A STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN WATER AND WATER + MONOHYDROXY ALCOHOLS

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DECLARATION

I declare that the thesis entitled A STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN WATER AND WATER + MONOHYDROXY ALCOHOLS has been prepared by me under the guidance of Dr. M.L. Parmar, Former Professor and Dean, Department of Chemistry, Himachal Pradesh University, Shimla and Dr. R.C. Thakur, Professor and Associate Dean, Department of Chemistry, Lovely Professional University, Phagwara. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

We certify that Mrs. Sonika Singh has prepared her thesis entitled, “A STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN WATER AND WATER + MONOHYDROXY ALCOHOLS”, for the award of Ph.D. degree of the Lovely Professional University under our guidance. She has carried out the work at the Department of Chemistry, Lovely Professional University.

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I dedicate this thesis to
my family and my husband, Harminder Singh
for their constant support and unconditional love.
I love you all dearly.

PREFACE

Studies of solute – solvent interactions in electrolytic solutions have been the subject of active interest. The inference regarding the interactions is generally derived from thermodynamic and transport properties like partial molar volume, viscosity and conductance studies. Since the partial molar volume and viscometric methods are known to give valuable information regarding solute – solvent, solute – solute as well as solvent – solvent interactions, therefore studies on partial molar volume and viscosity of ionic solutions are of great help in characterizing the structure and properties of the solutions. These thermodynamic investigations play an important role in understanding type and extent of the pattern of molecular associations that exist in liquid mixtures and their sensitivities of variations in compositions, temperature, pressure and chemical nature.

The transport properties are fascinating studies in themselves because their industrial and practical values lie in the way they control important reaction rates. These transport properties are very useful for the study of ionic salvation. These properties can give information on the effective size of a moving particle in solution. These properties are sensitive to strong ion – solvent interactions, which increase the effective size of the ions, and also to any modification in the structure of solvents.

The present work has been carried out with some divalent transition metal chlorides namely manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water and binary aqueous mixtures of alcohols (methanol and ethanol) in five different compositions viz; 5,10,15,20 and 35 wt% of alcohols.

Partial molar volumes of above mentioned divalent transition metal chlorides have been determined in water and in binary aqueous mixtures of methanol and ethanol at one temperature with the help of density measurements. Effect of temperature on the partial molar volumes was also analysed in 5% (w/w) methanol + water as well as in 5% (w/w) ethanol + water mixtures for these salts by taking five equidistant temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K). Magnesium chloride was taken as reference electrolyte (divalent cation) in whole of the study. The density measurements were made by using Ward and Millero method and results have been analysed by Masson’s equation. The experimental values of slopes and partial molar volumes of these transition metal chlorides have been interpreted in terms of ion-ion or ion –solvent interactions. The partial molar volumes vary with temperature as a power series of temperature. Structure making or breaking capacities of transition metal chlorides have been deduced by following the Hepler's criterion.

Viscosities measurements were made with the help of the suspended level type viscometer and the measured viscosity data has been analysed using Jones – Dole equation. The obtained parameters have been interpreted in terms of ion –ion and ion – solvent interactions. The viscosity data has also been analysed on the basis of transition state treatment of relative viscosity as proposed by Feakins and from this hypothesis activation parameters have also been determined which explains the mechanism of viscous flow. The enthalpy and entropy of activation are positive for the transition metal chlorides and magnesium chloride taken in the present study. The positive values of $\Delta H_2^{0^*}$ and $T\Delta S_2^{0^*}$ parameters indicate that the transition state theory is associated with bond breaking and decrease in order.

The hydrodynamic permeabilities have also been carried in the same solvent systems in which densities and viscosities measurements were carried out, through an inorganic membrane of aluminium oxide. In present case, the membrane constant 'A/l' is fairly constant for the solutions of selected electrolytes in water as well as in binary aqueous mixtures of alcohols. This indicates that membrane constant 'A/l' is characteristic property of membrane only. On other side, the equivalent pore radius decreased with the increase in the concentration of all mentioned electrolytes in water as well as in a particular composition of methanol + water and ethanol + water; this may be attributed to the increase in the thickness of the electrical double layer at the walls of the pores of aluminium oxide membrane. Moreover, equivalent pore radius and mechanical filtration coefficient are not same for the same electrolyte in water as well as in binary aqueous mixtures of alcohols. This indicates that equivalent pore radius is not the characteristic property of membrane but is also affected by the nature of permeating fluid.

The rejection coefficient (σ) across the aluminium oxide membrane has been determined for the divalent transition metal chlorides, viz; manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water as well as in binary aqueous mixtures of alcohols. It decreases with the increase in concentration of each electrolyte at 303.15K thereby showing that the solute and solvent flow with almost

equal velocities and hence there is no rejection of the solute by the inorganic membrane of aluminium oxide.

Outcomes of this study show that addition of divalent transition metal chlorides enhances the structure of methanol + water as well as ethanol + water solvent systems. So selected divalent transition metal chlorides behave as structure promoters or makers in water and binary aqueous mixtures of methanol as well as in ethanol.

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GENERAL INTRODUCTION AND REVIEW

Introduction

In the domain of physical chemistry, the study of electrolyte solution has extended in multi-directions in modern times. The introduction of extensive range of solvents as reaction media is of major importance. With some exceptions [1, 2] the thermodynamic studies have been limited to relatively polar solvents, but large variations in the chemical nature of the solvents used have enabled significant advances to be made in getting the information of interactions among ions and solvent molecules [3]. Phase transfer catalysis [4] has highlighted the importance of the studies of organic reactions, a very large of which take place by anionic mechanism.

Knowledge of ionic solutions has increased immensely during the past few decades. Different type of interactions exists in solutions and of these, solute – solvent interactions appear to be most significant. With the help of these interactions we can understand the nature of the solute and solvent, i.e., whether the solute modifies or distorts the structure of the solvent. The nature of solute – solvent, solute – solute interactions has been deduced mainly from thermodynamic properties like partial molar volume, free energy of transfer, heats, volume of mixing and the transport properties like viscous flow, conductance etc.

The volumetric and viscosity behaviour of solutes in solution provides information regarding solute – solvent and solute – solute interactions [5, 6]. At infinite dilution apparent molar volumes are, by definition, independent of solute-solute interactions and thus can be used to examine solute – solvent interactions. During last few years much interest has been centred on the behaviour of solutes in mixed solvent systems. It has been realized that the solvation of solutes can be better understood in mixed solvents than in pure solvents, because the dielectric constant and viscosity of the medium can be varied to a desired value only in the mixed solvents. Due to easy availability and high dielectric constant, water has been used as one of the co solvent in the mixed solvents If an organic solvent is added to water it brings a big change in the solvation of ions. The peculiarities of the aqua-organic mixtures are well reflected in the sudden changes in the reaction rates [7-9] and medium effect on the free energies of transfer of ions which cannot be explained only on the basis of the change in the dielectric constants. In a mixed solvent, ions will in general interact in preference with one of the solvent component. Under favourable condition it is possible to observe the stepwise replacement of molecules of one solvent component in the ion solvation shell by those of the other component as solvent composition is varied.

Ion-solvent interactions have been studied in detail in water and some other organic solvents, but less consideration has been given to solvent systems in which water is mixed with various organic solvents. Thermodynamic studies of water at infinite dilution in organic liquids are especially rare. Such studies are interesting because one is able to see what happens to the physical properties of water and aqueous solutions when diluted.

The entropies and enthalpies of transfer of electrolytes show a very complex dependence upon solvent composition when we shift from water to other an aqueous mixed solvent. These have been discussed in terms of change in solvent – solvent interactions in the bulk solvent brought about by the ions. The results obtained in mixed aqueous systems highlight the importance of solvent- solvent interactions between co-ordinated ions and solvent molecules in hydrogen – bonding media.

Dimethyl sulphoxide (DMSO) and water mixtures remain popular solvent media for the study of ionic solvation [10]. In these mixtures there is a little information of preferred solvation. This is attributed in part to the very strong interactions between water and DMSO molecules and in part to the transmission of Lewis basicity of the DMSO molecules in water and DMSO mixtures through H – bonds [11, 12].When dimethyl formamide (DMF) is taken as one of the solvent and is added to water it generally breakdown the normal structure of water and in turn a more structured solvent is formed as a consequence of enhanced hydrogen bonding between DMF and water molecules [13]. The water structure is already broken up to some extent at a higher temperature due to increased thermal motion and therefore, more free water molecules may be available at an earlier stage of DMF content for the formation of most structured solvent.

Dioxane is an aprotic solvent whereas water is amphoteric in nature. Both are miscible solvents to each other in all solvent compositions and are different in dielectric and dipole moments, but some of their physical properties like boiling point, vapour pressure and density are same [14]. These and many other several properties make studies of aqueous mixtures an interesting field to research, particularly of ionic processes in solutions of strong electrolytes. These studies of ion-solvations of strong electrolytes form the backbone of solution chemistry [15, 17].

Many phenomena like solubilities of electrolytes, rates of chemical reactions, phase separation processes and redox potentials are strongly influenced by the selective solvation of ions in mixed solvents [18, 19]. Various technological applications such as electro-deposition [20], metal refining [21] and in high energy density batteries [22, 23] are dependent on this principle.

The selective solvation behaviour of few copper (II) salts, viz., copper (II) benzoate, copper (II) formate and copper (II) iodate in water + dimethylformamide (DMF) mixtures have been reported[24]. A need is felt to have accurate aqueous data in many fields besides chemistry including geology [25], oceanography [26], boiler engineering [27] and oil recovery systems [28]. These areas require aqueous data over wide range of temperature, pressure and composition. One group of electrolytes that have not been extensively studied are the divalent transition metal chlorides in solvents like methanol and ethanol.

A need has developed for accurate thermodynamic data for transition metal salts in aqueous solutions because of its importance in geology [25], industrial [27] and biological [29] systems. In biological systems metals like copper, iron and manganese are required for various purposes [29], while other metals like nickel and cadmium can poison enzymes by substituting for their required metals. Transition metals are also important in geology because they are components of various minerals [25] and on the other hand engineers [27] are interested in their role in corrosion processes. Scientists, engineers and biologists working in various disciplines of science and technological processes are interested in various transport phenomenons studies as these studies are helpful in various biological processes.

The study of solvent flow through porous media is also of great importance and has attracted the attention of many chemists, chemical engineers and biologists. The interest in the study of flows through various porous media lies in the fact that these are useful in engineering and medical fields. Some of the important technological applications of membranes include their use in dialysis as a means of industrial, chemical and biological separations. Exchange of matter and energy, which is the principle function of organisms, takes place through membranes.

The use of porous media (membrane) in also useful in conversion of sea water to fresh water. The transport mechanism of flow of liquids and ions through inorganic membranes is not well established; however the studies involving inorganic membranes [30, 31] are of fundamental importance because they throw light on problems like sorption of ions by precipitates, the electrophoretic behaviour of suspensions etc. For the sake of convenience of presentation various thermodynamic and transport properties are briefly described as follows:

1.1 Thermodynamic Properties

Dissociation of a salt depends upon many factors like dielectric constant, polarity of the solvent and on the lattice energy. The process may be observed by dissociation of the crystal lattice in to gaseous ions which are then solvated in the solvents as shown below:

$$C^+A^- \longrightarrow C_g^+ + A_g^- \quad \triangle G_{\text{lattice}} \tag{1.1}$$

and

$$C_g^+ + A_g^- \longrightarrow C_g^+ + A_g^- \quad \triangle G_{\text{solvation}} \tag{1.2}$$

Since the free energy of solution, $\triangle G_{\text{sol.}}$ is thermodynamically given by the following relation:

$$\triangle G_{\text{sol.}} = \triangle G_{\text{solvation}} - \triangle G_{\text{lattice}} \tag{1.3}$$

therefore, the free energy of solvation of the ions must be considerably larger in order to overcome the lattice energy. This might possibly explain why solubility in water is greater than in non-aqueous solvents. However, the standard free energy, in practice is expressed as

$$\triangle G^o_{\text{sol.}} = -RT \ln K \tag{1.4}$$

where R is the universal gas constant, T is the absolute temperature, K is the equilibrium constant for the reaction.

$$MX \longrightarrow M^+ + X^- \tag{1.5}$$

which afford one of the methods by which free energies of solvation and transfer are derived [32]. Of many theories that have been applied to predict changes in solubility with the solvation of the solvent, most of them are dependent upon changes in the electrostatic properties of the solvent.

The quantitative relation between the solubility of simple salts and the dielectric constant of the solvent was proposed by Bjerrum [33]. But the formula proposed by Bjerrum gave poor results in the solubility calculations [34]. From these observations it is clear that the dielectric constant is not the main determinant of solubility rather ion-solvation depends on the solvent base strength of the hydrogen bonding capability.

The thermodynamics of transfer of a pair of gaseous ions into a solvent has been widely used to describe the ion-solvent interactions, which take place at infinite dilution. The thermodynamic solvation process in general is represented by the following expression:

$$C^{+}{}_{g} + A^{-}{}_{g} \xrightarrow{\qquad\qquad} C^{+}{}_{sol.} + A^{-}{}_{sol.} \quad \triangle Y^{o}{}_{sol.} \qquad (1.6)$$

where $C^{+}A^{-}$ is the ion pair and $\triangle Y^{o}{}_{sol.}$ represents the change in the thermodynamic function involved. The various thermodynamic properties are explained below:

(a) Solvation Enthalpies: Solvation enthalpies are obtained either through a Born-Haber cycle, as the difference between the enthalpy part of the lattice energy and the heats of solution at infinite dilution or from the spectrometric study of ion-solvent interactions in the gas phase [35, 36].

(b) Solvation Entropies: The various methods for the determination of entropies of solvation have been reviewed by Conway and Bockris [37]. The entropies of the gaseous ions are calculated from the Sackur-Tetrode equation for mono atomic gases, as given below:

$$\overline{S}^{o}{}_{g} = R[\ln V + 3/2 \ln T + 3/2 \ln M] + C \qquad (1.7)$$

where M is the atomic weight, V is the molar volume, R is the gas constant and C is a constant. The entropies of the ions can be obtained from electromotive force (e.m.f) measurements and from solubility studies or from Born equation applied to free energies [38]. The entropy of solvation is given by:

$$\Delta S^{o} = \overline{S_{2}}^{o} - \overline{S_{g}}^{o} \qquad (1.8)$$

where $\overline{S_{2}}^{o}$ is the partial molal entropy of the electrolyte and $S_{g}\overline{^{o}}$ is the standard molal entropy of the gaseous electrolyte.

(c) Gibbs Free Energies: The Gibbs free energy, △G, may be obtained from the following thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S \qquad (1.9)$$

where $\triangle H$ is the change in enthalpy, $\triangle S$ is the change in entropy and T is the absolute temperature. But some methods give a direct determination of the free energy of solution. The e.m.f of a cell is directly related to the change in free energy involved in the solvation of ion. In cells which are reversible w.r.t. anions and cations such as amalgam cell:

$$\text{MyHg} \;\Big|\; \text{MX} \;\Big|\; \text{AgX} - \text{Ag} \tag{1.10}$$

the standard free energy of solution of an electrolyte, $\triangle G^{o}_{sol.}$ is obtained directly from the standard electrode potential(E^{0}) of the cell as given below:

$$-\ \Delta\, G^{o}_{sol.} = \ Z\, F\, E^{o} \tag{1.11}$$

The free energies of transfer may be obtained by using electrochemical cells with transport. This may be realized by combining two amalgam cells in which the electrolyte is not in the same medium, e.g. water and another solvent:

$$\text{Ag-AgX} \;\Big|\; \text{MX}_{\text{water}} \;\Big|\; \text{MyHg} \;\Big|\; \text{MX}_{\text{solvent}} \;\Big|\; \text{AgX- Ag} \tag{1.12}$$

the net effect of the cell reaction is the transfer of MX from water to the other solvent. The standard potential of this double cell is given by the difference in the standard potential of the aqueous cell $W^{E0}MX$ and the non-aqueous cell $S^{E0}MX$. This is known as “medium effect” [39] and may be represented as:

$$\text{In}\gamma_{0} = \frac{W^{E0}MX - S^{E0}MX}{RT} \tag{1.13}$$

Sarma and Ahluwalia [40] proposed that the free energy change in case of structure breaking solutes, such as common electrolytes should be accompanied by positive free energy change, on the other hand, the structure making solutes are accompanied by negative free energy change, thereby making transfer of such solutes from water to mixed solvents favourable.

(d) Partial Molar volumes: The change in volume of water upon addition of one mole of electrolyte to the large reservoir of volume V, is known as partial molar volume of the electrolyte at the indicated concentration, at constant temperature T, pressure P, and moles of other components n_1, n_2 ---------.

Mathematically, partial volume, $\overline{V_2}$ may be written as:

$$\overline{V_2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n,---------}. \tag{1.14}$$

The partial molar volume of an electrolyte$\overline{V_2}$, can be calculated from density measurements [41]. The use of apparent molar volumes, ϕ_v, is more convenient, particularly for binary solutions, which may be calculated with the help of following relation:

For binary solutions, the use of apparent molar volume, ϕ_v is more convenient. The apparent molar volume of an electrolyte is defined by the relation:

$$\phi_v = \frac{M_2}{d^0} - \frac{1000(d-d^0)}{mdd^0} \tag{1.15}$$

where M_2 is the molecular weight of an electrolyte, d the density of electrolytic solution, d^0 is the density of water and m the molal concentration of the electrolyte.

When the molar concentration is used, the above relation may be written as:

$$\phi_v = \frac{M_2}{d^0} - \frac{1000(d-d^0)}{cd^0} \tag{1.16}$$

Molarity is most frequently used to express the concentration dependence of $\overline{V_2}$ and ϕ_v, since theoretical limiting Debye –Huckel equation uses this scale. At infinite dilution, the partial molar volume and the apparent molar volume are equal ($\phi_v^0 = \overline{V_2}^0$).

The extrapolation of the apparent molar volume of an electrolyte to infinite dilution and the expansion of concentration dependence of apparent molar volume have been made by three major equations: the Masson equation [42], the Redlich-Meyer equation [43] and Owen Brinkley equation [44].

Masson found that the apparent molar volume, ϕ_v of electrolyte varies with the square root of the molar concentration and can be represented by linear equation:

$$\phi_v = \phi_v^0 + S_v \sqrt{C} \tag{1.17}$$

where ϕ_v^0 is the apparent molar volume at infinite dilution and is equal to partial molar volume $\overline{V_2}^0$ and S_v is the experimental slope varying with electrolyte type and charge.

Redlich and Meyer have suggested the use of following extrapolation equation:

$$\phi_v = \phi_v^0 + S_v \sqrt{C} + b_v C \qquad (1.18)$$

where S_v is the theoretical limiting slope and b_v is a deviation constant determined from experimental results.

The ideal method is to make the measurements in very dilute solutions where the deviations from the limiting law are very small and hence b_v and higher order terms of the Owen – Brinkley equation do not have to be considered. Since the limiting law is not known above 70°C, the Masson equation must still be used at high temperatures.

1.2 Transport Properties

The transport properties such as relaxation of dielectric polarization, conductance and viscosity reflect the displacement of solvent molecules in solutions.. In general, an escalation in the structure due to increased rigidity leads decline in the rates of displacement of molecules and vice versa. If any system which is in the state of non – equilibrium, will always have tendency to get a state of equilibrium. As in this state of equilibrium, gradients of parameters are absent, spontaneous processes do not take place and there is no net transfer of matter between system and its surroundings. On other side, if such conditions are not fulfilled then system is known to be in state of non – equilibrium.

If a system which is in state of equilibrium, is disturbed to a non – equilibrium due to some extrinsic or intrinsic hindrance, one of the state parameter become a function of position and when this change is withdrawn, an irreversible decay process takes place simultaneously and the system approaches through a series of non equilibrium states until equilibrium is attained. This process is a transport process, because some quantity is transferred throughout the system as the system tries to make all parameters independent of position. Thus any process in which some physical quantity such as mass, energy, electrical charge etc. is transported from one region of system to another is known as transport process. The amount of physical quantity transported per unit time is called flux and is proportional to the gradient of some other physical quantities like temperature, pressure, concentration and electrical potential. The agency causing flux is known as force.

A transport process mathematically can be represented as:

$$J = L.X \qquad (1.19)$$

here J is the flux, X is the force and L is the proportionality constant called 'transport coefficient' or 'phenomenological coefficient', which is a measure of the rate at which the system approaches equilibrium state. Equation (1.19) can be written in general form as follows:

$$J_i = \sum_{k=1}^{n} L_{ik}\ X_k \ (i = 1, 2, 3 \ldots\ldots., n) \tag{1.20}$$

where X is a generalized force, J is generalized flux and L_{ik} is transport coefficient. In non-equilibrium thermodynamics X is called a thermodynamic driving force.

It is convenient to write equation (1.20) in matrix notation as follows:

$$J = L\ X \tag{1.20 a}$$

$$\begin{bmatrix} J_1 \\ J_2 \\ . \\ . \\ J_n \end{bmatrix} = \begin{bmatrix} L_{11}\ L_{12} \ldots \ldots L_{1n} \\ L_{21} L_{22} \ldots \ldots L_{2n} \\ .\ \ .\ \ . \\ .\ \ .\ \ . \\ L_{n1} L_{n2} \ldots \ldots L_{nn} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ . \\ . \\ X_n \end{bmatrix}$$

Thus if n = 2

$$J_1 = L_{11}\ X_1 + L_{12}X_2 \tag{1.20 b}$$

$$J_2 = L_{21}\ X_2 + L_{22}X_2 \tag{1.20 c}$$

Equation (1.20 c) expresses that if the off diagonal element of L exists, the i_{th} flux depends in a linear manner on the k_{th} force as well as upon its conjugate force X_i. The relation between J_i and X_k is called "thermodynamic coupling". Coupling here means a direct linear relation expressed by equation (1.20) and has a more definite and restricted meaning than interaction.

There are numbers of transport processes which are taking place in biological and non-biological systems are similar and obey all the principles of physics. Biological systems/living systems involve steadily transfer of heat and mass with its surrounding. In many biological systems of chemical reactions and flows, there is resultant coupled flow of certain substances even against a gradient. This type of flow is called active transport.

The transport processes can be classified into two categories as described below :

A. Uncoupled Transport Process

B. Coupled Transport Processes

A. Uncoupled Transport Processes

When $L_{ik} = 0$ ($i \neq k$) relation $J = LX$ become $J_i = L_{ii}X_i$. It is a phenomenological representation of several familiar empirical laws involving systems which are in non – equilibrium because of the presence of gradient of temperature, density of macroscopic velocity. They are associated with most familiar examples of transport processes such as heat conduction, diffusion and viscosity etc. For these examples the empirical laws are defined as follows:

(i) Fourier's Law of Heat Conduction: According to this law

$$q = -\lambda \text{ grad } T \qquad (1.21)$$

here q is a heat flux resulting from the transfer of heat caused by molecular interactions (pure heat flow) , λ is a coefficient of thermal conductivity and grad T is a gradient of temperature.

(ii) Fick's Law of Diffusion: According to this Law $J_i = - D \text{ grad } C_i$ (1.22)
where J_i is flux of chemical species i, C_i is concentration of i and D is the diffusion coefficient and is a characteristic of fluid only.

For the fluid flow through a membrane the equivalence of Fick's Law is D 'Arcy's law:

$$J_i = k \, dP/ l \qquad (1.23)$$

where k is known as permeability coefficient, which is a constant in the flux force law resulting from a pressure difference dP across the thickness l. The coefficient k can be the characteristic of the fluid and the membrane and it differ from D in respect that D is always a characteristic of the fluid only.

(iii) Newton's Law of Viscosity: This can be represented as follows:

$$\pi_{yx} = \eta \, . \, \partial U_x/\partial U_y \qquad (1.24)$$

where π_{yx} is a term which represents a momentum flux in the Y direction caused by a fluid flowing in X direction with velocity component U_x and η is a coefficient of shear viscosity.

B. Coupled Transport Processes

If a transport process involves two or more forces, the flow J_i will be influenced by other forces X_k ($k \neq i$) as well as its conjugate force X_i .Such transport processes are called coupled transport processes. Thermal diffusion, thermo- molecular pressure difference and electro-kinetic effects are known as coupled transport processes. These processes are briefly described as follows:

(i) Thermal Diffusion: When L_{ik} coefficients in equation J= L X (where J is the flux, X is the force and L is the proportionality constant and is called "transport coefficient") are different from zero, coupled transport phenomenon arises. Thermal diffusion is one of the best known coupled transport processes. If a bulb filled with gaseous component at a certain temperature is connected to other gaseous component at different temperature, it is found that the diffusion of both gaseous components depends not only on the concentration gradient but also on the temperature gradient. If the two bulbs are kept originally at the same temperature then the diffusion processes cause temperature difference between the two blubs. This phenomenon is as "Dufour Effect" or Diffusion thermo Effect" [45]. If thermal energy flow is represented as J_q and its conjugate gradient as X_q and diffusion flux of species i as J_i and its conjugate gradient as X_i , equation can be written as follows :

$$J_q = L_{qq}X_q + L_{qk} X_k \tag{1.25}$$

$$J_i = L_{iq} X_q + L_{ik} X_k \ (i=1,2------n) \tag{1.26}$$

If X_k, the concentration gradient of any component, is zero , then equation 1.25 becomes

$$J_q = L_{qq}X_q \tag{1.27}$$

This is a form of Fourier's Law of heat conduction. If X_q, which represents the temperature gradient, is zero, equation 1.26 becomes :

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \tag{1.28}$$

This is a form of Fick's law of diffusion. The terms L_{qk} X_k and L_{ik} X_q represent the coupling of heat conduction and diffusion process which results in the phenomena of thermal diffusion and the Dufour Effect, respectively.

(ii) Thermo- molecular Pressure Difference: The thermo molecular pressure difference is observed experimentally in an apparatus consisting of two large reservoirs I and II connected by a membrane, capillary or an orifice. The reservoirs are maintained at different but constant temperatures T_I and T_{II} and a gas is introduced into the systems at a pressure such that mean free path of the gas is of the order of the diameter of the capillary. It has been observed that the gas flows from the cold to the hot reservoir till a constant pressure difference is obtained. When the flow of gas stops, the pressure difference is given by the Maxwell's equation given below:

$$P_I / P_{II} = (T_1 / T_{II})^{1/2} \qquad (1.29)$$

where P_1 and P_{II} represents the pressures difference in two reservoirs respectively.

(iii) Electro- Kinetic Effects: The electro-kinetic phenomenon is a transport process across a membrane or capillary and is observed when a potential gradient is applied. It arises due to the formation of an electrical double layer at the surface of pores or capillary. According to the thermodynamics of irreversible processes [46] the electro-kinetic effects are described mathematically by the following relations:

$$I = L_{II}\Delta\phi + L_{12}\Delta P \qquad (1.30)$$

$$J = L_{2I}\Delta\phi + L_{22}\Delta P \qquad (1.31)$$

where, L_{11}, $L_{12} = L_{21}$ represent phenomenological coefficients, I the current flow, J the mass flow, $\Delta\phi$ and ΔP the potential gradient and pressure gradient respectively across a membrane or capillary. Relations (1.30) and (1.31) show that there are two forces involved in electro-kinetic phenomenon and corresponding to these forces there are two fluxes viz; current flux and volume flux. The terms L_{12} ΔP and $L_{21}\Delta\phi$ represent the coupling of electrical current flow and volume flow respectively.

1.3 Review of Literature

The objective of present work is to study the thermodynamic and transport properties of some divalent transition metal chlorides and magnesium chloride in water and water + monohydroxy alcohols. As studies in mixed aqueous organic systems highlight the importance of solvent – solvent interactions and also of interactions between coordinated ions and solvent molecules in hydrogen bonding media, therefore the thermodynamic and transport properties of electrolytic solutions with or without membrane has been investigated with a special emphasis on binary aqueous organic mixtures. For the sake of convenient presentation, the present review has been described under the following headings:

A. Thermodynamic properties
B. Transport properties

A. Thermodynamic Properties

The Standard thermodynamic quantities of ionic and non – ionic solutes in ionic and non-ionic solvents are exactly related with the solvent effect on the physico-chemical properties of the solutes are widely known. In general, the kinetics and equilibria of reactions involving those solutes in particular. It is also well recognized that composition profiles of transfer Gibbs energies, ΔG^0_{tr} (i), of various solutes in different aqueous ionic [47] and non-ionic co-solvents [48-50] systems are usually monotonic, while those for transfer enthalpies, ΔH^0_{tr} (i), and transfer entropies ΔS^0_{tr} (i), of various solutes exhibit extremum with mirror – images relationship to each other [47-54]. It is widely believed that the genesis of the observed mirror images relationship of ΔH^0_{tr} (i) and $T\Delta S^0_{tr}$ (i) in aquo-cosolvent systems lies in the involved solute induced perturbations of the three dimensional 3D - structure of aquo - cosolvent media, if any, relative to that in water.

It is known fact that amphiphatic solutes or molecular ions with polar sites draw more water molecules in the vicinity of them to arrange in a way identical to clathrate hydrates bringing hydrophobic hydration [55- 59] and result in an important increment in Gibb's free energy and decrease in entropy of the system [60].Preferential solvation and its impact is also evident in a variety of systems. For example, appreciable changes brought about in the electrode behavior of organic depolarizers in aprotic media such as tetrahyrofuran (THF) by the addition of Li^+ have been shown to occur in the presence of trace amounts of water in the solvent [61].The effects are associated to proton transfer from water molecules activated by the formation of hydrated $Li(H_2O)_g^+$ in the aprotic media.

Many researchers in the fields of biochemistry and physical chemistry have discussed the phenomenon of hydrophobicity [62]. Hydrobhobicity has been a much debated area among biochemists and physical chemist in the past. It manifests itself in the hydrophobic hydration: the entropically unfavorable solution of apolar molecules in water. Later on model was proposed to describe the enthalphic effect of hydrophobic hydration [63]. In the present case, this is expected that around a polar group there is existence of a co-operative arrangement of hydrogen bonded clathrate like "structures" of water. These entities which are differentially structured from bulk water; break up the introduction of cosolvent. N,N-dimethyl formamide (DMF) confirmed to be a specifically appropriate co solvent as it is aprotic and its dielectric constant is not low as to cause extensive association of ions.

Values of free energy of transfer of the protons, ΔG^0_{tr} (H^+), from water to binary aqueous mixture of DMSO have been calculated by Wells [64]. Values of, ΔG^0_{tr} (X^-) are then produced from, ΔG^0_{tr} (HX) and these, ΔG^0_{tr} (X^-) used to produce values for, ΔG^0_{tr} (M^{n+}) from the free energies of transfer of salts. In general, ΔG^0_{tr} for anions are positive and , ΔG^0_{tr} for the cations are negative.

The first row divalent transition metal divalent ions are known to form well defined co-ordination clusters in solutions and in the strongly coordinating donor solvents. In absence of coordinately active anions, the divalent transition metal cations exists as the M $(\text{solvent})^{2+}{}_6$ or M $(\text{solvent})^{2-}{}_4$ types solvates [65-67]. However, it should be noted that in some of the solvents the configurational equilibria between the hexa-bis and tetra – bis (solvent) species were detected [68, 69]. Furthermore, the equilbria between tetrahedral and square planar tetrasolvates were observed in hexamethylphosphatriamide solutions of divalent first row transition – metal per chlorates [70, 71]. This is related to the fact that the factors controlling the solvation processes are the donor properties of the solvents, as well as their space requirements, along with the electronic structure of the central metal cation.

Chauhan and co- workers [72] determined the apparent molar volumes of tetra-alkyl ammonium salts in binary aqueous mixtures of tert.butyl alcohols of varying dielectric constant. Molar volumes have been plotted against square root of concentration for MeNI, Et_4NI and Pr_4NI in aqueous tert. butanol mixtures of varying dielectric constant in order to study the effect of strongly water-structure promoting influence of tert.butanol on the nature of slope. The results show negligible influence of the water – structure promoting property of tert.butanol and nature of slope depends mainly upon dielectric constant of the medium.

Kumar [73] determined the densities of aqueous calcium chlorides solutions for molalities up to 6.4 mol.kg^{-1} at different temperatures ranging from 50^{0}C - 200^{0}C and at pressure of 20 -27 bar. Apparent molar volumes calculated were fitted to the equations of Roger and Pitzer and the obtained standard deviation of fit for the apparent molar volumes was found 0.21 cm^3 mol^{-1} from 50 – 200^{0}C at 20-27 bars.

Molar volumes of cadmium bromide and cadmium iodide have been reported [74] in aqueous ethylene glycol (10, 20, 30 and 40% wt%) in the temperature range 30 – 45^{0}C. The partial molar volume has been determined from Masson's equation and found increase with the increase in temperature, for both the electrolytes, thereby showing that these salts act as structure makers in binary aqueous ethylene glycol mixtures.

Roy and Sarkar [75] determined the apparent molar volumes and viscosity B-coefficients for nicotinic and benzoic acid in mixed solvents containing 10, 20, 30 mass % of *n*-amyl alcohol or isoamyl alcohol in methanol and in pure methanol from the density and viscosity measurements at 298.15K as function of concentrations of nicotinic acid and benzoic acid. These results were also found in agreement with the results so obtained in pure methanol and were used to calculate the partial molar volumes of transfer and viscosity B-coefficients for nicotinic acid and benzoic acid from methanol to different mixed methanol solvents, in order to rationalize the various interactions in the ternary solutions. An increase in the transfer properties of nicotinic acid and benzoic acid with increasing wt. % of *n*-amyl alcohol and isoamyl alcohol in methanol was observed and explained by the effect of structural changes and preferential solvation. The free energies of viscous flow, $\Delta\mu^{0\neq}{}_1$ and $\Delta\mu^{0\neq}{}_2$, per mole of solvent and solute, respectively, were also calculated and analyzed on the basis of the transition state theory of relative viscosity.

Parmar and Rao [76] analysed the data of density and viscosity for some multi – charged electrolytes namely ammonium aluminium sulphate and potassium aluminium sulphate in four different compositions of dimethyl sulphoxide in water (5, 10 15 and 20 weight percentage) in different concentrations and temperature range, with the help of Masson equation and Jones – Dole equation respectively. The interaction between selected multi charged electrolytes and different compositions of aqueous mixture of dimethyl sulphoxide has been interpreted in terms of structure making/breaking capacity. Both the electrolytes in this study have been found as structure makers.

lokhra et. al. [77] determined apparent molar volumes (ϕ_V) and experimental slopes (S_V) of calcium acetate in different compositions of acetic acid in water at different temperatures and the results obtained have been interpreted in terms of solute – solvent interactions and structure making / breaking capacity of the electrolyte. The apparent molar expansibilities at infinite dilution ($\phi^0{}_E$) have also been found to be determined. In the present study calcium acetate has been found structure breaker.

The partial molar volumes and viscosities of some common electrolytes, tetra-alkyl salts and multi- charged electrolytes, viz; ammonium nitrate and ammonium sulphate; tetra-methyl ammonium chloride and tetra-methyl ammonium iodide; ammonium ceric nitrate and ammonium cerium(IV) sulphate, respectively have been determined [78] in water at different temperatures. The density data have been analysed by means of Masson's equation. The experimental results of viscosity have also been interpreted using the Jones – Dole equation. All the different types of electrolyte behave similarly in water and acts as structure breakers.

Roy et. al. [79] have studied the apparent molar volumes and viscosity B-coefficients for glycine in concentration range (0.005, 0.010, 0.015, and 0.020) mol.dm^{-3} aqueous silver sulphate (Ag_2SO_4) solutions at various temperatures (25, 35, and 45^{0}C) as a function of glycine concentration. The standard partial molar volumes and experimental slopes (S_V^*) have also been analyzed by using Masson equation and interpreted in terms of solute-solvent and solute-solute interaction. The viscosity data was analyzed using the Jones-Dole equation, in which the derived parameters A and B were interpreted in terms of solute-solute and solute-solvent interactions, respectively. The standard volumes of transfer and viscosity B-coefficients of transfer of glycine from water to aqueous Ag_2SO_4 solutions were also determined. The structure making or breaking behaviour of glycine has also been discussed.

Huque et.al. [80] have reported the densities of aqueous solutions of potassium chloride, potassium nitrate, magnesium chloride and magnesium nitrate over temperature range (30, 35, 40, 45, 50)^{0}C.The apparent molar volume and limiting apparent molar volumes for all these electrolytes have been calculated by using the density data and the values of these parameters were discussed in terms of solute – solute and solute solvent interactions.

Parmar and Guleria [81] determined the densities , apparent molar volumes and partial molar volumes of oxalic acid and its salts like ammonium oxalate, sodium oxalate and potassium oxalate in binary aqueous mixtures of tetrahydrofuran (THF) [5,10,15 and 20 wt. % of THF] at 298.15K and in 5% (w/w) THF + water at five equidistant temperatures. The data have been analysed by using Masson equation and the obtained results have been interpreted in terms of solute-solute and solutes-solvent interactions.

Densities and apparent molar volumes of binary aqueous solutions of Me_4NBr, Et_4NBr, Bu_4NBr, CsBr and LiBr in the concentration range 0.02 – 0.2 m at 25^{0}C have been determined [82].Similar data has also been obtained for these salts in aqueous NaCl and KBr at 25^0 C. These results along with volumetric transfer data have been discussed in terms of cation - cation hydrophobic interactions and the salting in and salting out effects involving structural change of solvent water.

Sinha et. al.[83] determined apparent molar volumes and viscosity B-coefficients for nicotinamide in water and in aqueous tetra butyl ammonium bromide solutions in concentration range from (0.05, 0.10,and 0.15) mol.dm^{-3} over the range of temperature from (298.15 to 318.15) K as function of concentration of nicotinamide .These results are in conjunction with the results obtained in pure water and are used to deduce the standard volumes of transfer and viscosity B-coefficients of transfer for nicotinamide from water to aqueous TBAB solutions for rationalizing various interactions in the ternary solutions. The structure making or breaking ability of nicotinamide has also been discussed in terms of the sign of [$\partial^2\phi_v^0/\partial T^2$]. An increase in the transfer volume of nicotinamide with increasing TBAB concentration has been explained by Friedman–Krishnan co-sphere model. The activation parameters of viscous flow for the ternary solutions investigated were also determined and discussed by using transition state theory.

Li et. al. [84] have reported the apparent molar volumes, standard partial molar volumes and the viscosity B- coefficients of cefepime hydrochloride in pure water and normal saline solution from 278.15K to 313.15K with the help of density and viscosity data. The obtained results were discussed in terms of ion – ion interactions and ion – solvent interactions. Ion – solvent interactions and structural breaking or making nature of cefepime hydrochloride have been interpreted in terms of Hepler and Jones- Dole equations.

Parmar and others [85] determined partial molar volumes of ammonium aluminum sulphate and potassium aluminum sulphate in acetonitrile + water (0 -20 wt %) mixtures at different concentrations and temperatures from density measurements. The partial molar volumes from water to acetonitrile have been found to be negative and vary with temperature as a power series. Both the electrolytes in this study were found as structure makers.

The densities of aqueous solution of tetra – alkyl (tetra methyl ammonium, tetra –ethyl ammonium, tetra- n- propyl ammonium, tetra – propyl ammonium and tetra – n- butyl ammonium) hydroxides have been determined [86] at 25^0C in the concentration range 0.1 – 1.0 molkg^{-1}. The apparent and partial molar volumes have been calculated by density measurements. The apparent molar volumes showed considerable deviations from Debye-

Huckel limitations law; even at high dilution. The reaction for the concentration dependence of the limiting molar volumes is given in an analytical form. The limiting molar volumes of the solutes have been split into their ionic compounds by extra thermodynamic approach and discussed in terms of ion – solvent interactions. In this way, the limiting partial molar volume for the hydroxide ion is found to be 2 cm^3mol^{-1}.

S.Kant and others [86] determined molar volumes and viscosity of lithium chloride (LiCl), sodium chloride (NaCl) and potassium chloride (KCl) in 0.01 m aqueous ascorbic acid from density measurements at temperatures 303.15, 308.15, 313.15 and 318.15 K. The solute–solvent interactions for LiCl, NaCl and KCl have been analysed from ϕ_v^o, *B*-coefficient of Jones–Dole equation and Λ_m^o values. The structure making/breaking nature of electrolytes is inferred from the sign of $[\partial^2\phi_v^o/\partial T^2]_p$, dB/dT and temperature coefficient of Walden product i.e. $d(\Lambda_m^o\eta_o)$/dT values. It has been found that LiCl, NaCl and KCl behaves as structure-breaker in 0.01 m aqueous ascorbic

Chauhan and Kumar [87] have reported the partial molar volumes, isentropic compressibilities and partial molar isentropic compression for some saccharides at concentration range from (0.050 to 0.100) $mol.kg^{-1}$ in aqueous solutions of leucine at temperature range (293.15 to 313.15) K by using density and sound velocity data. The order of variation of these parameters have been interpreted in terms of solute- solute and solute – solvent interactions.

Dubey and Kaur [88] have studied the densities, sound velocity of binary mixtures of 1-tert –butoxy – 2- propanol with some selected alcohols namely 1- hexanol, 1- octanol and 1- decanol at five different temperature ranges from 298.15K to 313.15K over the entire composition range. These experimental quantities were used to calculate the values of excess molar volumes, excess molar isentropic compressibilities and deviation in sound velocities.

Chauhan and Chaudhary [89] have studied the apparent molar volume, apparent molar adiabatic compression, isentropic compression for amino acids namely glycine and methionine in aqueous solution of an antibiotic drug namely amikacin sulphate over temperature range from 293K to 313K. The experimental results of apparent molar volume were found positive for both amino acids which suggest the presence of strong solute –

solvent interactions over all temperatures range. All other parameters are also explained in terms of solute – solvent and solvent – solvent interactions.

B. Transport Properties

(a) Transport Properties of Electrolyte Solutions in Aqueous And Binary Aqueous Mixtures.

Viscosity, conductance and diffusion are some of the fundamental transport properties which are used to study the behavior of electrolytes in solution. Study of these transport properties help in understanding the nature of ion –ion and ion –solvent interactions. During past two decades various studies have been done on the transport properties and a lot of data has been reported in literature for different types of electrolytes in aqueous and in mixtures of organic solvents and the same have been summarized as follows:

Parmar and Thakur [90] have determined relative viscosities of some divalent transition metal sulphates, viz., manganese sulphate, cobalt sulphate, nickel sulphate, copper sulphate and zinc sulphate and magnesium sulphate at different concentrations in water and binary aqueous mixtures of ethylene glycol (5, 10, 15, 20 and 25 % by wt. of EG) at 303.15K .Temperature effect has also been analysed in 5% (w/w) EG+water and data has been analysed by using the Jones-Dole equation [91] and the obtained parameters have been interpreted in terms of ion-ion and ion-solvent interactions.

The viscosity of tetra-ethyl ammonium bromide solutions in binary mixtures of DMF + H_2O have been reported by Domenech and Costa [92] at different temperatures. The obtained data has been analyzed with the help of Jones- Dole equation and interpreted in terms of structure making or promoting capacities of ions. Activation parameters of viscous flow have also been calculated by using the applications of transition state theory.

Parmar and Guleria [93] have determined the viscosities of oxalic acid and its salts in water and in binary aqueous mixtures of THF mixtures at five temperatures ranges from 298.15 to 318.15K and in four different compositions of water + THF (5, 10, 15 and 20% by weight of THF). Experimental results and the activation parameters of viscous flow obtained have been interpreted in terms of solute – solute and solute – solvent interactions. In these studies, electrolytes were found structure breakers in water and water + THF mixtures.

Verma and Kumar [94] have reported the viscosities of barium and strontium butyrates in water and have shown two critical micellization concentration (CMC) in dilute concentration ranges. The experimental data have been examined by Vand , Moulik and Jones – Dole equations. The fluidity of soap which is temperature dependent has been studied with the help of Arrhenius and Erying's equations. The activation parameters of viscous flow have also been calculated in water.

Viscosity B-Coefficients of N – Phenylbenzohydroxamic acid (PBHA) in Dimethylsulfoxide at temperature range of 298.15 to 318.15K have been studied by Pande et al. [95]. The viscosity B- coefficients have been calculated with Jones –Dole equation. The behavior of N – Phenylbenzohydroxamic acid (PBHA) has been explained in terms of the structuring effect on the overall structure of the solvent.

In the binary aqueous mixture of N,N-dimethylformamide the viscosity B – coefficient of sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate and sulphates of Mn^{2+}, Ni^{2+}, Cd^{2+} has been studied at 293K by Tsierkzos and Molinou [96]. The viscosity B – coefficients for all these salts have been examined by using Jones – Dole equation and interpreted in terms of ion – ion and ion – solvent interactions. The salts of thiocyantes showed negative values of viscosity B- coefficients indicated a maximum structure breaking abilities in 40 wt% of DMF in water compositions, which indicated about stronger ion –solvent interactions at these compositions. On other side bivalent ions of sulphates showed positive values of viscosity B- coefficient in all solvent compositions, which informed about the structure making tendency of these taken bivalent ions.

Yan et. al. [97] have reported viscosity B- coefficients of some alpha amino acids in water at four temperatures 5, 15, 25 and 35°C. Activation free energy, activation enthalpy and activation entropy were calculated with the help of Eyring transition – state theory. The alpha amino acids with zwitterions groups showed the positive values of B – coefficients confirmed that they are structure- breakers with increasing temperature. On the other hand, amino acids with hydrophobic structure- making -CH_2 group showed negative B – coefficients values with increase in temperature. This explains that the non-polar part of these amino acids effect the charged end group (NH_3^+, COO^-) of glycine on water structure predominates, whereas, for the other amino acids, the reverse is true.

Volumetric studies of $MgCl_2$, $MgBr_2$ and $Mg(NO_3)_2$ have been reported [98][47] in dioxane+water and glycol+water mixtures at different temperatures and results have been interpreted in terms of ion-solvent interactions. The ion-solvent interactions are found stronger in dioxane+water than glycol+water. The volumes of transfer ($\triangle v^{0}_{tr}$) from water to mixed solvents have also been calculated. From these values it has been concluded that the structures breaking effect of electrolytes is more in dioxane+water and less in glycol+water.

Moattar and Salabat [99] have studied the viscosities, densities and water activities for binary and ternary systems of polypropylene glycol 425 + water and polypropylene glycol 425 + water + magnesium sulphate at 298K. The experimental values of density and viscosity for the binary systems have been analysed with Redlich – Kister type equation and for ternary systems were correlated using a semi – empirical equation.

Parvinder Khanuja [100] explained the structure making and breaking nature of amino acids in binary aqueous solution of sucrose.Free energy of activation and viscosity B-coefficients were also reported. Structure making and breaking capacity has also been analysed by studying the effect of temperature also.

Daabes and Awwad [101] measured densities and viscosities, of aqueous solutions of N-(2-hydroxyethyl) morpholine in the entire composition range at T = (293.15, 303.15, 313.15, 323.15, 333.15)K and at atmospheric pressure. The excess molar volumes and viscosity deviations of aqueous solutions were also calculated from the experimental results of density and viscosity measurements and fitted to the Redlich–Kister polynomial equation. Apparent molar volumes V_{Φ}, partial molar volume at infinite dilution V^{∞}, and the thermal expansion coefficient were also calculated.

Relative viscosities of N-phenyl-2-chlorobenzo-hydroxamic and N-o-tolyl-4-chlorobenzo-hydroxamic acids have been measured [102] at 30 and 40°C temperatures in water + acetone mixtures. Jones –Dole equation and transition state theory have been used to examine the viscosity data and activation parameters of viscous flow respectively. The results were interpreted in the light of solute–solvent interactions in aquo-organic media.

Riyazuddeen and Usmani [103] have studied the viscosities of some amino acids viz; L-alanine, L –threonine and glycylglycine in aqueous solutions of D- glucose and sucrose solvent systems as a function of molal concentration of amino acids at different temperatures ranges from 298.15 to 328.15K. With the help of the experimental viscosity data of the solutions, viscosity B – coefficients, activation free energy, activation enthalpy and activation entropy data have been calculated and these values of activation parameters have been discussed in terms of ion – ion, ion- solvent and solvent – solvent interactions; and structure promoter or structure breaking capacity of amino acids or peptide molecules.

Dubey et.al. [104] have reported the viscosities, densities and speed of sound for different compositions of 1- butanol with n- alkanes namely hexane, octane and decane at three temperatures 25, 30 and 35°C. This experimental data has been used to calculate the partial molar volumes, deviation in speed of sound, deviation in viscosity and partial molar adiabatic compressibility. The experimental results of viscosity have been examined by using the Redlich–Kister polynomial equation. The activation parameter viz. partial Gibbs free energy of activation has also been calculated to know the mechanism of viscous flow. The sign and values of magnitudes of these calculated parameters have given information about the existence of weak dispersive forces in butan-1-ol and alkane binary mixtures.

Saxena and others [105] reported the studies of sound velocity, density and viscosity of binary mixture of ethylamine + benzyl alcohol at 303K, 308K and 313K temperatures. Along with these experimental data, other experimental parameters viz; intermolecular free length, available volume, isentropic compressibility and molar volumes have also been calculated for ethylamine and benzyl alcohol in the pure state as well as in ethylamine + benzyl alcohol mixtures over entire selected temperature range. These experimental parameters informed about the significant results of molecular structure, molecular movement and other various types of intermolecular interactions and their strength influenced by content, structure and chemical properties of constituent molecules.

Bhattarai [106] have reported the partial molar volumes and densities of dodecyltrimethylammonium bromide (DTAB) in water as well as in four different binary aqueous mixtures of methanol at four different temperatures ranging from 25°C to 50°C and in different concentrations from 0.4 x 10^{-1} mol kg^{-1} to 1.2 x 10^{-1} mol kg^{-1}. From the results it has been found that with the increase in the concentration of DTAB, there was increase in the densities. Not only this, the densities were found to decline with the rising temperature over the whole concentration range selected in a given mixed solvent medium.

Deosarkar et. al. [107] reported the densities and viscosities of glycine in aqueous and binary aqueous solutions of urea at 25°C. The obtained data of densities has been used to calculate apparent molar volumes of glycine in water as well as in binary aqueous solutions of urea at above mentioned temperature. The obtained values of partial molar volumes and viscosities of glycine solutions have been analysed in terms of Masson's equation and Jones

– Dole relation respectively and interpreted in terms of various interactions and structural fitting in studied solutions.

Patial [108] studied the activation parameters in binary mixture of N,N – dimethylformamide (DMF) and (EMK) for viscous flow process of tetrahexylammonium (Hex_4NI) iodide at 25°C, 35°C and 45°C and in pure dimethylformamide and 20,40,60,100 mol% of dimethylformamide. These parameters have been examined as a function of solvent composition to analyse the nature of tetraethylammonium iodide in binary mixtures of dimethylformamide and ethylmethylketone. Also, these parameters suggested the strong ion –solvent interactions in these solvent systems as well as indicated that tetrahexylammonium iodide behaves as structure – promoter in dimethylformamide and ethylmethylketone mixed solvents.

Akhtar [109] has carried the volumetric and viscometric studies of ion – ion and ion – solvent interactions of glycine in water and in water + electrolyte solutions viz; NaCl and $MgCl_2$ solvent systems at 303K. The experimental data of densities and viscosities have been used to calculate ion – solvent and ion – ion interactions and free energies of activation of viscous flow of solvent and solute. The obtained results were interpreted in terms of the dehydration effects of the electrolytes on the amino acids and weak ion – ion and strong ion- solvent interactions. The nature of this amino acid in water as well as water + electrolytes was explained in terms of the charge, volume and effect of hydrogen bonding

Viscosities of sodium dodecyl sulphate (SDS) in aqueous solutions of antioxidant Butylated Hydroxy Anisole (BHA) at different temperatures and the viscosity data have been analyzed by using Jones–Dole equation [110]. A – coefficients of the Jones Dole equation in the present study are found to be negligible indicating weak ion–ion interactions on the other hand B – coefficients are found positive thereby showing significant solute–solvent interactions. BHA have been found structure-makers/promoters due to hydrophobic hydration of the antioxidant or surfactant molecules.

(b) Transport Phenomena across Membranes / Interfaces of Different Types

During last few decades, number of researchers applied the thermodynamics of irreversible processes for analysing the transport phenomena across various types of diaphragms/membranes. A brief account of transport phenomenon involving various electrolytic solutions has been mentioned below:

Radhakrishnamurty and Santhakumari [111] proposed a new model under the effect of concentration gradient to acquire permeabilities and mobilities of sodium, potassium, chloride ions and many other ions through natural and three different artificial lipid membranes in aqueous potassium chloride solutions of different concentrations. This simple model based on the potential measurements of all considered ions taken in this study.

Elsherif et. al. [112] reported the ion selective properties of multivalent charged salts across silver chloride supported parchment membrane. The movement of different salts across this membrane has been calculated in terms of permeation rate. The permeation rate affected by concentration of salts, type of ion and the diameter of ion has also been studied and experimental measurements have reported that the permeation rate reduced with increase in the concentration of salt and the diameter of ion. In this study, permeation rate increases with decrease in the charge of positive ion and reduces with the charge of negative ion. This confirmed the cation exchange nature of membrane.

Many workers [113,114] reported that under the simultaneous action of gradients of hydrodynamic pressure and electric field, non – equilibrium thermo-dynamic analysis is frequently used for the explanation of membrane transport phenomena. They have studied the structural details of the membrane and characterization of membrane system in forms of a set of experimentally accessible phenomenological coefficients and calculated the various parameters like effective cross- sectional area, equivalent pore radius, in addition, an electrical nature of membrane permeant interface are needed for a proper understanding and prediction of a membrane permeation characteristics.

The phenomenological coefficients and the nature of membrane has been reported [115] for the movement of LiCl solutions in four different concentration range (10, 20, 30 and 40%) as function of concentration of dioxane in aqueous binary mixtures of dioxane across membrane treated completely with cellulose. The permeable nature of membrane examined by determination of the efficiencies of electro – kinetic energy conversion and zeta potential.

Blokhra et. al. [116] reported the experimental results for the streaming potential of $NaNO_3$, NH_4NO_3 and $(NH_4)_2SO_4$ in water at 308K temperature across chemically treated oak wood membrane. The experimental investigations have given the results that the electro-kinetic energy conversion efficiency was maximum at the half of streaming potential in each salt solution.

Blokhra et. al. [117] have also examined the filtration coefficient for ammonium sulphate, ammonium nitrate and ammonium phosphate for water at different temperatures and aqueous solutions of these salts at different concentrations and at 303K temperature through deodar wood membrane. The experimental data have shown that the ion selectivity was maximum in water and increase with rise of temperature, while in case of solutions it reduces due to increase in ionic radii of the ions of solute in the solution. The effect of concentration of solutes on the friction coefficients has also been reported and estimated.

The phenomenological permeation coefficients [118] for ammonium sulphate, ammonium nitrate and ammonium phosphate in water and their aqueous solutions have been determined at 318K temperature in different concentrations for a soil membrane of known water amount. The results have been analysed in terms of non-equilibrium theories. It has been indicated by the experimental results that the frictional coefficient affected a lot by the concentration of solute and permeation coefficients was found higher in water than that of ammonium salt solutions.

Hydrodynamic permeability for water and aqueous solutions of ammonium sulphate, magnesium sulphate and potassium sulphate across a soil membrane at 303K have been reported [119] and data has been explained in terms of the non-equilibrium thermodynamic theories. Permeability coefficients have been found to be minimum for water and maximum for potassium sulphate. The frictional coefficient and the equivalent pore radius of the soil membrane have also been determined. With the help of flow of solute and solvent across the soil interface and the effect of solute concentration on coefficient has also been calculated and discussed.

Parmar and Gupta [120] reported the studies of hydrodynamic permeability for water and aqueous solutions of urea and manganese sulphate, copper sulphate and zinc sulphate across a soil sample interface of known thickness at 303K.The experimental data and results have been interpreted in terms of irreversible thermodynamics theories and calculated the various types of permeability coefficients for the selected solutions under study. The frictional coefficient between matrix and water has been calculated and its dependence on solute concentration has also been discussed.

Transport of sodium, potassium, calcium and magnesium ions through liquid membrane containing non –cyclic inophores composed of furan units has been reported by Sharma and Asrani [121]. These oligomers exhibits the abilities to transport alkali and alkanline earth metal ions through chloroform membrane and are selective for sodium and magnesium ions. Transport of alkali metal ions is relatively more facile than that of alkaline earth metal ions. Selectivity for sodium and potassium is reduced when a mixture of cations is used. These carriers are highly selective for the pair sodium /magnesium ions as compared to the pair potassium / calcium ions.

Singh et. al. [122] have reported the electrochemical nature of membranes when permeation of electrolyte mixtures is involved. Mixed membranes potentials in conjugation with membrane conductance behaviour of cellulose acetate membrane using sodium chloride and potassium chloride solutions of different compositions have been studied for this purpose. The results showed the presence of additional electrolyte even if its concentration is same on both sides of the membranes, significantly influences electro-chemical nature of membrane.

Shahi and Co-workers [123] reported the electrochemical transport properties of cation and anion- exchange membranes in aqueous solutions of NaCl, KCl and Na_2SO_4 at different concentrations. It was observed that the ion- exchange capacity of these membrane decreases while membrane resistance increases with the increase in membrane thickness. The electrolyte concentration corresponding to iso – conductance point has been determined and it shows that thinner membranes exhibit improved electrical conductivity. On the basis of Nikonenko and Zabolotsky, describing the micro – structure of the membrane material, the counter-ion diffusion coefficient in the membrane phase has been determined. A very good relation has been found between the counter ion diffusion coefficient across the ion –exchange membrane and their ion – exchange capacity value.

Objectives of the Study

The behaviour of ions in water and mixed solvent systems in particular has highlighted the importance of specific interactions between ions and the immediate neighbour solvent molecules. During recent years there has been an increasing interest in the study of the behaviour of electrolytes in mixed solvents, as the use of mixed solvents enables one to study the nature of ion – ion and ion –solvent interactions under the varied conditions simply by changing the solvent compositions. The study of thermodynamic and transport properties of these solutions provides an opportunity for extending the range of properties from which the structure of electrolyte solution may be inferred. Thermodynamic investigations play an important role in helping to understand the nature of and extent of pattern of molecular aggregation that exist in binary mixture and their sensitivities to variations in compositions, temperature, pressure and the molecular structure of electrolyte solution.

During the last few years it has been found that ion – solvation can be better understood in mixed solvents than in pure solvents, because many physical properties like dielectric constant and viscosities can be varied to a desired value in the mixed solvents. For the study of ion – solvent interactions, water has been used extensively as a component in mixed solvents due to its easy availability, high dielectric constant and unique physiochemical properties.

In addition, It has been found that the mixed binary aqueous solvents behaves in an unexpected way as correlated with the behaviour of mixed non - aqueous solvents. These investigations have given a new impetus to a detailed study of the structure of binary aqueous mixtures. The information drawn from the studies of thermodynamic and transport properties have been related to structural aspect of the solvent and the effect of electrolyte on the structure of the liquid on the microscopic scale in terms of solute – solvent interactions and structure making/breaking capacity of various solutes. Survey of literature showed that although many studies on thermodynamic ad transport properties of electrolytes have been carried out both in single and mixed solvent systems, but a little attention has been paid to the behaviour of divalent transition metal chlorides in mixed solvent system.

Since the results in mixed aqueous organic systems highlight the importance of solvent – solvent interactions and also of interactions between co – ordinated ions and solvent molecules in H – bonding media, therefore the main objectives of the present study will be to investigate thermodynamic properties viz; partial molar volumes, and transport processes such as viscous flow and permeabilities of some divalent transition metal cholrides in the mixtures of monohyodroxy alcohols with or without inorganic membrane.

The main objectives of the present investigations are:

1. To estimate the partial molar volumes of some divalent transition metal chlorides such as manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water and water + monohydroxy alcohols.

2. To analyse the various theories used for identifying the uncoupled transport property i:e; viscous flow of some selected transition metal chlorides and magnesium chloride in water and water + monohydroxy alcohols at various temperatures .

3. To investigate the coupled transport phenomenon viz; hydrodynamic permeabilities of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water and water + monohydroxy alcohols across an inorganic membrane of aluminum oxide.

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CHAPTER – II

PARTIAL MOLAR VOLUMES OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNISUM CHLORIDES IN BINARY AQUEOUS MIXTURES OF ALCOHOLS

2.1 Introduction

From the literature survey it is clear that partial molar volume is one of the important tools in elucidating the various types of interactions occurring in aqueous and non aqueous solutions. Partial molar volume is one of the thermodynamic properties which have industrial and practical applications. It may be used to get information about how the various changes will influence a solution at equilibrium and of these ions – solvent interactions are most important. Recently, the information of ionic solutions has increased immensely. With the study of partial molar volumes of electrolytes we can also analyse the solute-solvent interactions [1-8]. It has also been realized that the solvation of solutes can be better understood in mixed solvents rather than a pure solvent.

The partial molar volume of an electrolyte or any solute, $\overline{V_2^0}$, may be visualized by considering a large reservoir of water, so that the addition of one mole of solute will not alter the concentration. The change in volume of water upon the addition of one mole of electrolyte or solute to this large reservoir of volume V is known as partial molar volume of electrolyte or solute at the indicated concentration, at constant temperature T, Pressure P, and moles of other components, $n_1, n_2, n_3, \ldots\ldots\ldots\ldots$.

Mathematically, the partial molar volume $\overline{V_2^0}$, can be represented by the partial derivation of total volume w.r.t concentration at constant T,P and n_1,..........(n_1 = number of moles of water or any other solvent).

$$\overline{V_2^0} = \left[\frac{\partial V}{\partial n_2}\right]_{TP\, n_1} \qquad (2.1)$$

The concept of partial molar volume is useful because it can be shown mathematically that

$$V = n_1\overline{V_1^0} + n_2\overline{V_2^0} + n_3\overline{V_3^0} + \text{---------},\ T,\ P \text{ constant.} \qquad (2.2)$$

The partial molar volume of an electrolyte or solute, $\overline{V_2^0}$, may be determined from the density measurements [9].

For the binary solutions the use of apparent molar volume, ϕ_V , is more convenient. The apparent molar volume of salts or solute is defined by the following relation:

$$\phi_V \left(\frac{V\text{-}n_1 v_1^0}{n_2}\right)_{T,P} \qquad (2.3)$$

where n_1 is the number of moles of water or any other solvent, n_2 is the number of moles of electrolyte or solute, V is the volume of solution containing n_1 moles of water or solvent and n_2 moles of electrolyte or solute and $\overline{V_1^0}$ is the molar volume of pure water or solvent at a given temperature, T and Pressure, P and is given by the relation:

$$\overline{V_1^0} = \frac{M_1}{d_0} \tag{2.4}$$

where M_1 and d_0 represent the molecular weight and density of water or solvent respectively at given temperature T.

The apparent molar volume in terms of experimentally measured density, d and molecular weight M_1 and M_2 of water or solvent and electrolyte or solute respectively is given by the relation:

$$\phi_v = \frac{1}{n_2}\left(\frac{n_1 M_1 + n_2 M_2}{d}\right) - n_1\overline{V_1^0} \tag{2.5}$$

When molal concentration scale is used, $n_2 = m$, the molality and n_1 is equal to the number of moles of water or solvent in 1000g, so that

$$\phi_v = \frac{M_2}{d_0} - \frac{1000(d-d_0)}{mdd_0} \tag{2.6}$$

here d_0 represents the density of pure water or solvent and d represents the density of solution.

Using the molar concentration scale $n_2 = c$, the apparent molar volume is given by the following relation:

$$\phi_v = \frac{M_2}{d_0} - \frac{1000(d-d_0)}{cd_0} \tag{2.7}$$

The partial molar volume and the apparent molar volume at infinite dilution are equal ($\phi_v^0 = \overline{V_1^0}$). To obtain reliable ϕ_v^0 or $\overline{V_2^0}$ values, it is essential to determine the density, d or the density difference between the solution and pure solvent, $(d - d_o)$ with great precision. This can be demonstrated by examining the probable error in ϕ_v, due to uncertainties in density and concentration. By differentiating equation (2.7) w.r.t c at constant d and w.r.t d at constant c, is obtained as [10]:

$$\text{Probable error in } \phi_v = \left[\frac{M_2}{d_0} - \phi_v\right]\frac{\delta c}{c} \qquad (2.8)$$

and

$$\text{Probable error in } \phi_v = \left[\frac{-1000}{c}\right]\frac{\delta d}{d_0} \qquad (2.9)$$

Equations (2.8) and (2.9) demonstrate that in dilute solutions, ϕ_v is not seriously influenced by error in c, however, error in d causes a large uncertainty in ϕ_v (e.g. when c = 0.01 M, a 1ppm error in d causes an error of 0.1 cm^3/mole in ϕ_v).

The extrapolation of the partial molar volume of solutes to infinite dilution and the expression of concentration dependence of the apparent molar volume have been made by three major equations viz; Masson equation [11], the Redlich – Meyer equation [12] and Owen – Brinkley equation [13]. Masson found that apparent molar volumes of electrolytes vary linearly with the square root of the molar concentration by the linear relation:

$$\phi_v = \phi_v^0 + S_V^* \sqrt{C} \qquad (2.10)$$

where ϕ_v^0 is the apparent molar volume at infinite dilution and S_V^* is the experimental slope which varies with electrolyte type and charge.

Redlich – Meyer [12] have suggested the use of the following extrapolation equation for given electrolyte:

$$\phi_v = \phi_v^0 + S_v \sqrt{C} + b_v C \qquad (2.11)$$

where S_v is the theoretical limiting slope and b_v is an empirical constant determined from the experimental results.

Geffecken [14] and Scott [15] have also determined the apparent molar volumes of electrolytes by equation (2.10) and found that it appropriately shows the concentration dependence over a wide temperature range (0 – 100^0C).

It is concluded by Redlich and Rosenfeld [16] that for a given salt a constant limiting slope should be obtained at constant temperature and pressure, By differentiating the Debye – Huckel limiting law for activity coefficient with respect to pressure, Redlich and Meyer[17] have calculated the theoretical limiting law slope, S_v, using the equation:

$$S_v = kw^{3/2} \tag{2.12}$$

where
$$k = N^2 e^3 \left[\frac{8\pi}{1000D^3RT}\right]^{1/2} \left[\frac{\partial \text{In D}}{\partial p} - \frac{\beta}{3}\right] \tag{2.13}$$

and e is the electrostatic charge, D the dielectric constant of the solvent and β the compressibility of the solvent and other symbols have their usual significance [10] and

$$w = 0.5 \sum_i \gamma_i Z_i^2 \tag{2.14}$$

where γ_i is the number of ions of species i and Z_i is the valency formed by one molecule of electrolyte. For electrolytes of fixed valency, w is constant and limiting slope depends only on temperature and the physical properties (D, $\frac{\partial \text{In D}}{\partial p}$ and β) of the pure solvent. Since the limiting law is not known above 70^0C, Masson equation must still be used at higher temperature.

The Redlich – Meyer extrapolation equation represents the concentration dependence of ϕ_V of many 1:1 and 2:1 electrolytes in dilute solutions; however, the studies [18 - 20] for some 2:1, 1:1 and 4:1 electrolytes show deviations from this equation.

Hepler [21] has developed a technique of examining the sign of $\left[\frac{\partial^2 \phi_V^0}{\partial T^2}\right]_P$ for different solutes in terms of long range structure promoting and breaking capacity of solutes in aqueous solutions using the general thermodynamic relation:

$$\left[\frac{\partial \overline{C_P}}{\partial P}\right]_T = -T\left[\frac{\partial^2 \phi_V^0}{\partial T^2}\right]_P \tag{2.15}$$

With help of this equation, it is concluded that solutes which have positive values act as structure promoters and solutes with negative values act as structure breakers.

The apparent molar expansibility is defined as the change in ϕ_V^0 with temperature and is given as follows:

$$\phi_E^0 = \left[\frac{\partial \phi_V^0}{\partial T}\right]_P \tag{2.16}$$

The increase in the magnitude of ϕ_E^0 per degree temperature indicates that the behaviour of electrolytes is just like the nature of symmetrical tetra - alkyl ammonium salts [22] and reverse happens in case of common [23,24] electrolytes.

In the present study, the apparent molar volumes and apparent molar expansibilities of some transition metal chlorides and magnesium chloride in water and in binary aqueous mixtures of alcohols of five different compositions viz; (5%, 10%, 15%, 20% and 35%) w/w at 303.15K were determined. These parameters were also determined in water and 5% binary aqueous mixtures of alcohol at five different temperatures 298.15, 303.15, 308.15, 313.15 and 318.15K. The results obtained have been analysed in terms of ion – ion and ion – solvent interactions.

2.2 Experimental Details

The experimental part has been explained under the following sections:

(i) Materials

(ii) Preparation of solutions

(iii) Apparatus

(iv) Experimental procedure

(v) Sources of error

(i) Materials

(a) Conductivity water: The water used for the calibration of apparatus and for preparing various solutions was obtained by distilling the water thrice over alkaline $KMnO_4$, $K_2Cr_2O_7$ and quartz having specific conductance of the order 10^{-6} $Ohm^{-1}cm^{-1}$.

(b) Reagents: The reagents, magnesium chloride [$MgCl_2.6H_2O$, M.W. 203.30 g], manganese chloride [$MnCl_2.4H_2O$, M.W. 197.9 g], nickel chloride [$NiCl_2.6H_2O$, M.W. 237.71 g] , copper chloride [$CuCl_2.2H_2O$, M.W. 170.48 g], cobalt chloride [$CoCl_2.6H_2O$, M.W. 237.93 g] and cadmium chloride [$CdCl_2.H_2O$, M.W. 201.32] were of AnalR grade and used as such only after drying over anhydrous calcium oxide in a desiccator.

(c) Purifications of methanol and ethanol: Methanol and ethanol of AnalR grade were used after purification as follows:

Purification of methanol and ethanol was done using distillation method which purify the solvent on the basis of the difference in boiling point of various components present in the impure solvents. Solvents were first kept standing over calcium hydroxide for about 48 hours and then distilled. The first and last fractions were discarded. The central fraction was refluxed again and refractioned to obtain the methanol and ethanol for the present studies. The density of purified methanol was found to be 0.7817 gcm^{-3} is in good agreement with literature value d = 0.7818 gcm^{-3} and density of purified ethanol was found to be 0.7820 gcm^{3} [25] is in good agreement with literature value d = 0.7818 gcm^{-3} [25].

(ii) Preparation of solutions

The different compositions of methanol + water and ethanol + water and solutions of different salts were prepared by weight. The molality (m) of different salt solutions was converted into molarity (c) using the following relation [26]:

$$c = \frac{md1000}{1000 + mM_2} \tag{2.17}$$

where c is molarity, d is density of salt solution, m is molality and M_2 is molecular weight of salt.

(iii) Apparatus

For the calculation of partial molar volumes, densities of above mentioned salts were measured with the help of an apparatus shown in Fig.1, similar to the one described by “Ward and Millero [26].

In this apparatus a glass float A is suspended from a balance pan G with the help of a nylon thread H into a cylindrical sample container B of 250 ml capacity. The glass cell has a Bakelite top F with a hole in the centre of nylon thread to pass through. The cell was placed in water-bath having a stirrer E and thermometer D. The whole assembly of sample container and water-bath was placed in thermostat whose temperature was controlled with the help of an electronic relay. The fluctuation in the temperature was always within $\underline{+}$ 0.01^{0}C.

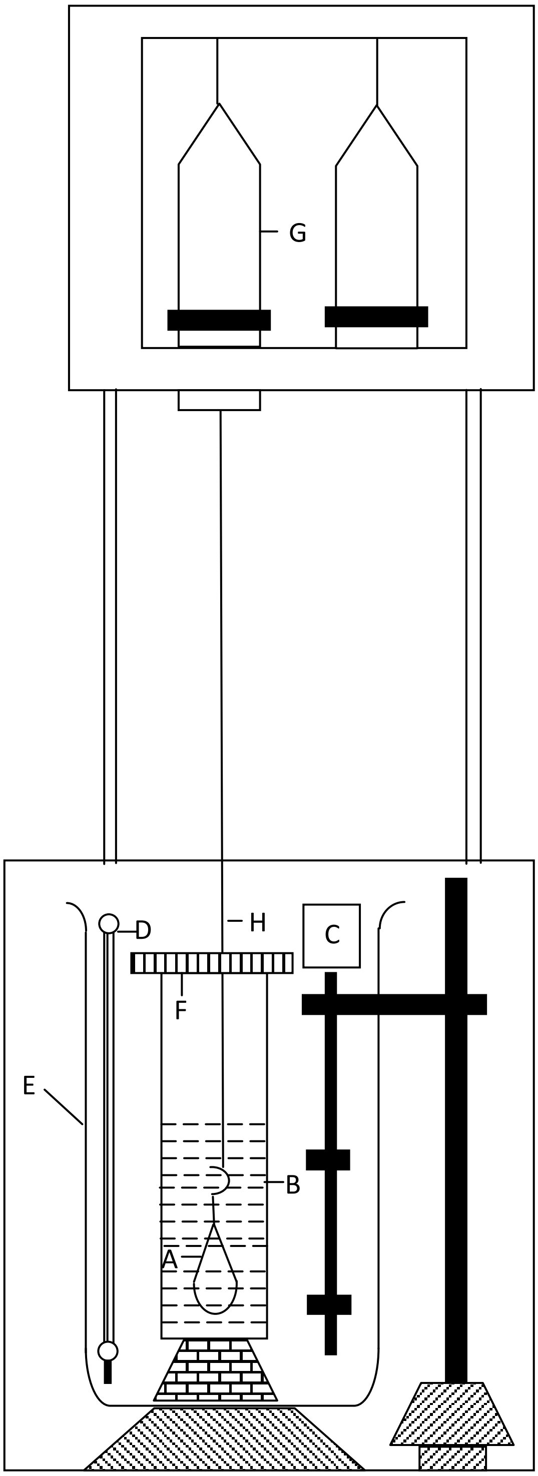

Fig.1: APPARATUS FOR MEASUREMENT OF DENSITY

(iv) Experimental procedure

The sample container and glass float was thoroughly cleaned by washing them with chromic acid first and then with acetone. The float was completely dried with the help of hot air blower.

A 28.895 g float of volume 26.528 ± 0.004 cm^3 at 308.15K was used. The volume of float was determined with the help of following equation [27]:

$$V_f = \left[\frac{W_{air} - W_{water}}{d_0}\right]_T$$

where W_{air} is the weight of float in air and W_{water} is weight of float in water. The quantity $W_{air} - W_{water}$ is the loss of weight of float in water and d_0 is the density of water at a particular temperature T. To obtainW_{water}, sample container was filled with water so that the level of water comes up to a fixed mark in the container. The densities of solutions were calculated using the following relation:

$$d - d_0 = \frac{W_0 - W}{V_f}$$

where d is the density of solution under study and d_0 is the density of pure water at a particular temperature, W_0 is the weight of float in pure water, W is the weight of float in solution under study and V_f is the volume of float.

The calibration of float was checked by determining density of pure methanol at 308.15K. Our value of density of methanol d = 0.77701 g cm^{-3} is in good agreement with literature value [28] d = 0.77703 g cm^{-3}.

(v) Sources of Error

(a) Fluctuation of temperature: Density is a function of temperature, and it changes to a large extent by a small change in temperature than by any other variables. So even a small change in temperature of thermostat will cause a larger error in density. This error has been avoided by placing the glass cell in a water bath where the temperature fluctuations are always controlled within ± 0.01^0C.

(b) Evaporation of the solution: A small change in the level of solution in the cell introduces a major error in the reproducibility of the weight of float in the solution. The solution can evaporate and this was avoided by having a Bakelite top with a hole in it and the level of the solution just before and after taking the weight of float was checked and no change has been observed.

(c) Improper suspension of float: A significant error is caused in the weight of float, if the float slightly touches the sides of cell or if the suspension thread touches the sides of lid. This has been avoided by careful suspension.

(d) Entrapped air bubbles: Solution in the sample container was stirred in order to avoid error due to the air bubble attached to the float.

(e) Solvent and solute purity: The error due to these impurities was minimized by using AnalaR grade chemicals and conductivity water for making the solutions.

2.3 Results and Discussion

In the present study, the apparent molar volumes of some divalent transition metal chlorides and magnesium chloride have been estimated in water and in binary aqueous mixtures of methanol and ethanol from the density measurements in various concentrations of electrolytes and at different temperatures.

The results for different systems studied have been explained under the following sections A, B and C.

Section –A

Discussion on the Results of Some Divalent Transition Metal Chlorides and Magnesium Chloride in Water.

Densities of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride have been determined by Ward and Millero method in water at 303.15K. The apparent molar volumes (ϕ_V) have been calculated directly from the density data using equation (2.7). The densities and apparent molar volumes of the above mentioned electrolytes in water at 303.15K are given in Table 2.I.

It has been noticed that the apparent molar volumes (ϕ_v) of above mentioned divalent transition metal chlorides and magnesium chloride vary linearly with the square root of molar concentration of the electrolyte solution in water in conformity with Masson’s equation (2.10) in the concentration range, studied here, at 303.15K. Plots for all above mentioned transition metal chlorides and magnesium chloride in water at 303.15K are shown in Fig 2.

TABLE - 2.I

DENSITIES, APPARENT MOLAR VOLUMES FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

Concentration c X 10^2 (mol dm^{-3})	Density d (g cm^{-3})	Apparent molar volume ϕ_V (cm^3 mol^{-1})
		d_0 = 0.99565 gcm^{-3}
	Manganese chloride	
0.497	0.99625	77.67
0.696	0.99648	79.09
0.994	0.99682	80.65
2.979	0.99893	88.18
4.955	1.00090	92.36
6.922	1.00256	98.50
9.852	1.00478	105.7
	Cobalt chloride	
0.497	0.99622	123.90
0.696	0.99644	125.00
0.994	0.99677	125.80
2.975	0.99890	129.30
4.945	1.00090	132.40
6.905	1.00286	134.10
9.822	1.00565	136.70
	Nickel chloride	
0.497	0.99640	87.36
0.696	0.99667	91.66
0.994	0.99708	94.36
2.978	0.99980	98.79
4.952	1.00229	104.09
6.917	1.00471	107.21
9.848	1.00830	109.74
	Copper chloride	
0.497	0.99629	42.08
0.696	0.99652	45.81
0.995	0.99686	49.11
2.982	0.99924	50.33
4.965	1.00146	53.69
6.943	1.00373	54.34

9.899	1.00682	57.90

Cadmium chloride

0.497	0.99633	64.96
0.696	0.99659	66.67
0.995	0.99697	68.95
2.980	0.99954	71.11
4.959	1.00192	75.22
6.931	1.00418	78.60
9.875	1.00743	82.39

Magnesium Chloride

0.497	0.99595	143.62
0.696	0.99607	143.61
0.994	0.99624	144.59
2.973	0.99727	149.48
4.940	0.99818	152.76
6.894	0.99897	155.83
9.801	1.00007	158.90

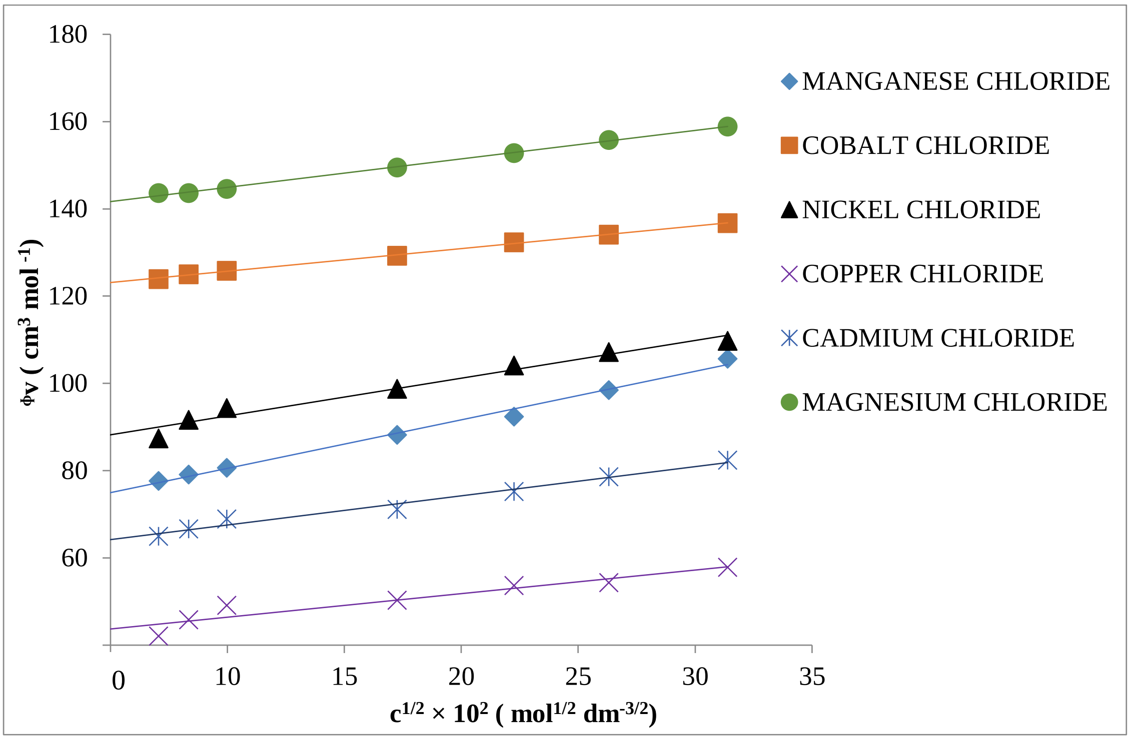

Fig.2: PLOTS OF ϕ_V VS $c^{1/2}$ FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

The limiting apparent molar volume ($\phi_V^0 = \overline{V_2^0}$), known as the partial molar volume has been calculated by using the least square fit to the linear plots of the experimental values of ϕ_V vs $\sqrt{c}$, using Masson's equation (2.10).The values of limiting apparent molar volumes (partial molar volumes) (ϕ_V^0) and experimental slopes (S_V^*) obtained for above mentioned salts in water at 303.15K are recorded in Table 2.II.

It is clear from Table 2.II. that values of S_V^* are positive and large for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride thereby showing the presence of strong ion – ion interactions. Further, as ϕ_V^0 is a measure of ion – solvent interactions (ion – ion interactions vanish at infinite dilution), therefore, it is clear from Table 2.II. that the values of ϕ_V^0 are positive for all the salts studied here in water at 303.15K, thereby showing the presence of strong ion – solvent interactions. It is also concluded from the ϕ_V^0 values that ion – solvent interactions follow the order for the divalent transition metal chlorides and magnesium chloride in water at 303.15K as:

Magnesium chloride > Cobalt chloride > Nickel chloride > Manganese chloride > Cadmium chloride > Copper chloride

As chloride ion (Cl^-) is a common ion in all the salts studied here in water at 303.15K, so it may be inferred that the solvation order for different cations in water follow the order:

$$Mg^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+} > Cd^{2+} > Cu^{2+}$$

TABLE - 2.II

LIMITING APPARENT MOLAR VOLUMES (ϕ_V^0) AND EXPERIMENTAL SLOPES (S_V^*) FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

Electrolyte	$\phi_V^0 = \overline{V_2^0}$ ($cm^3 mol^{-1}$)	S_V^* ($cm^3\ dm^{3/2}\ mol^{-3/2}$)
Manganese chloride	69.39	1.11
Cobalt chloride	120.51	0.51
Nickel chloride	83.88	0.86
Copper chloride	41.01	0.53
Cadmium chloride	60.80	0.66
Magnesium chloride	138.39	0.65

Effect of temperature:

Densities and apparent molar volumes, for all the above mentioned divalent transition metal chlorides and magnesium chloride in water at five different equidistant temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K) are given in Table – 2.III**.** Values of apparent molar volumes are plotted against the square root of concentration and linear plots have been found for all the electrolytes in water at different temperatures. A sample plot for cobalt chloride is shown in Fig.3.The values of limiting apparent molar volume (ϕ_V^0) and experimental slopes(S_V^*) obtained by using least – squares treatment to the Masson equation (2.10) are also recorded in Table 2.IV.

It is evident from Table 2.IV that the values of S_V^* are positive for all the divalent transition metal chlorides and magnesium chloride at temperatures studied here, hence showing the presence of strong ion – ion interactions. Also, it is clear that the values of S_V^* increase with increase in temperature from 298.15K to 318.15K for all above mentioned electrolytes thereby indicating that ion –ion interactions further improve with the increase in temperature.

It is also clear from Table 2.IV that the values of ϕ_V^0 are positive for all the above mentioned salts and magnesium chloride in water in whole of the temperature range. This shows the presence of strong ion – solvent interactions. It is also clear from Table 2.IV that the value of ϕ_v^0 for (for the above mentioned) individual electrolyte decreases with rise in temperature thereby showing that ion – solvent interactions further decrease with the increase of temperature. In other words it may be said that the solvation of all the ions is further reduced with the rise in temperature.

The temperature dependence of ϕ_v^0 in water for all the selected divalent transition metal chlorides and magnesium chloride can be expressed by the following equations:

$$\phi_v^0 = 4425.42 - 27.14\ T + 0.042T^2 \text{ for manganese chloride} \qquad (2.18)$$

$$\phi_v^0 = 643.41 - 2.11\ T + 0.001T^2 \text{ for cobalt chloride} \qquad (2.19)$$

$$\phi_v^0 = 5065.59 - 31.53\ T + 0.049T^2 \text{ for nickel chloride} \qquad (2.20)$$

$$\phi_v^0 = 5831.60 - 37.25\ T + 0.050T^2 \text{ for copper chloride} \qquad (2.21)$$

$$\phi_\nu^0 = 4679.46 - 37.25\ T + 0.040T^2 \text{ for cadmium chloride} \qquad (2.22)$$

TABLE - 2.III

DENSITIES AND APPARENT MOLAR VOLUMES OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT DIFFERENT TEMPERATURES.

Concentration $c \times 10^2$ (mol dm^{-3})	Density d (g cm^{-3})	Partial molar volume ϕ_V (cm^3 mol^{-1})
Manganese chloride		
Temperature = 298.15K		**d_o = 0.99705 g cm^{-3}**
0.498	0.99762	83.76
0.697	0.99784	84.89
0.996	0.99814	88.74
2.983	1.00022	91.90
4.962	1.00225	93.38
6.931	1.00395	98.65
9.866	1.00614	106.1
Temperature = 303.15		**d_o = 0.99565 g cm^{-3}**
0.497	0.99625	77.67
0.696	0.99648	79.09
0.994	0.99682	80.65
2.979	0.99893	88.18
4.955	1.00090	92.36
6.922	1.00256	98.50
9.852	1.00478	105.70
Temperature = 308.15K		**d_o = 0.99403 g cm^{-3}**
0.496	0.99467	69.50
0.695	0.99490	73.24
0.993	0.99524	76.54
2.974	0.99742	84.44
4.947	0.99934	91.12
6.912	1.00115	95.47
9.838	1.00330	104.30
Temperature = 313.15K		**d_o = 0.99220 g cm^{-3}**
0.495	0.99285	67.36
0.694	0.99310	68.79
0.991	0.99348	69.35
2.969	0.99574	79.31
4.939	0.99774	86.42
6.901	0.99963	90.96
9.823	1.00181	100.90
Temperature = 318.15K		**d_o = 0.99022 g cm^{-3}**
0.495	0.99094	52.96
0.692	0.99120	57.02

0.989	0.99158	61.07
2.964	0.99402	70.40
4.932	0.99624	76.60
6.891	0.99820	82.92
9.813	1.00076	91.39

Cobalt chloride

Temperature = 298.15K		**d_o = 0.99705 g cm^{-3}**
0.498	0.99759	129.92
0.697	0.99708	130.76
0.995	0.99811	131.87
2.979	1.00012	135.28
4.951	1.00206	137.15
6.912	1.00395	138.52
9.832	1.00663	140.91
Temperature = 303.15K		**d_o = 0.99565 g cm^{-3}**
0.497	0.99622	123.90
0.696	0.99644	125.02
0.994	0.99677	125.85
2.975	0.99890	129.27
4.945	1.00090	132.35
6.905	1.00286	134.10
9.822	1.00565	136.72
Temperature = 308.15K		**d_o = 0.99403 g cm^{-3}**
0.496	0.99463	117.84
0.695	0.99486	119.26
0.992	0.99520	120.81
2.971	0.99742	124.57
4.938	0.99953	127.33
6.895	1.00153	129.94
9.810	1.00440	133.02
Temperature = 313.15K		**d_o = 0.99220 g cm^{-3}**
0.495	0.99283	111.74
0.694	0.99307	113.45
0.991	0.99344	113.70
2.966	0.99578	118.16
4.931	0.99797	121.87
6.886	1.00012	123.88
9.798	1.00313	127.37
Temperature = 318.15K		**d_o = 0.99022 g cm^{-3}**
0.494	0.99090	101.51
0.692	0.99116	103.23
0.989	0.99154	105.52
2.961	0.99406	109.32
4.923	0.99647	112.09
6.876	0.99873	115.30
9.787	1.00208	117.91

Nickel chloride

Temperature = 298.15K		**d_o = 0.99705 g cm^{-3}**
0.498	0.99776	95.50
0.697	0.99803	97.48
0.996	0.99841	101.46
2.982	1.00108	102.86
4.959	1.00365	104.93
6.926	1.00602	108.53
9.857	1.00915	115.29
Temperature = 303.15K		**d_o = 0.99565 g cm^{-3}**
0.497	0.99640	87.36
0.696	0.99667	91.66
0.994	0.99708	94.36
2.978	0.99980	98.79
4.952	1.00229	104.09
6.917	1.00471	107.21
9.848	1.00830	109.74
Temperature = 308.15K		**d_o = 0.99403 g cm^{-3}**
0.496	0.99486	71.078
0.695	0.99516	75.67
0.993	0.99561	79.10
2.974	0.99867	82.22
4.949	1.00161	85.06
6.914	1.00421	91.02
9.845	1.00794	97.00
Temperature = 313.15K		**d_o = 0.99220 g cm^{-3}**
0.495	0.99303	70.89
0.694	0.99337	69.71
0.991	0.99382	74.89
2.969	0.99687	81.07
4.940	0.99981	84.32
6.903	1.00260	87.74
9.830	1.00645	93.48
Temperature = 318.15K		**d_o = 0.99022 g cm^{-3}**
0.495	0.99109	62.54
0.692	0.99142	65.14
0.989	0.99195	63.51
2.964	0.99515	72.10
4.932	0.99820	76.67
6.893	1.00114	80.07
9.817	1.00513	86.69

Copper chloride

Temperature = 298.15K		**d_o = 0.99705 g cm^{-3}**
0.498	0.99765	50.24
0.697	0.99788	51.67
0.996	0.99822	53.23

2.986	1.00048	55.78
4.970	1.00263	58.40
6.949	1.00467	61.02
9.907	1.00768	63.38
Temperature = 303.15K		**d_o = 0.99565 g cm^{-3}**
0.497	0.99629	42.08
0.696	0.99652	45.81
0.995	0.99686	49.11
2.982	0.99924	50.33
4.965	1.00146	53.69
6.943	1.00373	54.34
9.899	1.00682	57.90
Temperature = 308.15K		**d_o = 0.99403 g cm^{-3}**
0.496	0.99471	33.84
0.695	0.99497	35.57
0.993	0.99535	37.86
2.978	0.99787	41.80
4.959	1.00033	43.71
6.935	1.00255	47.91
9.890	1.00587	51.07
Temperature = 313.15K		**d_o = 0.99220 g cm^{-3}**
0.496	0.99288	33.65
0.694	0.99314	35.38
0.991	0.99352	37.69
2.972	0.99605	41.30
4.950	0.99846	44.36
6.922	1.00068	48.35
9.872	1.00407	50.64
Temperature = 318.15K		**d_o = 0.99022 g cm^{-3}**
0.495	0.99094	25.29
0.693	0.99120	29.36
0.989	0.99161	30.36
2.967	0.99429	33.67
4.942	0.99685	36.69
6.912	0.99922	40.67
9.858	1.00268	44.53

Cadmium chloride

Temperature = 298.15K		**d_o = 0.99705 g cm^{-3}**
0.498	0.99769	73.11
0.697	0.99792	76.83
0.996	0.99826	80.1
2.983	1.00059	82.92
4.964	1.00282	85.34
6.936	1.00489	88.56
9.880	1.00795	91.27
Temperature = 303.15K		**d_o = 0.99565 g cm^{-3}**
0.497	0.99633	64.96

0.696	0.99659	66.67
0.995	0.99697	68.95
2.980	0.99954	71.12
4.959	1.00192	75.23
6.931	1.00418	78.6
9.875	1.00743	82.39
Temperature = 308.15K		**d_o = 0.99403 g cm^{-3}**
0.496	0.99474	58.78
0.695	0.99501	60.78
0.993	0.99542	61.77
2.976	0.99799	68.67
4.952	1.00044	72.32
6.921	1.00278	75.36
9.863	1.00624	78.00
Temperature = 313.15K		**d_o = 0.99220 g cm^{-3}**
0.496	0.99294	52.53
0.694	0.99322	54.83
0.991	0.99363	57.56
2.971	0.99635	62.13
4.944	0.99891	66.14
6.912	1.00136	69.34
9.850	1.00487	73.27
Temperature = 318.15K		**d_o = 0.99022 g cm^{-3}**
0.495	0.99100	44.18
0.692	0.99130	45.91
0.989	0.99175	47.20
2.965	0.99459	54.51
4.936	0.99730	58.48
6.901	0.99986	62.25
9.836	1.00347	67.28

Magnesium chloride

Temperature = 298.15K		**d_o = 0.99705 g cm^{-3}**
0.498	0.99728	157.60
0.697	0.99737	157.88
0.995	0.9975	158.57
2.976	0.99829	162.13
4.944	0.99897	164.97
6.898	0.99958	167.13
9.805	1.00044	169.24
Temperature = 303.15K		**d_o = 0.99565 g cm^{-3}**
0.497	0.99595	143.63
0.696	0.99607	143.61
0.994	0.99624	144.60
2.973	0.99727	149.48
4.940	0.99818	152.77
6.894	0.99897	155.83
9.801	1.00007	158.91

Temperature = 308.15K		**d_o = 0.99403 g cm^{-3}**
0.496	0.99436	137.69
0.695	0.99448	139.41
0.992	0.99466	140.68
2.969	0.99569	148.28
4.932	0.99659	152.32
6.883	0.99738	155.57
9.785	0.9984	159.60
Temperature = 313.15K		**d_o = 0.99220 g cm^{-3}**
0.495	0.99258	127.66
0.693	0.99273	127.93
0.990	0.99292	131.68
2.964	0.99416	138.27
4.926	0.99533	140.88
6.876	0.99638	143.65
9.773	0.99718	153.55
Temperature = 318.15K		**d_o = 0.99022 g cm^{-3}**
0.494	0.99063	121.64
0.692	0.99078	123.66
0.989	0.99101	124.65
2.959	0.99240	130.92
4.917	0.99353	137.34
6.865	0.99470	139.42
9.760	0.99587	146.86

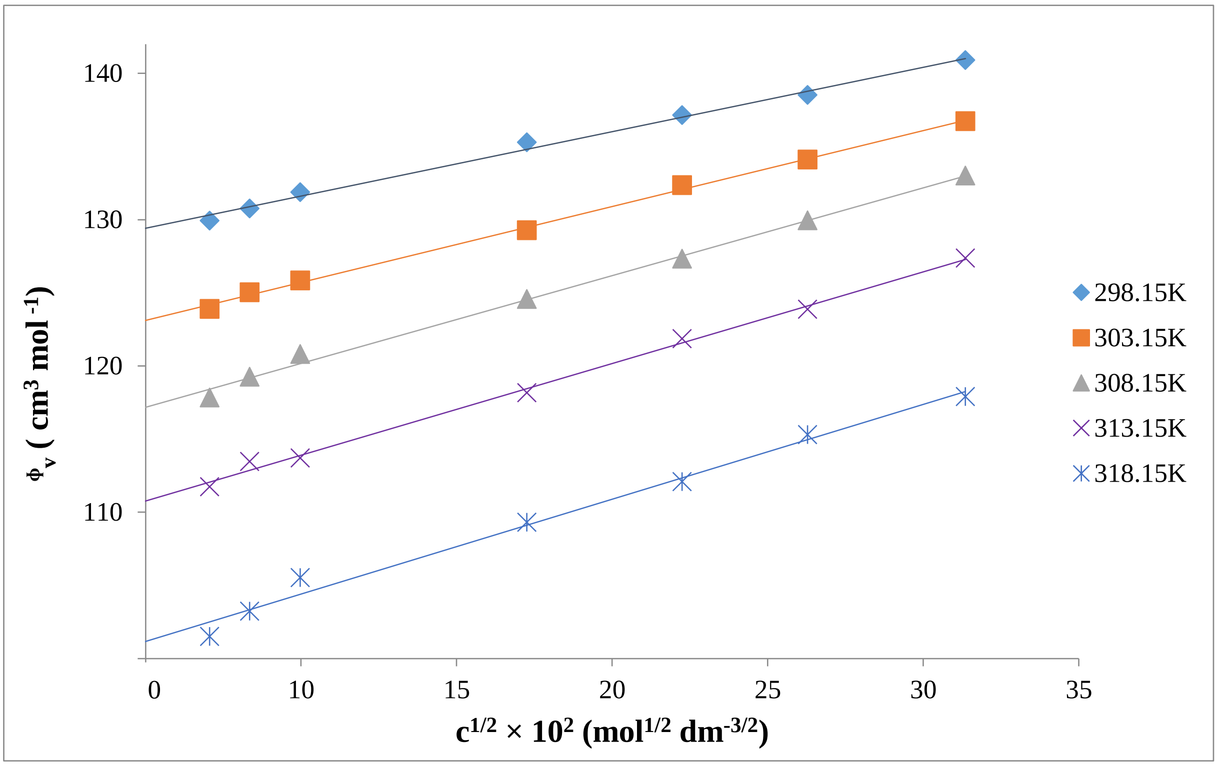

Fig.3: PLOTS OF ϕ_V VS $\sqrt{c}$ FOR COBALT CHLORIDE IN WATER AT DIFFERENT TEMPERATURES

TABLE - 2.IV

VALUES OF LIMITING APPARENT MOLAR VOLUMES (ϕ_V^0) AND EXPERIMENTAL SLOPES (S_V^*) FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT DIFFERENT TEMPERATURES.

Temperature (K)	$\phi_V^0 = \overline{V_2^0}$ **(cm^{3}mol^{-1})**	S_V^* **(cm^3 dm$^{3/2}$ mol$^{-3/2}$)**
	Manganese chloride	
298.15	78.40	0.80
303.15	69.39	1.11
308.15	61.62	1.33
313.15	56.82	1.35
318.15	44.33	1.48
	Cobalt chloride	
298.15	127.20	0.44
303.15	120.51	0.51
308.15	114.19	0.60
313.15	107.63	0.62
318.15	97.93	0.64
	Nickel chloride	
298.15	91.81	0.67
303.15	83.88	0.86
308.15	67.02	0.91
313.15	64.06	0.92
318.15	55.53	0.96
	Copper chloride	
298.15	47.26	0.51
303.15	41.01	0.53
308.15	30.03	0.66
313.15	29.78	0.67
318.15	22.16	0.69
	Cadmium chloride	
298.15	71.08	0.65
303.15	60.80	0.66
308.15	53.98	0.79
313.15	48.11	0.80
318.15	37.94	0.93
	Magnesium chloride	
298.15	153.80	0.49
303.15	138.39	0.65
308.15	131.82	0.90
313.15	120.63	0.97
318.15	114.71	0.99

$$\phi_v^0 = 4886.95 - 28.45\, T + 0.040 T^2 \text{ for magnesium chloride} \tag{2.23}$$

where T is the temperature expressed in Kelvin (K).

The limiting molar expansibilities , $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]_P$ values were calculated using equations (2.18 to 2.23) for selected divalent transition metal chlorides and magnesium chloride in water and are recorded in Table 2.V. It is clear, from Table 2.V, that the values of ϕ_E^0 for all the selected transition metal chlorides and magnesium chloride at different temperatures are negative but increase in the magnitude with rise in temperatures, which shows that these transition metal chlorides and magnesium chloride behave like those of symmetrical tetra alkyl ammonium salts [22] and not like common electrolytes [23, 24]. The increase in the magnitude of ϕ_E^0 values with increase in temperature may be ascribed to the presence of "packing effect" [22 - 24]. The variation of ϕ_E^0 with temperature has been found to be linear in water for all the transition metal chlorides and magnesium chloride and sample plots for manganese chloride and magnesium chloride are shown in Figs. 4 and 5 respectively.

During the recent years, it has been proposed by a number of workers that S_V^* is not the sole criterion for determining the structure making or breaking nature of any solute. Hepler [21] has developed a method of examining the sign of $\left[\frac{\partial^2 \phi_V^0}{\partial T^2}\right]_P$ for various solutes in terms of long range structure making/breaking behaviour of the solutes in aqueous solution using general thermodynamic relation $(\partial Cp)/\partial P) = -T\left(\frac{\partial^2 \phi_V^0}{\partial T^2}\right)p$

With the help of this relationship, it has been derived that the structure making solutes should have positive values, while structure breaking solutes should have negative values. In the present case, the values of $\left(\frac{\partial^2 \phi_V^0}{\partial T^2}\right)p$ for all transition metal chlorides and magnesium chloride are positive in water. This reveals that all the selected transition metal chlorides and magnesium chloride act as structure promoters in water.

TABLE - 2.V

VALUES OF LIMITING MOLAR EXPANSIBILITIES (ϕ_E^0) FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT DIFFERENT TEMPERATURES.

Electrolyte	**ϕ_E^0 (cm^3 mol^{-1} K^{-1})**				
Temperature (K)	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
Manganese chloride	-2.09	-1.68	-1.26	-0.84	-0.42
Cobalt chloride	-1.33	-1.32	-1.30	-1.29	-1.28
Nickel chloride	-2.31	-1.82	-1.33	-0.84	-0.35
Copper chloride	-7.43	-6.93	-6.43	-5.94	-5.43
Cadmium chloride	-2.27	-1.83	-1.39	-0.95	-0.51
Magnesium chloride	-4.59	-4.19	-3.79	-3.39	-2.99

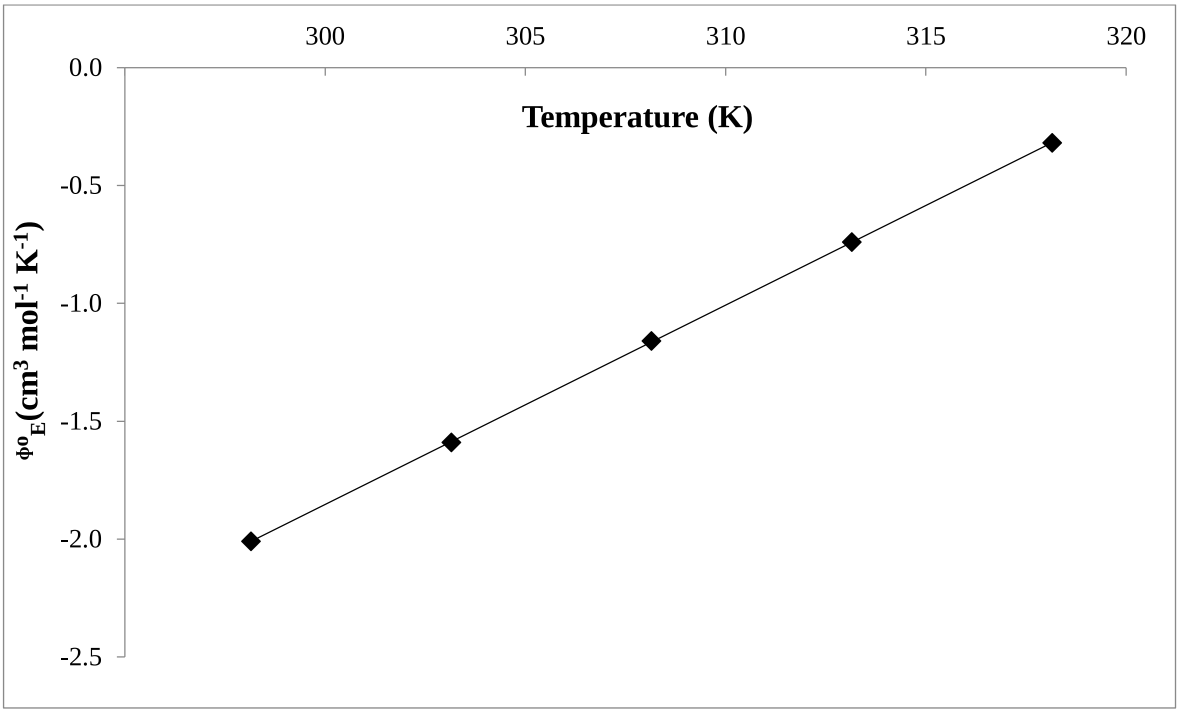

Fig. 4: VARIATION OF ϕ_E^0 WITH TEMPERATURE FOR MANGANESE CHLORIDE IN WATER.

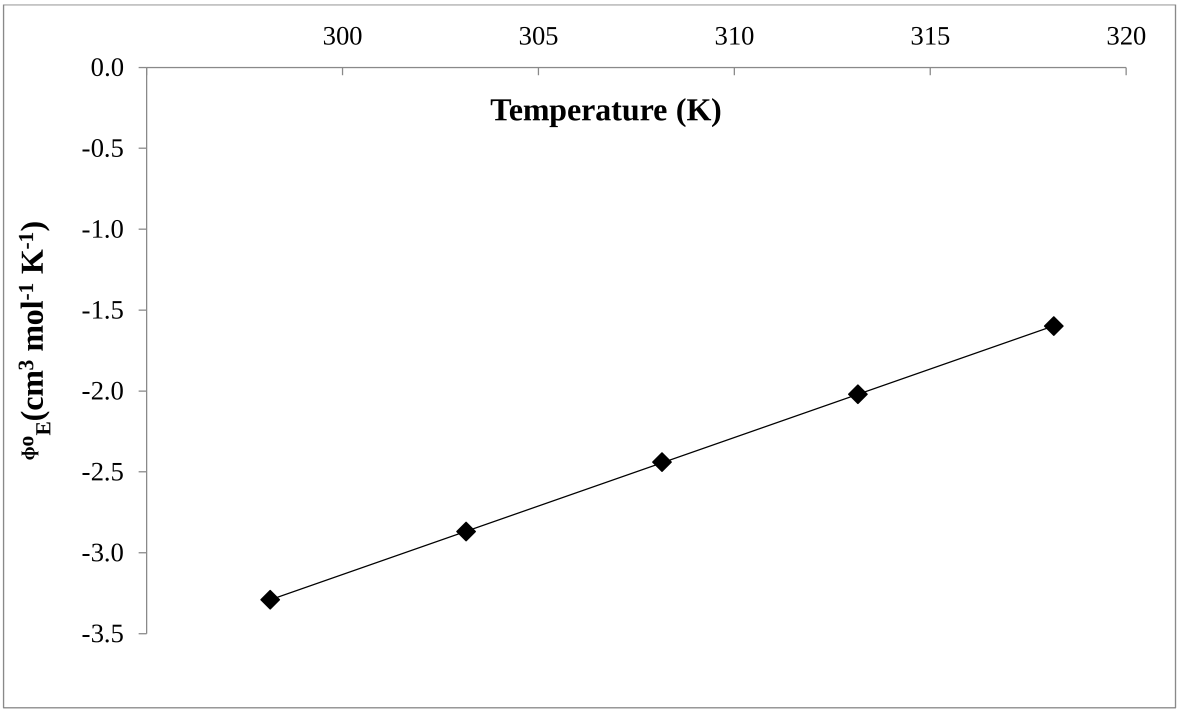

Fig. 5: VARIATION OF ϕ_E^0 WITH TEMPERATURE FOR MANGENSIUM CHLORIDE IN WATER.

Section-B

Discussion on the Results of Some Divalent Transition Metal Chlorides and Magnesium Chloride in Binary Aqueous Mixtures of Methanol

Densities and apparent molar volumes of divalent transition metal chlorides viz; manganese chloride, cobalt chloride, nickel chloride, copper chloride cadmium chloride and magnesium chloride in different compositions of binary aqueous mixtures of methanol (5, 10, 15, 20, 35 wt. percentage of methanol) at 303.15K are given in Table – 2.VI.

According to Masson equation apparent molar volumes (ϕ_V) should vary linearly with the square root of molar concentration ($\sqrt{c}$) and the same has been found true for all the selected divalent transition metal chlorides and magnesium chloride in different binary aqueous mixtures of methanol at 303.15K. Sample plots for nickel chloride and magnesium chloride are shown in Figs. 6 and 7 respectively.

The values of limiting apparent molar volumes(ϕ_V^0) and the experimental slopes (S_V^*), calculated by using the least square fit to linear plots of ϕ_V vs $\sqrt{c}$ for the divalent transition metal chlorides and magnesium chloride in different compositions of binary aqueous mixture of methanol at 303.15 K are also recorded in Table – 2.VII.

It is clear from Table – 2.VII, that the values of slopes (S_V^*) are positive for all the divalent transition metal chlorides and magnesium chloride in the different compositions of binary aqueous mixtures of methanol at 303.15K, thereby showing the presence of strong ion – ion interactions. It is also clear from Table – 2.VII that the values of S_V^* for an individual electrolyte increases with the increase in methanol content in water thereby suggesting that ion – ion interactions are further strengthened with the increase of methanol content. In other words, it may be said that the solvation of ions decreases with the increase of methanol in water which may be attributed to greater solvent – solvent (methanol - water) interactions i.e. methanol has more affinity for water than that of electrolyte. These results in binary mixtures of methanol also suggest the possible explanation for the absence of negative S_V^* values (i.e. negative slopes) for the divalent transition metal chlorides and magnesium chloride in different methanol + water mixtures at 303.15K.

Although, at infinite dilution all the above mentioned electrolytes are completely dissociated in different compositions of methanol + water, the situation would be different at higher

TABLE - 2.VI

DENSITIES AND APPARENT MOLAR VOLUMES FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K.

Concentration $c \times 10^2$ ($mol\ dm^{-3}$)	**Density** d ($g\ cm^{-3}$)	**Partial molar volume** ϕ_V ($cm^3\ mol^{-1}$)
Manganese chloride		
5% (w/w) Methanol + water		**$d_o = 0.98560\ g\ cm^{-3}$**
0.492	0.98626	64.86
0.689	0.98651	66.90
0.984	0.98688	68.93
2.950	0.98934	72.18
4.909	0.99164	75.97
6.862	0.99387	78.51
9.778	0.99715	80.94
10% (w/w) Methanol + water		**$d_o = 0.98208\ g\ cm^{-3}$**
0.490	0.98275	62.53
0.687	0.98300	65.18
0.981	0.98336	68.71
2.940	0.98585	70.94
4.892	0.98816	74.97
6.838	0.99046	76.73
9.744	0.99371	79.98
15% (w/w) Methanol + water		**$d_o = 0.97420\ g\ cm^{-3}$**
0.487	0.97488	59.80
0.681	0.97514	61.59
0.973	0.97552	63.97
2.916	0.97805	67.65
4.854	0.98050	69.93
6.784	0.98269	74.70
9.670	0.98617	76.08
20% (w/w) Methanol + water		**$d_o = 0.97089\ g\ cm^{-3}$**
0.485	0.97160	53.15
0.679	0.97187	55.26
0.970	0.97229	55.23
2.907	0.97485	63.54
4.838	0.97734	66.54
6.764	0.97980	68.18

9.643	0.98342	70.00
35% (w/w) Methanol + water		**d_o = 0.94954 g cm^{-3}**
0.474	0.95025	50.89
0.664	0.95053	51.50
0.949	0.95094	53.06
2.843	0.95354	60.28
4.733	0.95607	63.13
6.617	0.95849	65.99
9.434	0.96207	68.54

Cobalt chloride

5% (w/w) Methanol + water		**d_o = 0.98560 g cm^{-3}**
0.492	0.98613	132.21
0.689	0.98634	132.48
0.984	0.98664	134.20
2.944	0.98858	138.72
4.893	0.99039	142.09
6.830	0.99209	145.00
9.714	0.99455	147.92
10% (w/w) Methanol + water		**d_o = 0.98208 g cm^{-3}**
0.490	0.98263	128.14
0.686	0.98284	129.60
0.980	0.98315	131.18
2.934	0.98514	136.09
4.877	0.98702	139.13
6.807	0.98876	142.36
9.682	0.99129	145.41
15% (w/w) Methanol + water		**d_o = 0.97420 g cm^{-3}**
0.486	0.97477	124.04
0.681	0.97499	125.21
0.973	0.97531	127.12
2.911	0.97737	132.46
4.838	0.9793	136.04
6.755	0.98111	139.23
9.607	0.98364	143.37
20% (w/w) Methanol + water		**d_o = 0.97089 g cm^{-3}**
0.485	0.97147	121.93
0.679	0.97169	123.72
0.969	0.97202	125.04
2.901	0.9741	131.11
4.822	0.97602	135.50
6.732	0.97784	138.74
9.575	0.98036	143.20
35% (w/w) Methanol + water		**d_o = 0.94954 g cm^{-3}**

0.474	0.95013	119.62
0.664	0.95036	120.54
0.948	0.95070	121.76
2.838	0.95282	128.86
4.717	0.95479	133.38
6.586	0.95660	137.68
9.369	0.95924	141.54

Nickel chloride

5% (w/w) Methanol + water		**d_o = 0.98560 g cm^{-3}**
0.492	0.98627	103.17
0.689	0.98653	104.32
0.984	0.98692	105.16
2.947	0.98941	110.02
4.900	0.99179	113.03
6.844	0.99406	115.77
9.741	0.99734	118.91
10% (w/w) Methanol + water		**d_o = 0.98208 g cm^{-3}**
0.490	0.98276	100.97
0.687	0.98303	101.24
0.981	0.98342	102.97
0.293	0.98597	107.18
4.883	0.98838	110.70
6.821	0.99069	113.52
9.709	0.99401	116.93
15% (w/w) Methanol + water		**d_o = 0.97420 g cm^{-3}**
0.486	0.97490	96.42
0.681	0.97517	97.90
0.973	0.97557	99.51
2.913	0.97816	104.50
4.845	0.98062	108.00
6.768	0.98296	111.15
9.634	0.98635	114.56
20% (w/w) Methanol + water		**d_o = 0.97089 g cm^{-3}**
0.485	0.97160	94.12
0.679	0.97187	96.21
0.970	0.97229	96.17
2.904	0.97489	102.96
4.829	0.97738	106.43
6.746	0.97976	109.41
9.603	0.98320	112.81
35% (w/w) Methanol + water		**d_o = 0.94954 g cm^{-3}**
0.474	0.95026	90.56
0.664	0.95054	91.80
0.948	0.95094	94.92

2.840	0.95362	99.07
4.724	0.95618	102.34
6.599	0.95852	107.05
9.396	0.96200	110.69

Copper chloride

5% (w/w) Methanol + water		**d_o = 0.98560 g cm^{-3}**
0.492	0.98622	45.29
0.689	0.98646	46.46
0.985	0.98681	48.35
2.952	0.98907	53.71
4.914	0.99122	56.94
6.871	0.99333	58.83
9.795	0.99627	62.45
10% (w/w) Methanol + water		**d_o = 0.98208 g cm^{-3}**
0.490	0.98272	40.85
0.687	0.98296	43.21
0.981	0.98333	43.93
2.941	0.98563	50.72
4.897	0.98782	54.25
6.847	0.98989	57.45
9.762	0.99288	60.94
15% (w/w) Methanol + water		**d_o = 0.97420 g cm^{-3}**
0.487	0.97484	40.10
0.681	0.97509	40.99
0.973	0.97545	43.23
2.918	0.97779	48.73
4.858	0.97998	52.88
6.793	0.98205	56.38
9.686	0.98511	59.37
20% (w/w) Methanol + water		**d_o = 0.97089 g cm^{-3}**
0.485	0.97155	35.53
0.679	0.97181	36.13
0.970	0.97218	38.69
2.908	0.97455	45.99
4.842	0.97682	49.47
6.771	0.97893	53.30
9.655	0.98203	56.76
35% (w/w) Methanol + water		**d_o = 0.94954 g cm^{-3}**
0.474	0.95019	35.33
0.664	0.95044	36.91
0.949	0.95082	37.52
2.844	0.95316	45.53
4.736	0.95539	49.47
6.623	0.95750	52.97

9.444	0.96052	57.10

Cadmium chloride

5% (w/w) Methanol + water		**d_o = 0.98560 g cm^{-3}**
0.492	0.98624	72.45
0.689	0.98649	73.31
0.984	0.98686	74.46
2.949	0.98919	80.78
4.907	0.99145	83.32
6.858	0.99364	85.33
9.770	0.99674	88.58
10% (w/w) Methanol + water		**d_o = 0.98208 g cm^{-3}**
0.490	0.98275	66.01
0.687	0.98300	68.66
0.981	0.98339	69.08
2.939	0.98585	74.41
4.891	0.98816	78.43
6.836	0.99038	81.37
9.741	0.99371	83.42
15% (w/w) Methanol + water		**d_o = 0.97420 g cm^{-3}**
0.486	0.97488	63.31
0.681	0.97515	63.59
0.973	0.97555	64.32
2.916	0.97805	71.15
4.853	0.98047	74.05
6.784	0.98281	76.38
9.665	0.98605	80.81
20% (w/w) Methanol + water		**d_o = 0.97089 g cm^{-3}**
0.485	0.97159	58.79
0.679	0.97186	60.29
0.970	0.97228	59.81
2.907	0.97489	65.64
4.837	0.97727	71.52
6.762	0.97965	73.93
9.636	0.98308	77.07
35% (w/w) Methanol + water		**d_o = 0.94954 g cm^{-3}**
0.474	0.95024	56.70
0.664	0.95051	58.27
0.949	0.95090	61.09
2.843	0.95350	65.34
4.732	0.95592	70.03
6.614	0.95830	72.55
9.427	0.96169	76.29

Magnesium chloride		
5% (w/w) Methanol + water		**d_o = 0.98560 g cm^{-3}**
0.492	0.98587	150.65
0.689	0.98597	151.81
0.984	0.98612	152.66
2.942	0.98696	159.39
4.888	0.98764	163.94
6.820	0.9882	167.60
9.691	0.98888	171.94
10% (w/w) Methanol + water		**d_o = 0.98208 g cm^{-3}**
0.490	0.98236	148.91
0.686	0.98246	150.67
0.980	0.98261	151.98
2.932	0.98348	158.40
4.871	0.98416	163.54
6.796	0.98476	166.86
9.658	0.98548	171.17
15% (w/w) Methanol + water		**d_o = 0.97420 g cm^{-3}**
0.486	0.9745	145.43
0.681	0.97461	146.92
0.972	0.97477	148.55
2.909	0.97571	155.42
4.833	0.9765	159.85
6.744	0.97714	163.95
9.584	0.97797	168.32
20% (w/w) Methanol + water		**d_o = 0.97089 g cm^{-3}**
0.485	0.9712	143.59
0.679	0.97132	144.17
0.969	0.97149	145.66
2.899	0.97248	152.93
4.817	0.97327	158.52
6.722	0.97395	162.52
9.553	0.97478	167.47
35% (w/w) Methanol + water		**d_o = 0.94954 g cm^{-3}**
0.474	0.94987	140.86
0.664	0.95000	141.16
0.948	0.95018	143.03
2.836	0.95124	150.99
4.712	0.95214	156.01
6.576	0.95290	160.31
9.349	0.95392	164.78

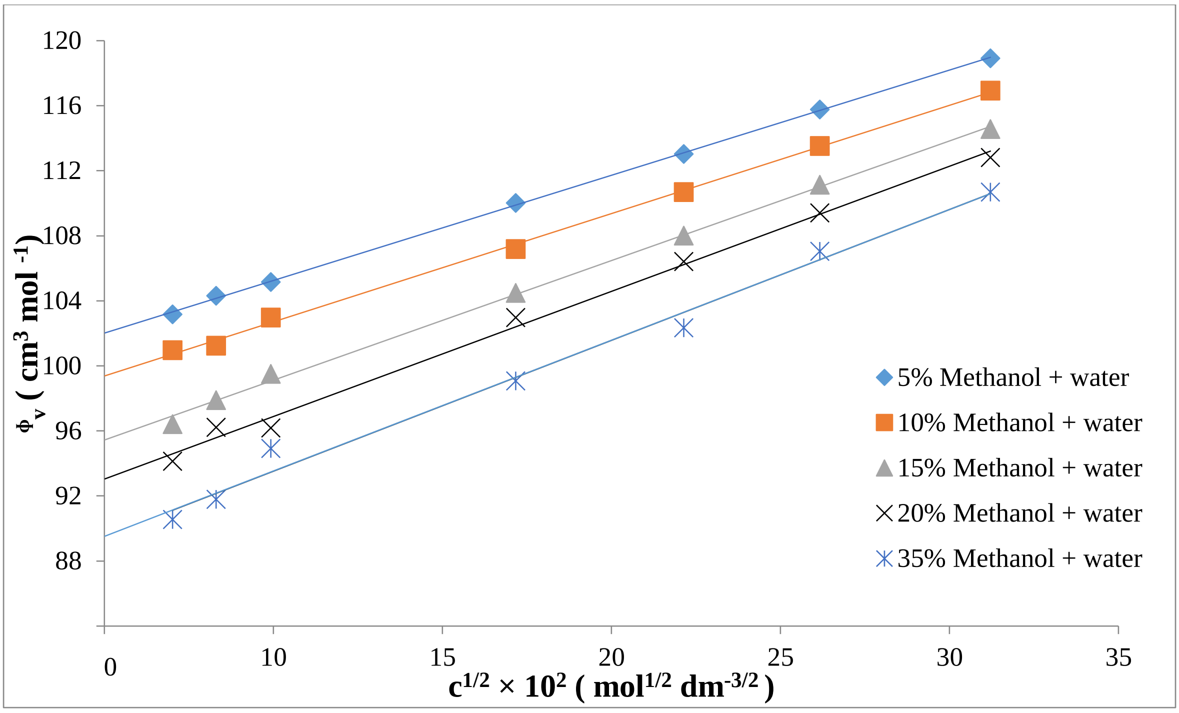

Fig.6. PLOTS OF Φ_V VS. $\sqrt{c}$ FOR NICKEL CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K.

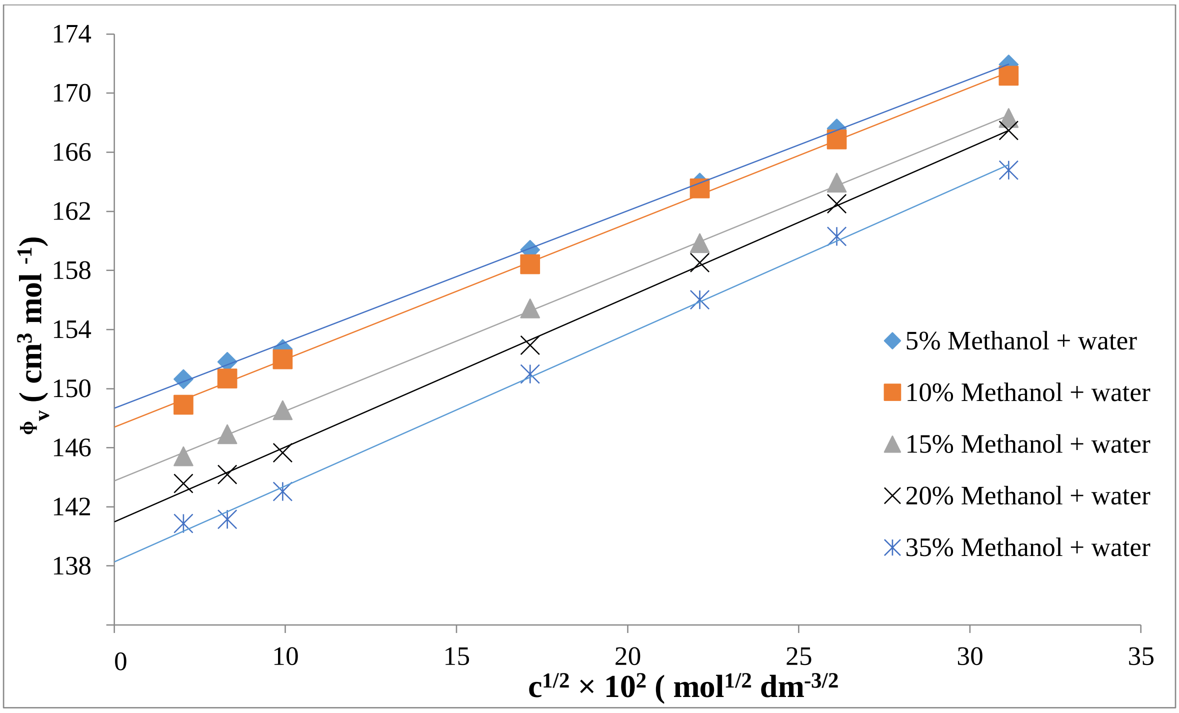

Fig.7: PLOTS OF Φ_V VS. $\sqrt{c}$ FOR MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K

TABLE - 2.VII

LIMITING APPARENT MOLAR VOLUMES (Φ_V^0) AND EXPERIMENTAL SLOPES (S_V^*) FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K.

Methanol + water (%w/w)	$\phi_V^0 = \overline{V_2^0}$ (cm^{3}mol^{-1})	S_V^* (cm^3 dm$^{3/2}$ mol$^{-3/2}$)	$\Delta\overline{V_{tr}^0}$ (cm^3 mol^{-1})
Manganese chloride			
0 (water)	69.39	1.112	----
5	61.50	0.637	-7.89
10	59.91	0.654	-9.48
15	56.22	0.660	-13.17
20	49.07	0.729	-20.32
35	45.79	0.774	-23.60
Cobalt chloride			
0 (water)	120.51	0.519	----
5	127.37	0.665	6.86
10	123.76	0.703	3.25
15	118.85	0.788	-1.66
20	116.29	0.869	-4.22
35	112.87	0.947	-7.64
Nickel chloride			
0 (water)	83.88	0.865	----
5	98.79	0.646	14.91
10	96.05	0.666	12.17
15	91.75	0.740	7.87
20	89.19	0.775	5.31
35	85.49	0.818	1.61
Copper chloride			
0 (water)	41.01	0.538	----
5	41.01	0.695	0.00
10	35.98	0.816	-5.03
15	34.72	0.812	-6.29

20	29.49	0.902	-11.52
35	29.16	0.923	-11.85

Cadmium chloride

0 (water)	60.80	0.668	----
5	68.02	0.672	7.22
10	62.03	0.715	1.23
15	57.72	0.737	-3.08
20	53.05	0.789	-7.74
35	52.06	0.799	-8.73

Magnesium chloride

0 (water)	138.39	0.654	----
5	144.21	0.891	5.82
10	142.81	0.920	4.42
15	139.03	0.951	0.64
20	135.92	1.020	-2.47
35	133.15	1.046	-5.24

concentrations. In the solvents like methanol + water, these salts would remain incompletely ionized and inter – ionic penetration does not occur and this may give rise to positive slopes of ϕ_V vs $\sqrt{c}$ curves.

Since, at infinite dilution the apparent molar volumes are independent of ion – ion interactions, hence can be used to examine the ion – solvent interactions. It is clear from Table – 2.VII that ϕ_V^0 values are positive for the divalent transition metal chlorides and magnesium chloride, studied here, in the entire composition range of methanol + water, thereby showing the presence of strong ion – solvent interactions. It is also clear from Table – 2.VII that the values of ϕ_V^0 decrease, for an individual electrolyte, with the increase of methanol content in water which may be attributed to the decrease in solvation of ions with the increase of methanol composition in water at 303.15K. This confirms our earlier conclusions from S_V^* data that methanol has more affinity for water than that of electrolyte. Further, It is also evident from Table – 2.VII that the magnitude of ϕ_V^0 values are greater than that of S_V^*, of all the divalent transition metal chlorides and magnesium chloride, means that ion – solvent interactions dominate over the ion – ion interactions in methanol + water at 303.15K.

The volume of transfer ($\Delta\overline{V_{tr}^0}$) has been calculated by using the relation:

$$\Delta\overline{V_{tr}^0} = \phi_V^0(M.S) - \phi_V^0(w) \qquad (2.24)$$

here $\phi_V^0(M.S)$ and $\phi_V^0(w)$ are the partial molar volumes of transition metal chlorides in mixed solvent (methanol + water) and water respectively. The values of volume of transfer of transition metal chlorides were recorded in Table- 2.VII. It is clear from Table- 2.VII that the values of $\Delta\overline{V_{tr}^0}$ continuously decrease with the increase in methanol content in water. The decrease in ϕ_V^0 and $\Delta\overline{V_{tr}^0}$ may be attributed to the increase in electrostriction in the presence of methanol. The electrostriction effect, which leads to the contraction in the volume of the solvent, is enhanced in the mixed solvents as compared to pure water. This electrostriction effect, again confirms the earlier conclusion of greater affinity of methanol for water. As Cl^- ion is common in all transition metal chlorides and in magnesium chloride, the values of volume of transfer in a particular composition of binary aqueous mixture of methanol, the electrostriction for the cations i.e. Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Mg^{2+} follows the order:

$$Mn^{2+} > Cu^{2+} > Mg^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+}.$$

Thus it may be concluded from this order that Ni^{2+} ion is highly solvated by methanol + water and Mn^{2+} is least. The order of preferential solvation of these cations is as given below:

$Ni^{2+} > Cd^{2+} > Co^{2+} > Mg^{2+} > Cu^{2+} > Mn^{2+}$.

Further, since the values of $\Delta\overline{V}_{tr}^{0}$ for an individual electrolyte, decreases with the increase in composition of methanol in water for all the divalent transition metal chlorides and magnesium chloride, therefore, the extent of preferential salvation for a particular cation decreases with the increase of methanol content in water, which may be attributed to the increase in solvent – solvent interactions i.e. between methanol and water.

Effect of temperature:

As the behaviour of all the electrolytes (taken in the present study) in binary aqueous mixtures of methanol + water at 303.15K was found to be identical, therefore only one composition system (5% w/w) of methanol + water has been selected for analysing the effect of temperature.

The experimentally determined values of densities and apparent molar volumes for different divalent transition metal chlorides viz; manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in 5% composition of methanol in water at five different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K) are given in Table. 2VIII.

TABLE - 2.VIII

DENSITIES AND APPARENT MOLAR VOLUMES FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AT DIFFERENT TEMPERATURES.

Concentration $c \times 10^2$ (mol dm^{-3})	**Density d (g cm^{-3})**	**Apparent molar volume ϕ_V (cm^3 mol^{-1})**
	Manganese chloride	
Temperature = 298.15K		**d_o = 0.98610 g cm^{-3}**
0.493	0.98674	69.01
0.689	0.98699	69.87
0.985	0.98736	71.02
2.952	0.98972	76.32
4.912	0.99202	78.46
6.864	0.99421	80.88
9.780	0.99734	84.14
Temperature = 303.15K		**d_o = 0.98560 g cm^{-3}**
0.492	0.98626	64.86
0.689	0.98651	66.9
0.984	0.98688	68.93
2.950	0.98934	72.18
4.909	0.99164	75.97
6.862	0.99387	78.51
9.778	0.99715	80.94
Temperature = 308.15K		**d_o = 0.98204 g cm^{-3}**
0.490	0.98271	62.53
0.687	0.98297	63.70
0.981	0.98336	64.56
2.940	0.98585	69.56
4.892	0.98822	72.90
6.838	0.99052	75.26
9.744	0.99373	79.36
Temperature = 313.15K		**d_o = 0.98042 g cm^{-3}**
0.490	0.98110	60.32
0.686	0.98136	62.09
0.979	0.98176	62.36
2.935	0.98427	68.07
4.885	0.98668	71.15
6.828	0.98902	73.40
9.73	0.99226	77.74

Temperature = 318.15K		**d_o = 0.97542 g cm^{-3}**
0.4876	0.97611	57.80
0.6825	0.97638	58.69
0.9749	0.97678	59.86
2.9207	0.97934	65.29
4.8608	0.98178	68.75
6.7947	0.98412	71.62
9.6835	0.98751	74.89

Cobalt chloride

Temperature = 298.15K		**d_o = 0.98610 g cm^{-3}**
0.492	0.98661	136.32
0.689	0.98681	136.88
0.984	0.98710	138.30
2.945	0.98897	142.49
4.895	0.99070	145.99
6.832	0.99236	148.37
9.715	0.99470	151.52
Temperature = 303.15K		**d_o = 0.98560 g cm^{-3}**
0.492	0.98613	132.22
0.689	0.98634	132.48
0.984	0.98664	134.20
2.944	0.98858	138.73
4.893	0.99039	142.10
6.831	0.99213	144.42
9.715	0.99462	147.20
Temperature = 308.15K		**d_o = 0.98204 g cm^{-3}**
0.490	0.98258	130.22
0.686	0.98279	131.08
0.980	0.98310	132.23
2.934	0.98506	137.48
4.876	0.98690	140.80
6.807	0.98864	143.55
9.681	0.99116	146.36
Temperature = 313.15K		**d_o = 0.98042 g cm^{-3}**
0.489	0.98097	128.17
0.685	0.98118	129.63
0.979	0.98149	131.22
2.929	0.98348	136.14
4.868	0.98537	138.99
6.796	0.98709	142.58
9.666	0.98969	144.87
Temperature = 318.15K		**d_o = 0.97542 g cm^{-3}**
0.487	0.97598	126.14

0.682	0.9762	126.71
0.974	0.97652	128.17
2.914	0.97858	132.79
4.844	0.98047	137.06
6.763	0.98227	140.09
9.619	0.98483	143.64

Nickel chloride

Temperature = 298.15K		**d_o = 0.98610 g cm^{-3}**
0.492	0.98674	109.36
0.689	0.98699	110.21
0.985	0.98736	111.34
2.948	0.98972	116.54
4.901	0.99198	119.41
6.844	0.99409	122.68
9.7403	0.99718	125.70
Temperature = 303.15K		**d_o = 0.98560 g cm^{-3}**
0.492	0.98628	101.11
0.689	0.98654	102.85
0.984	0.98693	104.13
2.947	0.98945	108.65
4.900	0.99183	112.21
6.845	0.99413	114.75
9.742	0.99738	118.50
Temperature = 308.15K		**d_o = 0.98204 g cm^{-3}**
0.490	0.98273	98.894
0.687	0.98300	99.755
0.981	0.98340	100.90
2.936	0.98596	106.14
4.883	0.98837	110.07
6.821	0.99071	112.63
9.709	0.99406	116.00
Temperature = 313.15K		**d_o = 0.98042 g cm^{-3}**
0.49	0.98114	92.58
0.685	0.98142	93.74
0.979	0.98184	94.59
2.932	0.98453	99.51
4.877	0.98717	101.31
6.813	0.98958	105.34
9.698	0.99286	111.62
Temperature = 318.15K		**d_o = 0.97542 g cm^{-3}**
0.487	0.97615	90.18
0.682	0.97644	90.45
0.974	0.97687	91.16
2.918	0.97960	96.84

4.853	0.98220	100.48
6.779	0.98468	103.68
9.652	0.98815	108.49

Copper chloride

Temperature = 298.15K		**d_o = 0.9861 g cm^{-3}**
0.492	0.98671	47.39
0.69	0.98695	47.97
0.985	0.98731	48.39
2.953	0.98957	53.74
4.916	0.99175	56.35
6.874	0.99383	58.86
9.802	0.99692	60.94
Temperature = 303.15K		**d_o = 0.9856 g cm^{-3}**
0.492	0.98622	45.29
0.689	0.98646	46.46
0.985	0.98681	48.35
2.952	0.98911	52.34
4.914	0.99125	56.32
6.871	0.99337	58.24
9.795	0.99627	62.45
Temperature = 308.15K		**d_o = 0.98204 g cm^{-3}**
0.490	0.98267	42.92
0.687	0.98292	43.20
0.981	0.98329	43.93
2.941	0.98562	49.68
4.897	0.98788	52.18
6.848	0.99003	54.80
9.762	0.99286	60.73
Temperature = 313.15K		**d_o = 0.98042 g cm^{-3}**
0.490	0.98106	40.69
0.686	0.98131	41.58
0.98	0.98168	42.75
2.937	0.98404	48.17
4.889	0.98630	51.23
6.837	0.98845	54.10
9.748	0.99143	58.68
Temperature = 318.15K		**d_o = 0.97542 g cm^{-3}**
0.487	0.97607	38.12
0.682	0.97632	39.61
0.975	0.97669	41.24
2.922	0.97911	45.33
4.865	0.98138	49.19
6.803	0.98356	52.12
9.700	0.98658	56.83

	Cadmium chloride	
Temperature = 298.15K		**d_o = 0.9861 g cm^{-3}**
0.492	0.98672	76.58
0.689	0.98696	77.74
0.985	0.98732	78.59
2.951	0.98964	82.51
4.909	0.99187	84.98
6.861	0.99406	86.51
9.775	0.99722	88.79
Temperature = 303.15K		**d_o = 0.98204 g cm^{-3}**
0.492	0.98624	72.44
0.689	0.9865	71.83
0.984	0.98686	74.45
2.950	0.98930	77.00
4.908	0.99164	79.41
6.860	0.99387	81.95
9.773	0.99700	85.91
Temperature = 308.15K		**d_o = 0.98204 g cm^{-3}**
0.490	0.98270	68.08
0.687	0.98296	68.65
0.981	0.98334	70.11
2.939	0.98577	75.79
4.891	0.98807	79.46
6.836	0.99037	80.92
9.739	0.99357	84.45
Temperature = 313.15K		**d_o = 0.98042 g cm^{-3}**
0.490	0.98110	63.80
0.686	0.98137	64.08
0.979	0.98177	64.80
2.935	0.98430	70.51
4.884	0.98672	73.78
6.827	0.98905	76.40
9.727	0.99233	80.45
Temperature = 318.15K		**d_o = 0.97542 g cm^{-3}**
0.487	0.97612	59.20
0.682	0.97639	60.68
0.974	0.97680	61.26
2.920	0.97937	67.73
4.860	0.98182	71.39
6.792	0.98408	75.69
9.680	0.98751	78.35

Magnesium chloride		
Temperature = 298.15K		**d_o = 0.9861 g cm^{-3}**
0.492	0.98634	156.77
0.689	0.98643	157.64
0.984	0.98656	158.80
2.944	0.98731	164.50
4.89	0.98795	167.81
6.822	0.98848	170.80
9.694	0.98912	174.58
Temperature = 303.15K		**d_o = 0.9856 g cm^{-3}**
0.492	0.98588	148.59
0.689	0.98598	150.34
0.984	0.98613	151.64
2.942	0.98696	159.39
4.888	0.98768	163.11
6.820	0.98824	167.01
9.692	0.98896	171.11
Temperature = 308.15K		**d_o = 0.98204 g cm^{-3}**
0.490	0.98234	144.77
0.686	0.98245	146.23
0.980	0.98261	147.84
2.932	0.98351	155.99
4.872	0.98430	159.79
6.798	0.98498	162.99
9.661	0.98581	167.29
Temperature = 313.15K		**d_o = 0.98042 g cm^{-3}**
0.489	0.98073	142.82
0.685	0.98085	143.40
0.979	0.98102	144.86
2.928	0.98200	152.33
4.864	0.98283	156.84
6.788	0.98355	160.34
9.647	0.98438	165.50
Temperature = 318.15K		**d_o = 0.97542 g cm^{-3}**
0.487	0.97575	139.02
0.682	0.97587	140.80
0.974	0.97605	142.13
2.913	0.97711	148.97
4.840	0.97798	154.22
6.755	0.97877	157.59
9.601	0.97971	162.63

The linear plots of ϕ_V verses $\sqrt{c}$ have also been obtained at different temperatures for all the above mentioned divalent transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water mixture. Sample plots for manganese chloride and magnesium chloride The linear plots of ϕ_V verses $\sqrt{c}$ have also been obtained at different temperatures for all the above mentioned divalent transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water mixture. Sample plots for manganese chloride and magnesium chloride are shown in Figs. 8 and 9 respectively. The values of limiting apparent molar volumes (ϕ_V^0) and experimental slopes (S_V^*) calculated by applying the least square method to the above mentioned linear plots of ϕ_V vs $\sqrt{c}$ (using 2.10 equation) are recorded in Table – 2.IX.

From Table 2.IX it is clear that the values of S_V^* are positive for all the above mentioned divalent transition metal chlorides in 5% (w/w) aqueous mixture of methanol in the entire temperature range, therefore these results indicate that ion – ion interactions are quite strong in divalent transition metal chlorides and magnesium chloride solutions in 5% (w/w) methanol + water mixture. Further values of S_V^* increases with the increase of temperature for an individual divalent transition metal chloride and magnesium chloride thereby suggesting that ion – ion interactions further improve with the rise in temperature, which may be due to the decrease in solvation of ions.

On the other hand, it is clear from the table 2.IX that values of ϕ_V^0 decrease with the increase of temperature for all the divalent transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water mixture, indicate the decrease in ion – solvent interactions with the increase in temperature i.e. ion – solvation decreases with the rise in temperature.

The temperature dependence of ϕ_V^0 in 5% (w/w) methanol + water mixture for different divalent transition metal chlorides viz; manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride can be expressed by the following relations:

ϕ_v^0 = 1468.37 - 8.66 T + 0.01 T^2 for manganese chloride (2.25)

ϕ_v^0 = 2664.80 – 16.03T + 0.02 T^2 for cobalt chloride (2.26)

ϕ_v^0 = 1585.11 – 8.31T + 0.01 T^2 for nickel chloride (2.27)

ϕ_v^0 = 663.80 – 3.68 T + 5.37 x 10^{-3} T^2 for copper chloride (2.28)

ϕ_v^0 = 793.92 – 3.72T + 4.39 x 10^{-3} T^2 for cadmium chloride (2.29)

ϕ_v^0 = 6210.87–38.54 T + 0.06 T^2 for magnesium chloride (2.30)

here, T represents the absolute temperature.

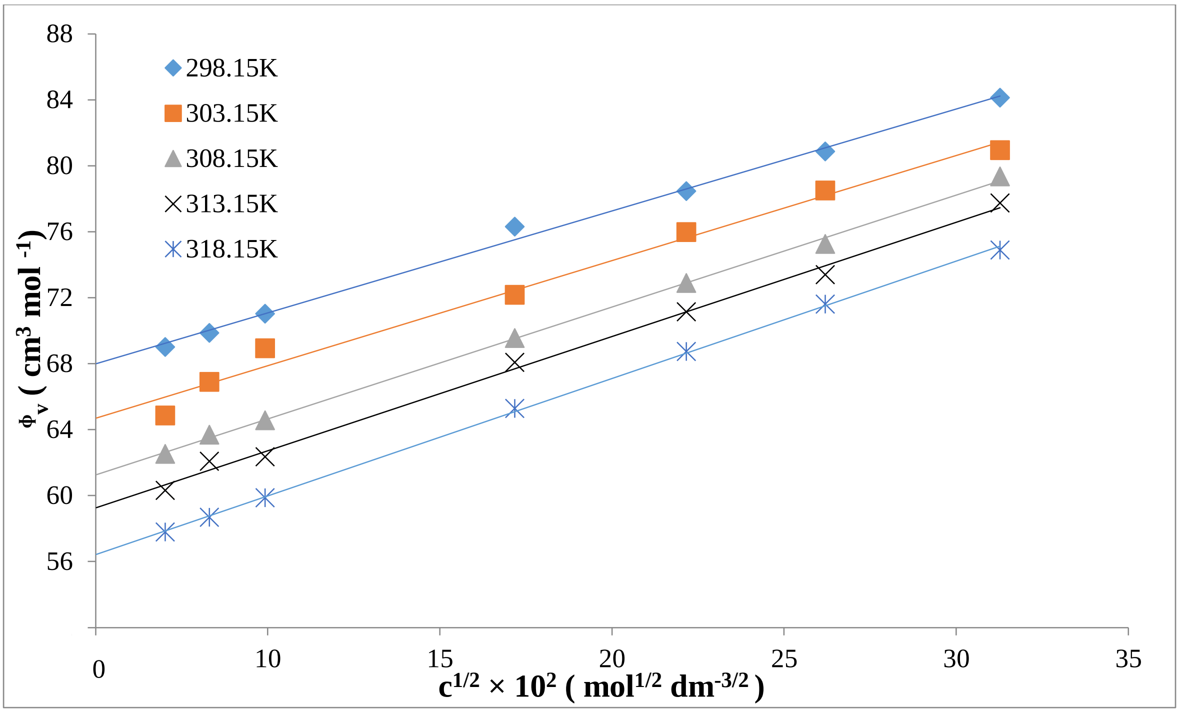

Fig.8: PLOTS OF Φ_V VS. $\sqrt{c}$ FOR MANGANESE CHLORIDE IN 5% (w/w) COMPOSITION OF METHANOL + WATER AT FIVE DIFFERENT TEMPERATURES.

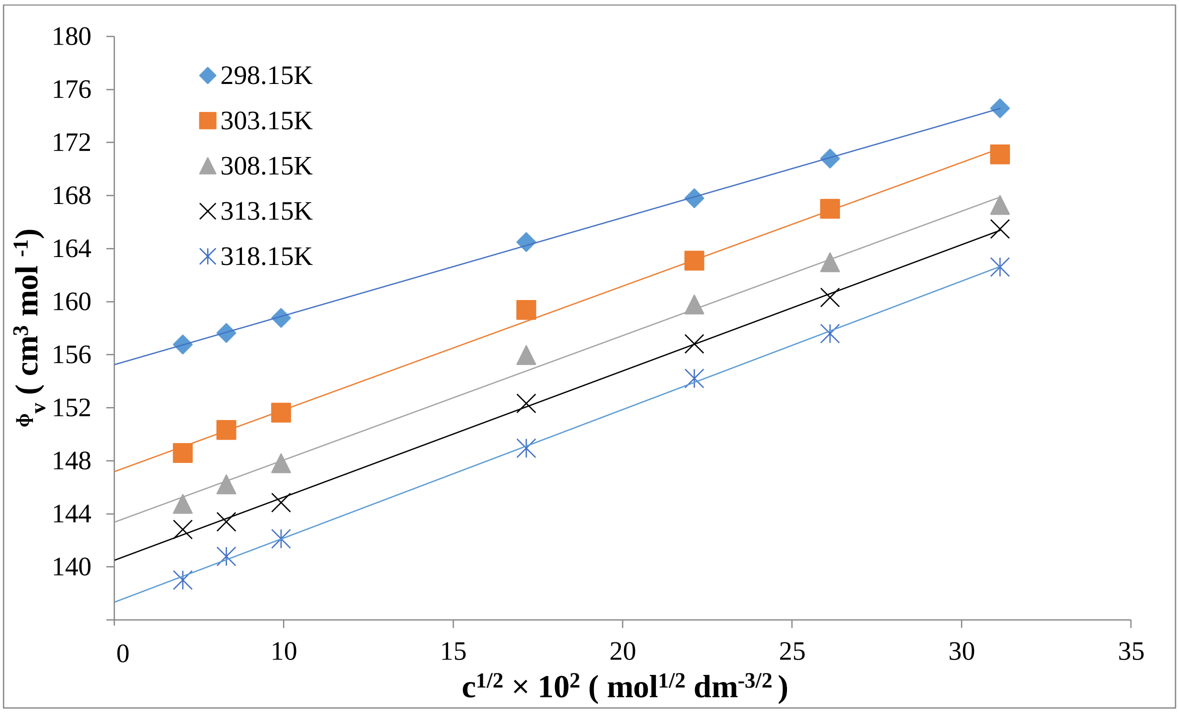

Fig.9: PLOTS OF Φ_V VS. $\sqrt{c}$ FOR MAGNESIUM CHLORIDE IN 5% (w/w) COMPOSITION OF METHANOL + WATER AT FIVE DIFFERENT TEMPERATURES.

TABLE - 2.IX

LIMITING APPARENT MOLAR VOLUMES (Φ_V^0) AND EXPERIMENTAL SLOPES (S_V^*) FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AT DIFFERENT TEMPERATURES.

Temperature K	$\phi_V^0 = \overline{V_2^0}$ **(cm^{3}mol^{-1})**	S_V^* **(cm^3 dm$^{3/2}$ mol$^{-3/2}$)**
	Manganese chloride	
298.15	64.89	0.618
303.15	61.50	0.637
308.15	57.86	0.679
313.15	55.80	0.694
318.15	52.86	0.715
	Cobalt chloride	
298.15	131.81	0.633
303.15	127.68	0.636
308.15	125.55	0.681
313.15	123.95	0.691
318.15	120.75	0.737
	Nickel chloride	
298.15	104.61	0.680
303.15	96.83	0.691
308.15	93.87	0.717
313.15	87.21	0.724
318.15	84.09	0.763
	Copper chloride	
298.15	43.16	0.585
303.15	40.89	0.681
308.15	37.27	0.710
313.15	35.53	0.726
318.15	33.29	0.735
	Cadmium chloride	
298.15	73.56	0.498
303.15	68.13	0.541
308.15	63.37	0.688
313.15	58.38	0.699
318.15	53.66	0.812
	Magnesium chloride	
298.15	151.56	0.739
303.15	142.52	0.932
308.15	138.67	0.949
313.15	135.74	0.954
318.15	132.5	0.972

Partial molar volume expansibilities $\phi_{\mathrm{E}}^{0}=\left[\frac{\partial \phi_{\mathrm{V}}^{0}}{\partial \mathrm{T}}\right]_{\mathrm{P}}$, calculated from equations (2.25) to (2.30) for the different divalent transition metal chlorides and magnesium chloride at different temperatures in 5% (w/w) methanol + water, are recorded in Table 2.X. The results of Table 2.X show that ϕ_{E}^{0} values are negative but increase in magnitude with increase in temperature for all the divalent transition metal chlorides and magnesium chloride (mentioned above) thereby suggesting that the behaviour of these electrolytes is just like symmetrical tetra alkyl ammonium salts [22] and not like common salts [23, 24] in methanol + water, because in case of common electrolytes the molar volume expansibilities ϕ_{E}^{0} should decrease with the increase of temperature.

The variation of ϕ_{E}^{0} with temperature for all the divalent transition metal chlorides and magnesium chloride is linear. Sample plots for copper chloride and manganese chloride are shown in Figs. 10 and 11, respectively. The positive increase in ϕ_{E}^{0}, for all the electrolytes studied here, in 5% (w/w) methanol + water, with the increase in temperature may be ascribed to the presence of " caging effect" [22,25]. From these results it may also be noted that the behaviour of the divalent transition metal chlorides and magnesium chloride do not change when the solvent is changed from water to methanol + water.

By applying the Hepler [21] criterion for the relations of (2.25) to (2.30) for divalent transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water mixture, it is found that the values of $\left(\frac{\partial^{2} \phi_{\mathrm{V}}^{0}}{\partial \mathrm{T}^{2}}\right)$ p is positive for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride, thereby suggesting that all divalent transition metal chlorides and magnesium chloride acts as structure makers/promoters in the binary aqueous mixtures of methanol.

TABLE - 2.X

VALUES OF LIMITING MOLAR VOLUME EXPANSIBILITIES ϕ_E^0 FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AT DIFFERENT TEMPERATURES.

Electrolyte	ϕ_E^0 (cm^3 mol^{-1}K^{-1})				
Temperature (K)	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
Manganese chloride	-2.69	-2.59	-2.49	-2.39	-2.29
Cobalt chloride	-4.10	-3.90	-3.70	-3.50	-3.30
Nickel chloride	-2.35	-2.24	-2.14	-2.04	-1.94
Copper chloride	-0.47	-0.42	-0.37	-0.31	-0.26
Cadmium chloride	-1.10	-1.05	-1.01	-0.97	-0.92
Magnesium chloride	-2.76	-2.16	-1.56	-0.96	-0.36

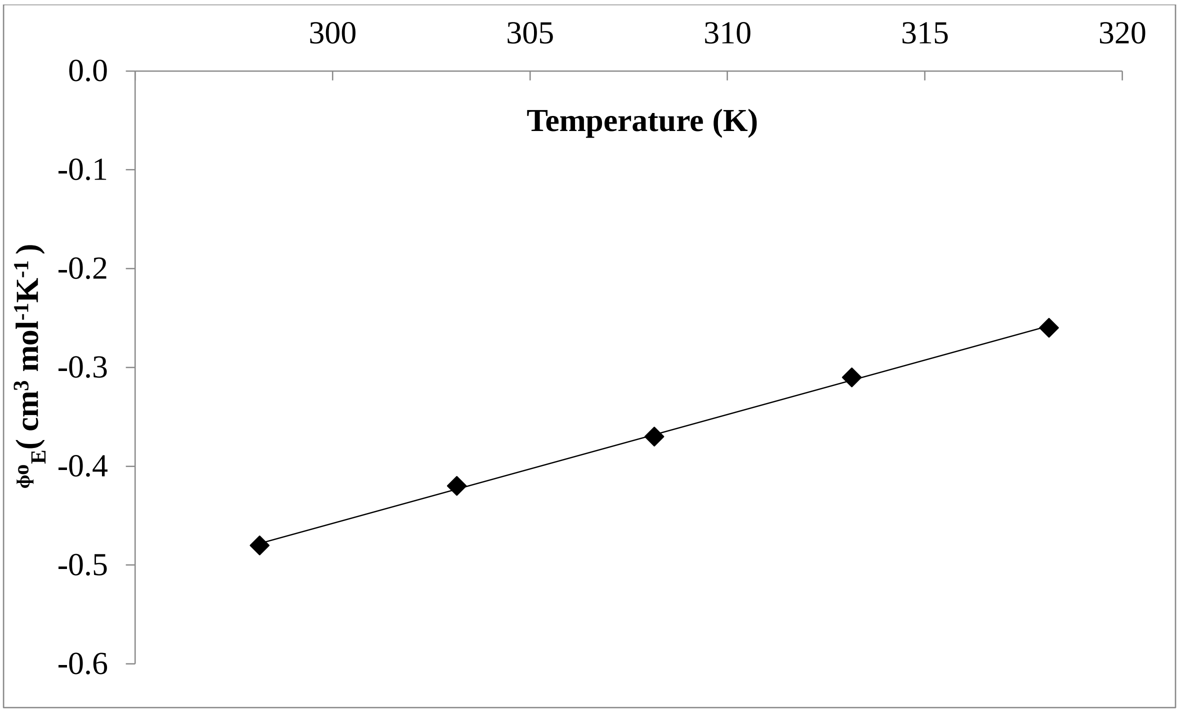

Fig.10: VARIATION OF Φ_E^0 WITH TEMPERATURE FOR COPPER CHLORIDE IN 5% (w/w) COMPOSITION OF METHANOL + WATER.

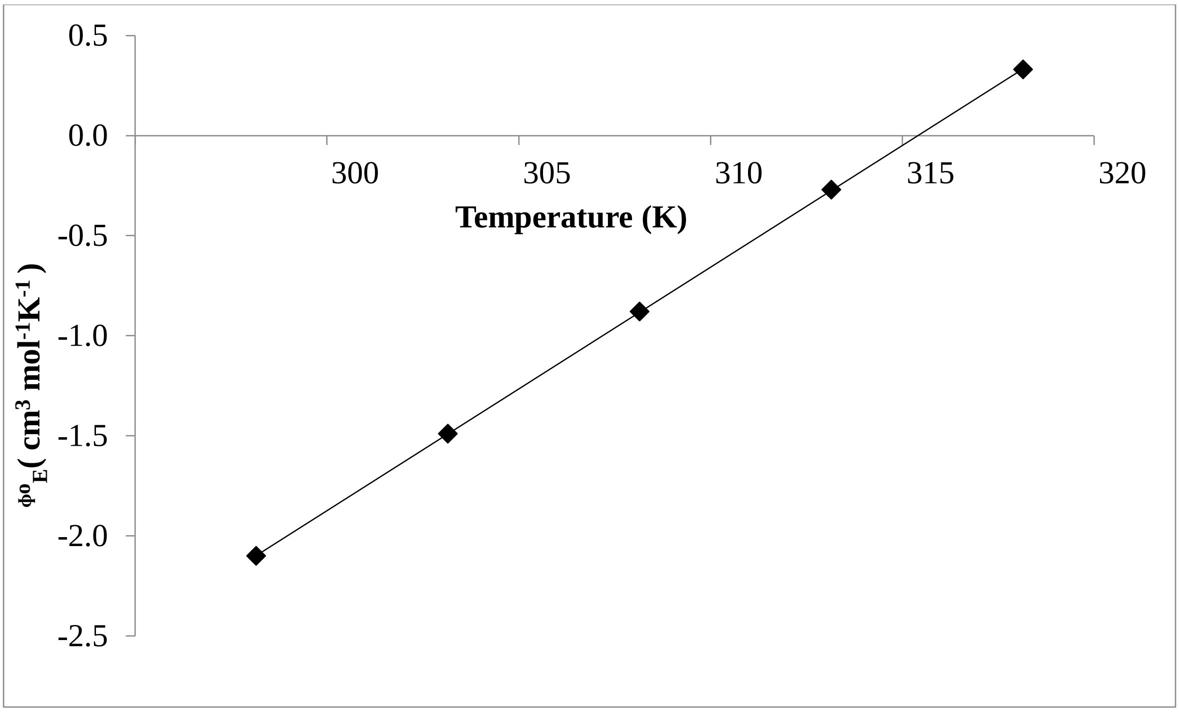

Fig.11: VARIATION OF Φ_E^0 WITH TEMPERATURE FOR MAGENSIUM CHLORIDE IN 5% (w/w) COMPOSITION OF METHANOL + WATER

Section - C

Discussion on the Results of Some Transition Metal Chlorides and Magnesium Chloride in Binary Aqueous Mixtures of Ethanol.

Densities and apparent molar volumes of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in different compositions of binary aqueous mixtures of ethanol (5, 10, 15, 20, 35 wt. percent of ethanol) at 303.15K are given in Table 2.XI.The apparent molar volumes (ϕ_V) vary linearly with square root of molar concentration ($\sqrt{c}$) in accordance with Masson's equation (2.10) for all the above mentioned divalent transition metal chlorides and magnesium chloride in different compositions of ethanol + water at 303.15K and sample plots for nickel chloride and magnesium chloride are shown in Figs. 12 and 13 respectively.

The values of limiting apparent molar volumes/partial molar volumes (ϕ_V^0) and the experimental slopes (S_V^*), for all the above mentioned divalent transition metal chlorides and magnesium chloride in different compositions of binary aqueous mixtures of ethanol at 303.15K are given in Table 2. XII.

It is clear from Table 2. XII that the values of slopes S_V^* are positive and large for all the mentioned divalent transition metal chloride and magnesium chloride, studied here in different binary mixtures of ethanol at 303.15K, thereby showing the presence of strong ion – ion interactions. It is also clear from Table 2. XII, that the value of S_V^*, for an individual electrolyte, increases with the increase in the amount of ethanol in water thereby suggesting that ion – ion interactions are further strengthened with the increase of ethanol content. In other words, it may be said that the solvation of ions decreases with the increase of ethanol in water which may be attributed to greater solvent – solvent (ethanol – water) interactions i.e. ethanol has more affinity for water than that of electrolyte. These results also suggest a possible explanation for the absence of negative S_V^* values for the divalent transition metal chlorides and magnesium chloride in different ethanol + water mixtures at 303.15K.

At infinite dilution, all the above mentioned salts are completely dissociated in different compositions of ethanol + water.

TABLE - 2.XI

DENSITIES AND APPARENT MOLAR VOLUMES FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL + WATER AT 303.15K.

Concentration c X 10^2 (mol dm^{-3})	**Density d (g cm^{-3})**	**Partial molar volume ϕ_V (cm^3 mol^{-1})**
	Manganese chloride	
5% (w/w) Ethanol + water		**d_o = 0.98626 g cm^{-3}**
0.493	0.98696	56.69
0.690	0.98724	56.67
0.985	0.98765	57.68
2.953	0.99034	60.59
4.916	0.99298	62.06
6.873	0.99555	63.62
9.799	0.99932	65.53
10% (w/w) Ethanol + water		**d_o = 0.98227 g cm^{-3}**
0.491	0.98299	52.19
0.687	0.98327	53.36
0.981	0.98369	54.22
2.941	0.98642	57.86
4.897	0.98914	58.66
6.847	0.99174	60.67
9.761	0.99548	63.70
15% (w/w) Ethanol + water		**d_o = 0.97602 g cm^{-3}**
0.487	0.97675	49.46
0.683	0.97704	49.75
0.975	0.97746	51.52
2.923	0.98025	54.51
4.866	0.983	55.82
6.805	0.98565	57.78
9.703	0.9895	60.42
20% (w/w) Ethanol + water		**d_o = 0.97104 g cm^{-3}**
0.485	0.97178	46.81
0.679	0.97207	47.70
0.970	0.9725	48.89
2.908	0.97531	52.62
4.842	0.97806	54.51
6.771	0.98078	55.68
9.656	0.98474	57.69

35% (w/w) Ethanol + water		**d_o = 0.95412 g cm^{-3}**
0.477	0.95487	42.61
0.667	0.95516	44.16
0.953	0.95559	45.87
2.858	0.95842	49.74
4.759	0.96122	51.05
6.655	0.96390	53.39
9.490	0.96782	56.12

Cobalt chloride

5% (w/w) Ethanol + water		**d_o = 0.98626 g cm^{-3}**
0.492	0.98674	142.48
0.689	0.98692	144.21
0.984	0.98721	143.44
2.945	0.98894	149.00
4.894	0.99056	152.16
6.831	0.99211	154.41
9.711	0.99426	157.72
10% (w/w) Ethanol + water		**d_o = 0.98227 g cm^{-3}**
0.490	0.98278	136.43
0.686	0.98298	137.00
0.980	0.98328	137.40
2.934	0.98514	142.65
4.876	0.98691	145.35
6.806	0.98854	148.44
9.678	0.99084	152.07
15% (w/w) Ethanol + water		**d_o = 0.97602 g cm^{-3}**
0.487	0.97654	134.53
0.682	0.97674	135.70
0.974	0.97704	136.55
2.916	0.97893	141.52
4.845	0.98070	144.82
6.764	0.98240	147.13
9.618	0.98478	150.46
20% (w/w) Ethanol + water		**d_o = 0.97104 g cm^{-3}**
0.485	0.97157	132.53
0.679	0.97178	132.81
0.969	0.97209	133.52
2.901	0.97402	139.25
4.821	0.97583	142.72
6.730	0.97753	145.72
9.572	0.98002	148.41
35% (w/w) Ethanol + water		**d_o = 0.95412 g cm^{-3}**
0.476	0.95466	130.66

0.667	0.95487	131.57
0.952	0.95520	130.58
2.851	0.95718	136.88
4.738	0.95903	140.77
6.615	0.96084	142.91
9.409	0.96333	146.78

Nickel chloride

5% (w/w) Ethanol + water		**d_o = 0.98626 g cm^{-3}**
0.492	0.98688	113.47
0.689	0.98712	114.61
0.985	0.98748	115.45
2.948	0.98981	118.94
4.901	0.99204	121.46
6.845	0.99419	123.56
9.740	0.99721	127.03
10% (w/w) Ethanol + water		**d_o = 0.98227 g cm^{-3}**
0.490	0.98291	109.26
0.687	0.98316	110.12
0.981	0.98353	111.26
2.936	0.98589	116.50
4.882	0.98812	120.02
6.818	0.99031	121.96
9.703	0.99337	125.53
15% (w/w) Ethanol + water		**d_o = 0.97602 g cm^{-3}**
0.487	0.97667	107.01
0.682	0.97692	108.48
0.975	0.97730	109.04
2.918	0.97968	115.05
4.852	0.98198	117.70
6.776	0.98417	120.32
9.643	0.98731	123.60
20% (w/w) Ethanol + water		**d_o = 0.97104 g cm^{-3}**
0.485	0.97170	104.73
0.679	0.97196	105.31
0.970	0.97234	106.78
2.903	0.97478	112.15
4.828	0.97708	115.96
6.743	0.97931	118.49
9.596	0.98248	122.03
35% (w/w) Ethanol + water		**d_o = 0.95412 g cm^{-3}**
0.476	0.95479	101.87
0.667	0.95505	103.09
0.953	0.95543	105.09
2.853	0.95786	111.75

4.744	0.96016	115.71
6.626	0.96239	118.33
9.431	0.96552	122.45

Copper chloride

5% (w/w) Ethanol + water		**$d_o = 0.98626$ g cm^{-3}**
0.493	0.98675	72.06
0.690	0.98694	72.93
0.985	0.98722	74.089
2.952	0.98905	77.027
4.912	0.99078	79.55
6.865	0.99248	80.99
9.782	0.99489	83.40
10% (w/w) Ethanol + water		**$d_o = 0.98227$ g cm^{-3}**
0.491	0.98278	67.80
0.687	0.98298	68.38
0.981	0.98328	68.80
2.940	0.98518	72.80
4.893	0.98703	74.52
6.839	0.98876	76.95
9.747	0.99133	78.92
15% (w/w) Ethanol + water		**$d_o = 0.97602$ g cm^{-3}**
0.487	0.97655	63.36
0.682	0.97676	63.64
0.975	0.97707	64.37
2.922	0.97906	68.08
4.863	0.98096	70.59
6.798	0.98281	72.34
9.689	0.98549	74.53
20% (w/w) Ethanol + water		**$d_o = 0.97104$ g cm^{-3}**
0.485	0.97158	60.99
0.679	0.97179	61.88
0.970	0.97210	63.07
2.907	0.97414	65.76
4.839	0.97610	67.88
6.764	0.97795	70.37
9.641	0.98055	73.98
35% (w/w) Ethanol + water		**$d_o = 0.95412$ g cm^{-3}**
0.476	0.95466	60.00
0.667	0.95487	60.93
0.953	0.95519	61.07
2.857	0.95725	63.85
4.755	0.95922	66.27
6.647	0.96103	69.73
9.474	0.96359	73.91

	Cadmium chloride	
5% (w/w) Ethanol + water		**d_o = 0.98626 g cm^{-3}**
0.493	0.98696	60.15
0.690	0.98723	61.60
0.985	0.98764	62.17
2.953	0.99030	65.41
4.915	0.99290	67.15
6.870	0.99528	71.00
9.792	0.99898	72.42
10% (w/w) Ethanol + water		**d_o = 0.98227 g cm^{-3}**
0.491	0.98299	55.67
0.687	0.98328	55.36
0.981	0.9837	56.66
2.941	0.98638	62.70
4.895	0.98899	65.21
6.843	0.9914	69.13
9.754	0.99507	71.36
15% (w/w) Ethanol + water		**d_o = 0.97602 g cm^{-3}**
0.487	0.97675	52.96
0.683	0.97704	53.25
0.975	0.97747	53.97
2.922	0.98017	60.79
4.864	0.98278	63.90
6.800	0.98523	67.51
9.693	0.98889	70.24
20% (w/w) Ethanol + water		**d_o = 0.97104 g cm^{-3}**
0.485	0.97179	48.21
0.679	0.97208	49.71
0.970	0.97251	51.35
2.908	0.97531	56.13
4.841	0.97795	60.33
6.768	0.98048	63.68
9.645	0.98395	69.48
35% (w/w) Ethanol + water		**d_o = 0.95412 g cm^{-3}**
0.477	0.95487	46.19
0.667	0.95518	44.61
0.953	0.95561	47.25
2.857	0.95839	54.41
4.757	0.96107	57.89
6.652	0.96375	59.28
9.480	0.96718	66.63

Magnesium chloride		
5% (w/w) Ethanol + water		**d_o = 0.98626 g cm^{-3}**
0.492	0.98653	150.59
0.689	0.98663	151.75
0.984	0.98678	152.60
2.945	0.98766	157.94
4.892	0.98845	160.76
6.827	0.98917	162.92
9.703	0.99011	165.91
10% (w/w) Ethanol + water		**d_o = 0.98227 g cm^{-3}**
0.490	0.98256	146.82
0.686	0.98267	147.70
0.980	0.98283	148.86
2.933	0.98378	154.58
4.873	0.98461	158.10
6.800	0.98537	160.57
9.667	0.98642	163.28
15% (w/w) Ethanol + water		**d_o = 0.97602 g cm^{-3}**
0.487	0.97632	145.28
0.682	0.97644	145.26
0.974	0.9766	147.33
2.915	0.97761	152.42
4.843	0.97847	156.48
6.758	0.97923	159.64
9.607	0.98025	163.19
20% (w/w) Ethanol + water		**d_o = 0.97104 g cm^{-3}**
0.485	0.97136	141.45
0.679	0.97148	142.65
0.969	0.97166	143.53
2.900	0.97270	150.43
4.819	0.97364	153.81
6.725	0.97444	157.31
9.560	0.97553	161.01
35% (w/w) Ethanol + water		**d_o = 0.95412 g cm^{-3}**
0.476	0.95446	138.34
0.667	0.95458	140.83
0.952	0.95478	140.49
2.850	0.95589	148.00
4.736	0.95688	152.01
6.610	0.95774	155.69
9.399	0.95906	158.00

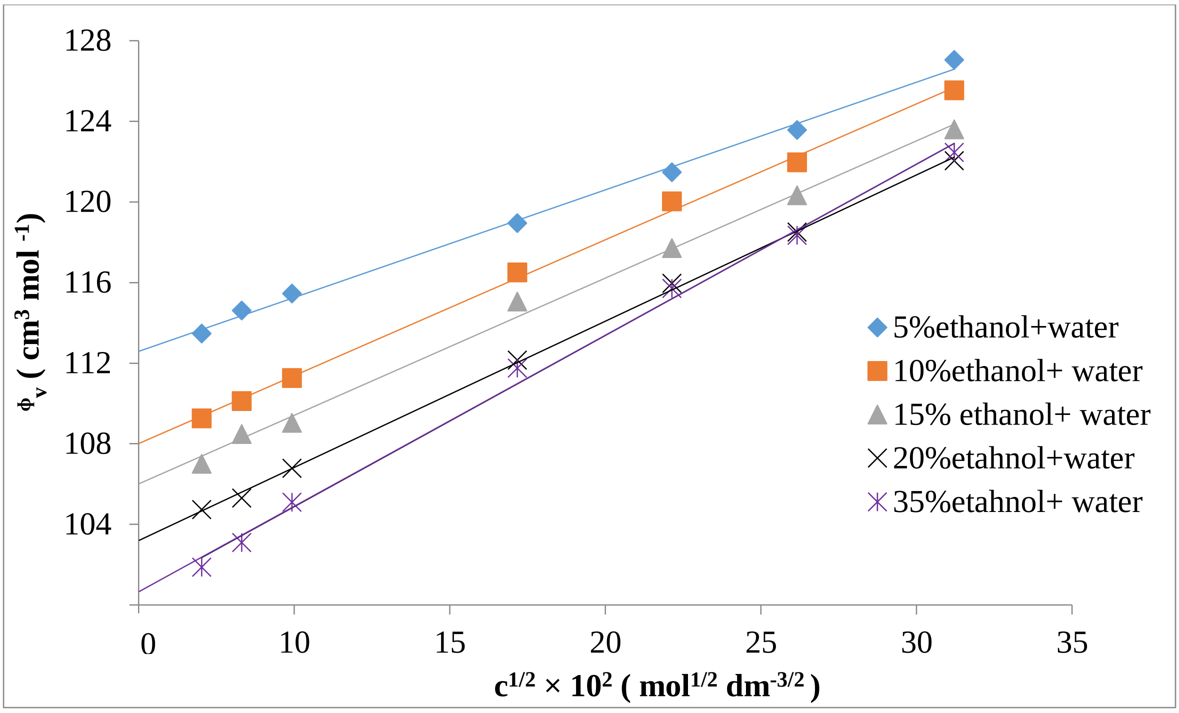

Fig.12: PLOTS OF Φ_V VS. √c FOR NICKEL CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL + WATER AT 303.15K.

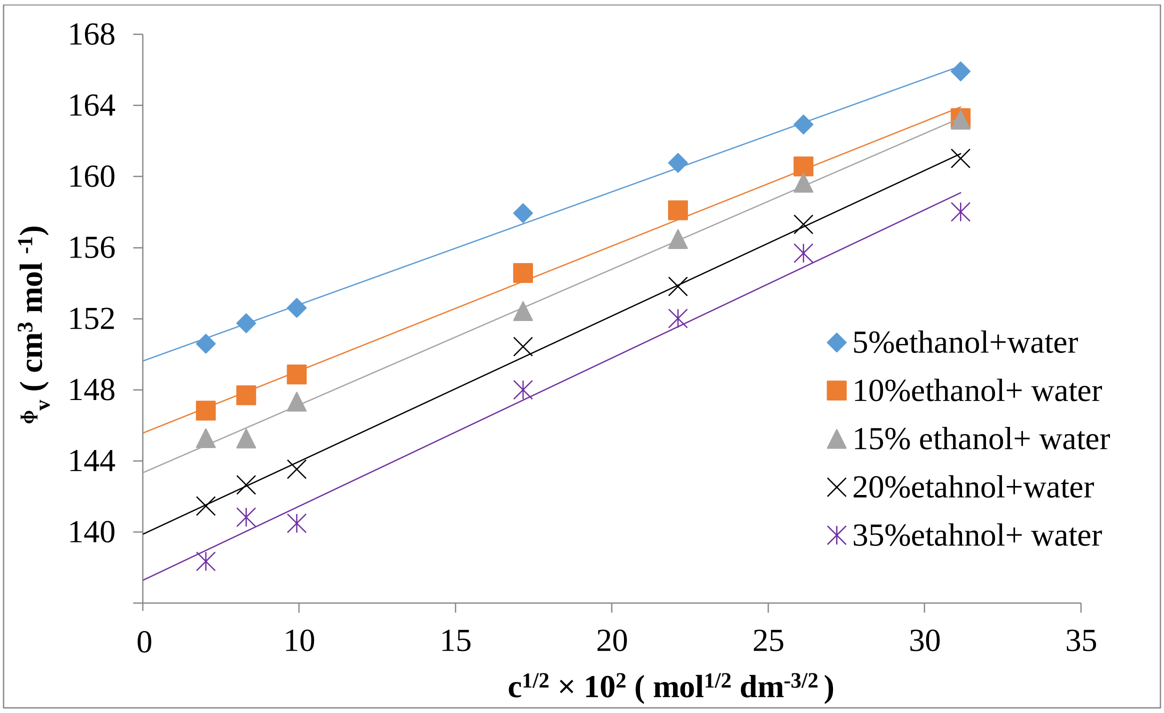

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Fig.13. PLOTS OF Φ_V VS. √C FOR MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL + WATER AT 303.15K.

TABLE - 2.XII

LIMITING APPARENT MOLAR VOLUMES (Φ_V^0) AND EXPERIMENTAL SLOPES (S_V^*) FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL + WATER AT 303.15K.

Ethanol + water (%w/w)	$\phi_V^0 = \overline{V_2^0}$ (cm^{3}mol^{-1})	S_V^* (cm^3 dm$^{3/2}$ mol$^{-3/2}$)	$\Delta\overline{V_{tr}^0}$ (cm^3 mol^{-1})
Manganese chloride			
0 (water)	69.39	1.112	------
5	53.93	0.370	-15.46
10	49.57	0.439	-19.82
15	46.57	0.437	-22.82
20	44.24	0.447	-25.15
35	39.97	0.528	-29.48
Cobalt chloride			
0 (water)	120.51	0.519	-----
5	138.15	0.626	17.64
10	131.43	0.652	00.92
15	130.13	0.658	09.62
20	127.23	0.697	06.72
35	125.21	0.698	04.70
Nickel chloride			
0 (water)	83.88	0.865	------
5	109.92	0.534	26.04
10	104.64	0.675	20.76
15	102.6	0.684	18.72
20	99.56	0.731	15.68
35	96.40	0.862	12.52
Copper chloride			
0(water)	41.01	0.538	------
5	69.19	0.454	28.18
10	64.45	0.467	23.44

15	59.85	0.477	18.84
20	57.56	0.503	16.55
35	55.73	0.546	14.72
Cadmium chloride			
0(water)	60.8	0.668	-----
5	57.02	0.497	-3.771
10	50.21	0.694	-10.59
15	47.24	0.756	-13.55
20	42.49	0.836	-18.30
35	38.97	0.861	-21.82
Magnesium chloride			
0(water)	138.39	0.654	------
5	146.45	0.634	8.06
10	142.07	0.702	3.68
15	139.52	0.767	1.13
20	135.79	0.824	-2.60
35	133.12	0.847	-5.27

Since above mentioned divalent transition metal chlorides and magnesium chloride are not ionized at higher concentrations in different mixtures of ethanol + water at 303.15K, therefore an appreciable inter –ionic penetration does not occur and this gives rise to the positive slope (i.e. strong ion – ion interactions) in ϕ_V vs $\sqrt{c}$ plots i.e. the absence of negative slopes.

The glance of Table 2. XII also shows that the values of ϕ_V^0 are positive and large for all divalent transition metal chlorides and magnesium chloride in the entire composition range of ethanol + water at 303.15K, thereby showing the presence of strong ion - solvent interactions. Further, it is also clear from Table 2. XII that the values of ϕ_V^0, in case of each transition metal chloride and magnesium chloride, decrease with the increase of ethanol content in water which may be attributed to the decrease in solvation of ions. It means that ion – solvent interactions decrease with the increase of ethanol compositions in water.

The values of volumes of transfer ($\Delta\overline{V_{tr}^0}$) have been determined by using the relation (2.24) for all divalent transition metal chlorides and magnesium chloride in different binary aqueous mixtures of ethanol at 303.15K and the corresponding values are recorded in Table 2.XII. It is clear that the values of $\Delta\overline{V_{tr}^0}$ continuously decrease in magnitude with the increase of ethanol content in water, may be attributed to the increase in electrostriction in the presence of ethanol. Thus, the electrostriction effect, which brings shrinkage in the volume of the solvent, is enhanced in the mixed solvents as compared with that in pure water. Electrostriction primarily reflects electrolyte – solvent or ion – solvent interactions, so it can be inferred that ion – solvent interactions decrease with the increase in ethanol content in water, again confirming the earlier conclusion of greater affinity of ethanol for water.

Since, Cl^- ion is common in all divalent transition metal chlorides and magnesium chloride, therefore from the values of $\Delta\overline{V_{tr}^0}$, it may be inferred that in a particular composition of ethanol + water, the electrostriction for these transition metal cations follows the following order:

$$Mn^{2+} > Cd^{2+} > Mg^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$$

Thus it may be concluded from this order that Cu^{2+} ion is preferentially solvated by ethanol + water and the order of preferential salvation of the cations is given below:

$$Cu^{2+} > Ni^{2+} > Co^{2+} > Mg^{2+} > Cd^{2+} > Mn^{2+.}$$

Further, the values of $\Delta\overline{V_{tr}^{0}}$, for an individual electrolyte, decrease with the increase in composition of ethanol in water for all the divalent transition metal chlorides and magnesium chloride, therefore the extent of preferential solvation for a particular cation decreases with the increase in ethanol content and leads to increase in solvent – solvent interactions i.e. between ethanol and water.

Effect of temperature

Since behaviour of all divalent transition metal chlorides and magnesium chloride in binary aqueous mixtures of ethanol + water was found to be similar at 303.15K, therefore only one composition 5% (w/w) of ethanol + water has been taken for analysing the effect of temperature.

Values of densities and apparent molar molar volumes for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in 5% (w/w) ethanol + water at different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15) K are given in Table – 2.XIII.

On plotting the values of apparent molar volumes against the square root of concentration linear plots of ϕ_V verses $\sqrt{c}$ have been obtained at different temperatures for all the above mentioned divalent transition metal chlorides and magnesium chloride in 5% (w/w) ethanol + water mixture. Sample plots for manganese chloride and magnesium chloride are shown in Figs. 14 and 15 respectively. The values of limiting apparent molar volumes ϕ_V^0 and experimental slopes S_V^* calculated by applying the least square theory to the above mentioned linear plots of ϕ_V vs $\sqrt{c}$ (using 2.10 equation) are given in Table – 2.XIV.

It is clear from Table 2.XIV that the values of S_V^* are positive and large for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in 5% (w/w) aqueous mixture of ethanol in the entire temperatures range, studied here. Since S_V^* is a measure of ion – ion interactions, therefore from the results it is clear that ion – ion interactions are quite strong in the entire temperature range for all the divalent transition metal chlorides and magnesium chloride. Further values of S_V^* increase with the increase of temperature for an individual divalent transition metal chloride as well as magnesium chloride thereby suggesting that ion – ion interactions are further strengthened with the rise in temperature, which may be attributed to the decrease in solvation of ions.

TABLE - 2.XIII

DENSITIES AND APPARENT MOLAR VOLUMES FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL + WATER AT DIFFERENT TEMPERATURES.

Concentration c X 10^2 (mol dm^{-3})	**Density d (g cm^{-3})**	**Partial molar volume ϕ_V (cm^3 mol^{-1})**
	Manganese chloride	
Temperature = 298.15K		**d_o = 0.98729 g cm^{-3}**
0.493	0.98797	60.88
0.690	0.98824	61.15
0.986	0.98864	61.86
2.956	0.99125	64.76
4.920	0.99377	67.04
6.878	0.99623	68.80
9.804	0.99981	71.10
Temperature = 303.15K		**d_o = 0.98626 g cm^{-3}**
0.493	0.98697	54.63
0.690	0.98725	55.20
0.985	0.98767	55.62
2.953	0.99034	60.59
4.916	0.99298	62.06
6.873	0.99555	63.62
9.799	0.99932	65.53
Temperature = 308.15K		**d_o = 0.98340 g cm^{-3}**
0.491	0.98413	50.23
0.688	0.98442	50.51
0.982	0.98485	51.23
2.945	0.98762	55.55
4.903	0.99034	57.31
6.855	0.99294	59.74
9.773	0.99671	62.76
Temperature = 313.15K		**d_o = 0.97866 g cm^{-3}**
0.489	0.97941	45.57
0.684	0.9797	47.04
0.978	0.98014	47.62
2.931	0.983	50.94
4.880	0.98571	54.61
6.823	0.98824	58.75
9.732	0.99246	57.32

Temperature = 318.15K		**d_o = 0.97419 g cm^{-3}**
0.487	0.97494	45.06
0.681	0.97524	45.04
0.973	0.97568	46.07
2.918	0.97856	49.43
4.858	0.98127	53.55
6.793	0.98394	55.82
9.687	0.98793	57.55

Cobalt chloride

Temperature = 298.15K		**d_o = 0.98729 g cm^{-3}**
0.493	0.98775	146.54
0.690	0.98793	147.09
0.985	0.98819	148.52
2.948	0.98989	151.68
4.899	0.99147	154.57
6.837	0.99298	156.69
9.72	0.99513	159.29
Temperature = 303.15K		**d_o = 0.98626 g cm^{-3}**
0.492	0.98674	142.48
0.689	0.98692	144.21
0.984	0.98720	144.46
2.945	0.98894	149.00
4.894	0.99056	152.16
6.831	0.99211	154.41
9.711	0.99426	157.72
Temperature = 308.15K		**d_o = 0.98340 g cm^{-3}**
0.491	0.98389	140.53
0.687	0.98408	141.39
0.982	0.98436	142.53
2.937	0.98611	148.12
4.880	0.98777	150.90
6.811	0.98932	153.57
9.684	0.99150	156.89
Temperature = 313.15K		**d_o = 0.97866 g cm^{-3}**
0.489	0.97916	138.63
0.684	0.97935	140.10
0.977	0.97964	140.65
2.923	0.98145	145.60
4.858	0.98315	148.67
6.780	0.98473	151.64
9.639	0.98688	155.98
Temperature = 318.15K		**d_o = 0.97419 g cm^{-3}**
0.486	0.97470	136.68
0.681	0.97490	137.25

0.972	0.97519	138.72
2.910	0.97705	143.36
4.836	0.97878	146.81
6.750	0.98040	149.80
9.598	0.98266	153.65

Nickel chloride

Temperature = 298.15K		**d_o = 0.98729 g cm^{-3}**
0.493	0.98790	115.54
0.690	0.98814	116.10
0.986	0.98849	117.52
2.951	0.99076	121.68
4.906	0.99291	124.75
6.850	0.99498	127.08
9.746	0.99785	131.03
Temperature = 303.15K		**d_o = 0.98626 g cm^{-3}**
0.492	0.98689	111.42
0.689	0.98714	111.68
0.985	0.98750	113.40
2.948	0.98985	117.57
4.902	0.99207	120.85
6.845	0.99419	123.56
9.740	0.99724	126.73
Temperature = 308.15K		**d_o = 0.98340 g cm^{-3}**
0.491	0.98404	109.29
0.687	0.98429	110.15
0.982	0.98466	111.29
2.940	0.98702	116.52
4.888	0.98928	119.40
6.826	0.99143	122.11
9.714	0.99452	125.32
Temperature = 313.15K		**d_o = 0.97866 g cm^{-3}**
0.489	0.97931	107.09
0.684	0.97956	108.55
0.977	0.97994	109.11
2.926	0.98232	115.08
4.865	0.98462	117.72
6.794	0.98684	119.88
9.669	0.98993	123.80
Temperature = 318.15K		**d_o = 0.97419 g cm^{-3}**
0.486	0.97485	104.85
0.681	0.97511	105.42
0.973	0.97549	106.89
2.913	0.97792	112.57
4.843	0.98025	115.58

6.765	0.98251	117.76
9.628	0.98571	121.19

Copper chloride

Temperature = 298.15K		**d_o = 0.98729 g cm^{-3}**
0.493	0.98776	76.20
0.690	0.98794	77.36
0.986	0.98821	78.22
2.954	0.98997	80.81
4.916	0.99162	83.46
6.870	0.99321	85.40
9.787	0.99547	88.03
Temperature = 303.15K		**d_o = 0.98626 g cm^{-3}**
0.493	0.98675	72.07
0.69	0.98694	72.94
0.985	0.98723	73.06
2.952	0.98905	77.03
4.912	0.99078	79.55
6.865	0.99248	80.99
9.781	0.99478	84.53
Temperature = 308.15K		**d_o = 0.98340 g cm^{-3}**
0.491	0.9839	69.92
0.688	0.98409	71.38
0.982	0.98438	71.95
2.943	0.98623	75.60
4.898	0.98796	78.69
6.845	0.98966	80.37
9.754	0.99207	82.97
Temperature = 313.15K		**d_o = 0.97866 g cm^{-3}**
0.489	0.97918	65.58
0.684	0.97938	66.76
0.978	0.97968	67.63
2.929	0.9816	71.66
4.875	0.98345	73.81
6.815	0.98522	75.84
9.711	0.98771	78.98
Temperature = 318.15K		**d_o = 0.97419 g cm^{-3}**
0.486	0.97472	63.27
0.681	0.97492	65.06
0.973	0.97523	65.34
2.916	0.97717	70.12
4.853	0.97898	73.69
6.784	0.98075	75.74
9.669	0.98339	77.33

Cadmium chloride		
Temperature = 298.15K		**d_o = 0.98729 g cm^{-3}**
0.493	0.98799	60.24
0.690	0.98826	61.69
0.986	0.98867	62.25
2.956	0.99129	66.85
4.919	0.99385	68.85
6.877	0.99638	70.04
9.802	0.99996	72.99
Temperature = 303.15K		**d_o = 0.98626 g cm^{-3}**
0.493	0.98697	58.10
0.690	0.98725	58.67
0.985	0.98766	60.11
2.953	0.99034	64.04
4.915	0.9929	67.15
6.870	0.99528	71
9.792	0.99894	72.83
Temperature = 308.15K		**d_o = 0.98340 g cm^{-3}**
0.491	0.98412	55.77
0.688	0.9844	56.94
0.982	0.98482	57.8
2.944	0.98751	62.79
4.901	0.99011	65.50
6.851	0.99252	69.35
9.765	0.99625	70.92
Temperature = 313.15K		**d_o = 0.97866 g cm^{-3}**
0.489	0.97939	53.23
0.684	0.97968	53.52
0.978	0.98012	53.19
2.930	0.98288	58.59
4.878	0.98552	62.03
6.82	0.98801	65.62
9.722	0.99177	67.92
Temperature = 318.15K		**d_o = 0.97419 g cm^{-3}**
0.487	0.97494	48.56
0.681	0.97523	50.05
0.973	0.97567	50.63
2.917	0.97844	57.13
4.857	0.98119	58.72
6.790	0.98375	62.14
9.680	0.98756	64.88

	Magnesium chloride	
Temperature = 298.15K		**d_o = 0.98729 g cm^{-3}**
0.493	0.98754	154.59
0.690	0.98763	156.04
0.985	0.98777	156.60
2.947	0.98857	161.94
4.896	0.98929	164.55
6.832	0.98993	166.78
9.709	0.99072	170.14
Temperature = 303.15K		**d_o = 0.98626 g cm^{-3}**
0.492	0.98653	150.59
0.689	0.98663	151.75
0.984	0.98678	152.60
2.945	0.98766	157.94
4.892	0.98845	160.76
6.827	0.98917	162.92
9.703	0.99007	166.33
Temperature = 308.15K		**d_o = 0.98340 g cm^{-3}**
0.491	0.98369	146.72
0.687	0.98380	147.59
0.982	0.98396	148.75
2.936	0.98495	153.07
4.879	0.98581	156.52
6.809	0.98657	159.40
9.679	0.98758	162.83
Temperature = 313.15K		**d_o = 0.97866 g cm^{-3}**
0.489	0.97896	145.05
0.684	0.97907	146.53
0.977	0.97924	147.10
2.922	0.98024	152.51
4.856	0.98115	155.35
6.777	0.98194	158.29
9.634	0.98303	161.40
Temperature = 318.15K		**d_o = 0.97419 g cm^{-3}**
0.486	0.97451	141.21
0.681	0.97463	142.4
0.972	0.97481	143.28
2.909	0.97588	149.08
4.835	0.97683	152.65
6.747	0.97765	156.06
9.591	0.97867	160.75

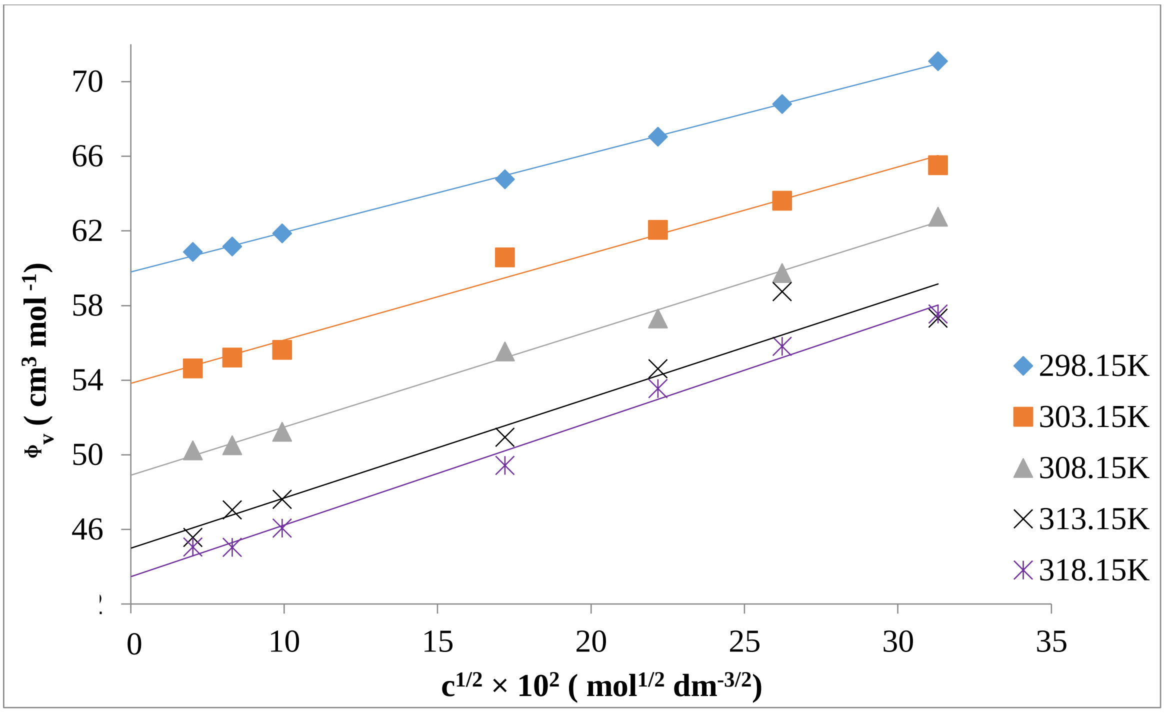

Fig.14. PLOTS OF Φ_V VS. $\sqrt{c}$ FOR MANGANESE CHLORIDE IN 5% (w/w) ETHANOL + WATER AT DIFFERENT TEMPERATURES.

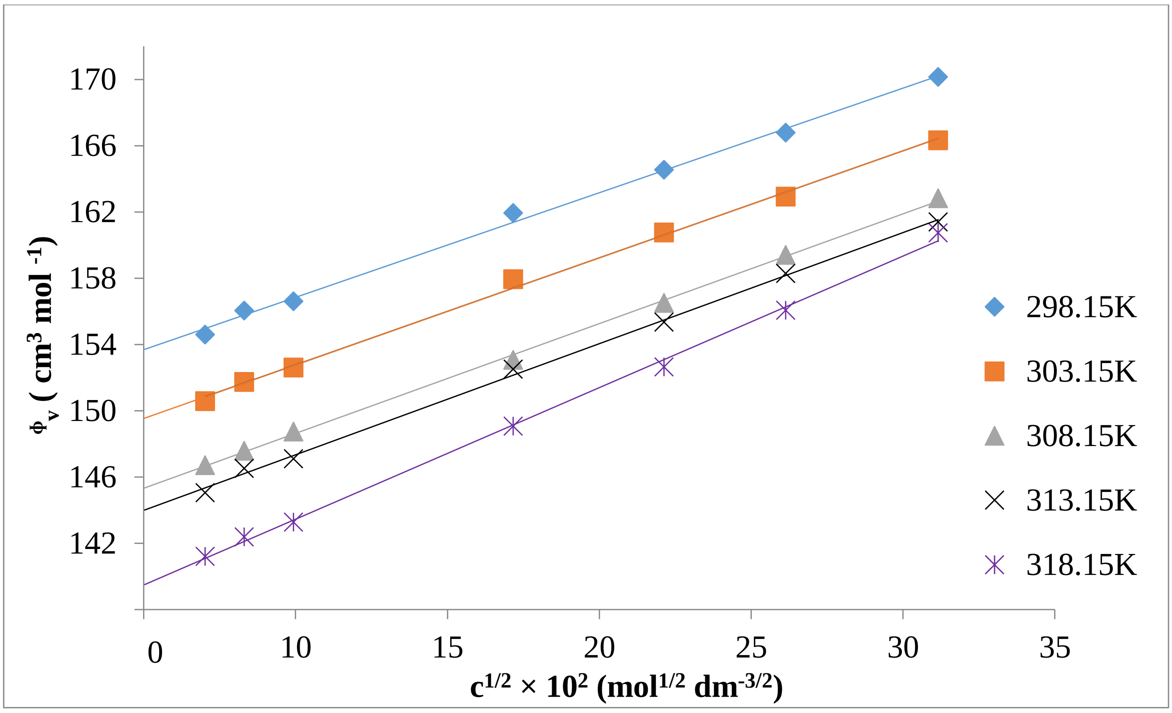

Fig.15. PLOTS OF Φ_V VS. $\sqrt{c}$ FOR MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL + WATER AT DIFFERENT TEMPERATURES.

TABLE - 2.XIV

LIMITING APPARENT MOLAR VOLUMES (ϕ_V^0) AND EXPERIMENTAL SLOPES (S_V^*) FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5%(w/w) ETHANOL + WATER AT DIFFERENT TEMPERATURES.

Temperature (K)	$\phi_V^0 = \overline{V_2^0}$ (cm^{3}mol^{-1})	S_V^* (cm^3 dm$^{3/2}$ mol$^{-3/2}$)
	Manganese chloride	
298.15	57.68	0.424
303.15	51.51	0.464
308.15	46.32	0.517
313.15	42.30	0.540
318.15	40.70	0.556
	Cobalt chloride	
298.15	142.91	0.525
303.15	138.55	0.612
308.15	135.89	0.680
313.15	133.87	0.693
318.15	131.59	0.703
	Nickel chloride	
298.15	111.02	0.627
303.15	106.74	0.639
308.15	104.73	0.660
313.15	102.71	0.677
318.15	100.14	0.687
	Copper chloride	
298.15	73.21	0.466
303.15	68.45	0.499
308.15	66.66	0.526
313.15	62.19	0.533
318.15	59.75	0.595
	Cadmium chloride	
298.15	57.30	0.505
303.15	53.63	0.626
308.15	51.51	0.643
313.15	47.85	0.650
318.15	44.33	0.673
	Magnesium chloride	
298.15	150.53	0.631
303.15	146.32	0.645
308.15	142.03	0.663
313.15	140.64	0.673
318.15	135.53	0.798

Also values of ϕ_V^0 decrease with the increase of temperature for all the divalent transition metal chlorides and magnesium chloride in 5% (w/w) ethanol + water mixture in the entire temperature range, which may be attributed to the decrease in ion – solvent interactions.

The temperature dependence of ϕ_V^0 in 5% (w/w) ethanol + water mixture for different divalent transition metal chlorides viz; manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride can be expressed by the following relations:

$\phi_V^0 = 2365.18 - 14.13\ T + 0.021T^2$ for manganese chloride (2.31)

$\phi_V^0 = 2517.88 - 14.94\ T + 0.023\ T^2$ for cobalt chloride (2.32)

$\phi_V^0 = 2408.91 - 14.44\ T + 0.022\ T^2$ for nickel chloride (2.33)

$\phi_V^0 = 623.73 - 2.72\ T + 2.91 \times 10^{-3}\ T^2$ for copper chloride (2.34)

$\phi_V^0 = 284.21 - 0.78\ T + 9.03 \times 10^{-5}\ T^2$ for cadmium chloride (2.35)

$\phi_V^0 = 2950.40 - 17.79\ T + 0.028\ T^2$ for magnesium chloride (2.36)

where T represents the absolute temperature.

The partial molar volume expansibilities, $\phi_E^0 = \left[\frac{\partial \phi_V^0}{\partial T}\right]_P$, calculated from equations (2.31) to (2.36) for different divalent transition metal chlorides and magnesium chloride at different temperatures in 5% (w/w) ethanol + water, are recorded in Table 2.XV. The results of Table 2.XV show that the values of ϕ_E^0 are negative but increase in magnitude with the increase in temperature for all the divalent transition metal chlorides and magnesium chloride (mentioned above) thereby suggesting that the behaviour of these salts is just like symmetrical tetra alkyl ammonium salts [22] but not like common salts [23,24] in ethanol + water mixtures, because in case of common salts the molar expansibility ϕ_E^0 should decrease with the increase in temperature.

The variation of ϕ_E^0 with temperature for all the divalent transition metal chlorides and magnesium chloride is linear and the sample plots for cobalt chloride and magnesium chloride are shown in Figs.16 and 17, respectively. The increase in ϕ_E^0, for all the electrolytes studied here, in 5% (w/w) ethanol + water, with the increase in temperature may be ascribed to the presence of "caging effect" [22,25]. From these results it may also be noted that the behaviour of the divalent transition metal chlorides and magnesium chloride do not change when the solvent is changed from water to ethanol + water.

TABLE - 2.XV

VALUES OF LIMITING MOLAR EXPANSIBILITIES ϕ_E^0 FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL + WATER AT DIFFERENT TEMPERATURES.

Electrolyte	ϕ_E^0 (cm^{3}mol^{-1}K^{-1})				
Temperature (K)	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**
Manganese chloride	-1.60	-1.39	-1.18	-0.97	-0.76
Cobalt chloride	-1.22	-0.99	-0.76	-0.53	-0.30
Nickel chloride	-1.32	-1.10	-0.88	-0.66	-0.44
Copper chloride	-0.98	-0.95	-0.92	-0.89	-0.86
Cadmium chloride	-0.726	-0.725	-0.724	-0.723	-0.722
Magnesium chloride	-1.09	-0.81	-0.53	-0.25	0.02

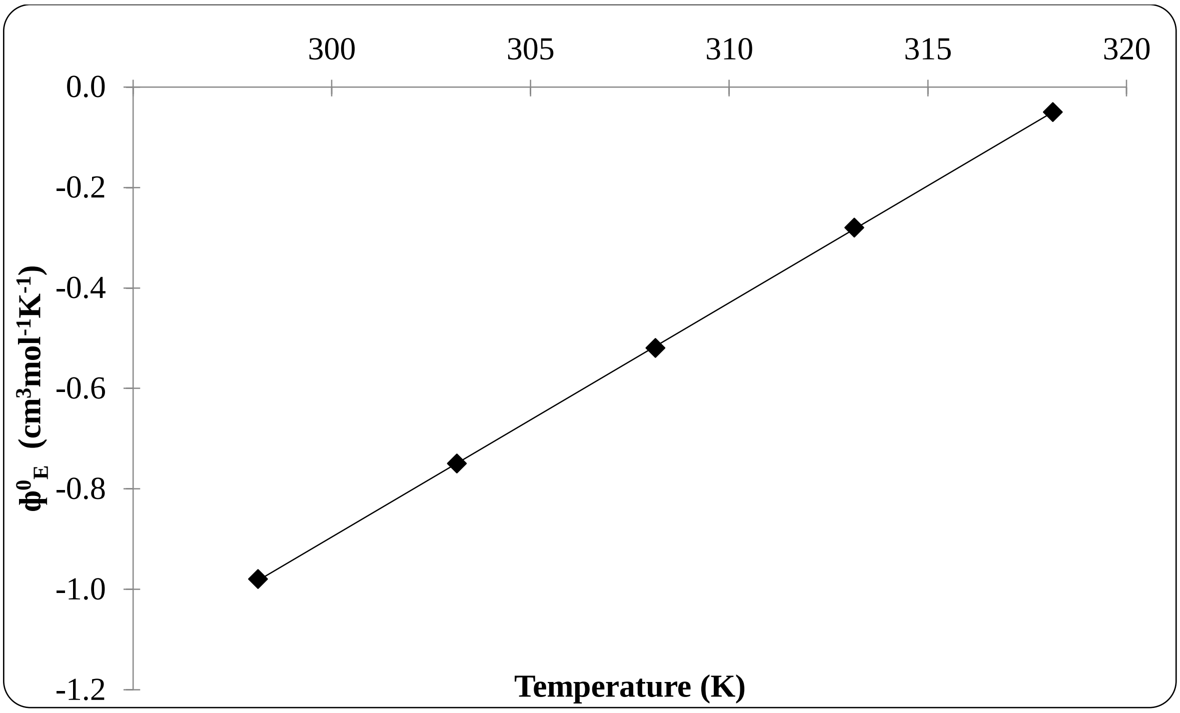

Fig.16. VARIATION OF ϕ^0_E WITH TEMPERATURE FOR COBALT CHLORIDE IN 5% (w/w) COMPOSITION OF ETHANOL IN WATER.

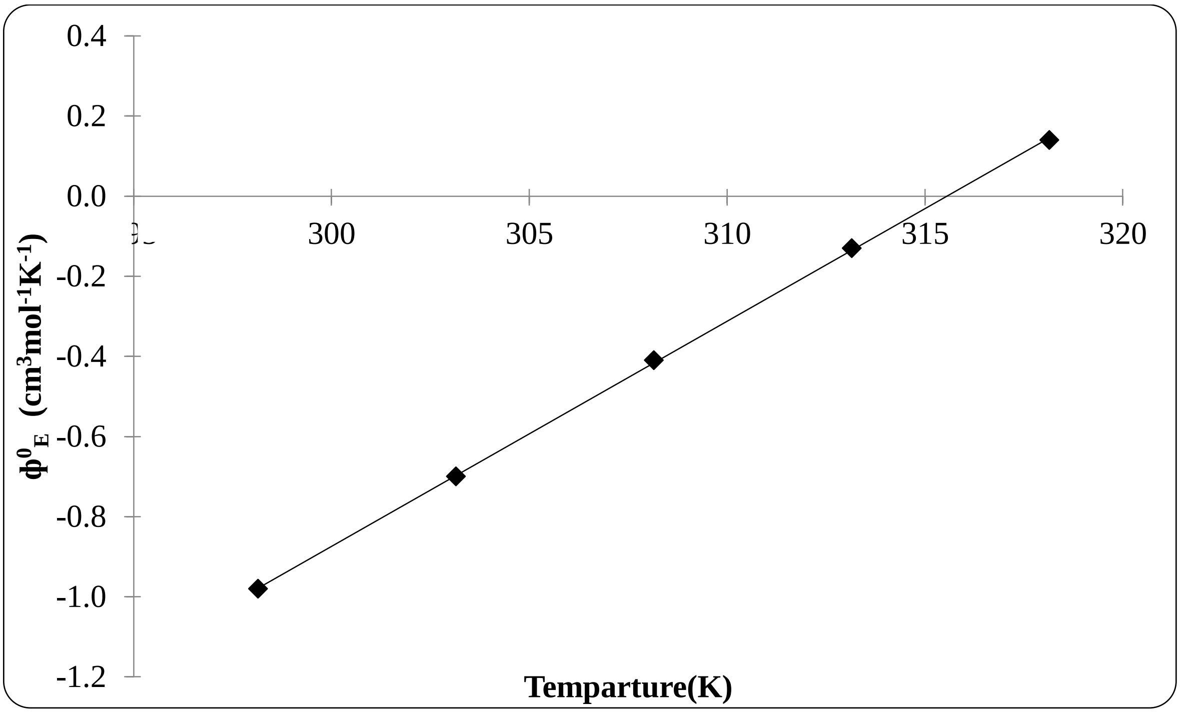

Fig.17. VARIATION OF ϕ^0_E WITH TEMPERATURE FOR MAGENISUM CHLORIDE IN 5% (w/w) COMPOSITION OF ETHANOL IN WATER

By applying the criteria of Hepler [21] to relations (2.31) to (2.36) for divalent transition metal chlorides and magnesium chloride in 5% (w/w) ethanol + water mixture, it is found that values of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)p$ is positive suggesting that manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride behave as structure makers/promoters in ethanol + water mixture.

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CHAPTER – III

VISCOSITIES OF SOME DIVALANT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN BINARY AQUEOUS MIXTURES OF ALCOHOLS

3.1 Introduction

The viscosity of a liquid is defined as a measure of resistance to its flow. As flow takes place by the displacement of the molecules, so studies of viscosity can lead to information about these displacements. Number of researchers revealed that the addition of an electrolyte either breaks or makes the structure of the solvent. The making and breaking structure of fluids have been considered as a measure of solute –solvent interactions.

The interstitial solvent between the cosphere of ions is unmodified in very dilute solutions and has the same properties as in the pure solvent [1], each species of ion would be expected to contribute towards a change in viscosity, but electrostatic forces between oppositely charged ions must be taken into consideration.

The study of viscosity of electrolyte solutions is usually done to get information of ion – solvent interactions [2-5]. Generally, relative viscosity variation with the molar concentration (c) is represented by Jones – Dole relation [6]:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \tag{3.1}$$

where η and η_0 are the viscosity coefficients of the solution and solvent respectively. A is the Falkenhagen coefficient [7] that takes into account the ionic interactions and B is the Jones – Dole Coefficient related to the size of ions and to the different ion – solvent interactions. Moreover, B – coefficient has been used as a measure of structure breaking or making capacity of an electrolyte in a particular solvent [8] , therefore its estimation will throw light on the strength of self association of the solvent molecules.

The negative B – coefficient indicates a decrease in the viscosity in the presence of a solute and hence increase in the fluidity which results into net decrease in the structure of the solvent. Conversely, an increases in the structure increases the rigidity and hence viscosity of the solvent resulting in a positive B – coefficient.

The shapes and size of electrolytes were correlated with the B – coefficient through Vand equation [9]. Strokes [10] assumption of a rigid solvated volume independent of the concentration is valid only at high dilution. Assuming that the large tetra – alkyl ammonium ions have a spherical symmetry, a correlation between the partial molar volumes and viscosity measurements have been proposed through the Einstein equation [11].

It was shown [12] that following factors are responsible for the variation of the B – coefficient from solvent to solvent.

(i) Structure breaking which is more important in three dimensional solvents than in other classes of solvents.

(ii) High molal volumes and low dielectric constants, which yield high B – values for the similar solvents and,

(iii) Reduced B – values when the primary solvation of ions is sterically hindered in high molal volume of solvents or if either ion of the binary electrolyte is not specifically solvated.

As it is difficult to separate the ionic size effect from the structural effect of B – coefficients, better criteria [13] for the solvent structural influence would be the temperature dependence of the value of B – coefficient i.e. $\frac{\mathrm{dB}}{\mathrm{dT}}$. This criterion suggests that structure makers will have negative values of $\frac{\mathrm{dB}}{\mathrm{dT}}$. Kay et. al. [14] had deduced that viscosity B – coefficient measurements of R_4NBr in water as a function of temperature and by comparison with the corresponding B – values in methanol solutions shows that Bu_4NBr and Pr_4NBr are strong structure makers where as Et_4NBr has almost no effect on water structure. This must be due to the large size of R_4N^+ ions in Bu_4NBr and Pr_4NBr, since the contribution from Br- ion to the B – values is very small.

The viscosity data can also be interpreted on the basis of transition state theory of relative viscosity of electrolytic solution as suggested by Feakins et. al. [15]. The B – coefficient in the light of this theory can be related by the equation:

$$\mathrm{B} = \frac{\overline{\mathrm{V}}_1^0 - \overline{\mathrm{V}}_2^0}{1000} + \frac{\overline{\mathrm{V}}_1^0}{1000}\left[\frac{\Delta\mu_2^{0*} - \Delta\mu_1^{0*}}{\mathrm{RT}}\right] \tag{3.2}$$

Here $\overline{\mathrm{V}}_1^0$ and $\overline{\mathrm{V}}_2^0$ are the partial molar volumes of the solvent and solute (at infinite dilution) respectively. $\Delta\mu_2^{0*}$ is activation free energy for the viscous flow per mole of the solution, $\Delta\mu_1^0$ is activation free energy of activation per mole of the pure solvent and is given by the following expression[16]:

$$\Delta\mu_1^{0*} = \Delta\mathrm{G}_1^0 = \mathrm{RTIn}\left({}^{\eta_0\overline{\mathrm{V}}_1^0}\!\big/_{\mathrm{Nh}}\right) \tag{3.3}$$

where h is plank's constant and N is the Avogadro's number, η_0 is the viscosity of the solvent.

The equation (3.2) may be rearranged as follows:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + \frac{RT}{V}[1000\ B - (\overline{V}_1^0 - \overline{V}_2^0)] \qquad (3.4)$$

Therefore in order to determine $\Delta\mu_2^{0*}$, the values of $\Delta\mu_1^{0*}$ should be known which can be calculated by using equation (3.3). Greater values of $\Delta\mu_2^{0*}$ represent the strong ion – solvent interactions. The enthalpy and entropy of activation for viscous flow can also be calculated if the B – coefficient is determined at different temperatures.

A number of extensive viscometric studies have been done recently in various solvents and their aqueous mixtures involving different electrolytes but literature provides less information regarding the viscometric studies of 2 : 1 salts in binary aqueous mixtures of alcohols. This led to the study of transition metal chlorides viz; manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in binary aqueous mixtures of alcohols (methanol and ethanol).

3.2 Experimental Details

The experimental part of this chapter has been discussed under the following sections:

(i) Materials

(ii) Measurements of viscosity

(iii) Sources of error

(i) Materials

For the measurements, all the materials used were of AR grade and used as such only after drying as described in chapter 2. The water required for the preparation of various types of solutions was also prepared as described in chapter 2.

(ii) Measurement of Viscosity

Viscosity measurements were made with the help of suspended level type viscometer. The viscometer, shown in Fig.18, consists of a U-tube with two bulbs 'D' and 'E', along with a side arm 'F'. The left limb is a pipette with two definite marks 'A' and 'B' above and below

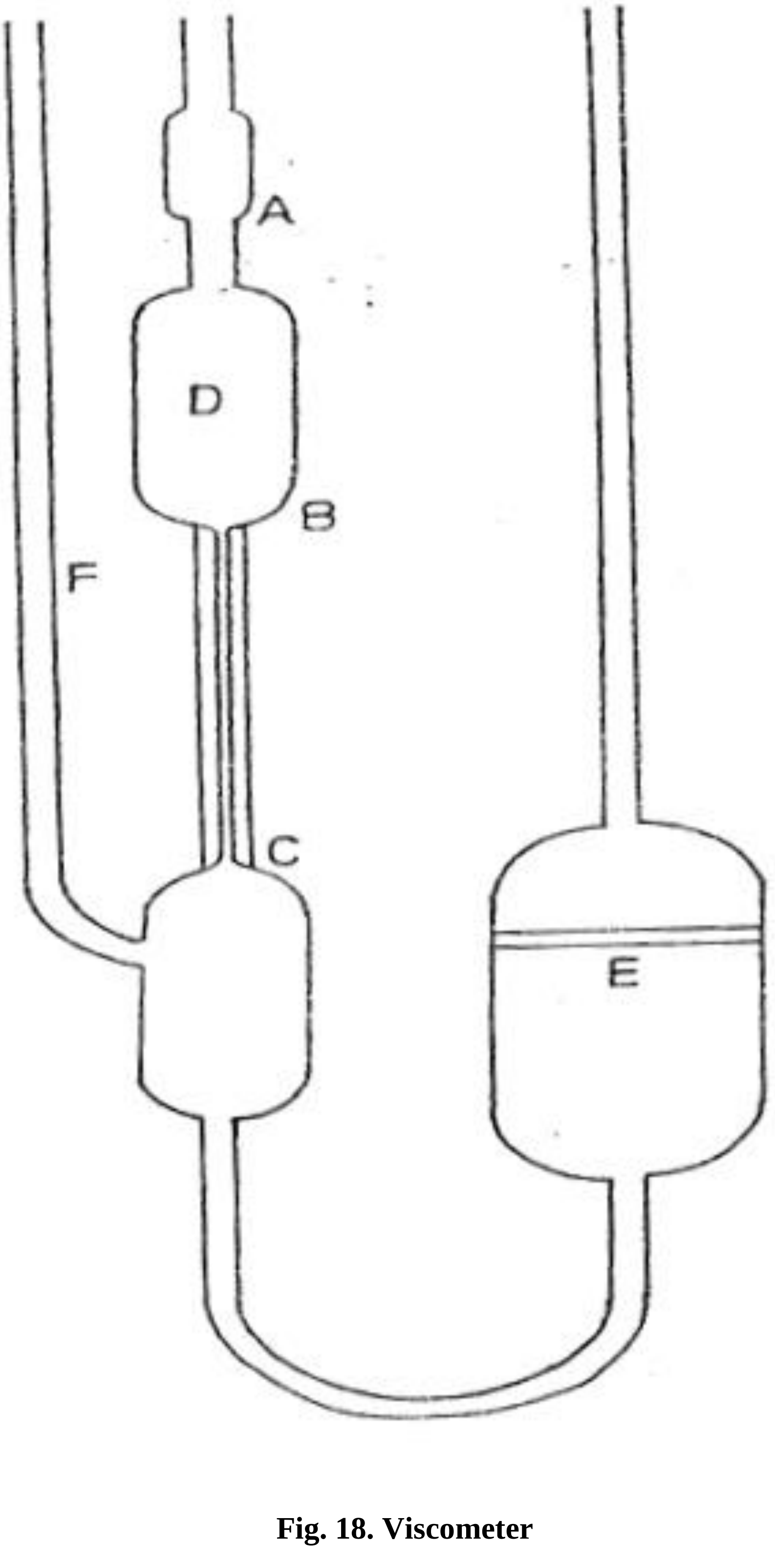

Fig. 18. Viscometer

the bulb ‘D’ and a fine capillary ‘C’ about 10" long through which the liquid contained in the bulb “D’ flows under gravity into bulb ‘E’.

The viscometer was thoroughly cleaned with chromic acid, followed by washing with water and finally with acetone. The viscometer was then dried by applying vacuum. Flow time for volume of solution through the capillary, between the marks A and B was measured with the help of a stop watch capable of recording time upto 0.1 second. Viscosities of solutions were determined at different temperatures in water thermostat controlled upto $\pm 0.01^0$C by means of an electronic relay and contact thermometer.

Procedure: A known volume of solution was introduced into the bulb ‘E’ keeping the side arm ‘F’ closed, the solution was forced through the capillary tube ‘C’ until the meniscus stood above the mark ‘A’. On opening the side arm ’F’, while keeping capillary limb closed, the solution below ‘ C’ falls back and the column of solution CA is held suspended. On opening the capillary tube the flow time between marks ‘A’ and ‘B’ was noted. The column of the liquid CA is same in each case, independent of the volume of the solution in viscometer. The flow time between marks ‘A’ and ‘B’ was determined by visual observations.

The relative viscosities of solutions were calculated by using the following relation:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{d\,t}{d_0 t_0} \qquad (3.5)$$

where d and d_0 are densities, η and η_0 are viscosities of the solution and solvent respectively, t and t_0 are the times of flow of solution and solvent respectively. Since all the flow times were greater than 100 seconds, so kinetic energy correction is not required. Also the densities needed for the purpose of the calculation of viscosity were measured as described in chapter 2.

All the solutions were made by weight and the molality was converted into molarity as described in Chapter – 2.

The calibration of the viscometer was done with the help of conductivity water, used as a standard liquid. This calibration was further checked by determining the viscosity of methanol = 0.5073 cP is in good agreement with the corresponding literature value of 0.5064 cP at 303.15K .

(iii) Sources of Error

The various sources of error and factors affecting the reproducibility of the results are discussed as follows:

(a) Fluctuation of temperature: Viscosity of solution is very sensitive to temperature change. With every one degree rise in temperature there is decrease in viscosity of solution by one to two percent, which can lead to a large change in viscosity. So in order to minimize this error, viscometer is suspended in a water thermostat where the temperature fluctuation was controlled with in $\pm 0.01^0$C.

(b) Solute and solvent purity: To obtain the viscosity data with maximum accuracy, the solute and solvent of AR Grade are used after drying and using triple distilled water.

(3.3) Results and Discussion

Here in the present study, viscosities of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride have been determined in water and in binary aqueous mixtures methanol and ethanol at various concentrations of the solute and at five different temperatures. For the convenience, results have been explained in sections A, B and C.

Section - A

Discussion on the Results of Viscous Flow of Some Divalent Transition Metal Chlorides and Magnesium Chloride in Water.

Densities, viscosities and relative viscosities for the solutions of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water have been determined at 303.15K, and the values are recorded in Table 3.I. It is clear that the values of relative viscosities for all the divalent transition metal chlorides and magnesium chloride increase with the increase in concentration of individual electrolyte in water.

TABLE - 3.I

DENSITIES, VISCOSITIES AND RELATIVE VISCOSITIES OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

Concentration $c \times 10^2$ (mol dm^{-3})	**Density** d (g cm^{-3})	**Viscosity** η (cP)	**Relative Viscosity** $\frac{\eta}{\eta_o}$
		η_0 = 0.8007 cP	
		Manganese chloride	
0.497	0.99625	0.8270	1.0328
0.696	0.99648	0.8321	1.0392
0.994	0.99682	0.8386	1.0474
2.979	0.99893	0.8698	1.0863
4.955	1.00090	0.8933	1.1157
6.922	1.00256	0.9131	1.1403
9.852	1.00478	0.9383	1.1719
		Cobalt chloride	
0.497	0.99622	0.8186	1.0223
0.696	0.99644	0.8229	1.0278
0.994	0.99677	0.8281	1.0342
2.975	0.99890	0.8516	1.0636
4.945	1.00090	0.8673	1.0832
6.905	1.00286	0.8810	1.1003
9.822	1.00565	0.9004	1.1245
		Nickel chloride	
0.497	0.99640	0.8173	1.0208
0.696	0.99667	0.8210	1.0255
0.994	0.99708	0.8256	1.0311
2.978	0.99980	0.8461	1.0567
4.952	1.00229	0.8608	1.0751

6.917	1.00471	0.8727	1.0900
9.848	1.00830	0.8935	1.1160
Copper chloride			
0.497	0.99629	0.8270	1.0329
0.696	0.99652	0.8321	1.0392
0.995	0.99686	0.8387	1.0474
2.982	0.99924	0.8701	1.0867
4.965	1.00146	0.8938	1.1163
6.943	1.00373	0.9141	1.1417
9.899	1.00682	0.9402	1.1743
Cadmium chloride			
0.497	0.99633	0.8222	1.0268
0.696	0.99659	0.8273	1.0332
0.995	0.99697	0.8332	1.0406
2.980	0.99954	0.8598	1.0739
4.959	1.00192	0.8781	1.0966
6.931	1.00418	0.8941	1.1167
9.875	1.00743	0.9154	1.1432
Magnesium Chloride			
0.497	0.99595	0.8225	1.0273
0.696	0.99607	0.8268	1.0326
0.994	0.99624	0.8326	1.0398
2.973	0.99727	0.8572	1.0706
4.940	0.99818	0.8755	1.0934
6.894	0.99897	0.8909	1.1126
9.801	1.00007	0.9108	1.1375

Relative viscosities of all the divalent transition metal chlorides and magnesium chloride studied here in water at 303.15K can be represented by Jones – Dole equation and a straight line plot should be obtained if $(\eta_r - 1)/\sqrt{c}$ is plotted against the square root of molar concentration $\sqrt{c}$ according to this equation and the same has been found true in the present study also for all the above mentioned transition metal chlorides and magnesium chloride in water at 303.15K. Plots for all the selected divalent transition metal chlorides and magnesium chloride are shown in Fig. 19. The values of A and B parameters of Jones – Dole equation, obtained by using least squares method for the plots of $(\eta_r - 1)/\sqrt{c}$ verses $\sqrt{c}$ are recorded in Table 3.II.

It is clear from Table 3.II that the values of A parameter are positive thereby indicating the presence of specific ion-ion interactions. It is also clear from Table 3.II that the values of B – coefficients, for all the divalent transition metal chlorides and magnesium chloride, studied here, are positive and smaller in comparison to the values of A parameters. This suggests the existence of weak ion – solvent interactions in water at 303.15K.

Effect of temperature:

Densities, viscosities and relative viscosities for the solutions of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water at five equidistant temperatures 298.15, 303.15, 308.15, 313.15 and 318.15K are determined and are given in Table 3.III. From the perusal of Table 3.III, it is clear that values of relative viscosities for the solutions of above mentioned divalent transition metal chlorides and magnesium chloride in water at all the temperatures increase with the increase in concentration of an individual electrolyte. Moreover, the variation of relative viscosity of the solutions of the selected salts in water at different temperatures can be described by Jones- Dole equation (3.1). According to this equation a straight line plot should be obtained if $(\eta_r - 1)/\sqrt{c}$ is plotted against $\sqrt{c}$ and same has been found to be true in the present study for all the above mentioned divalent transition metal chlorides and magnesium chloride in water. Sample plots for manganese chloride and magnesium chloride are shown in Figs. 20 and 21 respectively. The values of A and B parameters obtained with the help of least square method to the linear plots of $(\eta_r - 1)/\sqrt{c}$ verses $\sqrt{c}$ for all the above mentioned divalent transition metal chlorides are recorded in Table 3.IV.

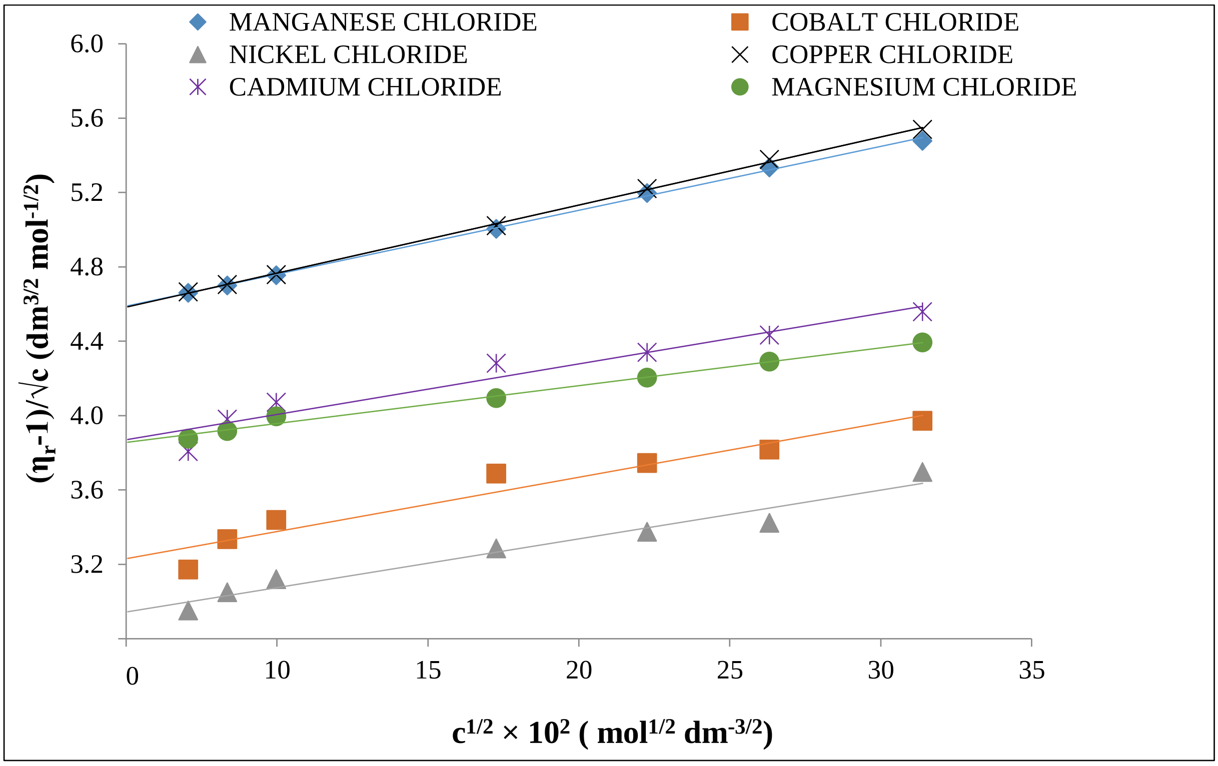

Fig. 19: PLOTS OF $(\eta_r\text{-}1)/\sqrt{c}$ VS $\sqrt{c}$ FOR MANGANESE CHLORIDE, COBALT CHLORIDE,NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGANISUM CHLORIDE IN WATER AT 303.15K.

TABLE 3.II

VALUES OF A AND B PARAMETERS OF THE JONES – DOLE EQUATION FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

Electrolyte	**A** **($dm^{3/2}\ mol^{-1/2}$)**	**B** **($dm^{3}\ mol^{-1}$)**
Manganese chloride	4.417	0.0344
Cobalt chloride	3.083	0.0293
Nickel chloride	2.812	0.0262
Copper chloride	4.401	0.0365
Cadmium chloride	3.734	0.0272
Magnesium chloride	3.753	0.0204

TABLE - 3.III

DENSITIES, VISCOSITIES AND RELATIVE VISCOSITIES OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT DIFFERENT TEMPERATURES.

Concentration c X 10^2 (mol $dm^{-3/2}$)	**Density d (g cm^{-3})**	**Viscosity η (cP)**	**Relative Viscosity $\frac{\eta}{\eta_o}$**
	Manganese chloride		
Temperature = 298.15K			**η_0= 0.8937 cP**
0.498	0.99762	0.9226	1.0324
0.697	0.99784	0.9281	1.0385
0.996	0.99814	0.9358	1.0472
2.980	1.00022	0.9701	1.0855
4.962	1.00225	0.9954	1.1138
6.931	1.00395	1.0182	1.1393
9.866	1.00614	1.0461	1.1705
Temperature = 303.15K			**η_0= 0.8007 cP**
0.497	0.99625	0.8270	1.0328
0.696	0.99648	0.8321	1.0392
0.994	0.99682	0.8386	1.0474
2.979	0.99893	0.8698	1.0863
4.955	1.00090	0.8933	1.1157
6.922	1.00256	0.9131	1.1403
9.852	1.00478	0.9383	1.1719
Temperature = 308.15K			**η_0= 0.72250cP**
0.496	0.99467	0.7465	1.0332
0.695	0.99490	0.7514	1.0400
0.993	0.99524	0.7577	1.0487
2.974	0.99742	0.7863	1.0884
4.947	0.99934	0.8075	1.1176
6.912	1.00115	0.8252	1.1422
9.838	1.00330	0.8487	1.1747
Temperature = 313.15K			**η_0= 0.6560 cP**
0.495	0.99285	0.6781	1.0338
0.694	0.99310	0.6827	1.0407
0.991	0.99348	0.6885	1.0495
2.969	0.99574	0.7145	1.0892
4.939	0.99774	0.7338	1.1186
6.901	0.99963	0.7504	1.1440
9.823	1.00181	0.7720	1.1769
Temperature = 318.15K			**η_0= 0.5988 cP**

0.495	0.99094	0.6197	1.0350
0.692	0.99120	0.6239	1.0419
0.989	0.99158	0.6294	1.0511
2.964	0.99402	0.6535	1.0914
4.932	0.99624	0.6716	1.1216
6.891	0.99820	0.6870	1.1472
9.813	1.00076	0.7068	1.1803

Cobalt chloride

Temperature = 298.15K			**η_0= 0.8937 cP**
0.498	0.99759	0.9129	1.0214
0.697	0.99780	0.9168	1.0258
0.995	0.99811	0.9223	1.0320
2.979	1.00012	0.9467	1.0593
4.951	1.00206	0.9643	1.0790
6.912	1.00395	0.9797	1.0963
9.832	1.00663	0.9997	1.1186
Temperature = 303.15K			**η_0= 0.8007 cP**
0.497	0.99622	0.8186	1.0223
0.696	0.99644	0.8229	1.0278
0.994	0.99677	0.8281	1.0342
2.975	0.99890	0.8516	1.0636
4.945	1.00090	0.8673	1.0832
6.905	1.00286	0.8810	1.1003
9.822	1.00565	0.9004	1.1245
Temperature = 308.15K			**η_0=0.7225 cP**
0.496	0.99463	0.7390	1.0229
0.695	0.99486	0.7426	1.0278
0.992	0.99520	0.7476	1.0347
2.971	0.99742	0.7674	1.0622
4.938	0.99953	0.7826	1.0832
6.895	1.00153	0.7950	1.1004
9.810	1.00440	0.8129	1.1252
Temperature = 313.15K			**η_0= 0.6560 cP**
0.495	0.99283	0.6715	1.0237
0.694	0.99307	0.6750	1.0290
0.991	0.99344	0.6792	1.0354
2.966	0.99578	0.6980	1.0640
4.931	0.99797	0.7114	1.0845
6.886	1.00012	0.7236	1.1031
9.798	1.00313	0.7398	1.1277
Temperature = 318.15K			**η_0=0.5988 cP**
0.494	0.9909	0.6131	1.0239
0.692	0.99116	0.6165	1.0297
0.989	0.99154	0.6208	1.0367

2.961	0.99406	0.6376	1.0648
4.923	0.99647	0.6511	1.0874
6.876	0.99873	0.6606	1.1033
9.787	1.00208	0.6762	1.1293

Nickel chloride

Temperature = 298.15K			**η_0= 0.8937 cP**
0.498	0.99776	0.9115	1.0200
0.697	0.99803	0.9155	1.0245
0.996	0.99841	0.9204	1.0299
2.98	1.00108	0.9424	1.0545
4.959	1.00365	0.9583	1.0724
6.926	1.00602	0.9727	1.0884
9.857	1.00915	0.9939	1.1122
Temperature = 303.15K			**η_0= 0.8007 cP**
0.497	0.99640	0.8173	1.0208
0.696	0.99667	0.8210	1.0255
0.994	0.99708	0.8256	1.0311
2.978	0.99980	0.8461	1.0567
4.952	1.00229	0.8608	1.0751
6.917	1.00471	0.8727	1.09
9.848	1.00830	0.8935	1.116
Temperature = 308.15K			**η_0= 0.7225 cP**
0.496	0.99486	0.7385	1.0223
0.695	0.99516	0.7421	1.0272
0.993	0.99561	0.7458	1.0324
2.974	0.99867	0.7650	1.0589
4.949	1.00161	0.7795	1.0789
6.914	1.00421	0.7910	1.0949
9.845	1.00794	0.8103	1.1216
Temperature = 313.15K			**η_0= 0.6560 cP**
0.495	0.99303	0.6710	1.0229
0.694	0.99337	0.6739	1.0273
0.991	0.99382	0.6775	1.0328
2.969	0.99687	0.6954	1.0602
4.940	0.99981	0.7081	1.0795
6.903	1.00260	0.7194	1.0967
9.830	1.00645	0.7362	1.1223
Temperature = 318.15K			**η_0= 0.5988cP**
0.495	0.99109	0.6132	1.0241
0.692	0.99142	0.6160	1.0289
0.989	0.99195	0.6197	1.035
2.964	0.99515	0.6370	1.0638
4.932	0.99820	0.6496	1.0849
6.893	1.00114	0.6602	1.1026

9.817	1.00513	0.6743	1.1261

Copper chloride

Temperature = 298.15K			**η_0= 0.8937 cP**
0.498	0.99765	0.9227	1.0324
0.697	0.99788	0.9281	1.0385
0.996	0.99822	0.9359	1.0472
2.986	1.00048	0.9711	1.0866
4.970	1.00263	0.9958	1.1142
6.949	1.00467	1.0204	1.1418
9.907	1.00768	1.0484	1.1731
Temperature = 303.15K			**η_0= 0.8007 cP**
0.497	0.99629	0.8270	1.0329
0.696	0.99652	0.8321	1.0392
0.995	0.99686	0.8387	1.0474
2.982	0.99924	0.8701	1.0867
4.965	1.00146	0.8938	1.1163
6.943	1.00373	0.9141	1.1417
9.899	1.00682	0.9402	1.1743
Temperature = 308.15K			**η_0= 0.7225 cP**
0.496	0.99471	0.7465	1.0332
0.695	0.99497	0.7514	1.0400
0.993	0.99535	0.7578	1.0488
2.978	0.99787	0.7860	1.0879
4.959	1.00033	0.8076	1.1178
6.935	1.00255	0.8257	1.1428
9.890	1.00587	0.8495	1.1758
Temperature = 313.15K			**η_0= 0.6560 cP**
0.496	0.99288	0.6786	1.0345
0.694	0.99314	0.6829	1.0411
0.991	0.99352	0.6885	1.0495
2.972	0.99605	0.7154	1.0905
4.950	0.99846	0.7343	1.1194
6.922	1.00068	0.7512	1.1452
9.872	1.00407	0.7731	1.1785
Temperature = 318.15K			**η_0= 0.5988 cP**
0.495	0.99094	0.6200	1.0355
0.693	0.99120	0.6241	1.0423
0.989	0.99161	0.6292	1.0508
2.967	0.99429	0.6537	1.0917
4.942	0.99685	0.6714	1.1212
6.912	0.99922	0.6863	1.1462
9.858	1.00268	0.7061	1.1793

	Cadmium chloride		
Temperature = 298.15K			**η_0= 0.8937 cP**
0.498	0.99769	0.9167	1.0257
0.697	0.99792	0.9214	1.0310
0.996	0.99826	0.9277	1.0381
2.983	1.00059	0.9554	1.0691
4.964	1.00282	0.9764	1.0925
6.936	1.00489	0.9927	1.1108
9.880	1.00795	1.0207	1.1421
Temperature = 303.15K			**η_0= 0.8007 cP**
0.497	0.99633	0.8222	1.0268
0.696	0.99659	0.8273	1.0332
0.995	0.99697	0.8332	1.0406
2.980	0.99954	0.8598	1.0739
4.959	1.00192	0.8781	1.0966
6.931	1.00418	0.8941	1.1167
9.875	1.00743	0.9154	1.1432
Temperature = 308.15K			**η_0= 0.7225 cP**
0.496	0.99474	0.7428	1.0281
0.695	0.99501	0.7467	1.0336
0.993	0.99542	0.7518	1.0405
2.976	0.99799	0.7753	1.0731
4.952	1.00044	0.7928	1.0973
6.921	1.00278	0.8075	1.1177
9.863	1.00624	0.8267	1.1442
Temperature = 313.15K			**η_0= 0.6560 cP**
0.496	0.99294	0.7467	1.0336
0.694	0.99322	0.7518	1.0405
0.991	0.99363	0.7753	1.0731
2.971	0.99635	0.7928	1.0973
4.944	0.99891	0.8075	1.1177
6.912	1.00136	0.8267	1.1442
9.850	1.00487	0.7428	1.0281
Temperature = 318.15K			**η_0= 0.5988 cP**
0.495	0.99100	0.6709	1.0228
0.692	0.99130	0.6738	1.0271
0.989	0.99175	0.6780	1.0336
2.965	0.99459	0.6990	1.0656
4.936	0.99730	0.7141	1.0886
6.901	0.99986	0.7252	1.1054
9.836	1.00347	0.7430	1.1327

	Magnesium chloride		
Temperature = 298.15K			**η_0= 0.8937 cP**
0.498	0.99728	0.9163	1.0253
0.697	0.99737	0.9209	1.0304
0.995	0.9975	0.9263	1.0364
2.976	0.99829	0.9532	1.0666
4.944	0.99897	0.9734	1.0892
6.898	0.99958	0.9897	1.1074
9.805	1.00044	1.0124	1.1328
Temperature = 303.15K			**η_0= 0.8007 cP**
0.497	0.99595	0.8225	1.0273
0.696	0.99607	0.8268	1.0326
0.994	0.99624	0.8326	1.0398
2.973	0.99727	0.8572	1.0706
4.940	0.99818	0.8755	1.0934
6.894	0.99897	0.8909	1.1126
9.801	1.00007	0.9108	1.1375
Temperature = 308.15K			**η_0= 0.7225 cP**
0.496	0.99436	0.7425	1.0278
0.695	0.99448	0.7463	1.0330
0.992	0.99466	0.7512	1.0397
2.969	0.99569	0.7742	1.0716
4.932	0.99659	0.7904	1.0940
6.883	0.99738	0.8045	1.1136
9.785	0.9984	0.8223	1.1381
Temperature = 313.15K			**η_0= 0.6560 cP**
0.495	0.99258	0.6753	1.0295
0.693	0.99273	0.6790	1.0350
0.990	0.99292	0.6837	1.0422
2.964	0.99416	0.7054	1.0754
4.926	0.99533	0.7208	1.0988
6.876	0.99638	0.7335	1.1181
9.773	0.99718	0.7499	1.1432
Temperature = 318.15K			**η_0= 0.5988 cP**
0.494	0.99063	0.6169	1.0302
0.692	0.99078	0.6203	1.0359
0.989	0.99101	0.6247	1.0432
2.959	0.9924	0.6448	1.0768
4.917	0.99353	0.6592	1.1009
6.865	0.99470	0.6713	1.1210
9.760	0.99587	0.6860	1.1457

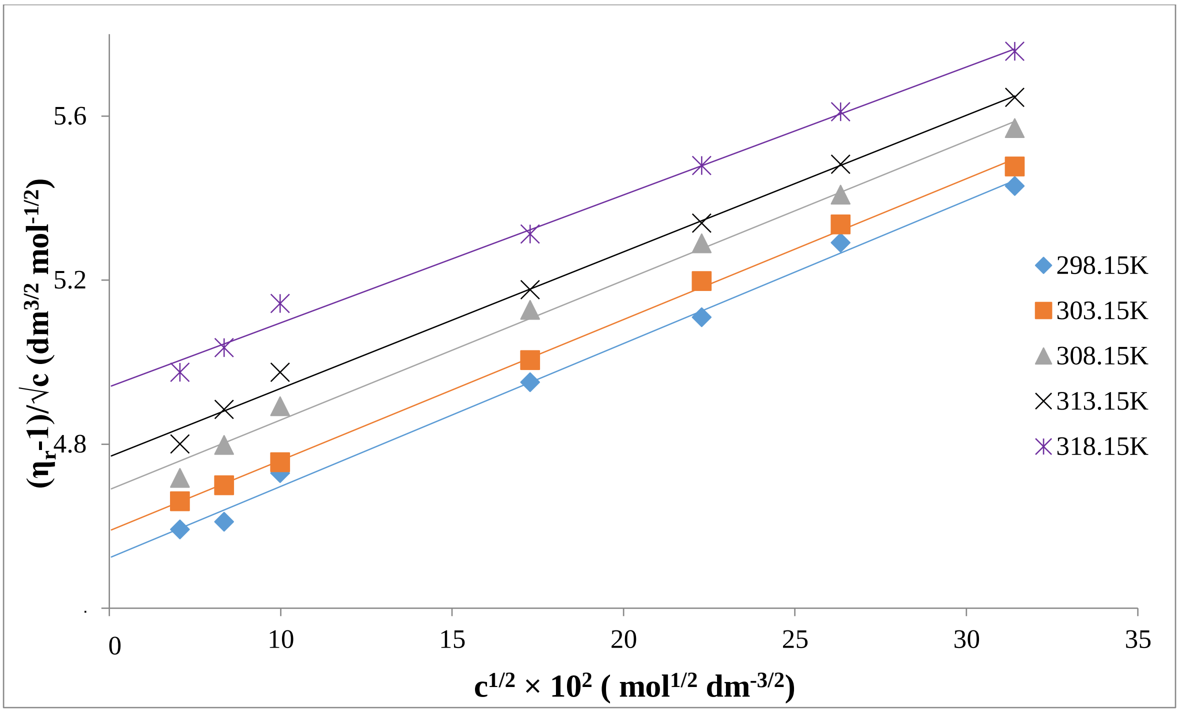

Fig. 20. PLOTS OF $(\eta_r - 1)/\sqrt{c}$ VS $\sqrt{c}$ FOR MANGANESE CHLORIDE IN WATER AT DIFFERENT TEMPERATURES.

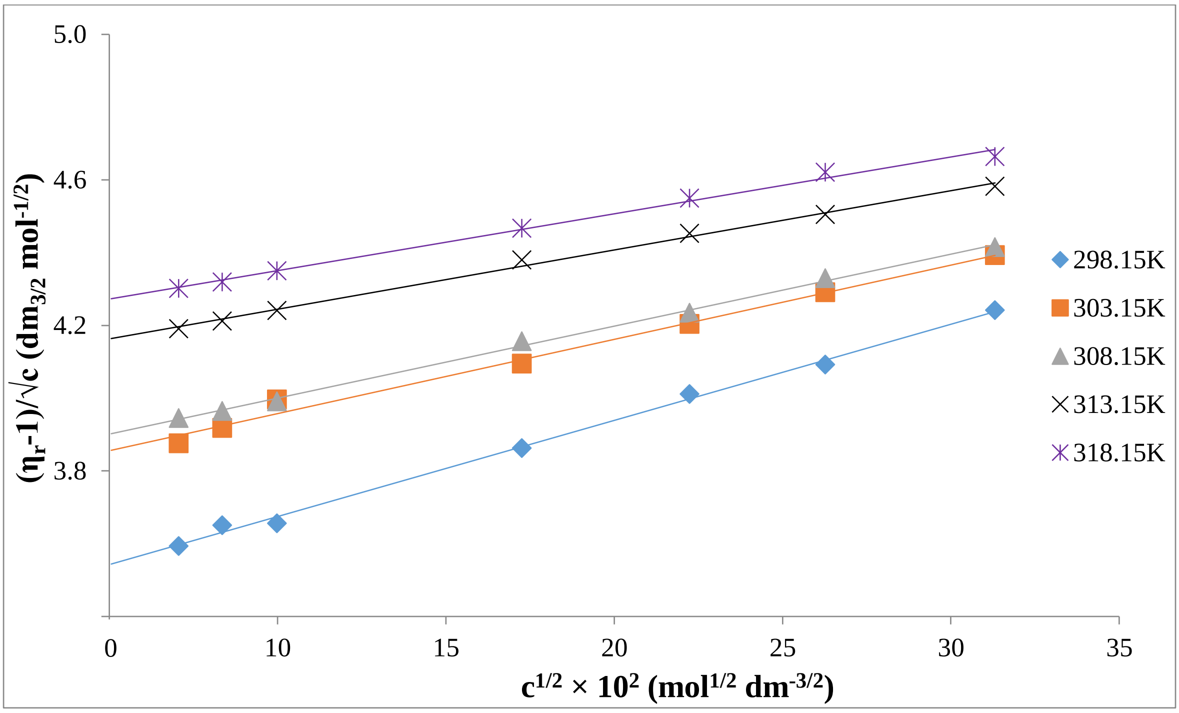

Fig. 21. PLOTS OF $(\eta_r - 1)/\sqrt{c}$ VS $\sqrt{c}$ FOR MAGNESIUM CHLORIDE IN WATER AT DIFFERENT TEMPERATURES.

TABLE - 3.IV

VALUES OF A AND B PARAMETERS OF THE JONES – DOLE EQUATION FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT DIFFERENT TEMPERATURES.

Temperature (K)	A ($dm^{3/2}$ $mol^{-1/2}$)	B (dm^3 mol^{-1})
	Manganese chloride	
298.15	4.348	0.034
303.15	4.417	0.034
308.15	4.519	0.034
313.15	4.603	0.033
318.15	4.784	0.031
	Cobalt chloride	
298.15	2.876	0.029
303.15	3.083	0.029
308.15	3.125	0.027
313.15	3.245	0.026
318.15	3.336	0.025
	Nickel chloride	
298.15	2.680	0.027
303.15	2.812	0.026
308.15	2.993	0.025
313.15	3.057	0.025
318.15	3.266	0.024
	Copper chloride	
298.15	4.33	0.037
303.15	4.401	0.036
308.15	4.517	0.034
313.15	4.672	0.032
318.15	4.857	0.027
	Cadmium chloride	
298.15	3.448	0.032
303.15	3.734	0.027
308.15	3.818	0.024
313.15	2.971	0.041
318.15	2.840	0.044
	Magnesium chloride	
298.15	3.410	0.026
303.15	3.753	0.020
308.15	3.802	0.019
313.15	4.081	0.016
318.15	4.194	0.015

It is clear from Table 3.IV that the values of parameter A are positive for the solutions of all the divalent transition metal chlorides and magnesium chloride in water at all temperature, thereby showing the presence of strong ion – ion interactions. Also, from Table 3.IV it is evident that the value of the A parameter increases with the rise in temperature for the solution of an individual electrolyte in water and this suggests that ion – ion interactions are further strengthened with the rise of temperature. Also, from Table 3.IV, it is clear that the values of B coefficient are positive thereby showing the existence of specific ion –solvent interactions, but these values for all the above mentioned divalent transition metal chlorides and magnesium chloride decrease with rise in temperature indicating that ion – solvent interactions are further weakened. The negative temperature coefficient of B i.e $(\frac{dB}{dT})$ for the solutions of above mentioned salts in water suggests that these salts act as structure maker in water. These conclusions from viscous flow for the solutions of divalent transition metal chlorides and magnesium chloride in water are in good agreement with our previous finding from the studies of partial molar volumes (explained in chapter II).

Section - B

Discussion on the Results of Viscous Flow of Some Divalent Transition Metal Chlorides and Magnesium Chloride in Binary Aqueous Mixtures of Methanol

Densities, viscosities and relative viscosities of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride; and magnesium chloride in five different compositions of methanol + water (5,10,15,20 and 35 by weight percentage of methanol) at 303.15K are given in Table 3.V.

It is clear from Table 3.V that the values of relative viscosities for the solutions of above mentioned divalent transition metal chlorides and magnesium chloride in the different binary aqueous mixtures of methanol at 303.15K increase with the increase in the concentration of each salt. The concentration dependence of relative viscosity of the solutions of the above mentioned salts in different binary aqueous compositions of methanol can be represented by the Jones- Dole equation (3.1) and for all the above mentioned salts linear plots have been obtained between $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$ in all compositions of methanol + water at 303.15K.

TABLE – 3.V

DENSITIES, VISCOSITIES AND RELATIVE VISCOSITIES OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K.

Concentration $c \times 10^2$ ($mol\ dm^{-3}$)	Density d ($g\ cm^{-3}$)	Viscosity η (cP)	Relative Viscosity $\frac{\eta}{\eta_0}$
	Manganese chloride		
5% (w/w) Methanol + water			**η_0 = 0.8002 cP**
0.492	0.98626	0.8580	1.0723
0.689	0.98651	0.8688	1.0857
0.984	0.98688	0.8843	1.1051
2.950	0.98934	0.9572	1.1962
4.909	0.99164	1.0204	1.2752
6.862	0.99387	1.0659	1.3320
9.778	0.99715	1.1254	1.4064
10% (w/w) Methanol +water			**η_0= 0.8362 cP**
0.490	0.98275	0.89579	1.0711
0.687	0.98300	0.90754	1.0852
0.981	0.98336	0.92414	1.1050
2.940	0.98585	1.00125	1.1972
4.892	0.98816	1.06288	1.2709
6.838	0.99046	1.10837	1.3253
9.744	0.99371	1.17162	1.40101
15% (w/w) Methanol + water			**η_0= 0.9022 cP**
0.487	0.97488	0.9692	1.0741
0.681	0.97514	0.9831	1.0896

0.973	0.97552	1.0020	1.1105
2.916	0.97805	1.0848	1.2023
4.854	0.98050	1.1473	1.2716
6.784	0.98269	1.2022	1.3324
9.670	0.98617	1.2749	1.4130
20% (w/w) Methanol + water		**η_0= 0.9247 cP**	
0.485	0.9716	0.9948	1.0758
0.679	0.97187	1.0094	1.0916
0.970	0.97229	1.0283	1.1119
2.907	0.97485	1.1123	1.2028
4.838	0.97734	1.1761	1.2718
6.764	0.9798	1.2326	1.3329
9.643	0.98342	1.3082	1.4146
35% (w/w) Methanol + water		**η_0= 1.0568 cP**	
0.474	0.95025	1.1402	1.0788
0.664	0.95053	1.1565	1.0943
0.949	0.95094	1.1777	1.1143
2.843	0.95354	1.2765	1.2078
4.733	0.95607	1.3502	1.2776
6.617	0.95849	1.4121	1.3361
9.434	0.96207	1.4943	1.4138
Cobalt chloride			
5% (w/w) Methanol + water		**η_0= 0.8002 cP**	
0.492	0.98613	0.8144	1.0178
0.689	0.98634	0.8192	1.0238
0.984	0.98664	0.8280	1.0348

2.944	0.98858	0.8706	1.0880
4.893	0.99039	0.9086	1.1355
6.830	0.99209	0.9466	1.1830
9.714	0.99455	1.0015	1.2515
10% (w/w) Methanol + water		**η_0= 0.8362 cP**	
0.490	0.98263	0.8529	1.0200
0.686	0.98284	0.8586	1.0267
0.980	0.98315	0.8656	1.0351
2.934	0.98514	0.9101	1.0884
4.877	0.98702	0.9514	1.1376
6.807	0.98876	0.9919	1.1861
9.682	0.99129	1.0505	1.2562
15% (w/w) Methanol + water		**η_0= 0.9022 cP**	
0.486	0.97477	0.9219	1.0217
0.681	0.97499	0.9283	1.0288
0.973	0.97531	0.9375	1.0390
2.911	0.97737	0.9854	1.0921
4.838	0.9793	1.0326	1.1444
6.755	0.98111	1.0724	1.1885
9.607	0.98364	1.1358	1.2588
20% (w/w) Methanol + water		**η_0= 0.9247 cP**	
0.485	0.97147	0.9471	1.0241
0.679	0.97169	0.9548	1.0324
0.969	0.97202	0.9612	1.0394
2.901	0.97410	1.0131	1.0955
4.822	0.97602	1.0589	1.1450

6.732	0.97784	1.1027	1.1924
9.575	0.98036	1.1742	1.2698
35% (w/w) Methanol + water		**η_0= 1.0568 cP**	
0.474	0.95013	1.0861	1.0277
0.664	0.95036	1.0944	1.0355
0.948	0.95070	1.1048	1.0453
2.838	0.95282	1.1647	1.1020
4.717	0.95479	1.2146	1.1492
6.586	0.95660	1.2665	1.1983
9.369	0.95924	1.3298	1.2583
Nickel chloride			
5% (w/w) Methanol + water		**η_0= 0.8002 cP**	
0.492	0.98627	0.8284	1.0352
0.689	0.98653	0.8345	1.0429
0.984	0.98692	0.8454	1.0565
2.947	0.98941	0.8879	1.1096
4.900	0.99179	0.9298	1.1619
6.844	0.99406	0.9618	1.2019
9.741	0.99734	1.0103	1.2625
10% (w/w) Methanol + water		**η_0= 0.8362 Cp**	
0.490	0.98276	0.8666	1.0363
0.687	0.98303	0.8730	1.0439
0.981	0.98342	0.8828	1.0556
2.937	0.98597	0.9306	1.1128
4.883	0.98838	0.9731	1.1636
6.821	0.99069	1.0068	1.2039

9.709	0.99401	1.0561	1.2629
15% (w/w) Methanol + water		**η_0= 0.9022 cP**	
0.486	0.9749	0.9364	1.0378
0.681	0.97517	0.9442	1.0464
0.973	0.97557	0.9541	1.0575
2.913	0.97816	1.0067	1.1157
4.845	0.98062	1.0505	1.1643
6.768	0.98296	1.0861	1.2037
9.634	0.98635	1.1396	1.2630
20% (w/w) Methanol + water		**η_0= 0.9247 cP**	
0.485	0.9716	0.9615	1.0397
0.679	0.97187	0.9692	1.0481
0.97	0.97229	0.9799	1.0596
2.904	0.97489	1.0331	1.1171
4.829	0.97738	1.0775	1.1652
6.746	0.97976	1.1165	1.2073
9.603	0.9832	1.1638	1.2585
35% (w/w) Methanol + water		**η_0= 1.0568 cP**	
0.474	0.95026	1.1043	1.0448
0.664	0.95054	1.1139	1.0540
0.948	0.95094	1.1264	1.0658
2.840	0.95362	1.1890	1.1250
4.724	0.95618	1.2378	1.1712
6.599	0.95852	1.2791	1.2103
9.396	0.96200	1.3357	1.2638

Copper chloride			
5% (w/w) Methanol + water		**η_0= 0.8002 cP**	
0.492	0.98622	0.8402	1.0500
0.689	0.98646	0.8490	1.0610
0.985	0.98681	0.8598	1.0745
2.952	0.98907	0.9140	1.1422
4.914	0.99122	0.9577	1.1969
6.871	0.99333	1.003	1.2542
9.795	0.99627	1.0532	1.3161
10% (w/w) Methanol + water		**η_0= 0.8362 cP**	
0.490	0.98272	0.8808	1.0533
0.687	0.98296	0.8892	1.0633
0.981	0.98333	0.9003	1.0766
2.941	0.98563	0.9595	1.1474
4.897	0.98782	1.0053	1.2021
6.847	0.98989	1.0483	1.2536
9.762	0.99288	1.1035	1.3196
15% (w/w) Methanol + water		**η_0= 0.9022 cP**	
0.487	0.97484	0.9514	1.0544
0.681	0.97509	0.9598	1.0638
0.973	0.97545	0.9725	1.0778
2.918	0.97779	1.0351	1.1472
4.858	0.97998	1.08903	1.2069
6.793	0.98205	1.13127	1.2537
9.686	0.98511	1.19212	1.3212
20% (w/w) Methanol + water		**η_0= 0.9247cP**	

0.485	0.97155	0.97714	1.0566
0.679	0.97181	0.9869	1.0672
0.970	0.97218	1.0002	1.0816
2.908	0.97455	1.0696	1.1566
4.842	0.97682	1.1207	1.2119
6.771	0.97893	1.1643	1.2590
9.655	0.98203	1.2333	1.3337
35% (w/w) Methanol + water		**η_0= 1.0568 cP**	
0.474	0.95019	1.1168	1.0567
0.664	0.95044	1.1291	1.0683
0.949	0.95082	1.1456	1.0839
2.844	0.95316	1.2239	1.1580
4.736	0.95539	1.2790	1.2101
6.623	0.9575	1.3301	1.2585
9.444	0.96052	1.4070	1.3313
Cadmium chloride			
5% (w/w) Methanol + water		**η_0= 0.8002 cP**	
0.492	0.98624	0.8495	1.0615
0.689	0.98649	0.8596	1.0742
0.984	0.98686	0.8731	1.0911
2.949	0.98919	0.9353	1.1688
4.907	0.99145	0.9818	1.2269
6.858	0.99364	1.0252	1.2811
9.770	0.99674	1.0863	1.3575
10% (w/w) Methanol + water		**η_0= 0.8362 cP**	
0.490	0.98275	0.8896	1.0638

0.687	0.983	0.9000	1.0763
0.981	0.98339	0.9140	1.0929
2.939	0.98585	0.9815	1.1737
4.891	0.98816	1.0335	1.2359
6.836	0.99038	1.0796	1.2909
9.741	0.99371	1.1359	1.3584
15% (w/w) Methanol + water		**η_0= 0.9022 cP**	
0.486	0.97488	0.9603	1.0643
0.681	0.97515	0.9722	1.0775
0.973	0.97555	0.9876	1.0946
2.916	0.97805	1.0608	1.1757
4.853	0.98047	1.1150	1.2357
6.784	0.98281	1.1659	1.2921
9.665	0.98605	1.2264	1.3592
20% (w/w) Methanol + water		**η_0= 0.9247 cP**	
0.485	0.97159	0.9860	1.0662
0.679	0.97186	0.9999	1.0812
0.970	0.97228	1.0146	1.0972
2.907	0.97489	1.0877	1.1762
4.837	0.97727	1.1472	1.2406
6.762	0.97965	1.19607	1.2933
9.636	0.98308	1.2574	1.3597
35% (w/w) Methanol +water		**η_0= 1.0568 cP**	
0.474	0.95024	1.12692	1.0662
0.664	0.95051	1.1425	1.0810
0.949	0.9509	1.1603	1.0979

2.843	0.9535	1.2417	1.1749
4.732	0.95592	1.3098	1.2393
6.614	0.9583	1.3668	1.2933
9.427	0.96169	1.4330	1.3559
Magnesium chloride			
5% (w/w) Methanol + water		**η_0= 0.8002 cP**	
0.492	0.98587	0.8379	1.0472
0.689	0.98597	0.8479	1.0596
0.984	0.98612	0.8586	1.0729
2.942	0.98696	0.9213	1.1513
4.888	0.98764	0.9714	1.21403
6.820	0.9882	1.0136	1.2667
9.691	0.98888	1.0797	1.3493
10% (w/w) Methanol + water		**η_0= 0.8362 cP**	
0.490	0.98236	0.8764	1.0480
0.686	0.98246	0.8860	1.0595
0.980	0.98261	0.8990	1.0750
2.932	0.98348	0.9629	1.1514
4.871	0.98416	1.0158	1.2147
6.796	0.98476	1.0599	1.2674
9.658	0.98548	1.1306	1.3520
15% (w/w) Methanol + water		**η_0= 0.9022 cP**	
0.486	0.9745	0.9462	1.0487
0.681	0.97461	0.9566	1.0602
0.972	0.97477	0.9704	1.0755
2.909	0.97571	1.0384	1.1509

4.833	0.97650	1.0954	1.2140
6.744	0.97714	1.1461	1.2702
9.584	0.97797	1.2184	1.3503
20% (w/w) Methanol + water		**η_0= 0.9247 cP**	
0.485	0.97120	0.9706	1.0496
0.679	0.97132	0.9809	1.0608
0.969	0.97149	0.9941	1.0749
2.899	0.97248	1.0653	1.1519
4.817	0.97327	1.1228	1.2141
6.722	0.97395	1.1740	1.2696
9.553	0.97478	1.2488	1.3504
35% (w/w) Methanol + water		**η_0= 1.0568 cP**	
0.474	0.94987	1.1105	1.0507
0.664	0.95000	1.1219	1.0615
0.948	0.95018	1.1361	1.0750
2.836	0.95124	1.2161	1.1506
4.712	0.95214	1.2853	1.2161
6.576	0.95290	1.3391	1.2670
9.349	0.95392	1.4228	1.3462

Sample plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$ for nickel chloride and manganese chloride are shown in Figs. 22 and 23 respectively.

The values of A and B parameters of Jones – Dole equation have been calculated by using the least square method to the linear plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$, and are recorded in Table 3.VI. From Table 3.VI, it is clear that the values of A coefficient are positive for an individual salt in the entire composition range of methanol + water at 303.15K, thereby showing the presence of ion – ion interactions and further these values increase with the increase of methanol content in water at 303.15K, thereby showing that ion –ion interactions are further strengthened with the increase of methanol content in water, which may be attributed to the decrease in ion – solvation.

It is also clear from Table 3.VI that the values of B – parameter for all the studied divalent transition metal chlorides and magnesium chloride are positive but are smaller in magnitude in comparison of the values of A – parameter in the entire compositions of methanol + water at 303.15K which indicates the dominance of ion- ion interactions over ion- solvent interactions. This may be attributed to the weak solvation of these ions by the binary mixtures of methanol + water. Moreover, it is also clear from the Table 3.VI that the values of B-parameter decrease with the addition of methanol content in water thereby resulting in the decrease of ion-solvent interactions which shows that water has more affinity for methanol than that for salt. These conclusions from viscous flow are in agreement with those drawn from the density data for the above mentioned divalent transition metal chlorides and magnesium chloride.

The viscosity data for the solutions of above mentioned divalent transition metal chlorides and magnesium chloride in binary aqueous mixtures of methanol at 303.15K have also been examined on the basis of transition state theory of relative viscosities according to equation (3.3) as suggested by Feakins *et al* [15].

In order to determine $\Delta\mu_2^{0*}$, it is important to evaluate $\Delta\mu_1^{0*}$ and this parameter has been calculated with the help of relation (3.3) for the different compositions of methanol + water at 303.15K and the corresponding values are given in Table 3.VII. For the mixed solvent (methanol + water), each solvent mixture can be treated as pure solvent and the molar volume has been taken as a mean value and is defined [17-19] as follows:

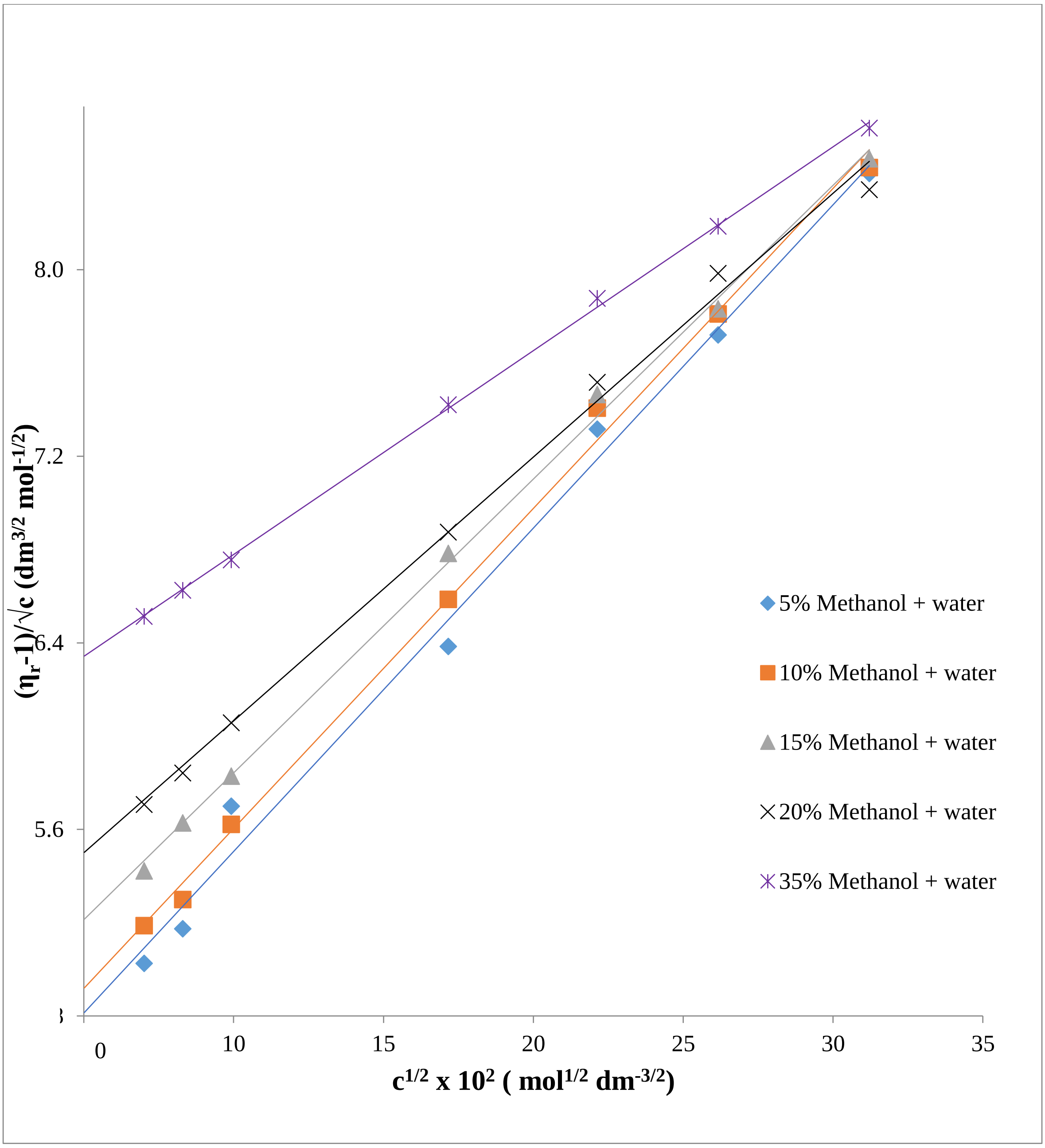

Fig.22: PLOTS OF $(\eta_r\text{-}1)/\sqrt{c}$ VS $\sqrt{c}$ FOR NICKEL CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K.

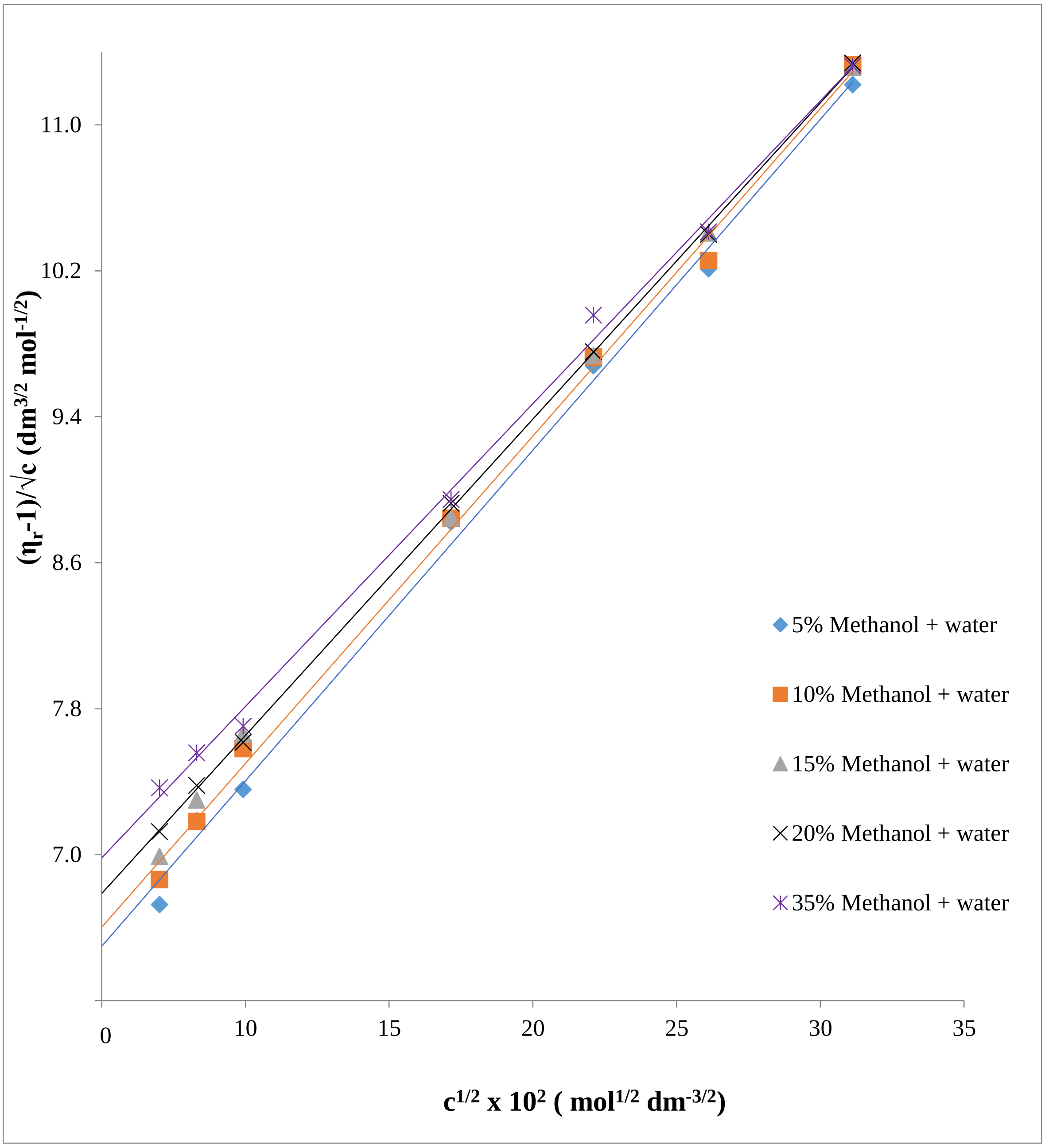

Fig.23: PLOTS OF $(\eta_r\text{-}1)/\sqrt{c}$ VS $\sqrt{c}$ FOR MANGANESE CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL +WATER AT 303.15K.

TABLE – 3.VI

VALUES OF A AND B PARAMETERS OF THE JONES – DOLE EQUATION FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K.

Methanol + water % (w/w)	**A ($dm^{3/2} mol^{-1/2}$)**	**B ($dm^3 mol^{-1}$)**
	Manganese Chloride	
5	09.421	0.121
10	09.428	0.116
15	10.007	0.105
20	10.290	0.096
35	10.890	0.085
	Cobalt Chloride	
5	1.093	0.226
10	1.349	0.221
15	1.736	0.215
20	2.015	0.212
35	2.822	0.182
	Nickel chloride	
5	4.119	0.138
10	4.232	0.137
15	4.583	0.126
20	4.934	0.113
35	5.906	0.089
	Copper chloride	
5	6.263	0.123
10	6.714	0.111
15	6.871	0.11
20	7.296	0.107
35	7.580	0.101
	Cadmium chloride	
5	8.060	0.104
10	8.392	0.102
15	8.590	0.097
20	9.032	0.084
35	9.178	0.081
	Magnesium chloride	
5	5.590	0.181
10	5.704	0.179
15	5.831	0.177
20	5.919	0.174
35	6.153	0.169

Table – 3.VII

VALUES OF $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0*}$ AND $\Delta\mu_2^{0*}$ FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF METHANOL + WATER AT 303.15K.

Methanol + water % (w/w)	$\overline{V_1^0}$ (cm^3 mol^{-1})	$\overline{V_2^0}$ (cm^3 mol^{-1})	$\Delta\mu_1^{0*}$ (kJ mol^{-1})	$\Delta\mu_2^{0*}$ (kJ mol^{-1})
		Manganese chloride		
5	18.68	61.50	61.36	83.45
10	19.18	59.91	61.54	82.13
15	19.79	56.22	61.81	79.82
20	20.33	49.07	61.94	77.40
35	22.40	45.79	62.52	74.71
		Cobalt chloride		
5	18.68	127.37	61.36	106.50
10	19.18	123.76	61.54	104.31
15	19.79	118.85	61.81	101.80
20	20.33	116.29	61.94	100.10
35	22.40	112.87	62.52	93.17
		Nickel chloride		
5	18.68	98.79	61.36	90.77
10	19.18	96.05	61.54	89.64
15	19.79	91.75	61.81	87.02
20	20.33	89.19	61.94	84.48
35	22.40	85.49	62.52	79.63
		Copper chloride		
5	18.68	41.01	61.36	80.96
10	19.18	35.98	61.54	78.33
15	19.79	34.72	61.81	77.71
20	20.33	29.49	61.94	76.33
35	22.40	29.16	62.52	74.64
		Cadmium chloride		
5	18.68	68.02	61.36	82.04
10	19.18	62.03	61.54	80.57
15	19.79	57.72	61.81	78.99
20	20.33	53.05	61.94	76.40
35	22.40	52.06	62.52	74.96
		Magnesium Chloride		
5	18.68	144.21	61.36	102.70
10	19.18	142.81	61.54	101.30
15	19.79	139.03	61.81	99.53
20	20.33	135.92	61.94	97.83
35	22.40	133.15	62.52	93.99

$$\overline{V_1^0} = (X_1M_1 + X_2M_2)/d_1 \qquad (3.6)$$

where X_1, M_1, X_2 and M_2 are the mole fractions and molecular weights of water and methanol respectively and d_1: the density of solvent mixture (methanol + water). The values of $\overline{V_1^0}$ for the different binary aqueous mixtures of methanol, $\overline{V_2^0}$ the partial molar volumes at infinite dilution and $\Delta\mu_2^0$ for the solutions of divalent transition metal chlorides and magnesium chloride in methanol + water at 303.15K are also recorded in Table 3.VII.

It is clear from Table 3.VII, that the value of $\Delta\mu_1^0$ for the solutions of divalent transition metal chlorides does not change appreciably with the change in the composition of methanol in water at 303.15K. In other words it may be said that $\Delta\mu_1^0$ is practically held constant in the entire range of composition of binary aqueous mixtures of methanol, studied here, at 303.15K. Thus according to the relation (3.4), the value of $\Delta\mu_2^0$ is determined, by the values of $\overline{V_1^0}$, $\overline{V_2^0}$ and B- coeffiecent. The values of $\Delta\mu_2^0$, thus calculated with the help of relation (3.4) are recorded in Table 3.VII. The positive values of $\Delta\mu_2^0$ indicate that the formation of transition state is less favoured in the presence of these salts meaning thereby that the formation of transition state is followed by breaking and distortion of intermolecular bonds. Moreover, the larger values of $\Delta\mu_2^0$ than $\Delta\mu_1^0$ suggest that all the divalent transition metal chlorides and magnesium chloride behave as structure promoters in different binary aqueous mixtures of methanol at 303.15K.

It has been highlighted by number of researchers that $\frac{dB}{dT}$ is a better criterion for determining the structure making/breaking behaviour of any salt rather than simply from the B-coefficient. So it means that in order to follow this criterion, the temperature effect must be studied.

Effect of temperature:

Since the behaviour of all the divalent transition metal chlorides and magnesium chloride was found similar in all the different compositions of methanol + water hence the effect of temperature has been studied only in 5% (w/w) composition of methanol + water at five different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K). It may be stated here that for the sake of comparison of results the same composition was selected to study the effect of temperature as done in case of partial molar volumes study.

Densities, viscosities and relative viscosities for manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in 5% wt. of methanol + water at different temperatures (298.15, 303.15, 308.15, 313.15, and 318.15K) are given in Table 3.VIII. The plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$ for the solutions of above mentioned divalent transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water mixture at different temperatures have been found to be linear in accordance to Jones- Dole equation (3.1) and sample plots for nickel chloride and magnesium chloride are given in Figs. 24 and 25 respectively.

The values A and B coefficients of Jones- Dole equation have been calculated by applying least square method to the above linear plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$ for all the above mentioned divalent salts in 5% (w/w) methanol + water at 303.15K and are noted in Table 3.IX. From Table 3.IX ,it is clear that the values of A parameter are positive for all the divalent transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water mixture, in the entire temperature range, studied here, thereby showing the presence of strong ion – ion interactions. It is also clear from Table 3.IX that the value of parameter A increases with the increase of temperature for an individual electrolyte thereby suggesting that ion – ion interactions are further strengthened with the rise in temperature which may be attributed to the decrease in ion – solvation with the increase of temperature. In other words, the presence of strong ion – ion interactions may be attributed to decrease in the ion solvation of transition metal chlorides as well as of magnesium chloride. From Table 3.IX the values of parameter B are also positive for the selected transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water at all temperatures. These positive values indicate the presence of ion – solvent interactions which are weakened with the rise in temperature for the transition metal chlorides and magnesium chloride taken in the present study.

It is also clear from the Table 3.IX that the value of $\frac{dB}{dT}$ is negative for the solutions of above mentioned divalent transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water mixture thereby suggesting that these salts act as structure makers in methanol + water mixture. These conclusions from viscosity data are in excellent agreement with those drawn from the studies on the effect of temperature on partial molar volumes.

TABLE - 3.VIII

DENSITIES, VISCOSITIES AND RELATIVE VISCOSITIES OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER MIXTURE AT DIFFERENT TEMPERATURES.

Concentration c X 10^2 (mol dm^{-3})	**Density** d (g cm^{-3})	**Viscosity** η (cP)	**Relative Viscosity** $\frac{\eta}{\eta_0}$
Manganese Chloride			
Temperature = 298.15K		**η_0 = 0.9266 cP**	
0.492	0.98674	0.9919	1.0704
0.689	0.98699	1.0050	1.0849
0.985	0.98736	1.0234	1.1044
2.951	0.98972	1.1076	1.1953
4.911	0.99202	1.1804	1.2738
6.864	0.99421	1.2318	1.3293
9.779	0.99734	1.3018	1.4049
Temperature = 303.15K		**η_0 = 0.8002 cP**	
0.492	0.98626	0.8580	1.0723
0.689	0.98651	0.8688	1.0857
0.984	0.98688	0.8843	1.1051
2.950	0.98934	0.9573	1.1962
4.909	0.99164	1.0204	1.2752
6.862	0.99387	1.0659	1.3320
9.778	0.99715	1.1254	1.4064
Temperature = 308.15K		**η_0 = 0.6990 cP**	
0.490	0.98271	0.7509	1.0742
0.687	0.98297	0.7605	1.0879
0.981	0.98336	0.7734	1.1063
2.940	0.98585	0.8388	1.1999
4.892	0.98822	0.8900	1.2732
6.838	0.99052	0.9319	1.3331
9.744	0.99373	0.9862	1.4108
Temperature = 313.15K		**η_0 = 0.6132 cP**	
0.490	0.9811	0.6589	1.0744
0.686	0.98136	0.6687	1.0904
0.979	0.98176	0.6808	1.1102
2.935	0.98427	0.7410	1.2084
4.885	0.98668	0.7838	1.2781
6.828	0.98902	0.8187	1.3351
9.73	0.99226	0.8695	1.4178
Temperature = 318.15K		**η_0 = 0.5451 cP**	
0.487	0.97611	0.5878	1.0783

0.682	0.97638	0.5967	1.0947
0.974	0.97678	0.6078	1.1150
2.920	0.97934	0.6607	1.2120
4.860	0.98178	0.7007	1.2855
6.794	0.98412	0.7362	1.3506
9.683	0.98751	0.7768	1.4252

Cobalt Chloride

Temperature = 298.15K		**η_0 = 0.9266 cP**	
0.492	0.98661	0.9418	1.0163
0.689	0.98681	0.9471	1.0221
0.984	0.9871	0.9555	1.0311
2.945	0.98897	1.0029	1.0823
4.895	0.9907	1.0490	1.1320
6.832	0.99236	1.0958	1.1825
9.715	0.9947	1.1547	1.2461
Temperature = 303.15K		**η_0 = 0.8002 cP**	
0.492	0.98613	0.8144	1.0178
0.689	0.98634	0.8192	1.0238
0.984	0.98664	0.8280	1.0348
2.944	0.98858	0.8706	1.0880
4.893	0.99039	0.9086	1.1355
6.831	0.99213	0.9467	1.1831
9.715	0.99462	1.0016	1.2516
Temperature = 308.15K		**η_0 = 0.6990 cP**	
0.490	0.98258	0.7176	1.0265
0.686	0.98279	0.7221	1.0330
0.980	0.9831	0.7299	1.0441
2.934	0.98506	0.7684	1.0992
4.876	0.9869	0.8045	1.1508
6.807	0.98864	0.8387	1.1997
9.681	0.99116	0.8838	1.2643
Temperature = 313.15K		**η_0 = 0.6132 cP**	
0.489	0.98097	0.6311	1.0291
0.685	0.98118	0.6357	1.0367
0.979	0.98149	0.6422	1.0472
2.929	0.98348	0.6792	1.1075
4.868	0.98537	0.7117	1.1606
6.796	0.98709	0.7409	1.2081
9.666	0.98969	0.7816	1.2746
Temperature = 318.15K		**η_0 = 0.5451 cP**	
0.487	0.97598	0.5614	1.0299
0.682	0.9762	0.5661	1.0386
0.974	0.97652	0.5720	1.0494
2.914	0.97858	0.6043	1.1085
4.844	0.98047	0.6319	1.1592

6.763	0.98227	0.6569	1.2051
9.619	0.98483	0.6972	1.2790

Nickel Chloride

Temperature = 298.15K		**η_0 = 0.9266 cP**	
0.492	0.98674	0.9581	1.0339
0.689	0.98699	0.9649	1.0413
0.985	0.98736	0.9748	1.0520
2.948	0.98972	1.0266	1.1078
4.901	0.99198	1.0703	1.1550
6.844	0.99409	1.1133	1.2014
9.740	0.99718	1.1642	1.2564
Temperature = 303.15K		**η_0 = 0.8002 cP**	
0.492	0.98628	0.8284	1.0352
0.689	0.98654	0.8346	1.0429
0.984	0.98693	0.8454	1.0565
2.947	0.98945	0.8879	1.1096
4.900	0.99183	0.9298	1.1620
6.845	0.99413	0.9619	1.2020
9.742	0.99745	1.0104	1.2627
Temperature = 308.15K		**η_0 = 0.6990 cP**	
0.490	0.98273	0.7283	1.0419
0.687	0.983	0.7348	1.0512
0.981	0.9834	0.7439	1.0641
2.936	0.98596	0.7886	1.1281
4.883	0.98837	0.8239	1.1786
6.821	0.99071	0.8575	1.2266
9.709	0.99406	0.8991	1.2861
Temperature = 313.15K		**η_0 = 0.6132 cP**	
0.49	0.98114	0.6402	1.0440
0.685	0.98142	0.6472	1.0554
0.979	0.98184	0.6554	1.0688
2.932	0.98453	0.6935	1.1309
4.877	0.98717	0.7284	1.1878
6.813	0.98958	0.7547	1.2307
9.698	0.99286	0.7944	1.2954
Temperature = 318.15K		**η_0 = 0.5451 cP**	
0.487	0.97615	0.5702	1.0461
0.682	0.97644	0.5756	1.0559
0.974	0.97687	0.5825	1.0687
2.918	0.9796	0.6184	1.1344
4.853	0.9822	0.6475	1.1879
6.779	0.98468	0.6715	1.2320
9.652	0.98815	0.7073	1.2977

Copper chloride			
Temperature = 298.15K		**η_0 = 0.9266 cP**	
0.492	0.98671	0.9669	1.0434
0.69	0.98695	0.9759	1.0532
0.985	0.98731	0.9888	1.0670
2.953	0.98957	1.0485	1.1315
4.916	0.99175	1.0966	1.1834
6.874	0.99383	1.1433	1.2338
9.802	0.99692	1.1988	1.2937
Temperature = 303.15K		**η_0 = 0.8002 cP**	
0.492	0.98622	0.8402	1.0500
0.689	0.98646	0.8490	1.0610
0.985	0.98681	0.8598	1.0745
2.952	0.98911	0.9141	1.1423
4.914	0.99125	0.9578	1.1969
6.871	0.99337	1.0036	1.2542
9.795	0.99627	1.0532	1.3161
Temperature = 308.15K		**η_0 = 0.6990 cP**	
0.490	0.98267	0.7371	1.0544
0.687	0.98292	0.7454	1.0663
0.981	0.98329	0.7557	1.0811
2.941	0.98562	0.8066	1.1538
4.897	0.98788	0.8500	1.2159
6.848	0.99003	0.8834	1.2637
9.762	0.99286	0.9347	1.3371
Temperature = 313.15K		**η_0 = 0.6132 cP**	
0.490	0.98106	0.6475	1.0559
0.686	0.98131	0.6551	1.0682
0.98	0.98168	0.6644	1.0834
2.937	0.98404	0.7108	1.1591
4.889	0.9863	0.7460	1.2164
6.837	0.98845	0.7806	1.2730
9.748	0.99143	0.8230	1.3420
Temperature = 318.15K		**η_0 = 0.5451 cP**	
0.487	0.97607	0.5759	1.0565
0.682	0.97632	0.5827	1.0691
0.975	0.97669	0.5917	1.0856
2.922	0.97911	0.6320	1.1595
4.865	0.98138	0.6662	1.2221
6.803	0.98356	0.6957	1.2764
9.700	0.98658	0.7313	1.3415
Cadmium chloride			
Temperature = 298.15K		**η_0 = 0.9266 cP**	

0.492	0.98672	0.98087	1.0585
0.689	0.98696	0.99140	1.0698
0.985	0.98732	1.00573	1.0853
2.951	0.98964	1.07884	1.1642
4.909	0.99187	1.13149	1.2210
6.861	0.99406	1.18284	1.2764
9.775	0.99722	1.24452	1.3430
Temperature = 303.15K		**η_0 = 0.8002 cP**	
0.492	0.98624	0.8495	1.0615
0.689	0.9865	0.8596	1.0742
0.984	0.98686	0.8731	1.0911
2.950	0.9893	0.9354	1.1689
4.908	0.99164	0.9820	1.2272
6.860	0.99387	1.0254	1.2814
9.773	0.997	1.0866	1.3579
Temperature = 308.15K		**η_0 = 0.6990 cP**	
0.490	0.9827	0.7459	1.0670
0.687	0.98296	0.7561	1.0816
0.981	0.98334	0.7689	1.1000
2.939	0.98577	0.8300	1.1872
4.891	0.98807	0.8722	1.2477
6.836	0.99037	0.9109	1.3030
9.739	0.99357	0.9664	1.3825
Temperature = 313.15K		**η_0 = 0.6132 cP**	
0.490	0.98110	0.6561	1.0698
0.686	0.98137	0.6653	1.0849
0.979	0.98177	0.6775	1.1047
2.935	0.98430	0.7314	1.1927
4.884	0.98672	0.7707	1.2568
6.827	0.98905	0.8062	1.3146
9.727	0.99233	0.8489	1.3843
Temperature = 318.15K		**η_0 = 0.5451 cP**	
0.487	0.97612	0.5857	1.0745
0.682	0.97639	0.5936	1.0890
0.974	0.97680	0.6037	1.1075
2.920	0.97937	0.6524	1.1968
4.860	0.98182	0.6883	1.2627
6.792	0.98408	0.7195	1.3200
9.680	0.98751	0.7612	1.3964

Magnesium chloride

Temperature = 298.15K		**η_0 = 0.9266 cP**	
0.492	0.98634	0.9687	1.0454
0.689	0.98643	0.9791	1.0566
0.984	0.98656	0.9917	1.0702
2.944	0.98731	1.0593	1.1432

4.89	0.98795	1.1181	1.2066
6.822	0.98848	1.1725	1.2653
9.694	0.98912	1.2388	1.3368
Temperature = 303.15K		**η_0 = 0.8002 cP**	
0.492	0.98588	0.8379	1.0472
0.689	0.98598	0.8479	1.0596
0.984	0.98613	0.8586	1.0730
2.942	0.98696	0.9213	1.1513
4.888	0.98768	0.9715	1.2140
6.820	0.98824	1.0136	1.2667
9.692	0.98896	1.0798	1.3494
Temperature = 308.15K		**η_0 = 0.6990 cP**	
0.490	0.98234	0.7337	1.0496
0.686	0.98245	0.7419	1.0613
0.980	0.98261	0.7527	1.0767
2.932	0.98351	0.8061	1.1531
4.872	0.98430	0.8526	1.2196
6.798	0.98498	0.8946	1.2798
9.661	0.98581	0.9463	1.3537
Temperature = 313.15K		**η_0 = 0.6132 cP**	
0.489	0.98073	0.6451	1.0519
0.685	0.98085	0.6525	1.0640
0.979	0.98102	0.6628	1.0808
2.928	0.9820	0.7110	1.1594
4.864	0.98283	0.7507	1.2242
6.788	0.98355	0.7858	1.2814
9.647	0.98438	0.8387	1.3677
Temperature = 318.15K		**η_0 = 0.5451 cP**	
0.487	0.97575	0.5757	1.0561
0.682	0.97587	0.5830	1.0695
0.974	0.97605	0.5913	1.0849
2.913	0.97711	0.6369	1.1685
4.840	0.97798	0.6732	1.2350
6.755	0.97877	0.7089	1.3005
9.601	0.97971	0.7526	1.3806

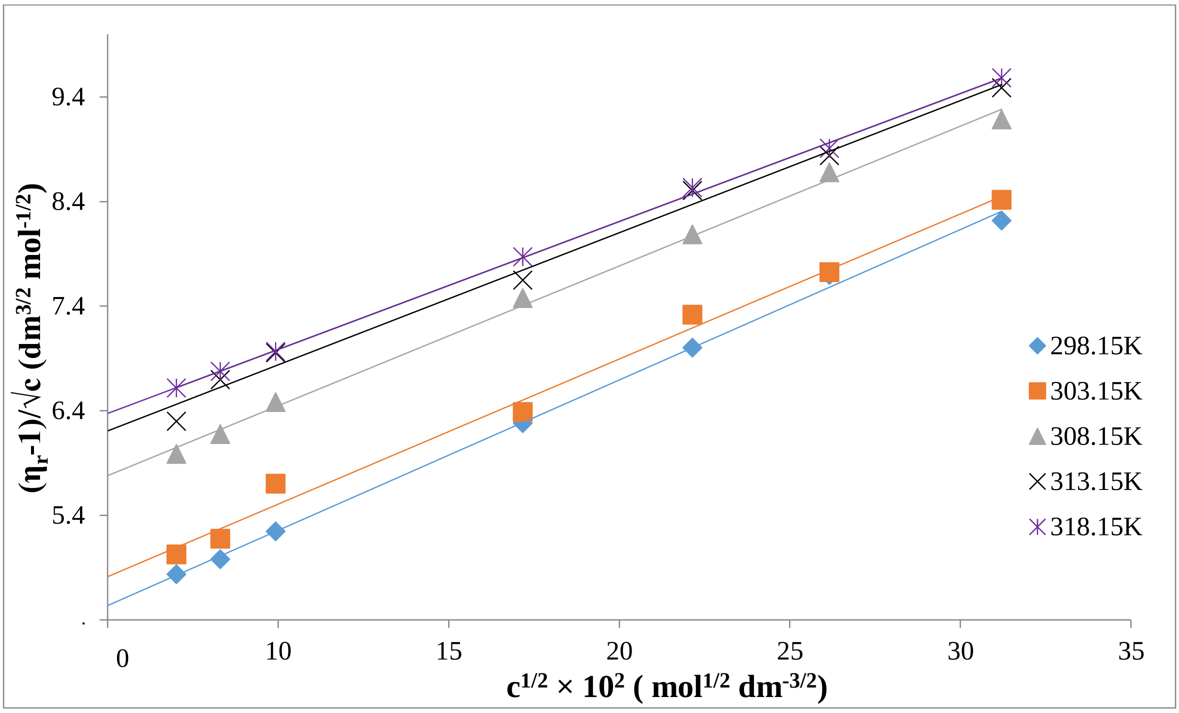

Fig.24: PLOTS OF $(\eta_r\text{-}1)/\sqrt{c}$ VS$\sqrt{c}$ FOR NICKEL CHLORIDE IN 5% (w/w) METHANOL + WATER MIXTURE AT DIFFERENT TEMPERATURES.

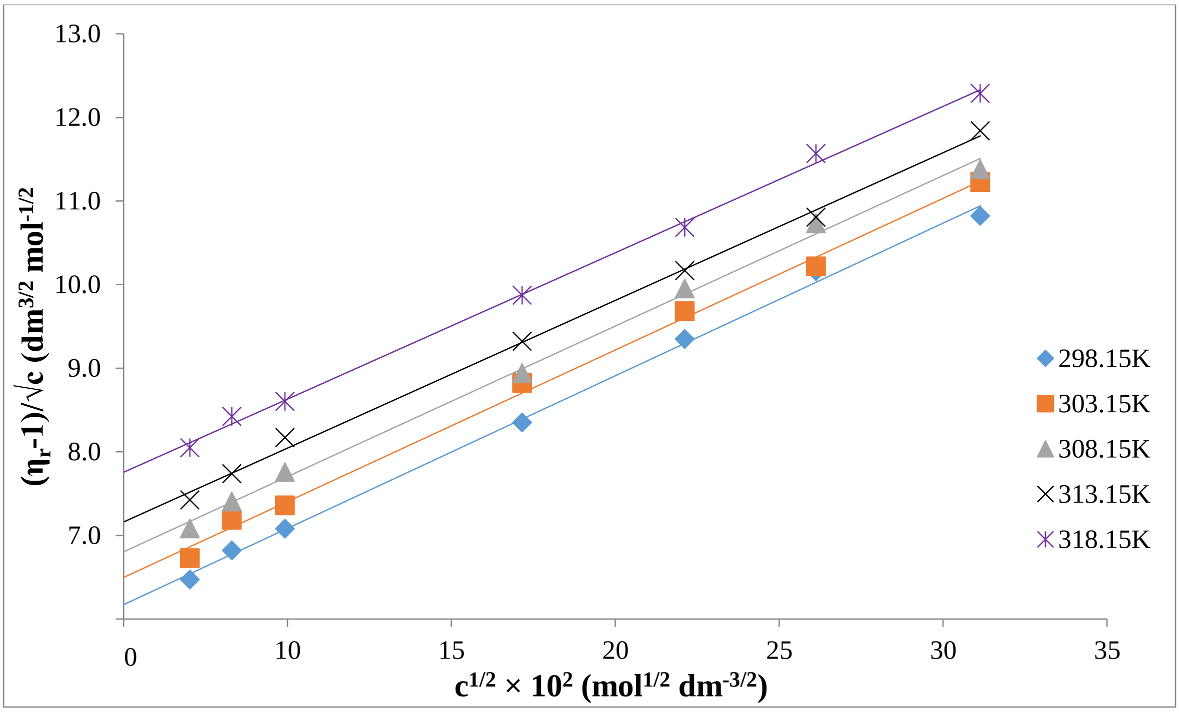

Fig.25: PLOTS OF $(\eta_r\text{-}1)/\sqrt{c}$ VS $\sqrt{c}$ FOR MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL +WATER MIXTURE AT DIFFERENT TEMPERATURES.

TABLE- 3.IX

VALUES OF A AND B PARAMETERS OF THE JONES – DOLE EQUATION FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) COMPOSITIONS OF METHANOL + WATER AT DIFFERENT TEMPERATURES.

Temperature (K)	**A ($dm^{3/2}\ mol^{-1/2}$)**	**B ($dm^3\ mol^{-1}$)**
	Manganese chloride	
298.15	9.239	0.125
303.15	9.421	0.121
308.15	9.713	0.113
313.15	10.020	0.111
318.15	10.600	0.103
	Cobalt chloride	
298.15	0.767	0.233
303.15	1.092	0.226
308.15	2.422	0.197
313.15	2.842	0.196
318.15	3.074	0.189
	Nickel chloride	
298.15	3.817	0.143
303.15	4.119	0.138
308.15	5.111	0.133
313.15	5.575	0.126
318.15	5.763	0.122
	Copper chloride	
298.15	5.346	0.132
303.15	6.263	0.123
308.15	6.951	0.122
313.15	7.201	0.120
318.15	7.376	0.119
	Cadmium chloride	
298.15	7.522	0.112
303.15	8.057	0.104
308.15	8.979	0.103
313.15	9.503	0.094
318.15	10.066	0.085
	Magnesium chloride	
298.15	5.259	0.182
303.15	5.590	0.181
308.15	5.904	0.180
313.15	6.278	0.177
318.15	6.881	0.175

The data of viscosity B- coefficients at different temperatures have also been examined on the basis of transition state theory as explained earlier. The values of $\Delta\mu_1^0$ and $\Delta\mu_2^0$ have been determined at different temperatures with the help of (3.3) and (3.4) relations respectively and the corresponding values are recorded in Table 3.X.The corresponding values of $\overline{V_1^0}$ and $\overline{V_2^0}$ required for the calculation of $\Delta\mu_1^0$ and $\Delta\mu_2^0$ are also recorded in Table 3.X.

According to Feakins model [15], $\Delta\mu_2^{0*} > \Delta\mu_1^{0*}$ for the solutes having positive B – values and greater the value of $\Delta\mu_2^{0*}$, the larger is the structure making capacity of the solute. On the basis of this model, it is concluded that all the divalent cations (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Mg^{2+}) are structure maker (Cl^- ion is a common ion).Similarly according to the Feakins theory, $\Delta\mu_2^{0*}$ should decrease with the increase of temperature for the solutes having negative values of $\frac{dB}{dT}$. This is nicely shown by all the divalent transition metal ions i.e. Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Mg^{2+}, which act as structure makers.

The quantity $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, the change in activation energy per mole of solute, on replacing one mole of solvent by one mole of solute at infinite dilution, is given in Table 3.XI. Values the quantity $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ are found positive and large for all the divalent transition metal chloride and magnesium chloride studied in 5% (w/w) methanol + water mixture at various temperatures which shows that the formation of transition state is accompanied by breaking of intermolecular bonds. In other words, it may be said that the formation of transition state is favoured less in the presence of these divalent transition metal chlorides and magnesium chloride in the entire temperature range studied here.

The values of $\Delta\mu_2^{0*}$ at different temperatures can also be used to calculate the activation entropy for different salts with the help of following relation (3.7) [15]:

$$\frac{d(\Delta\mu_2^{0*})}{dT} = -\Delta S_2^{0*} \tag{3.7}$$

The values of ΔS_2^{0*} have been determined from the slopes of the linear plots of $\Delta\mu_2^{0*}$ vs temperature T. A sample plot for manganese chloride, nickel chloride and copper chloride in 5% (w/w)methanol + water mixture is shown in Fig. 26.The values of $T\Delta S_2^{0*}$ at different

TABLE - 3.X

VALUES OF $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0*}$AND $\Delta\mu_2^{0*}$ FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) OF METHANOL + WATER MIXTURE AT DIFFERENT TEMPERATURES.

Temperature (K)	$\overline{V_1^0}$, ($cm^3 mol^{-1}$)	$\overline{V_2^0}$ ($cm^3 mol^{-1}$)	$\Delta\mu_1^{0*}$ ($kJ mol^{-1}$)	$\Delta\mu_2^{0*}$ ($kJ mol^{-1}$)
Manganese chloride				
298.15	18.68	64.90	60.71	83.52
303.15	18.69	61.50	61.36	83.49
308.15	18.75	57.87	62.04	82.91
313.15	18.79	55.80	62.71	83.23
318.15	18.88	52.86	63.41	82.72
Cobalt chloride				
298.15	18.68	131.81	60.71	106.67
303.15	18.69	127.68	61.36	106.63
308.15	18.75	125.55	62.04	103.64
313.15	18.79	123.95	62.71	104.50
318.15	18.88	120.75	63.41	104.18
Nickel chloride				
298.15	18.68	104.61	60.71	91.20
303.15	18.69	96.83	61.36	90.61
308.15	18.75	93.87	62.04	90.59
313.15	18.79	87.21	62.71	89.73
318.15	18.88	84.09	63.41	89.76
Copper chloride				
298.15	18.68	43.16	60.71	81.50
303.15	18.69	40.89	61.36	81.05
308.15	18.75	37.27	62.04	81.26
313.15	18.79	35.53	62.71	81.78
318.15	18.88	33.29	63.41	82.10
Cadmium chloride				
298.15	18.68	73.56	60.71	82.95
303.15	18.69	68.13	61.36	82.15
308.15	18.75	63.37	62.04	82.29
313.15	18.79	58.38	62.71	81.32
318.15	18.88	53.66	63.41	80.21
Magnesium chloride				
298.15	18.68	151.56	60.71	102.57
303.15	18.69	142.52	61.36	102.53
308.15	18.75	138.67	62.04	103.04
313.15	18.79	135.74	62.71	103.46
318.15	18.88	132.5	63.41	103.96

TABLE – 3.XI

VALUES OF $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, $T\Delta S_2^{0*}$ AND ΔH_2^{0*} FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER MIXTURE AT DIFFERENT TEMPERATURES.

Temperature (K)	$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ (kJ mol^{-1})	$T\Delta S_2^{0*}$ (kJ mol^{-1})	ΔH_2^{0*} (kJ mol^{-1})
Manganese chloride			
298.15	22.82	51.31	134.84
303.15	22.13	52.17	135.67
308.15	20.87	53.03	135.95
313.15	20.53	53.89	137.13
318.15	19.31	54.75	137.48
Cobalt chloride			
298.15	45.96	82.62	189.29
303.15	45.28	84.00	190.64
308.15	41.61	85.39	189.04
313.15	41.79	86.77	191.28
318.15	40.77	88.16	192.35
Nickel chloride			
298.15	30.49	62.52	153.72
303.15	29.25	63.57	154.18
308.15	28.55	64.62	155.21
313.15	27.03	65.67	155.41
318.15	26.35	66.72	156.48
Copper chloride			
298.15	20.79	28.74	110.25
303.15	19.69	29.22	110.28
308.15	19.22	29.71	110.97
313.15	19.08	30.19	111.97
318.15	18.69	30.67	112.77
Cadmium chloride			
298.15	22.24	77.76	160.71
303.15	20.79	79.06	161.22
308.15	20.26	80.37	162.66
313.15	18.61	81.67	162.99
318.15	16.81	82.97	163.19
Magnesium chloride			
298.15	41.86	17.92	120.49
303.15	41.17	18.22	120.75
308.15	41.01	18.52	121.57
313.15	40.75	18.82	122.28
318.15	40.56	19.12	123.09

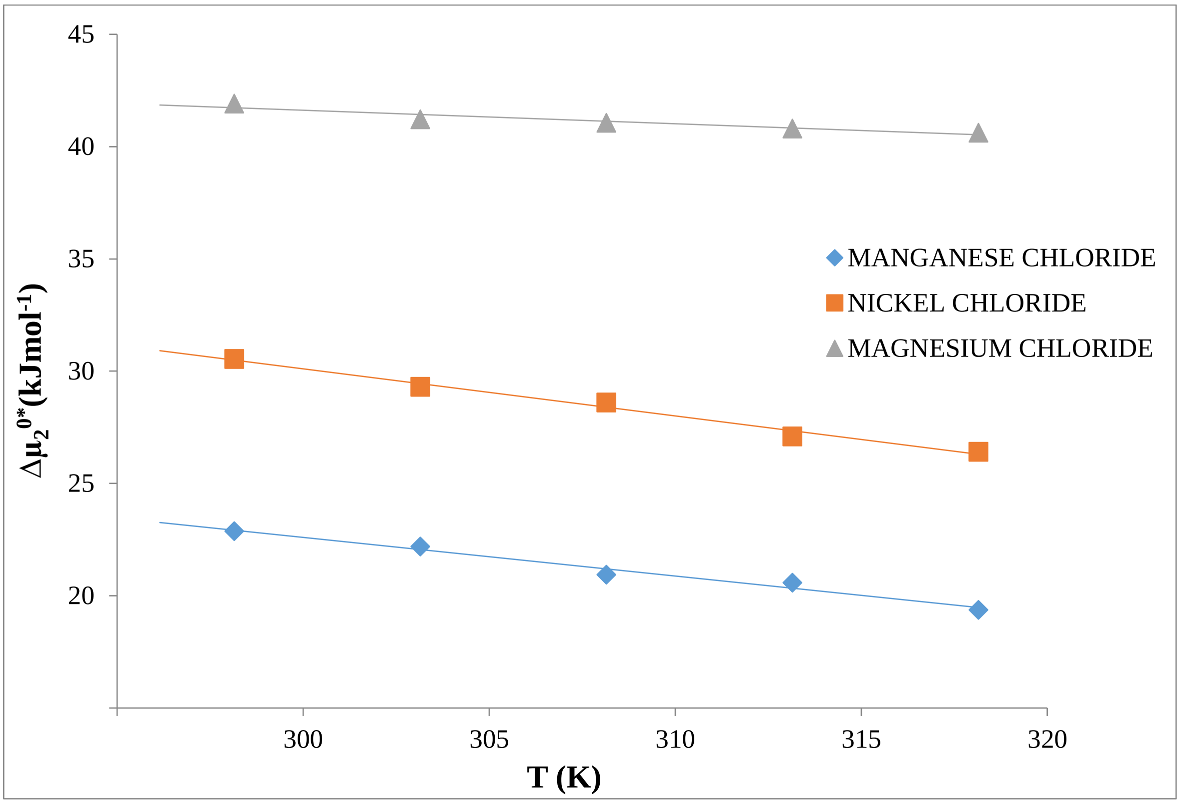

Fig.26: VARIATION of $\Delta\mu_2^{0*}$ WITH TEMPERATURE FOR MANGANESE CHLORIDE, NICKEL CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER MIXTURES.

temperatures for the divalent transition metal chlorides and magnesium chloride are also shown in Table 3.XI.

The activation enthalpy ΔH_2^0 has been calculated with the help of following relation (3.8) [15]:

$$\Delta H_2^{0*} = \Delta \mu_2^{0*} + T\Delta S_2^{0*} \tag{3.8}$$

The corresponding values of ΔH_2^{0*} are also recorded in Table 3.XI and It is clear from Table 3.XI that the values of activation enthalpy and activation entropy are positive for all the selected transition metal chlorides and magnesium chloride which indicate that the transition state is associated with the structure breaking and decrease in order.

Section – C

Discussion on the Results of Viscous Flow of Some Divalent Transition Metal Chlorides and Magnesium Chloride in Binary Aqueous Mixtures of Ethanol

Densities, viscosities and relative viscosities of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in five different compositions of ethanol + water (5, 10, 15, 20 and 35 by weight percentage of ethanol) at 303.15K are shown in Table 3.XII.

It is clear from Table 3.XII that the values of relative viscosities for the solutions of above mentioned divalent transition metal chlorides and magnesium chloride in the different binary aqueous mixtures of ethanol at 303.15K increase with the increase in concentration of each salt. The concentration dependence of relative viscosity of the solutions of the above mentioned salts in different binary aqueous compositions of ethanol can be represented by the Jones- Dole equation (3.1) and for all the above mentioned salts linear plots have been obtained between $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$ in all compositions of ethanol + water at 303.15K. Sample plots for cobalt chloride and magnesium chloride are shown in Figs. 27 and 28 respectively.

The values of A and B parameters of Jones – Dole equation have been calculated by using least square method to the linear plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$ and are given in Table - 3.XIII.

TABLE - 3.XII

DENSITIES, VISCOSITIES AND RELATIVE VISCOSITIES FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL + WATER AT 303.15K.

Concentration $c \times 10^2$ (mol dm^{-3})	**Density** d (g cm^{-3})	**Viscosity** η (cP)	**Relative Viscosity** $\frac{\eta}{\eta_0}$
	Manganese chloride		
5% (w/w) Ethanol + water			**η_0= 0.8228 cP**
0.493	0.98696	0.8841	1.0744
0.690	0.98724	0.8953	1.0880
0.985	0.98765	0.9100	1.1059
2.953	0.99034	0.9775	1.1879
4.916	0.99298	1.0261	1.2470
6.873	0.99555	1.0659	1.2954
9.799	0.99932	1.1183	1.3591
10% (w/w) Ethanol + water			**η_0= 0.9104 cP**
0.491	0.98299	0.9803	1.0767
0.687	0.98327	0.9931	1.0908
0.981	0.98369	1.0100	1.1094
2.941	0.98642	1.0863	1.1931
4.897	0.98914	1.1397	1.2518
6.847	0.99174	1.1846	1.3011
9.761	0.99548	1.2418	1.3639
15% (w/w) Ethanol + water			**η_0= 0.9758 cP**
0.487	0.97675	1.0522	1.0783
0.683	0.97704	1.0663	1.0927
0.975	0.97746	1.0844	1.1112
2.923	0.98025	1.1674	1.1963
4.866	0.983	1.2258	1.2562
6.805	0.98565	1.2746	1.3062
9.703	0.9895	1.3358	1.3689
20% (w/w) Ethanol + water			**η_0= 1.1158 cP**
0.485	0.97178	1.2047	1.0796
0.679	0.97207	1.2213	1.0945
0.970	0.9725	1.2421	1.1131
2.908	0.97531	1.3379	1.1990
4.842	0.97806	1.4054	1.2594
6.771	0.98078	1.4606	1.3089
9.656	0.98474	1.5326	1.3734
35% (w/w) Ethanol + water			**η_0= 1.3780 cP**

0.477	0.95487	1.4883	1.0800
0.667	0.95516	1.5086	1.0947
0.953	0.95559	1.5348	1.1138
2.858	0.95842	1.6529	1.1994
4.759	0.96122	1.7362	1.2598
6.655	0.9639	1.8048	1.3097
9.490	0.96782	1.8925	1.3733
	Cobalt chloride		
5% (w/w) Ethanol + water			**η_0= 0.8228 cP**
0.492	0.98674	0.8478	1.0303
0.689	0.98692	0.8527	1.0363
0.984	0.98721	0.8598	1.0449
2.945	0.98894	0.8941	1.0866
4.894	0.99056	0.9189	1.1166
6.831	0.99211	0.9443	1.1476
9.711	0.99426	0.9704	1.1793
10% (w/w) Ethanol + water			**η_0= 0.9104 cP**
0.490	0.98278	0.9399	1.0323
0.686	0.98298	0.9460	1.0391
0.980	0.98328	0.9542	1.0481
2.934	0.98514	0.9917	1.0892
4.876	0.98691	1.0206	1.1210
6.806	0.98854	1.0468	1.1498
9.678	0.99084	1.0798	1.1860
15% (w/w) Ethanol + water			**η_0= 0.9758 cP**
0.487	0.97654	1.0089	1.0339
0.682	0.97674	1.0150	1.0402
0.974	0.97704	1.0238	1.0492
2.916	0.97893	1.0651	1.0914
4.845	0.9807	1.0965	1.1236
6.764	0.9824	1.1233	1.1511
9.618	0.98478	1.1603	1.1890
20% (w/w) Ethanol + water			**η_0= 1.1158 cP**
0.485	0.97157	1.1562	1.0361
0.679	0.97178	1.1636	1.0428
0.969	0.97209	1.1744	1.0525
2.901	0.97402	1.2238	1.0967
4.821	0.97583	1.2608	1.1298
6.730	0.97753	1.2931	1.1588
9.572	0.98002	1.3293	1.1913
35% (w/w) Ethanol + water			**η_0= 1.3780 cP**
0.476	0.95466	1.4280	1.0362
0.667	0.95487	1.4398	1.0448
0.952	0.9552	1.4518	1.0535
2.851	0.95718	1.5131	1.0979

4.738	0.95903	1.5609	1.1327
6.615	0.96084	1.5960	1.1581
9.409	0.96333	1.6439	1.1929

Nickel chloride

5% (w/w) Ethanol + water			**η_0= 0.8228 cP**
0.492	0.98688	0.8588	1.0437
0.689	0.98712	0.8672	1.0539
0.985	0.98748	0.8771	1.0659
2.948	0.98981	0.9277	1.1274
4.901	0.99204	0.9682	1.1766
6.845	0.99419	1.0026	1.2185
9.740	0.99721	1.0532	1.2800
10% (w/w) Ethanol + water			**η_0= 0.9104 cP**
0.490	0.98291	0.9512	1.0448
0.687	0.98316	0.9600	1.0545
0.981	0.98353	0.9716	1.0672
2.936	0.98589	1.0275	1.1286
4.882	0.98812	1.0716	1.1770
6.818	0.99031	1.1105	1.2197
9.703	0.99337	1.1672	1.2820
15% (w/w) Ethanol + water			**η_0= 0.9758 cP**
0.487	0.97667	1.0221	1.0474
0.682	0.97692	1.0309	1.0564
0.975	0.9773	1.0430	1.0689
2.918	0.97968	1.1039	1.1312
4.852	0.98198	1.1517	1.1802
6.776	0.98417	1.1938	1.2233
9.643	0.98731	1.2510	1.2820
20% (w/w) Ethanol + water			**η_0= 1.1158 cP**
0.485	0.9717	1.1694	1.0479
0.679	0.97196	1.1801	1.0576
0.97	0.97234	1.1930	1.0691
2.903	0.97478	1.2673	1.1357
4.828	0.97708	1.3181	1.1812
6.743	0.97931	1.3691	1.2269
9.596	0.98248	1.4262	1.2781
35% (w/w) Ethanol + water			**η_0= 1.3780 cP**
0.476	0.95479	1.4441	1.0479
0.667	0.95505	1.4580	1.0580
0.953	0.95543	1.4783	1.0728
2.853	0.95786	1.5648	1.1355
4.744	0.96016	1.6263	1.1801
6.626	0.96239	1.6900	1.2263
9.431	0.96552	1.7588	1.2763

Copper chloride			
5% (w/w) Ethanol + water			**η_0= 0.8228 cP**
0.492	0.98674	0.8608	1.0460
0.689	0.98692	0.8684	1.0554
0.984	0.98721	0.8803	1.0698
2.945	0.98894	0.9339	1.1349
4.894	0.99056	0.9793	1.19018
6.831	0.99211	1.0146	1.2330
9.711	0.99426	1.0680	1.2979
10% (w/w) Ethanol + water			**η_0= 0.9104 cP**
0.490	0.98278	0.9557	1.0497
0.686	0.98298	0.9671	1.0622
0.980	0.98328	0.9786	1.0749
2.934	0.98514	1.0426	1.1452
4.876	0.98691	1.0962	1.2040
6.806	0.98854	1.1373	1.2491
9.678	0.99084	1.1887	1.3057
15% (w/w) Ethanol + water			**η_0= 0.9758 cP**
0.487	0.97654	1.0279	1.0533
0.682	0.97674	1.0392	1.0649
0.974	0.97704	1.0532	1.0793
2.916	0.97893	1.1234	1.1513
4.845	0.9807	1.1761	1.2052
6.764	0.9824	1.2296	1.2600
9.618	0.98478	1.2803	1.3120
20% (w/w) Ethanol + water			**η_0= 1.1158 cP**
0.485	0.97157	1.1797	1.0572
0.679	0.97178	1.1917	1.0679
0.969	0.97209	1.2090	1.0834
2.901	0.97402	1.2919	1.1578
4.821	0.97583	1.3528	1.2123
6.730	0.97753	1.4170	1.2699
9.572	0.98002	1.4803	1.3263
35% (w/w) Ethanol + water			**η_0= 1.3780 cP**
0.476	0.95466	1.4618	1.0608
0.667	0.95487	1.4781	1.0726
0.952	0.9552	1.4997	1.0882
2.851	0.95718	1.6060	1.1654
4.738	0.95903	1.6966	1.2311
6.615	0.96084	1.7590	1.2764
9.409	0.96333	1.8455	1.3392
Cadmium chloride			
5% (w/w) Ethanol + water			**η_0= 0.8228 cP**

0.493	0.98696	0.8725	1.0604
0.690	0.98723	0.8830	1.0731
0.985	0.98764	0.8970	1.0901
2.953	0.99030	0.9645	1.1721
4.915	0.99290	1.0137	1.2319
6.870	0.99528	1.0546	1.2817
9.792	0.99898	1.1186	1.3594
10% (w/w) Ethanol + water			**η_0= 0.9104 cP**
0.491	0.98299	0.9678	1.0630
0.687	0.98328	0.9780	1.0741
0.981	0.9837	0.9929	1.0905
2.941	0.98638	1.0677	1.1727
4.895	0.98899	1.1223	1.2326
6.843	0.9914	1.1669	1.2817
9.754	0.99507	1.2393	1.3612
15% (w/w) Ethanol + water			**η_0= 0.9758 cP**
0.487	0.97675	1.0379	1.0636
0.683	0.97704	1.0493	1.0753
0.975	0.97747	1.0680	1.0945
2.922	0.98017	1.1450	1.1734
4.864	0.98278	1.2052	1.2351
6.800	0.98523	1.2543	1.2854
9.693	0.98889	1.3317	1.3646
20% (w/w) Ethanol + water			**η_0= 1.1158 cP**
0.485	0.97179	1.1877	1.0644
0.679	0.97208	1.2011	1.0764
0.970	0.97251	1.2212	1.0944
2.908	0.97531	1.3098	1.1738
4.841	0.97795	1.3796	1.2364
6.768	0.98048	1.4352	1.2861
9.645	0.98395	1.5234	1.3652
35% (w/w) Ethanol + water			**η_0= 1.3780 cP**
0.477	0.95487	1.4692	1.0661
0.667	0.95518	1.4888	1.0804
0.953	0.95561	1.5106	1.0961
2.857	0.95839	1.6201	1.1756
4.757	0.96107	1.7025	1.2354
6.652	0.96375	1.7743	1.2875
9.480	0.96718	1.8776	1.3625
	Magnesium chloride		
5% (w/w) Ethanol + water			**η_0= 0.8228 cP**
0.485	0.97136	0.8653	1.0516
0.679	0.97148	0.8743	1.0625
0.969	0.97166	0.8867	1.0776
2.900	0.9727	0.9448	1.1482

4.819	0.97364	0.9852	1.1973
6.725	0.97444	1.0270	1.2480
9.560	0.97553	1.0800	1.3124
10% (w/w) Ethanol + water		**η_0= 0.9104 cP**	
0.490	0.98256	0.9594	1.0538
0.686	0.98267	0.9688	1.0641
0.980	0.98283	0.9821	1.0787
2.933	0.98378	1.0464	1.1493
4.873	0.98461	1.0948	1.2025
6.800	0.98537	1.1419	1.2543
9.667	0.98642	1.1968	1.3145
15% (w/w) Ethanol + water		**η_0= 0.9758 cP**	
0.487	0.97632	1.0289	1.0544
0.682	0.97644	1.0395	1.0652
0.974	0.9766	1.0527	1.0788
2.915	0.97761	1.1211	1.1489
4.843	0.97847	1.1764	1.2055
6.758	0.97923	1.2244	1.2547
9.607	0.98025	1.2840	1.3158
20% (w/w) Ethanol + water		**η_0= 1.1158 cP**	
0.485	0.97136	1.1774	1.0552
0.679	0.97148	1.1893	1.0658
0.969	0.97166	1.2065	1.0812
2.900	0.9727	1.2867	1.1531
4.819	0.97364	1.3481	1.2081
6.725	0.97444	1.4021	1.2565
9.560	0.97553	1.4724	1.3195
35% (w/w) Ethanol + water		**η_0= 1.3780 cP**	
0.476	0.95446	1.4545	1.0554
0.667	0.95458	1.4700	1.0667
0.952	0.95478	1.4895	1.0808
2.850	0.95589	1.5871	1.1517
4.736	0.95688	1.6649	1.2082
6.610	0.95774	1.7318	1.2567
9.399	0.95906	1.8150	1.3171

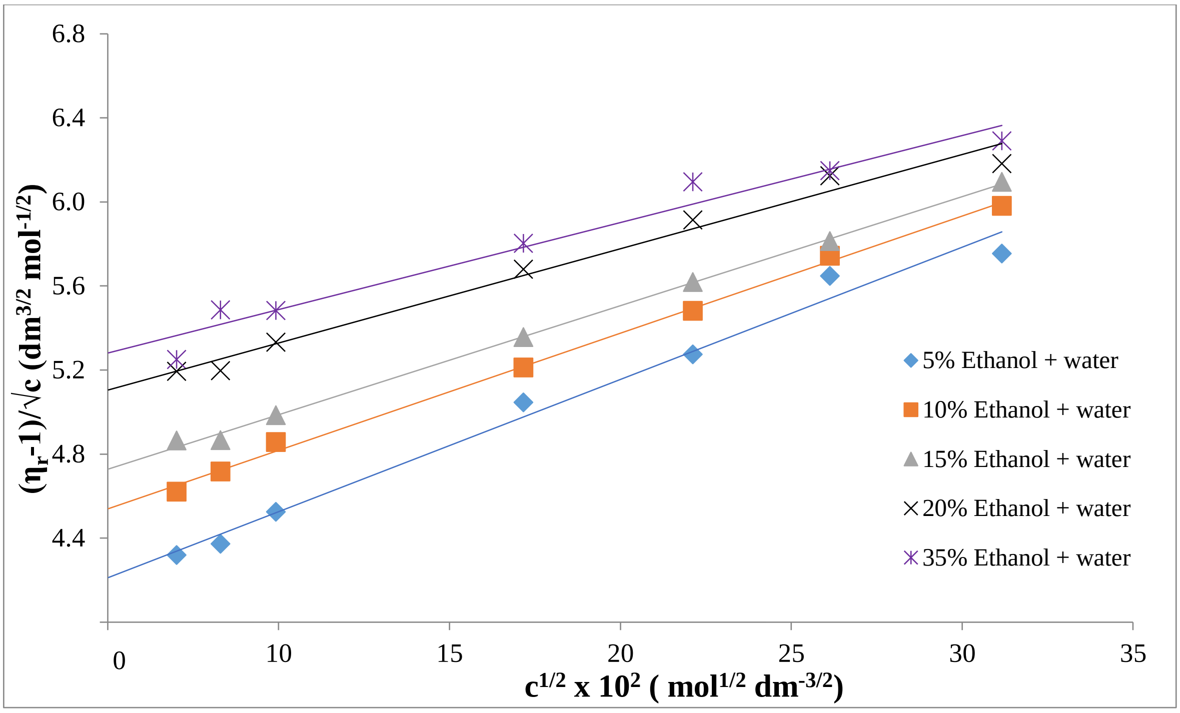

Fig.27: PLOTS OF $(\eta_r - 1) / \sqrt{c}$ VS $\sqrt{c}$ FOR COBALT CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL+ WATER AT 303.15K

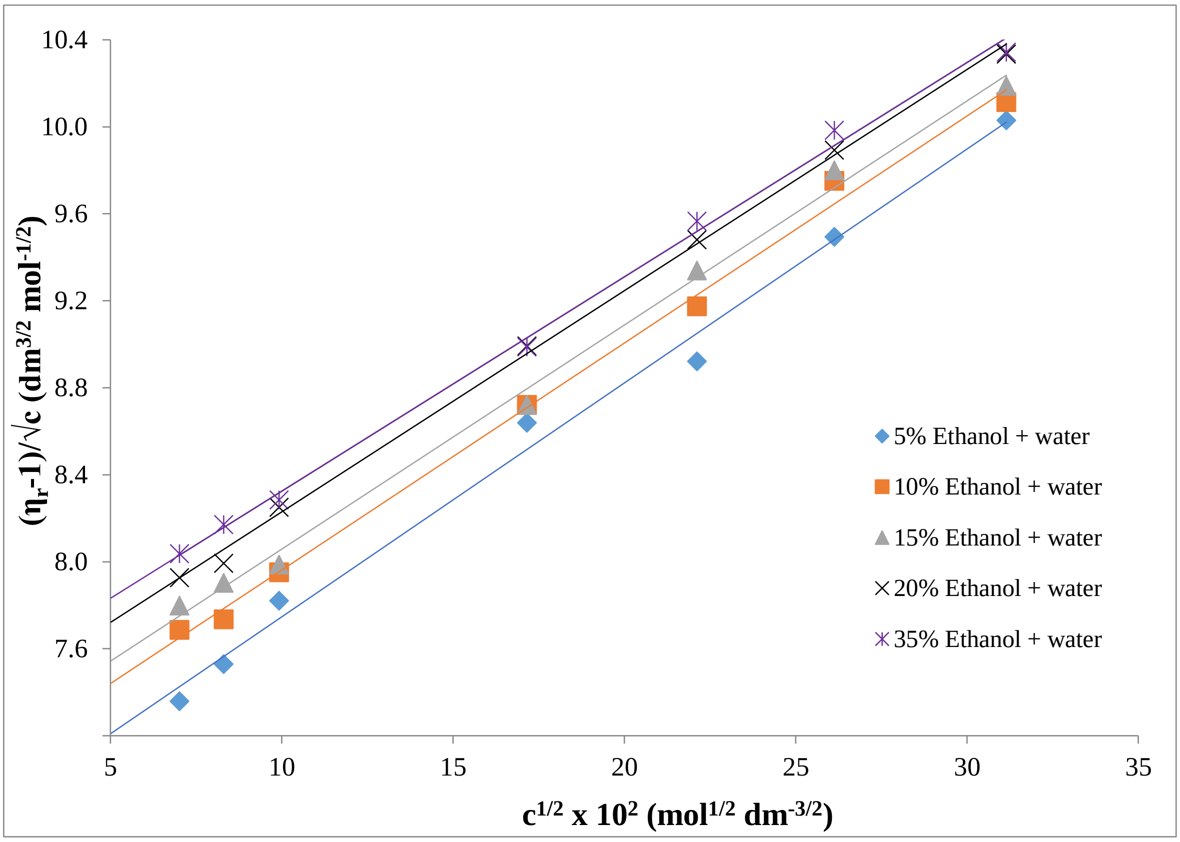

Fig.28: PLOTS OF $(\eta_r - 1) / \sqrt{c}$ VS $\sqrt{c}$ FOR MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL+ WATER AT 303.15K

TABLE - 3.XIII

VALUES OF A AND B PARAMETERS OF THE JONES – DOLE EQUATION FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN DIFFERENT COMPOSITIONS OF ETHANOL + WATER AT 303.15K.

Ethanol + water % (w/w)	A ($dm^{3/2}$ $mol^{-1/2}$)	B (dm^3 mol^{-1})
	Manganese Chloride	
5	10.320	0.036
10	10.742	0.029
15	11.009	0.027
20	11.262	0.024
35	11.427	0.022
	Cobalt Chloride	
5	3.896	0.063
10	4.268	0.056
15	4.469	0.052
20	4.881	0.045
35	5.074	0.042
	Nickel chloride	
5	5.532	0.109
10	5.680	0.106
15	6.054	0.096
20	6.235	0.092
35	6.474	0.085
	Copper chloride	
5	5.735	0.123
10	6.482	0.113
15	7.003	0.104
20	7.466	0.103
35	8.120	0.100
	Cadmium chloride	
5	7.891	0.114
10	8.145	0.106
15	8.379	0.103
20	8.509	0.101
35	9.019	0.085
	Magnesium chloride	
5	6.671	0.107
10	6.917	0.104
15	7.027	0.103
20	7.213	0.102
35	7.339	0.100

It is clear from Table 3.XIII that the A coefficient values are positive for an individual salt in the entire composition range of ethanol + water at 303.15K. This indicates the presence of ion – ion interactions and values of A – parameter increases continuously with the increase of amount of ethanol in water at 303.15K thereby suggesting that ion –ion interactions are further strengthened with the increase of ethanol content in water, which may be referred to the decrease in ion – salvation. It is also clear from Table 3.XIII that the values of B – parameter for all the selected divalent transition metal chlorides and magnesium chloride are positive but are smaller in comparison with the values of A – parameter in the entire compositions of ethanol + water at 303.15K indicating the presence of specific ion- solvent interactions but these interactions are weaker as compared to ion – ion interactions. This may also to be attributed to the weak solvation of these ions by mixtures of ethanol + water. Moreover, it is also clear from the Table 3.XIII that the values of B-parameter are decreasing with the addition of ethanol content in water thereby resulting in the decrease of ion-solvent interactions meaning thereby water has more affinity for solvent than that for salt. These conclusions from viscous flow are in agreement with those drawn from the density data for the above mentioned divalent transition metal chlorides and magnesium chloride described in chapter –II.

The viscosity data for the solutions of the above mentioned transition metal chlorides in the binary aqueous mixtures of ethanol at 303.15K have also been examined on the basis of transition state theory of relative viscosities according to the relation (3.2). The values of $\Delta\mu_1^0$ and $\overline{V_1^0}$ for the different binary aqueous mixtures of ethanol have been calculated with the help of relations (3.3) and (3.6) respectively and the respective values are given in Table – 3.XIV. The values of $\overline{V_2^0}$ for the solutions of the divalent transition metal chlorides and magnesium chloride in binary aqueous mixtures of ethanol, determined from density data, have also been recorded in Table – 3.XIV.From Table – 3.XIV, it is clear that $\Delta\mu_1^0$ does not change appreciably with the change in the composition of ethanol in water at 303.15K. In other words, it may be said that $\Delta\mu_1^0$ values for the different compositions of ethanol + water at 303.15K are practically held constant. It is also clear from Table – 3.XIV that the values of $\Delta\mu_2^0$ change with solvent composition for each salt, studied here, in ethanol + water mixtures at 303.15K. Moreover, the positive values of $\Delta\mu_2^0$ suggest that the formation of transition state is less favoured in the presence of selected divalent transition metal chlorides and magnesium chloride. In other words, formation of transition state in accompanied by breaking of intermolecular bonds.

TABLE - 3.XIV

VALUES OF $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0*}$AND $\Delta\mu_2^{0*}$ FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5%(w/w) OF ETHANOL + WATER MIXTURE AT 303.15K.

Ethanol + water (%w/w)	$\overline{V_1^0}$ (cm^3 mol^{-1})	$\overline{V_2^0}$ (cm^3 mol^{-1})	$\Delta\mu_1^{0*}$ (kJ mol^{-1})	$\Delta\mu_2^{0*}$ (kJ mol^{-1})
Manganese chloride				
5	18.85	53.93	61.46	71.04
10	19.53	49.57	61.8	69.44
15	20.35	46.57	62.08	68.71
20	21.13	44.24	62.51	68.13
35	24.11	39.91	63.38	67.38
Cobalt chloride				
5	18.85	138.15	61.46	85.82
10	19.53	131.43	61.8	83.46
15	20.35	130.13	62.08	82.11
20	21.13	127.23	62.51	80.55
35	24.11	125.21	63.38	78.34
Nickel chloride				
5	18.85	109.92	61.46	88.29
10	19.53	104.64	61.80	86.54
15	20.35	102.60	62.08	84.26
20	21.13	99.56	62.51	82.90
35	24.11	96.40	63.38	79.88
Copper chloride				
5	18.85	69.19	61.46	84.63
10	19.53	64.45	61.80	82.17
15	20.35	59.85	62.08	79.85
20	21.13	57.56	62.51	79.14
35	24.11	55.73	63.38	77.13
Cadmium chloride				
5	18.85	57.02	61.46	81.85
10	19.53	50.21	61.80	79.51
15	20.35	47.24	62.08	78.25
20	21.13	42.49	62.51	77.11
35	24.11	38.97	63.38	73.83
Magnesium chloride				
5	18.85	146.45	61.46	92.90
10	19.53	142.07	61.80	91.10
15	20.35	139.52	62.08	89.66
20	21.13	135.79	62.51	88.41
35	24.11	133.12	63.38	85.23

Greater values of $\Delta\mu_2^0$ than that of $\Delta\mu_1^0$ suggest that the all the selected transition metal chlorides and magnesium chloride in ethanol + water solvent systems behave as structure promoters. This conclusion is in the excellent agreement with that drawn from partial molar volume studies (described in chapter II).
Since it has been described in Section –B of this chapter that structure making or breaking capacity of any electrolyte cannot be predicted only on the basis of B-Coefficient, rather dB/dT is a better criterion for determining this property, so in order to follow this criterion the effect of temperature must be studied.

Effect of temperature

It is evident that the behaviour of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in different compositions of ethanol + water at 303.15K is found similar, so only one composition 5% (w/w) ethanol + water is selected to study the effect of temperature, as the same composition was also selected in case of density data to study the effect of temperature described in chapter II. Values of densities, viscosities and relative viscosities for various concentrations of the solutions of divalent transition metal chlorides and magnesium chloride in 5% (w/w) ethanol + water mixtures at different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K) are recorded in Table – 3.XV.

The plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$ for all the above mentioned divalent transition metal chlorides and magnesium chloride in 5% (w/w) ethanol + water at five different temperatures have been found to be linear in accordance with Jone –Dole equation (3.1) and sample plots for nickel chloride and magnesium chloride are shown in Figs.29 and 30, respectively. The values of A and B parameters of the Jones – Dole equation for all the above mentioned transition metal chloride and magnesium chlorides in 5% (w/w) ethanol + water at different temperatures have been calculated using least square method and the corresponding values have been recorded in Table – 3.XVI.

From Table 3.XVI, it is clear that the values of A parameter of the Jones - Dole equation are positive in the entire temperature range for all the salts in 5%(w/w) ethanol + water indicating the existence of ion – ion interactions.

TABLE - 3.XV

DENSITIES, VISCOSITIES AND RELATIVE VISCOSITIES FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL + WATER MIXTURE AT DIFFERENT TEMPERATURES.

Concentration $c \times 10^2$ ($mol\ dm^{-3}$)	Density d ($g\ cm^{-3}$)	Viscosity η (cP)	Relative Viscosity $\frac{\eta}{\eta_0}$
Manganese Chloride			
Temperature = 298.15K		**η_0 = 0.9960 cP**	
0.493	0.98797	1.0693	1.0735
0.690	0.98824	1.0835	1.0878
0.986	0.98864	1.1009	1.1053
2.956	0.99125	1.1820	1.1867
4.920	0.99377	1.2402	1.2451
6.878	0.99623	1.2884	1.2935
9.804	0.99981	1.3516	1.3570
Temperature = 303.15K		**η_0 = 0.8228 cP**	
0.493	0.98697	0.8841	1.0745
0.690	0.98725	0.8953	1.0880
0.985	0.98767	0.9100	1.1059
2.953	0.99034	0.9775	1.1879
4.916	0.99298	1.0261	1.2470
6.873	0.99555	1.0659	1.2954
9.799	0.99932	1.1183	1.3591
Temperature = 308.15K		**η_0 = 0.7343 cP**	
0.491	0.98413	0.7904	1.07632
0.688	0.98442	0.8012	1.0911
0.982	0.98485	0.8147	1.1094
2.945	0.98762	0.8764	1.1935
4.903	0.99034	0.9203	1.2532
6.855	0.99294	0.9567	1.3028
9.773	0.99671	1.0045	1.3680
Temperature = 313.15K		**η_0 = 0.6377 cP**	
0.489	0.97941	0.6867	1.0768
0.684	0.97970	0.6959	1.0913
0.978	0.98014	0.7076	1.1095
2.931	0.98300	0.7612	1.1935
4.880	0.98571	0.7996	1.2538
6.823	0.98824	0.8313	1.3035
9.732	0.99246	0.8726	1.3682
Temperature = 318.15K		**η_0 = 0.5713 cP**	
0.487	0.97494	0.6162	1.0785

0.681	0.97524	0.6247	1.0933
0.973	0.97568	0.6352	1.1118
2.918	0.97856	0.6846	1.1981
4.858	0.98127	0.7191	1.2585
6.793	0.98394	0.7475	1.3082
9.687	0.98793	0.7844	1.3728

Cobalt Chloride

Temperature = 298.15K		**η_0 = 0.9960 cP**	
0.493	0.98775	1.0219	1.0260
0.690	0.98793	1.0275	1.0316
0.985	0.98819	1.0355	1.0396
2.948	0.98989	1.0729	1.0771
4.899	0.99147	1.1025	1.1069
6.837	0.99298	1.1282	1.1327
9.72	0.99513	1.1649	1.1695
Temperature = 303.15K		**η_0 = 0.8228 cP**	
0.492	0.98674	0.8478	1.0303
0.689	0.98692	0.8527	1.0363
0.984	0.98721	0.8598	1.0449
2.945	0.98894	0.8941	1.0866
4.894	0.99056	0.9189	1.1166
6.831	0.99211	0.9443	1.1476
9.711	0.99426	0.9704	1.1793
Temperature = 308.15K		**η_0 = 0.7343 cP**	
0.493	0.98389	0.7577	1.0319
0.690	0.98408	0.7629	1.0389
0.985	0.98437	0.7700	1.0485
2.948	0.98615	0.8014	1.0913
4.899	0.98781	0.8227	1.1204
6.837	0.98939	0.8441	1.1495
9.72	0.9915	0.8717	1.1871
Temperature = 313.15K		**η_0 = 0.6377 cP**	
0.489	0.97916	0.6589	1.0332
0.684	0.97935	0.6630	1.0396
0.977	0.97964	0.6694	1.0496
2.923	0.98145	0.6972	1.0932
4.858	0.98315	0.7165	1.1236
6.780	0.98473	0.7364	1.1547
9.639	0.98688	0.7573	1.1876
Temperature = 318.15K		**η_0 = 0.5713 cP**	
0.486	0.9747	0.5914	1.0351
0.681	0.9749	0.5951	1.0416
0.972	0.9752	0.6005	1.0509
2.910	0.97705	0.6258	1.0953
4.836	0.97878	0.6440	1.1270

6.750	0.9804	0.6600	1.1551
9.598	0.98266	0.6797	1.1895

Nickel Chloride

Temperature = 298.15K		**η_0 = 0.9960 cP**	
0.493	0.9879	1.0360	1.0401
0.690	0.98814	1.0447	1.0489
0.986	0.98849	1.0575	1.0617
2.951	0.99076	1.1226	1.1271
4.906	0.99291	1.1778	1.1825
6.850	0.99498	1.2222	1.2271
9.746	0.99785	1.2882	1.2933
Temperature = 303.15K		**η_0 = 0.8228 cP**	
0.492	0.98689	0.8588	1.0437
0.689	0.98714	0.8672	1.0539
0.985	0.98751	0.8771	1.0659
2.948	0.98985	0.9278	1.1275
4.902	0.99207	0.9683	1.1767
6.845	0.99419	1.0026	1.2185
9.740	0.99724	1.0533	1.2800
Temperature = 308.15K		**η_0 = 0.7343 cP**	
0.491	0.98404	0.7678	1.0456
0.687	0.98429	0.7749	1.0552
0.982	0.98466	0.7845	1.0684
2.940	0.98702	0.8302	1.1306
4.888	0.98928	0.8641	1.1767
6.826	0.99143	0.8968	1.2212
9.714	0.99452	0.9437	1.2851
Temperature = 313.15K		**η_0 = 0.6377 cP**	
0.489	0.97931	0.6675	1.0466
0.684	0.97956	0.6738	1.0566
0.977	0.97994	0.6820	1.0694
2.926	0.98232	0.7233	1.1341
4.865	0.98462	0.7528	1.1804
6.794	0.98684	0.7829	1.2276
9.669	0.98993	0.8184	1.2834
Temperature = 318.15K		**η_0 = 0.5713 cP**	
0.486	0.97485	0.5982	1.0470
0.681	0.97511	0.6040	1.0571
0.973	0.9755	0.6115	1.0702
2.913	0.97796	0.6486	1.1351
4.843	0.98029	0.6760	1.1830
6.765	0.98251	0.7013	1.2274
9.628	0.98571	0.7332	1.2833

Copper chloride

Temperature = 298.15K		**η_0 = 0.9960 cP**	
0.493	0.98776	1.0412	1.0454
0.690	0.98794	1.0507	1.0549
0.986	0.98821	1.0649	1.0691
2.954	0.98997	1.1271	1.1316
4.916	0.99162	1.1832	1.1879
6.870	0.99321	1.2278	1.2327
9.787	0.99547	1.2913	1.2964
Temperature = 303.15K		**η_0 = 0.8228 cP**	
0.493	0.98675	0.8608	1.0460
0.69	0.98694	0.8684	1.0554
0.985	0.98723	0.8803	1.0698
2.952	0.98905	0.9339	1.1349
4.912	0.99078	0.9793	1.1901
6.865	0.99248	1.0146	1.2330
9.782	0.99489	1.0680	1.2979
Temperature = 308.15K		**η_0 = 0.7343 cP**	
0.4915	0.9839	0.7683	1.0463
0.688	0.98409	0.7754	1.0559
0.9827	0.98438	0.7856	1.0698
2.943	0.98623	0.8333	1.1348
4.898	0.988	0.8730	1.1888
6.846	0.9897	0.9059	1.2336
9.754	0.99211	0.9534	1.2983
Temperature = 313.15K		**η_0 = 0.6377 cP**	
0.489	0.97918	0.6696	1.0500
0.684	0.97938	0.6765	1.0609
0.978	0.97968	0.6846	1.0736
2.929	0.9816	0.7278	1.1413
4.875	0.98348	0.7627	1.1959
6.815	0.98522	0.7907	1.2399
9.712	0.98778	0.8309	1.3029
Temperature = 318.15K		**η_0 = 0.5713 cP**	
0.486	0.97472	0.6012	1.0522
0.681	0.97492	0.6075	1.0632
0.973	0.97523	0.6154	1.0771
2.916	0.97717	0.6553	1.1468
4.853	0.97898	0.6854	1.1995
6.784	0.98075	0.7125	1.2469
9.669	0.98339	0.7476	1.3084

Cadmium chloride

Temperature = 298.15K		**η_0 = 0.9960 cP**	

0.493	0.98799	1.0546	1.0588
0.690	0.98826	1.0673	1.0715
0.986	0.98867	1.0847	1.0890
2.956	0.99129	1.1666	1.1712
4.919	0.99385	1.2271	1.2319
6.877	0.99638	1.2754	1.2804
9.802	1.00003	1.3496	1.3549
Temperature = 303.15K		**η_0 = 0.8228 cP**	
0.493	0.98697	0.8725	1.0604
0.690	0.98725	0.8830	1.0731
0.985	0.98766	0.8971	1.0901
2.953	0.99034	0.9645	1.1721
4.915	0.9929	1.0137	1.2319
6.870	0.99528	1.0546	1.2817
9.792	0.99898	1.1186	1.3594
Temperature = 308.15K		**η_0 = 0.7343 cP**	
0.491	0.98412	0.7797	1.0618
0.688	0.9844	0.7893	1.0749
0.982	0.98482	0.8028	1.0932
2.944	0.98751	0.8638	1.1763
4.901	0.99011	0.9050	1.2324
6.851	0.99252	0.9449	1.2868
9.766	0.99629	1.0003	1.3622
Temperature = 313.15K		**η_0 = 0.6377 cP**	
0.489	0.97939	0.6782	1.0635
0.684	0.97968	0.6863	1.0762
0.978	0.98012	0.6979	1.0944
2.930	0.98288	0.7503	1.1765
4.878	0.98552	0.7887	1.2367
6.82	0.98801	0.8208	1.2871
9.721	0.99174	0.8702	1.3645
Temperature = 318.15K		**η_0 = 0.5713 cP**	
0.487	0.97494	0.6080	1.0641
0.681	0.97523	0.6154	1.0771
0.973	0.97567	0.6254	1.0946
2.917	0.97844	0.6726	1.1772
4.857	0.98119	0.7066	1.2366
6.790	0.98375	0.7359	1.2880
9.680	0.98756	0.7809	1.3668

Magnesium chloride

Temperature = 298.15K		**η_0 = 0.9960 cP**	
0.493	0.98754	1.0472	1.0513
0.690	0.98763	1.0581	1.0623
0.985	0.98777	1.0729	1.0772
2.947	0.98861	1.1418	1.1463

4.896	0.98933	1.1975	1.2023
6.832	0.98997	1.2424	1.2473
9.709	0.99072	1.3053	1.3105
Temperature = 303.15K		**η_0 = 0.8228 cP**	
0.492	0.98653	0.8653	1.0516
0.689	0.98663	0.8743	1.0625
0.984	0.98678	0.8867	1.0776
2.945	0.98766	0.9448	1.1482
4.892	0.98845	0.9852	1.1973
6.827	0.98917	1.0270	1.2480
9.703	0.99011	1.0800	1.3124
Temperature = 308.15K		**η_0 = 0.73434 cP**	
0.491	0.98369	0.7725	1.0520
0.687	0.98380	0.7807	1.0632
0.982	0.98396	0.7908	1.0770
2.936	0.98495	0.8428	1.1478
4.879	0.98581	0.8811	1.1998
6.809	0.98660	0.9174	1.2493
9.679	0.98766	0.9629	1.3112
Temperature = 313.15K		**η_0 = 0.63774 cP**	
0.489	0.97896	0.6723	1.0542
0.684	0.97907	0.6791	1.0649
0.977	0.97925	0.6877	1.0784
2.923	0.98028	0.7331	1.1495
4.856	0.98119	0.7677	1.2038
6.777	0.98202	0.8011	1.2562
9.635	0.98311	0.8383	1.3145
Temperature = 318.15K		**η_0 = 0.5713 cP**	
0.486	0.97451	0.6031	1.0556
0.681	0.97463	0.6099	1.0674
0.972	0.97481	0.6187	1.0829
2.909	0.97588	0.6606	1.1561
4.835	0.97683	0.6931	1.2131
6.747	0.97765	0.7179	1.2565
9.591	0.97867	0.7543	1.3202

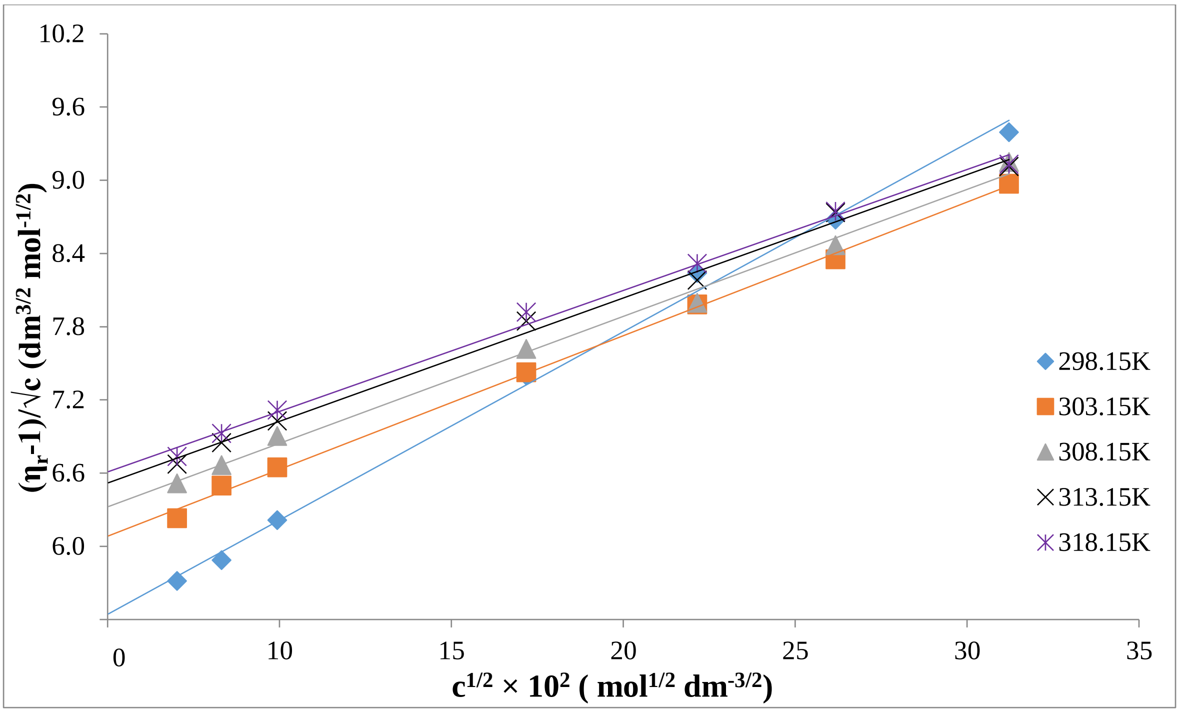

FIG.29: PLOTS OF $(\eta_r - 1) / \sqrt{c}$ VS $\sqrt{c}$ FOR NICKEL CHLORIDE IN 5% (w/w) ETHANOL+ WATER AT DIFFERENT TEMPERATURES.

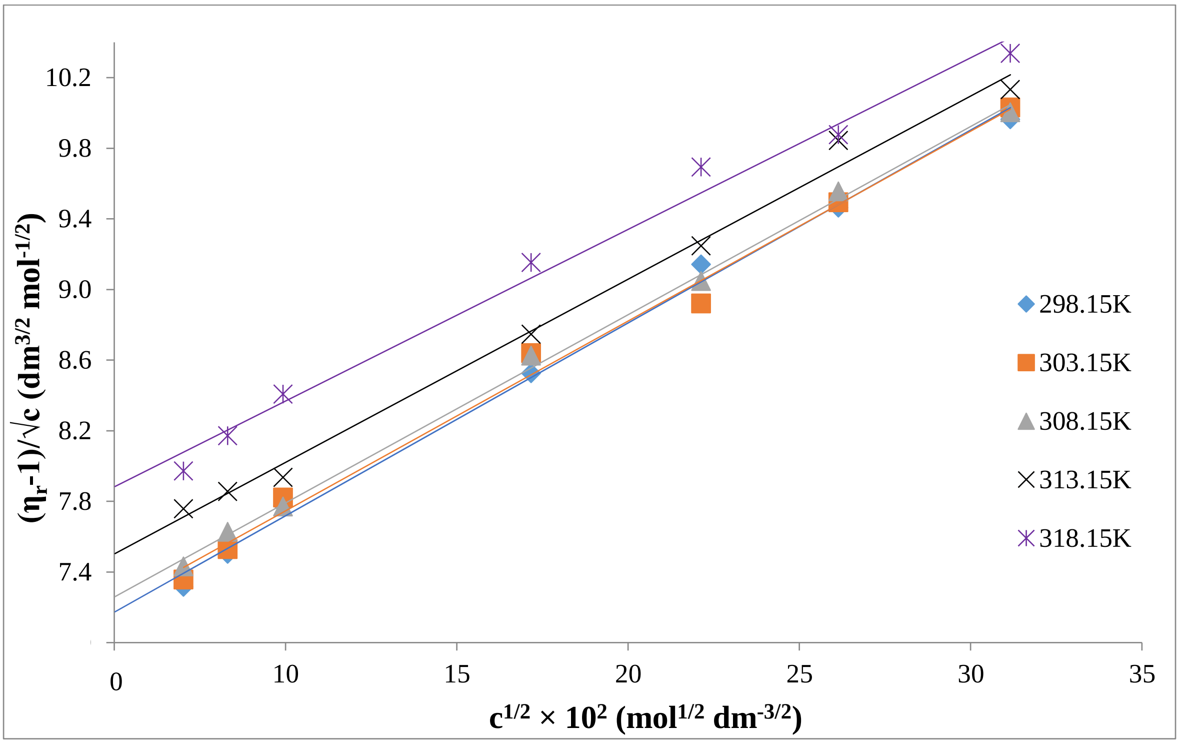

FIG.30: PLOTS OF $(\eta_r - 1) / \sqrt{c}$ VS $\sqrt{c}$ FOR MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL+ WATER AT DIFFERENT TEMPERATURES.

TABLE - 3.XVI

VALUES OF A AND B PARAMETERS OF THE JONES – DOLE EQUATION FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) COMPOSITIONS OF ETHANOL + WATER AT DIFFERENT TEMPERATURES.

Temperature (K)	A ($dm^{3/2}$ $mol^{-1/2}$)	B (dm^3 mol^{-1})
	Manganese chloride	
298.15	10.22	0.037
303.15	10.32	0.036
308.15	10.67	0.034
313.15	10.75	0.033
318.15	11.05	0.030
	Cobalt chloride	
298.15	3.24	0.070
303.15	3.89	0.062
308.15	4.24	0.057
313.15	4.41	0.055
318.15	4.70	0.047
	Nickel chloride	
298.15	4.67	0.154
303.15	5.53	0.109
308.15	5.80	0.104
313.15	6.01	0.101
318.15	6.11	0.099
	Copper chloride	
298.15	5.62	0.124
303.15	5.73	0.122
308.15	5.78	0.121
313.15	6.44	0.106
318.15	6.82	0.101
	Cadmium chloride	
298.15	7.69	0.118
303.15	7.89	0.114
308.15	8.20	0.108
313.15	8.43	0.103
318.15	8.52	0.102
	Magnesium chloride	
298.15	6.62	0.109
303.15	6.67	0.107
308.15	6.72	0.106
313.15	6.98	0.104
318.15	7.39	0.097

Also, from Table – 3.XVI, it is clear that for each salt the value of A parameter increases with rise in temperature. This shows that ion – ion interactions are further strengthened with the increase in temperature. This may be attributed to the decrease in solvation of ions with the increase of temperature. On the other hand values of the B – parameter are positive but smaller in magnitude than the values of A parameter for all the solutions of divalent transition metal chlorides and magnesium chloride in 5% (w/w) ethanol + water composition at different temperatures thereby showing the presence of ion – solvent interactions, which dominate over the ion – ion interactions. Further, the values of B – coefficient decrease with the increase in temperature for each salt solution in 5% (w/w) ethanol + water composition thereby showing that the ion – solvent interactions are further weakened with the rise in temperature which may be attributed to the decrease in the solvation of ions. Also, the values of $\frac{dB}{dT}$ are negative for the solutions of divalent transition metal chlorides and magnesium chloride in 5% (w/w) ethanol + water composition indicating that all the selected divalent transition metal chlorides and magnesium chloride act as structure makers. This conclusion from $\frac{dB}{dT}$ is in good agreement with that drawn from the study of temperature effect on partial molar volumes as explained in chapter – II.

Viscosity B- coefficient data at different temperatures have also been interpreted in terms of transition state theory as already explained in section B. The values of $\Delta\mu_1^0$ and $\Delta\mu_2^0$ for viscous flow of the various salt solutions in 5% (w/w) ethanol + water have been determined at different temperatures with the help of relations (3.3) and (3.4) respectively and are given in Table – 3.XVII and corresponding values of $\overline{V_1^0}$ and $\overline{V_2^0}$ required for the calculation of $\Delta\mu_1^0$ and $\Delta\mu_2^0$ are also recorded in Table – 3.XVII.

According to Feakins model [15], $\Delta\mu_2^0 > \Delta\mu_1^0$ for the solutes having positive B – values. The greater the value of $\Delta\mu_2^0$, the larger is the structure making capacity of the solute. On the basis of this point of view, it is concluded from the present study all the divalent cations are structure makers.

According to the Feakins theory, $\Delta\mu_2^0$ decreases with the increase of temperature for the solutes having negative values of $\frac{dB}{dT}$. This is nicely shown by all the divalent transition metal ions i.e. Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Mg^{2+} which act as structure makers (Cl^- ion being common ion).

TABLE - 3.XVII

VALUES OF $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0*}$AND $\Delta\mu_2^{0*}$ FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL + WATER MIXTURE AT DIFFERENT TEMPERATURES.

Temperature (K)	$\overline{V_1^0}$ (cm^3 mol^{-1})	$\overline{V_2^0}$ (cm^3 mol^{-1})	$\Delta\mu_1^{0*}$ (kJ mol^{-1})	$\Delta\mu_2^{0*}$ (kJ mol^{-1})
Manganese chloride				
298.15	18.82	57.68	60.91	70.93
303.15	18.84	51.51	61.45	70.71
308.15	18.89	46.32	62.18	70.59
313.15	18.99	42.30	62.84	70.63
318.15	19.07	40.70	63.56	70.72
Cobalt chloride				
298.15	18.82	142.91	60.91	86.57
303.15	18.84	138.55	61.45	85.88
308.15	18.89	135.89	62.18	85.8
313.15	18.99	133.87	62.84	86.22
318.15	19.07	131.59	63.56	85.78
Nickel chloride				
298.15	18.82	111.02	60.91	93.39
303.15	18.84	106.74	61.45	87.88
308.15	18.89	104.73	62.18	87.95
313.15	18.99	102.71	62.84	88.24
318.15	19.07	100.14	63.56	88.63
Copper chloride				
298.15	18.82	73.21	60.91	84.43
303.15	18.84	68.45	61.45	84.49
308.15	18.89	66.66	62.18	85.11
313.15	18.99	62.19	62.84	83.34
318.15	19.07	59.75	63.56	83.23
Cadmium chloride				
298.15	18.82	57.30	60.91	81.64
303.15	18.84	53.63	61.45	81.40
308.15	18.89	51.51	62.18	81.26
313.15	18.99	47.85	62.84	80.95
318.15	19.07	44.33	63.56	81.24
Magnesium chloride				
298.15	18.82	150.53	60.91	92.64
303.15	18.84	146.32	61.45	92.90
308.15	18.89	142.03	62.18	93.36
313.15	18.99	140.64	62.84	93.80
318.15	19.07	135.53	63.56	93.28

The values of quantity$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, the change in activation energy per mole of solute, on replacing one mole of solvent by one mole of solute at infinite dilution, is given in Table 3.XVIII which are found positive and large for all the divalent transition metal chlorides and magnesium chloride studied in 5% (w/w) ethanol + water mixture at various temperatures. These values indicate that the formation of transition state is accompanied by breaking of intermolecular bonds. In other words, it may be said that the formation of transition state is less favoured in the presence of these divalent transition metal chlorides and magnesium chloride in the entire temperature range studied here.

The values of $\Delta\mu_2^{0*}$ at different temperatures can also be used to calculate the activation entropy ΔS_2^{0*} for different salts with the help of relation (3.7). The values of ΔS_2^{0*} have been determined from the slopes of the linear plots of $\Delta\mu_2^{0*}$ vs temperature T. Sample plots for manganese chloride, nickel chloride and copper chloride in 5% (w/w) ethanol + water mixture are shown in Fig. 31. The values of $T\Delta S_2^{0*}$ at different temperatures for the divalent transition metal chlorides and magnesium chloride are also recorded in Table 3.XVIII.

The activation enthalpy ΔH_2^{0*} has been calculated with the help of relation (3.8) and the corresponding values of ΔH_2^{0*} are also recorded in Table 3.XVIII. From Table 3.XVIII, it is clear that the activation enthalpy and activation entropy are positive for all the transition metal chlorides and magnesium chloride studied in 5% (w/w) composition of ethanol + water at different temperatures thereby indicating that the transition state is associated with the structure breaking and decreases in order. If we compare the results of the solutions of divalent transition metal chlorides and magnesium chloride in the binary aqueous solutions of methanol and ethanol, it can be very easily concluded that both systems behave identically to each other except the structure making abilities of the different cations.

TABLE - 3XVIII

VALUES OF$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, $T\Delta S_2^*$ AND ΔH_2^{0*} FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL + WATER MIXTURE AT DIFFERENT TEMPERATURES.

Temperature (K)	$(\Delta\mu_2^{0*}-\Delta\mu_1^{0*})$ (kJ mol^{-1})	$T\Delta S_2^*$ (kJ mol^{-1})	ΔH_2^{0*} (kJ mol^{-1})
Manganese chloride			
298.15	10.01	42.78	113.71
303.15	9.25	43.50	114.21
308.15	8.41	44.22	114.81
313.15	7.79	44.93	115.57
318.15	7.16	45.65	116.38
Cobalt chloride			
298.15	25.65	47.22	133.79
303.15	24.43	48.01	133.90
308.15	23.62	48.81	134.61
313.15	23.37	49.60	135.82
318.15	22.21	50.39	136.18
Nickel chloride			
298.15	32.48	94.45	187.85
303.15	26.42	96.03	183.91
308.15	25.76	97.62	185.57
313.15	25.40	99.20	187.44
318.15	25.06	100.79	189.42
Copper chloride			
298.15	23.52	61.12	145.56
303.15	23.03	62.14	146.64
308.15	22.92	63.17	148.28
313.15	20.50	64.19	147.54
318.15	19.66	65.22	148.45
Cadmium chloride			
298.15	20.72	47.31	128.96
303.15	19.94	48.11	129.51
308.15	19.08	48.90	130.17
313.15	18.11	49.69	130.64
318.15	17.67	50.49	131.73
Magnesium chloride			
298.15	31.73	26.95	119.6
303.15	31.44	27.40	120.31
308.15	31.17	27.85	121.22
313.15	30.95	28.30	122.10
318.15	29.71	28.76	122.04

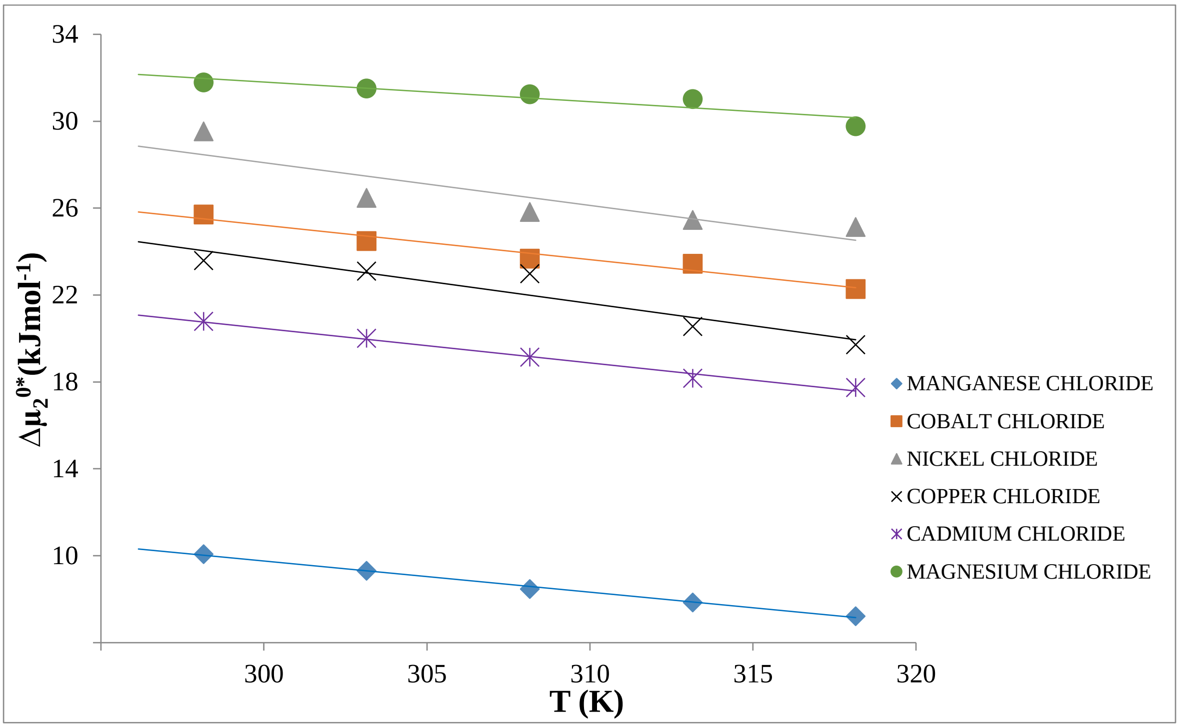

Fig. 31: VARIATION OF $\Delta\mu_2^{0*}$ WITH TEMPERATURE FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) ETHANOL + WATER MIXTURE.

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CHAPTER – IV

STUDIES ON HYDRODYNAMIC PERMEABILITIES OF SOME TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN BINARY AQUEOSUS MIXTURES OF ALCOHOLS ACROSS AN INORGANIC MEMBRANE

4.1 Introduction

When two forces i.e. potential gradient and pressure gradient couple, they give rise to current and volume flux. Some interesting electro-kinetic effects like streaming potential, electrophoresis, sedimentation potential (Dorn effect) and electro-osmosis are observed at the interfacial boundary, when two different phases are brought in contact with each other. These effects are associated with the existence of electrical double layer at the interfacial boundary. The various electro-kinetic effects have been briefly discussed as follows:

(i) Streaming potential: If a system of liquid is forced through a capillary tube or a porous diaphragm, potential difference is set up between the two sides called streaming potential [1].Potential difference so developed was found to be directly proportional to the applied pressure for any given solution. Kruyt [2] designed an apparatus for studying the streaming potential using glass capillary which was later on modified by Freundlich and Rona [3]. Kruyt and Willingen [4] have shown that E/ P for any capillary or diaphragm is constant, where E is the streaming potential developed and P is the pressure difference across the capillary or diaphragm.

(ii) Electrophoresis: Migration of suspended solids or liquids particles [5, 6] under the influence of an applied e.m.f. is called electrophoresis and quantitative interpretation of the same has been provided by Smoluchwski [7] , Debye and Huckel [8] .

(iii) Sedimentation potential (Dorn effect): Dorn[9] observed that when charged particles are allowed to fall through a standing liquid, an electrical potential gradient is set up and it opposes the motion of particles. Strock [10] was the first to show experimentally a relation between electrical potential and Zeta potential. Quist and Washburn [11] have obtained results with aqueous solutions. They measured electrical potential brought about by the fall of pyrex glass powder through conductivity water using silver – silver electrodes. They found that electrical potential between the electrodes is directly proportional to the rate of flow of powder and distance between the electrodes.

(iv) Electro – Osmosis: Flow of liquids per unit electric current under a zero potential difference is called electro-osmosis. Reuss [12] observed the phenomenon of movement of liquid with respect to a solid diaphragm on the application of e.m.f. Wiedmann [13] later on observed that the pressure gradient across the two sides of a porous diaphragm is proportional to the applied e.m.f. and is independent of the dimensions of the diaphragm.

Hepburn[14] found that the direction and velocity of the liquid stream depends upon the nature of plug and the liquid. The theoretical interpretation of electro- osmosis has been given by Helmholtz [15] and Lamb [16].

Importance of inorganic membranes

Due to the stable nature and applications of inorganic membranes, an aluminium oxide membrane has been used in the present study for the determination of hydrodynamic permeabilities of some divalent transition metal chloride namely, manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in binary aqueous solutions of methanol and ethanol.

The main objectives of the present study are:

(i) To calculate the filtration coefficient Lp as a function of hydrodynamic pressure and the concentration of the solute.

(ii) To evaluate the rejection coefficient σ as a function of solute concentration.

4.2 Experimental

The experimental part of this study has been discussed under following sections:

(i) Materials

(ii) Preparation of the membrane

(iii) The apparatus

(iv) The experimental detail

(v) Sources of error

(i) Materials: Conductivity water of specific conductance of order 10^{-6} ohm^{-1}cm^{-1}has been used. Both the solvents namely methanol and ethanol were purified and used as explained in chapter II. Manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride and aluminium oxide of AnalaR grade were used after drying over calcium oxide for more than 24 hours.

(ii) Preparation of the membrane: Inorganic membrane of aluminium oxide is prepared in the laboratory .The aluminium oxide was bloated in conductivity water and casted in the form of a plug. 10 gm of swollen material along with small amount of an adhesive namely araldite was placed in a pyrex glass tube having a constriction in the middle and compressed mechanically at the site of constriction with the help of a mechanical device shown in Fig. 32. It was left as such for about 24 hours for the complete setting of the plug. The thickness and diameter of the plug thus prepared were 1.745 cm and 1.850 cm, respectively. The maximum variation in the permeability of aluminium oxide membrane prepared after one week was only of the order of 5-10%.

In order to know the directional nature of the membrane for the permeation of water, the flow of water was noted in both the directions at 303.15K and the values were found to be the same in both the directions which ensures the isotropic nature of the membrane.

(iii) Apparatus: The apparatus and its experimental set up is shown in Fig. 33. It consists of a pyrex glass tube of 29 cm in length having a slight constriction in the middle with an internal diameter 1.85 cm where the plug of aluminium oxide is set up. This tube has two standard female joints B-24 at the ends. To the standard B-24 male joints are fixed the coiled platinum electrodes F and G. The ends of the electrodes are fused in glass tubes of diameter 5 mm, so that the electrode ends are insulated from the permeant. The length of these glass tubes are adjusted in such a way that when standard joints are kept in position, the electrodes touch the cross-sectional surface of the membrane. The main tube has two side tubes H and K, bearing B-14 female standard joints D and E. Through the joint E a capillary tube, J, of length 18 cm and diameter 0.15 cm bent at 90^0 is connected to the side tube K. A graduated tube I of length about 50 cm and 1.0 cm in diameter is connected to the side tube H through another standard joint D.

(iv)The Experimental Procedure: For equilibration of the membrane the experimental cell was filled with water and left overnight. It was then thoroughly washed with fresh distilled water under pressure gradient to ensure the proper cleanliness. The apparatus was filled by adding conductivity water on one side of the membrane and then sucking it to the other side under a pressure gradient by means of a vacuum pump. This ensured the complete filling of the capillaries of the membrane. The tubes J and I were then introduced and the

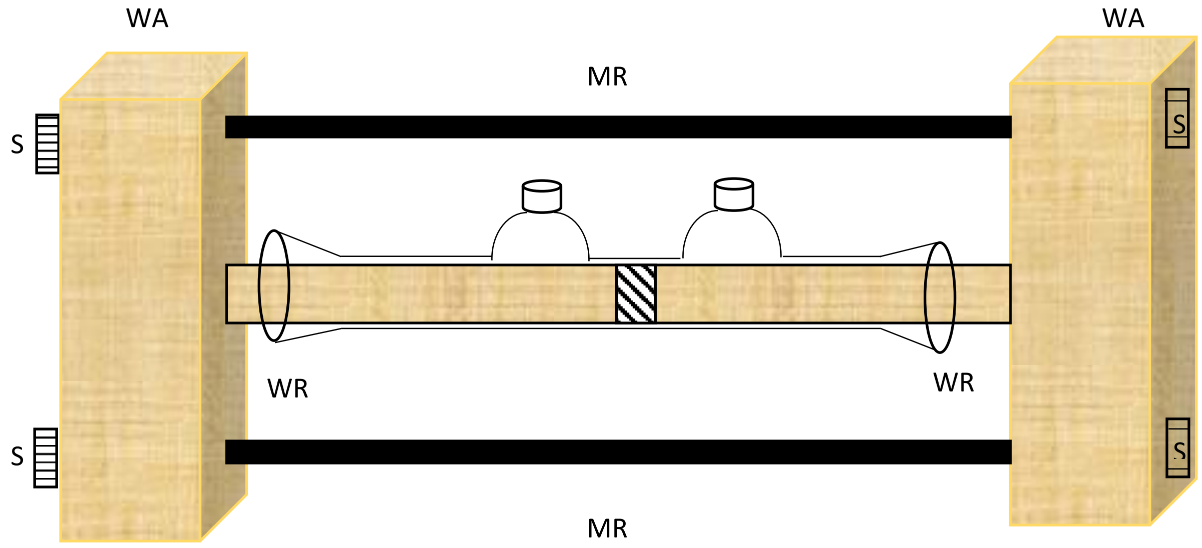

Fig 32: MECHANICAL DEVICE FOR THE PREPARATION OF MEMBRANE

WA=WOODEN ASSEMBLY

WR=WOODEN ROD

S=SCREWS

MR=METAL ROD

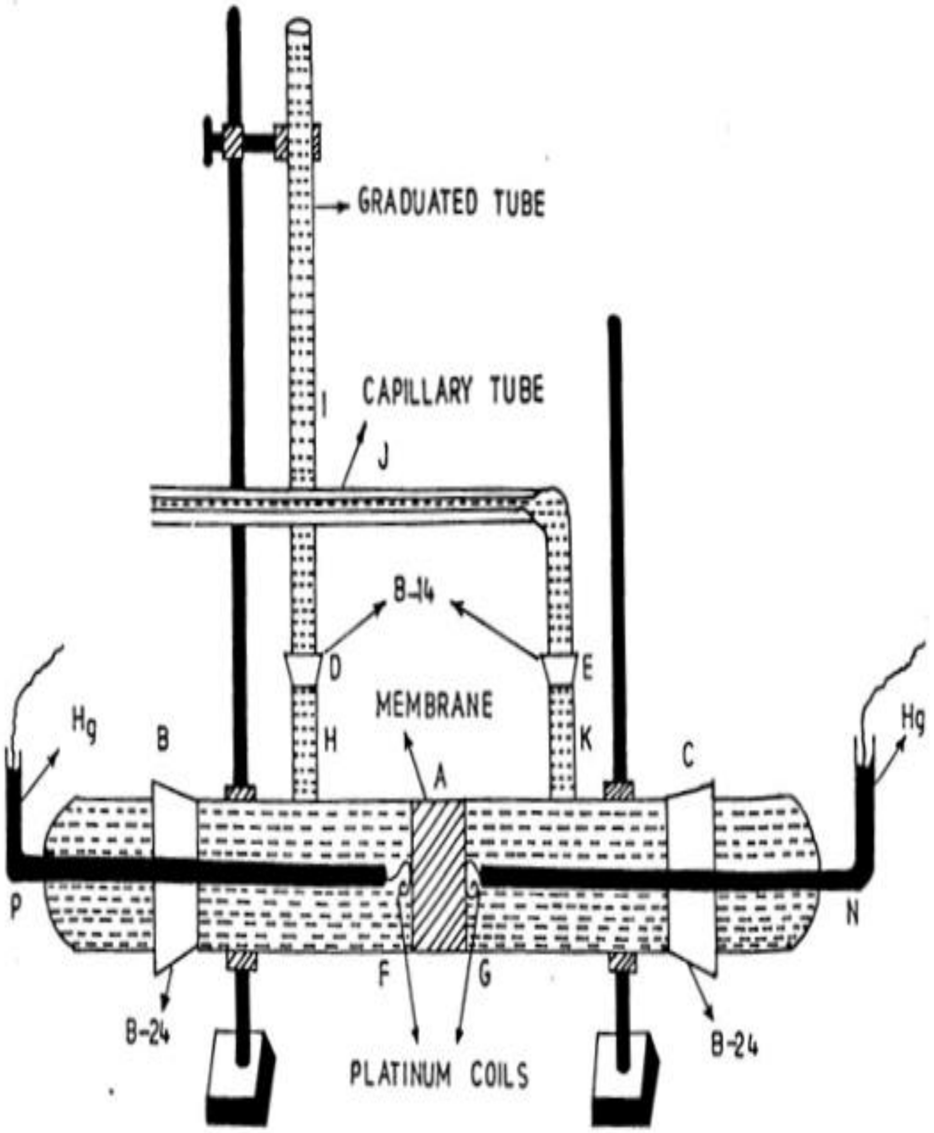

Fig 33.SCHEMATIC SET UP OF THE APPARATUS

apparatus suitably mounted inside the thermostat, where it was allowed to attain a constant temperature. The temperature was adjusted with the help of an electronic relay.

In order to measure the hydrodynamic permeability, desired pressure difference was introduced across one side of the cell with the help of a pressure head. The system was kept in the thermostat for about two hours to allow the experimental solution to attain the temperature of the thermostat. The rate of flow of liquid at desired pressure difference was measured by noting the time taken by the solution to move a certain distance through horizontal capillary. The flow time was recorded with the help of a stop watch of least count 0.01 second. In this way the flow was recorded at different pressures. For measurement of coupling coefficient (σ) one chamber of the apparatus was filled with a particular solution of the solute and other chamber with pure solvent. A desired pressure head of solvent was then applied on the side of the solvent chamber and the capillary was attached on the side of solution to note the net (resultant) volume flow, J'_V. The values of L'_P and $(J'_V)_{\Delta P'=0}$ were calculated from the slope and intercept of the plots of J'_V vs $\Delta P'$ respectively. Conductance of the system (membrane + solution) and specific conductance of the solution was also noted with the help of a digital conductivity bridge.

(v) Sources of Error: The various sources of error and factors responsible for effecting the reproducibility of results are discussed below:

(a) Incomplete wetting of the membrane: The rate of flow of liquid depends upon the actual number of capillaries transmitting the liquid. So, if all the capillaries are not wetted, poor reproducibility can result from one experiment to other. This was ensured by introducing the solution after evacuation of apparatus and by preparation of solution from distilled water.

(b) Temperature control: Variation in temperature causes the change in permeability of the permeant through the membrane. The temperature within the thermostat was maintained constant with the help of an electronic relay with an accuracy of ±0.01^{0}C.

4.3 Results and Discussion

In the present study, the hydrodynamic permeabilties of some divalent transition metal chlorides namely; manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water and in binary aqueous mixtures of methanol and ethanol through an inorganic membrane of aluminum oxide have been determined.

For the sake of ease the results of experiments carried out in the present study, have been explained under the sections A and B.

Section – A

Hydrodynamic Permeabilities of Divalent Transition Metal Chlorides and Magnesium Chloride in Water across an Inorganic Membrane of Aluminum Oxide

The permeability of any membrane depends upon the molecular size of the permeating fluid, the state of aggregation of the liquid, the number of hydrogen bonds etc. So it is very important to understand the nature of membrane as none of the properties explained above determines the nature of any membrane. So, before using any membrane into its use, it is important to know its effective cross-sectional area, equivalent pore radius and electrical nature of the membrane. These characteristics have been determined as given below:

1. Membrane characterization: The thickness of the inorganic membrane of aluminum oxide was measured with the help of a cathetometer, which measures upto 0.001 cm and found to be 1.750 cm. The diameter of membrane was noted with the help of travelling microscope and found to be 1.855 cm.

The rate of flow through any membrane under the influence of hydrostatic pressure depends on the effective cross – sectional area ‘A’ and effective length ‘ l’ of the pores of the membrane. Determination of either of these quantities is difficult due to complex geometry of the opening within a membrane, however it is possible to determine the ratio ‘A/l’ called membrane constant, in terms of which permeant nature of any membrane can be expressed quantitatively.

For a membrane having ‘n’ number of pores of equivalent radius ‘r’, the effective cross-sectional area ‘A’, through which permeation occurs, is $n\pi r^2$. The electrical conductance ‘K’ of the membrane equilibrated with a permeant having specific conductance ‘k’ is given by the following relation [17] :

$$K = n\pi r^2 \times \frac{k}{l} = \frac{A}{l} \times k \tag{4.1}$$

So that the membrane constant can be written as follows:

$$\frac{A}{l} = K/k \tag{4.2}$$

This constant is a characteristic parameter of the membrane and is independent of the nature of permeation fluid, as long as the interaction between the permeant and membrane matrix is not strong enough to alter its equivalent pore radius [18]. The membrane constant thus estimated from the relation (4.2) for different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride are given in Table – 4.I.

It is clear from the Table – 4.I. that the value of membrane constant (A/l) is fairly constant for all the binary aqueous solutions of divalent transition metal chlorides and magnesium chloride and it is in accordance with the findings of Singh et. al.[17] which clearly shows that the membrane constant ‘A/l’ is a characteristic property of the membrane and is independent of the nature of permeating fluid.

The average pore radius of any membrane can be calculated from the following expression:

$$\left(\frac{J_v}{\Delta P}\right)_{\Delta\pi=0} = \frac{n\pi r^4}{8\eta l} = \frac{n\pi r^2 \times r^2}{8\eta l}$$

$$= \frac{n\pi r^2}{l} \times \frac{r^2}{8\eta} = \frac{A}{l} \times \frac{r^2}{8\eta}$$

or $$r = \left(\frac{8\eta (J_v/\Delta P)_{\Delta\pi=0}}{A/l}\right)^{1/2} \qquad (4.3)$$

where η represents the coefficient of viscosity of the permeating fluid J_v is the volume flow through the membrane, ΔP is the pressure difference across the interface in centimetres of the permeating fluid and Δπ is the osmotic pressure across the membrane.

The values of J_v, volume flow for different concentrations of binary aqueous solutions of some selected divalent transition metal chlorides and magnesium chloride at 303.15K are given in Table – 4.II. The densities and viscosities required for the calculation of “equivalent pore radius “r” of the membrane, for the different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride are also given in Table – 4.III.

TABLE -4.I

MEMBRANE CHARACTERISTICS ASCERTAINED FROM CONDUCTANCE DATA FOR SOLUTIONS OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K

Concentration m (mol kg^{-1})	K × 10^5 (Ohm^{-1})	k × 10^5 (Ohm^{-1} cm^{-1})	A/l (cm)
Manganese chloride			
0.005	0.82	0.93562	0.876
0.007	0.88	1.00408	0.879
0.010	0.95	1.08395	0.88
0.030	1.31	1.49471	0.876
0.050	1.81	2.06521	0.877
0.070	2.37	2.70417	0.878
0.100	2.90	3.30890	0.876
Cobalt chloride			
0.005	0.88	1.00408	0.876
0.007	0.96	1.09536	0.88
0.010	1.05	1.19805	0.882
0.030	1.45	1.65445	0.878
0.050	1.89	2.15649	0.879
0.070	2.47	2.81827	0.875
0.100	2.98	3.40018	0.879
Nickel chloride			
0.005	0.28	0.31948	0.875
0.007	0.35	0.39935	0.877
0.010	0.49	0.55909	0.876
0.030	0.68	0.77588	0.883
0.050	1.88	2.14508	0.876
0.070	2.08	2.37328	0.878
0.100	3.14	3.58274	0.877
Copper chloride			
0.005	0.9	1.0269	0.882

0.007	0.97	1.10677	0.876
0.010	1.14	1.30074	0.877
0.030	1.70	1.93970	0.876
0.050	2.25	2.56725	0.879
0.070	2.82	3.21762	0.878
0.100	3.14	3.58274	0.876
Cadmium chloride			
0.005	0.83	0.94703	0.882
0.007	0.88	1.00408	0.880
0.010	0.89	1.01549	0.890
0.030	1.31	1.49471	0.879
0.050	1.62	1.84842	0.880
0.070	1.89	2.15649	0.879
0.100	2.33	2.65853	0.879
Magnesium chloride			
0.005	0.60	0.6846	0.875
0.007	0.66	0.75306	0.876
0.010	0.69	0.78729	0.877
0.030	1.20	1.36920	0.882
0.050	1.66	1.89406	0.878
0.070	1.98	2.25918	0.880
0.100	2.42	2.76122	0.877

TABLE – 4.II

HYDRODYNAMIC VOLUME FLOW (J_V) FOR DIFFERENT CONCENTRATIONS OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K (PER UNIT AREA OF MEMBRANE).

$\Delta P \times 10^{-4}$ (dyne cm^{-2})	$J_V \times 10^5$ (cm sec^{-1})						
Concentration of electrolytic solution (m) mol.kg^{-1}	**0.005**	**0.007**	**0.010**	**0.030**	**0.050**	**0.070**	**0.100**
Manganese chloride							
0.49	3.86	3.77	3.68	3.32	3.29	2.94	2.71
0.98	6.01	5.53	5.46	5.45	5.36	5.30	4.33
1.47	9.30	9.21	8.39	7.59	7.46	7.36	6.87
1.96	11.81	11.30	10.15	9.91	9.84	9.21	9.01
2.45	14.39	12.97	12.36	11.39	10.96	10.64	10.12
Cobalt chloride							
0.49	2.45	2.39	2.31	2.21	1.64	1.63	1.62
0.98	4.25	4.14	3.91	3.70	2.93	2.35	2.53
1.47	6.07	5.93	5.89	5.48	4.21	3.19	3.24
1.96	8.39	8.13	7.90	6.84	5.89	3.92	4.27
2.45	9.16	9.33	9.16	8.36	7.20	4.97	4.82
Nickel chloride							
0.49	4.53	4.01	3.12	2.43	1.89	1.89	1.63
0.98	6.95	6.41	6.29	5.28	4.84	3.28	3.24
1.47	8.82	8.56	7.88	6.56	6.43	5.47	5.35
1.96	11.00	10.37	9.61	8.64	8.53	7.59	7.71
2.45	14.32	14.04	12.10	11.76	10.68	9.84	9.52
Copper chloride							
0.49	1.62	1.57	1.56	1.42	1.40	1.38	1.34
0.98	2.77	2.70	2.61	2.58	2.45	2.38	2.23
1.47	4.20	4.00	3.84	3.76	3.60	3.55	3.36

1.96	5.38	5.10	5.08	4.89	4.64	4.56	4.57
2.45	6.59	6.37	6.21	6.18	5.08	4.97	4.88

Cadmium chloride

0.49	1.85	1.82	1.76	1.75	1.71	1.69	1.47
0.98	3.21	3.15	3.07	3.01	2.94	2.73	2.56
1.47	4.83	4.73	4.64	4.53	4.41	3.94	3.44
1.96	6.46	5.80	5.64	5.56	5.10	4.91	4.66
2.45	7.59	7.29	7.09	6.76	6.28	5.94	5.35

Magnesium chloride

0.49	2.45	2.36	2.26	2.20	2.06	1.93	1.77
0.98	4.24	4.00	3.80	3.51	3.43	2.79	2.44
1.47	5.74	5.63	5.38	4.95	4.90	4.29	3.60
1.96	7.51	6.82	6.65	6.36	6.18	5.17	4.42
2.45	9.24	8.41	8.27	8.13	7.42	6.74	5.46

TABLE - 4.III

DENSITIES, MOLAR VOLUMES AND VISCOSITIES FOR DIFFERENT CONCENTRATIONS OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K

Concentration (m) (mol kg^{-1})	Density (d) (g cm^{-3})	Viscosity (η) (cP)	Molar volume (V) (cm^3 mol^{-1})
	Manganese chloride		
0.005	0.99625	0.82703	198.64
0.007	0.99648	0.83211	198.60
0.010	0.99682	0.83868	198.53
0.030	0.99893	0.86987	198.11
0.050	1.00090	0.89334	197.72
0.070	1.00256	0.9131	197.39
0.100	1.00478	0.93837	196.96
	Cobalt chloride		
0.005	0.99622	0.81862	238.83
0.007	0.99644	0.82299	238.78
0.010	0.99677	0.82816	238.70
0.030	0.99890	0.85164	238.19
0.050	1.00090	0.86738	237.72
0.070	1.00286	0.88103	237.25
0.100	1.00565	0.9004	236.59
	Nickel chloride		
0.005	0.99640	0.81737	238.57
0.007	0.99667	0.82109	238.50
0.010	0.99708	0.82562	238.41
0.030	0.99980	0.8461	237.76
0.050	1.00229	0.86085	237.17
0.070	1.00471	0.87279	236.60
0.100	1.00830	0.89359	235.75

Copper chloride			
0.005	0.99629	0.82706	171.11
0.007	0.99652	0.83214	171.08
0.010	0.99686	0.83872	171.02
0.030	0.99924	0.87014	170.61
0.050	1.00146	0.89384	170.23
0.070	1.00373	0.91417	169.85
0.100	1.00682	0.94028	169.33
Cadmium chloride			
0.005	0.99633	0.82220	202.06
0.007	0.99659	0.82731	202.01
0.010	0.99697	0.83322	201.93
0.030	0.99954	0.85989	201.41
0.050	1.00192	0.8781	200.93
0.070	1.00418	0.89416	200.48
0.100	1.00743	0.91542	199.84
Magnesium chloride			
0.005	0.99595	0.82259	204.13
0.007	0.99607	0.82688	204.1
0.010	0.99624	0.83261	204.07
0.030	0.99727	0.85724	203.86
0.050	0.99818	0.87552	203.67
0.070	0.99897	0.89092	203.51
0.100	1.00007	0.91083	203.29

The equivalent pore radii, calculated with the help of relation (4.3) for different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride are noted in Table – 4.IV.

It is clear from Table – 4.IV that the equivalent pore radius of the membrane decreases with the increase in the concentration of individual divalent transition metal chloride and magnesium chloride in water at 303.15K and may be attributed to increase in the electrical double layer at the walls of the pores of aluminium oxide membrane. These results suggest that the divalent transition metal chlorides and magnesium chloride form cross links at the walls of the pores of inorganic membrane of aluminium oxide, thereby resulting decrease in the equivalent pore radius.

It is also clear from Table – 4.IV that the equivalent pore radii, for different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride are different so it can be concluded from the experimental results that the equivalent pore radius is not a characteristic property of the inorganic membrane of aluminum oxide only, but is seriously influenced by the nature as well as concentration of the permeating fluid.

TABLE – 4.IV

EQUIVALENT PORE RADIUS (r) AND MECHANICAL FILTRATION COEFFICIENT (L_p) FOR DIFFERENT CONCENTRATIONS OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDEIN WATER AT 303.15K.

Concentration m (mol kg^{-1})	Equivalent pore radius, r x 10^4 (cm)	Filtration coefficient Lp × 10^9 (cm^3 dyne^{-1} sec^{-1})
Manganese chloride		
0.005	2.44	5.48
0.007	2.41	4.93
0.010	2.39	4.50
0.030	2.32	4.20
0.050	2.34	4.04
0.070	2.23	3.94
0.100	2.18	3.83
Cobalt chloride		
0.005	1.93	3.70
0.007	1.91	3.64
0.010	1.88	3.60
0.030	1.87	3.15
0.050	1.63	2.87
0.070	1.64	1.68
0.100	1.64	1.66
Nickel chloride		
0.005	2.63	4.82
0.007	2.47	4.77
0.010	2.19	4.50
0.030	1.95	4.33
0.050	1.74	4.15
0.070	1.75	4.15
0.100	1.65	4.13

Copper chloride		
0.005	1.57	2.56
0.007	1.56	2.44
0.010	1.56	2.39
0.030	1.52	2.41
0.050	1.52	1.94
0.070	1.53	1.91
0.100	1.53	1.88
Cadmium chloride		
0.005	1.68	3.00
0.007	1.67	2.77
0.010	1.64	2.70
0.030	1.67	2.56
0.050	1.67	2.30
0.070	1.68	2.17
0.100	1.58	2.00
Magnesium chloride		
0.005	1.94	3.44
0.007	1.91	3.04
0.010	1.87	3.03
0.030	1.87	2.99
0.050	1.83	2.74
0.070	1.79	2.44
0.100	1.73	1.91

II. Filtration Coefficient (L_P): The thermodynamic relation for the volume flow (J_v), as a function of applied pressure difference (ΔP) and the osmostic pressure difference ($\Delta\pi$) across any membrane is given by the following expression [14]:

$$J_V = L_P\Delta P - \sigma L_P\Delta\pi \qquad (4.4)$$

where symbols have their usual significance.

It is convenient to determine the filtration coefficient, L_P at $\Delta\pi = 0$ i.e. at equal concentrations of the solute on both sides of a membrane so that the above expression (4.4) can be written as follows:

$$L_P = \left[\frac{J_V}{\Delta P}\right]_{\Delta\pi=0} \qquad (4.5)$$

The values of volume flow, J_V, for the different binary aqueous solutions of selected divalent transition metal chlorides and magnesium chloride at 303.15K have been recorded in Table – 4.II. The expression (4.5) shows that the volume transported per unit area of the membrane per unit time, should vary linearly with hydrodynamic pressure difference, ΔP, across the membrane. Present study shows that the volume transported per unit time is linearly proportional to the pressure head for all the binary aqueous solutions of selected divalent transition metal chlorides and magnesium chloride in water at 303.15K and a sample plot for the different concentrations of manganese chloride in water at 303.15K is shown in Fig.34.

The permeability coefficient, L_p, has been determined from the slopes of linear plots of J_v vs ΔP for different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride through inorganic membrane of aluminium oxide at 303.15K and these values are noted in Table – 4.IV.

The variation of L_p with concentration for different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride is linear. Fig.35 shows the plots of all the selected divalent transition metal chlorides and magnesium chloride.

It is clear from Table – 4.IV and Fig. 35 that L_p decreases with the increase in the concentration of each divalent transition metal chloride and magnesium chloride in water at 303.15K through inorganic membrane of aluminium oxide. Since L_p is a constant which expresses the interactions between the membrane matrix and permeating fluid, therefore it

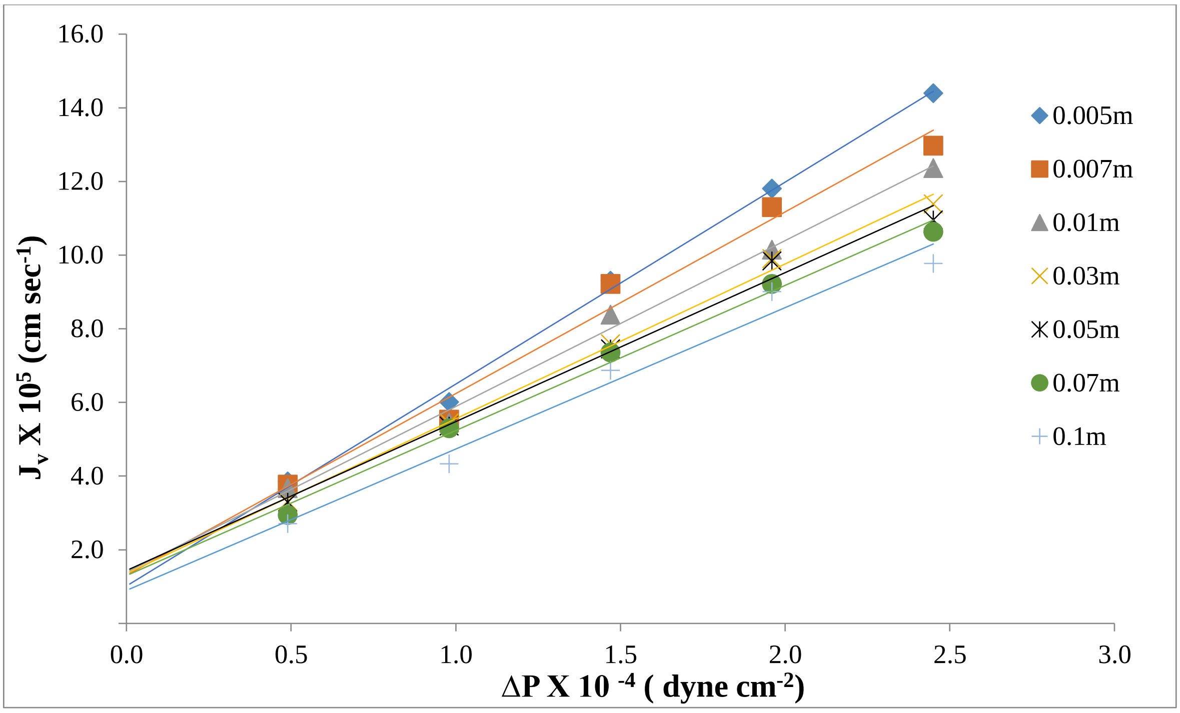

Fig. 34: PLOTS OF J_v VS ΔP FOR MANGANESE CHLORIDE IN WATER AT 301.15

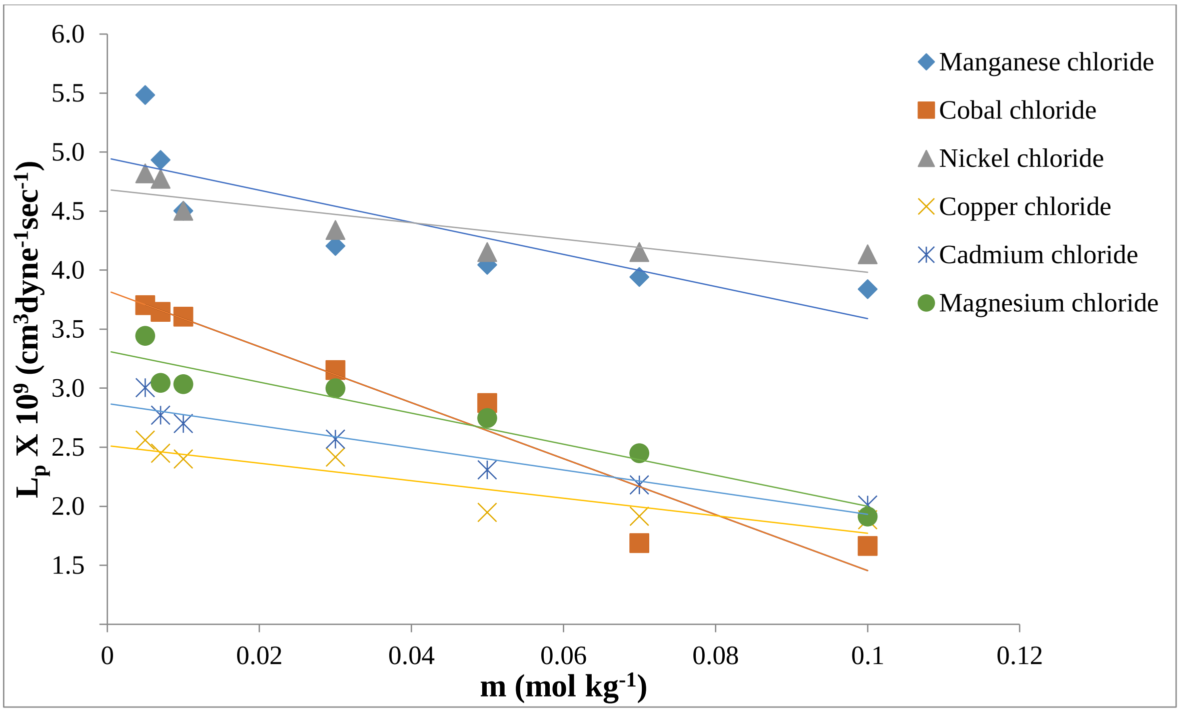

Fig. 35: PLOTS OF L_p VS c For MANGANESE CHLORIDE ,COBLAT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

may be inferred from these results that the friction between the interface of aluminium oxide and permeating fluids increases with the increase in concentration of each divalent transition metal chloride and magnesium chloride in water at 303.15K through inorganic membrane of aluminium oxide in water at 303.15K. It is also clear from Table - 4.IV that L_p is different for the different salts, studied here, so it may be concluded from these results that L_p is not the characteristic property of the inorganic interface of aluminum oxide only but it is seriously influenced by nature of the permeating fluid.

III. Rejection or coupling coefficient($\boldsymbol{\sigma}$): The thermodynamic relation for the resultant volume flow, J'_V, as a function of applied pressure difference, $\Delta P'$ and the osmotic pressure difference, $\Delta\pi$, through an inorganic membrane is given by the following relation[19]:

$$J'_V = L'_P\Delta P - \sigma L'_P\Delta\pi \qquad (4.6)$$

Or

$$J'_V = L'_P[\Delta P - \sigma\Delta\pi] \qquad (4.7)$$

here σ is known as rejection or coupling coefficient or membrane selectivity and the other symbols have their usual significance.

Since $\Delta\pi = RT\Delta C$, the above expression (4.7) may also be written as follows:

$$J'_V = L'_P[\Delta P' - \sigma RT\Delta C] \qquad (4.8)$$

where J'_V: net or resultant volume flow, R; gas constant, T; absolute temperature and ΔC; concentration difference across the inorganic membrane of aluminium oxide.

The values of the resultant volume flow, J'_V for various concentration differences across the inorganic membrane of aluminium oxide for different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride are given in Table – 4.V at 303.15K.According to relation 4.8, the plot of J'_V vs $\Delta P'$should be linear and same have been found to be true in case of all the selected divalent transition metal chlorides and magnesium chloride in water at 303.15K. Fig. 36 shows a sample plot for magnesium chloride in water at 303.15K.

The filtration coefficient L'_P and $(J'_V)_{\Delta P'=0}$ has been calculated by the least square fit to the slopes and intercepts of the straight line plots of J'_V vs $\Delta P'$, respectively and these values have

TABLE - 4.V

THE NET VOLUME FLOW, J_v' (FOR THE DETERMINATION OF REJECTION COEFFICIENT) FOR VARIOUS CONCENTRATION OF DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

$\Delta P' \times 10^{-4}$ (dyne cm^{-2})	**$J_v' \times 10^5$ (cm sec^{-1})**						
Concentration of electrolytic solution (m) mol.kg^{-1}	**0.005**	**0.007**	**0.01**	**0.03**	**0.05**	**0.07**	**0.1**
Manganese chloride							
0.49	3.36	3.07	3.01	2.87	2.7	2.61	2.52
0.98	7.52	7.08	6.77	6.53	5.4	6.08	5.9
1.47	11.71	10.05	10.64	10.33	10.1	9.66	9.3
1.96	16.03	15.11	14.57	14.09	13.8	13.26	12.86
2.45	18.31	19.06	18.49	17.79	16.38	16.77	16.4
Cobalt chloride							
0.49	1.95	1.93	1.89	1.79	1.65	1.61	1.51
0.98	5.9	5.59	5.52	5.32	5.07	4.99	4.74
1.47	8.82	8.55	7.78	7.92	7.49	7.36	6.97
1.96	11.7	11.3	10.98	10.49	9.69	9.69	9.17
2.45	14.6	14.1	13.6	13	12.4	11.9	11.3
Nickel chloride							
0.49	2.92	2.74	2.67	2.61	2.56	2.46	2.36
0.98	7.09	7.02	6.79	6.56	6.36	6.27	6.13
1.47	10.39	10.24	9.87	9.56	9.27	9.13	8.78
1.96	13.69	13.47	13	12.57	12.21	11.92	11.52
2.45	16.98	16.5	15.98	15.5	15.07	14.7	14.23
Copper chloride							
0.49	3.04	2.89	2.78	2.63	2.63	2.41	2.31
0.98	7.23	6.9	6.64	6.64	6.41	6.17	5.99
1.47	10.25	9.96	9.56	9.56	9.17	8.93	8.69
1.96	13.42	13.05	12.48	12.48	12	11.6	11.44

2.45	18.67	17.69	16.85	16.25	15.7	14.63	14
Cadmium chloride							
0.49	2.3	2.69	2.3	1.98	1.89	1.78	1.88
0.98	6.8	5.36	5.99	5.74	5.52	5.3	5.19
1.47	9.91	9.28	8.79	8.38	8.03	7.74	7.57
1.96	13	12.21	11.57	11.04	10.48	10.13	9.9
2.45	16.14	14.98	14.8	13.59	13.02	12.38	12.13
Magnesium chloride							
0.49	2.97	2.94	2.66	2.54	2.43	2.21	2.11
0.98	7.89	7.6	7.21	6.95	6.73	6.36	5.18
1.47	11.78	11.3	10.71	10.39	10.01	9.61	9.2
1.96	15.61	15.11	14.21	13.31	13.31	12.71	12.21
2.45	20.56	19.88	18.7	17.87	16.95	15.95	14.01

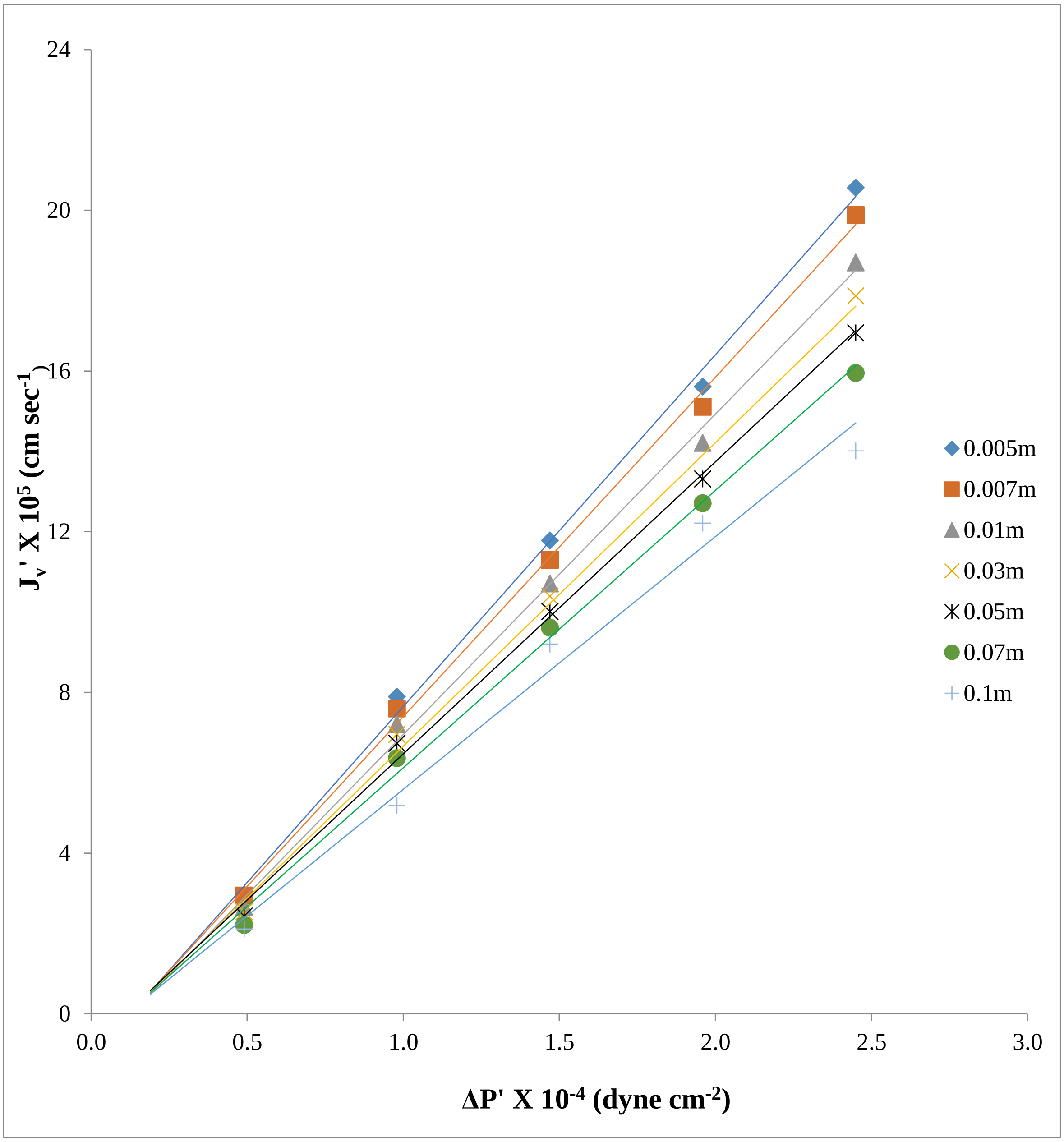

Fig. 36: PLOTS OF J_v' VS ΔP' FOR MAGNESIUM CHLORIDE IN WATER AT 303.15K

been recorded in Table – 4.VI. It is clear from Table – 4.VI that the values of L'_P and $(J'_V)_{\Delta P'=0}$ are different for various concentrations of an individual solute in water at 303.15K.

If the hydrostatic pressure across the inorganic membrane of aluminium oxide is kept constant i.e., $\Delta P' = 0$, then the relation 4.8 can be written as:

$$(J'_V)_{\Delta P'=0} = -\sigma L'_P RT\Delta C$$

Or $$\sigma = -\left[\frac{J'_V}{L'_P RT\Delta C}\right]_{\Delta P'=0} \tag{4.9}$$

here the negative sign indicates that the hydrostatic and osmotic pressures act in opposite directions to each other. The values of rejection coefficients, σ ,can be obtained with the help of relation (4.9). These values of σ calculated for the solutions of manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in water at 303.15K are also recorded in Table – 4.VI.

The rejection coefficient σ is a measure of membrane selectivity and according to Staverman [20] when σ = 1, whole of the solute is rejected by the membrane,while $\sigma < 1$ means a part of the solute passes through a membrane. σ can also be interpreted in terms of velocity of the solute as explained below:

When $\sigma = 1$, velocity of the solute is zero, which means that solute cannot cross the membrane. When $\sigma = 0$, solute and solvent flow with equal velocity across the membrane. According to the pore model [21] of transport through membrane, rejection coefficient is also known as coupling coefficient and measure the coupling between total volume flux and solute transmission. As the value of σ goes towards zero, the coupling between two processes increases and when it becomes equal to zero, the coupling is complete, which means that solute and solvent flow with equal velocities. This is possible only when solute is identical with the solvent.

It is clear from Table – 4.VI that the value of σ for different binary aqueous solutions of divalent transition metal chlorides and magnesium chloride decreases with increase in the concentration of each salt at 303.15K. It means that σ approaches zero as the concentration of each salt increases thereby indicating that the coupling between the above processes

TABLE – 4VI

THE RESULTANT VOLUME FLOW, $(J'_V)_{\Delta p'=0}$, MECHANICAL FILTRATION COEFFICIENT, L'_p, AND REJECTION COEFFICIENT (σ), FOR VARIOUS CONCENTRATIONS OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN WATER AT 303.15K.

Concentration, m (mol kg^{-1})	$(J_V')_{\Delta p'=0} \times 10^5$ (cm sec^{-1})	$L_p' \times 10^9$ (cm^3 dyne^{-1} sec^{-1})	$\sigma \times 10^6$
Manganese chloride			
0.005	-2.20	9.51	1.84
0.007	-1.92	8.57	1.27
0.010	-1.73	8.31	0.83
0.030	-1.69	8.04	0.28
0.050	-1.59	7.91	0.16
0.070	-1.47	7.53	0.11
0.100	-1.38	7.31	0.07
Cobalt chloride			
0.005	-0.74	6.34	0.93
0.007	-0.72	6.13	0.67
0.010	-0.71	5.89	0.48
0.030	-0.59	5.63	0.14
0.050	-0.58	5.33	0.09
0.070	-0.47	5.13	0.05
0.100	-0.46	4.9	0.04
Nickel chloride			
0.005	-0.20	7.09	0.22
0.007	-0.20	6.93	0.16
0.010	-0.19	6.70	0.11
0.030	-0.18	6.49	0.04
0.050	-0.17	6.3	0.02
0.070	-0.14	6.15	0.01
0.100	-0.14	5.95	0.01
Copper chloride			
0.005	-0.71	7.64	0.74
0.007	-0.63	7.30	0.49
0.010	-0.53	6.93	0.3
0.030	-0.41	6.75	0.08

0.050	-0.33	6.47	0.04
0.070	-0.21	6.09	0.02
0.100	-0.16	5.88	0.01
Cadmium chloride			
0.005	-0.53	6.91	0.61
0.007	-0.53	6.41	0.47
0.010	-0.49	6.24	0.31
0.030	-0.41	5.82	0.09
0.050	-0.38	5.56	0.05
0.070	-0.34	5.31	0.04
0.100	-0.23	5.14	0.02
Magnesium chloride			
0.005	-1.11	8.76	1.01
0.007	-1.05	8.45	0.70
0.010	-1.03	7.98	0.51
0.030	-0.89	7.56	0.16
0.050	-0.80	7.27	0.09
0.070	-0.78	6.90	0.06
0.100	-0.71	6.29	0.04

increases with the increase in the concentration of each salt and hence solute and solvent flow with almost same velocity only at higher concentration. Further, it is also clear from Table – 4.VI that value of σ is very small and further decreases with the increase in concentration difference of a particular solute in water at 303.15K. This indicates that there is no rejection of the solute by the inorganic membrane of aluminium oxide.

SECTION - B

Hydrodynamic Permeabilities of Solutions of Divalent Transition Metal Chlorides and Magnesium Chloride in Binary Aqueous Mixtures of Alcohols across an Inorganic Membrane of Aluminium Oxide.

In this section hydrodynamic permeabilities of divalent transition metal chlorides namely manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in binary aqueous mixtures of alcohols have been determined in order to access the combined effect of alcohols (methanol and ethanol).

It has been described in previous section of this chapter that the rate of permeation through any membrane matrix, under the influence of hydrostatic pressure depends upon the effective cross – sectional area 'A' and thickness 'l' of the membrane. The determination of these quantities is difficult due to the complex geometry of the openings, within the membrane. However, 'A/l', the so called membrane constant may be determined in terms of which the permeant behaviour of any membrane matrix can be expressed.

Also in the previous section we have seen that 'A/l' is a characteristic property of a membrane and is independent of the nature of permeating fluid as long as the interactions between the membrane matrix and permeating fluid are not strong enough to alter its equivalent pore radius. This statement has to be verified by determining the membrane constant 'A/l' for the ternary systems (Transition metal chloride +alcohol+water). The membrane constant 'A/l' has been determined from the conductometric measurements of the solutions of divalent transition metal chlorides, namely; manganese chloride, cobalt chloride, nickel chloride, copper chloride, cadmium chloride and magnesium chloride in binary aqueous mixtures of methanol and ethanol only at 303.15K. The values of membrane constant 'A/l' thus calculated are given in Table – 4.VII and it is clear that the values of membrane constant 'A/l' are same

TABLE -4.VII

MEMBRANE CHARACTERISTICS ASCERTAINED FROM CONDUCTANCE DATA FOR SOLUTIONS OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AND 5% (w/w) ETHANOL + WATER AT 303.15K

Concentration m , (mol kg^{-1})	**K × 10^3 (Ohm^{-1})**	**k × 10^3 (Ohm^{-1} cm^{-1})**	**A/l (cm)**
5% (w/w) Methanol + Water			
Manganese chloride			
0.005	0.41	0.468	0.872
0.007	0.46	0.525	0.885
0.010	0.57	0.65	0.877
0.030	0.89	1.015	0.873
0.050	1.37	1.563	0.878
0.070	1.78	2.031	0.876
0.100	2.17	2.476	0.875
Cobalt chloride			
0.005	0.44	0.502	0.876
0.007	0.53	0.605	0.877
0.010	0.61	0.696	0.876
0.030	0.95	1.084	0.88
0.050	1.53	1.746	0.879
0.070	1.84	2.099	0.88
0.100	2.42	2.761	0.877
Nickel chloride			
0.005	0.36	0.411	0.878
0.007	0.42	0.479	0.877
0.010	0.51	0.582	0.876
0.030	0.98	1.118	0.875
0.050	1.31	1.495	0.879
0.070	1.74	1.985	0.874
0.100	2.03	2.316	0.875
Copper chloride			
0.005	0.53	0.605	0.876
0.007	0.6	0.685	0.876
0.010	0.73	0.833	0.876
0.030	0.98	1.118	0.875
0.050	1.56	1.780	0.881
0.070	1.87	2.134	0.878
0.100	2.49	2.841	0.876

Cadmium chloride			
0.005	0.37	0.422	0.876
0.007	0.43	0.491	0.877
0.010	0.51	0.582	0.876
0.030	0.79	0.901	0.877
0.050	1.02	1.164	0.879
0.070	1.63	1.860	0.881
0.100	2.19	2.499	0.88
Magnesium chloride			
0.005	0.43	0.491	0.877
0.007	0.52	0.593	0.877
0.010	0.69	0.787	0.876
0.030	0.98	1.118	0.875
0.050	1.34	1.529	0.876
0.070	1.59	1.814	0.878
0.100	2.23	2.544	0.878
5% (w/w) Ethanol + Water			
Manganese chloride			
0.005	0.43	0.491	0.878
0.007	0.58	0.662	0.876
0.010	0.79	0.901	0.877
0.030	0.98	1.118	0.875
0.050	1.35	1.540	0.877
0.070	1.50	1.712	0.877
0.100	1.69	1.928	0.875
Cobalt chloride			
0.005	0.45	0.513	0.877
0.007	0.56	0.639	0.876
0.010	0.78	0.890	0.876
0.030	0.89	1.015	0.881
0.050	1.31	1.495	0.876
0.070	1.52	1.734	0.876
0.100	1.66	1.894	0.876
Nickel chloride			
0.005	0.46	0.525	0.876
0.007	0.57	0.650	0.877
0.010	0.75	0.856	0.876
0.030	0.93	1.061	0.877
0.050	1.23	1.403	0.877
0.070	1.47	1.677	0.876
0.100	1.61	1.837	0.876
Copper chloride			
0.005	0.54	0.616	0.876

0.007	0.63	0.719	0.876
0.010	0.72	0.822	0.876
0.030	0.83	0.947	0.876
0.050	1.05	1.198	0.876
0.070	1.16	1.324	0.876
0.100	1.30	1.483	0.877

Cadmium chloride

0.005	0.38	0.434	0.876
0.007	0.48	0.548	0.875
0.010	0.53	0.605	0.876
0.030	0.79	0.901	0.877
0.050	0.89	1.015	0.877
0.070	1.02	1.164	0.876
0.100	1.24	1.415	0.876

Magnesium chloride

0.005	0.43	0.491	0.876
0.007	0.52	0.593	0.877
0.010	0.69	0.787	0.876
0.030	0.98	1.118	0.877
0.050	1.34	1.529	0.876
0.070	1.59	1.814	0.877
0.100	2.23	2.544	0.877

for ternary systems of above mentioned divalent transition metal chlorides and magnesium chloride in binary aqueous mixtures of alcohols (methanol + water and ethanol + water) at 303.15K as were found to be in case of binary aqueous solutions described in previous section of this chapter. It again confirms our earlier conclusion that the membrane constant ‘A/l’ is a characteristic property of the membrane matrix only and does not depend upon the nature of the permeating fluid across the membrane.

IV. The Equivalent Pore Radius: Combined effect of alcohols and the divalent transition metal chlorides and magnesium chloride have also been analysed and equivalent pore radii for the different ternary systems have also been determined at 303.15K.

Volume flow, J_v, for the different solutions of above mentioned divalent transition metal chlorides and magnesium chloride in different binary aqueous mixtures of alcohols (methanol and ethanol) at 303.15K have been determined and values are recorded in Table – 4.VIII. The densities and viscosities for the above mentioned ternary systems at 303.15K have also been given in Table – 4.IX .By substituting the values of various quantities in relation (4.3) the average pore radii have been calculated for different ternary systems and are recorded in Table – X. It is evident from Table – X that the equivalent pore radius decreases with the increase in concentration of the each electrolyte in 5% (w/w) methanol + water and 5% (w/w) ethanol + water at 303.15K. The decrease in equivalent pore radius with the increase in the concentration of each electrolyte can be attributed to increase in the thickness of electrical double layer at the walls of the pores of inorganic membrane of aluminium oxide. Moreover the equivalent pore radius is different for different concentrations in 5% (w/w) methanol + water and 5% (w/w) ethanol + water mixtures at 303.15K thereby concluding that the equivalent pore radius is not the characteristic property of inorganic membrane of aluminium oxide only but it is seriously influenced by the nature of permeating fluid. This again confirms our earlier conclusions drawn from binary aqueous solutions of electrolytes.

TABLE – 4.VIII

HYDRODYNAMIC VOLUME FLOW (J_V) FOR DIFFERENT CONCENTRATIONS OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AND 5% (w/w) ETHANOL + WATER AT 303.15K (PER UNIT AREA OF MEMBRANE).

$\Delta P \times 10^{-4}$ (dyne cm^{-2})	**$J_v \times 10^5$ (cm sec^{-1})**						
concentration of electrolytic solution (m) mol.kg^{-1}	**0.005**	**0.007**	**0.010**	**0.030**	**0.050**	**0.070**	**0.10**
5% (w/w) Methanol + Water							
Manganese chloride							
0.49	3.59	3.44	3.40	3.29	3.18	3.08	2.95
0.98	8.06	7.81	7.70	7.43	7.28	7.09	6.90
1.47	11.58	11.26	10.98	10.64	10.37	10.13	9.85
1.96	15.11	14.63	14.28	13.86	13.5	13.15	12.76
2.45	18.62	18.17	16.98	16.98	16.48	16.04	15.65
Cobalt chloride							
0.49	3.71	3.29	2.95	2.63	2.45	2.21	2.05
0.98	8.32	7.53	6.80	6.26	5.48	5.45	5.12
1.47	11.90	10.73	9.67	8.86	8.24	7.58	7.17
1.96	15.50	13.93	12.52	11.52	10.65	9.86	9.27
2.45	19.13	17.13	15.43	14.23	13.03	12.23	11.30
Nickel chloride							
0.49	3.25	3.11	3.04	2.93	2.84	2.74	2.68
0.98	7.39	7.27	7.10	6.67	6.72	6.52	6.32
1.47	10.72	10.46	10.19	9.853	9.52	9.28	8.99
1.96	13.90	13.59	13.27	12.8	12.38	12.10	11.64
2.45	17.05	16.61	16.20	15.59	15.16	14.76	14.22
Copper chloride							
0.49	3.13	3.03	2.94	2.81	2.76	2.69	2.58
0.98	7.18	7.04	6.86	6.68	6.49	6.34	6.12
1.47	10.36	10.12	9.82	9.52	9.24	9.01	8.73
1.96	13.48	13.16	12.70	12.39	12.04	11.72	11.28
2.45	16.53	16.05	15.58	15.69	14.70	14.32	13.85
Cadmium chloride							
0.49	3.09	2.89	2.74	2.5	2.42	2.34	2.28
0.98	7.10	6.80	6.44	6.10	5.84	5.70	5.59
1.47	10.21	9.65	9.14	8.60	8.28	8.10	7.90
1.96	13.27	12.54	11.73	11.15	10.72	10.38	10.16
2.45	16.28	15.35	14.41	13.58	13.07	12.73	12.45

Magnesium chloride

0.49	3.34	3.23	3.19	3.08	2.95	2.92	2.84
0.98	7.72	7.47	7.30	7.13	6.96	6.84	6.67
1.47	11.14	10.78	10.49	10.19	9.95	9.77	9.56
1.96	14.47	14.03	13.68	13.28	12.91	12.71	12.37
2.45	17.72	17.22	16.78	16.24	15.79	15.47	15.22

5% (w/w) Ethanol + Water

Manganese chloride

0.49	3.11	3.04	2.89	2.78	2.68	2.61	2.51
0.98	7.29	7.08	6.79	6.75	6.44	6.25	6.08
1.47	10.35	10.05	9.66	9.43	9.17	8.76	8.53
1.96	13.50	13.11	12.57	12.26	11.89	11.48	11.12
2.45	16.59	16.08	15.39	15.05	14.58	14.08	13.58

Cobalt chloride

0.49	3.08	2.65	2.35	2.23	2.00	1.76	1.54
0.98	7.22	8.09	5.74	5.49	5.03	4.53	4.14
1.47	10.24	9.05	8.09	7.74	7.09	6.36	5.73
1.96	13.28	11.70	10.33	9.94	9.13	8.14	7.31
2.45	16.32	14.40	12.80	12.23	11.10	9.91	8.87

Nickel Chloride

0.49	2.81	2.73	2.63	2.58	2.52	2.45	2.40
0.98	6.62	6.48	6.30	6.17	5.95	5.87	5.76
1.47	9.43	9.20	8.95	8.73	8.50	8.32	8.20
1.96	12.21	11.92	11.60	11.37	9.98	10.78	10.52
2.45	15.02	14.64	14.20	12.90	13.44	13.16	12.93

Copper chloride

0.49	2.73	2.65	2.63	2.52	2.45	2.39	2.33
0.98	6.52	6.26	6.20	6.08	5.90	5.74	5.67
1.47	9.27	8.95	8.78	8.08	8.36	8.2	8.09
1.96	11.02	11.52	11.33	11.12	10.8	10.55	10.39
2.45	14.68	14.19	13.89	13.58	13.17	12.91	12.63

Cadmium chloride

0.49	2.63	2.54	2.43	2.39	2.31	2.28	2.21
0.98	6.28	6.09	5.92	5.81	5.64	5.56	5.38
1.47	8.93	8.63	8.36	8.23	7.97	7.89	7.66
1.96	11.6	11.19	10.82	10.64	10.27	10.15	9.86
2.45	14.62	13.6	12.15	12.9	12.59	12.35	12.06

Magnesium chloride

0.49	2.89	2.84	2.73	2.65	2.58	2.54	2.43
0.98	6.79	6.28	6.45	6.19	6.13	6.04	4.89
1.47	9.66	9.46	9.12	8.82	8.69	8.51	8.24
1.96	12.57	12.21	11.79	11.46	11.24	11.02	10.24
2.45	15.49	15.08	14.53	14.08	13.82	13.48	13.05

TABLE - 4.IX

DENSITIES, MOLAR VOLUMES AND VISCOSITIES FOR DIFFERENT CONCENTRATIONS OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AND 5% (w/w) ETHANOL + WATER AT 303.15K

Concentration (m) (mol kg^{-1})	Density (d) (g cm^{-3})	Viscosity (η) (cP)	Density (d) (g cm^{-3})	Viscosity (η) (cP)
	5% (w/w) Methanol + water		**5% (w/w) Ethanol + water**	
Manganese chloride				
0.005	0.98626	0.8899	0.98697	0.9293
0.007	0.98651	0.9074	0.98724	0.9489
0.010	0.98688	0.9299	0.98765	0.9743
0.030	0.98934	1.0328	0.99034	1.0915
0.050	0.99164	1.1096	0.99298	1.1745
0.070	0.99387	1.1755	0.99555	1.2431
0.100	0.99715	1.2577	0.99932	1.3326
Cobalt chloride				
0.005	0.98613	0.9022	0.98674	0.9291
0.007	0.98634	0.9218	0.98692	0.9493
0.010	0.98664	0.9463	0.98721	0.9752
0.030	0.98858	1.0604	0.98894	1.0927
0.050	0.99039	1.1429	0.99056	1.1771
0.070	0.99209	1.2117	0.99211	1.2465
0.100	0.99455	1.2997	0.99426	1.3370
Nickel chloride				
0.005	0.98627	0.9031	0.98688	0.9292
0.007	0.98653	0.9227	0.98712	0.9488
0.010	0.98692	0.9472	0.98748	0.9741
0.030	0.98941	1.0613	0.98981	1.0909
0.050	0.99179	1.1425	0.99204	1.1733
0.070	0.99406	1.2113	0.99419	1.2414
0.100	0.99734	1.2992	0.99721	1.3298
Copper chloride				
0.005	0.98622	0.8747	0.98674	0.9291
0.007	0.98646	0.8887	0.98692	0.9493
0.010	0.98681	0.9070	0.98721	0.9752
0.030	0.98907	0.9909	0.98894	1.0927

0.050	0.99122	1.0515	0.99056	1.1771
0.070	0.99333	1.1031	0.99211	1.2465
0.100	0.99627	1.1700	0.99426	1.3370
Cadmium chloride				
0.005	0.98624	0.9169	0.98696	0.9480
0.007	0.98649	0.9385	0.98723	0.9711
0.010	0.98686	0.9666	0.98764	1.0006
0.030	0.98919	1.0930	0.99030	1.1331
0.050	0.99145	1.1831	0.99290	1.2259
0.070	0.99364	1.2574	0.99528	1.3014
0.100	0.99674	1.3522	0.99898	1.3973
Magnesium chloride				
0.005	0.98587	0.9020	0.97136	0.9289
0.007	0.98597	0.9214	0.97148	0.9490
0.010	0.98612	0.9458	0.97166	0.9741
0.030	0.98696	1.0566	0.97270	1.0892
0.050	0.98764	1.1356	0.97364	1.1698
0.070	0.98820	1.2014	0.97444	1.2358
0.100	0.98888	1.2847	0.97553	1.3217

Table – 4.X

EQUIVALENT PORE RADIUS (r) AND MECHANICAL FILTRATION COEFFICIENT (L_P) FOR DIFFERENT CONCENTRATIONS OF MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AND 5% (w/w) ETHANOL + WATER AT 303.15K

Concentration (m) (mol kg^{-1})	Equivalent pore radius r x 10^4 (cm)	Filtration coefficient Lp x 10^9 (cm^{3}dyne^{-1}sec^{-1})	Equivalent pore radius r x 10^4 (cm)	Filtration coefficient Lp x 10^9 (cm^{3}dyne^{-1}sec^{-1})
	5% (w/w) Methanol + water		**5% (w/w) Ethanol + water**	
		Manganese chloride		
0.005	1.72	7.57	2.50	6.77
0.007	1.60	7.40	2.46	6.55
0.010	1.51	6.88	2.42	6.28
0.030	1.41	6.85	2.38	6.13
0.050	1.27	6.69	2.32	5.97
0.070	1.23	6.53	2.29	5.75
0.100	1.22	6.38	2.32	5.55
		Cobalt chloride		
0.005	1.77	7.76	2.31	6.64
0.007	1.65	6.96	2.17	5.94
0.010	1.56	6.26	2.13	5.20
0.030	1.44	5.81	2.07	4.99
0.050	1.29	5.37	2.09	4.55
0.070	1.26	4.99	2.02	4.06
0.100	1.23	4.62	1.96	3.64
		Nickel chloride		
0.005	1.78	6.96	2.44	6.12
0.007	1.66	6.80	2.38	5.97
0.010	1.54	6.63	2.35	5.80
0.030	1.45	6.42	2.29	5.27
0.050	1.32	6.18	2.20	5.48
0.070	1.28	6.04	2.19	5.37
0.100	1.20	5.80	2.21	5.27
		Copper chloride		
0.005	1.21	6.76	2.41	5.80
0.007	1.24	6.56	2.36	5.78
0.010	1.35	6.35	2.32	5.64
0.030	1.43	6.34	2.27	5.54
0.050	1.50	6.01	2.19	5.38
0.070	1.56	5.85	2.10	5.28
0.100	1.60	5.65	2.07	5.17

Cadmium chloride				
0.005	1.84	6.64	2.40	5.98
0.007	1.71	6.26	2.35	5.56
0.010	1.61	5.84	2.30	5.42
0.030	1.56	5.55	2.25	5.28
0.050	1.49	5.34	2.15	5.14
0.070	1.32	5.20	2.13	5.05
0.100	1.28	5.08	2.06	4.93
Magnesium chloride				
0.005	2.05	7.25	2.45	6.32
0.007	1.64	7.05	2.42	6.21
0.010	1.55	6.85	2.37	5.91
0.030	1.44	6.63	2.30	5.74
0.050	1.29	6.46	2.18	5.63
0.070	1.26	6.32	2.01	5.48
0.100	1.63	6.22	1.96	5.43

V. **The Mechanical Filtration Coefficient (L_p):** According to relation (4.5) the volume flow, J_v, should vary linearly with the hydrostatic pressure, ΔP, across the inorganic membrane of aluminium oxide and in the present study straight line plots (J_v vs ΔP) have been found for all the ternary systems permeating through inorganic membrane of aluminium oxide at 303.15K. Sample plots of J_v vs ΔP for different concentrations of cobalt chloride in 5% (w/w) methanol + water and 5% (w/w) ethanol + water mixtures at 303.15K are shown in Fig.37 and 38, respectively. The mechanical filtration coefficients, L_p, have been estimated by using the least square fit to the slopes of linear plots of J_v vs ΔP and the corresponding values of different ternary systems are also recorded in Table – 4 .X. Variation of the mechanical filtration coefficient, L_p, with concentration of individual electrolyte in binary aqueous mixtures of alcohols (methanol and ethanol) at 303.15K has also been found to be linear for all the ternary systems and plots of L_p vs c for all the transition metal chlorides and magnesium chloride in 5% (w/w) methanol + water and 5% (w/w) ethanol + water at 303.15K are shown in Fig. 39 and 40, respectively.

It is clear from Table – 4.X that L_p decreases with the increase in concentration of individual divalent transition metal chlorides and magnesium chloride in methanol + water and ethanol + water at 303.15K. Since the hydraulic conductivity, L_p, is a constant which expresses the interactions between the membrane matrix and the permeating fluid, therefore it may be inferred from Table – 4.X that the interactions between aluminium oxide membrane and electrolyte in binary aqueous mixtures of alcohols are enhanced at 303.15K. In other words, it may be said that on the addition of an electrolyte in binary aqueous mixtures of alcohols (methanol and ethanol), the friction between membrane matrix and flowing fluid is enhanced. Further, It is also clear from these results that L_p is different for the various ternary systems, studied at 303.15K, indicating that L_p is also not the characteristic property of the inorganic membrane of aluminium oxide, rather it is seriously influenced by the nature of the permeating fluids. This again confirms our earlier conclusion drawn from binary aqueous solutions.

VI. The Rejection Coefficient (σ): The rejection coefficient, σ, has also been determined for all the selected divalent transition metal chlorides and magnesium chloride in binary aqueous mixtures of alcohols (methanol and ethanol) [5% (w/w) of alcohols] by keeping alcohols + water as a solvent on one side of the inorganic

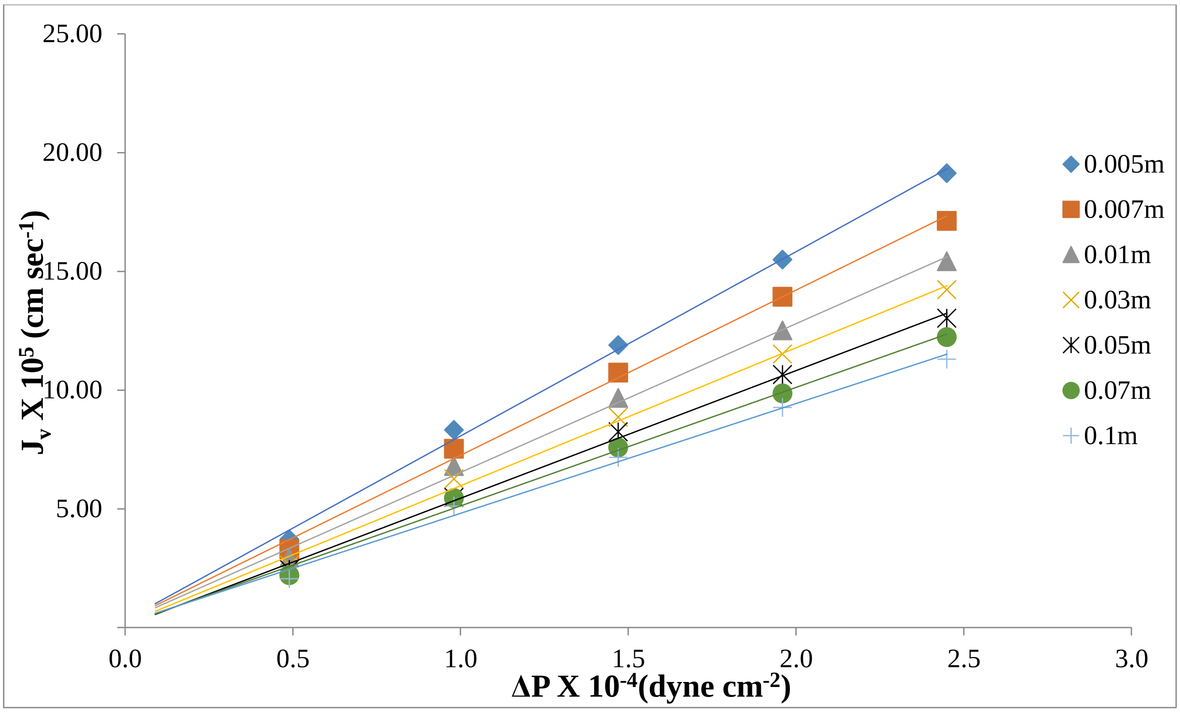

Fig. 37: PLOTS FOR J_v VS ΔP FOR COBALT CHLORIDE IN 5% (w/w) METHANOL + WATER AT 303.15K

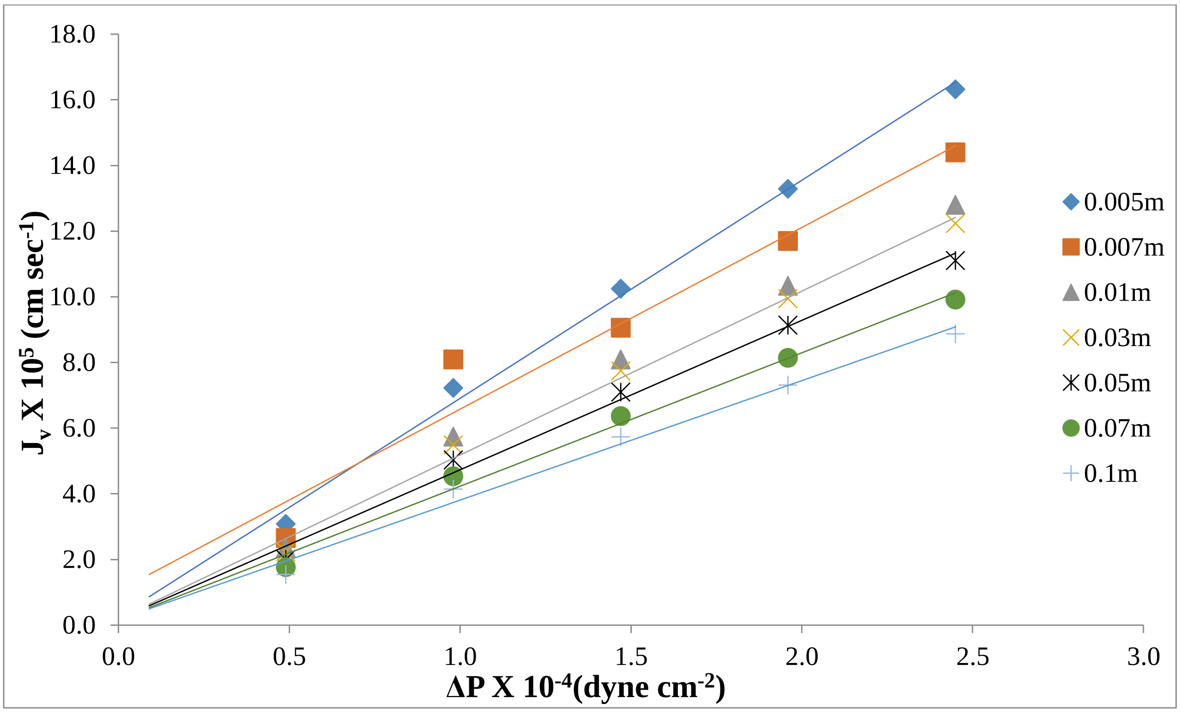

Fig. 38: PLOTS FOR J_v VS ΔP FOR COBALT CHLORIDE IN 5% (w/w) ETHANOL + WATER AT 303.15K

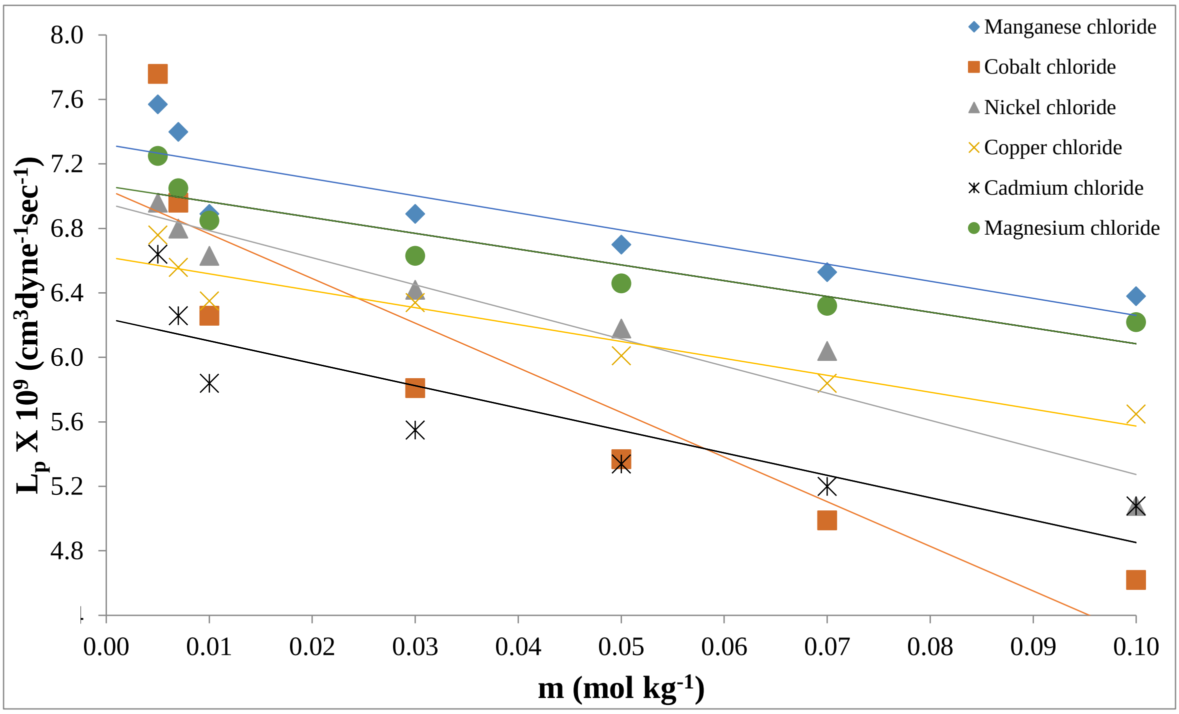

Fig.39: PLOTS OF L_P VS c FOR MAGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE,COPPER CHLORIDE,CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN METHANOL + WATER AT 303.15K.

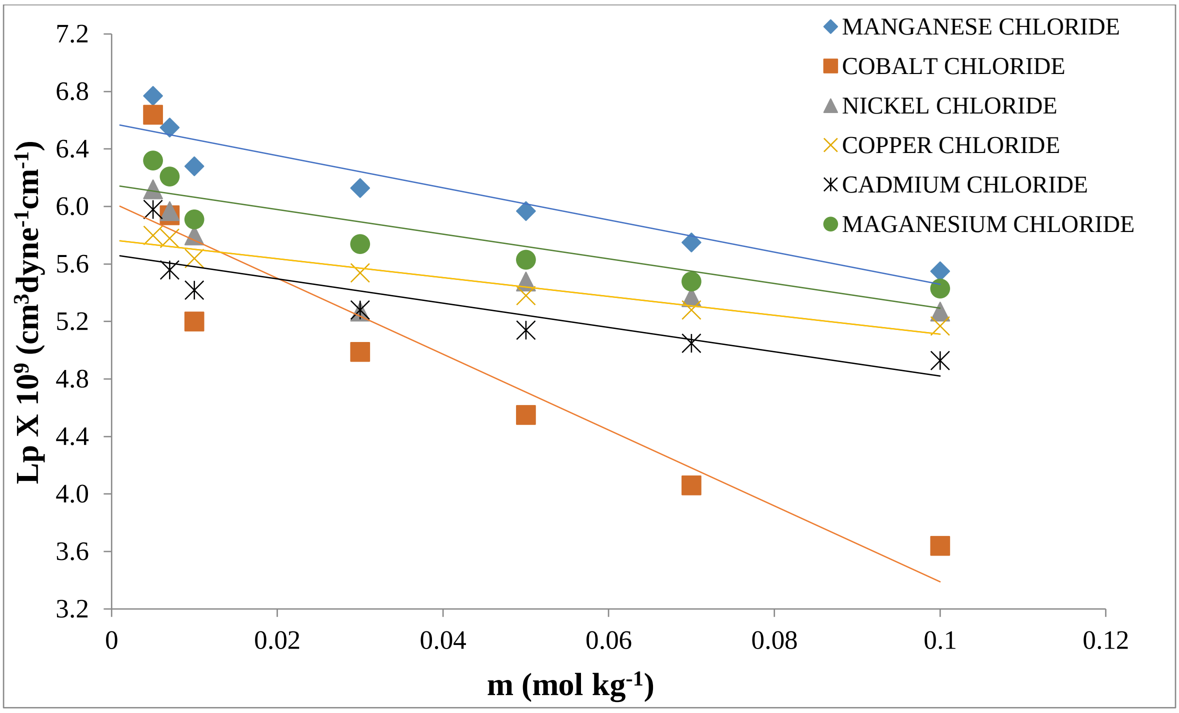

FIG. 40: PLOTS OF L_P VS c FOR MAGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE,COPPER CHLORIDE,CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN ETHANOL + WATER AT 303.15K.

membrane of aluminium oxide and the ternary solution on the other side. The resultant volume flow, $J_v^{'}$, is noted for each concentration difference (Δc) at different pressures across the aluminium oxide membrane at 303.15K. The values of net volume flow, $J_v^{'}$, for the different ternary systems, obtained under the simultaneous influence of osmotic pressure (Δπ) and the hydrostatic pressure (ΔP) at 303.15K are recorded in Table – 4.XI.

According to relation (4.8) $J_v^{'}$ should also vary linearly with $\Delta P^{'}$ and the same has been found true for all the ternary systems studied here at 303.15K. A sample plot of $J_v^{'}$ vs $\Delta P^{'}$ is shown in Fig.41 for nickel chloride in 5% (w/w) methanol + water at 303.15K. The values of $L_p^{'}$ and $(J_v^{'})_{\Delta P'=0}$ have been calculated from the slopes and intercepts of the straight line plots of $J_v^{'}$ vs $\Delta P^{'}$ by using least square method respectively. The values of $L_p^{'}$ and $(J_v^{'})_{\Delta P'=0}$ thus estimated, for different ternary systems at 303.15K are recorded in Table – 4.XII.

It is evident from Table – 4.XII that the values of $L_p^{'}$ and $(J_v^{'})_{\Delta P'=0}$ are different for various solutions of a particular electrolyte in alcohols (methanol and ethanol) + water mixtures at 303.15K.Futher, it is clear from Table – 4.XII the values of $L_p^{'}$ and $(J_v^{'})_{\Delta P'=0}$ are also different for particular electrolyte in methanol + water and ethanol + water mixtures at 303.15K.

The coupling coefficient, σ, for the different ternary systems at 303.15K has been evaluated from the relation (4.9) and the corresponding values are also recorded in Table – 4.XII. The rejection coefficient, σ, is a measure of membrane selectivity or the coupling between total volume flux and the solute transmission (As explained in the previous section). It is clear from the Table – 4.XII that the value of σ decreases with the increase in concentration difference for a particular salt in methanol + water and ethanol + water mixture at 303.15K. From these values of σ, it may be concluded that even in ternary systems the coupling between ternary solutions of electrolytes and binary mixtures of alcohols (methanol and ethanol) goes on increasing with the increase in the concentration of a particular electrolyte in aqueous mixtures of alcohols (methanol and ethanol) meaning thereby that the solute (electrolyte) and solvent (methanol + water and ethanol + water) flow with almost equal velocities, only at higher concentrations of a particular solute at 303.15K, through the inorganic membrane of aluminium oxide.

Further, It is clear that the value of σ is very small in magnitude and it further decreases with the increase in the concentration difference (Δc) of the solute in a particular solvent (methanol + water and ethanol + water) at 303.15K, indicating that there is no rejection of the solute by inorganic membrane of aluminium oxide even in ternary systems.

TABLE – 4.XI

NET VOLUME FLOW (J_V') FOR THE DETERMINATION OF REJECTION COEFFICIENT AT DIFFERENT CONCENTRATION DIFFERENCES (ΔC) ACROSS THE MEMBRANE FOR MANGANESE CHLORIDE, COBALT CHLORIDE, NICKEL CHLORIDE, COPPER CHLORIDE, CADMIUM CHLORIDE AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AND 5% (w/w) ETHANOL + WATER AT 303.15K PER UNIT AREA OF MEMBRANE.

$\Delta P \times 10^{-4}$ (dyne cm^{-2})	**$J_V' \times 10^{5}$ (cm sec^{-1})**						
concentration of electrolytic solution (m) mol.Kg^{-1}	**0.005**	**0.007**	**0.01**	**0.03**	**0.05**	**0.07**	**0.1**
5% (w/w) Methanol + Water							
Manganese chloride							
0.49	2.95	2.86	2.75	2.59	2.50	2.46	2.37
0.98	7.43	7.10	6.95	6.83	6.61	6.34	6.18
1.47	10.92	10.48	10.18	9.90	9.54	9.29	9.04
1.96	14.42	13.80	13.47	13.08	12.57	12.21	11.89
2.45	17.9	17.16	16.67	16.15	15.63	15.15	14.70
Cobalt chloride							
0.49	1.65	1.64	1.56	1.47	1.45	1.4	1.23
0.98	5.19	5.06	4.91	4.62	4.47	4.36	4.25
1.47	7.76	7.58	7.39	6.90	6.73	6.62	6.4
1.96	10.33	10.10	9.79	9.22	8.95	8.72	7.51
2.45	12.90	12.60	12.21	11.51	11.20	10.94	10.64
Nickel chloride							
0.49	2.00	1.97	1.91	1.88	1.86	1.65	1.62
0.98	5.99	5.76	5.58	5.38	5.25	4.99	5.07
1.47	8.86	8.61	8.31	8.04	7.89	7.49	7.6
1.96	11.79	11.44	11.08	10.77	10.55	8.97	10.18
2.45	14.56	14.15	13.72	13.33	13.04	12.44	11.83
Copper chloride							
0.49	2.81	2.70	2.68	2.45	2.37	2.26	2.14
0.98	6.79	6.56	6.66	6.26	5.99	5.90	5.67
1.47	9.66	9.83	9.20	8.93	8.67	8.42	8.13
1.96	12.64	12.3	11.92	11.64	11.27	11.05	10.58
2.45	16.47	16.12	15.96	14.86	14.28	13.82	13.06
Cadmium chloride							
0.49	2.13	1.97	1.94	1.89	1.81	1.75	1.65
0.98	5.82	5.52	5.35	5.29	5.16	4.99	4.86
1.47	8.5	8.01	7.86	7.63	7.46	7.23	6.99
1.96	11.17	10.58	10.27	10.07	9.82	9.48	9.17

2.45	13.81	12.95	12.62	12.37	12.00	11.59	11.14
Magnesium chloride							
0.49	2.31	2.28	2.24	2.20	2.12	2.09	1.97
0.98	6.56	6.36	6.23	6.07	5.74	5.67	5.45
1.47	9.77	9.39	9.09	8.86	8.47	8.31	7.89
1.96	12.02	12.39	12.02	11.64	11.15	10.94	10.33
2.45	16.14	15.47	14.86	14.52	13.8	13.58	12.79
5% (w/w) Ethanol + Water							
Manganese chloride							
0.49	2.13	2.07	1.81	1.69	1.61	1.48	1.37
0.98	6.09	5.94	5.52	5.35	5.23	5.03	4.82
1.47	9.08	8.73	8.24	8.01	7.82	7.43	7.22
1.96	12.13	11.6	10.95	10.65	10.33	9.96	9.64
2.45	15.13	14.73	13.58	13.02	12.59	11.94	11.28
Cobalt chloride							
0.49	1.67	1.55	1.48	1.38	1.32	1.21	1.16
0.98	4.57	4.45	4.33	4.15	3.98	3.87	3.79
1.47	6.56	6.35	6.18	6.02	5.82	5.52	5.46
1.96	8.42	8.23	8.1	7.82	7.59	7.18	7.05
2.45	10.98	10.45	9.98	9.49	9.08	8.63	8.42
Nickel chloride							
0.49	2.08	1.88	1.79	1.66	1.56	1.48	1.45
0.98	5.99	5.67	5.39	5.2	4.96	4.78	4.63
1.47	8.98	8.45	8.05	7.67	7.38	7.04	6.89
1.96	11.88	11.19	10.65	10.18	9.77	9.27	9.05
2.45	14.88	13.92	13.28	12.6	11.98	11.53	11.2
Copper chloride							
0.49	1.65	1.57	1.35	1.28	1.22	1.15	1.07
0.98	5.33	5.08	4.71	4.62	4.50	4.37	4.26
1.47	8.06	7.57	7.16	6.96	6.8	6.67	6.25
1.96	10.71	10.15	9.51	9.28	9.1	8.89	8.61
2.45	13.35	12.57	11.52	11.06	10.73	10.38	9.88
Cadmium chloride							
0.49	1.48	1.20	1.26	1.13	1.09	1.05	1.01
0.98	5.10	4.71	4.53	4.36	4.28	4.16	4.02
1.47	7.80	7.23	6.92	6.7	6.52	6.34	6.13
1.96	10.45	9.72	9.27	8.95	8.71	8.52	8.27
2.45	13.36	12.13	11.84	11.21	10.93	10.64	10.33
Magnesium chloride							
0.49	2.13	2.07	1.81	1.69	1.61	1.48	1.37
0.98	6.09	5.95	5.52	5.35	5.22	5.02	4.81
1.47	9.09	8.73	8.23	8.01	7.82	7.43	7.22
1.96	12.14	11.61	10.94	10.64	10.33	9.96	9.64
2.45	15.13	14.59	13.24	12.58	12.02	11.28	10.73

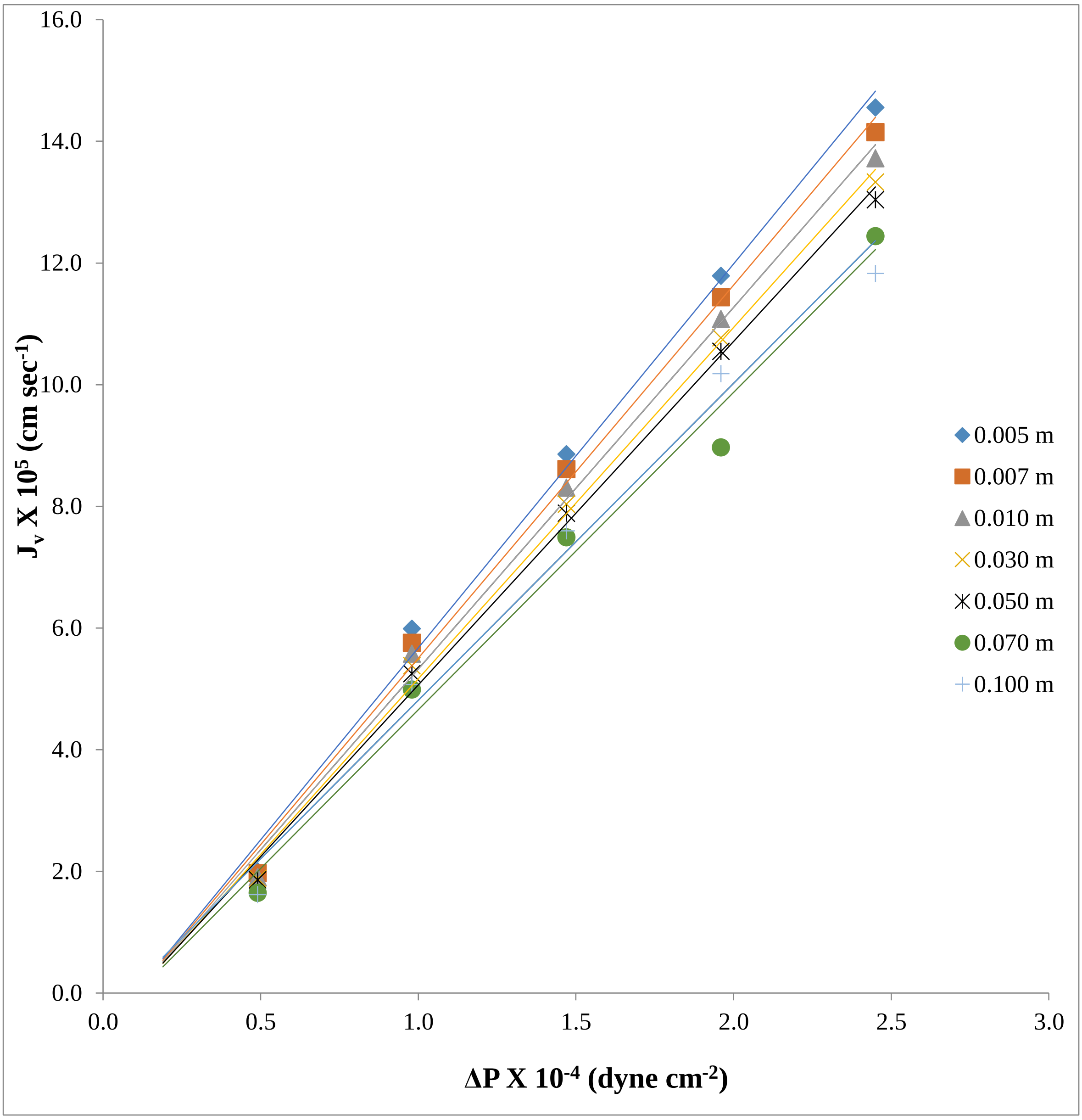

Fig. 41: PLOTS OF $J_v^{'}$ VS ΔP' FOR VARIOUS CONCENTRATIONS OF NICKEL CHLORIDE IN 5% (w/w) METHANOL + WATER MIXTURE AT 303.15 K.

Table – 4.XII

PERMEABILITY DATA AND REJECTION COEFFICIENT (σ), FOR DIFFERENT CONCENTRATION DIFFERENCE 'Δc' OF SOME DIVALENT TRANSITION METAL CHLORIDES AND MAGNESIUM CHLORIDE IN 5% (w/w) METHANOL + WATER AND 5% (w/w) ETHANOL + WATER AT 303.15K PER UNIT AREA OF THE MEMBRANE.

Concentration (m) mol kg^{-1}	$(J'_V)_{\Delta p=0} \times 10^5$ cm sec^{-1}	$L'_p \times 10^9$ cm^3 $dyne^{-1}$ sec^{-1}	$\sigma \times 10^6$
5% (w/w) Methanol + Water			
Manganese chloride			
0.005	-0.34	7.53	0.36
0.007	-0.31	7.20	0.24
0.010	-0.30	7.01	0.17
0.030	-0.30	6.81	0.06
0.050	-0.29	6.58	0.03
0.070	-0.28	6.38	0.02
0.100	-0.27	6.19	0.02
Cobalt chloride			
0.005	-0.72	5.64	1.01
0.007	-0.69	5.50	0.71
0.010	-0.68	5.34	0.51
0.030	-0.66	5.03	0.17
0.050	-0.63	4.89	0.1
0.070	-0.62	4.78	0.07
0.100	-0.61	4.5	0.05
Nickel Chloride			
0.005	-0.63	6.31	0.79
0.007	-0.62	6.13	0.57
0.010	-0.61	5.94	0.41
0.030	-0.60	5.77	0.14
0.050	-0.58	5.64	0.08
0.070	-0.56	5.22	0.06
0.100	-0.49	5.21	0.04
Copper chloride			
0.005	-0.28	6.76	0.33
0.007	-0.27	6.65	0.23
0.010	-0.26	6.49	0.16
0.030	-0.23	6.16	0.05
0.050	-0.21	5.93	0.03
0.070	-0.19	5.76	0.02
0.100	-0.10	5.45	0.01

Cadmium chloride			
0.005	-0.32	5.85	0.43
0.007	-0.30	5.51	0.31
0.010	-0.28	5.36	0.21
0.030	-0.27	5.25	0.07
0.050	-0.26	5.11	0.04
0.070	-0.24	4.93	0.03
0.100	-0.22	4.75	0.02
Magnesium chloride			
0.005	-0.58	6.76	0.68
0.007	-0.54	6.61	0.46
0.010	-0.42	6.33	0.26
0.030	-0.40	6.16	0.09
0.050	-0.37	5.87	0.05
0.070	-0.35	5.76	0.03
0.100	-0.27	5.41	0.02
5% (w/w) Ethanol + Water			
Manganese chloride			
0.005	-0.70	6.54	0.85
0.007	-0.68	6.32	0.61
0.010	-0.67	5.91	0.45
0.030	-0.64	5.71	0.15
0.050	-0.60	5.52	0.09
0.070	-0.59	5.28	0.06
0.100	-0.53	5.03	0.04
Cobalt chloride			
0.005	-0.30	4.59	0.52
0.007	-0.69	4.40	0.89
0.010	-0.68	4.24	0.64
0.030	-0.66	4.06	0.21
0.050	-0.63	3.90	0.13
0.070	-0.62	3.70	0.09
0.100	-0.61	3.63	0.07
Nickel chloride			
0.005	-0.69	6.43	0.85
0.007	-0.66	6.04	0.62
0.010	-0.64	5.76	0.44
0.030	-0.6	5.48	0.14
0.050	-0.57	5.23	0.09
0.070	-0.56	5.02	0.06
0.100	-0.53	4.88	0.04
Copper chloride			
0.005	-0.81	5.87	1.09

0.007	-0.73	5.24	0.79
0.010	-0.69	5.13	0.53
0.030	-0.63	4.94	0.17
0.050	-0.62	4.82	0.1
0.070	-0.60	4.69	0.07
0.100	-0.58	4.48	0.05
Cadmium chloride			
0.005	-1.10	5.94	1.47
0.007	-1.06	5.48	1.1
0.010	-1.01	5.29	0.76
0.030	-0.96	5.05	0.25
0.050	-0.93	4.92	0.15
0.070	-0.92	4.80	0.11
0.100	-0.92	4.67	0.08
Magnesium chloride			
0.005	-0.70	6.54	0.85
0.007	-0.62	6.26	0.56
0.010	-0.54	5.77	0.37
0.030	-0.47	5.52	0.11
0.050	-0.38	5.29	0.06
0.070	-0.33	5.01	0.04
0.100	-0.31	4.81	0.03

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List of Publications

1. Sonika, R.C.Thakur and Ravi Sharma, “Effect of temperature on the partial molar volumes of some Bivalent transition metal chlorides in water and binary aqueous mixtures of methanol” IJCRGG, ISSN: 0974-4290, Vol.7, No.5, pp 2222-2228, 2014-2015 in International Journal of ChemTech Research.

2. R.C. Thakur and Sonika, “Effect of Temperature on Partial Molar Volumes of Some Bivalent Transition Metal Chlorides and Magnesium Chloride in the Water-Rich Region of Binary Aqueous Mixtures of Ethanol” ISSN: 0975-8585, 5(6) Page No. 1298, 2014 in RJPBCS.

3. R.C. Thakur and Sonika,“Effect of Temperature on Viscosity B- Coefficients of Some Transition Metal Chlorides and Magnesium Chloride in Water and In Water + Methanol Mixtures” ISSN: 0975-8585, 6(1) Page No. 664, 2015 in RJPBCS.

4. S. Chauhan, M. S. Chauhan , G. S. Chauhan , Sonika and J. Jyoti, “Sound Speed and Density Studies of Interactions Between Cationic Surfactants and Aqueous Gelatin Solution” 33:279–288 , 2012 in Int J Thermophys.DOI 10.1007/s10765-011-1146-0

5. Sonika, R.C.Thakur, “Viscometric Study on Intermolecular Interactions of Some Transition Metal Chlorides in Water and Water + Ethanol Mixtures: Solvent and Temperature Effect” communicated in Indian Journal of Chemistry A.

Conference Papers

1. Sonika, Balwinder Saini and Ravi Sharma, “Low temperature synthesis of nano –structure TiO_2 for degradation of azo dye in National conference on analytical chemistry and molecular spectroscopy, 13-14th Oct. 2016 at National Institute of Technology, Hamirpur (HP).

2. Sonika, R.C.Thakur and Ravi Sharma, “Activation energy parameters for the hydrodynamic permeability of divalent transition metal sulphates and magnesium sulphate in binary aqueous mixtures of ethylene glycol” in International Conference: “Recent Advances in fundamental and Applied Science, 25-26th Nov. 2016 at the Lovely Professional University, Phagwara (PB).