Physico - Chemical Studies of Different Solutions of Electrolytes such as Chlorides of Fe^{3+}, Co^{3+}, Cu^{2+}, Mg^{2+}, Hg^{2+} and Ni^{2+} in Methanol-Water and Ethanol-Water System

BY

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DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

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Dedicated

TO

My Beloved Parents

The thesis titled "**Physico - Chemical Studies of Different Solutions of Electrolytes such as Chlorides of Fe^{3+}, Co^{3+}, Cu^{2+}, Mg^{2+}, Hg^{2+} and Ni^{2+} in Methanol-Water and Ethanol-Water System**" submitted by Md. Ferdaus Nowaz, Roll No.- 100103207 F, Session – October, 2001 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Philosophy on 30th October, 2006.

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ABSTRACT

The study of structure of water and of aqueous solutions of electrolytes and non-electrolytes are important from both theoretical and practical points of view. Water structure plays an important role in aqueous systems. The knowledge of water structure is a prerequisite to understand the various interactions in the aqueous solutions. In this investigation, the experimental measurements of density and viscosity of aqueous solution of $FeCl_3$, $CoCl_3$, $CuCl_2$, $MgCl_2$, $HgCl_2$ and $NiCl_2$ (electrolytes) in the presence of methanol and ethanol were carried out at different temperature (5-35^{0}C). Here, some parameters related to density and viscosity, such as *B*-coefficients of Jones-Dole equation, excess molar volume V_m^E, apparent molal volumes, enthalpy of activation $\Delta H_\eta^\#$, free energy of activation $\Delta G_\eta^\#$ and entropy of activation, $T\Delta S_\eta^\#$ for viscous flow were calculated by using standard equation in order to investigate the effect of methanol and ethanol on the structure modifying properties of $FeCl_3$, $CoCl_3$, $CuCl_2$, $MgCl_2$, $HgCl_2$ and $NiCl_2$ (electrolytes) on water. In this study the values apparent molar volumes of all solutions are found positive and increase almost linearly with increase mole fraction of electrolytes both in methanol-water and ethanol-water system. The experimentally determined viscosity values of different solutions were found to decrease with increase of temperature. The positive values of B-coefficient for the solution containing trivalent cation such as Fe^{3+}, Co^{3+} were observed higher than those of bivalent cation such as Mg^{2+}, Cu^{2+} etc. The positive values indicate that the electrolytic salts taken in this study are structure maker. The structure intensifying properties of these electrolytes were also supported by the calculated values of thermodynamic quantities such as $\Delta H_\eta^\#$, $\Delta G_\eta^\#$ and $T\Delta S_\eta^\#$.

CHAPTER-1

INTRODUCTION

CHAPTER-1

INTRODUCTION

1.1 GENERAL CONSIDERATION:

The study of structure of water and of aqueous solutions of electrolytes and non-electrolytes are important from both theoretical and practical points of view. It is well known that human body is mainly composed of water and the human body chemistry mainly deals with the aqueous solution of electrolytes and non-electrolytes. It has been recognized that the structure of water plays an important role in deciding the conformations of proteins and other bio-polymers in their aqueous solutions. In human body, the electrolytes are there to balance and solve many complicated problems and the non-electrolytes like protein, carbohydrates etc. are also there to involve in the metabolic activities. Some recent interesting observations have proved that mixed binary aqueous systems behave in a peculiar fashion compared with the mixed non-aqueous systems and have given a new impetus to a detail study of the structure of water and of aqueous solutions [1-4]. Recently some important observation on binary systems with water indicate the possibilities of extension and completion of data reported to the structure of water [5-16]

Theoretical models proposed to depict the bulk structure of water can be broadly classified into continuous models [17-19] and mixture models [20-21]. The continuous models treat liquid water as a uniform dielectric medium and averaged over a large number of molecules. The environment about a particular molecule is considered to be same as about any other molecules. So that the behaviour of all molecules is equivalent. The mixture models consider liquid water consists of two or more distinguishable species with different physical properties. Among the supporters of mixture model approach towards defining the intermolecular structure of water. There are differences of opinion about the particular form of species. Many models have been proposed which can be categorized under the mixture concept. The complexity in the properties of water and its typical nature precludes a simple model for representation of its structure. However, the presence of a bulky four co-ordinated species has been universally accepted. Weather the particular form of this species is ice-like or similar to any other form is still an open question. On this basis of these fundamental ideas it is possible to imagine a series of effective liquid water structure. The papers published in this field, without any doubt, indicate that the complete structure of water is still unknown. Specially, the change of these structures is not known when an electrolytic or non-electrolytic substance is added to water, except in a limited case [22,23].

Water structure plays an important role in aqueous systems. The knowledge of water structure is a prerequisite to understand the various interactions in the aqueous solutions. A brief account of the present status of the structure of water and aqueous solution is, therefore, included in this section along with the theories and reactions involved.

From the physical properties it appears that water is an 'anomalous' liquid whose many properties differ essentially from the normal liquids of simpler structure. The notable unique physical properties exhibited by liquid water are [24]:

i) negative change of volume of during melting.
ii) maximum density in the natural liquid range (at 4°C).
iii) minimum isothermal compressibility in the normal liquid range at 4.6°C).
iv) numerous crystalline polymorphs.
v) high dielectric constant.
vi) abnormally high melting, boiling and critical temperatures for such a low molecular weight substance that is neither ionic nor metallic.
vii) increasing liquid fluidity with increasing pressure
viii) high mobility transport for H^+ and OH^- ions [25]etc.

Liquid water possesses distinctive structural features which are roughly describable by the statement that retains a certain degree of similarity analogous to ice. Partial retention of the tetrahedral directed hydrogen bonding involved in the crystalline structure of ice [25,26]. In other words liquid water may be treated as a broken form of the ice lattice with the increase of the length of $O \cdots H \cdots O$ bond.

This view of water structure is supported strongly by the result of x-ray scattering experiments and studies of the infrared and Raman absorption spectra, which indicate that a considerable degree of short range order and the low coordination characteristics of the tetrahedral bonded structure persists in the liquid. Thus x-ray scattering studies indicate that the average number of nearest neighbors is 4.4 to 4.6 and the average distance between centers is 2.9A°. A high concentration of molecules is also found at 4.75 to 4.90A°, which is roughly the expected distance for the next nearest neighbors if the molecules tend to have a tetrahedral arrangement as in ice [27]. A distance maximum of 1.1A° is attributed to the closest O-H distance in the molecule [28] of water that can be regarded as a particular type of associated liquid in which the association penetrates through the whole volume of the liquid, forming a three dimensional network. Most modern theories of water take this view as a starting point that water is a mixture of certain three dimensional structures [28].

The different models proposed, although able to account for a number of distinctive features of liquid water, but they are contradictory in many respects [7, 29]. As a result, in spite of the exhaustive amount of work done on the properties of water [1, 23, 30-32] the clear understanding about liquid water is far from complete.

The properties of solution can be accounted for in terms of solvent-solvent solvent-solute and solute-solute interactions. The concentration dependence of a given property extrapolated to the limit of infinite dilution provides a measure of solute-solvent interactions. Solute-water interaction or hydration phenomena, can be conveniently classified into three basic types:

(i) **Hydrophilic hydration:** Where the solute-solvent interaction occurs via hydrogen bonding such as in the case of aqueous solution of simple sugar (non ionic solute).

(ii) **Ionic hydration**: Where the interaction occurs through electrostatic forces such as in the case of polar or ionic solute.

(iii) **Hydrophobic hydration**: Where there is no direct molecular interaction, rather there is a restructuring of water molecules around the solute particles. This is observed in solutions of essentially a large polar molecules such as long chain alcohols and long chain fatty acid salts.

The structure of water is profoundly influenced by the presence of solute molecule. Introduction of a solute produces changes in the properties of the liquid water that are analogous to those brought about by temperature or pressure changes. It is generally agreed that in aqueous solutions of ions not larger than I^-, the nearest neighbour water molecules are always immobilized by the direct ion dipole interaction. This idea explains the influence of Li ion on the viscosity of water in which it is dissolved. However, the more fluidity of 0.1 M solution of CsCI than pure water demonstrates that the idea cannot explain all the physico-chemical behaviour of aqueous solutions. This phenomenon was interpreted by Bernal and Fowler [33] that the ions of different salts influence the water structure differently. On the basis of the results obtained from analysis of entropy of hydration by Frank and Evans [34] with the estimated entropy losses arising from (i) restriction of the ions in "free volume" cells in the condensed phases (ii) immobilization of first-layer water and (iii) dielectric polarization of more distant water, Frank and Wen [20] suggested a model of structure liquid water which is sketched in Fig. 1.1. According to figure 1.1 the ions of solute are surrounded by three concentric regions.

The innermost region (A), called the primary solvation sheath, consists of ordered co-ordinate water molecules, is immobilised by the strong ion-dipole interactions. In outermost region (C) water molecules have a normal liquid water. The water molecules in the intermediate region (B) are more random in organisation than normal water due to an approximate balance between the dielectric field of the central ion and the orienting influence of neighbouring water molecules (Fig. 1. 1). The cause of structure breaking and making is presumably the shift in balance in the region (B) between two competing orienting influences. The ion with low charge density has relatively weak electrostatic fields so that the region (A) is very small thereby causing a net breaks of water structure. On the other hand, for the ions with high charge density the region (A) exceeds the region (B) which results in a net structural increase around these ions.

The development of solution chemistry is still far from being adequate to account for the properties of solutions in terms of the properties of the constituent molecules. It is clear that if the solute and solvent are interacting, as indeed they do in some cases then the chemistry of the solute in solution must be different. In such cases the presence of a solvent modifies the properties of a solute in a different manner. There are several experimental procedures that can in principle be used to obtain information on the solvation of molecules. The experimental results on various macroscopic properties provide useful information for proper understanding of specific interactions between the components and structure of the solution. The thermodynamic and transport properties are sensitive to the solute-solvents solute-solute and solvent-solvent interactions. In solution systems these three types of interaction are possible but solute-solute interactions are negligible

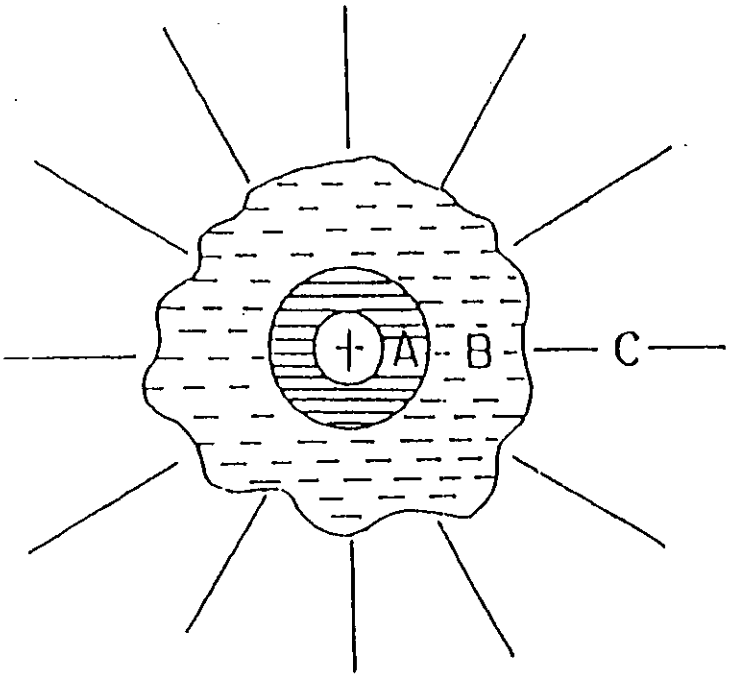


Fig. 1.1: Frank and Wen model for the structure modification produced by an ion.

at dilute solutions. The concentration dependences of the thermodynamic properties is a measure of solute-solute interaction and in the limit of infinite dilution these parameters serve as a measure of solute-solvent interactions. The solute induced changes in water structure also result in a change in solution viscosity. The variation of viscosity of solution with solute concentration is related to the size of the solute as well as solute-solvent interactions.

Many workers reported and discussed the role of water structure in water electrolytes interaction in aqueous and mixed aqueous solutions. The aqueous solutions of electrolytes contain at least two solute species, a cation and an anion. The degree of ordering of water molecules in the vicinity of an ion depends in the first instance on the ionic surface charge density. This is determined by the charge and the ion radius, so that one might expect highly charged and small ions to posses well ordered hydration spheres, whereas singly charged, large ions would not be able to align the water dipole and to overcome the effect of hydrogen bond interactions that exist in bulk water. Such ions would be classified as structure breakers, where as the former type would be classified as structure makers. The structure in question produces spherically symmetric orientations of water molecules, quite incompatible with the tetrahedral hydrogen bonded network in unperturbed water. Where as one, two or possibly even more water layers will perhaps be so oriented by a structure making ion, that there must also be a region where the magnitudes of the transmitted ion-dipole effects and hydrogen bonding between water molecules become equal, and this must lead to a structural mismatch where the water molecules are structurally and dynamically highly perturbed. The temperature sensitivity of the ionic hydration sphere is well demonstrated by the so-called viscosity coefficient B, defined by the empirical equation of Jones-Dole [35].

$$\eta_r = \eta / \eta_o = 1 + A\sqrt{C} + BC \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1.1)$$

Where η is the viscosity of a solutions of concentration C and η_o is the viscosity of the solvent. In equation (1.1) the second term on the right hand side accounts for electrostatic effects and the constant A can be estimated from Debye-Huckel type calculation. The third term arises from the short range ion-ion interactions. At 25° C the constant B is positive for structure making ions and negative for structure breaking ions.

Structure making or breaking by ions has also been studied by various dynamic methods. In particular, the life times of water molecules in the ionic hydration shell have been examined by n m r and dielectric methods. Thus in pure water at 25°C the life time of the water molecule at a given site is 1pico second (ps) [36]. The life time of a water molecule in the hydration shells of Mn^{2+} is 25000 ps. Whereas in the hydration shell of F^- it is only marginally affected (4 ps) [36]. Intermediate value has been estimated for the hydration shells of other ions, for instance Na^+ (10 ps) and Cl^- (5 ps). The diffusions rates of water molecules within the hydration shells are also affected. In the vicinity of an I^-, water rotates more rapidly than it does in bulk water, whereas the opposite effects are observed for structure making ions, where the rotational diffusion is retarded [36]. From such dynamic data it is possible to estimate the approximate height of the energy barrier for rotation of water, relative to the energy barrier in pure water [37].

Thermodynamic and transport properties furnish important information regarding the nature of solute-solvent and solute-solute interactions. The concentration dependence of these properties gives an idea of the solute-solute interaction. While their limiting values are measures of solute-solvent interactions. In the recent past thermodynamic studies on a number of nonpolar or polar solutes with nonpolar side chains have been undertaken to apprehend the so called "hydrophobic effect [38-41], Cabani [42] has critically reviewed such studies in aqueous solutions of none-electrolytes. Physico-chemical behaviour of amino acids and peptides in aqueous solution were systematically reviewed by Greenstein and Winitz [43], Lilley [44], Zamyatnin [45] Wadi and Natarajan [46] and Ahluwalia [47] respectively. They discussed the water structure in water-amino acid and water-peptide group interaction in aqueous and mixed aqueous solutions using the results from the investigation of thermodynamic properties. Lark et al [48] reviewed the viscometric studies involving the solutions of amino acid in water.

It is well known that the concentrated salt solutions induce conformational changes in proteins. Though relatively large concentrations are needed to significantly perturb the molecular structure, there is evidence that at much lower concentrations too the protein-ion (from salt) interactions are not insignificant.

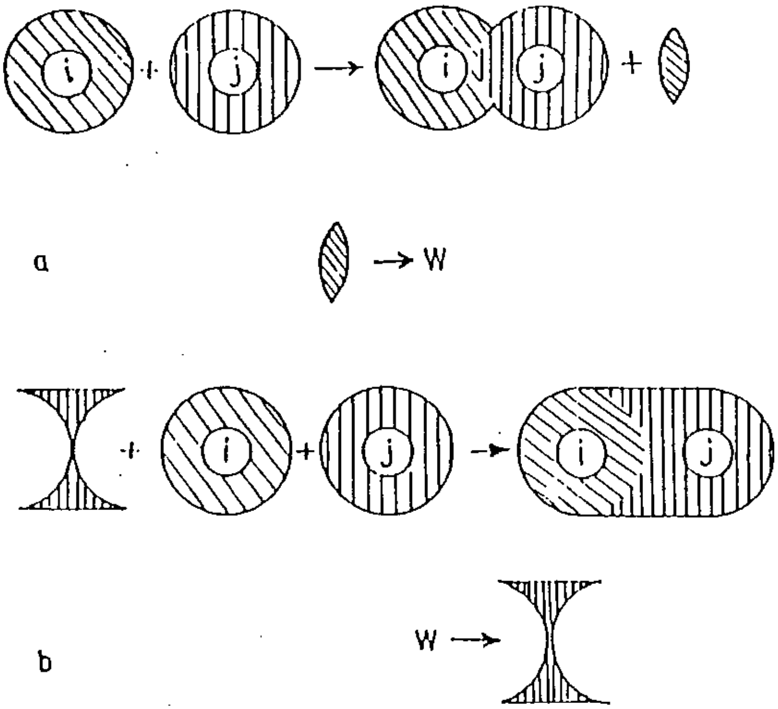


Fig. 1.2: Schematic representation of overlap of the hydration cospheres.

Friedman and Krishman [49] have suggested a model for ionic solutions based on the concepts of Frank and Evans [34], were enables to interpret the physicochemical properties of solutions. It is assumed that around an ion there is a cosphere (figure 1.2) in which the solvent properties are affected by the solutes, characterized by thermodynamics of the process:

n [solvent (bulk)] → n [solvent (cosphere)]

Where, n is the number of solvent molecules in the cosphere. When two solute particles come close together for their cospheres to overlap, as shown in Fig 1.2 (a) some of the solvent molecules from the cospheres get displaced to the bulk. This overlap effect may be described as mutual destruction of the cospheres, if the solute species, namely i and j are different, one cosphere may be disrupted before the other. Conversely, the behaviour represented in Figure 1.2 (b) shows a mutual constructive interaction as the cospheres come close together. In this the solvent gets transferred to the cospheres from the bulk.

Nevertheless it may be hoped that the changes in structure of water brought about by solute may be helped towards better understanding of the structure of water. Any acceptable model should be able not only to account for the various properties of water but must also stand in rigorous test of interpreting the behaviour of structure of aqueous solutions. The model that is commonly adopted specially in the field of solution chemistry is the Flickering cluster model of Frank and Wen [20] developed by Namethy and Scherags[50]. In this model, there are short lived clusters of varying extent consisting of highly hydrogen bonded molecules which are mixed with and alternately roles with non-bonded monomers. According to this hypothesis the water molecules are considered to be a dynamic equilibrium between the bulky tetrahedral hydrogen boned clusters and the denser monomer molecules as represented by

$$n\,H_2O \Leftrightarrow (H_2O)_n$$

This dynamic equilibrium corresponds to the transportation of water monomer to the tetrahedral structure with an average life of 10-11 sec in pure water [20,51]. When a solute is put into water, it is assumed that the solute may shift the equilibrium in either direction. A solute which causes a shift so as to increase the number and average half life of the clusters is termed a structure maker and a solute which has and effect in the opposite direction is called a structure breaker [20]. Although the concept of structure making and breaking is not entirely satisfactory. It is proved useful in discussing the effects of solute on water structure. These effects can be detected experimentally by observing the changes brought by the solutes in the properties of water such as fluidity (Reorientation time, viscosity), conductivity, heat capacity, proton magnetic resonance, ultrasonic velocity, compressibility etc. For instance, structure makers are shown to decrease the fluidity of water by causing an increase in reorientation time and increase in viscosity. The reverse is true for structure breakers.

These effects are observed in the case of electrolytes and polar substances but in the case of non-polar hydrocarbon or polar substance with large hydrocarbon chains having polar hydroxyl group it is observed that water structure increases around the hydrocarbon chain through hydrophobic hydration [51]. The average life of cluster forming along the chain being increased that it by the formation of an extra structure of this type. In the case of non-polar hydrocarbon having cyclic ring and smaller molecules containing nitrogen atom nothing significant has been found in the current literature.

In solution chemistry the importance of water's (especially for ions) physical properties and its solvent power, its various and peculiar role as a reactant or product or solvent has been the inspiration of scientist. They take water very much for granted and rarely spare a thought for its possible role in influencing the course of chemical or biochemical processes. In the present work we tried to review our knowledge of liquid water, its remarkable physical properties in the presence of some electrolytes and how these give rise to a unique liquid "structure", and its influence on the interactions between dissolved solutes. In view of the above discussion it seems interesting to investigate the effect of some electrolytes on the thermodynamic and transport properties of aqueous solution and non-aqueous (methanol-water and ethanol-water) solution. The study deals with the determination of the apparent molal volume and viscosity of several electrolytes at various temperatures.

1.2 OBJECTIVE OF THIS THESIS:

In addition to the theoretical interest of the solution chemistry as discussed in the previous section, the studies of solution chemistry have some practical application in many ways. For example it has got wide application in textile dyeing printing, leather tanning and processing, pharmaceutical, pulp and paper, sugar, agricultural, secondary recovery of oil, paint industries etc. Therefore, one of the major objectives of this thesis is to study the behavior of methanol, ethanol (widely used as chemical in many industry). In aqueous medium in the presence of different type of electrolytes were chosen for the study. In one type the anions were same but cation were different. Same ionic radious but different charge and size of cation also may be affect on water structure. Different charge and size of the ions may affect water structure differently which may be reflected by the volumetric and viscometric study of the respective solutions.

Therefore another important objective of the study is to enrich the data available in the literature in this field.

CHAPTER-2

REVIEW OF LITERATURE

2. Review of literature:

In the literature it has been seen that quite a large number of publication has been made on various aspects of liquid solutions. Among those a considerable amounts of work has been carried out on ternary mixture, although their number in comparison to the binary mixture is very limited. In this work both past and recent publications have been reviewed. A brief description of both theoretical and experimental research work related to the volumetric and viscometric studies of liquid solutions are presented here. From the beginning of 20th century a large number of equations have been proposed from time to time to explain volumetric, viscometric and thermodynamic behaviour of liquid solutions. But none of those has really been proved to be of general applicability. The first serious attempt to correlate viscosity of a solution with thermodynamic properties was made by Eyring [52] on the basis of the statistical-mechanical theory of reaction rates. More recently, the Flory's theory [53,54] of binary mixture has been extended to express mixture of viscosities.

M. Azhar Ali et. al. [55] measured V_m^E values of binary mixture of n-hexane, n-heptane and water with aniline at 298.15 and 358.15°K over the entire composition range. The systems n-hexane + aniline and n-heptane + aniline shows negative V_m^E values at higher aniline concentration and positive at lower concentration. In explaining the negative values of V_m^E they assumed the possibility of some segment of linear chain molecules being accommodated in the interstitial space between the aniline molecules.

Using batch dilatometers Kaur, et. al. [56] measured molar excess volume for binary mixtures of n-propanol, n-butanol, n-pentanol and n-hexanol with n-octane, n-decane, n-dodacane at 293.15K. The molar excess volumes were found to decrease with the increase of $-CH_2-$ groups in n-alkanol.

Chaudhury, S. X. et. al. [57] studied the molar excess volume of an n-alkanol (methanol, ethanol, n-propanol, n-butanol) and n-alkane (n-hexane, n-heptane and n-octane) + 1, 2-dichloroethane at 298.15K. They found the values of molar excess volume for all the mixtures except those with methanol and with ethanol at higher mole fraction of alkanol.

Dewan and Mehta [58] have determined the molar excess volumes (V_m^E) of different liquid mixtures of quinoline with alkanol as a function of composition at 30° C. The molar excess volumes were found negative over the entire composition range for all the mixtures which decrease with increasing the chain length of alkanols (C_1-C_{10}).

Treszeznowicz. et. al. [59] have determined the molar excess volume of mixtures of 1-alkanol + n-alkane over the entire range of composition. The V_m^E values have been found to vary from positive to negative depending on the size of chain length. In that study the changes of excess molar volume have been interpreted in terms of three contributions: effect of H-bonding, disruption of molecular order and negative effect due to interstitial accommodation of molecular segments.

Bhattacharjee et. al. [60] have measured viscosities of ternary mixtures of benzene-carbon tetrachloride, toluene-carbon tetrachloride and 0-xylene-carbon tetrachloride in cyclohexane at 298.15, 303.15 and 313.15 K. They have found that the negative value $\eta^{\Delta E}$ due to dispersion forces (non-specific interaction).

The viscosity and density of aqueous solutions of NaCl, KCl and $CaCl_2$ was determined at 25^0 C in the presence of polyvinyl alcohol by C. Holzsky, C. Suciu and D. Sandulescu [61]. They calculated the B-coefficient of Jone-Dole equation. From their experimental values and from the calculated values of B-coefficient they explained the effect of PVA on the structure forming and structure breaking properties of electrolytes. They proposed that a cage like structure is formed by the long chain PVA molecules around the smaller electrolytic ions. They explained the decreasing effect of the concentration of PVA on the structure modifying properties of electrolytes.

Singh & Yadav [62] have determined density, apparent molal volume (ϕ_v) and volume of transfer ($\Delta\phi_{v,tr}$) of urea from water to aqueous ammonium sulfate solution at 303.15 and 313.15 K. They also calculated thermodynamic quantities ($\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$) of viscous flow. They found ammonium sulfate in aqueous solutions enhance the water structure.

T.L Broadwater and L. Kay [63] have measured the density, viscosity and dielectric constant for tert-butyl alcohol-water system over the whole composition range at 25°C. They also measured the electrical conductance of KC1, $CaC1_2$, LiBr, NaBr, KBr, Me_4NBr, Bu_4NBr and Me_4NI for aqueous mixtures of *tert*-butyl alcohol upto 20 mol at 25°C. They have reported that the hydrophobic hydration of Bu_4N^+ disappears gradually as *tert*-butyl alcohol is added to water. Similar results were also reported with dioxane-water and ethanol-water mixtures.

Gangopadhy & Lahiri [64] have measured viscosity and B-coefficients of drugs (viz hydrochlorides of eyproheptadine, chloropromazine ethambutol, amodiaquin and pheniramine maleate) in water at three different temperature

(293, 298 and 303 K) They found that the single ion B_+ values to be high and positive but the dB_+/dt values to be negative. They show all drug cations can be regarded to be highly structure making in character and highly solvated.

The effect of tert-butanol on structural properties of alkali halides in water was studied by N.M Murthy and S.V. subrahmanyam [65]. In their study they observed that the effect of alkali halides on temperature corresponds to sound velocity maximum (T.S.V.M) in the order of NaCl > KCl > RbCl and KCl > KBr > KI . Their observations was explained on the basis of disruption and formation of hydrogen bonded structure of water due to the presence of different cations and anions by them.

Kapadi et al [66] have determined density, viscosity for the binary mixtures of ethanediol with water at five different temperatures 298.15 - 318.5 K From these data, molar excess volume, deviation in viscosity of the composite have been calculated. They have suggested from these result that weak hydrophobic interaction might be developed in the water rich region and its magnitude increases at low temperature.

N.M. Murthy and S.V. Subrahmanyam [67] investigated the binary solutions of water and tert-butanol, n-propanol, ethylene glycerol and glycol through the measurement of density and ultrasonic velocity at 25°C. During their investigation they observed that ethylene glycol and glycerol facilitate the breakdown of the hydrogen bonded structure of water, whereas *tret*-butanol and *n*-propanol enhance the hydrogen bonded structure of water.

Agarwal et al. [68] have determined densities and viscosities of binary mixtures of nitromethane with some polar and non-polar solvent viz.(methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, acetone, methyl ethyl ketone, methyl acetate, ethyl acetate, carbone tetrachloride, benzene and toluene) at 298.15K. From the densities and viscosities they also determined excess viscosities η^E, molar excess volume V^E and Gibbs free energy$\Delta G^{\#E}$. They proposed that negative values of η^E, V^E , $\Delta G^{\#E}$ are due to dominated dispersion type forces.

N. C. Day, H. K. Saika and I. Haque [69] have determined the relative viscosity and density of glycine in 5%, 10%, and 20% (w/w) acetonitrile-water mixture at 25°C, 30°C, 35°C and of DL alanine in water 5%, 10% and 20% (w/w) acetonitrile-water mixture. The viscosity B-coefficients have been found to increase with increasing concentration of acetonitrile and also with the increase of temperature in both cases.

M. M. Huque and D. Sandulescu [70] have investigated the effect of polyvinyl alcohol on structure breaking and structure forming properties of NaCl and KCl. They have calculated the values of *B*-coefficients of Jones-Dole equation, [η], $\Delta H^{\#}, \Delta G^{\#}$ and $T\Delta S^{\#}$ for the above solutions from the experimentally determined values of viscosity and density at 20, 25, 30, 35, and 40°C. They have mentioned that the thermodynamic of flow phenomena indicate a strong interaction between Na^+ ion and solvents.

Amaledu Pal et al. [71] have measured density and sound speeds of L-glycine in aqueous $(CH_3)_4NI$ and NaBr at 298.15K. From these data they determined apparent molar volume (V_ϕ) and compressibilities (K_ϕ).They observed that V_ϕ^o increases with increasing concentration of NaBr in solutions whereas it decreases with increasing $(CH_3)_4NI$ and NaI concentrations.

S.V. Subrahmanyam et al. [72] carried out an extensive investigation on the compressibility and temperature dependence of sound velocity maximum in water [73]. They found in their research that alkali halides indicate structure ordering effect for Li^+ & Na^+ ion and structure disordering effect for Rb^+ & K^+. In this regard, Li^+ ion was found to be more effective than Na^+ ion in structure making i.e. it enhances in the long range order in water and Rb^+ ion was found to be more effective than that of K^+ ion in structure breaking, i.e. the disruption of hydrogen bonded structure of water. For anions, the structure breaking effect was found to be in the order of $I^- > Br^- > Cl^-$.

Gunjan Maheshwar et al. [74] have determined density and viscosity of ternary liquid mixtures of pyridine with some polar (acetone and methyl ethyl ketone) and non polar (benzene, toluene and carbon tetrachloride) solvent at a constant temperature 303.15 K. Various excess functions viz. excess viscosity (η^E), excess volume (V^E), excess Gibbs free energy of activation of flow ($\Delta G^{\#E}$), interaction parameter (d) of Grunberg and Nissan equation were determined. According to their data the negative values of (η^E) due to dominance of dispersion forces between the unlike molecules. They also found that the value of $\Delta G^{\#E}$ changed from positive to negative one. This is due to interaction between the mixing components accompanied by the complex formation.

From the classical principle of thermodynamics Einstein deduced an equation, $\eta = \eta_o(1+2.5\Phi)$ for the viscosity of solution. For the expression, he considered the solute molecules were composed of spherical, incompressible, uncharged particle which were large in comparision to water molecules [75]. This equation proved valid only at low concentration.

The viscosity of electrolytic solution in terms of interionic forces was studied by Falkenhagen and Dole. They proposed that the electrical forces between ions in the solution tend to establish and maintain a preferred re-arrangement and thus to stiffen the solution, i.e. to increase its viscosity. The mathematical treatment of this effects resulted in the following limiting law for very dilute solution $\frac{\eta}{\eta_o} = \eta_{rel} = 1 + A\sqrt{C}$ Practically, this equation was of little use in calculating viscosities, since the square root term is swamped by much larger linear term expressed in the empirical equation of Jones and Dole [35]

$$\eta_{rel} = 1 + A\sqrt{C} + BC$$

Here, A is Falkenhagen's co-efficient while the empirical parameter 'B' supposedly represents the ion-solvent interaction. The B-coefficient was found to be greater or less than zero depending on the solute and to be highly specific for both electrolytes and temperature. The B-coefficients are fairly, accurately additive properties of the constituent ions. The positive values of B-coefficients correspond to the ions which are strongly hydrated (structure maker) such as Na^+, Li^+, Mg^{2+}, and La^{3+}. The negative values of B-coefficients were found for ions which exert a structure breaking effect on the solution such as Rb^+, Cs^+, I^-, ClO_3^- and NO_3^-. An extensive investigation on the effect of temperature on B-coefficient was carried out by H.S. Frank and Wen [20], R.W. Gurney[76] and H.S Frank and M.W. Evans [34]. As a result of these investigations they have drawn a conclusion that the positive value of dB/dT is for structure making effect and the negative value of dB/dT is for structure breaking effect of electrolyte.

Ali et al. [77] studied volumetric and viscometric properties of urea and D-glucose in aqueous glycine at 308.15 K. They also determined limiting apparent molar volume (ϕ_v^o) and the slope (S_v*) using Masson's equation, free energy of activation and refractive index. They found that the large positive value of (ϕ_v^o) for both glucose and urea in all the three aqueous glycine mixed solvent due to strong solute – solvent interaction.

In an investigation, A. Rashid et al. [78] measured the *B*-coefficient of Jones-dole equation, thermodynamic quantities of flow phenomena, apparent specific volume, velocity of ultrasound and adiabatic compressibility of NaCl and KCl in poly acrylamide solution within the temperature range of 20^0 to 40^0C. He observed that polyacrylamide increases the structure breaking effect of KCl but decreases the structure forming effect of NaCl.

M.M. Huque and S.T. Saad [79] studied the viscosities of aqueous solution of urotropine in the presence of NaCl and KCl and determined the thermodynamic quantities of $\Delta H_\eta^{\#}, \Delta G_\eta^{\#}$ and $T\Delta S_\eta^{\#}$ by measuring the viscosity coefficients at 20^0, 25^0, 30^0, 35^0 and 40^0C. They also calculated the value of $\Delta\mu^{\#}$ of the same solution. They have found that NaCl intensified and destroyed the structure of the solutions and urotropine reduced the structure intensifying property of NaCl but enhanced the structure destroying property of KCl.

Nikam et al. [80] have measured density and viscosity of sucrose and maltose in 0.5 M aqueous ammonium chloride solutions at 25, 30, 35 and 40° C. They analyzed density and viscosity data and calculated apparent molar volume of transfer from water to aqueous ammonium chloride solution. They found that sucrose and maltose act as structure maker in water and in aqueous ammonium chloride.

Singh and Sinha [81] determined viscosities, densities and activation energies of viscous flow of some system of alcohol and nonpolar solvents at 30^0, 40^0, 45^0 and 50^0C. They also determined the viscosities and densities of the partially miscible binary system of n-hexane and benzyl alcohol at 30^0, 40^0, 45^0 and 50^0C. They calculated the activation enthalpies and entropies of the system and have discussed their variation with concentration.

Parmar et al.[82] have determined partial molar volume of some mineral salts viz. sodium sulfate, potassium sulfate, ammonium sulfate, magnesium sulfate, di ammonium hydrogen sulfate, sodium di hydrogen phosphate and di-potassium hydrogen phosphate in water at various temperature and mineral salt concentration. They have found sodium sulfate , potassium sulfate and ammonium sulfate act as the structure breaker where as rest of these salt act as structure maker / promoter in water.

Sakurai, Masao and Nakagawa [83] determined the density of dilute solution of water in n- alkanols at 278.15, 298.15, 308.15 and 318.15K. They determined the partial molar volume of water in alkanols. The densities of dilute solutions of water in $Me(CH_2)_n$ OH, (n=0-7) was determined at 278.15, 288.15 and 318.15 K. They found that the value of ($V_m^{\propto}$) in alkanols increased with chain length of the alkanol and with temperature except for MeOH used as solvent.

Viscosities, densities, refractive indexes and enthalpies of ethylene glycol-water and dioxine-methanol system were determined by Solimo and his co-workers [84] at 25^0C. Volume change, partial molar volume, adiabatic compressibility, dielectric moment and molar viscosity was evaluated and compared with the related values in the systems of ethylene glycol-water and dioxin-methanol system. The results were interpreted on the basis of dissociation effect of the glycol by the dioxin and hydrogen bond formation.

Man Singh [85] studied densities and apparent molar volume for glycine, DL-α-alaline and β-alaline in water and water + (1,3,5 and 7M) urea solution at 288.15, 298.15 and 308.15K. He also found that the V_{ϕ}^{o} values of β-alaline were slightly higher than of DL-α-alaline and of glycine than urea for aqueous solution

F.H. Jumean [86] calculated the partial molal volume of *tris* (hydroxymethyl) aminomethane in the concentration range 0.02 to 0.05M in water and in the aqueous solutions containing 10, 20, 30, 40 and 50% (w/w) ethanol and *t*-butanol at 303.15 and 313.15K. He also calculated the partial molal volumes of transfer of *tris* from water to the aqueous alcohol solutions and found that all the transfer values are positive and they are well pronounced at 10% (w/w) alcohol. He found that the magnitude and position of maximum enhancements are temperature dependent. He also obtained the values for the partial molal expansibility of *tris* form as a function of solvent composition and observed the negative value in water and positive in most of the co-solvent system.

F.H. Jumean and M.I. Qaderi [87] determined the partial molal volume of N-methyl *tris* (hydroxymethyl) glycine (tricine) in aqueous solution containing 10, 20, 30, 40, and 50% (w/w) ethanol and *t*-butanol at 303.15 and 313.15K and observed the anomalous behaviour in the region of structure enhancement of water by both the alcohols. In water-*t*-butanol, a negative derivation in the partial molal volume at infinite dilution was observed. In water-ethanol, a positive deviation near 10% (w/w) ethanol was followed by a large drop. They also obtained the values for the infinite dilution partial molal expansibility and the infinite dilution partial molal volume of transfer from water to the mixed solvents and discussed their significance.

M. M. Huque et al.[88] have measured viscosities of different solutions containing NaCl, KCl and hexamethylene tetramine (HMTA) in 3.2% (w/v) methanol-water system at 20, 25, 30, 35 and 40°C. They also determined B-coefficient of Jone-Dole equation and $\Delta H_n^{\#}$ for viscous flow .They found that positive value of B-coefficient and dB/dT were negative for solution containing NaCl due to structure forming nature of NaCl. In mixed (CH_3OH +H_2O) solvent and in presence of HMTA, KCl changed its structure breaking effect.

T.Tomicic, K.Jvanovic, and Jovanka [89] reported that viscosity of aqueous solutions of Na-CM-cellulose containing NaCl and Na_2SO_4 was dependent on temperature, pH and concentrations. They interpreted the result according to the ionization theory of polyelectrolytes in diluted solutions.

Nikam et al [90] have measured viscosities of cesium halide (Cl^-,Br^-,I^-) $(C_4H_9)_4NBr$, NaBr and $NaBPh_4$ in (0,20,40,80) mass % aqueous acetone at 298.15K. They observed that viscosity B-coefficient for aqueous CsCl, CsBr and CsI solution were negative. For this they suggest that it may occur due to structure breaking tendency of these electrolytes in pure water.

Shirokuroiwa, Minoru Ogawa, and Motao Nakamura [91] used Na-CM-cellulose for a study of the superposition of frequency-dependent and shear rate dependent curves of viscosity and rigidity. Their results showed that: (1) superposition is possible. (2) the shift factors of the horizontal shift along the low ω (angular frequency) axis of the logω-logG` (dynamic rigidity) and logω-logη` (dynamic viscosity) curves are identical, (3) the vertical shift increases with concentration, (4) there is large dependence of η/η_o (ratio of initial to succeeding viscosities) on concentration. (5) the log η_o (non Newtonian viscosity) - logγ a (shear rate) curves and the logη-logω curves are both reduce to a composite curve by the same shift factor used in the case of a sodium polyacrylate solution.

Mandal et al. [92] have measured viscosity of 1:1and 2:2 salt in none aqueous solvent in the high concentration range at 35.0 ± 0.05°C. The result have been discussed by using Angel's equation.

Jan Wozniak [93] determined the effect of temperature, pH and concentration of commercial cellulose ethers on the viscosity and gelation temperature (T) of their 2% solution. The addition of Na_2SO_4, Na_3PO_4 lowered T. The addition of EtOH increased T and the addition of glycerol or sucrose had practically no effect on T.

Prasad et. al [94] have determined the equivalent conductance, density and viscosity of propanoate of lithium, sodium and potassium in 50% (w/w) propanoic acid + ethanol mixture at 35°C. They also determined ion pair association constant (λ_o and K_a) by using these conductance and Fuoss-Kraus and Shedlobsky extraplotation. They proposed that the positive and large value of P_v due to the presence of positive solute-solvent interaction.

They also proposed the positive B value due to alkali metal propanoate act as structure maker in this mixed solvent system.

The effect of temperature on the viscosities of cetyltrimethyl ammonium salts (CTAX, X=B_r^-, NO_3^-) in the presence of added salts was studied by Sepulveda, Luis; Gamboa, Consuelo [95]. The experimental results showed that the plots of relative viscosity vs 1/T were linear and the activation enthalpy of viscous flow were obtained from the slopes of such plots. The activation free energy ($\Delta G^{\#}$) and entropies ($\Delta S^{\#}$) for viscous flow were calculated. The $\Delta G^{\#}$ was interpreted in terms of the energy required to create a hole or an activation transition micellar structure capable of being transformed into smaller micelles and finally into spherical micelles. The $\Delta G^{\#}$ and $\Delta H^{\#}$ valued were slightly dependent on the nature of the concentrations. The more strongly bound counter ions produce the greatest effect on the energy of the rod to sphere transition.

Gupta et al. [96] have measured densities and viscosities of ternary systems involving maltose, alkali metal halides (NaCl, KCl, KBr and KI) and water at 293.15, 303.15 and 313.15 K. From this data they also determined limiting apparent molar volume. They proposed that large positive value of (ϕ_v^o) in purely aqueous medium due to interaction between solute and co-solute. They explain the nature of $V^o_{2,tr}$ following types of interaction between solute [maltose] and co-solute (NaCl, KCl, KBr and KI)

i. Interaction between the ions of co-solute (NaCl/ KCl/ KBr / KI) and hydrophilic –OH sites of maltose.

ii. Interaction between the ions of (NaCl / KCl / KBr /KI) and hydrophobic group of maltose.

Theoretical model of the structure of water were extensively and critically investigated in many review articles and books [97-99]. According to these studies each oxygen atom of water is considered to be approximately SP^3 hybridized and bonded with four approximately tetrahedral disposed hydrogen atoms. But the formation of these bonds is essentially a cooperative processes because of the mutual polarization of the participating water molecules which facilitate further bonding. Thus when favorable low energy fluctuation exists, it promotes the formation of a bond. Many of them simultaneously form a self establishing three dimensional hydrogen bonded clusters. These clusters exist and persist until these suffer collective destruction by an unfavorable (high) energy fluctuation. Thus the clusters are short lived as shown by their dielectric relaxation time (10-11s).

The interstitial model of liquid water proposed by Somoilov [98] was extensively reviewed in these articles. This model got a considerable success but in a manner places some emphasis on the concepts of quasi-crystallinity. The concept was found suitable for cold water. It would hardly be approximate over the whole temperature range within which water can exists as a liquid.

The effect of alkali ammonium bromide on the structure of water was studied by Kay et al. [100]. They determined the B-coefficient of Jone-Dole equation for these solutions and compare their result with the B-values in methanol solutions. They found that Pr_4NBr and Bu_4NBr are strong structure makers and Me_4NBr is a structure breaker but Et_4NBr has almost no effect on the structure of water.

P. S. Nikam and Mehdi Hasan [101] measured the density, viscosity and relative viscosity of mono, di and tri chloroacetic acid solutions in different compositions of water-EtOH at 30° and 36° C. From the measurement, the data obtained shows that (i) B-coefficients are positive and decreased with EtOH content in monochloroacetic acid and become negative in 34.4 and 54.1% EtOH solutions which suggest that the structure making tendency of monochloroacetic acid decreases with the increase of percentage of EtOH. (ii) B-coefficients are also positive in dichloroacetic acid solutions and decreases with increase of EtOH content, becomes minimum in 25.3 wt. % EtOH solution and then increase with further increase EtOH content. This trend suggests that the aqueous EtOH has a minimum structure order effect in 25.3 wt.% EtOH mixture in presence of dichloroacetic acid. (iii) In the case of trichloroacetic acid solutions the positive and large value of B-coefficients indicate that trichloroactic acid acts as strong structure maker in all solvent mixtures but it is found that B-value does not vary much with EtOH content indicating the same structure order ness of the aqueous EtOH solvent mixtures in the presence of trichloroacetic acid. They found that the structure making tendency of the acid follows the order, MCCA < DCAA < TCAA as evidenced by $B_{MCAA} < B_{DCAA} < B_{TCAA}$. They also found that the values of apparent molar volume at infinite dilution follow the order MCAA < DCAA < TCAA at each solvent composition.

J. S. Sandhu and Gurbir Singh [102] measured the densities of L-proline and L-hydroxy proline in MeOH-water mixtures at 298.15, 308.15 and 318.15 K and calculated the apparent molar volume of the solute. They found that the plots of apparent molar volume against concentration are linear and positive slope in the case of both the amino acids. They also found that apparent molar volume increases with increasing temperature in aqueous and MeOH-water mixtures in the temperature range 298.15- 318.15 K. It appears that primary and secondary solvation layers are found around the Zwitter ions. They noted that the value of apparent molar volume of two amino acids decreased with the addition of MeOH at all the three temperatures.

CHAPTER-3

THEORETICAL BACKGROUND

THEORETICAL BACKGROUND

3.1 General

The abnormal behaviour of water in many respects such as in viscosity, adiabatic compressibility negative relative or partial molar volume etc. (which have not yet been adequately understood) is found when many compounds of electrolytes and non-electrolytes when these are dissolved in water. It is found that the hydrogen bond plays an important role in the interaction of components which can not alone account for observed abnormal properties. The chemists generally believed that abnormalities in behaviour are structural in origin and it can be understood eventually in the light of full knowledge of structural behaviour of each component present in the solution. There are many physico-chemical methods of investigation to get an insight of the structure of the aqueous solutions. The various properties of the aqueous solutions can be explained with the help of those methods. The volumetric and viscometric measurements are more representative in character among various physico-chemical methods of study. The volumetric and the viscometric methods are the simplest and cheapest methods to measure. The structural effect on the properties of an aqueous solution can be explained by volumetric and viscometric measurements.

3.2 Physical properties and chemical constitutions:

The size, shape of molecules and their geometric arrangement is very essential to explain the composition, their structure of the molecules and the molecular interaction in the binary systems. The measurement of Bulk properties like density, viscosity, free energy, enthalpy, entropy etc. is important to study the typical properties of liquid solutions.

The various physical parameter base upon the measurement of density, viscosity, surface tension, refractive index, dielectric constant etc. have been found to fall into the following three categories:

i) **Additive properties**: An additives property is one, which for a given system is the sum of the corresponding properties of the individual constituents. Mass is strictly an additives property, as the mass of a molecule is exactly equal to the sum of the masses of its constituent atoms. Similarly, the mass of mixture is the sum of the separate masses of the constituent parts. Molecular properties such as molar volume, free energy, enthalpy etc. are the other examples of additive property.

ii) **Constitutive properties**: The property, which depends entirely upon the arrangement of atoms in the molecule and not on their number is said to be a constitutive property. The optical activity is the property of the asymmetry of the molecule and occurs in all compounds having a overall asymmetry.

iii) **Constitutive and additive properties**: These are additive properties, but the additive character is modified by the way in which the atoms or constituent parts of a system are linked together. For example, atomic volume of oxygen in hydroxyl (-OH) group is 7.8 while that in ketonic group (>CO) is 12.2. The parachor, molar refraction and viscosity etc. are other examples of this type.

3.3 Density and temperature

The density of a liquid is the mass of unit volume of the liquid. An increase in temperature of a liquid, increase the volume of the liquid, thus decreasing its density to some extent. The temperature increase brings about an increase in molecular velocity. These energetic molecules then move apart causing more holes in the bulk of the liquid. This causes the expansion of the liquid, thereby decreasing the number of molecules per unit volume and hence density.

3.4 Theories of solution

The macroscopic properties of liquids and their solutions are strictly dependent on the relative arrangement of component particles hence on the structure of the liquids. Since the structure of liquids depends on forces between molecules, their size and shapes hence their macroscopic properties must change with the change in composition. The above facts are often being ignored during their studies. However, some studies [103-106] of liquid mixture derive their comprehensive basis from the (i) cell model of liquids and also from the postulation of universal form for the intermolecular potential represented by $\epsilon_j = \epsilon^* ij\varphi\ (r_{ij} / r^*_{ij})$; where r_{ij} is the distance between centres of the molecules i and j, ϵ^*_{ij} and r^*_{ij} are the characteristic parameters for the pair and $\varphi\ (r / r^*)$ is the universal function of its argument. No attempt has been made in these studies to elaborate the details of this observance. Flory's theory [53,54] improved for predicting the excess functions of binary mixtures from the equation of state properties of pure liquids. The theory originally derived for non-polar liquids, its claims general applicability through the use of an adjustable parameter. As a matter of fact, this is the only theory which have been extended for application to mixtures in which the component molecules may appreciably differ in structure.

3.5 Flory's theory of liquid mixtures: In order to make the treatment applicable to even non-spherical molecules, any molecule of a liquid is considered to have r segments and each segment to have 3c outer degrees of freedom. The partition function Z of a liquid having N molecules has been given by the expression,

$$Z = Z_{comb} \, [\, \Gamma(V^{1/3} - V^{*\,1/3})^3]^{rNc} \exp(-E_o/KT) \qquad (3.2)$$

where Z_{comb} is the combined factor for accounting the number of ways of arranging all of the segments (rN), Γ is the geometric factor and v and v* are the volume per segment and hard core volume per segment, respectively. The molar volume of the liquid (V) and the characteristic molar volume (V*) are related to v and v* through the relations,

$$V = vrN \qquad (3.3)$$

and $$V^* = v^*rN \qquad (3.4)$$

respectively. E_o in equation (3.2) is the mean interaction energy given by the relation,

$$E_o = -Nrs\epsilon / 2v \qquad (3.5)$$

where s is the number of intermolecular contact sites per segment and ϵ is a constant characterising the energy of interaction for a pair of nearest sites. Defining curtail volume (v), curtail pressure (p) and curtail temperature (T), as

$$\bar{v} = {}^{v}\!/_{v^*} = {}^{V}\!/_{V^*} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \qquad (3.6)$$

$$\bar{P} = p/p^* = 2pv^{*2}/S\epsilon \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \qquad (3.7)$$

and $$\bar{T} = T/T^* = 2v^*CRT/s\in \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \qquad (3.8)$$

the partition function Z (equation 3.2) can be represented in its curtail form as, $Z = Z_{comb} (\Gamma v^*)^{rNC} (\bar{v}^{1/3} - 1)^{3rNC} \exp(rNC/ \bar{v}\bar{T}$ ... ... (3.9)

The curtail equation of state is given as

$\bar{p}\bar{v}/\bar{T} = \bar{v}^{1/3}/(\bar{v}^{1/3} - 1) - 1/\bar{v}\bar{T}$ ... .(3.10)

3.6 Application of Flory's Theory to Binary Solutions

For a binary solution of N_1 and N_2 molecules of mixture 1 and 2, the interaction energy (E_o) is given by the relation:

$-E_o = (A_{11} \in_{11} + A_{22} \in_{22} + A_{12} \in_{12})/v$ ... ... (3.11)

where A_{11}, A_{22} and A_{12} are the number of contacts of type 11, 22 and 12, respectively and $\in_{11}$, $\in_{22}$ and $\in_{12}$ are the corresponding interaction energies of different types of contacts. Let us consider r_1 and r_2 are the number of segments of the molecules of the two mixtures. Since same hard core volume is guessed at the segments of the two species, $r_1/r_2 = v_1^*/ v_2^*$. Let us also consider s_1 and s_2 to be the available contact sites on the segment of component 1 and 2 and are in the ratio of the molecular surface areas of contact per segment. It can be shown that

$$s_1/s_2 = (V_2^*/V_1^*)^{1/3}$$

Since, $A_{11} + A_{12} = s_1 r_1 N_1$ ... ... (3.12)

and $2A_{22} + A_{12} = S_2 r_2 N_2$... ... ... (3.13)

it follows that

$- E_o (s_1 r_1 N_1 \in_{11} + S_2 r_2 N_2 \in_{22} - A = \Delta \in)/2v$... ... ... (3.14)

Since $\Delta \in = \in_{11} + \in_{12} - 2\in_{12}$... ... ... (3.15)

On the assumption of perfect random mixing of molecules of the mixture, equation (3.14) may be written as

$-E_o / \bar{r}N = (s/2v)(\theta_1^2 \in_{11} + \theta_2^2 \in_{22} + \theta_1 \theta_2 \in_{12})$ ... ... (3.16)

where $\bar{r} = (r_1N_1 + r_2N_2) / N, (N = N_1 + N_2)$

and $\theta_1 = r_1s_1N_1/\Sigma r_jN_js_j$ ... ... (3.17)

The segment fraction is defined as

$\varphi_1 = r_1N_1 / Er_jN_j$ ... ... (3.18)

Substituting the values of $p_1^* = s_1 \in_{11} / 2v^{*2}$ and $P_2^* = S_2 \in_{22}/2V^{*2}$, it can be shown that equation (3.16) can be written as

$-E_o/ \bar{r}N = P^*v^*/ \bar{v}$ ... ...(3.19)

where $P^* = \varphi_1P_1^* + \varphi_2P_2^* - \varphi_1\theta_2X_{12}$ ... ...(3.20)

and $X_{12} = s_1\Delta \in /2V^{*2}$... ... ...(3.21)

X_{12} is a measure of interchange energy vertically of contacts between unlike species in a mixture at the expense of contact between like molecules. It is a disposable parameter of the theory and can be determined from the experimental values of an excess thermodynamic function (usually H_m^E or V_m^E at mole fraction 0.5. For instance, X_{12} may be obtained from the relation,

$H_m^E = x_1p_1{}^*V_1{}^* \left[\frac{1}{\bar{v}_1} - \frac{1}{v}\right] + x_2p_2{}^*V_2{}^* \left[\frac{1}{\bar{v}_2} - \frac{1}{v}\right] + (x_1V_1{}^*\theta_2 X_{12})/ V$... ... (3.22)

3.7 THEORY OF DENSITY OF LIQUID:

The density of a liquid may be defined as the mass per unit volume of the liquid, the unit volume being cubic centimeter (cm^3) or milliliter (ml). Since the milliliter is defined to be the volume occupied by one gram of water at temperature of maximum density (4°C), the density of water at this in C.G.S system is unity. The density of water at any other temperature is expressed relative to that at 4°C. and is expressed as $d_{4^0}^{t^o}$. The relative density d^{t^o} of a substance at any specific temperature is the ratio of the weight of a given volume of the substance to the weight of an equal volume of water at the same temperature. The absolute-density of a certain substance at t°C is equal to the relative density multiplied by the density of water at that temperature. Since the density of a liquid at different temperature is solely dependent on the volume of the liquid at the corresponding temperature, the volumetric study is fully based on density measurement.

3.8 Molar volume and apparent molar volume of binary mixtures:

Molar volume: The volume occupied by one gram molecule of a substance is called molar volume. It may be expressed as

$$V_m = \frac{M}{d} Cm^3.mol^{-1} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.23)$$

Molar volume is additive for ideal mixture. When two components are mixed together there may be either a positive or a negative deviation in volume. The positive deviation in molar volume i.e., volume expansion has often been explained by the break down of the mode of association through H-bonding of the associated liquids. The negative deviation in molar volume i. e., volume contraction may be due to the decrease in the intermolecular distance between the interacting molecules or by interstitial accommodation of smaller species in the structural network of the large species. The deviation of volume from ideal additivity for binary mixtures is given by excess molar volume.

Excess Molar volume: For binary systems the molar volumes of pure components, V^o and of mixtures, V_{mix} is given by the relation:

$$V^o = \frac{M}{d} \quad \dots \qquad (3.24)$$

$$V_{mix} = \frac{X_1M_1 + X_2M_2}{d_{mix}} \quad \dots \qquad (3.25)$$

and the ideal molar volume of this system is given by

$V_{ideal} = X_1V^o_1 + X_2V^o_2$

$$\text{Or, } V_{ideal} = \frac{X_1M_1}{d_1} + \frac{X_2M_2}{d_2} \quad \dots \qquad (3.26)$$

When M_1 and M_2 are the molecular weights of components 1 and 2, X_1 and X_2 are the mole fractions of components on 1 and 2, d_{mix} is the density binary mixture, d_1 and d_2 are densities of pure components 1 and 2. So the excess molar volume V^E_m is given by the relation.

$$V^E_m = V_{mix} - V_{ideal} \quad \dots \qquad (3.27)$$

3.8.1 Apparent / Partial molal volume

The apparent molal volume of a solute in a solution generally denoted by ϕ_v is defined by that relation [107]:

$$\varphi_V = \frac{V - n_1 \bar{V}_1^o}{n_2} \quad \dots \qquad (3.28)$$

Where, n_1 and n_2 are the number of moles of the solvent and solute respectively, and $\bar{V}_1^o$ is the molal volume of the solvent at specified temperature and pressure.

For binary solution, the apparent molal volume ϕ_v is determined from density measurements. In terms of the experimentally measured density (ρ), the apparent molal volume of an electrolyte in an aqueous solution is given by [108]:

$$\varphi_V = \frac{1}{n_2}\left(\frac{n_1 M_2 + n_2 M_2}{\rho} - n_1 \bar{V}_1^o\right) \dots \dots \dots\dots \dots \dots \dots\dots \qquad (3.29)$$

Where n_1 and n_2 are number of moles, M_1 and M_2 are molar masses of solvent and solute respectively.

For molal concentration scale $n_2 = m$, the molality and $n_1 = 55.51$, the number of moles of solvent (water) in 1000 g of solvent (water), then the equation for apparent molal volume takes the form [107,108]:

$$\phi_v = \frac{1}{\rho}\left[M_2 - \frac{1000}{m}\left(\frac{\rho - \rho_o}{\rho_0}\right)\right] \dots \dots \dots\dots \dots \dots \dots\dots \dots\dots \qquad (3.30)$$

$$= \frac{1}{\rho}\left[M_2 - \frac{1000}{m}\left(\frac{W - W_o}{W_o - W_e}\right)\right] \dots \dots \dots\dots \dots \dots \dots\dots \dots\dots \qquad (3.31)$$

Where, ρ_o and ρ are the densities of the solvent and solution and W_e, W_o and W are the weight of empty density bottle, weight of density bottle with solvent and weight of density bottle with solution respectively.

If the concentration is expressed in molarity, the equation (3.29) takes the form

$$\phi_v = \frac{M_2}{\rho_o} - \frac{1000(\rho - \rho_o)}{C\rho_o} \dots \dots \dots\dots \dots \dots \dots\dots \dots \qquad (3.32)$$

The relation,

$$C = \frac{m.\rho.1000}{1000+\phi_v.m.\rho_o} \quad \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots \quad (3.33)$$

is used for interconversion of the concentration on the two scales [108].

The partial molal volume of a solute is defined as the change in volume that takes place when one mole of the solute is added to an infinite amount of the solvent at constant temperature and pressure, so that the concentration of the solution remains unaltered [107, 108].

Mathematically, for the component i, it can be represented by the partial derivative of the total volume with respect to the concentration at constant T, P and n_j, where, n_j represents the number of moles of the component j as:

$$\bar{V}_1 = \left[\frac{\delta V}{\delta n_1}\right]_{TPn_j\,(j\neq i)} \quad \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots \quad (3.34)$$

The total volume V of the solution at constant T and P is given as [111].

$$V = n_1\,\bar{V}_1 + n_2\,\bar{V}_2 \quad \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots \quad (3.35)$$

For binary solution, $\bar{V}$ the solute partial molal volume of the solute. It can be expressed as,

$$V_2 = \left(\frac{\delta v}{\delta n_2}\right)_{T.P.n_1} \quad \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots\ \ldots \quad (3.36)$$

Where, the subscript 1 and 2 refer to solvent and solute respectively.

The partial molal volume of the solute and the solvent can be derived using the equation (3.28) as:

$$\bar{V}_2 = \left(\frac{\delta V}{\delta n_2}\right)_{T.P.n_1} = \phi_v + n_2\left(\frac{\delta\phi_v}{\delta n_2}\right)_{T.P.n_1} = \phi_V + m\left(\frac{d\delta_v}{dm}\right)_{T.P.n_1} \quad \ldots\ \ldots\ \ldots \quad (3.37)$$

and

$$\bar{V}_1 = \left(\frac{V - n_2\bar{V}}{n_1}\right) = \frac{1}{n_1}\left[n_1 V_1^o - n_2^2\left(\frac{\delta\phi_v}{\delta n_2}\right)\right]_{T.P.n_1} = \bar{V}_2^0 - \frac{m^2}{55.51}\left(\frac{d\phi_v}{dm}\right)_{T.P.n_1} \quad \dots\dots \quad (3.38)$$

For solutions of simple electrolytes, the apparent molal volume (ϕ_v) vary linearly with even up to moderate concentrations. This behaviour is in agreement with the prediction of the Deby-Huckel theory for dilute solutions.

Since,

$$\frac{d\phi_v}{dm} = \frac{d\phi_v}{d\sqrt{m}}.\frac{d\sqrt{m}}{dm} = \frac{1}{2\sqrt{m}}.\frac{d\phi_v}{d\sqrt{m}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.39)$$

If ϕ_v is available as a function of molal concentration, the partial molal volume of the solute and solvent can be obtained from equations (3.37) and (3.38) as

$$\bar{V}_2 = \phi_v + \frac{\sqrt{m}}{2}\left(\frac{\delta\phi_v}{\delta\sqrt{m}}\right) = \phi_v^o + \frac{3\sqrt{m}}{2}\left(\frac{\delta\phi_v}{\delta\sqrt{m}}\right) \quad \dots\dots\dots\dots\dots\dots\dots \quad (3.40)$$

and

$$\bar{V}_2 = \bar{V}_1^0 - \frac{m}{55.51}\left(\frac{\sqrt{m}}{2}.\frac{\delta\phi_v}{\delta\sqrt{m}}\right) = \bar{V}_1^o - \frac{M_1 m^{3/2}}{2000}\left(\frac{\delta\phi_v}{\delta\sqrt{m}}\right) \quad \dots\dots\dots\dots \quad (3.41)$$

Where, ϕ_v^o is the apparent molal volume to zero concentration.

When molar concentration scale is used to express ϕ_v as a function of concentration,

$$\bar{V}_2 = \phi_v + \left[\frac{1000 - C\phi_v}{2000 + C^{3/2}\left(\frac{\delta\phi_v}{\delta\sqrt{C}}\right)}\right]\sqrt{C} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.42)$$

and

$$\bar{V}_2 = \frac{2000\bar{V}_1^o(18.016/\rho_o)}{2000 + C^{3/2}(\frac{\delta\phi_v}{\delta\sqrt{C}})} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (3.43)$$

The partial molal volume and the apparent molal volume are identical at infinite dilution (m or c $\rightarrow$ o).

3.9 THEORY OF VISCOSITY OF LIQUIDS:

The viscosity of a simple fluid is it's physical characteristics of resistance to flow. The term viscosity co-efficient is usually defined as the force per unit area required to maintain a unit difference of velocity, i.e., one centimeter per second between two parallel plates of one centimeter apart. Mathematically this can be represented as:

$$\frac{F}{A} = \eta \frac{U}{S}$$

Where, η is the viscosity coefficient, S is the distance between two parallel plates of area one of which is being moved with a force F at a velocity U. The liquids having no coefficient of viscosity are said to be mobile, on the other hand the liquid of which viscosity coefficient is high does not flow readily is called viscous liquid. The theory of viscosity is developed by Eyring and co-workers, which illustrates the mechanism involved and does permit rough estimation of viscosity from other physical properties as described below:

In a pure liquid, at rest the individual molecules are constantly in motion, however, because of close packing, the motion is largely confined to vibration of each molecule within a cage formed by its nearest neighbours. This cage is represented by the energy barrier of height $\Delta G_o^{\#}/N$.

Eyring has suggested that a liquid at rest continuously undergoes rearrangements in which one molecule at a time escapes from its cage into an adjoining hole and thus the molecules move in each of the cartisian co-ordinate directions in jumps of length ‘a’ at a frequency ‘K’ per molecule, ‘K’ is given by the rate equation:

$$K = \frac{kT}{h} e^{-} \Delta G_o^{\#} / RT \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (3.44)$$

Here, k and h are Boltzman and Plank constant respectively, R is molar gas constant and $\Delta G_o^{\#}$ is the molar energy of 'activation in the stationary fluid.

In a fluid that flows in the X direction with a velocity gradient (dV_x/dY), the frequency of the molecular rearrangements is increased. This effect can be explained by considering the potential energy barrier as distorted under the applied stress 'τyx, so that

$$-\Delta G^{\#} = -\Delta G_o^{\#} \pm \left(\frac{a}{\partial}\right)\left(\frac{\tau yx V}{2}\right) \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (3.45)$$

Where,V is the volume of a molecular of liquid and ± (a/∂) $(\tau yx V/2)$ is an approximation to the work done on the molecules as they move to the top of the energy barrier, moving with the applied shear stress. Plus (+) sign indicates the movement along the applies shear stress and minus (-) indicates moment against the applied shear stress.

Defining K_f and K_b as the frequency of forward and backward jumps respectively, one can find from equations (3.44) and (3.45) that

$$K_f = \frac{KT}{h} e^{-\Delta G_o^{\#} / RT} . e^{a \tau yxv / 2\partial RT} \quad \dots \dots \dots \dots \dots \dots \dots \quad (3.46)$$

$$K_b = \frac{KT}{h} e^{-\Delta G_o^{\#} / RT} . e^{-a \tau yxv / 2\partial RT} \quad \dots \dots \dots \dots \dots \dots \dots \quad (3.47)$$

The net velocity at which the molecule ‘A’ slips ahead of those in layer ‘B’ is just the distance traveled per jump ‘a’ times the net frequency of forward jumps ($K_f - K_b$). Thus

$$V_{xA} - V_{xB} = a\,(K_f - K_b) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.48)$$

Considering the velocity profile as linear over small distance ∂ between layer 'A' and 'B' one can get

$$-\frac{dV_x}{dY} = \frac{a}{\partial}\,(K_f - K_b) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.49)$$

By combining equation (3.45), (3.46) and (3.47) finally it is found that

$$-\frac{dV_x}{dY} = \frac{a}{\partial}\left(\frac{KT}{h}e^{-\Delta G_o^{\#}/RT}\right)\left(2\sin h\frac{\partial \tau yx V}{2\partial RT}\right)\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.50)$$

It is interesting to note that equation (3.50) predicts non-Newtonian flow for liquids in general; in fact this equation has the same general form as the Eyring model,

$$\tau yx = A\ arc\ \sin h\left(-\frac{I}{B}\frac{dV_x}{dY}\right)$$

If $a\,\tau yx\,V/2\partial RT$ is small compared to unity, equation (3.50) becomes constant with the Newton's law of viscosity

$$\eta = \left(\frac{\partial}{a}\right)^2 \frac{N\,h}{V}\,e^{\Delta G_o^{\#}/RT} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.51)$$

Here N is the Avogadro's number. In most application ∂/a is taken as unity i.e., the distance between molecular layer '∂/a, is the same as the distance between the lattice points 'a'.

In the above equation the coefficient of viscosity is expressed in terms of free energy of activation $\Delta G_o^{\#}$, which is obtained empirically. Since the bonds between neighbouring molecules, which must be broken in order to make a hole, are the same as those which are broken in the process of vaporization. It follows that the energy required to form a hole is the energy of vaporization Δu_{vap}.

Therefore it can be considered that the energy of activation is proportional to energy of vaporization. It has been found that the free energy of activation $\Delta G_o^{\#}$, determined by fitting equation (3.50). Empirically it is found that: $G_o^{\#} = 0.408\ \Delta u_{vap}$. By using this empirical equation and considering $\partial/a = 1$, Equation (3.51) becomes

$$\eta = \frac{N h}{V} e^{0.408 \Delta u / RT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \tag{3.52}$$

The energy of vaporization at the normal boiling point can be roughly estimated from Trouton's rule:

$$\Delta u_{vap} = \Delta H_{vap} = 9.4\ RT_b \ldots \ldots \ldots \ldots \ldots \ldots \tag{3.53}$$

With this approximation equation (3.52) becomes

$$\eta = \frac{N h}{V} . e^{3.8 T_b / T} \quad \ldots \ldots \ldots \ldots \ldots \ldots \tag{3.54}$$

This model has got a great success and it leads to an expression for viscosity proportional to exp $\Delta G^{\#} / RT$. This Arrhenious form has long been observed to hold approximately for many liquids. One of the defects of this model, however, is that the viscosity of many liquids change exponentially with temperature only at low temperature. Further this model is unable to explain the properties such as of super cooling on glass transition region. Since the fluidity (the reciprocal of viscosity) of a liquid is proportional to the excess volume (V-V_s) i.e., to the number of vacancies introduced, Batschinski [109] pointed out that this should also be a part of an acceptable theory of liquid. A realistic theory was developed after many efforts given by Doiolittle

[110], Cohen and Tuenbull [111], Boche [112], Mc Cedo and Litovitz [113] and William, Landel and Ferry [114]. If it is considered that a fraction X_s of a shear surface is covered by solid like molecules and the remaining fraction, X_g, is covered by the gas like molecules, then the viscosity η, which is the ratio of shear stress 'f' to the rate of strain S is

$$\eta_g = \frac{f}{S} = \frac{X_s f_s + X_g g_g}{S} = X_s \mu_s + X_g \mu_g = \frac{V_s}{V}\mu_s + \frac{V - V_s}{V}\mu_s \quad \ldots\ldots\ldots\ldots\ldots (3.55)$$

The term η_g is taken as equal to the gas viscosity obtained from the kinetic theory of gases; i.e.,

$$\eta_s = \frac{2}{3d^2}\left(\frac{mKT}{\pi^3}\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.56)$$

Where, m is the molecular weight, d is the diameter of the molecules. In accordance with the generalization of Eyring's early procedure η_s is found to have the values:

$$\eta_s = \frac{Nh}{2K} \cdot \frac{b}{\sqrt{2}} \cdot \frac{V}{V_s} \, \frac{1}{V - V_s} \cdot \frac{1}{1 - e^{\theta/T}} \exp \frac{aE_s V_s}{RT(V - V_s)} \quad \ldots\ldots\ldots\ldots\ldots\ldots . \quad (3.57)$$

Here 'K' and 'a' are the transition coefficient and proportionality constant respectively, E_s is the heat of sublimation, θ is the Einstein characteristic temperature, V and V_s are the molar volume of the liquid and that of solid at the melting point respectively. Substituting the values of η_s and η_g in equation (3.55) it becomes,

$$\eta = \frac{Nh}{2K} \cdot \frac{b}{\sqrt{2}} \cdot \frac{1}{(V - V_s)} \cdot \frac{1}{(1 - e^{\theta/T})} \exp\left[\frac{aK_s V_s}{RT(V - V_s}\right] + \frac{V - V_s}{V} \cdot \frac{2}{2d^2}\left(\frac{mKT}{\pi^3}\right)^{\frac{1}{2}} \quad \ldots \,..(3.58)$$

This equation is self consist ant since if V approaches V_g the η becomes infinite and as V grows compared to V_s, η is reached to η_g. In general, this equation is adequate to predict viscosity. The V_s to be used is the molar volume of the solid like structure as it actually exists in the liquid due to the structural change and to thermal expansion or construction. The details of the experimental determination of viscosity of the liquid under study have been described in Chapter-4.

3.9.1 Poiseuille's equation and viscosity

For the determination of viscosity co-efficient usually called viscosity, can be determined by Poiseuille's equation

$$\eta = \frac{\pi r^4 P t}{8 l V} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.59)$$

Where, r is the radius of the tube, P is the driving pressure, and t is the time taken for the liquid of volume V to flow through a length *l* of the capillary tube. If the force of gravity is the driving pressure, then P can be, replaced by hρg, the product of the height of the liquid level, density of the liquid and acceleration due to gravity. So we can write equation (3.52) as follows:

$$\eta = \frac{\pi r^4 h \rho g t}{8 l V} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.60)$$

Thus the determination of absolute viscosity of a liquid by flow method is difficult and laborious one. These difficulties can be eliminated by measuring the relative viscosity of the liquid with respect to water or other standard liquid.

Let t_1, and t_2 be the times of flow of a fixed volume (V) of the two liquids through the same capillary. The expression for relative viscosity (η_1/η_2) can be derived from equation (3.60).

$$\frac{\eta_1}{\eta_2} = \frac{\pi r^4 h \rho_1 g t_1}{8 l V} \times \frac{8 l V}{\pi r^4 h \rho_2 g t_2}$$

$$= \frac{\rho_1 t_1}{\rho_2 t_2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (3.61)$$

Where, η_1 is the viscosity of solution and η_2 is the viscosity of water or standard solution ρ_1 and ρ_2 the density of solution and water respectively. We can easily determine relative viscosity from equation (3.61).

3.9.2 Viscosity and temperature

The viscosity of a liquid generally decrease with the increase of temperature, i.e. a liquid becomes more free moving at higher temperature. Numerous equations, connecting viscosity and temperature, have been proposed, but those of the exponential type, first derived independently by S. Arrhenius (1912) and J. De Guzmann (1913), are preferred due to their theoretical and practical importance

$$\eta = Ae^{-B/RT} \quad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (3.62)$$

Here 'A' and 'B' are constants for the given liquid. It follows from equation (3.62) that the plot of log η versus l/T will be a straight line. By analogy with the Arrhenius theory of reaction rates, 'B' has the dimension of work and can be regarded as the activation energy for viscous flow. It is probably related to the work needed to form 'holes' in the liquid, into which molecules can move, thus permitting relative motion to take place.

It has been suggested that before a molecule of liquid flow, it must acquire sufficient energy 'B', to push aside the molecules which surround it. As the temperature increases, the number of such molecules increase in proportion to the Boltzman factor $e^{-B/RT}$, and hence resistance in a reciprocal manner i.e. according to the factor $e^{-B/RT}$ as in equation (3.62)

At low temperature the viscosity of a liquid is usually greater because the intermolecular attractive forces simply dominate the disruptive kinetic forces. At elevated temperatures the kinetic energy of the molecules increase at the expense of intermolecular forces which diminish progressively. Therefore, the molecules of a liquid at high temperature offer less resistance to the flow and hence less viscosity.

Viscosity also depends on pressure, molecular weight or mass of the molecule, molecular size and particularly chain length, the magnitude of intermolecular forces. Non-polar liquids viz. benzene, toluene etc. have low viscosities, whereas, liquids in which direct bonding exists between the molecules e.g., glycerine, water etc. have high viscosities (where H-bonding occurs extensively).

3.9.3 Viscosity as a rate process

In a tube, liquid is considered as addition of concentric layers which follows as a rate process. When we treat the viscosity of any solution as a rate process we considered the followings:

i) The rate of motion of any layer with respect to another is assumed to involve a equilibrium state.

ii) In moving a molecule from an equilibrium state to another, a suitable 'hole' or 'site' should be available.

iii) The production of such a site requires the energy since work must be done in pushing back the molecules.

iv) The jump of the moving molecules from an equilibrium state to the next should be regarded as equivalent to the passage of the system over a plot of energy barrier.

Eyring and his co-workers using absolute reaction rate theory and partition function correlated the co-efficient of viscosity and temperature as follows:

$$\eta = \frac{hN}{V_m} e^{\Delta G^{*}/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.63)$$

Here, N = Avogrado number = 6.023×10^{23}

h = Planck's constant = 6.6252×10^{-34} Joule

R = Molar gas constant = 8.314 J mole^{-1} ^{o}K^{-1}

η = Viscosity in (poise)

V_m = Observed molar volume in cm^3

T = Temperature in Kelvin scale.

$\Delta G_\eta^{\#}$ is free energy of activation per mole for viscous flow. Again, it is known to us that $\Delta G_\eta^{\#} = \Delta H_\eta^{\#} - T\Delta S_\eta^{\#}$, so the equation (3.56) becomes

$$\eta = \frac{hN}{V_m} e^{\Delta H_\eta^{\#} - T\Delta S_\eta^{\#} / RT} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad \ldots \ldots \ldots (3.64)$$

or, $\ln \eta\, V_m/hN = -\Delta S_\eta^{\#} / R + \Delta H_\eta^{\#} /RT \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$ (3.65)

Where, $\Delta H_\eta^{\#}$ is the enthalpy of activation per mole for viscous flow and $\Delta S^{\#}$ is the entropy of activation. Since $\Delta S^{\#}$ does not much change within a range of temperature, so when in $\ln \eta\, V_m/hN$ is plotted against $1/T$ a straight line will be found. From the slope and intercept, $\Delta H^{\#}$ and $\Delta S^{\#}$ respectively can be calculated.

3.10 THEORY OF THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS:

Debye and Huckel first did the modern quantitative treatment on attractive forces between ions in electrolytic solutions. Onsasgar and Falkenhagen chiefly made the extension of this work. The essential postulate of Debye Huckel theory is that in electrolytic solution every ion may be considered as being surrounded by an ionic atmosphere of opposite sign. The net charge of the atmosphere is equal in magnitude but opposite in sign to that of central ion. The charge density is greater in the immediate vicinity of the central ion and fall off with increasing distance. This consideration of distribution of ions in solution produces an electrical potential, ϕ, for an electrolyte solution undistributed by external forces.

The electrical contribution to work content, ΔA of n_i ions and their atmosphere is given by

$$W_{(el)} = \Delta A_{(el)} = \sum_{i=1}^{n_i} \int_0^{ei} \phi(ej)de \quad \ldots \qquad (3.66)$$

Thus if an uncharged ion at constant composition is charged reversibly in a field of potential ϕ(ej) depends on the instantaneous charge e. The charging process of Debye is represented by

$$W_{(el)} = \Delta A_{(el)} = \sum_{i=1}^{n_i} \int_{\lambda=0}^{\lambda=1} ej\phi(\lambda ej)d\lambda \quad \ldots \qquad (3.67)$$

follows directly from equation (3.67) if the instantaneous charge is represented by λej. From the definition of chemical potential, μ, it is given by:

$$\mu_i = \left(\frac{\partial u}{\partial n_i}\right)_{V,T,n_1,n_2.....} = \left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_1,n_2....} \quad \ldots \qquad (3.68)$$

$$= \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_1,n_2.....} = \left(\frac{\partial F}{\partial n_i}\right)_{P,T,n_1,n_2....}$$

Gutenberg [115] suggested another charging process following equation (3.66) that the electrical contribution to the chemical potential for an ion is represented by

$$\Delta\mu_{(el)} = \left(\frac{\partial Acl}{\partial n_i}\right)_{V,T} = \int_0^{zie} \phi(ej)de \quad \ldots \qquad (3.69)$$

These two charging process give the same result for a dilute solution. In a theoretical analysis Onsasgar showed that for an electrolytic solution at higher concentration the potential of ionic atmosphere is no longer expected to be additive and thus Debye and Gutenberg charging process lead to somewhat different results. This fact was also mentioned by Gronwall, Lamer and Sandev [116]. They developed a complete integration by using Debye charging process.

CHAPTER-4

EXPERIMENTAL

EXPERIMENTAL

4.1 INTRODUCTION:

The structure changes in aqueous solution of an electrolyte to a considerable magnitude by the addition of some non-electrolytes can be visualized through the modification of some physico-chemical properties such as density, viscosity, electrical conductivity, compressibility, sound velocity, elasticity etc. In this investigation, the experimental measurements of density and viscosity of aqueous solution of $FeCl_3$, $CoCl_3$, $CuCl_2$, $MgCl_2$, $HgCl_2$ and $NiCl_2$ (electrolytes) in the presence of methanol and ethanol were carried out at different temperature (5-35^{0}C) . Here, some parameters related to density and viscosity, such as *B*-coefficients of Jones-Dole equation, apparent molar volume, thermodynamic quantities of flow phenomena were calculated from the experimental data in order to investigate the effect of methanol and ethanol on the structure modifying properties of $FeCl_3$, $CoCl_3$, $CuCl_2$, $MgCl_2$, $HgCl_2$ and $NiCl_2$ (electrolytes) on water.

4.2 REAGENTS AND CHEMICALS:

Analytical grade ferric chloride (BDH), cobalt chloride (E.Merck), cupper chloride (E.Merck), magnesium chloride (BDH), mercuric chloride, (E.Merck) and nickel chloride (E. Merck) were used as electrolytes in this study. These salts were dried for 24 hours in an oven at 105°C. The dried salts were kept in a desiccator containing anhydrous silica gel to avoid any kind of hygroscopic effect. Freshly prepared double distilled water was used as solvent to prepare stock solution of electrolytes. The double distilled water was prepared using small amount of $KMnO_4$ in a quick fit distillation plant of Pyrex glass. The specific conductance of the prepared distilled water was found to be, $Ls = 1.002\times10^{-6}$ $ohm^{-1}cm^{-1}$. In this study as non-electrolytes ethyl alcohol and methyl alcohol (E.Merck) were used. Solutions of all electrolyte salts were prepared by using an analytical balance (Metler) at room temperature. The amount of ethyl alcohol and methyl alcohol were measured with the help of pipette. The compositions of prepared solutions under investigation are presented in Table-4.1 & 4.2

Table-4.1

Concentration of different solutions with methanol investigated.

Solvent	Conc. of solvent cm^3/100cm^3	Conc. of electrolytes mol/ 100 cm^3					
		$FeCl_3$	$CoCl_3$	$CuCl_2$	$MgCl_2$	$HgCl_2$	$NiCl_2$
MeOH	0	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
MeOH	5	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
MeOH	10	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
MeOH	15	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
MeOH	20	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25

Table-4.2

Concentration of different solutions with ethanol investigated.

Solvent	Conc. of solvent $cm^3/100cm^3$	Conc. of electrolytes mol/ 100 cm^3					
		$FeCl_3$	$CoCl_3$	$CuCl_2$	$MgCl_2$	$HgCl_2$	$NiCl_2$
EtOH	0	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
EtOH	5	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
EtOH	10	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
EtOH	15	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25
EtOH	20	0.05	0.05	0.05	0.05	0.05	0.05
		0.10	0.10	0.10	0.10		0.10
		0.15	0.15	0.15	0.15		0.15
		0.20	0.20	0.20	0.20		0.20
		0.25	0.25	0.25	0.25		0.25

4.3 MEASUREMENT OF DENSITY:

In this investigation, density of each solution was measured at different temperature (5°, 15°, 25° and 35°C). For this measurement, the apparatus used was designed and made in the laboratory. Hydrostatic method (using Archimedes principle) was followed by using a glass made plumate of $2cm^3$. Both the plumate and the apparatus were first thoroughly cleaned with cleaning (chromic-sulfuric acid) mixture and then washed with enough distilled water. The weight of the plumate in air, in distilled water and in the solution under investigation were taken at different temperature. A polish made U.10 ultra thermostat was used to control the temperature within ± 0.5°C. The density of different solution were calculated by using the formula:

$$\text{Density} = \frac{\text{Weight of the plumate in air} - \text{Weight of the plumate in solution}}{\text{Volume of the plumate } (2cm^3)}$$

The temperature coefficient of the volume of plumate at low range of temperature (5°-35°C) was assumed to be negligible. The apparatus for density measurement was calibrated with redistilled water on the basis of the data (Table-4) at different temperature [117]. The density values of different solution at different temperature under investigation are presented in Appendix-1.

Table-4.4: DENSITY AND VISCOSITY OF WATER AT DIFFERENT TEMPREATURE.

Temperature	Density of water in gm/cm^3		Viscosity of water in Cp.	
	Literature Value	Obtained Value	Literature Value	Obtained Value
5°C	0.9996	0.9989	1.001	1.009
15°C	0.9985	0.9984	0.9685	0.9766
25°C	0.9971	0.9977	0.8900	0.8899
35°C	0.9941	0.9946	0.7190	0.7189

4.4 APPARENT / PARTIAL MOLAL VOLUME MEASUREMENTS:

The apparent molal volumes of different electrolytes solutions investigated were determined from the density values using the following equations [107,108]:

$$\phi_v = \frac{1}{\rho}\left\{M_2 - \frac{1000}{m}\left(\frac{W - W_o}{W_o - W_e}\right)\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.1)$$

or

$$\phi_v = \frac{1}{\rho}\left\{M_2 - \frac{1000}{m}\left(\frac{\rho - \rho_o}{\rho_o}\right)\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.2)$$

Where ρ is the density of the experimental solution, M_2 is the molar mass of electrolytes, m is the molality of the electrolyte solution and ρ_o is the density of the solvent.

The molality 'm' of a solution was calculated from molarity 'M' using the equation [107].

$$m = \frac{1}{\left(\frac{\rho}{M}\right) - \left(\frac{M_2}{1000}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.3)$$

Where M_2 is the molecular weight of solute and ρ is the density of the solution. The molarity 'M' of a solution were calculated from the following equation [118].

$$M = \frac{a}{M_2} \times \frac{1}{Vol.\ of\ solution\ in\ liter} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

Where, a = weight of solute (electrolyte) in gm.
M_2 = Solute molecule weight

Partial molal volume of electrolytes $\bar{V}_2$ and solvent $\bar{V}_1$ were calculated using the equation [107, 108].

$$\bar{V}_2 = \phi_v + \frac{\sqrt{m}}{2}\left(\frac{d\phi_v}{d\sqrt{m}}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.5)$$

and

$$\bar{V}_1 = \bar{V}_1^0 - \frac{M_1 m^{3/2}}{2000}\left(\frac{d\phi_v}{d\sqrt{m}}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.6)$$

where, ϕ_v = Apparent molar volume of electrolytes.
M_1 = molecular mass of solvent
$\bar{V}_1^0$ = Molal volume of solvent.

Molal volume of solvent (pure water) at experimental temperature was calculated using the following equation [117].

$$\bar{V}_1^0 = \frac{\text{Molecular masses of solvent}}{\text{Density of solvent (at exp. temp.)}}$$

The values of $d\phi_v / d\sqrt{m}$ were obtained from the slope of the plot of ϕ_v against $\sqrt{m}$ and the apparent molal volume. The partial molal volume of electrolytes at infinite dilution (ϕ_v^0 and $\bar{V}_1^0$ respectively) was determined from the intercept obtained by extrapolating the plot to zero concentration.

4.5 Measurement of viscosity:

The concept of viscosity is related to the flow of fluids, treated by hydrodynamics as a measure of frictional resistance that is offered by a fluid layer when another adjacent fluid layer tends to flow past over the previous layer. It is measured in terms of the steady force operative on the fluid, which is required to maintain a steady difference of velocity between two layer's of a defined area and at a defined distance from each other. When a fluid flows past a stationary plane boundary becomes almost stationary and successive layers, assume increasingly higher velocities. The frictional force (f) resisting the relative motion of any two adjacent layers is proportional to the area of interface (S) between them and to the velocity gradient

$\frac{dv}{dr}$ (According to the Newton's law viscous flow).

$$F = \eta S \frac{dv}{dr} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (4.7)$$

Where, η is known as the coefficient of viscosity or simple viscosity. It may be defined as "The force per unit area required to maintain a velocity distance of unity between two parallel layers of liquid unit distance a part".

The viscosity of different electrolytes solution taken under study was measured by using a viscometer of Ostwald type (SILVER BRAND NO. 11, 75-100 sec.) and a thermostat (B.BRAUN MELSUNGEN) were used for this purpose. The inside wall of the viscometer was first cleaned thoroughly with cleaning mixture so that there could not be obstacle due to grease or any other invisible dirt in capillary and the liquid could run freely without adhering to the inside wall of the viscometer. After that it was rinsed thoroughly with distilled water followed by acetone. The viscometer was then dried by blowing warm air. It was then clamped vertically in an open glass made transparent thermostatic bath containing clean water and a thermostat, having the temperature controlling capacity of ± 0.02°C. The viscometer was placed in such a way that the upper mark of the narrow limb was well below the water level. 10 ml. of the liquid to be investigated was taken into the viscometer with the help of a pipette and 10 minute was allowed to reach the temperature of the thermostat. A clean, dust free rubber tube was attached to the smaller arm of the viscometer and with the help of it, the liquid was sucked up of the capillary arm of the viscometer until the surface of the liquid was above the upper mark. The liquid was then released to flow freely. The time required for the surface of the liquid to pass from the upper mark to the lower mark was noted with the help of a digital stop watch. Flow time measurement was repeated for each solution until at least four successive measurements fall within 0.05 second. From the measurement of the time of flow the viscosity coefficient η was calculated by using the Poiseuille's equation

$$\eta = \frac{\pi p t r^4}{8lV}$$

Where, η is the viscosity coefficient in poise, l and r stand for the length and radius of the capillary tube, V is the volume of the liquid taken under investigation, t flow time in second by the influence of the deriving pressure p. The Poiseuille's equation can be written in the form of

$$\eta = KPt$$

Here, K is constant of proportionality given by $\pi r^4/8lV$. The pressure P at any instant driving the liquid of density ρ through the capillary of a viscometer is $h\rho g$, where h is the difference in height between the levels in each limb of the instrument. Although h varies throughout the experiment, the initial and the final values are the same in every case; so ρ is proportional to the density. The relationship between the viscosities η_1 and η_2 of two liquids 1 and 2 having densities ρ_1 and ρ_2 is

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

Here, t_1 and t_2 are the time of flow. The viscometer was calibrated by using redistilled water on the basis of the data presented in Table-4 and the viscosity data for different solutions under investigation is presented in **appendix-IV**

4.6 Determination of different thermodynamic parameters (enthalpy of activation $\Delta H_\eta^{\#}$, free energy of activation $\Delta G_\eta^{\#}$ and entropy of activation, $T\Delta S_\eta^{\#}$)for viscous flow

The value of enthalpy of activation were calculated from the plot lnη VS $\frac{1}{T}$. Other thermodynamic quantities of flow phenomena $\Delta G_\eta^{\#}$ and $T\Delta S_\eta^{\#}$ were measured by the following relations :

$$\Delta G_\eta^{\#} = RT\ln\frac{\eta V}{hN_A} = \Delta H_\eta^{\#} - T\Delta S_\eta^{\#}$$

$$\text{or}\quad \Delta S_\eta^{\#} = \frac{\Delta H_\eta^{\#} - \Delta G_\eta^{\#}}{T}$$

Therefore,

$$\Delta S_\eta^{\#} = \frac{\Delta H_\eta^{\#}}{T} + R\ln\frac{hN_A}{V\eta}$$

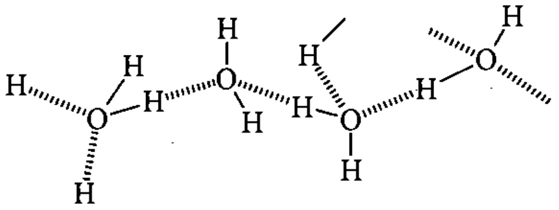
Were, $\Delta G_\eta^{\#}$, $\Delta H_\eta^{\#}$ and $T\Delta S_\eta^{\#}$ represent changes in free energy, enthalpy and entropy respectively. $\Delta H_\eta^{\#}$ has been taken as equal to activation energy of viscous flow.

RESULTS
&
DISCUSSION

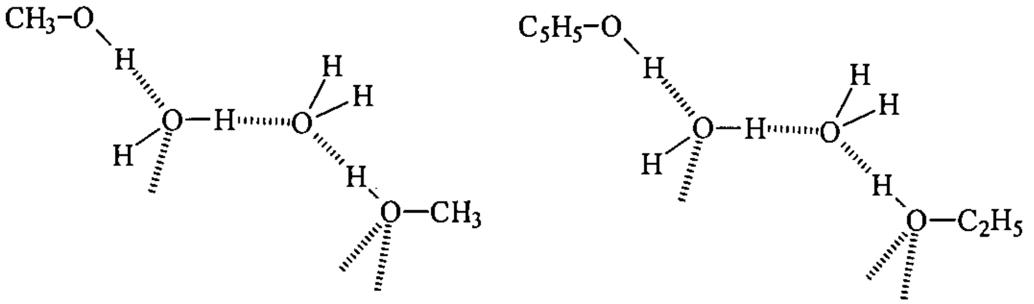
CHAPTER-5

RESULTS AND DISCUSSION

Volumetric study of an aqueous solution is important both from the theoretical and practical point of views. It gives us information about the structure of solute and solvent molecules. It also gives us information about the interaction between particles in liquid solution. In this work volumetric studies have been carried out by measuring experimentally the density of different solution of electrolytes such as chlorides of Fe^{3+}, Co^{3+}, Cu^{2+}, Mg^{2+}, Hg^{2+} & Ni^{2+} in methanol-water and ethanol-water system. The experimentally determined values are presented in appendix-I. It is observed from result that the values of density of water decrease with the increase of % of both methanol and ethanol at all temperatures. This may be due to the formation of hydrogen bonds between the water molecules and the three dimensional tetrahedral structure of methanol and ethanol molecules as shown below (Fig.5.1). It is also observed from the results presented in appendix-I that in the case of ethanol the increase density values is slightly higher than that in the case of methanol. This may be due to the bigger three dimensional molecular structure of ethanol of molecules than methanol molecules. The results represented in appendix –I also shows that for all cases the density value decreases with the increase of temperature. This follows the normal behaviour of liquid solution.



Hydrogen bonding in water



Hydrogen bonds between MeOH and water Hydrogen bonds between EtOH and watei

Fig. 5.1

The effects of different electrolytes ($FeCl_3$, $CoCl_3$, $CuCl_2$, $MgCl_2$, $HgCl_2$ and $NiCl_2$) added into the solvent mixtures are also observed in the results presented in appendix-I. The results on density values of different electrolytes presented in appendix-I shows that all the electrolytes have positive effects on the density of water and mixed solvents (water-methanol and water-ethanol). However, the extents of the effect are different for different electrolytes as discussed bellows:

It is seen in results presents in appendix-I that the positive effect of $FeCl_3$ is highest among all electrolytic salts. This may be due to the higher charge density and co-ordination number (6) than the other cations of the electrolytes. It is also observed from the results that $CuCl_2$ has minimum effect on the increase in density of water, water-methanol and water-ethanol solvents. This may be due to the lowest charge density of Cu^{2+}. However, with respect to the charge density of cations some anomalies are observed in the density values. For example, Hg^{2+} has lowest charge density but the increase of densities values is quite high, next to the Fe^{3+} ion.

The charge densities of Fe^{3+}, Co^{3+}, Cu^{2+}, Mg^{2+}, Hg^{2+} & Ni^{2+} are presented in Table 5.1.

Table 5.1: Charge density of different cations involved in this study

Cations	Coordination Numbers	Charge of ions	Radius of ions	Volume of ions	Charge density
Cu^{2+}	4	2+	0.71	1.50	1.33
Hg^{2+}	2	2+	0.83	2.40	0.83
Mg^{2+}	4	2+	0.71	1.50	1.33
Ni^{2+}	4	2+	0.69	1.38	1.45
Fe^{3+}	6	3+	0.69	1.38	2.18
Co^{3+}	6	3+	0.69	1.38	2.18

In the case of $HgCl_2$ it is also found that experiments could not carried out with higher than 0.05M concentration. Some undissolved $HgCl_2$ crystals are found to form. This may be due to the low solubility of $HgCl_2$ in water, water-methanol and water-ethanol mixed solvents.

The higher values of densities containing equimolar concentration of $MgCl_2$ than $CoCl_3$ and $NiCl_2$ may be due to the absence of d-orbital in Mg^{2+}. The presence of d-orbital in Co^{3+}, Ni^{2+} and Cu^{2+} may reduce the attraction of nucleus towards other polar water, water-methanol and water-ethanol solvent.

Information about interaction between particles in aqueous solutions of electrolytes and can be explained by the change of excess molar volume and apparent molal volume. The Excess molar volume was calculated by using the expression

$$V^{o} = M/d$$

$$V_{\text{mix}} = \frac{X_1M_1 + X_2M_2}{d_{mix}}$$

$$V^{E} = V_{\text{mix}} - (X_1V_1 + X_2V_2)$$

$$= \frac{X_1M_1 + X_2M_2}{d_{mix}} - (\frac{X_1M_1}{d_1} + \frac{X_2M_2}{d_2})$$

where

X_1=Mole fraction of solute

X_2= Mole fraction of solvent

M_1= Molecular weight of solute

M_2= Molecular weight of solvent

d_{mix}=Density of the liquid mixture experimentally determined

The apparent molal volume of different solution under study were calculated using the formula

$$\phi_v = \frac{1}{\rho}\left\{M_2 - \frac{1000}{m}\left(\frac{\rho - \rho_o}{\rho_o}\right)\right\}$$

Where ρ is the density of the experimental solution, M_2 the molar mass of the electrolytes, m is the molality of the electrolyte solution and ρ_o is the density of the solvent. The molality 'm' of the experimental solution was calculated by using the formula

$$m = \frac{1}{\left(\frac{\rho}{M}\right) - \left(\frac{M_2}{1000}\right)}$$

The calculated values of excess molar volume in appendix-II. A sample arrangement is shown tables 5.2-5.3 and in figures 5.2-5.43. It is evident from the table that excess molar volume of all solutions under study is found negative. It is observed from the results that the negative value of V^E increases with the increase of concentration both the alcohols (i.e., methanol & ethanol). However, after certain point it is found to increase with the increase of mole fraction of electrolytes and a minimum curvature is found in the diagram. The minimum of curvature indicates that at a certain composition maximum interaction take place.

Data table: 5.2 Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes($FeCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	-0.00655	-0.17278	-0.11521	-0.10594
	0.05	-0.01884	-0.01937	-0.02334	-0.02740
	0.10	-0.02074	-0.02185	-0.02436	-0.03209
	0.15	-0.02250	-0.02733	-0.02852	-0.03750
	0.20	-0.01804	-0.01972	-0.02327	-0.02692
	0.25	-0.00532	-0.01346	-0.01671	-0.01698
15°C	0.00	-0.00885	-0.18353	-0.12683	-0.11302
	0.05	-0.01458	-0.01496	-0.01925	-0.02079
	0.10	-0.01624	-0.01985	-0.02289	-0.02421
	0.15	-0.01720	-0.02184	-0.02852	-0.03396
	0.20	-0.01413	-0.02002	-0.02183	-0.02762
	0.25	-0.00773	-0.01287	-0.01340	-0.01489
25°C	0.00	-0.01033	-0.18675	-0.12996	-0.11766
	0.05	-0.01578	-0.01762	-0.02062	-0.02133
	0.10	-0.01912	-0.0202	-0.02365	-0.02684
	0.15	-0.02098	-0.02896	-0.03342	-0.03734
	0.20	-0.01218	-0.01675	-0.01717	-0.02382
	0.25	-0.00515	-0.00785	-0.00810	-0.01554
35°C	0.00	-0.01174	-0.18828	-0.13736	-0.12885
	0.05	-0.01134	-0.01677	-0.01928	-0.02135
	0.10	-0.01915	-0.02225	-0.02736	-0.02957
	0.15	-0.02100	-0.02826	-0.03345	-0.03904
	0.20	-0.01367	-0.01615	-0.01952	-0.02069
	0.25	-0.00119	-0.00503	-0.00955	-0.01703

Data table: 5.3 Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Concentration of Electrolytes ($FeCl_3$)in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	-0.01418	-0.18273	-0.12583	-0.11496
	0.05	-0.02269	-0.02665	-0.02840	-0.02995
	0.10	-0.02578	-0.03166	-0.04270	-0.04862
	0.15	-0.02620	-0.03706	-0.04788	-0.04972
	0.20	-0.01791	-0.02687	-0.02721	-0.03103
	0.25	-0.00692	-0.01550	-0.02231	-0.02959
15°C	0.00	-0.01651	-0.19353	-0.13965	-0.12666
	0.05	-0.01703	-0.01899	-0.02233	-0.02362
	0.10	-0.01852	-0.02071	-0.02593	-0.03503
	0.15	-0.02242	-0.02579	-0.02890	-0.03773
	0.20	-0.01538	-0.02012	-0.02392	-0.02673
	0.25	-0.01066	-0.01471	-0.02111	-0.02201
25°C	0.00	-0.01803	-0.19881	-0.14287	-0.13370
	0.05	-0.0191	-0.02173	-0.02692	-0.03021
	0.10	-0.02378	-0.02559	-0.03124	-0.03871
	0.15	-0.03256	-0.03873	-0.03963	-0.04932
	0.20	-0.01943	-0.02387	-0.02637	-0.03324
	0.25	-0.00555	-0.00981	-0.02026	-0.02812
35°C	0.00	-0.01949	-0.20652	-0.15473	-0.14507
	0.05	-0.02089	-0.02265	-0.02507	-0.03545
	0.10	-0.02818	-0.02931	-0.03138	-0.03875
	0.15	-0.0326	-0.03393	-0.03632	-0.04703
	0.20	-0.02094	-0.02473	-0.02552	-0.03165
	0.25	-0.00161	-0.00839	-0.01058	-0.02967

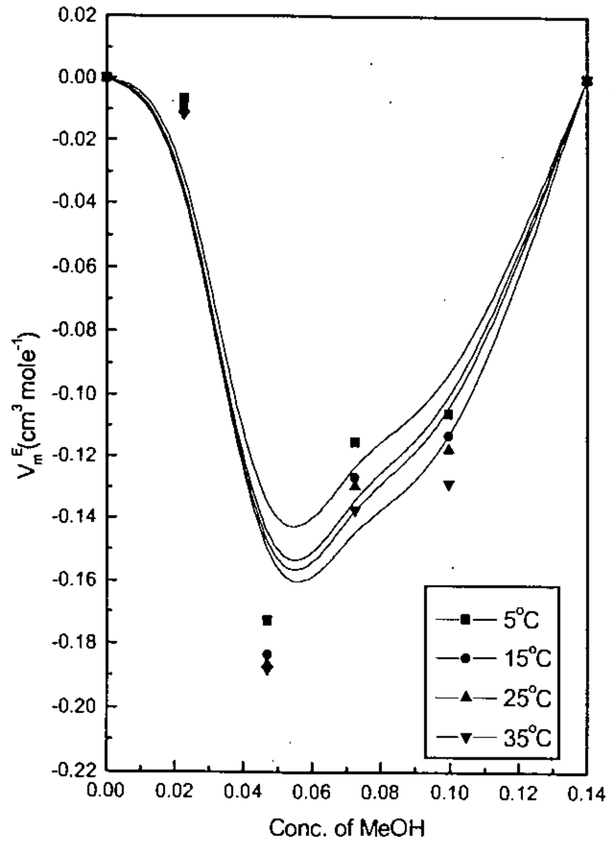


Fig.5.2 Excess molar volume of MeOH at different temperature .

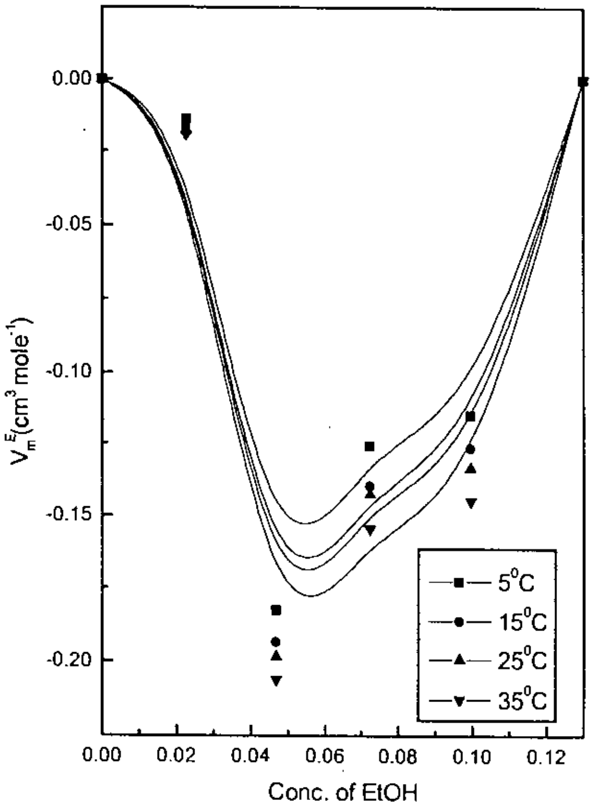


Fig.5.3 Excess molar volume of EtOH at different temperature .

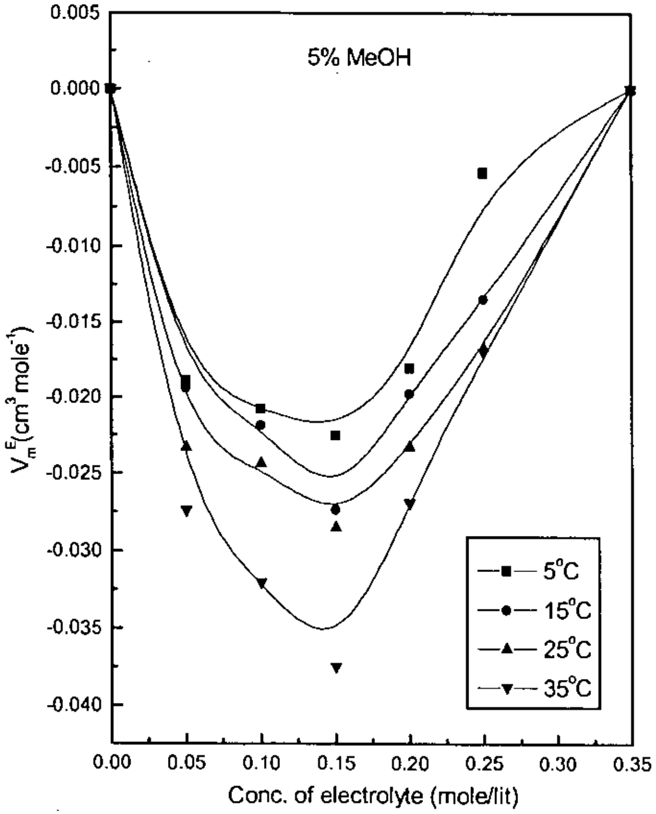


Fig.5.4: Excess molar volume of $FeCl_3$ at different temperature .

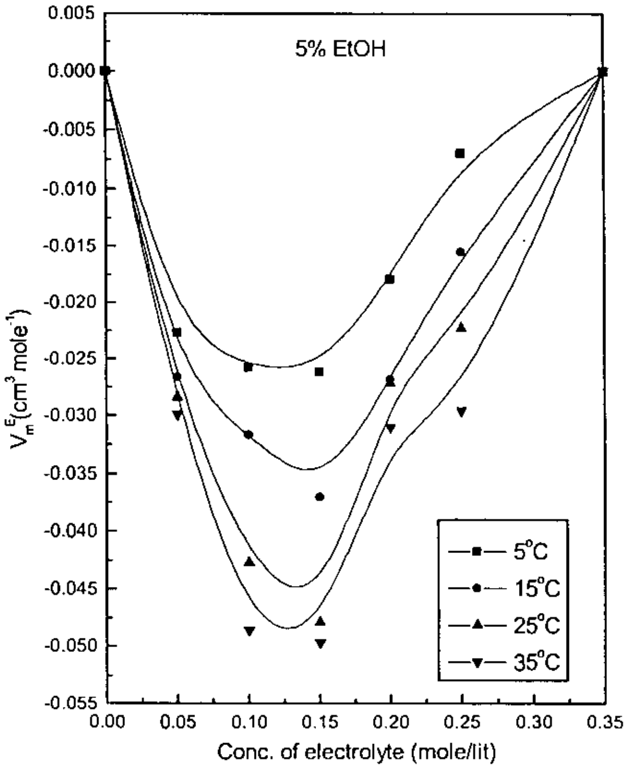


Fig.4.5: Excess molar volume of $FeCl_3$ at different temperature .

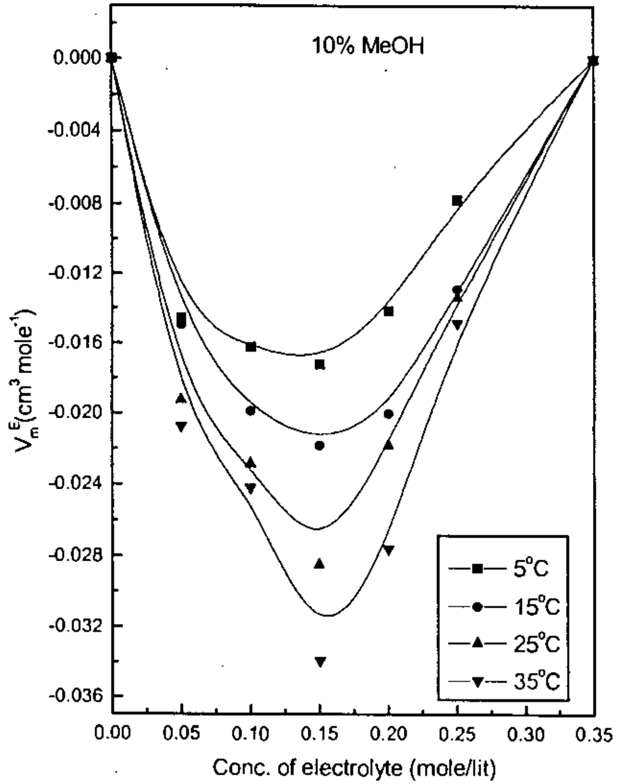


Fig.5.6: Excess molar volume of $FeCl_3$ at different temperature .

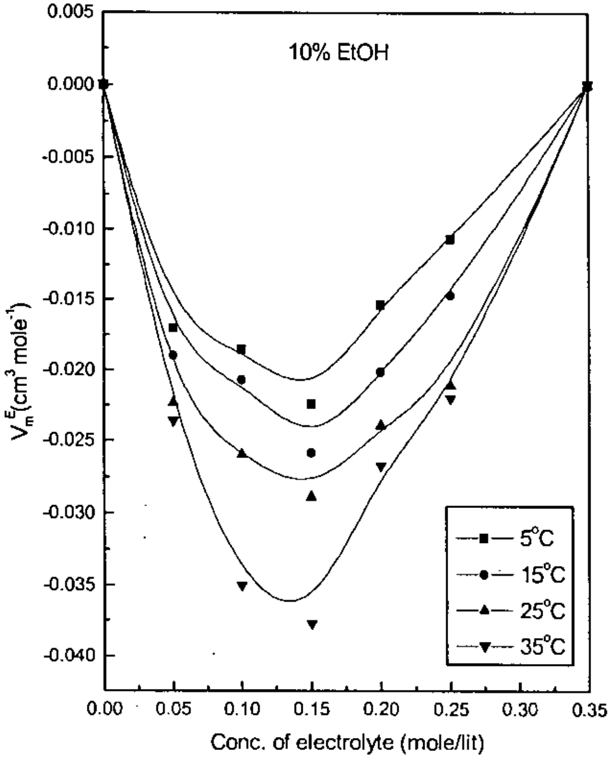


Fig.5.7: Excess molar volume of $FeCl_3$ at different temperature .

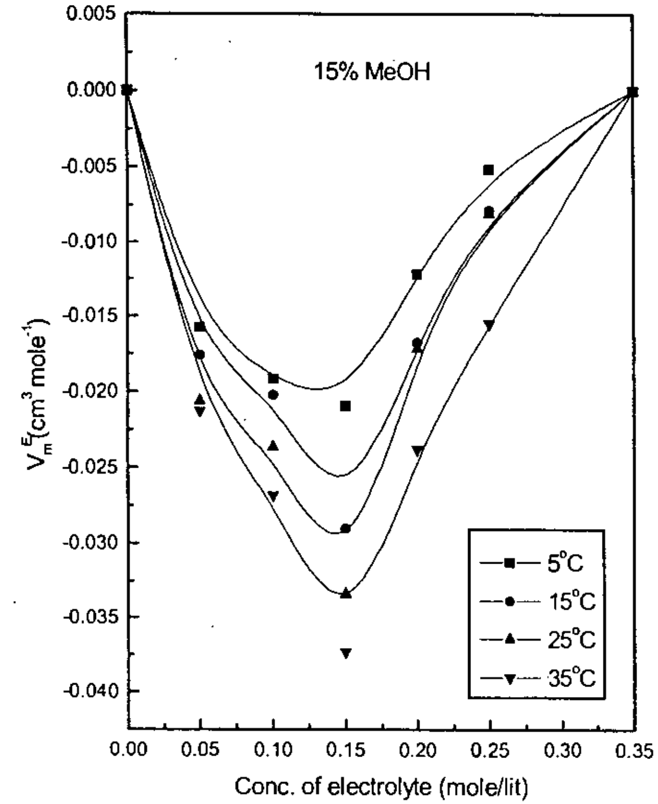


Fig. 5.8: Excess molar volume of $FeCl_3$ at different temperature .

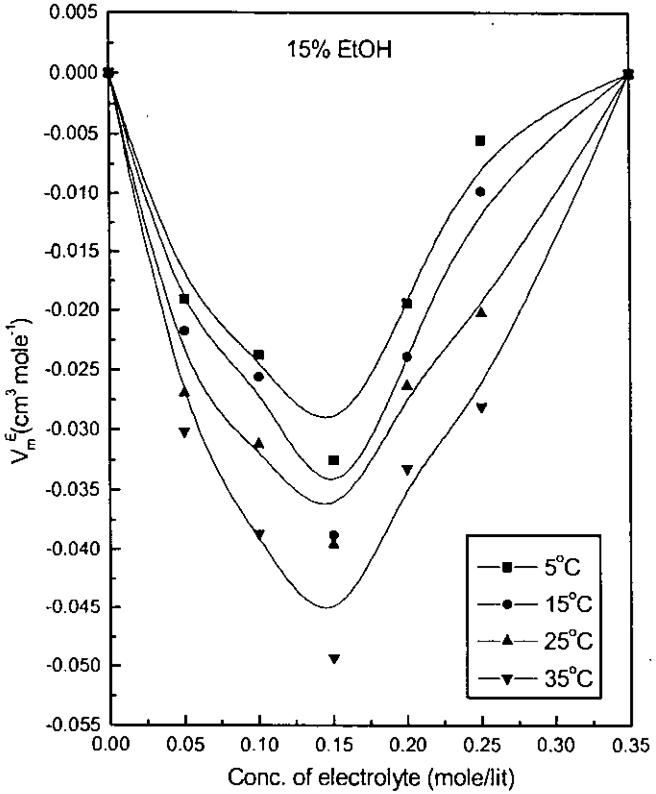


Fig.5.9: Excess molar volume of $FeCl_3$ at different temperature .

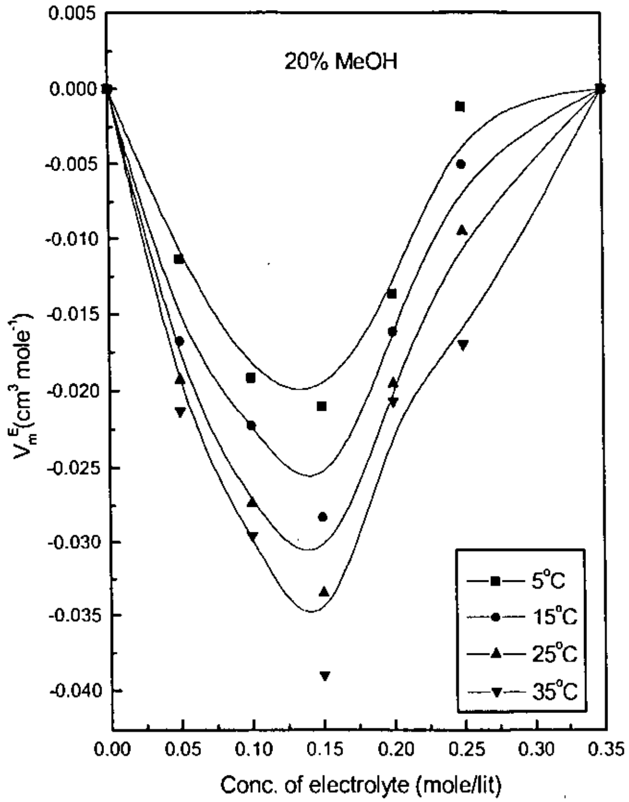


Fig. 5.10: Excess molar volume of $FeCl_3$ at different temperature .

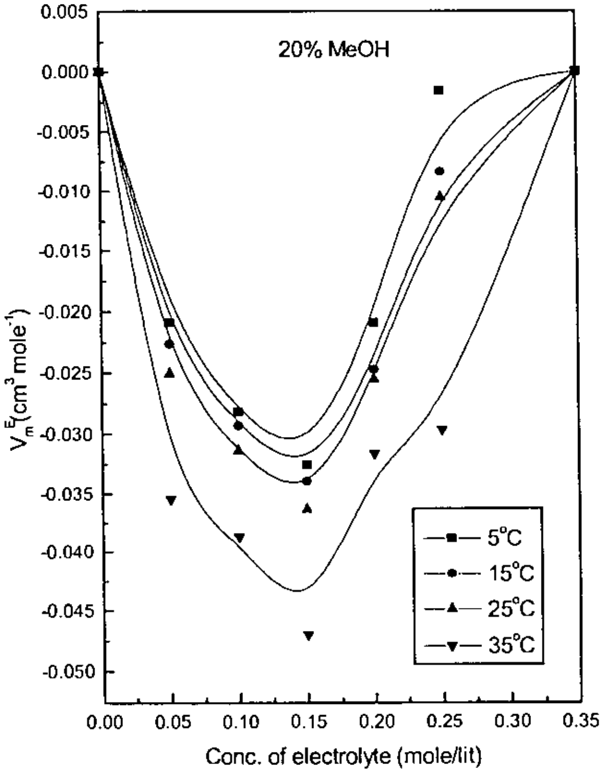


Fig.5.11: Excess molar volume of $FeCl_3$ at different temperature .

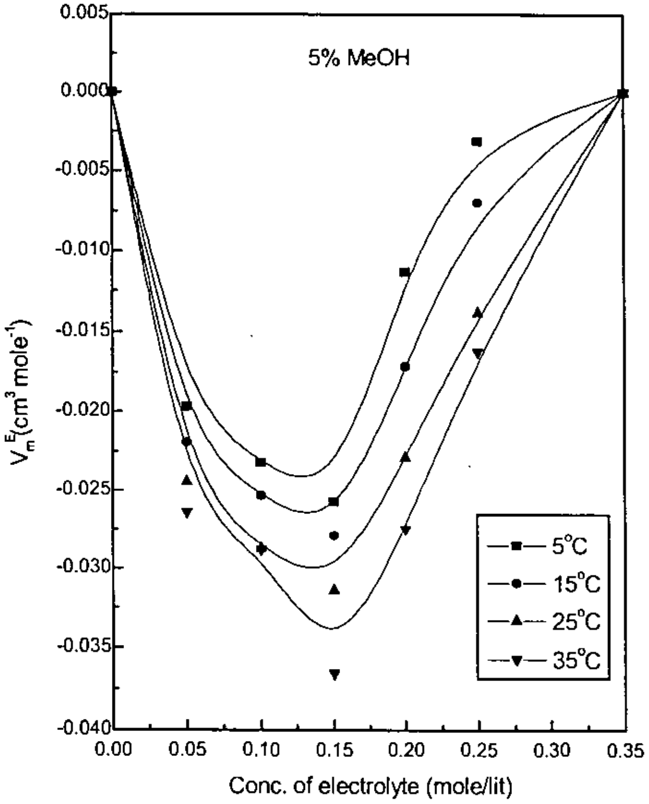


Fig. 5.12: Excess molar volume of $CoCl_3$ at different temperature .

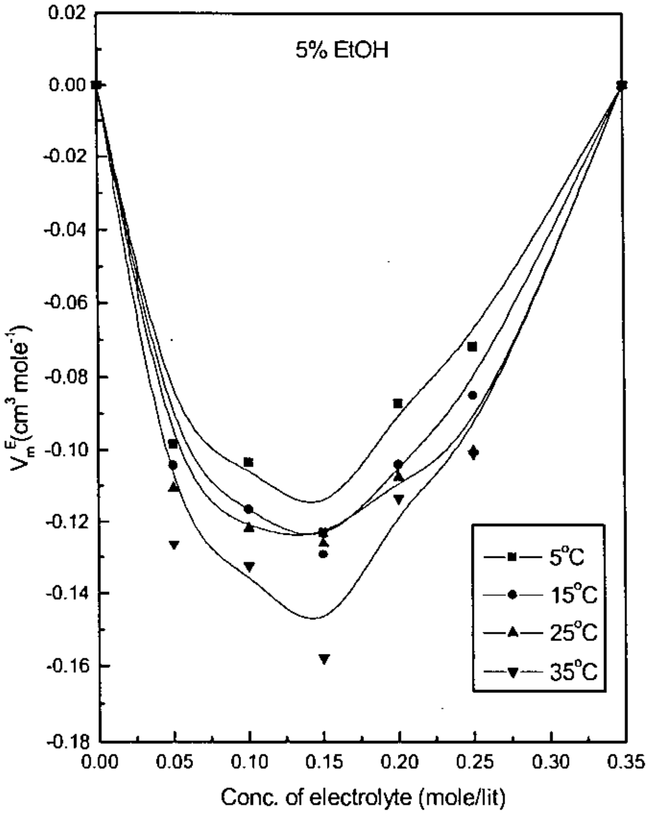


Fig.5.13: Excess molar volume of $CoCl_3$ at different temperature .

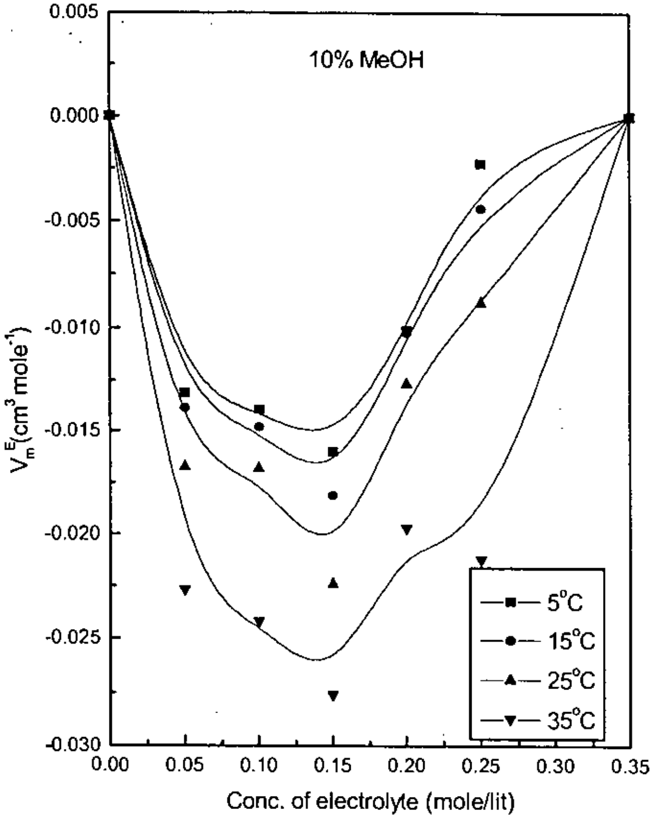


Fig. 5.14: Excess molar volume of $CoCl_3$ at different temperature .

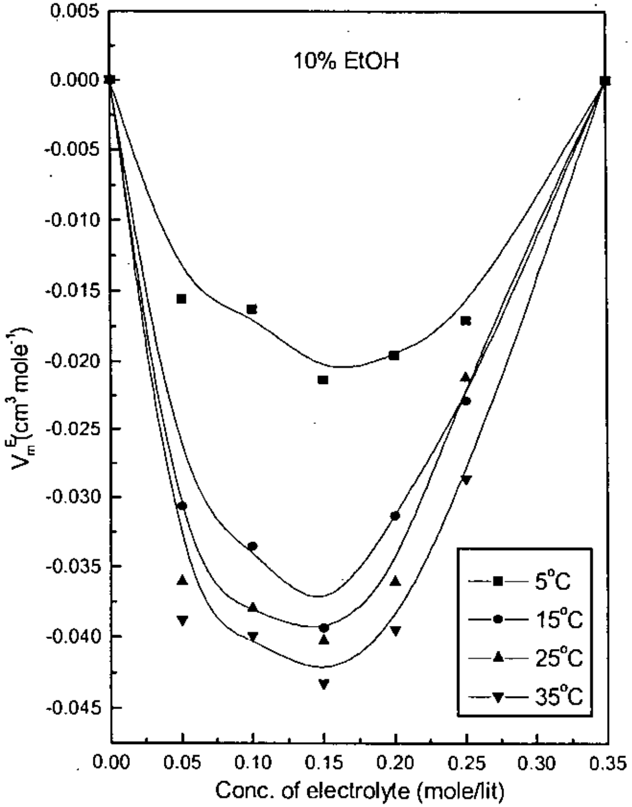


Fig. 5.15: Excess molar volume of $CoCl_3$ at different temperature .

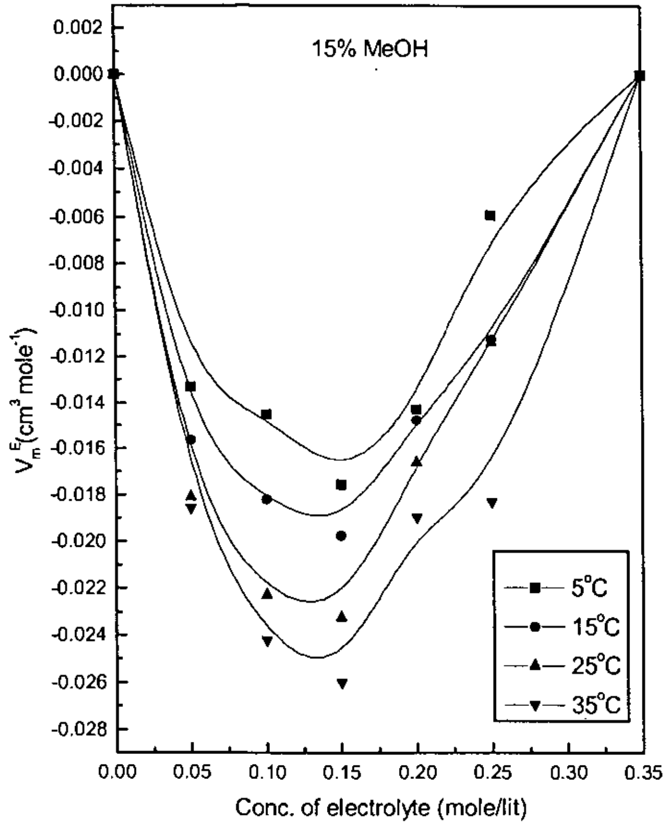


Fig.5.16: Excess molar volume of $CoCl_3$ at different temperature .

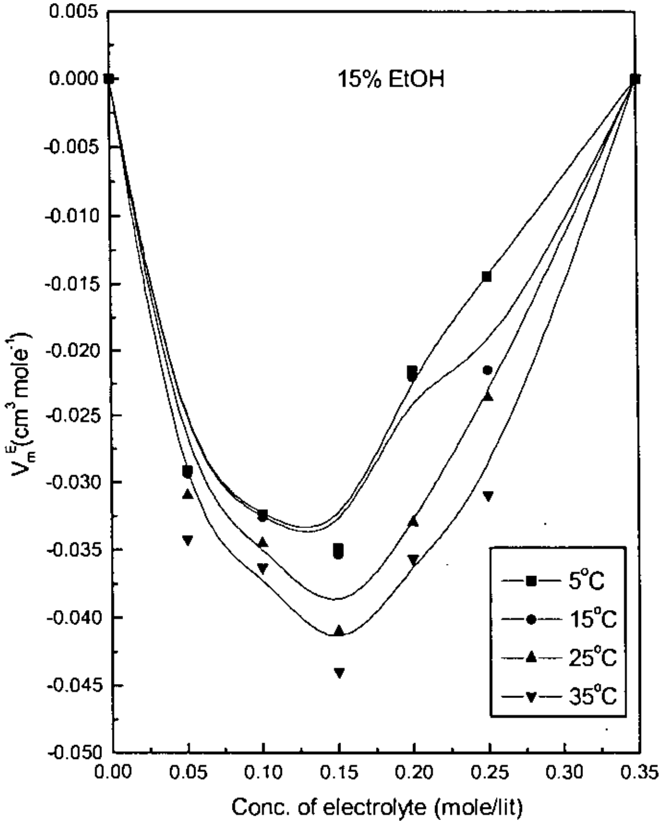


Fig.5.17: Excess molar volume of $CoCl_3$ at different temperature .

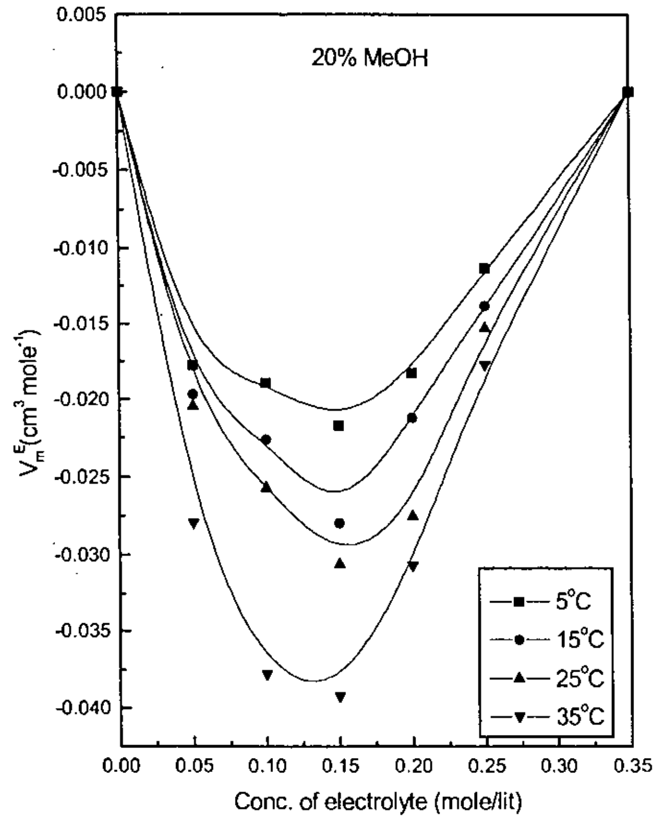


Fig. 5.18: Excess molar volume of $CoCl_3$ at different temperature .

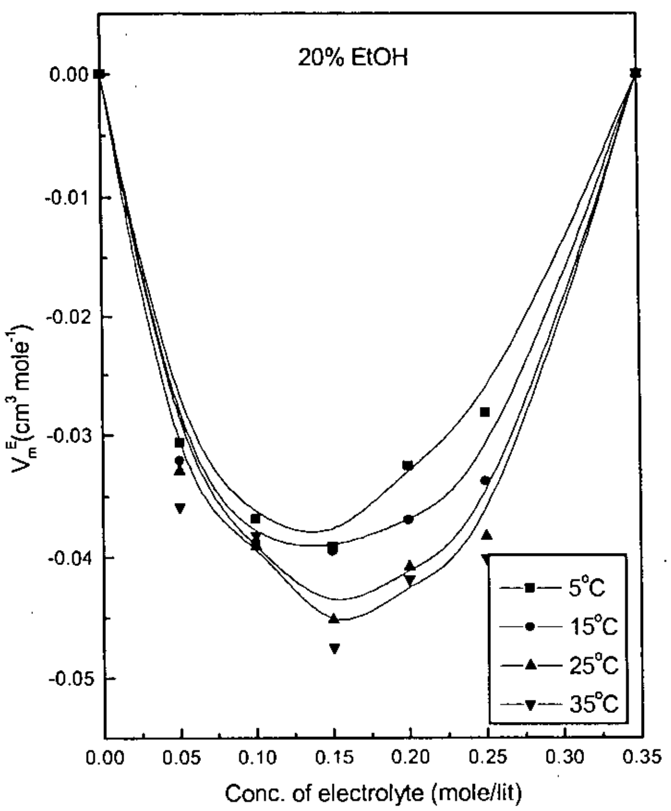


Fig. 5.19: Excess molar volume of $CoCl_3$ at different temperature .

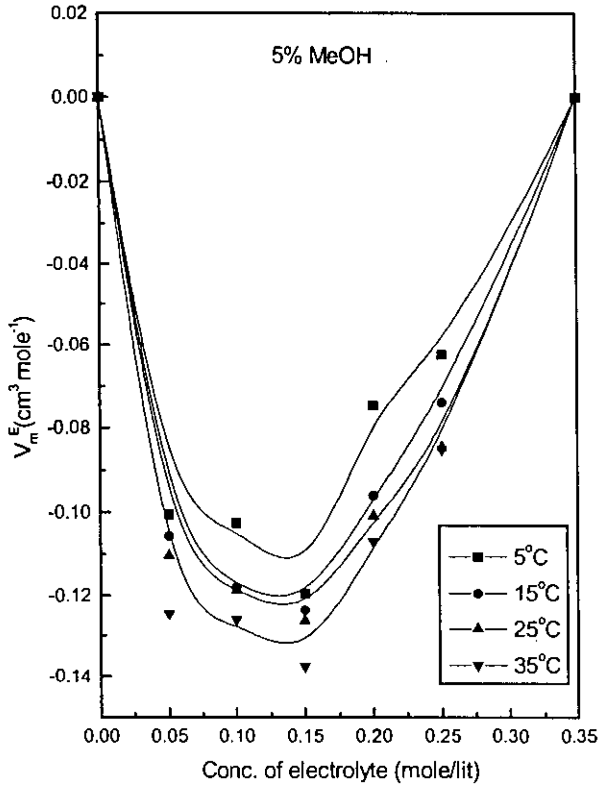


Fig. 5.20: Excess molar volume of $CuCl_2$ at different temperature .

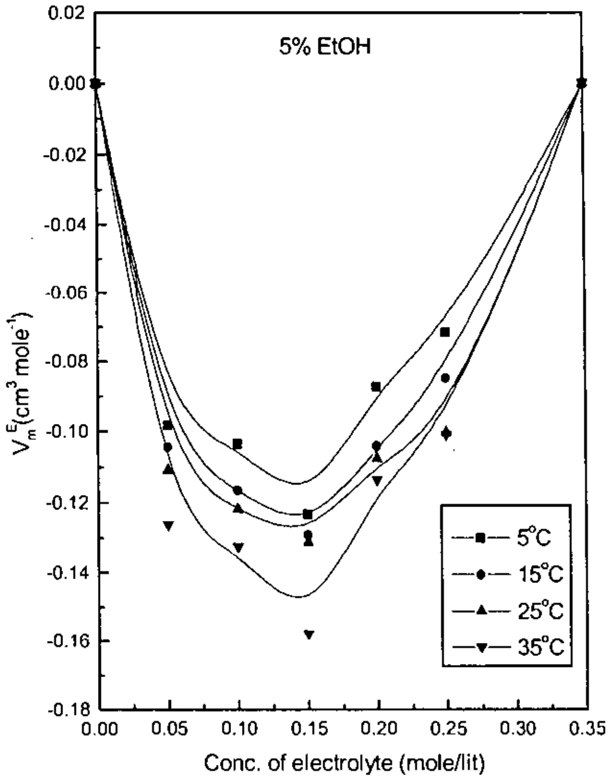


Fig. 5.21: Excess molar volume of $CuCl_2$ at different temperature .

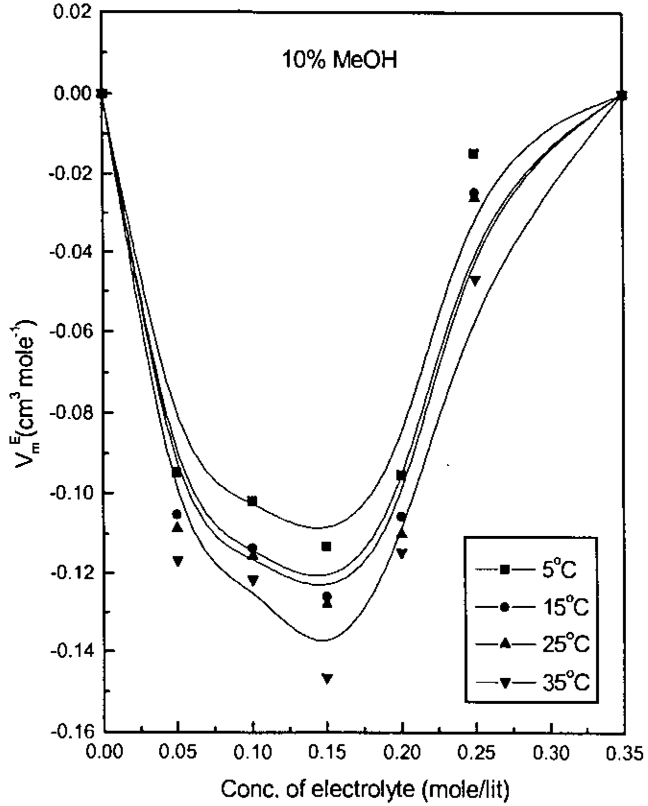


Fig. 5.22: Excess molar volume of $CuCl_2$ at different temperature .

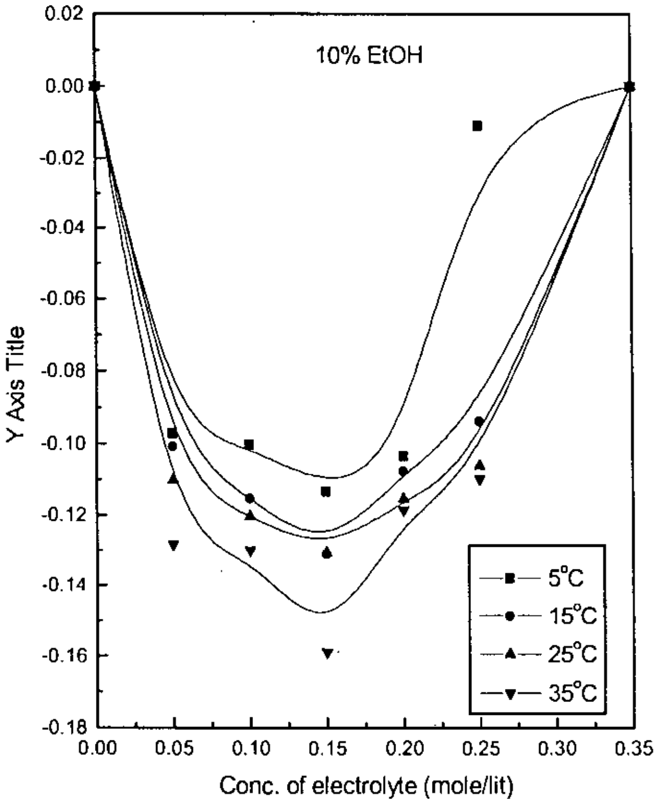


Fig. 5.23: Excess molar volume of $CoCl_2$ at different temperature .

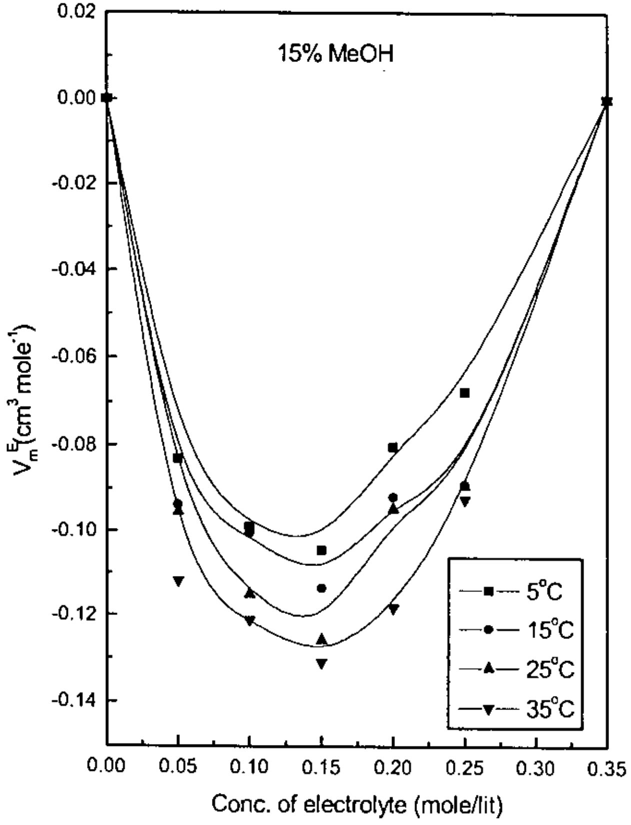


Fig. 5.24: Excess molar volume of $CuCl_2$ at different temperature .

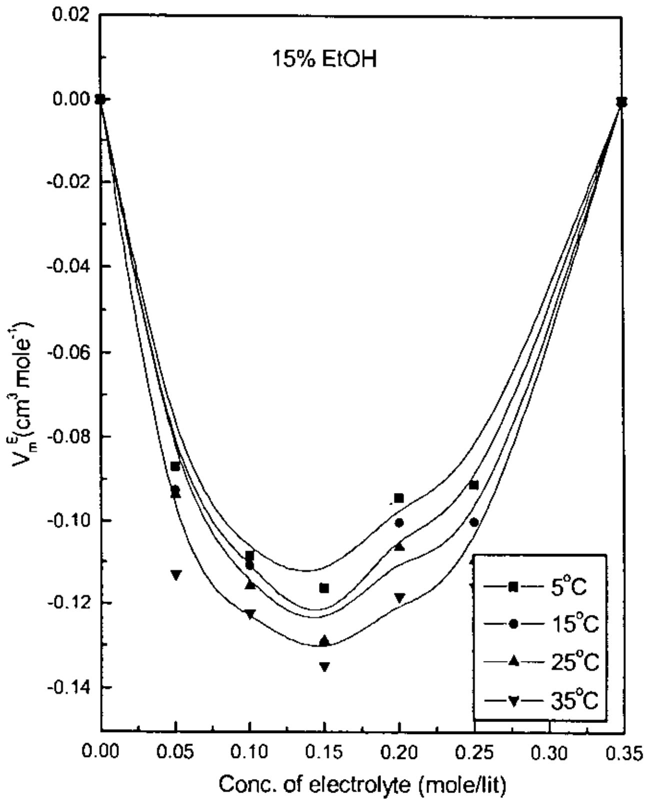


Fig.5.25: Excess molar volume of $CuCl_2$ at different temperature .

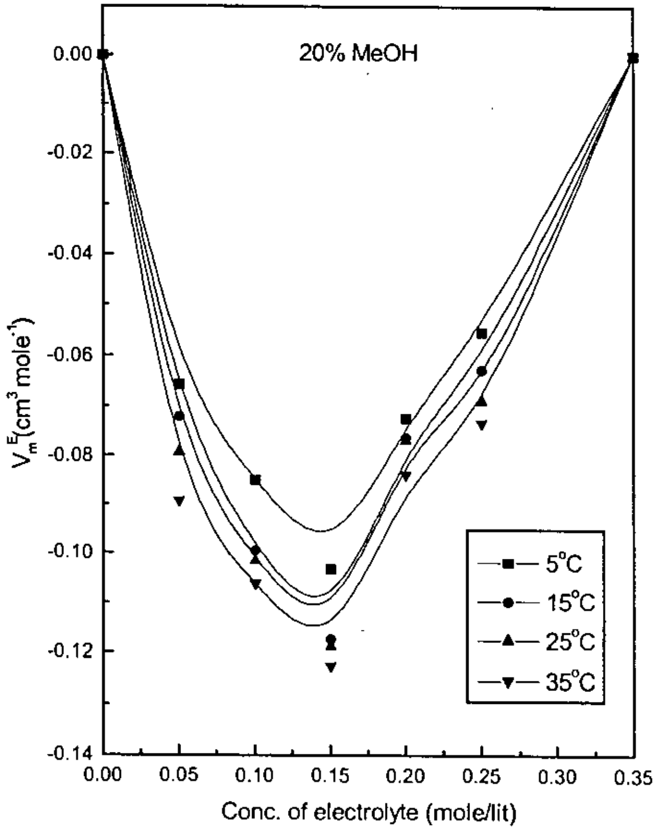


Fig. 5.26: Excess molar volume of $CuCl_2$ at different temperature .

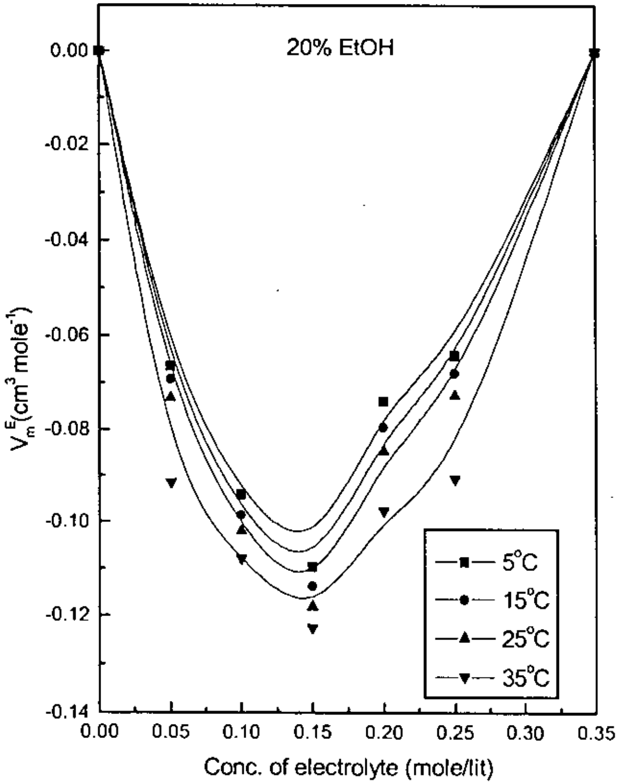


Fig.5.27: Excess molar volume of $CuCl_2$ at different temperature .

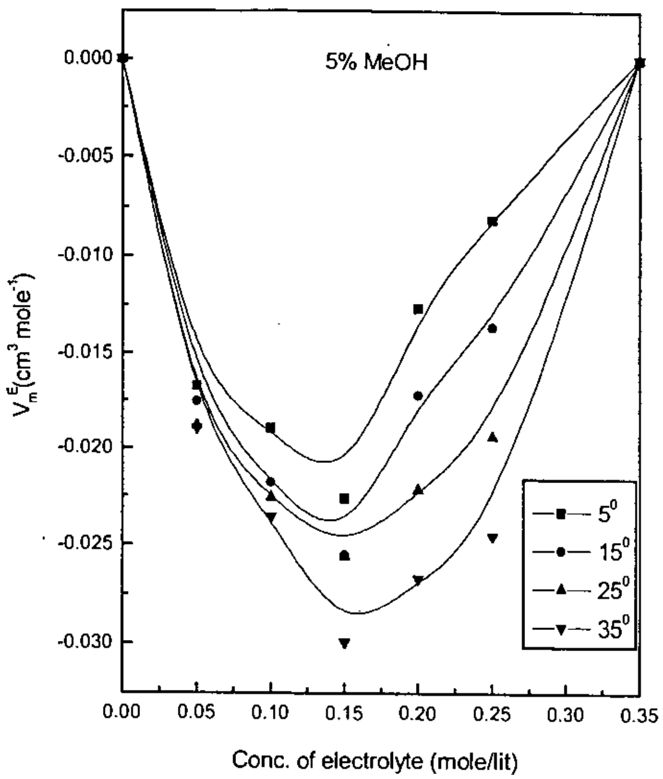


Fig.5.28: Excess molar volume of $MgCl_2$ at different temperature .

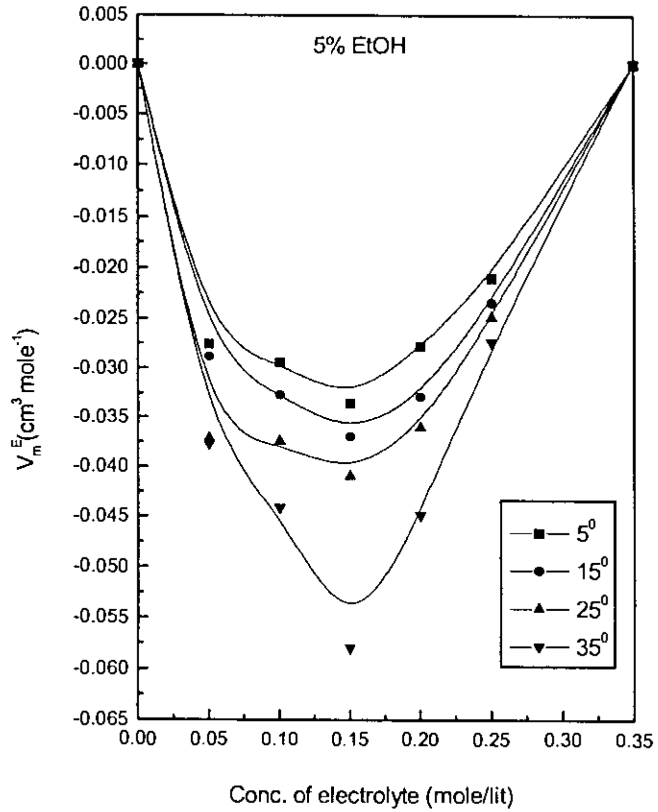


Fig.5.29: Excess molar volume of $MgCl_2$ at different temperature .

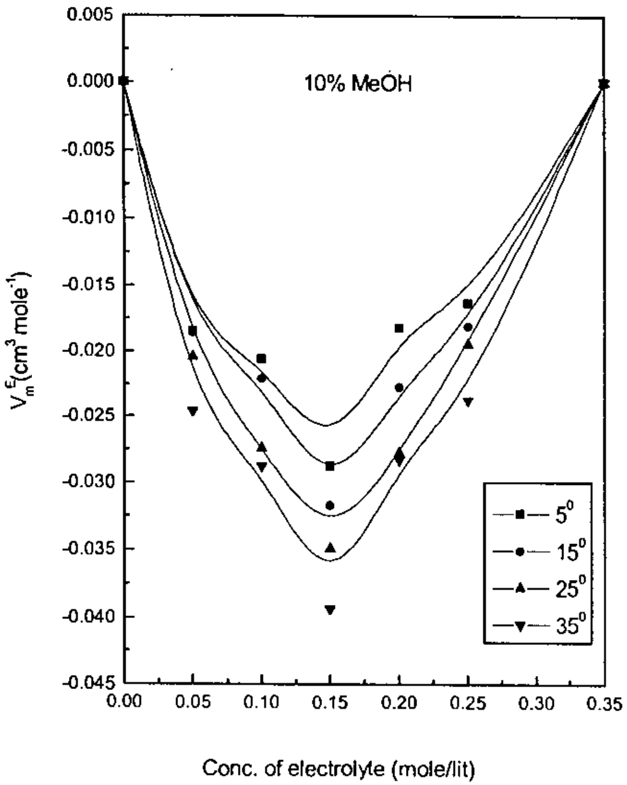


Fig.5.30: Excess molar volume of $MgCl_2$ at different temperature .

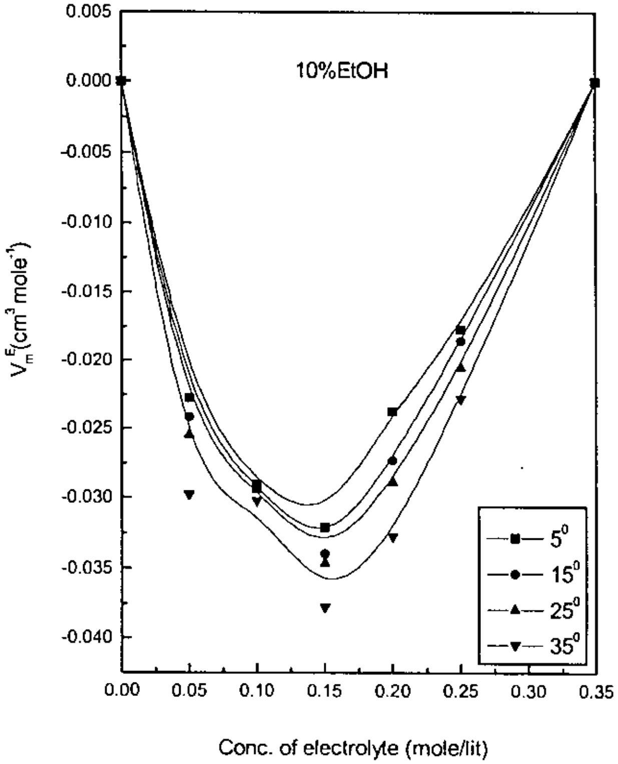


Fig. 5.31: Excess molar volume of $MgCl_2$ at different temperature .

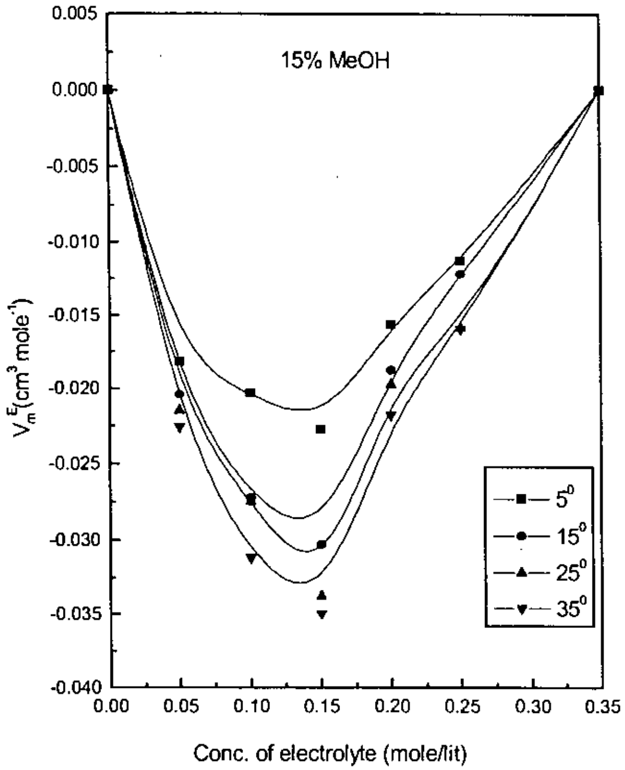


Fig. 5.32: Excess molar volume of $MgCl_2$ at different temperature .

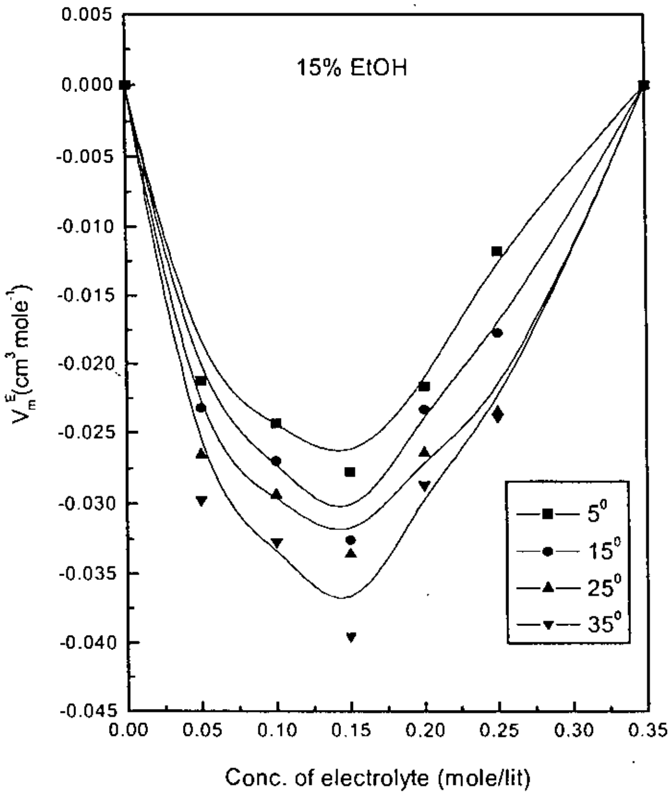


Fig. 5.33: Excess molar volume of $MgCl_2$ at different temperature .

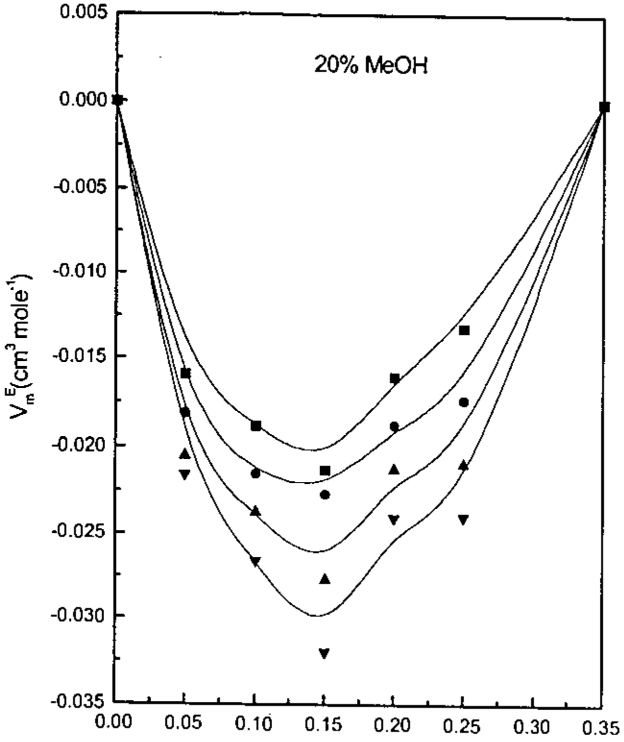


Fig. 5.34: Excess molar volume of $MgCl_2$ at different temperature .

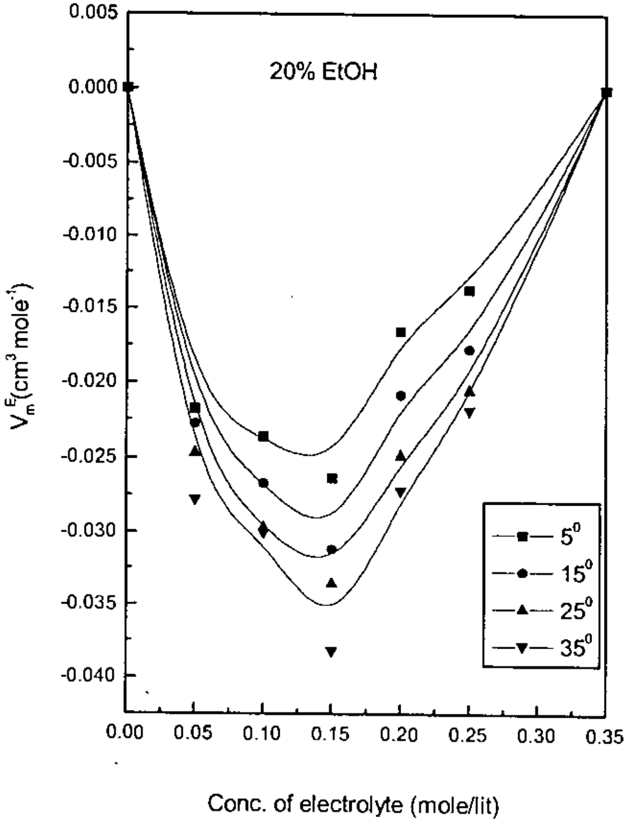


Fig.5.35: Excess molar volume of $MgCl_2$ at different temperature .

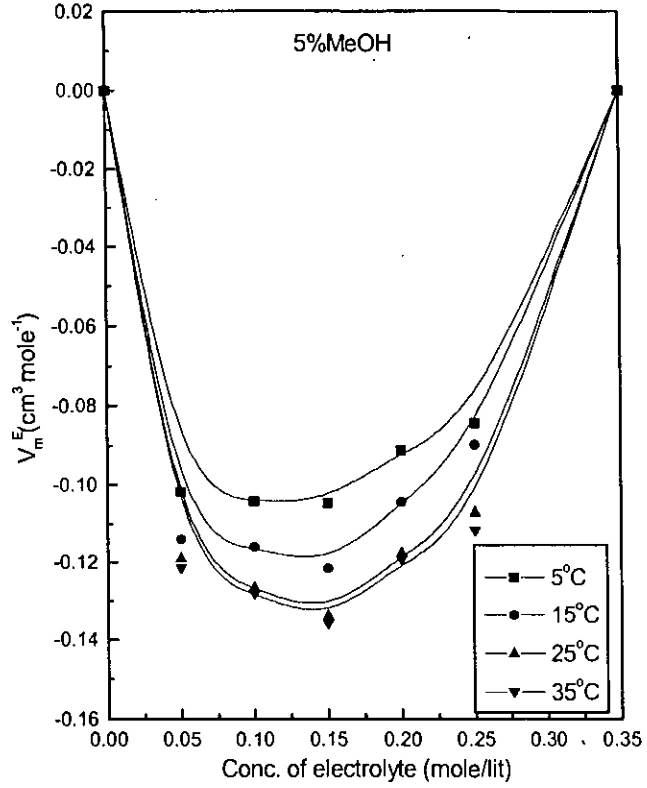


Fig. 5.36: Excess molar volume of $NiCl_2$ at different temperature .

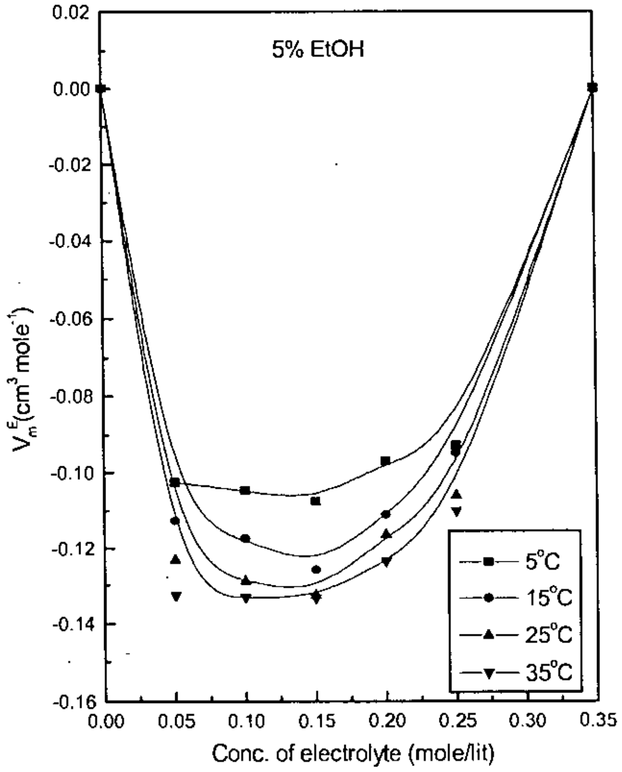


Fig. 5.37: Excess molar volume of $NiCl_2$ at different temperature .

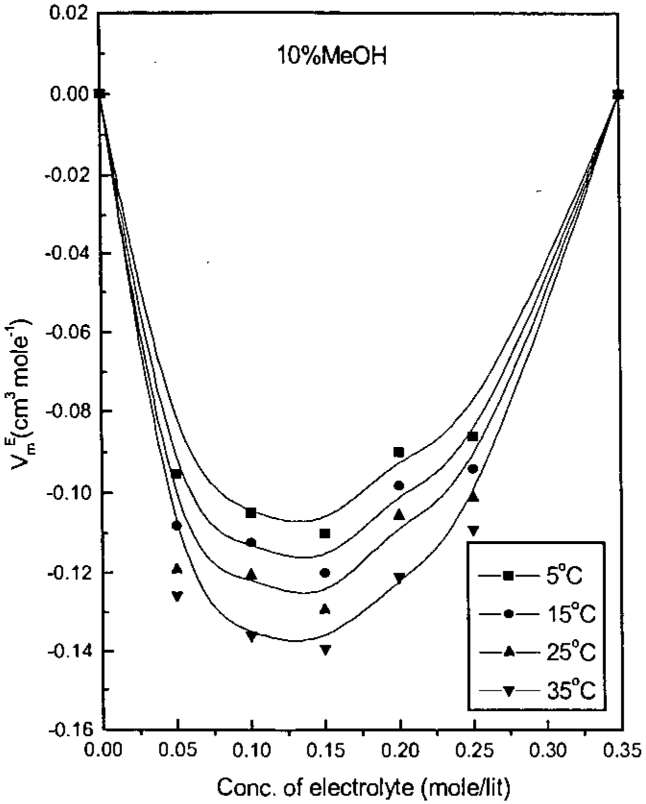


Fig. 5.38: Excess molar volume of $NiCl_2$ at different temperature .

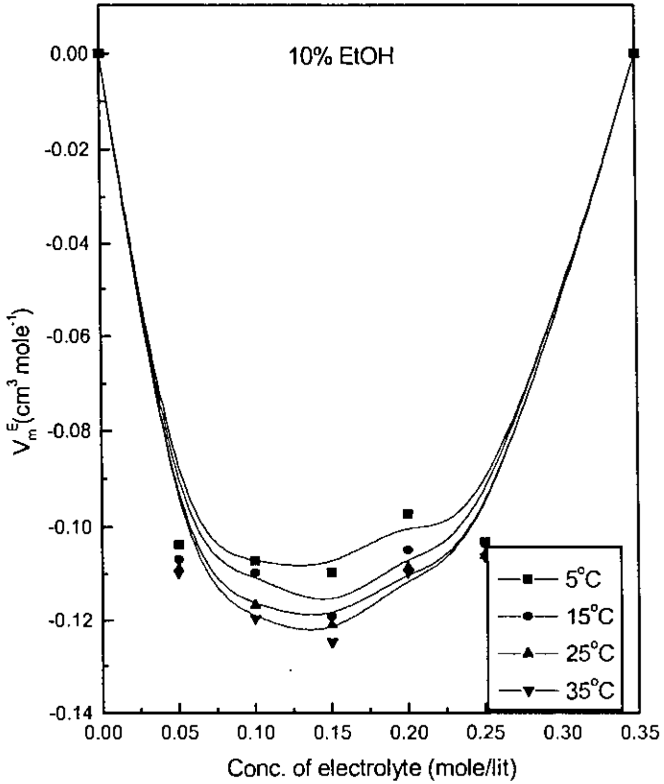


Fig. 5.39: Excess molar volume of $NiCl_2$ at different temperature .

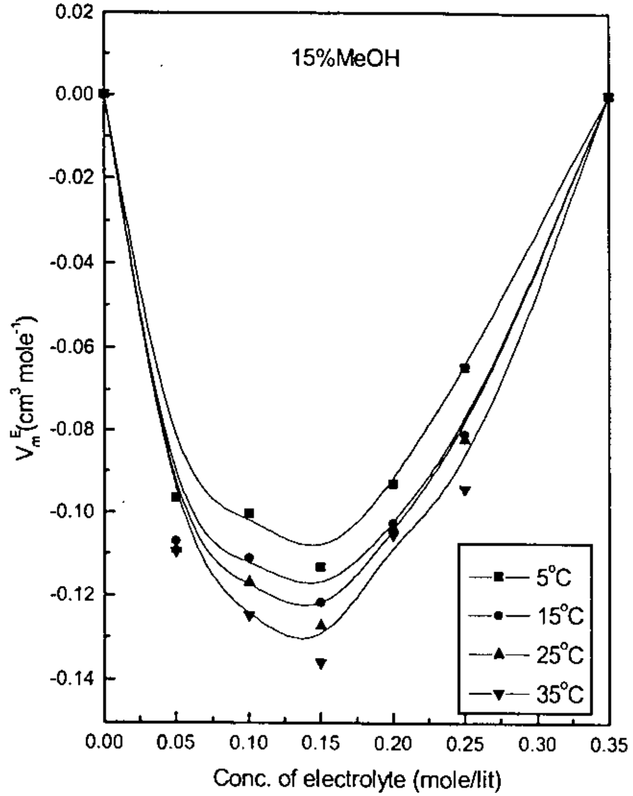


Fig. 5.40: Excess molar volume of $NiCl_2$ at different temperature .

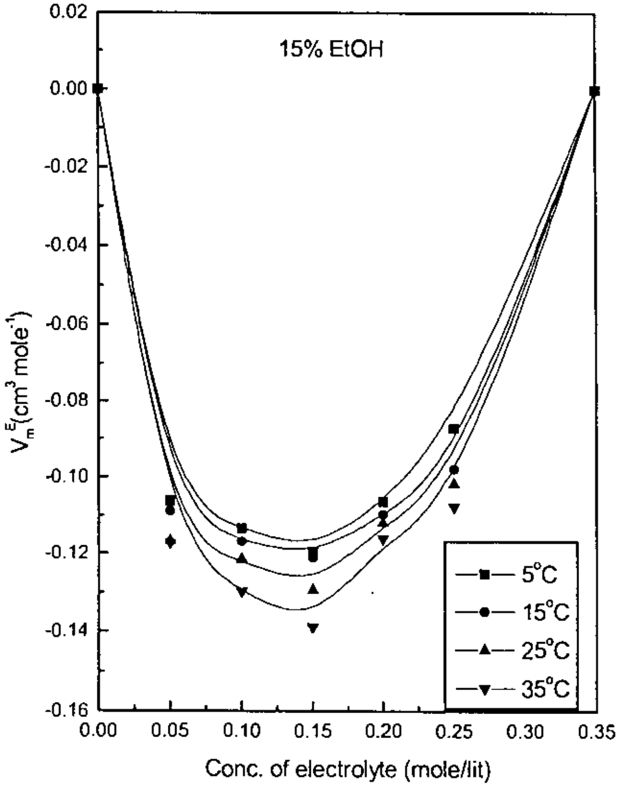


Fig. 5.41: Excess molar volume of $NiCl_2$ at different temperature .

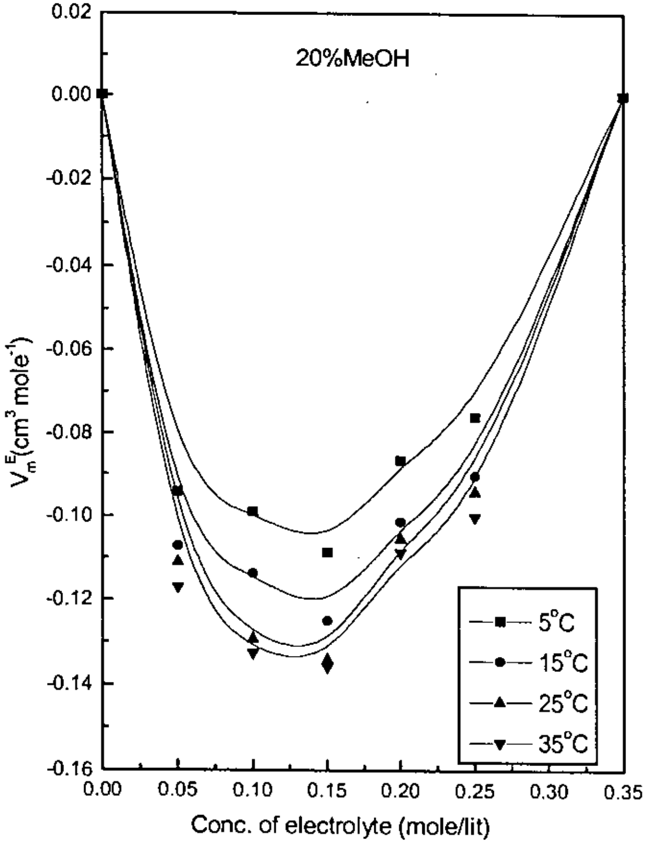


Fig. 5.42: Excess molar volume of $NiCl_2$ at different temperature .

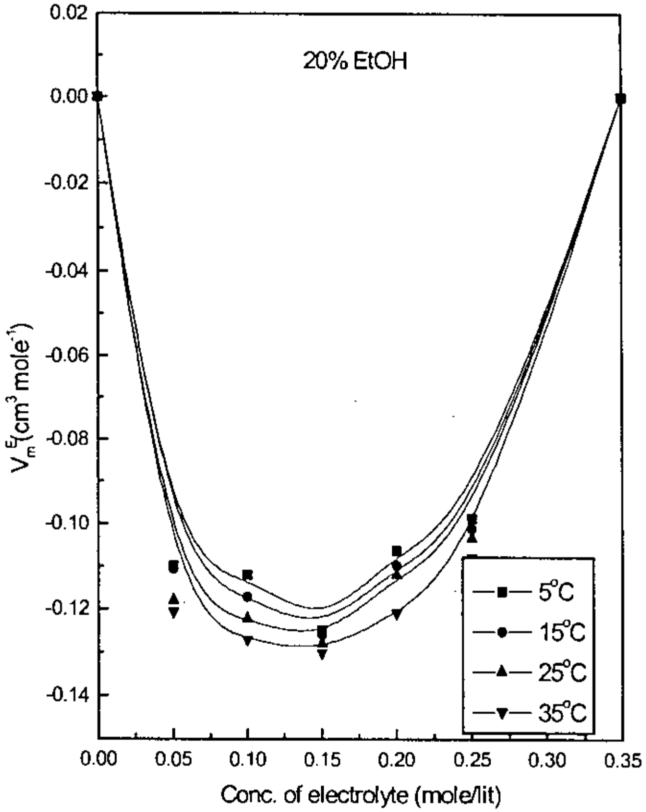


Fig. 5.43: Excess molar volume of $NiCl_2$ at different temperature .

The values of apparent molar volume are presented in appendices III. A two samples arrangement is shown in tables 5.4-5.5 and in figures 5.44-5.85. It is evident from the table that apparent molar volumes of all solutions under study are positive and the values increase almost linearly with increase of mole fraction of electrolytes both in methanol-water and ethanol-water system.

Similar results were also obtained by Nikam. et. al.[80] and Santhu et.al [119] with chloroacetic acid-aqueous ethanol system and methanol-water system respectively.

Data table: 5. 4 Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($FeCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	39.707251	48.077783	64.635163	79.188382
	0.05	244.15529	244.30798	244.37347	244.46085
	0.10	244.94954	245.12533	245.21332	245.30138
	0.15	245.85636	246.65921	246.74843	246.83771
	0.20	246.67726	247.35879	247.97439	248.10981
	0.25	247.54477	248.53003	248.66613	249.27431
15°C	0.00	40.193975	49.385000	64.989214	79.342613
	0.05	244.22071	244.35164	244.46085	244.54830
	0.10	245.03741	245.21332	245.32340	245.41153
	0.15	245.96710	246.72612	246.86004	247.62096
	0.20	246.81116	247.44857	247.56088	247.65081
	0.25	247.65721	248.17261	248.30827	248.91604
25°C	0.00	40.261895	49.703597	65.128095	79.897186
	0.05	244.30798	244.39531	244.46085	244.54830
	0.10	245.10335	245.21332	245.32340	245.41153
	0.15	246.05577	246.72612	246.86004	247.62096
	0.20	246.46398	247.44857	247.56088	247.65081
	0.25	247.05326	248.17261	248.30827	248.48939
35°C	0.00	40.408192	49.907641	65.308384	80.288923
	0.05	244.39531	244.57017	244.65768	246.64725
	0.10	245.19132	245.27936	245.38949	247.51380
	0.15	245.42937	246.83771	246.94940	247.71093
	0.20	245.50066	247.03464	247.16892	247.74080
	0.25	245.86488	248.71153	249.60931	251.78832

Data table: 5. 5 Values of apparent molar volume, ϕ_v ($cm^3.g^{-1}$) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($FeCl_3$)in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	53.409239	61.643275	78.962044	93.174424
	0.05	246.11351	246.20230	246.26894	246.33562
	0.10	246.95355	247.02064	247.13255	247.22215
	0.15	247.14970	247.93102	248.69094	248.75907
	0.20	247.63647	248.27389	248.88981	249.00358
	0.25	248.30352	249.73738	250.23168	250.36983
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	248.18270	248.31840	248.36367	248.45425
	0.10	249.04783	250.18787	250.25690	250.34900
	0.15	250.65296	251.43804	251.53109	251.57764
	0.20	251.42536	252.04443	252.13796	252.20815
	0.25	251.86466	252.78672	253.28369	253.78131
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	248.25053	248.40895	248.47690	248.54489
	0.10	249.13897	250.25690	250.34900	250.41812
	0.15	250.74538	250.83788	250.90729	250.97674
	0.20	250.99247	251.61150	251.65808	251.72799
	0.25	251.53209	252.05151	252.12165	252.19183
35°C	0.00	53.751890	62.307994	79.478060	94.103813
	0.05	248.31840	248.47690	248.54489	248.63560
	0.10	250.23389	250.30294	250.44116	251.53952
	0.15	250.81475	250.88415	250.97674	251.76401
	0.20	251.58822	251.70468	251.77461	251.84458
	0.25	251.60192	251.71839	251.81164	252.16204

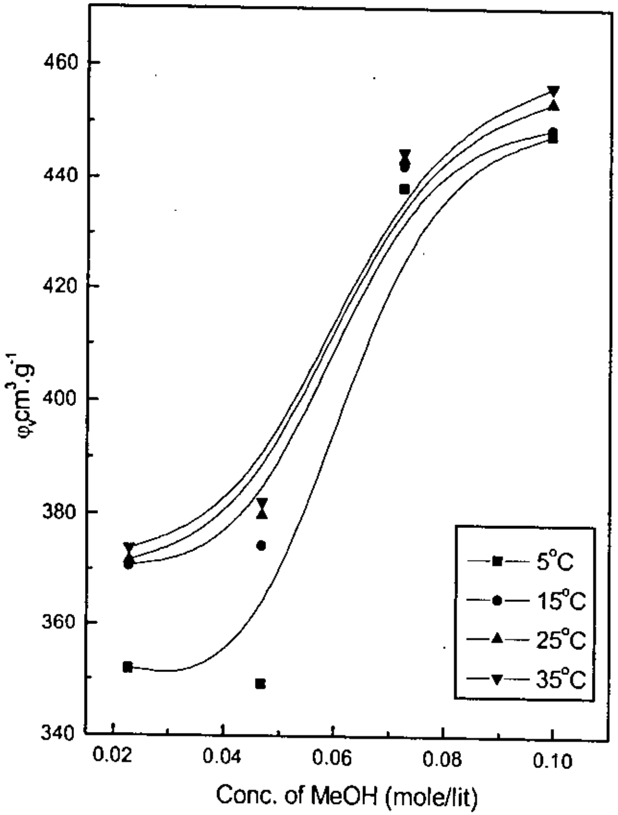


Fig. 5.44: Variation of apparent molar volume of MeOH at different temperature .

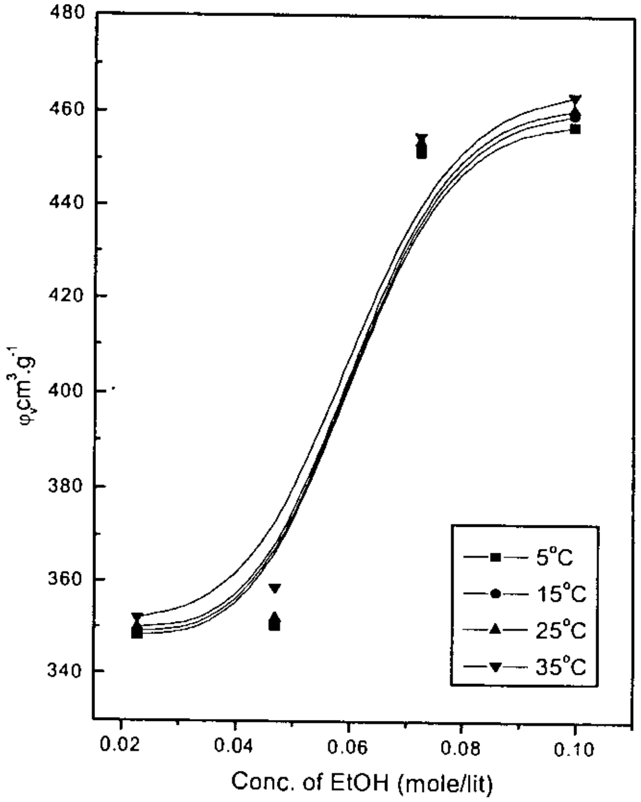


Fig. 5.45: Variation of apparent molar volume of EtOH at different temperature .

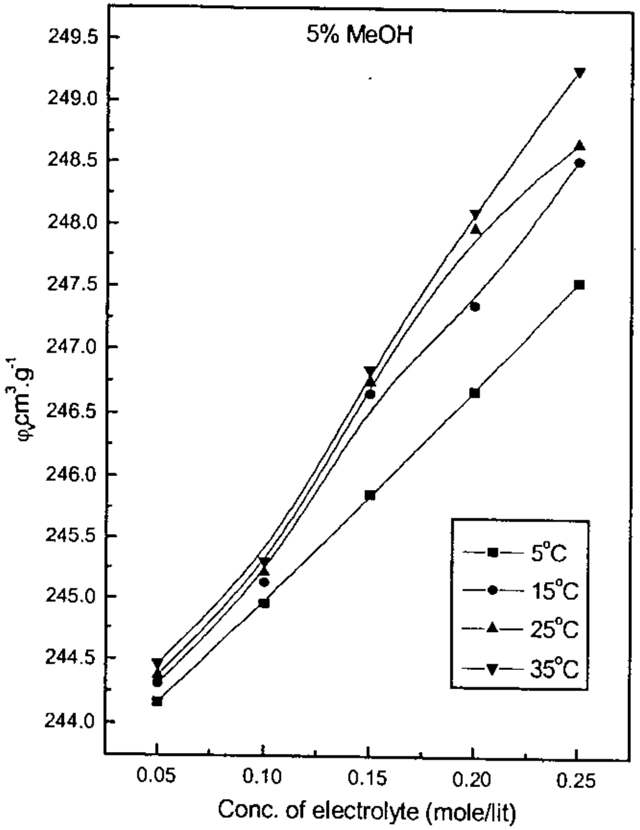


Fig. 5.46: Variation of apparent molar volume of $FeCl_3$ at different temperature .

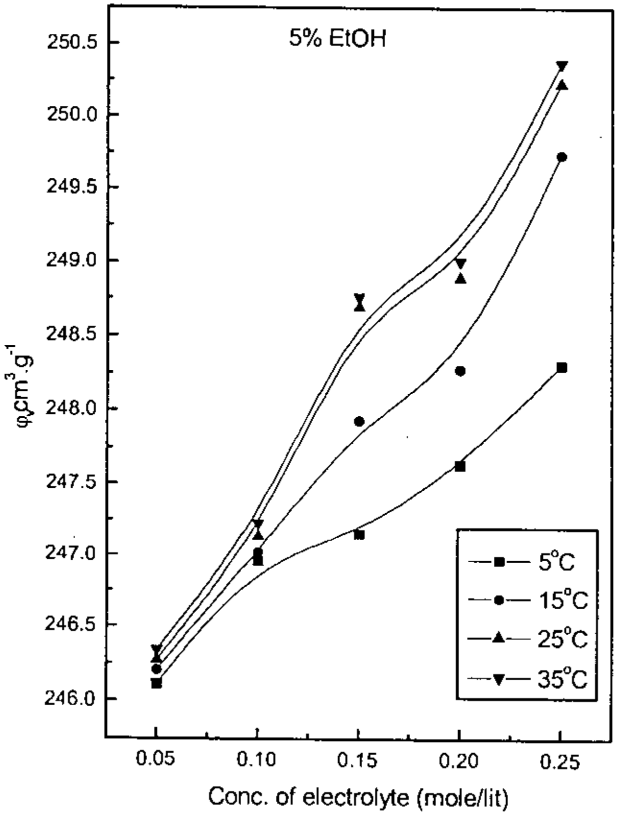


Fig. 5.47: Variation of apparent molar volume of $FeCl_3$ at different temperature .

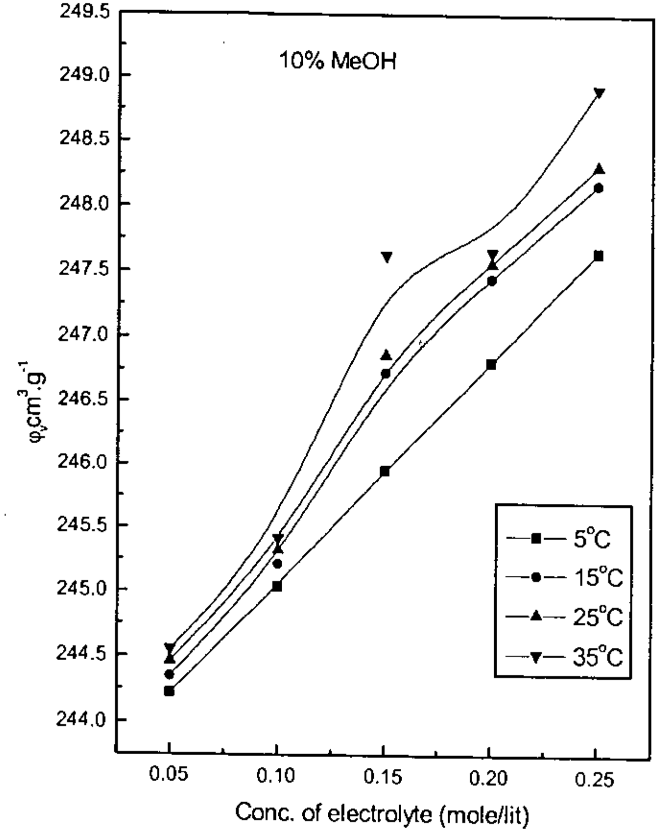


Fig. 5.48: Variation of apparent molar volume of $FeCl_3$ at different temperature.

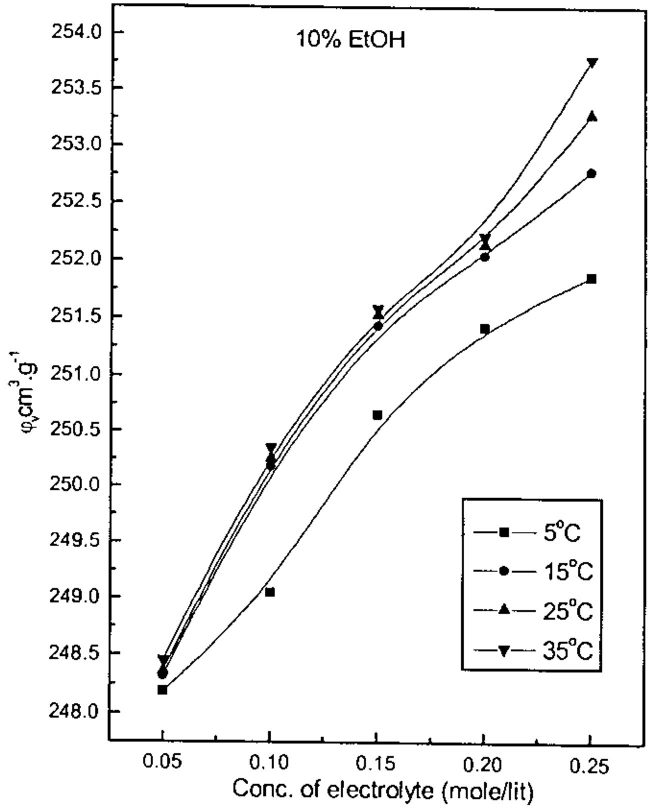


Fig. 5.49: Variation of apparent molar volume of $FeCl_3$ at different temperature.

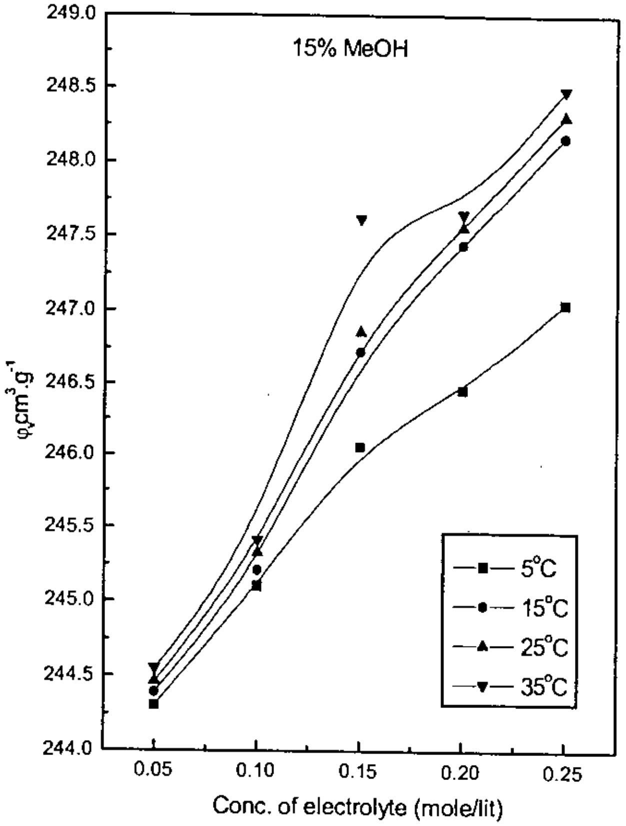


Fig. 5.50: Variation of apparent molar volume of $FeCl_3$ at different temperature.

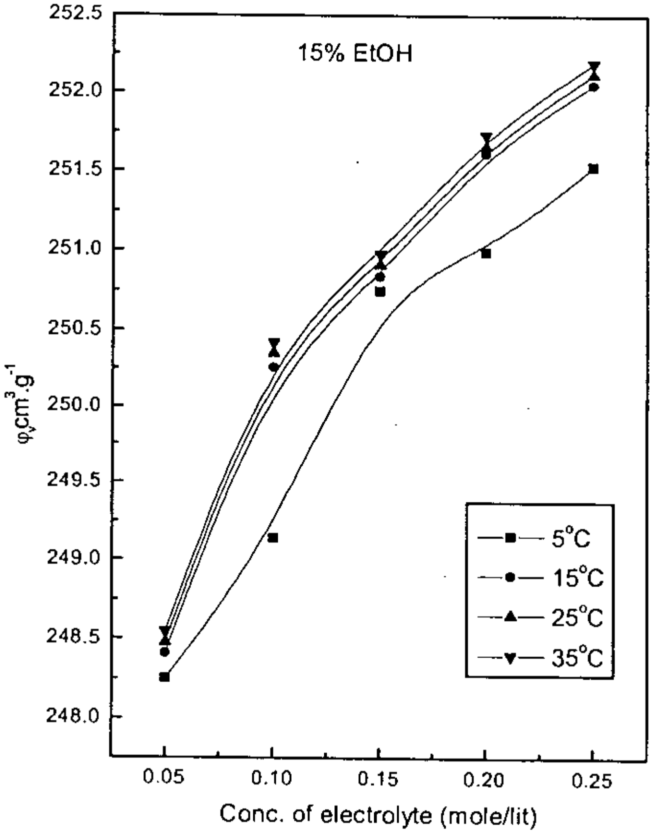


Fig. 5.51: Variation of apparent molar volume of $FeCl_3$ at different temperature.

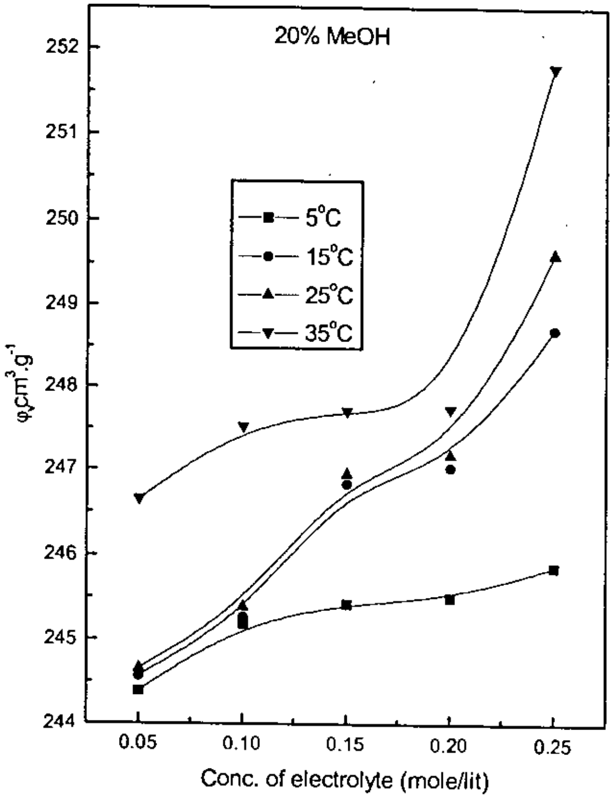


Fig. 5.52: Variation of apparent molar volume of $FeCl_3$ at different temperature .

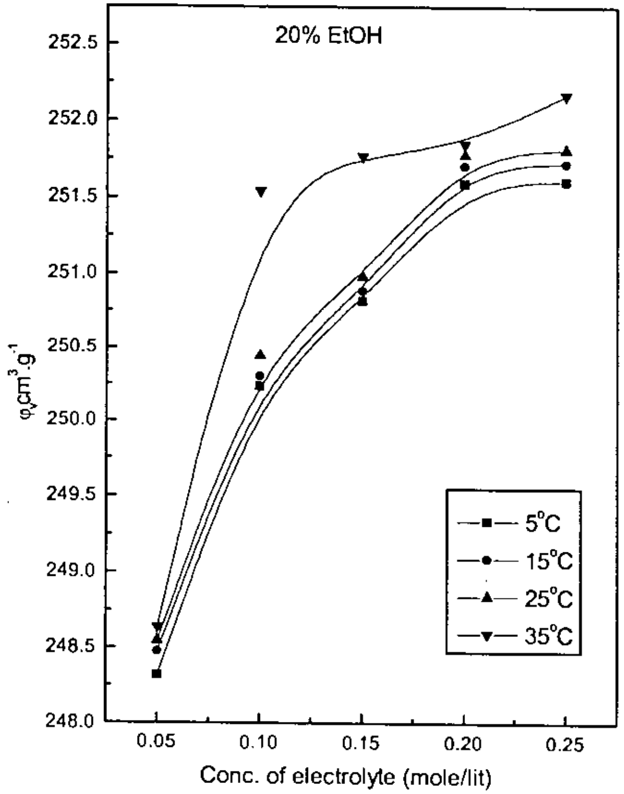


Fig. 5.53: Variation of apparent molar volume of $FeCl_3$ at different temperature.

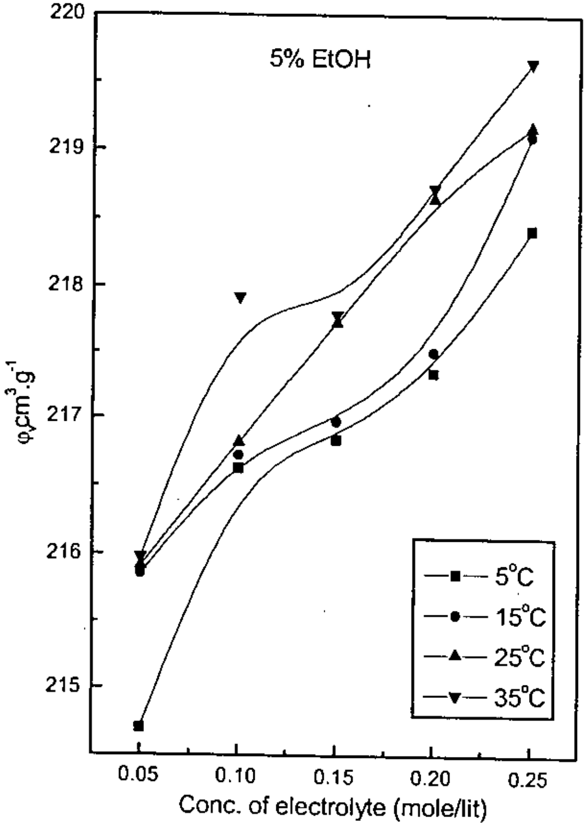


Fig. 5.54: Variation of apparent molar volume of $CoCl_3$ at different temperature .

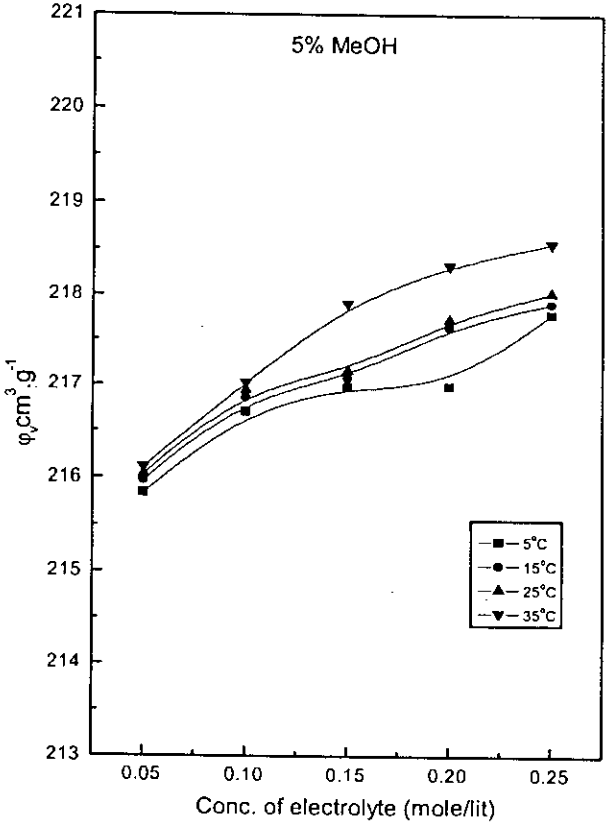


Fig. 5.55: Variation of apparent molar volume of $CoCl_3$ at different temperature.

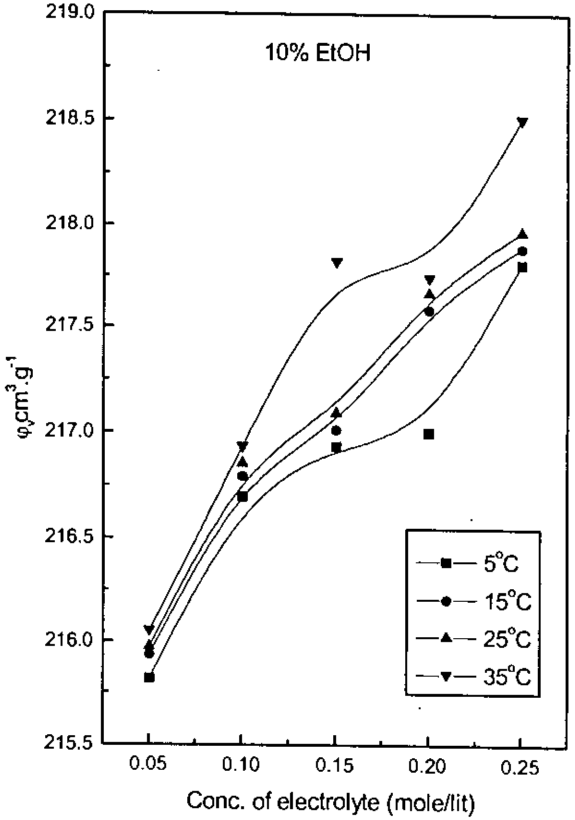


Fig. 5.56: Variation of apparent molar volume of $CoCl_3$ at different temperature.

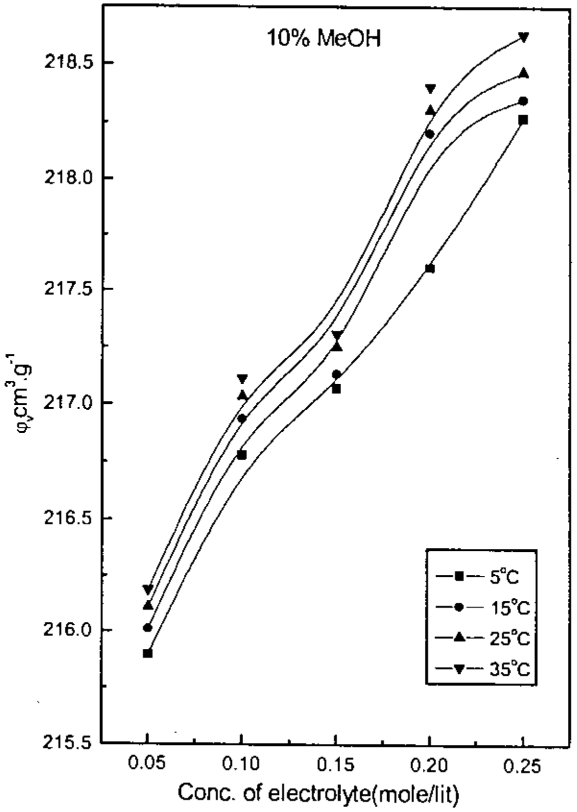


Fig. 5.57: Variation of apparent molar volume of $CoCl_3$ at different temperature.

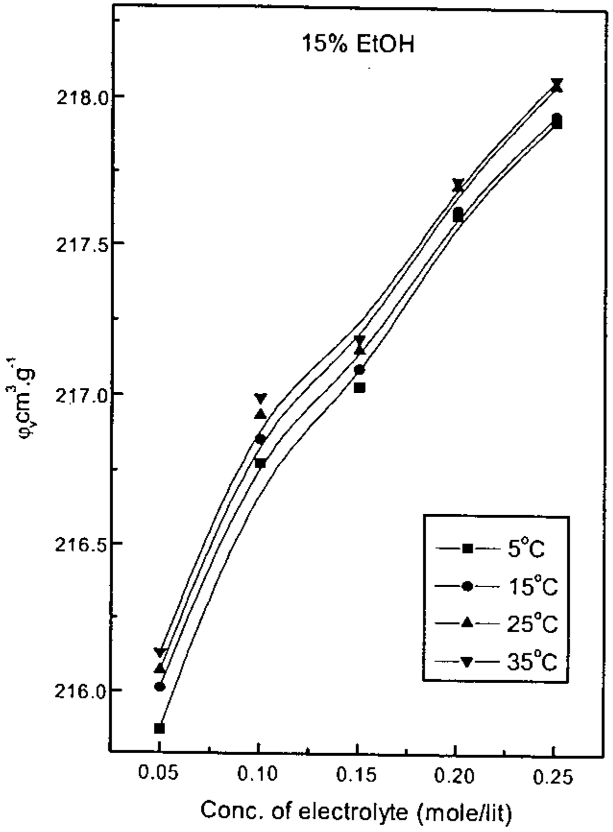


Fig. 5.58: Variation of apparent molar volume of $CoCl_3$ at different temperature.

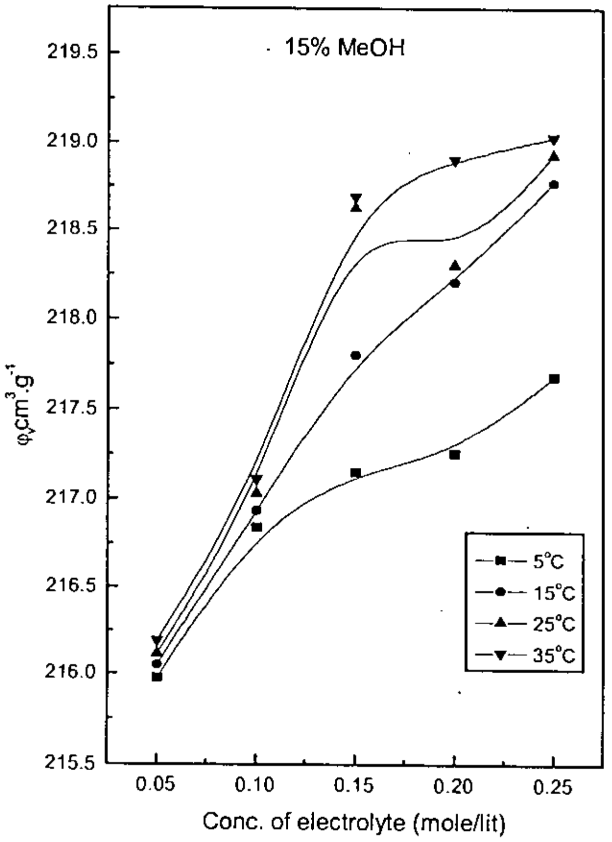


Fig. 5.59: Variation of apparent molar volume of $CoCl_3$ at different temperature.

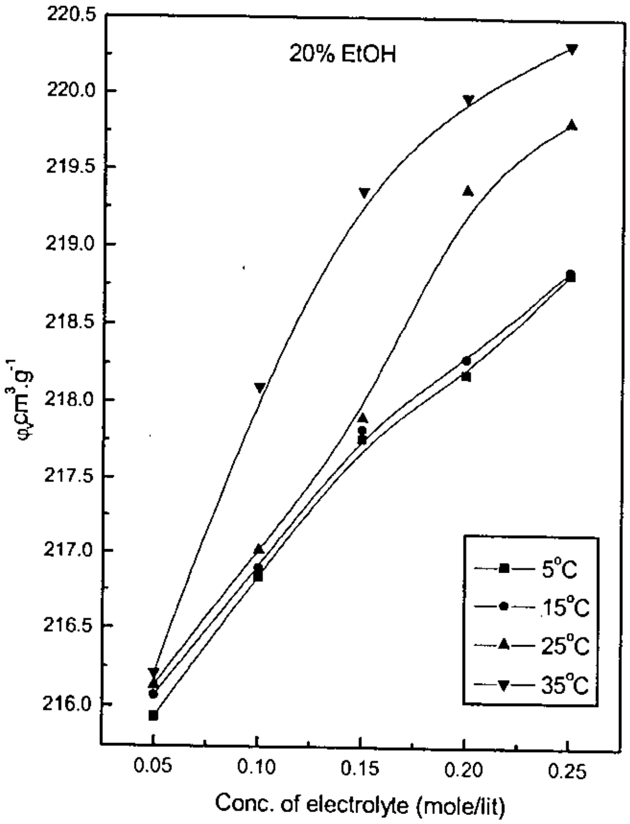


Fig. 5.60: Variation of apparent molar volume of $CoCl_3$ at different temperature.

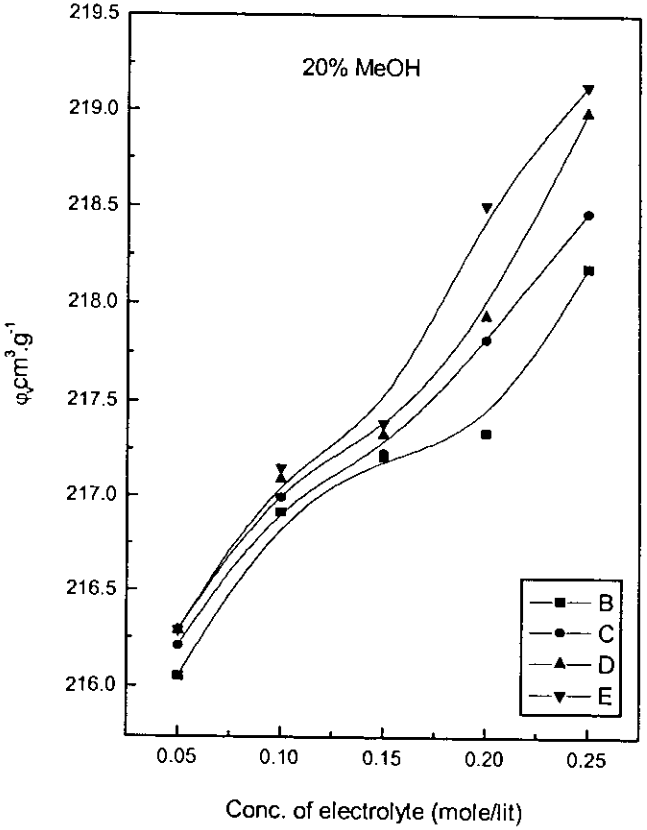


Fig. 5.61: Variation of apparent molar volume of $CoCl_3$ at different temperature.

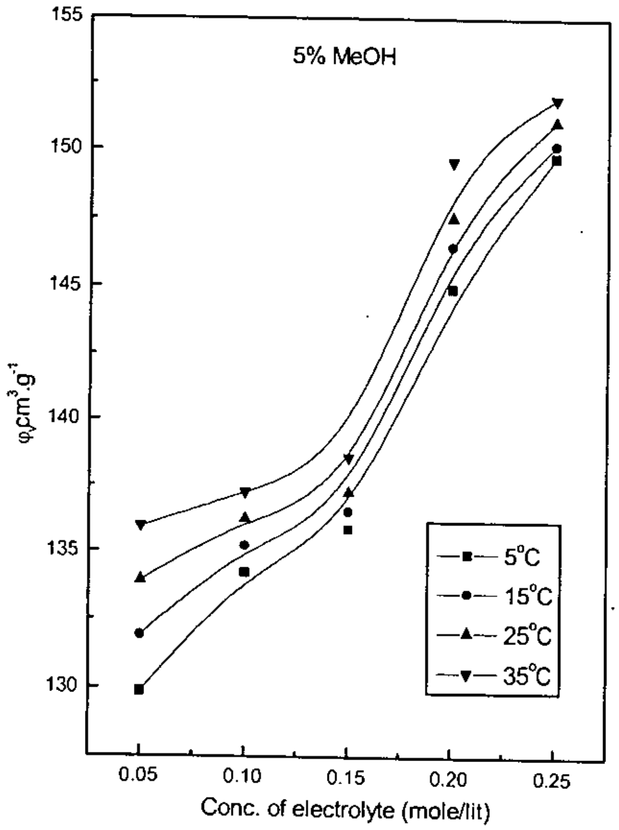


Fig. 5.62: Variation of apparent molar volume of $CuCl_2$ at different temperature.

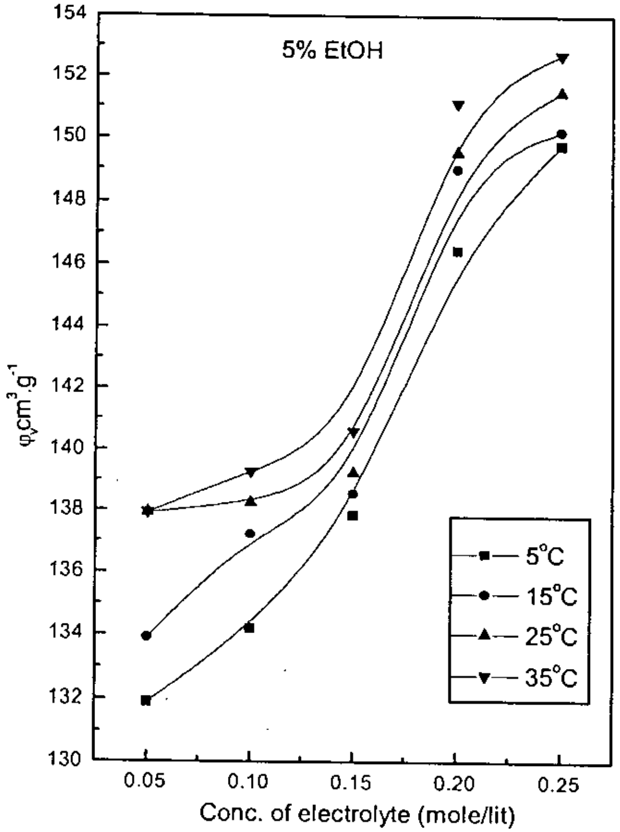


Fig. 5.63: Variation of apparent molar volume of $CuCl_2$ at different temperature.

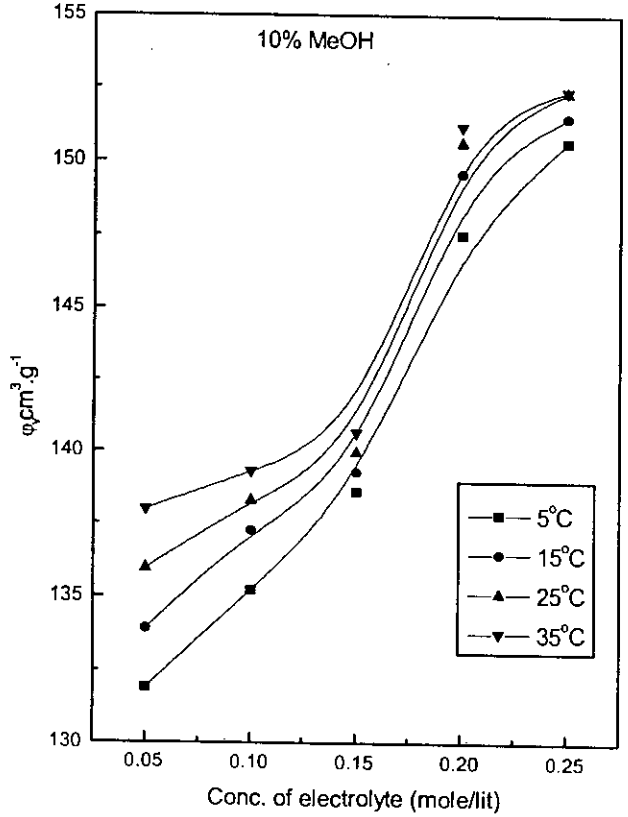


Fig. 5.64: Variation of apparent molar volume of $CuCl_2$ at different temperature.

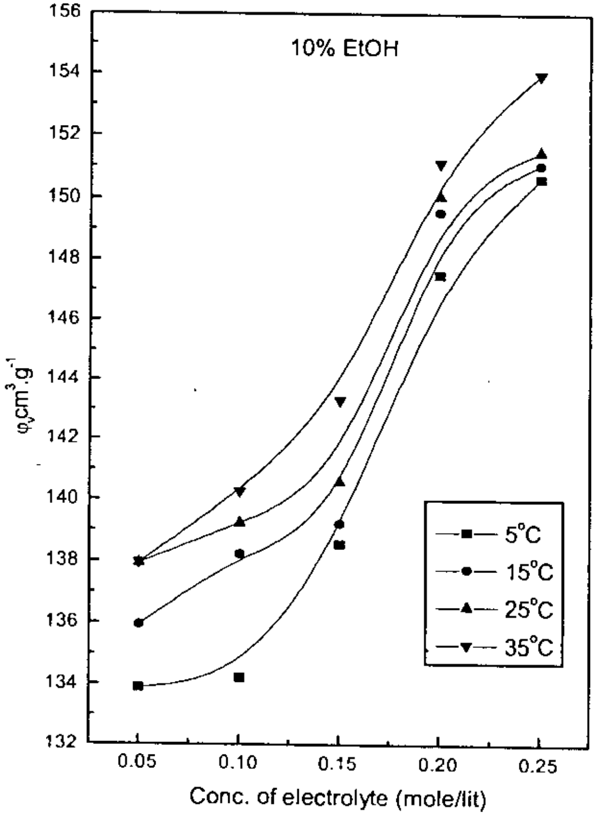


Fig. 5.65: Variation of apparent molar volume of $CuCl_2$ at different temperature.

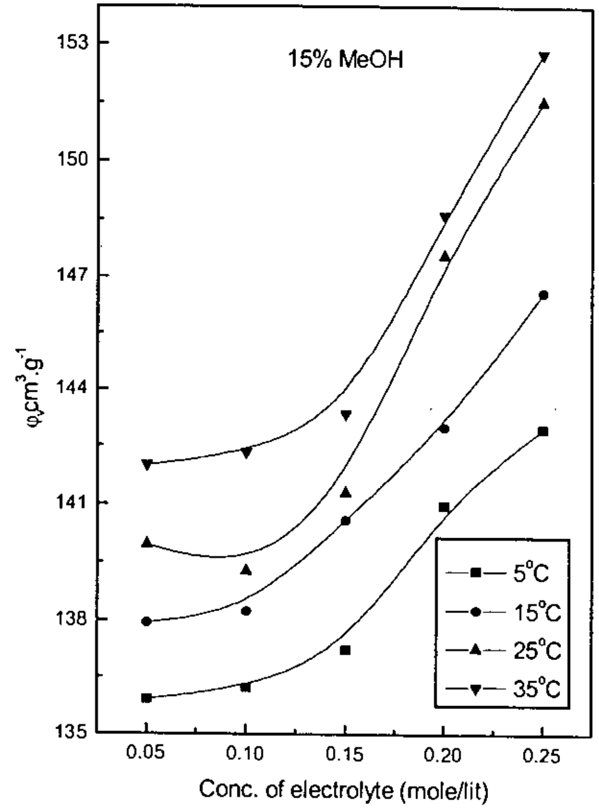


Fig. 5.66 : Variation of apparent molar volume of $CuCl_2$ at different temperature.

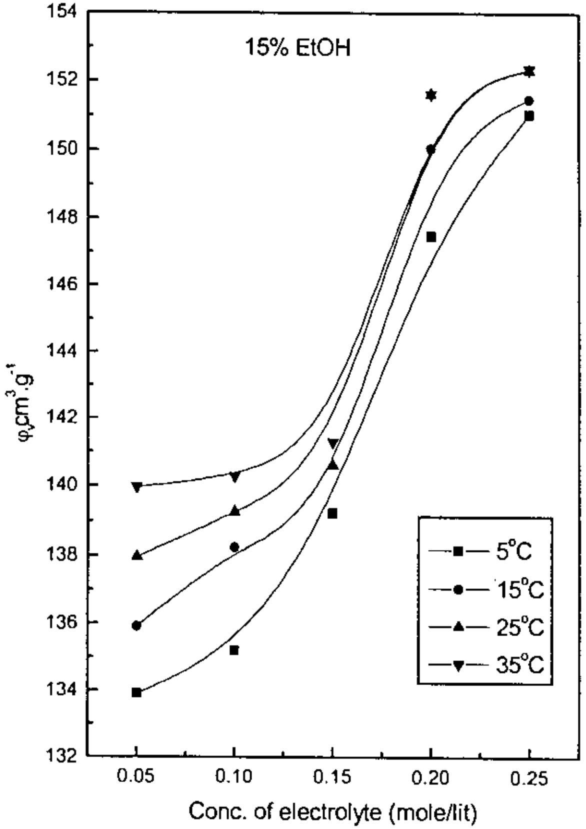


Fig. 5.67: Variation of apparent molar volume of $CuCl_2$ at different temperature.

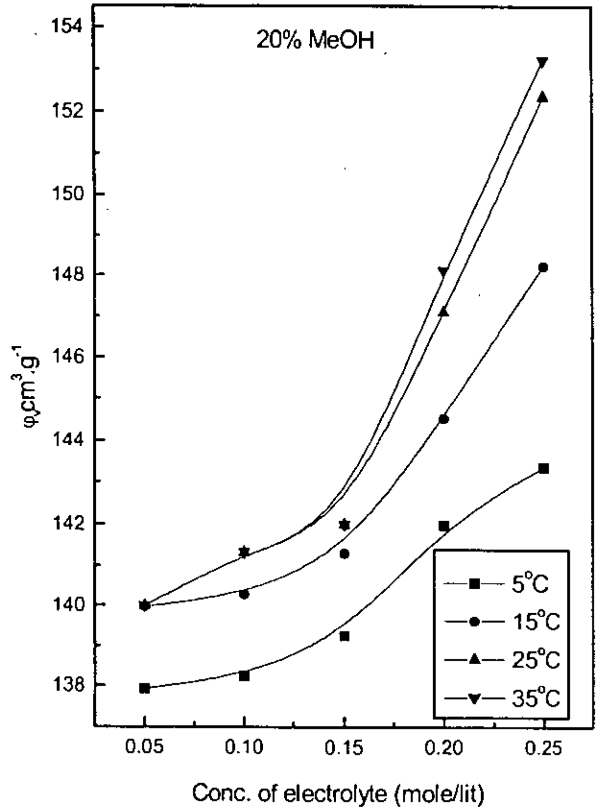


Fig. 5.68: Variation of apparent molar volume of $CuCl_2$ at different temperature.

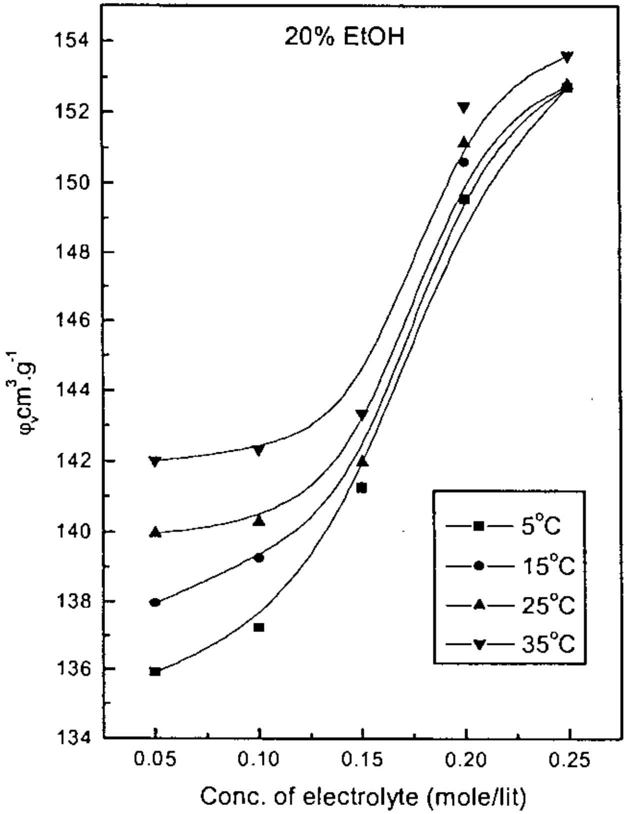


Fig. 5.69: Variation of apparent molar volume of $CuCl_2$ at different temperature.

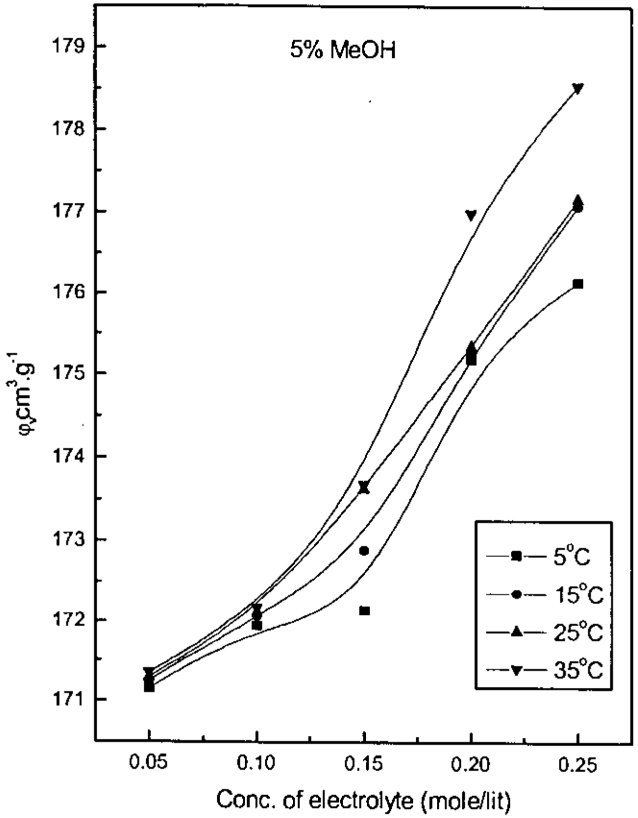


Fig. 5.70: Variation of apparent molar volume of $MgCl_2$ at different temperature.

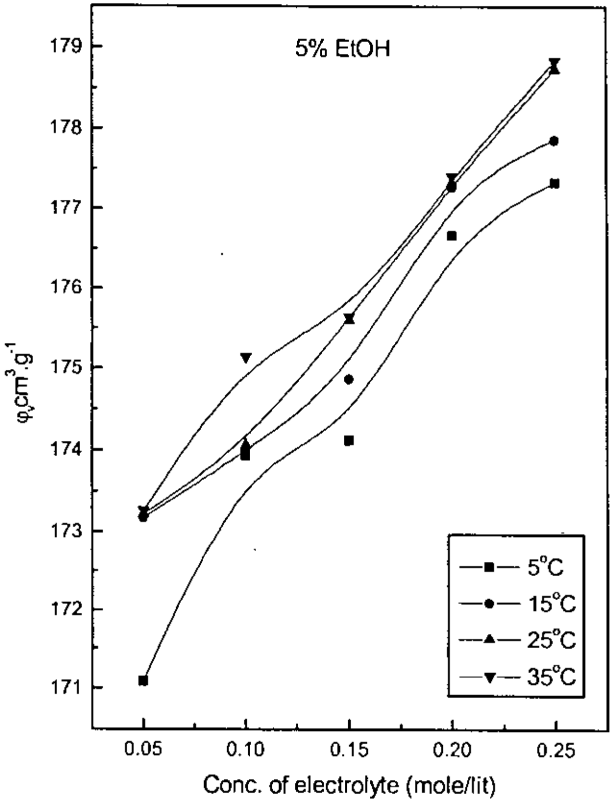


Fig. 5.71: Variation of apparent molar volume of $MgCl_2$ at different temperature.

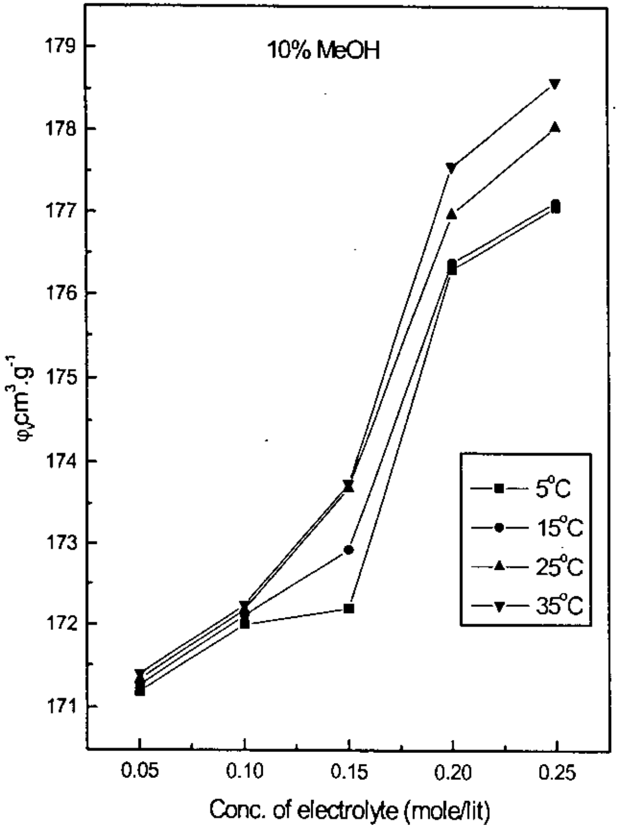


Fig. 5.72: Variation of apparent molar volume of $MgCl_2$ at different temperature.

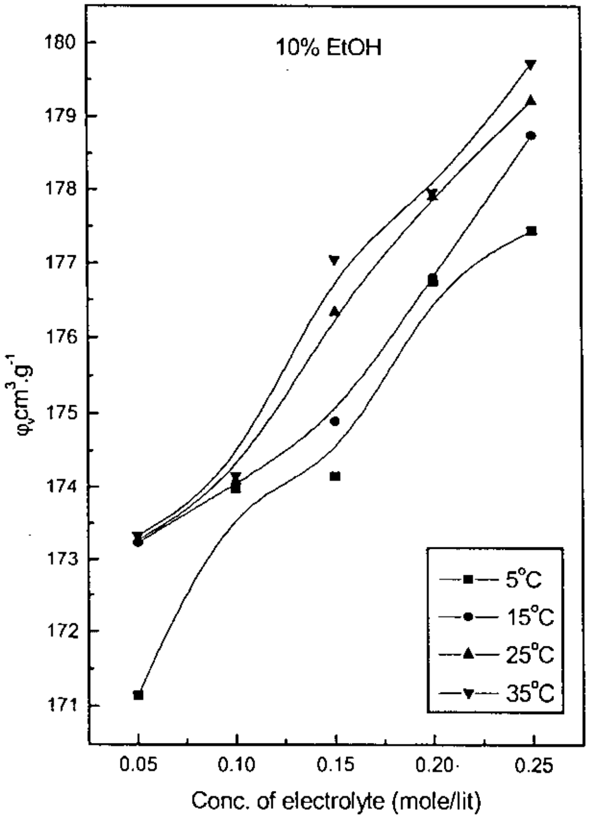


Fig. 5.73: Variation of apparent molar volume of $MgCl_2$ at different temperature.

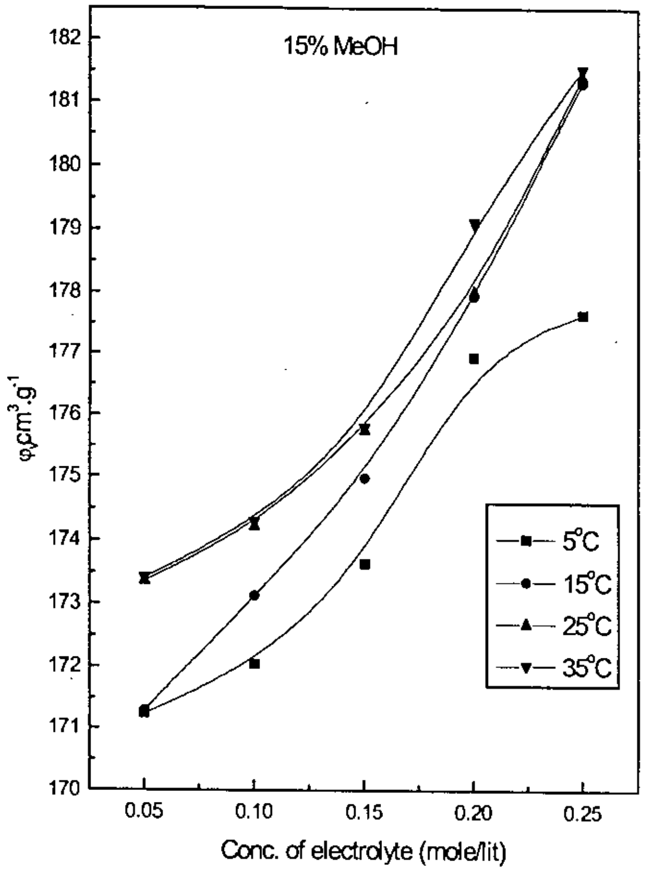


Fig. 5.74: Variation of apparent molar volume of $MgCl_2$ at different temperature.

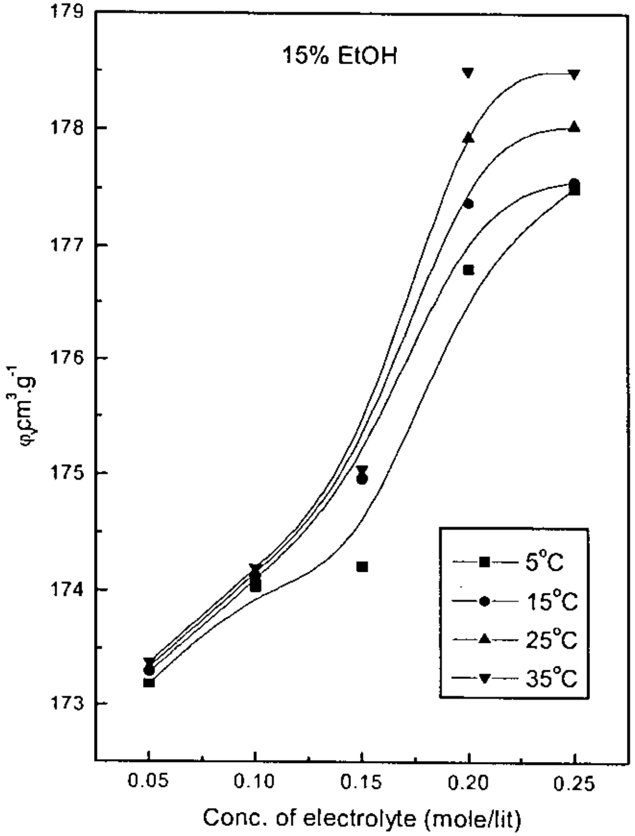


Fig. 5.75: Variation of apparent molar volume of $MgCl_2$ at different temperature.

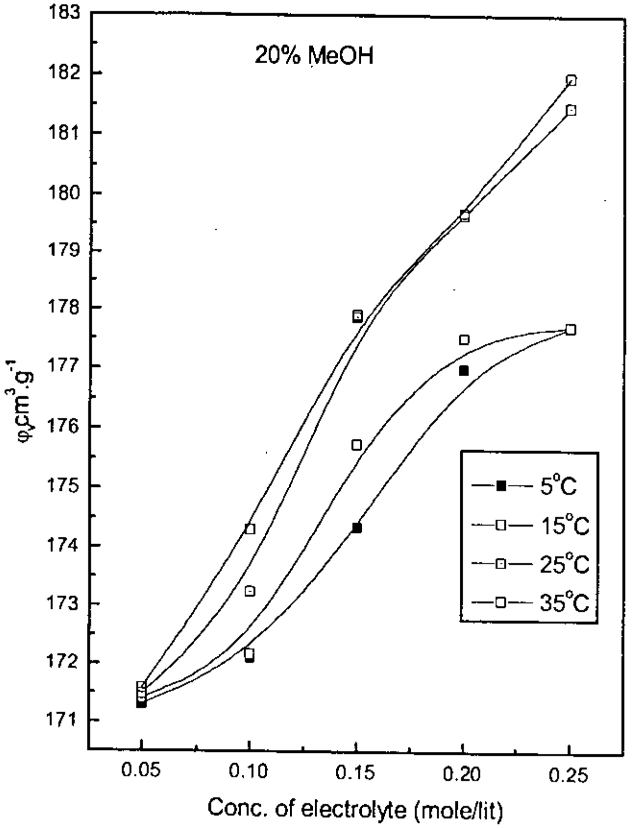


Fig. 5.76: Variation of apparent molar volume of $MgCl_2$ at different temperature.

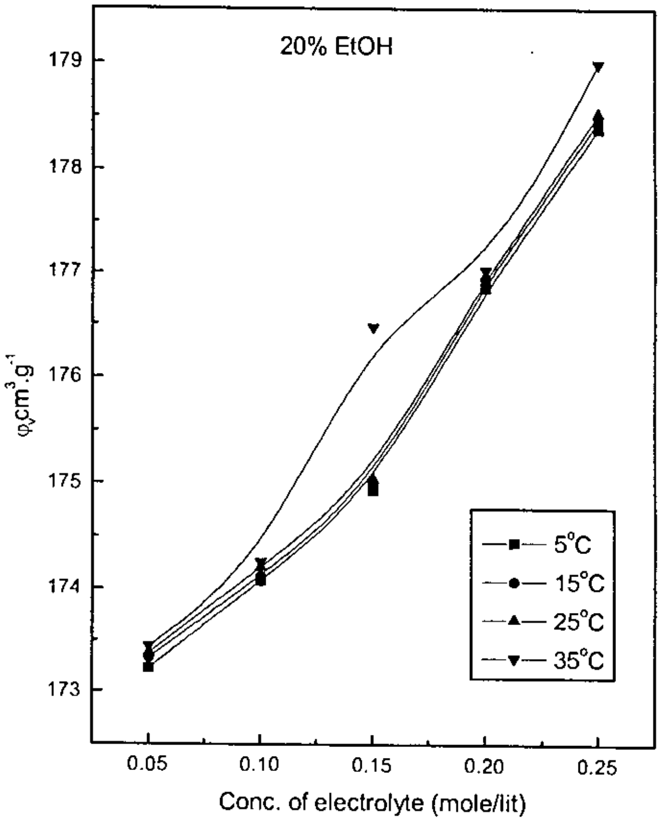


Fig. 5.77: Variation of apparent molar volume of $MgCl_2$ at different temperature.

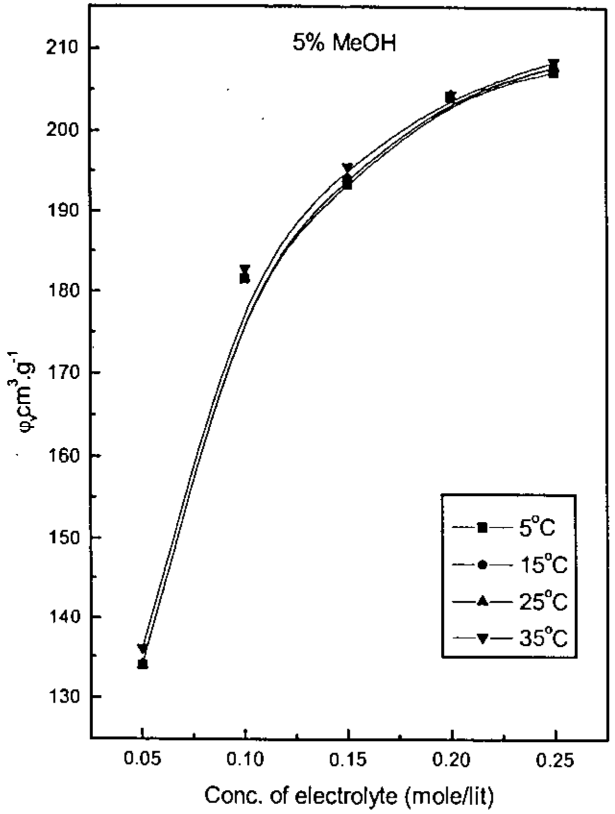


Fig. 5.78: Variation of apparent molar volume of $NiCl_2$ at different temperature.

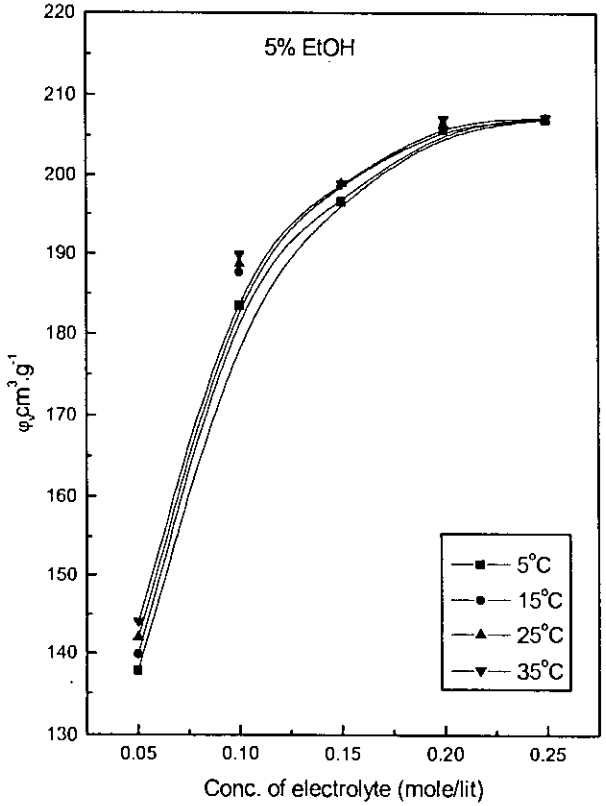


Fig. 5.79: Variation of apparent molar volume of $NiCl_2$ at different temperature.

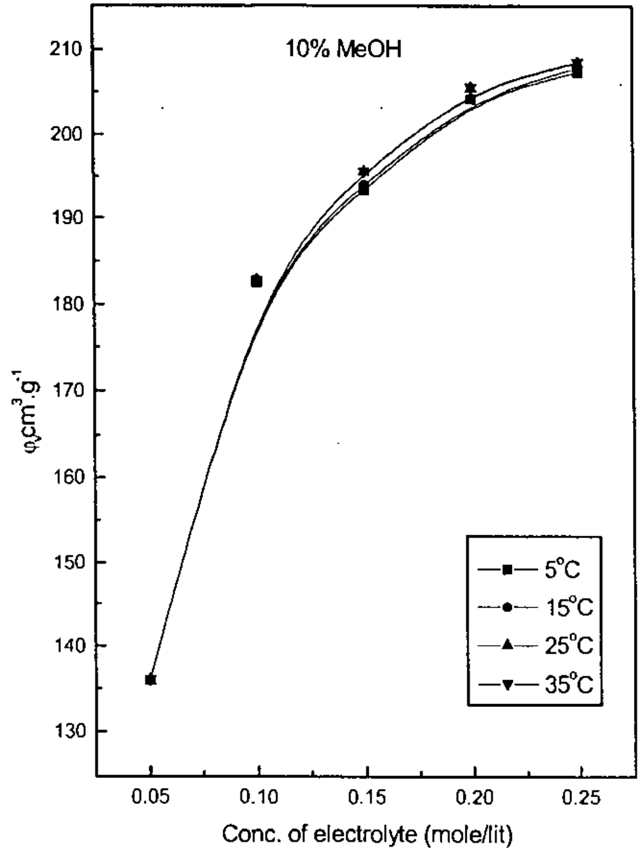


Fig. 5.80: Variation of apparent molar volume of $NiCl_2$ at different temperature.

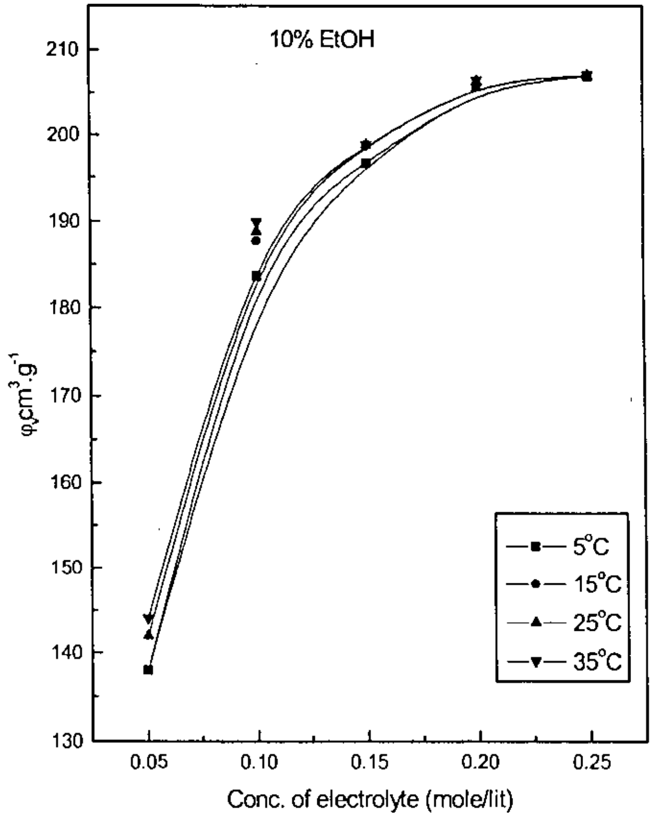


Fig. 5.81: Variation of apparent molar volume of $NiCl_2$ at different temperature .

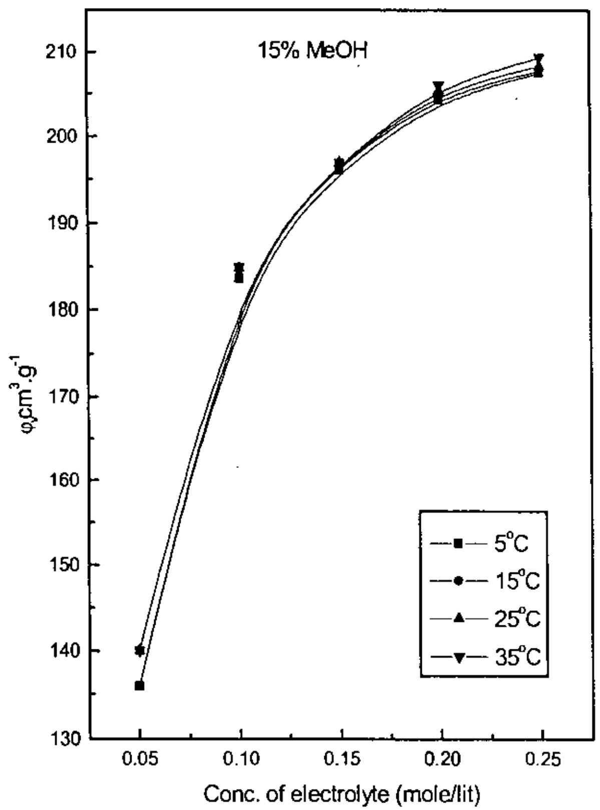


Fig. 5.82: Variation of apparent molar volume of $NiCl_2$ at different temperature.

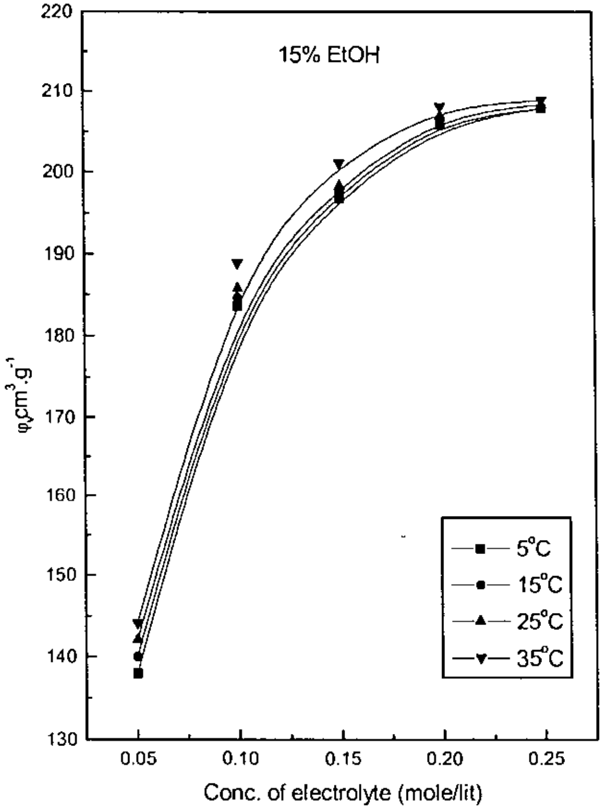


Fig. 5.83: Variation of apparent molar volume of $NiCl_2$ at different temperature.

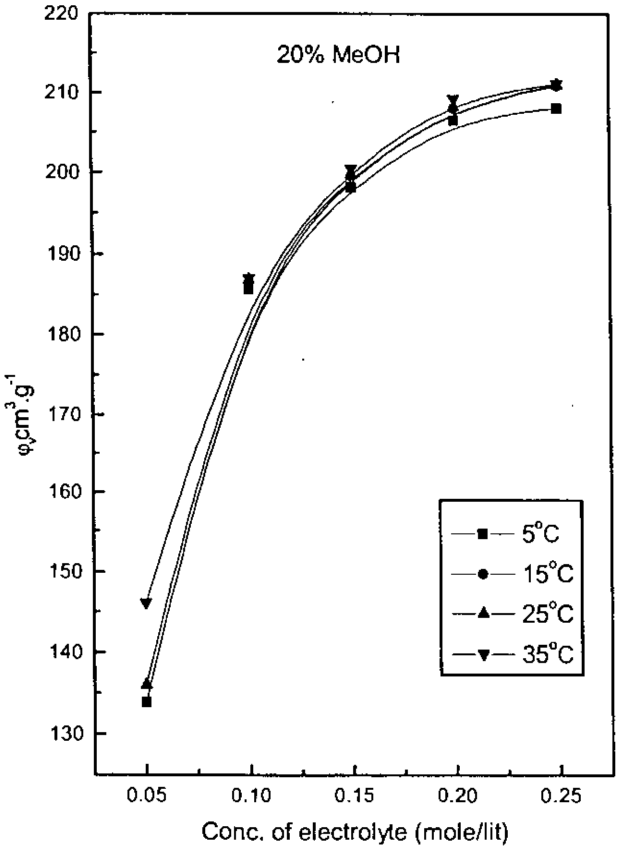


Fig. 5.84: Variation of apparent molar volume of $NiCl_2$ at different temperature.

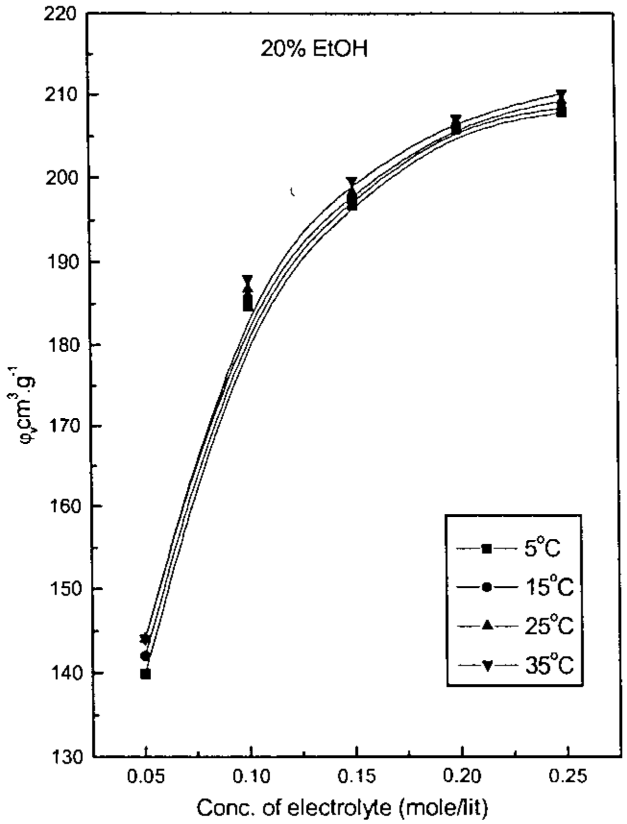


Fig. 5.85: Variation of apparent molar volume of $NiCl_2$ at different temperature.

The molecular movements of water molecules decrease if there is a structural increase and increase in the less structural molecular environment. The values of viscosity and it's related properties provide important information about the structure and on the interaction between the particles (ions and molecules) in liquid solution. The experimentally determined values of viscosity of different solutions at different temperature are presented in appendix-IV. From this data it is observed that viscosity values of different solutions decrease with increase of temperature. The values are found to increase with methanol or ethanol concentration and also with the increase of mole fraction of electrolytes.

To interprete the viscosity data of aqueous solutions of electrolytes Falkerenhagen and Dole [120] use an empirical equation

$$\eta_{rel} = 1 + A\sqrt{C} + BC$$

$$\text{or, } \frac{\eta}{\eta_0} - 1 = A\sqrt{C} + BC$$

Here, B is an empirical coefficient , which corresponds to an ion solvent interaction and has positive or negative values depending on the nature of electrolyte. The positive value of 'B' corresponds to intensification of the structure and negative value corresponds to the disruption of structure.

The values of B-coefficient for different solution under study were calculated by using equation $\frac{\eta - \eta_o}{\eta_o} = BC$, neglecting $A\sqrt{C}$ of the above equation.

The plot $\frac{\eta - \eta_o}{\eta_o}$ V_s C give a straight line which passes through the origin.

The B values were calculated from the slope of each straight lines. The calculated results are presented in tables 5.6-5.15 and also in figures 5.86-5.95. An examination of the data presented in the above mentioned tables reveals that for all solutions positive values are obtained, which indicates that the electrolytic salts taken in this study are structure maker. It is also observed from the results positive value of B-coefficient for the solution containing trivalent cation such as Fe^{3+},Co^{3+} has higher values than that of bivalent cation such as Mg^{2+},Cu^{2+} etc. The data presented in table also show that the concentration of methanol and ethanol does not have any significant change. This may be due to the fact that molecules of methanol and ethanol in aqueous medium bonded with water molecules through hydrogen bond. As a result they are not affected much.

The result presented in these tables and in diagrams 5.86-5.95 also show that the value of B-coefficient decreases with the increases of temperature. That is $\frac{dB}{dT}$ values are negative which also support the structure forming nature of electrolytes [121].

Data table: 5. 6 Values of B-coefficient of Jones-Dole equation of $FeCl_3$ at different temperature

Conc. Of MeOH	5°C	15°C	25°C	35°C
5%	0.14262	0.12691	0.12673	0.12633
10%	0.13741	0.12666	0.12639	0.12602
15%	0.1368	0.12657	0.12637	0.12630
20%	0.13604	0.12643	0.12634	0.12622

Data table:5. 7 Values of B-coefficient of Jones-Dole equation of $FeCl_3$ at different temperature

Conc. of EtOH	**5°C**	**15°C**	**25°C**	**35°C**
5%	0.14250	0.14263	0.14237	0.14110
10%	0.13730	0.13743	0.13719	0.13702
15%	0.13668	0.13651	0.13643	0.13617
20%	0.13593	0.13586	0.13578	0.13611

Data table: 5. 8 Values of B-coefficient of Jones-Dole equation of $CoCl_3$ at different temperature

Conc. Of MeOH	5°C	15°C	25°C	35°C
5%	0.12816	0.12791	0.12783	0.12733
10%	0.12790	0.12766	0.12759	0.12742
15%	0.12780	0.12757	0.12747	0.12738
20%	0.12725	0.12703	0.12694	0.12682

Data table: 5. 9 Values of B-coefficient of Jones-Dole equation of $CoCl_3$ at different temperature

Conc. of EtOH	5°C	15°C	25°C	35°C
5%	0.12805	0.12781	0.12693	0.12622
10%	0.12779	0.12755	0.12679	0.12601
15%	0.12770	0.12746	0.12657	0.12651
20%	0.12715	0.12692	0.12643	0.12615

Data table: 5.10 Values of B-coefficient of Jones-Dole equation of $CuCl_2$ at different temperature

Conc. of MeOH(v/v)	5°C	15°C	25°C	35°C
5%	0.11789	0.11691	0.11683	0.11633
10%	0.11754	0.11666	0.11659	0.11622
15%	0.11692	0.11657	0.11647	0.11618
20%	0.11680	0.11653	0.11614	0.11602

Data table: 5.11 Values of B-coefficient of Jones-Dole equation of $CuCl_2$ at different temperature

Conc. of EtOH(v/v)	5°C	15°C	25°C	35°C
5%	0.11882	0.11204	0.11175	0.11162
10%	0.11787	0.11248	0.11193	0.11151
15%	0.11752	0.11233	0.11143	0.11114
20%	0.11747	0.1117	0.11113	0.11104

Data table:5.12 Values of B-coefficient of Jones-Dole equation of $MgCl_2$ at different temperature

Conc. of MeOH	5°C	15°C	25°C	35°C
5%	0.11709	0.11691	0.11673	0.11633
10%	0.11618	0.11616	0.11609	0.11602
15%	0.11643	0.11637	0.11627	0.11618
20%	0.11627	0.11623	0.11614	0.11612

Data table: 5.13 Values of B-coefficient of Jones-Dole equation of $MgCl_2$ at different temperature

Conc. Of EtOH	5°C	15°C	25°C	35°C
5%	0.11699	0.11681	0.11672	0.11669
10%	0.11674	0.11669	0.11655	0.11641
15%	0.11633	0.11624	0.11614	0.11605
20%	0.11617	0.11609	0.11601	0.11605

Data table:5.1 4 Values of B-coefficient of Jones-Dole equation of $NiCl_2$ at different temperature

Conc. of MeOH	5°C	15°C	25°C	35°C
5%	0.14262	0.12691	0.12683	0.12633
10%	0.13741	0.12666	0.12649	0.12632
15%	0.1368	0.12657	0.12647	0.12628
20%	0.13604	0.12643	0.12634	0.12622

Data table: 5.15 Values of B-coefficient of Jones-Dole equation of $NiCl_2$ at different temperature

Conc. of EtOH	5°C	15°C	25°C	35°C
5%	0.11832	0.11822	0.11813	0.11808
10%	0.11829	0.11819	0.11813	0.11809
15%	0.11817	0.11816	0.11815	0.11814
20%	0.11718	0.11710	0.11704	0.11684

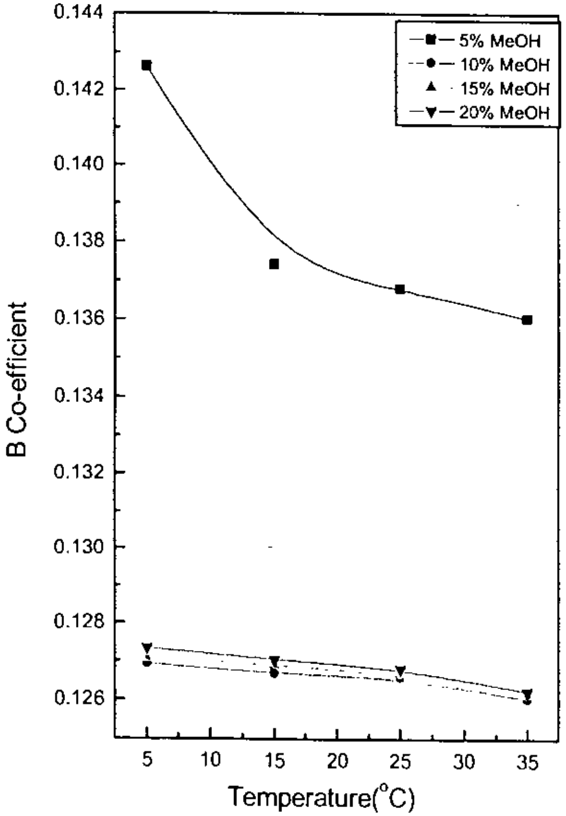


fig.5.86: Variation of B Co-efficient of diff. conc. of $FeCl_3$ at diff. temperature

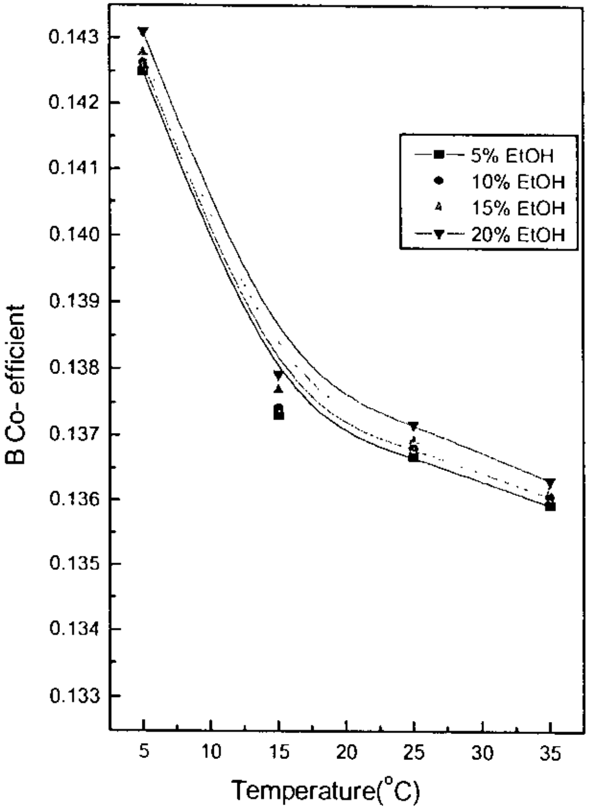


fig.5.87: Variation of B Co-efficient of diff. conc. of $FeCl_3$ at diff. temperature

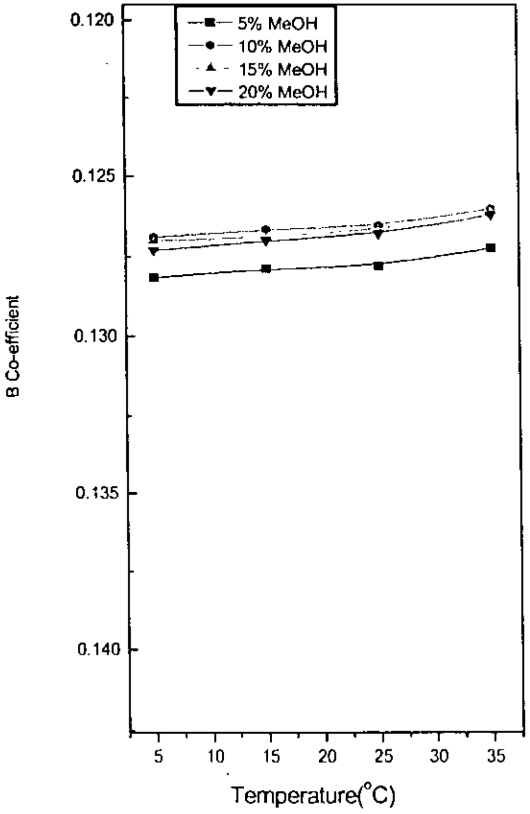


fig.5.88: Variation of B Co-efficient of diff. conc. of $CoCl_3$ at diff. temperature

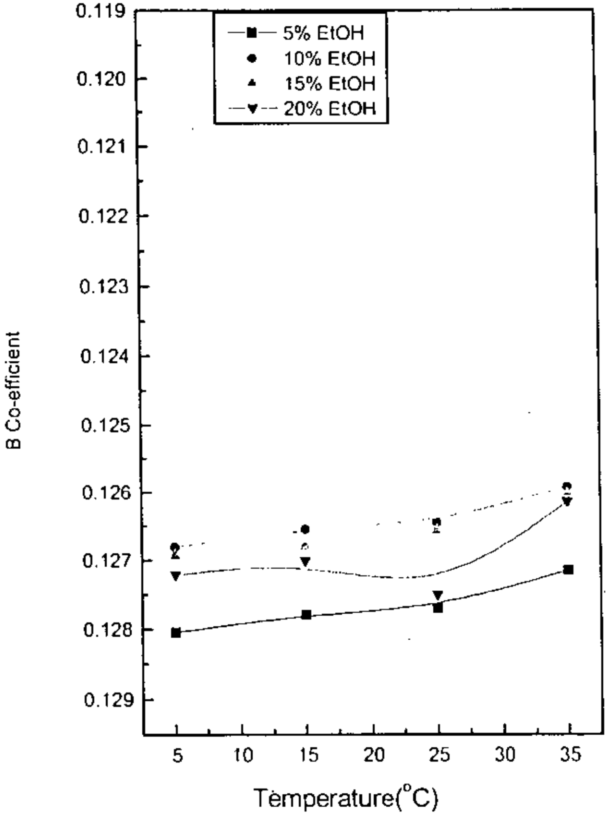


fig.5.89: Variation of B Co-efficient of diff. conc. of $CoCl_3$ at diff. temperature

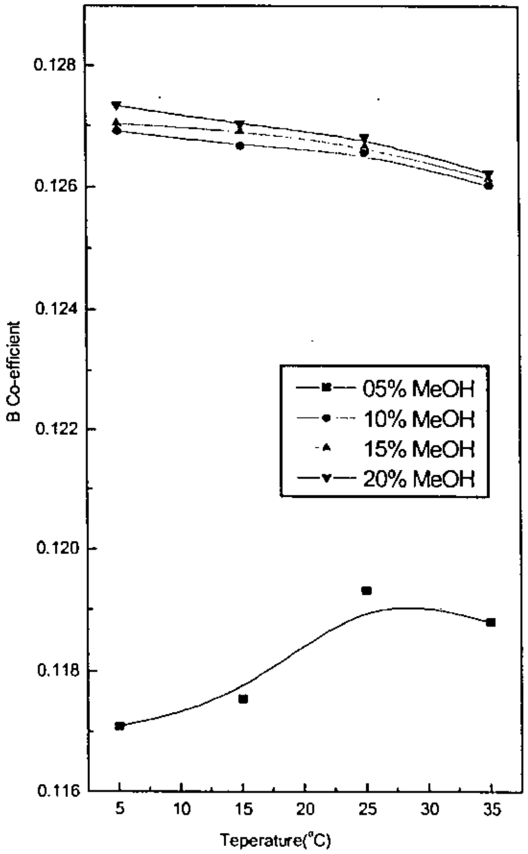


fig.5.90: Variation of B Co-efficient of diff. conc. of $CuCl_2$ at diff. temperature

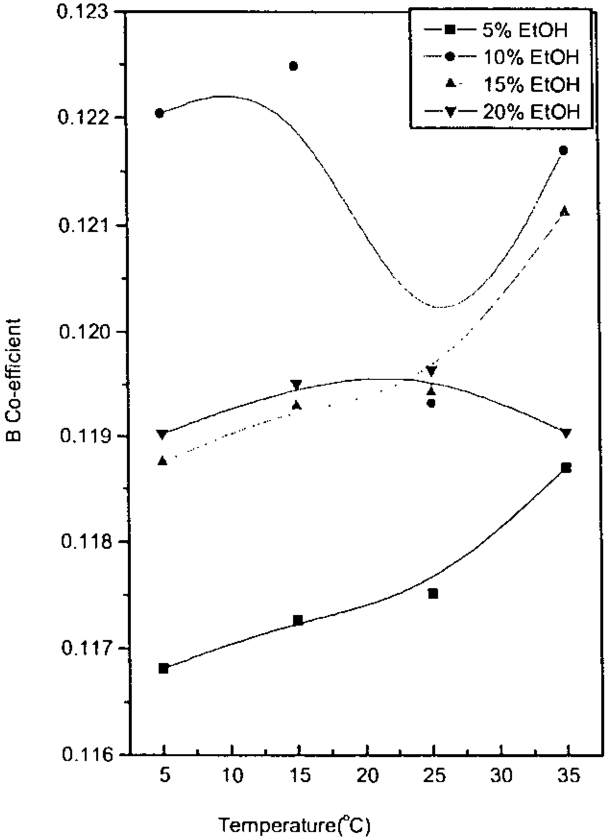


fig. 5.91: Variation of B Co-efficient of diff. conc. of $CuCl_2$ at diff. temperature

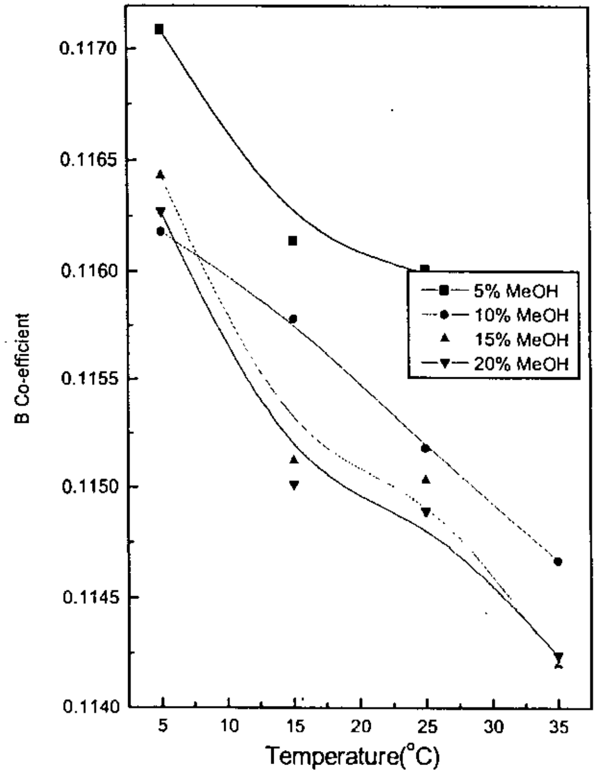


fig.5.92: Variation of B Co-efficient of diff. conc. of $MgCl_2$ at diff. temperature

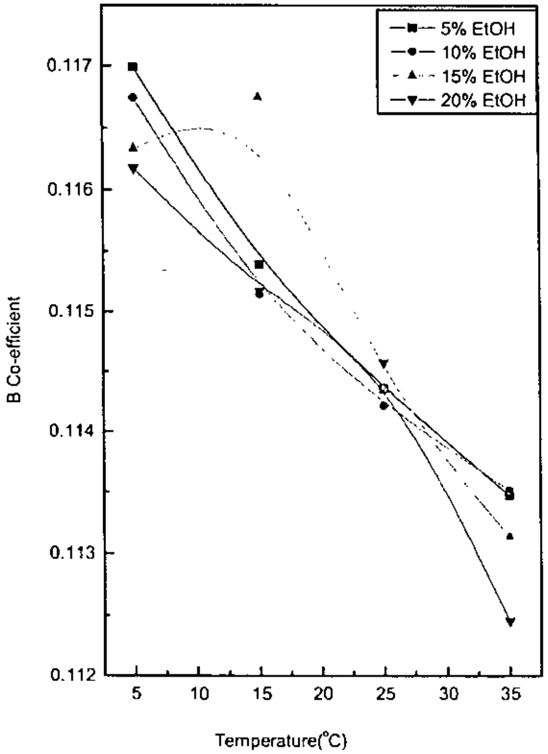


fig.5.93: Variation of B Co-efficient of diff. conc. of $MgCl_2$ at diff. temperature

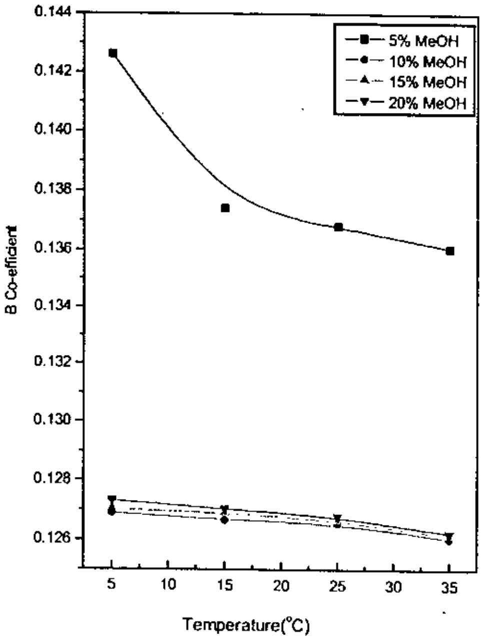


fig.5.94: Variation of B Co-efficient of diff. conc. of $NiCl_2$ at diff. temperature

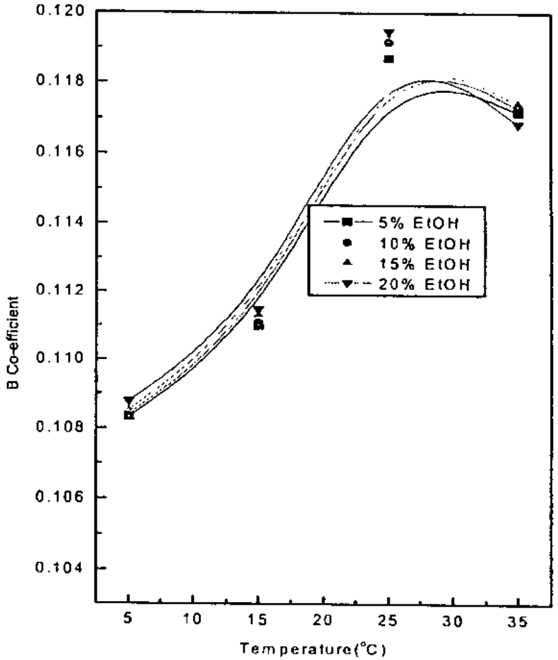


fig.5.95: Variation of B Co-efficient of diff. conc. of $NiCl_2$ at diff. temperature

If there is no chemical interaction in solution, the measurement of viscosity data and its corresponding result of flow process is related to the change in size and interaction between the hydrodynamic group which characterize the flow process. The variation of enthalpy of activation corresponds to the change of activation between hydrodynamic units. The energy (enthalpy) of activation of flow can be determined from the temperature dependence of viscosity. The temperature dependence of viscosity can be expressed mathematically by the linear equation [120]

$$\eta = A \exp[B/(T-T_o)]$$

Taking logarithim of the equation on can get

$$\ln\eta = \ln A + B(T-T_o)$$

In addition to these equation there are some other equation which also express the temperature dependence of viscosity of liquid solution:

$\eta = A \exp(B/T)$ ....a

$\eta= A \exp(B/T^n)$ ....b

$\eta= A\, T^{1/2}\exp[B/(T-T_0)]$ c

$\eta= A\, T^n \exp[B/(T-T_0)]$ ....d

$\eta= A\, T^{1/2}\exp[B/(T-T_0) + C/T]$ ....e

Here B represents energy change of activation of flow process . Among these , equation (a) was proposed by Eyring [52] and is considered as the simplest and most suitable over a small range of temperature. In this study this equation has been used to determine the enthalpy change of flow process of deferent solution investigated.

To determine the value of enthalpy of activation the logarithim form of this equation $\Delta H_\eta^\# \approx \Delta E_\eta^\# = R\frac{d\ln\eta}{d(\frac{1}{T})}$

The diagram drawn by taking $\ln\eta$ Vs $\frac{1}{T}$ gives straight lines of which the slope represents $\Delta H_\eta^{\#}$ or $\Delta E_\eta^{\#}$.

The calculated values of $\Delta H_\eta^{\#} \approx \Delta E_\eta^{\#}$ are presented in table 5.16-5.25. It is evident from the table that the enthalpy of flow process increase with the increase of concentration of electrolytes. The values of enthalpy of activation for electrolytes sequences are $FeCl_3 > CoCl_3 > CuCl_2 > MgCl_2 > NiCl_2$.

The increases of enthalpy of activation correspond to the increase in intensification of structure. From this it may be said that the presence of alcohol enhances the structure making property of different electrolytes under study. It is also from the above sequence that the enthalpy of activation i.e. structure intensification is higher in the case of electrolytes having higher charge density of cation. Among the studied electrolytes Fe^{3+} has highest and Ni^{2+} has lowest charge density. From the values of free energy of activation change and enthalpy change of activation , the value of change in entropy is calculated using the equations:

$$\Delta G_\eta^{\#}=\Delta H_\eta^{\#}-T\Delta S_\eta^{\#}$$

$$\text{or} \quad \Delta S_\eta^{\#} = \frac{\Delta H_\eta^{\#} - \Delta G_\eta^{\#}}{T}$$

Data table: 5.16 Enthalpy $\Delta H_{\eta}^{\#}$ ($K.cal.mol^{-1}$) of different solution of $FeCl_3$ at different temperature

Conc. of MeOH (v/v)	Concentration of $FeCl_3$				
	0.05	0.01	0.15	0.20	0.25
0 %	64.898	66.578	68.246	69.901	70.576
5%	64.901	66.587	68.256	69.904	70.579
10%	64.904	66.590	68.259	69.907	70.583
15%	64.905	66.914	68.260	69.909	70.596
20%	64.907	66.593	68.262	69.910	70.599

Data table:5.17 Enthalpy $\Delta H_{\eta}^{\#}$ ($K.cal.mol^{-1}$) of different solution of $FeCl_3$ at different temperature

Conc. of EtOH (v/v)	Concentration of $FeCl_3$				
	0.05	0.01	0.15	0.20	0.25
0%	64.898	66.578	68.246	69.901	70.576
5%	66.634	66.427	68.090	69.733	69.735
10%	66.635	66.428	68.091	69.734.	69.739
15%	63.637	66.430	68.093	69.736	69.742
20%	64.752	66.431	68.093	69.737	69.746

Data table:5.18 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $CoCl_3$ at different temperature

Conc. of MeOH (v/v)	Concentration of $CoCl_3$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.731	66.413	68.088	69.721	69.724
5%	64.705	66.383	68.045	69.684	69.689
10%	64.707	66.386	68.048.	69.687	69.692
15%	64.712	66.389	68.051	69.690	69.695
20%	64.713	66.392	68.054	69.693	69.699

Data table: 5.19 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $CoCl_3$ at different temperature

Conc. of EtOH (v/v)	Concentration of $CoCl_3$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.731	66.413	68.088	69.721	69.724
5%	64.748	66.427	68.090	69.733	69.789
10%	64.750	66.428	68.091	69.734	69.792
15%	64.750	66.430	68.093	69.736	69.795
20%	64.752	66.431	68.094	69.737	69.799

Data table: 5.20 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $CuCl_2$ at different temperature

Conc. of MeOH (v/v)	Concentration of $CuCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.959	66.646	68.312	69.959	69.961
5%	64.961	66.647	68.316	69.961	69.967
10%	64.961	66.648	68.318	69.963	69.968
15%	64.962	66.649	68.318	69.964	69.972
20%	64.964	66.650	68.320	69.966	69.979

Data table:5.21 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $CuCl_2$ at different temperature

Conc. of EtOH (v/v)	Concentration of $CuCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.959	66.646	68.312	69.959	69.724
5%	64.951	66.640	68.311	69.960	69.689
10%	64.956	66.645	68.316	69.965	69.692
15%	64.959	66.646	68.317	69.968	69.695
20%	64.965	66.642	68.323	69.975	69.699

Data table: 5.22 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $MgCl_2$ at different temperature.

Conc. of MeOH (v/v)	Concentration of $MgCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.663	66.338	67.999	69.638	70.21
5%	64.666	66.347	68.002	69.642	70.216
10%	64.667	66.345	68.003	69.643	70.224
15%	64.669	66.343	68.005	69.646	70.235
20%	64.671	66.342	68.007	69.648	70.256

Data table: 5.23 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $MgCl_2$ at different temperature.

Conc. of EtOH (v/v)	Concentration of $MgCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.663	66.338	67.999	69.638	70.124
5%	64.665	66.341	68.001	69.640	70.129
10%	64.666	66.343	68.003	69.643	70.131
15%	64.669	66.345	68.005	69.646	70.138
20%	64.713	66.392	68.054	69.693	69.699

Data table: 5.24 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $NiCl_2$ at different temperature

Conc. of MeOH (v/v)	Concetration of $NiCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.876	66.568	68.241	69.891	70.214
5%	64.892	66.577	68.245	69.893	70.219
10%	64.893	66.580	68.248	69.895	70.314
15%	64.895	66.581	68.249	69.898	70.318
20%	64.897	66.582	68.250	69.899	70.324

Data table: 5.25 Enthalpy $\Delta H_{\eta}^{\#}$ (K.cal.mol^{-1}) of different solution of $NiCl_2$ at different temperature

Conc. of MeOH (v/v)	Concetration of $NiCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	64.876	66.568	68.241	69.891	70.451
5%	64.744	66.422	68.082	69.724	70.462
10%	64.745	66.425	68.086	69.729	70.493
15%	64.747	66.427	68.086	69.731	70.498
20%	64.713	66.392	68.054	69.693	70.505

Among the different parameters of thermodynamics quantities of free energy change is most important The free energy change of flow process for different solutions under study were calculated using the equation:

$$\Delta G_{\eta}^{\#}=RTln\frac{V\eta}{hN_{A}}$$

Here,V is the molar volume of liquid solution, η is viscosity, h is Plank's constant and N_A is Avogrado number.

The values of free energy of activation $\Delta G_{\eta}^{\#}$ for viscous flow are represented in graph 5.96-5.137 appendix-V. It is observed from the results presented in graph that the value of $\Delta G_{\eta}^{\#}$ of different solutions of electrolytes under study increase with the increase of concentration of methanol or ethanol. From the figures it is also found that the value of $\Delta G_{\eta}^{\#}$ of different the solutions of electrolytes under study increases with temperature. It is also observed from the figures that the values of $\Delta G_{\eta}^{\#}$ of various electrolytes under study in water-methanol increase less than in water-ethanol. It is also observed that $\Delta G_{\eta}^{\#}$ values are all positive. These results indicates that the viscous flow is not favored. During the viscous flow the molecules have to overcome the transition state of higher energy compared to that of the ground state. The positive values of free energy of activation of viscous flow can be explained in the light of model proposed by Furth [122]. According this model the kinetic species involved in the viscous flow move into a cavity (hole) and the work involved in forming this hole in the liquid medium is given by the work required in forming the hole against surface tension of the liquid. The higher positive values indicate strong solute-solvent interaction rendering the solution more structured.

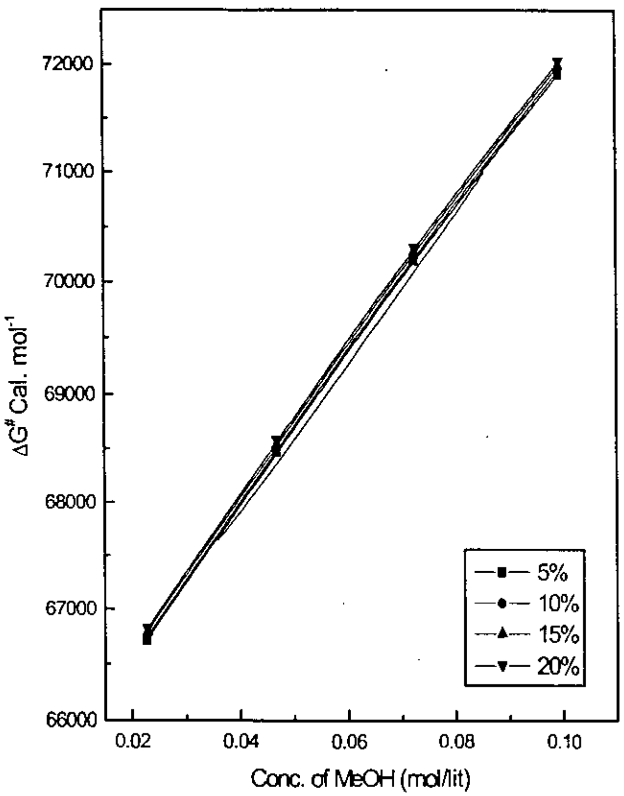


Fig.5.96: Variation of free energy of MeOH at different temperatur.

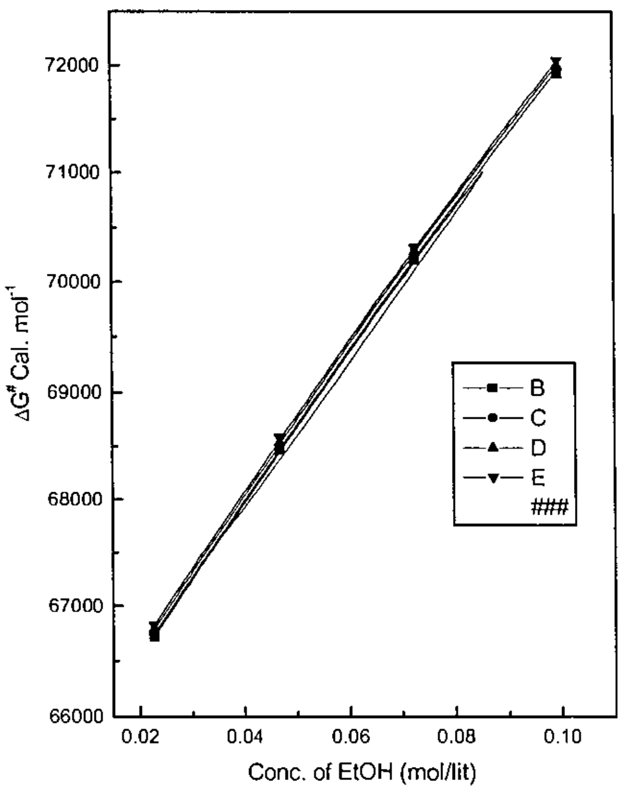


Fig.5.97 Variation of free energy of EtOH at different temperature

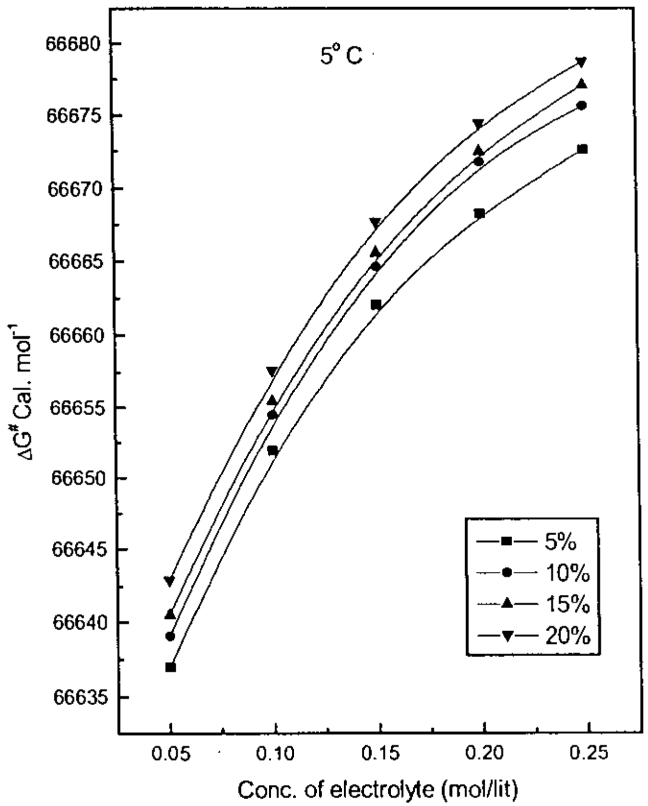


Fig.5.98: Variation of free energy of $FeCl_3$ at different concentration of MeOH.

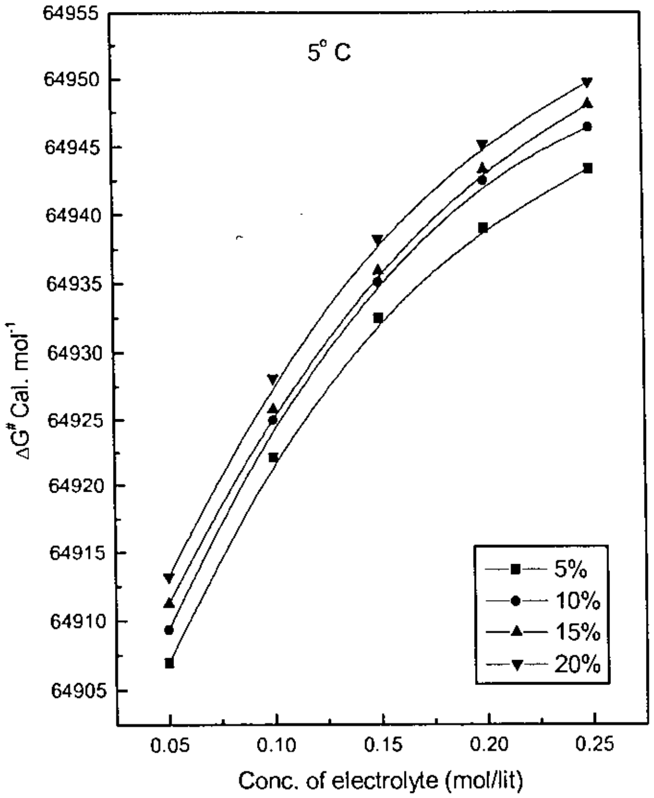


Fig. 5.99: Variation of free energy of $FeCl_3$ at different concentration of EtOH.

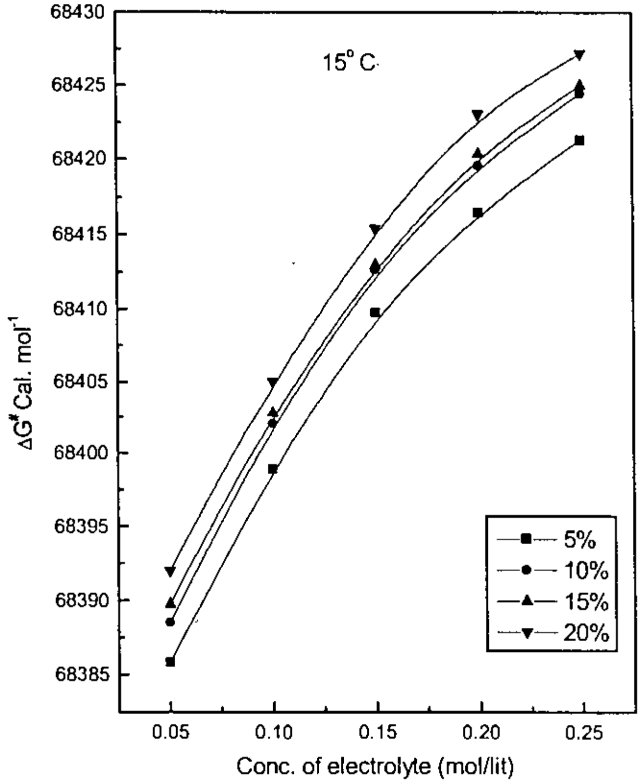


Fig. 5.100: Variation of free energy of $FeCl_3$ at different concentration of MeOH.

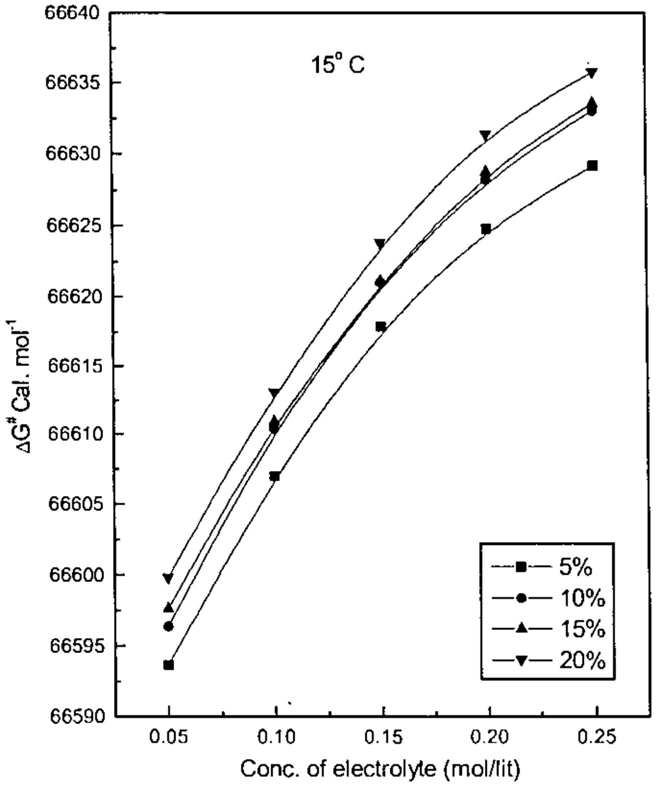


Fig. 5.101: Variation of free energy of $FeCl_3$ at different concentration of EtOH.

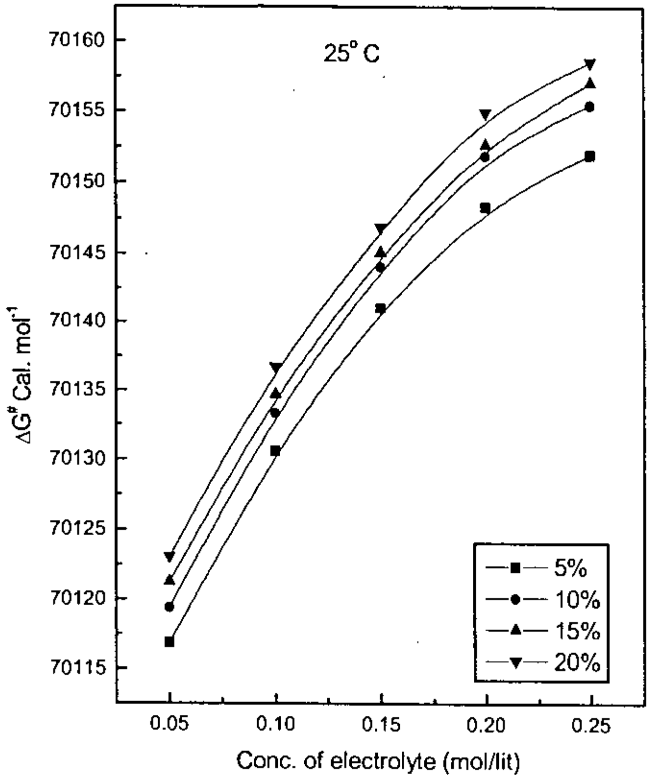


Fig. 5.102: Variation of free energy of $FeCl_3$ at different concentration of MeOH.

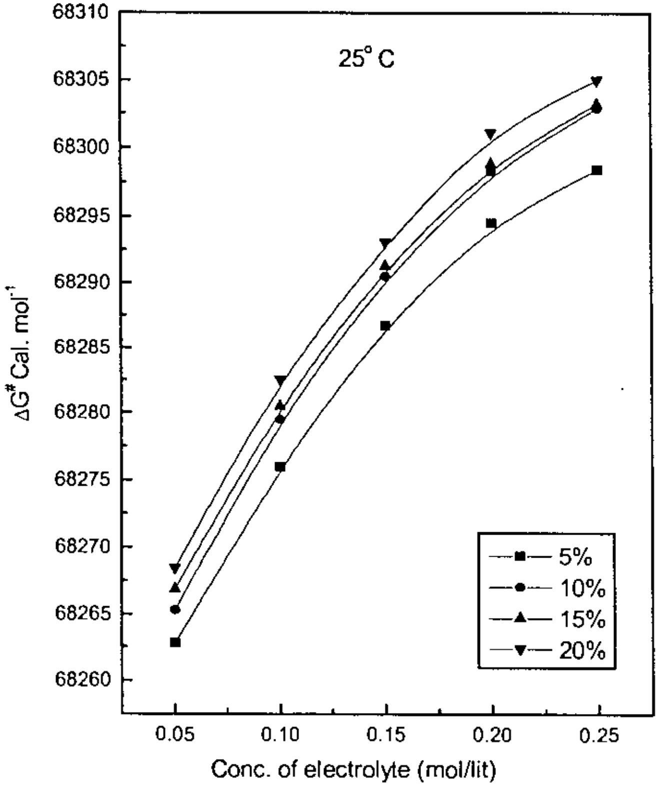


Fig. 5.103: Variation of free energy of $FeCl_3$ at different concentration of EtOH.

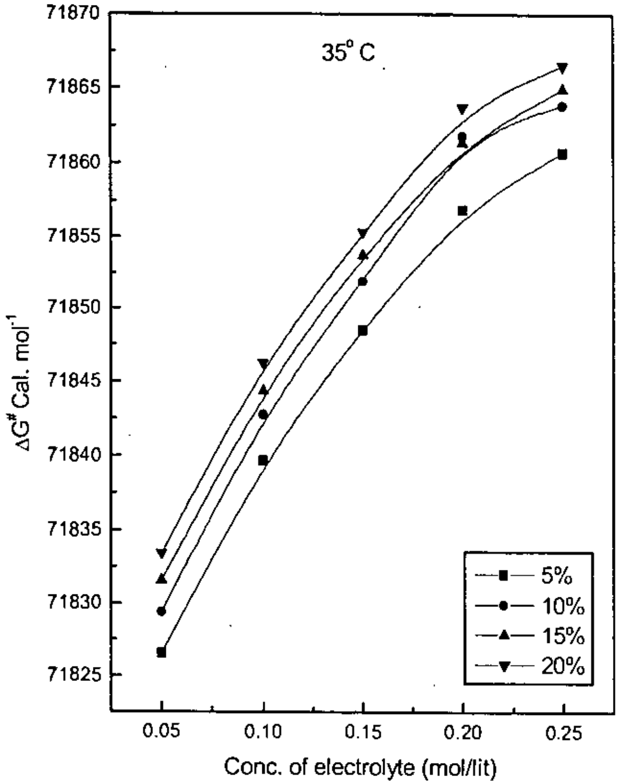


Fig. 5.104: Variation of free energy of $FeCl_3$ at different concentration of MeOH.

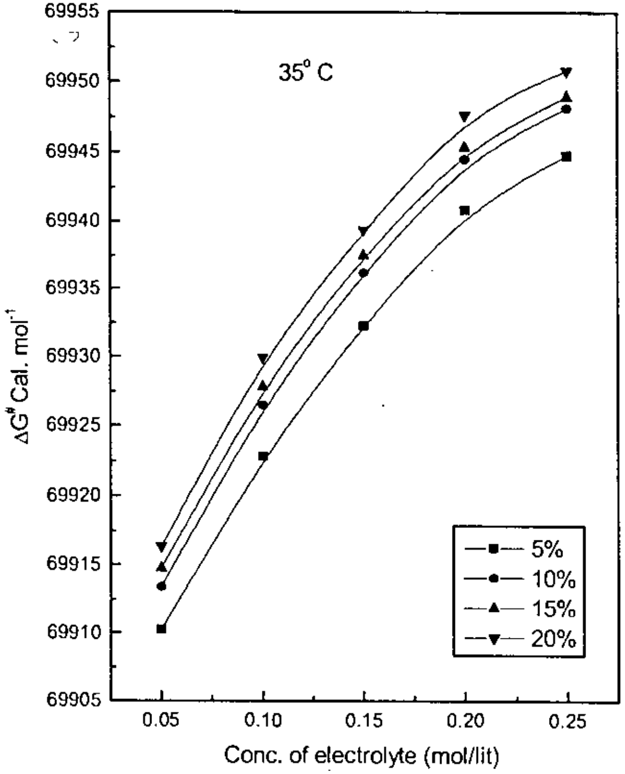


Fig. 5.105: Variation of free energy of $FeCl_3$ at different concentration of EtOH.

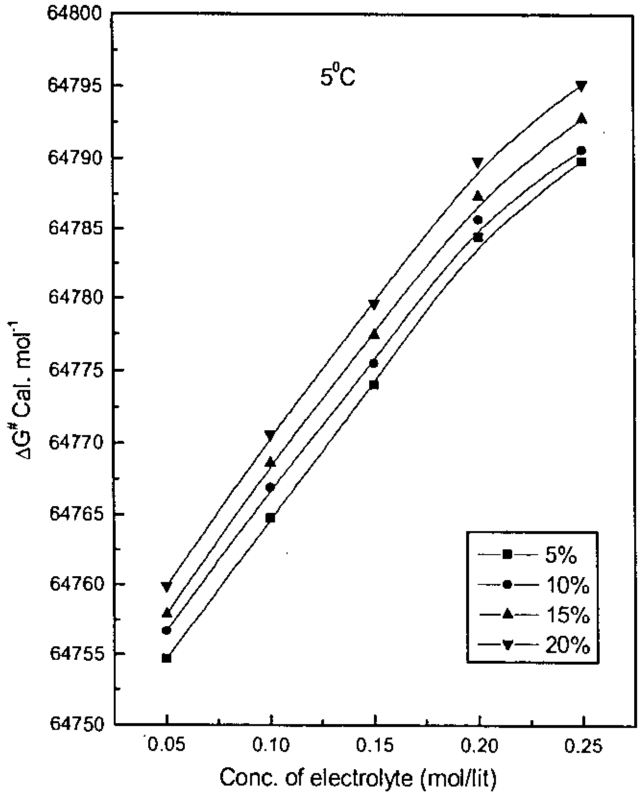


Fig. 5.106: Variation of free energy of $CoCl_2$ at different concentration of MeOH.

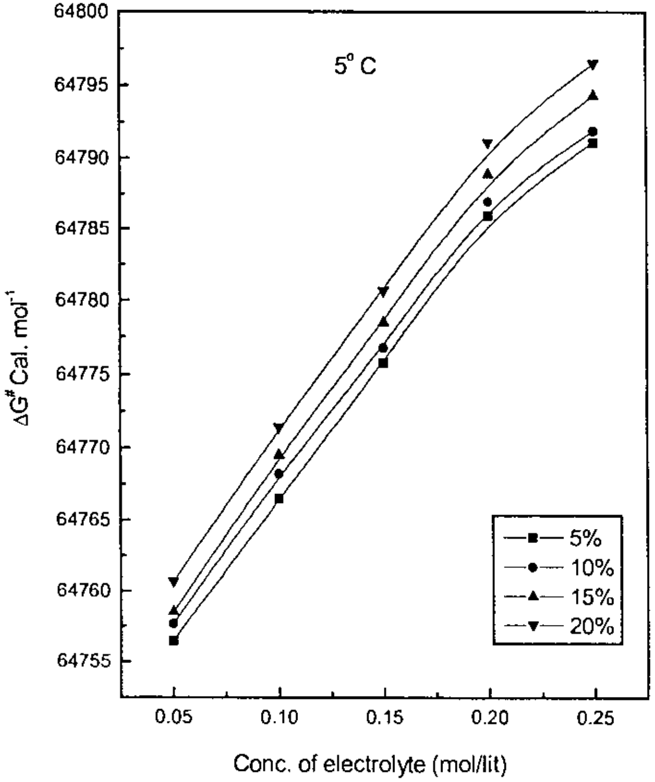


Fig. 5.107: Variation of free energy of $CoCl_2$ at different concentration of EtOH.

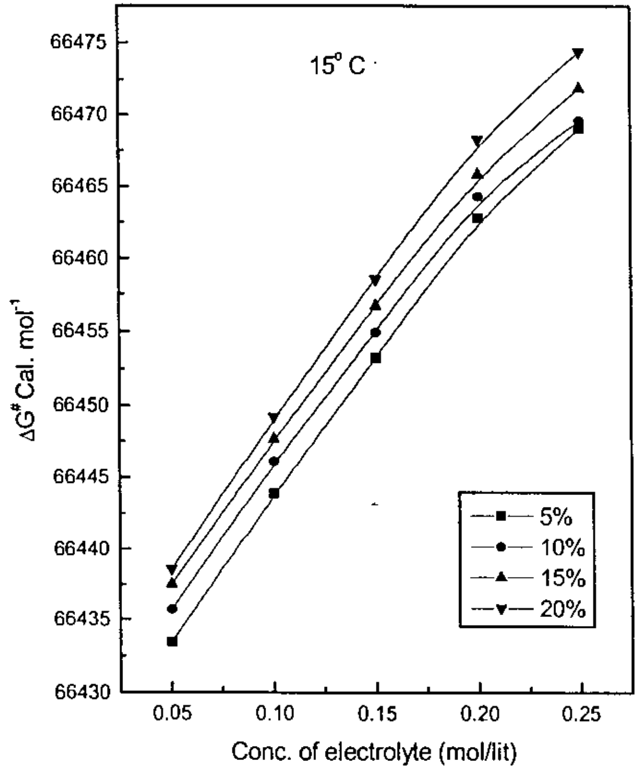


Fig. 5.108: Variation of free energy of $CoCl_2$ at different concentration of MeOH.

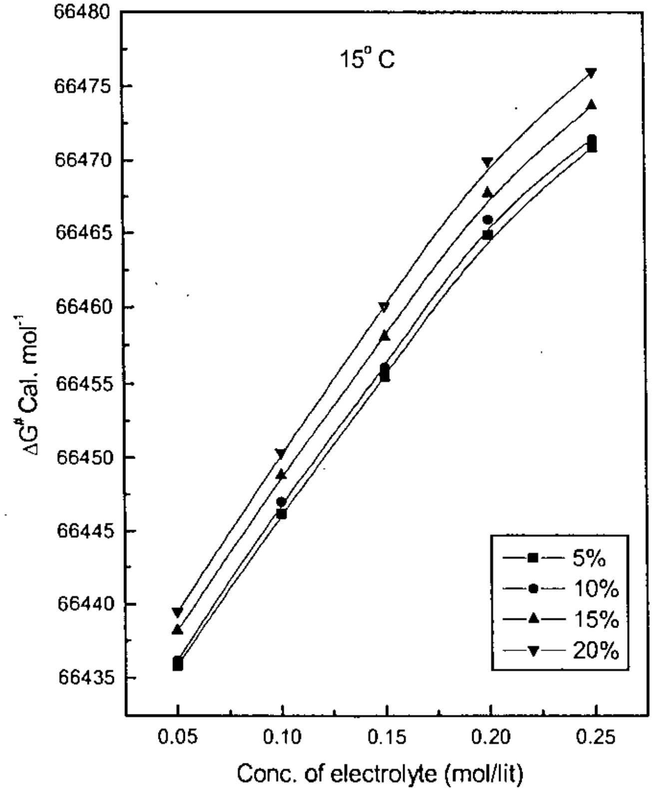


Fig. 5.109: Variation of free energy of $CoCl_2$ at different concentration of EtOH.

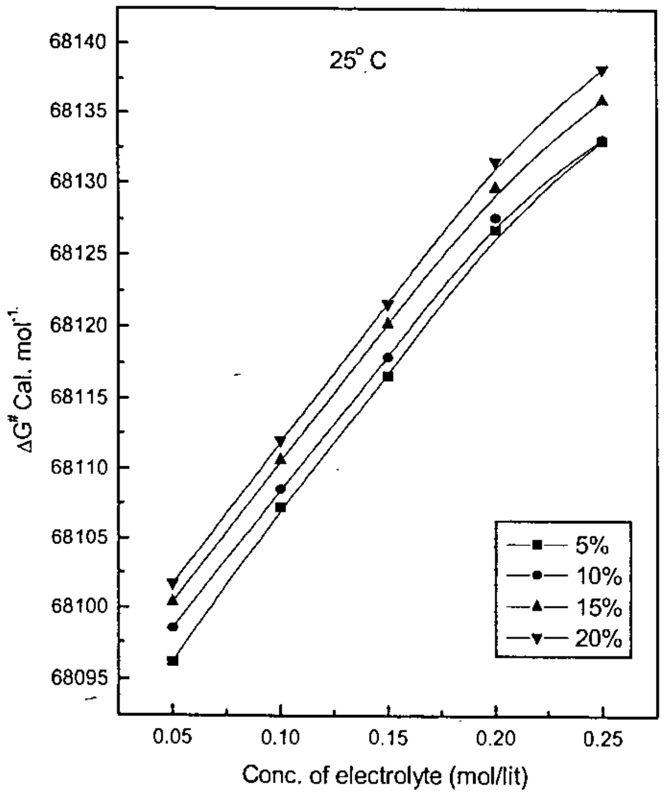


Fig. 5.110: Variation of free energy of $CoCl_2$ at different concentration of MeOH.

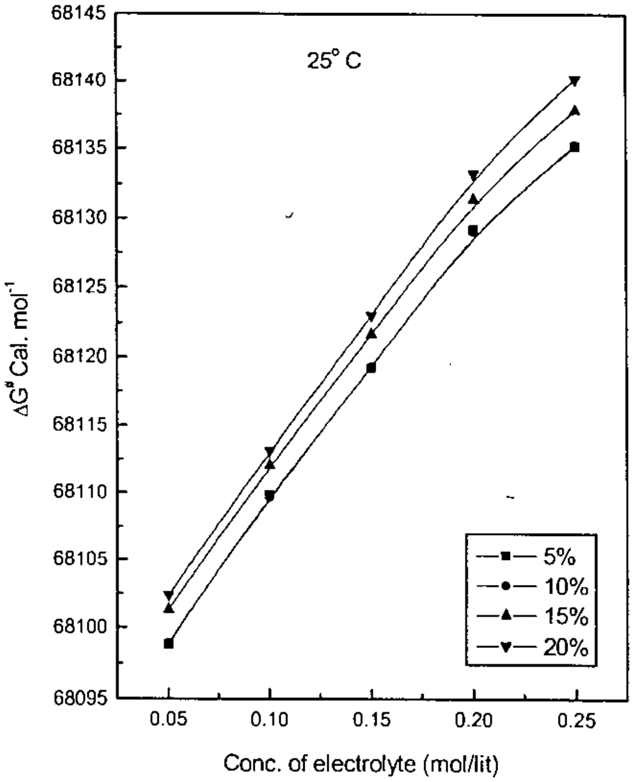


Fig. 5.111: Variation of free energy of $CoCl_2$ at different concentration of EtOH.

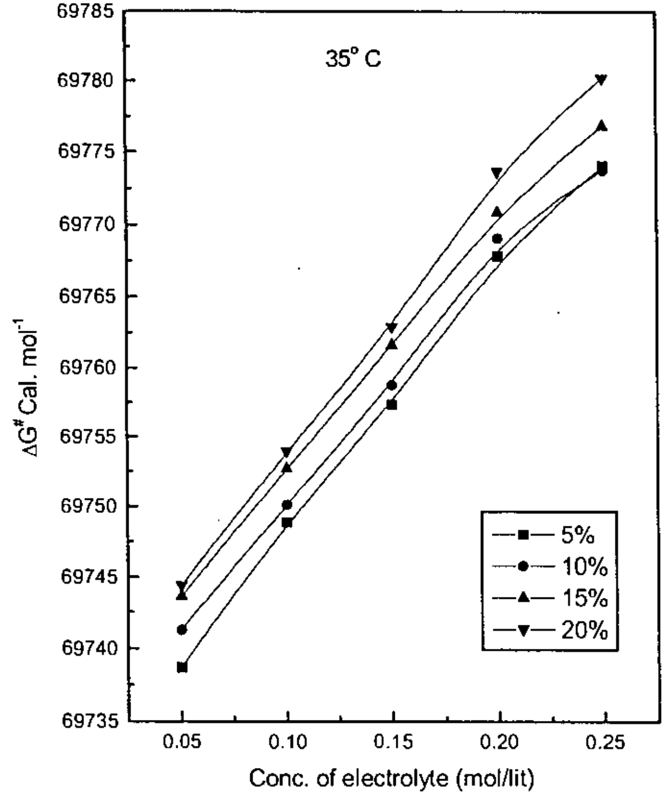


Fig. 5.112: Variation of free energy of $CoCl_2$ at different concentration of MeOH.

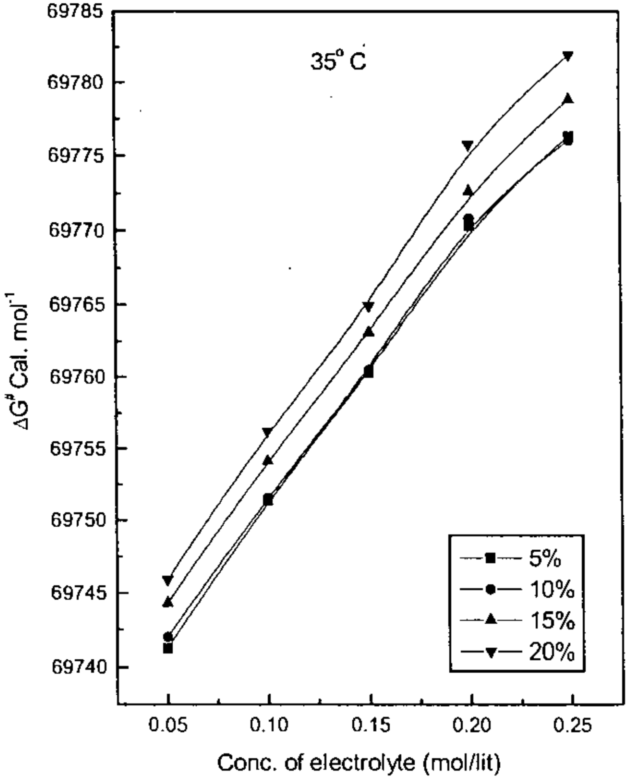


Fig. 5.113: Variation of free energy of $CoCl_2$ at different concentration of EtOH.

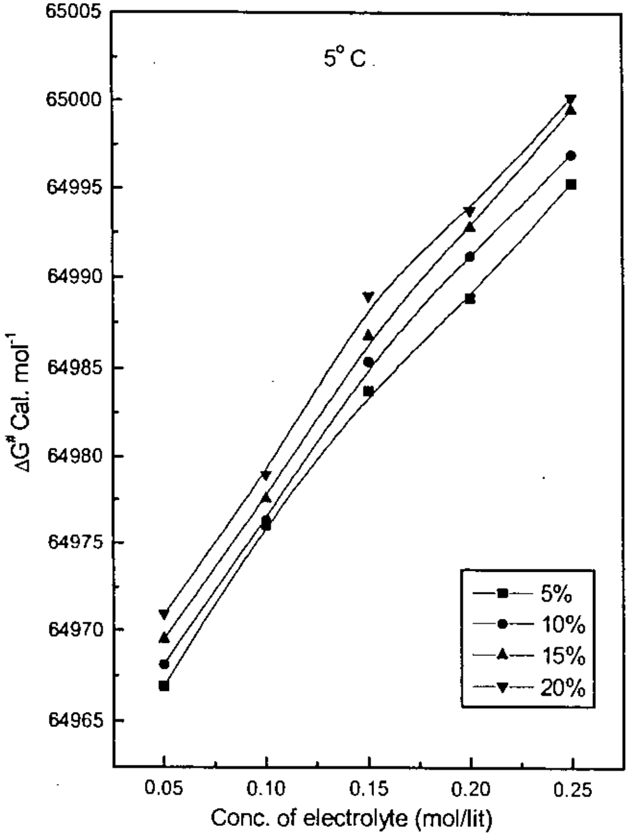


Fig. 5.114: Variation of free energy of $CuCl_2$ at different concentration of MeOH.

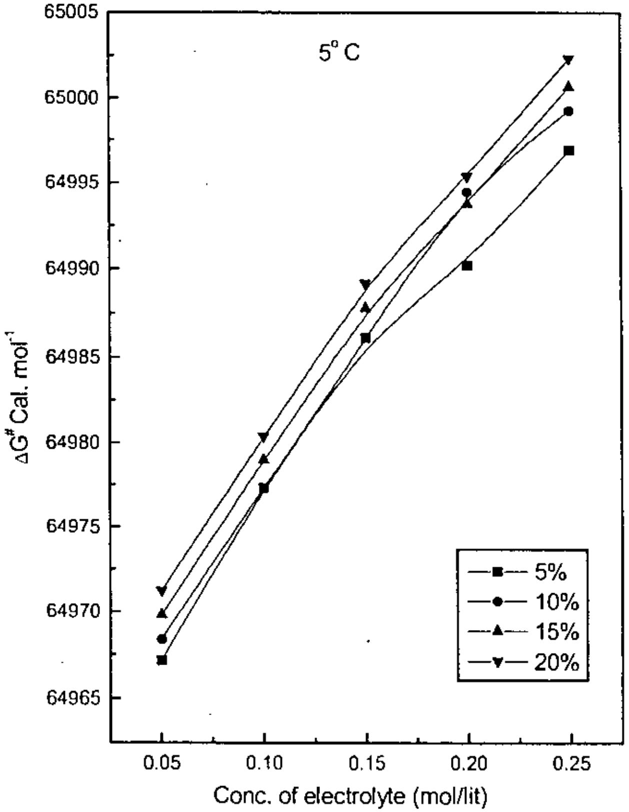


Fig. 5.115: Variation of free energy of $CuCl_2$ at different concentration of EtOH.

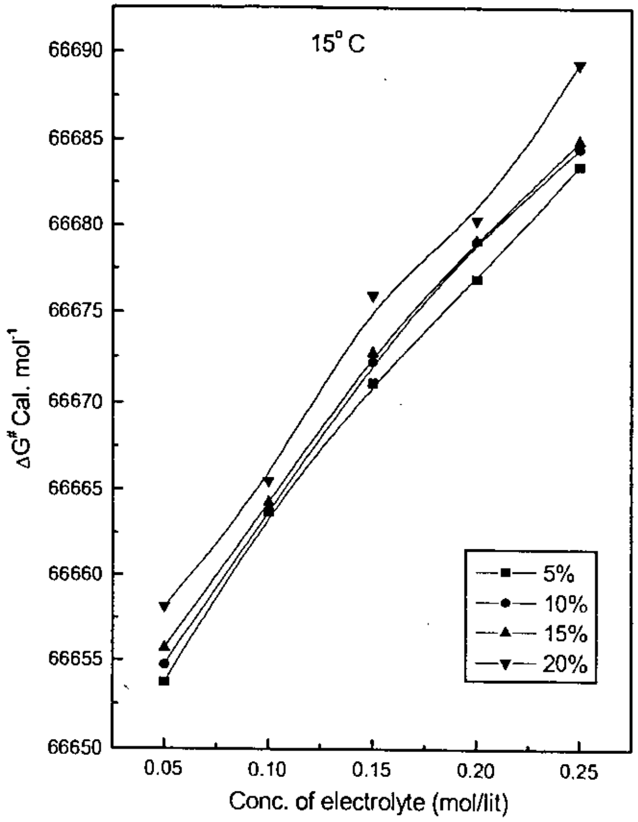


Fig. 5.116: Variation of free energy of $CuCl_2$ at different concentration of MeOH.

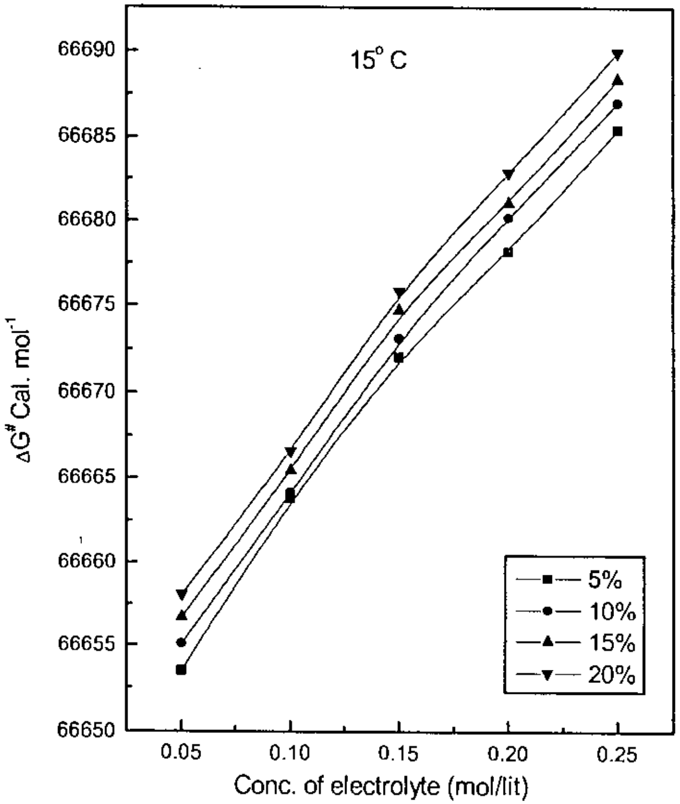


Fig. 5.117: Variation of free energy of $CuCl_2$ at different concentration of EtOH.

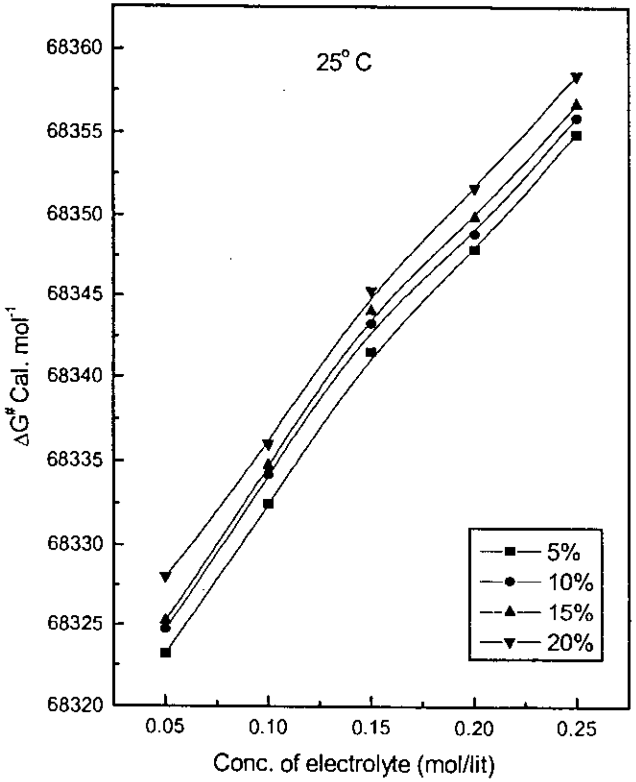


Fig. 5.118: Variation of free energy of $CuCl_2$ at different concentration of MeOH.

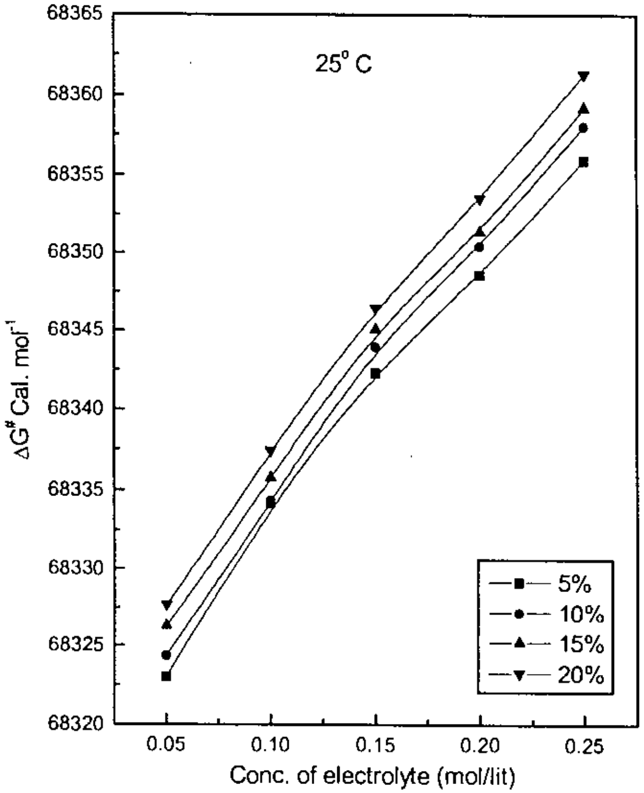


Fig. 5.119: Variation of free energy of $CuCl_2$ at different concentration of EtOH.

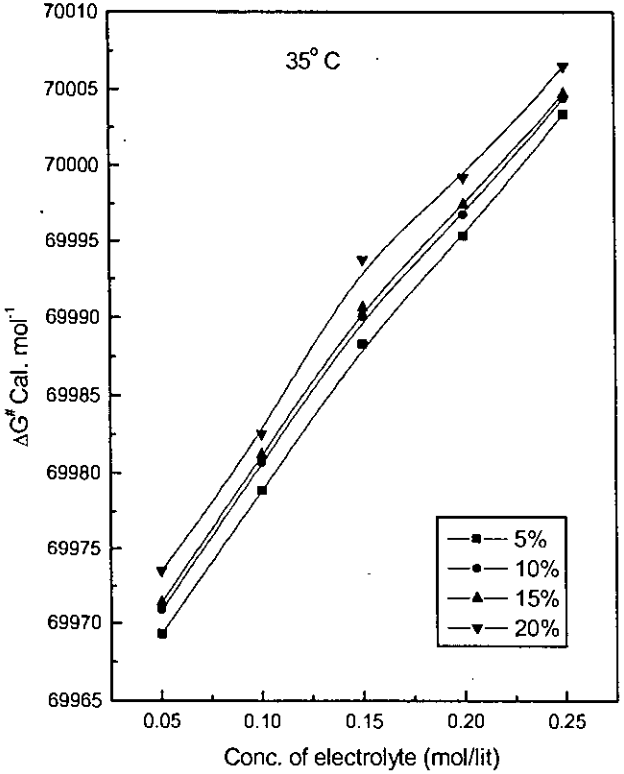


Fig. 5.120: Variation of free energy of $CuCl_2$ at different concentration of MeOH.

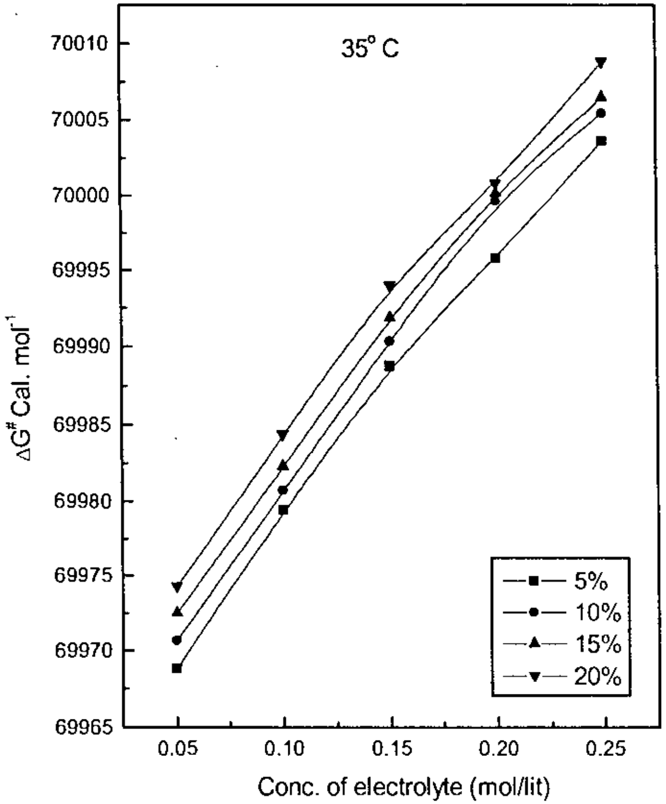


Fig. 5.121: Variation of free energy of $CuCl_2$ at different concentration of EtOH.

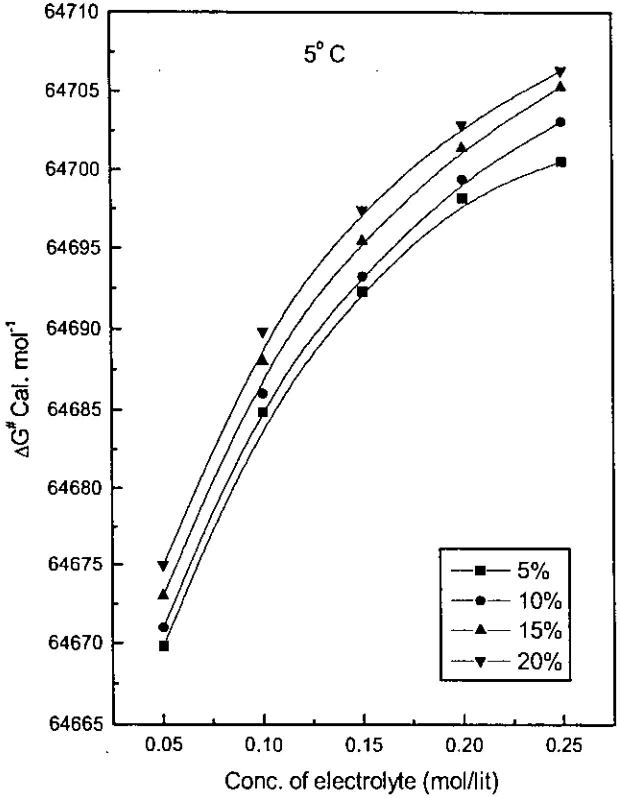


Fig. 5.122: Variation of free energy of $MgCl_2$ at different concentration of MeOH.

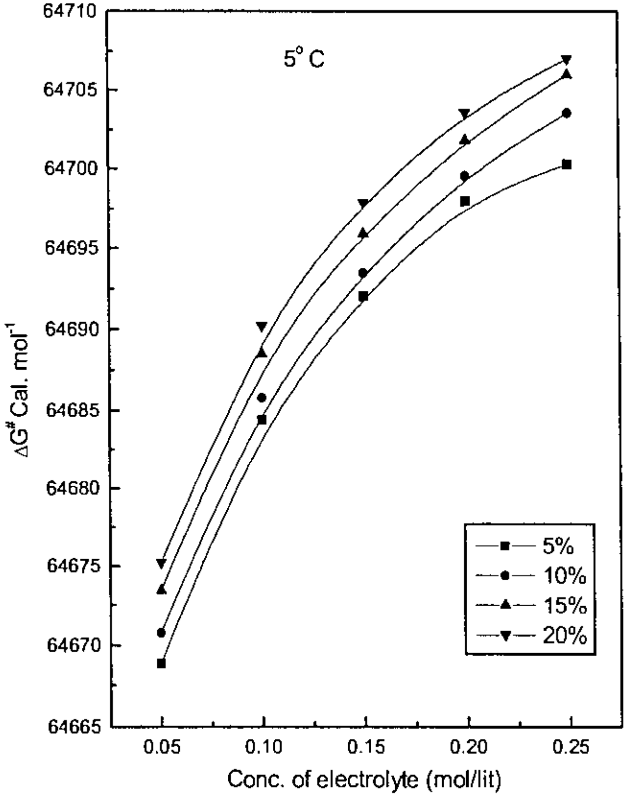


Fig. 5.123: Variation of free energy of $MgCl_2$ at different concentration of EtOH.

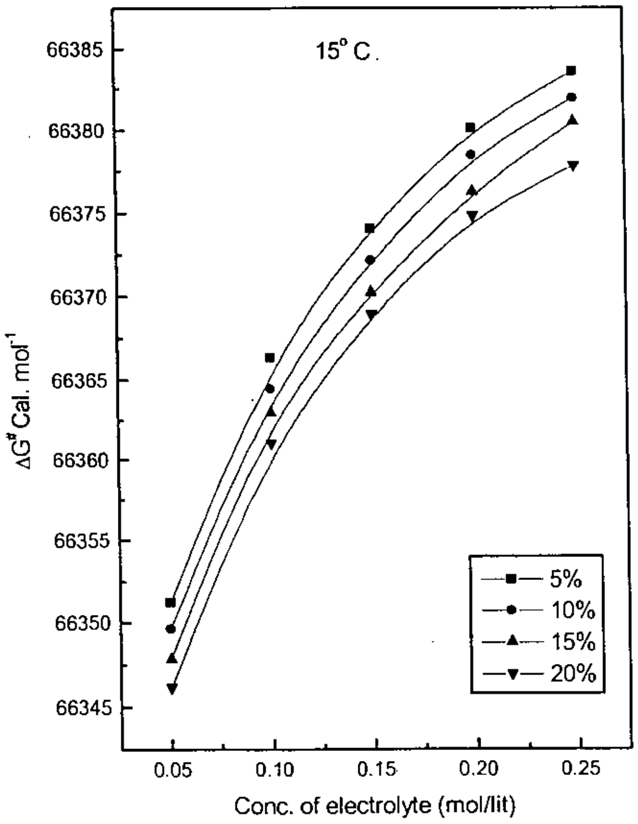


Fig. 5.124: Variation of free energy of $MgCl_2$ at different concentration of MeOH.

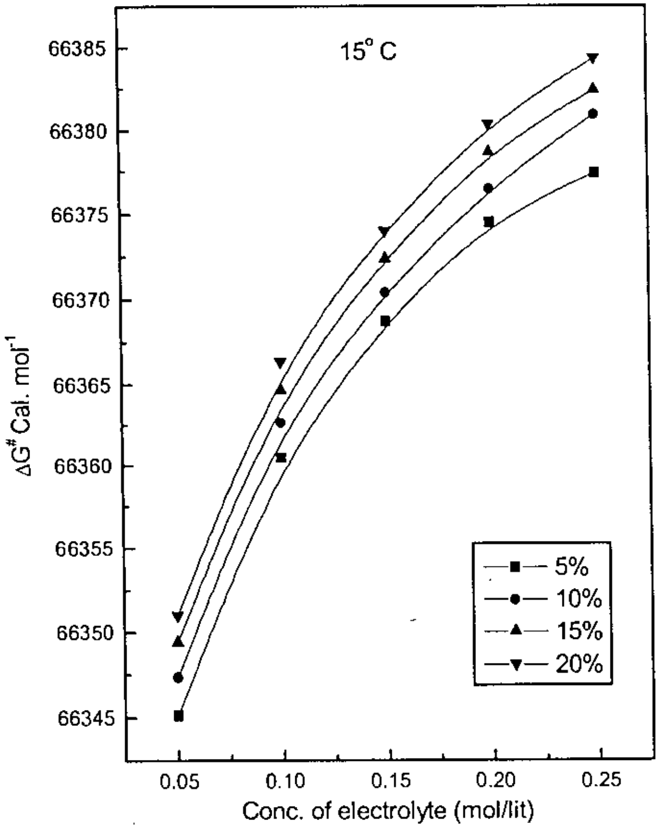


Fig. 5.125: Variation of free energy of $MgCl_2$ at different concentration of EtOH.

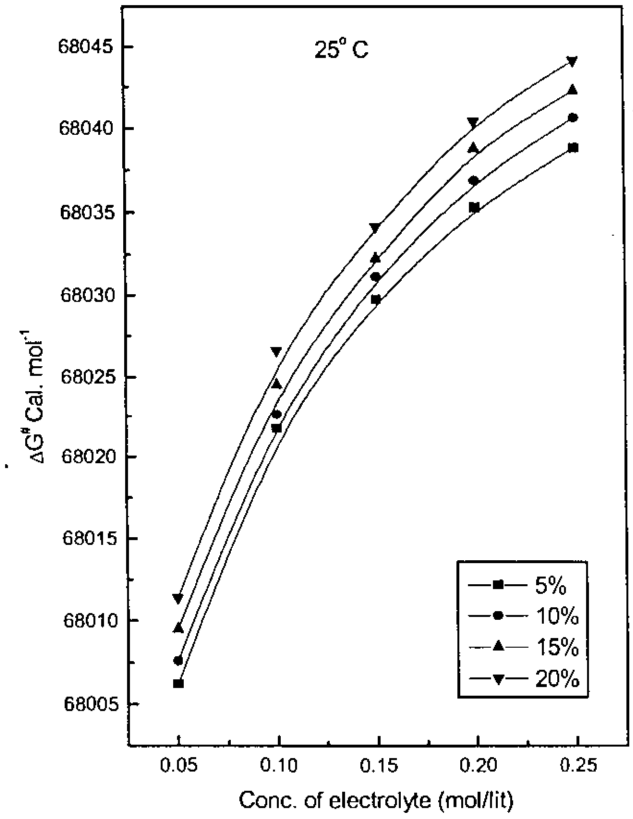


Fig. 5.126: Variation of free energy of $MgCl_2$ at different concentration of MeOH.

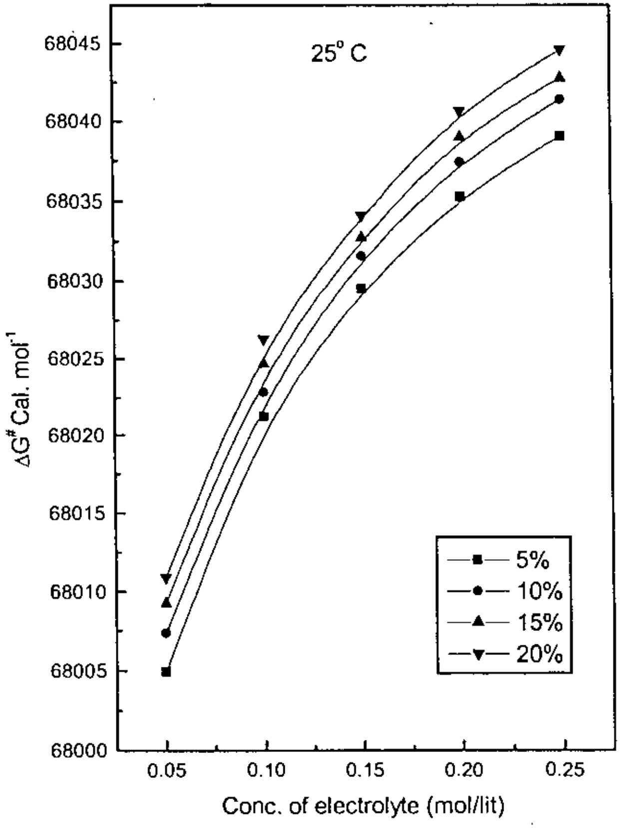


Fig. 5.127: Variation of free energy of $MgCl_2$ at different concentration of EtOH.

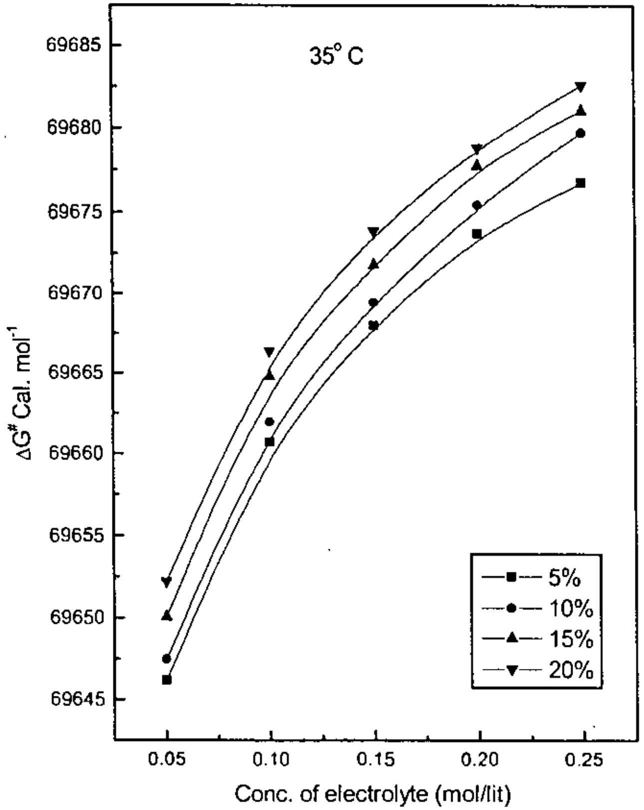


Fig. 5.127: Variation of free energy of $MgCl_2$ at different concentration of MeOH.

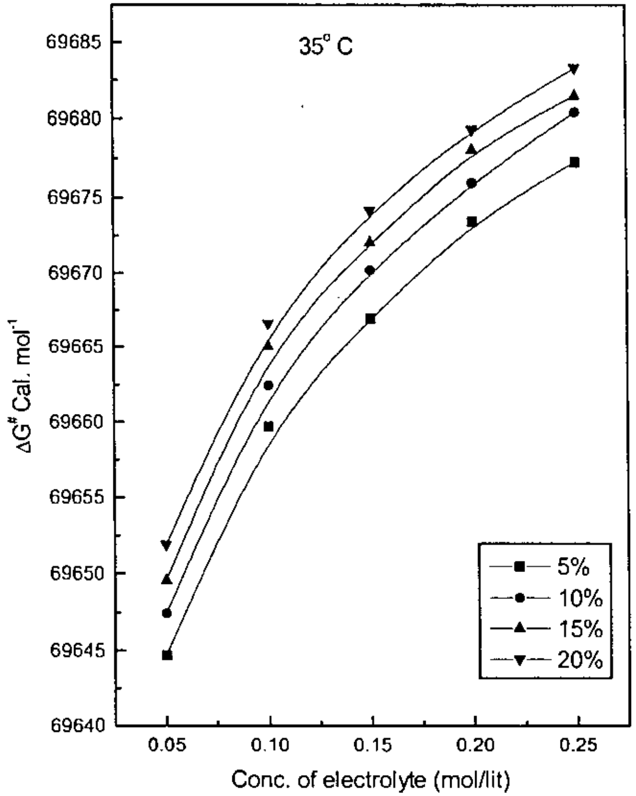


Fig. 5.128: Variation of free energy of $MgCl_2$ at different concentration of EtOH.

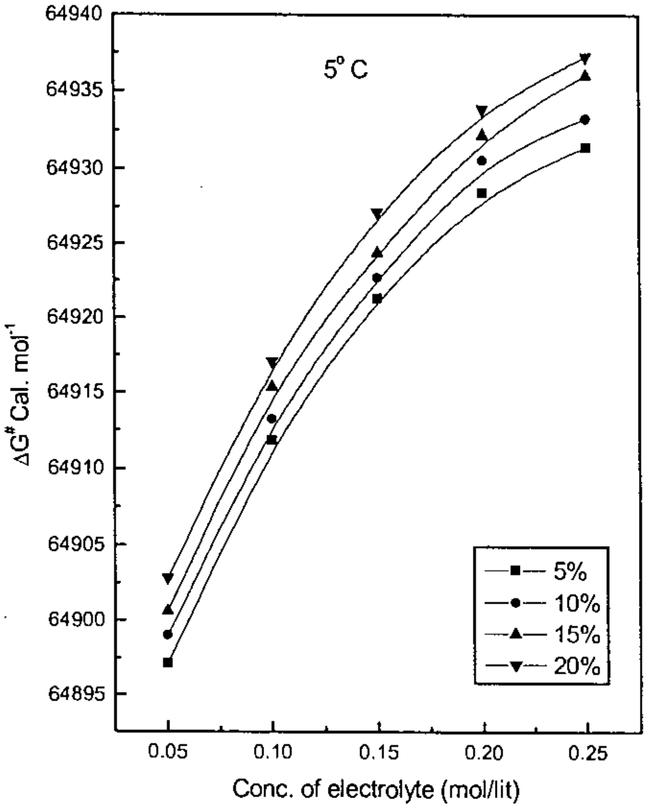


Fig. 5.129: Variation of free energy of $NiCl_2$ at different concentration of MeOH.

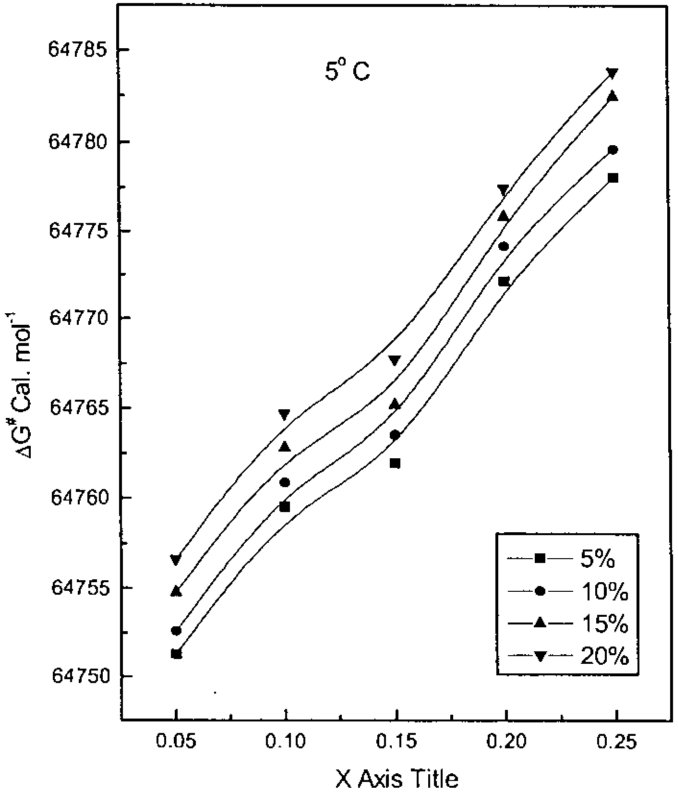


Fig. 5.130: Variation of free energy of $NiCl_2$ at different concentration of EtOH.

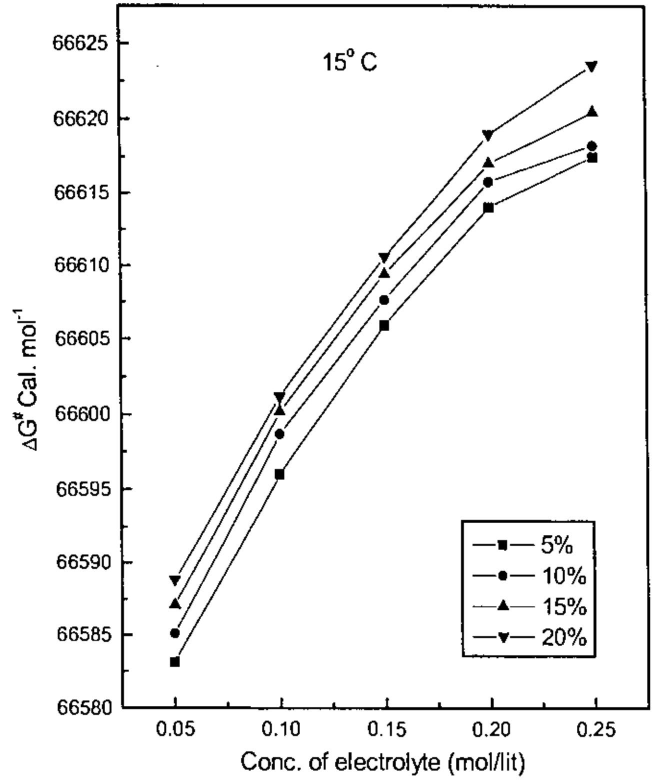


Fig. 5.131: Variation of free energy of $NiCl_2$ at different concentration of MeOH.

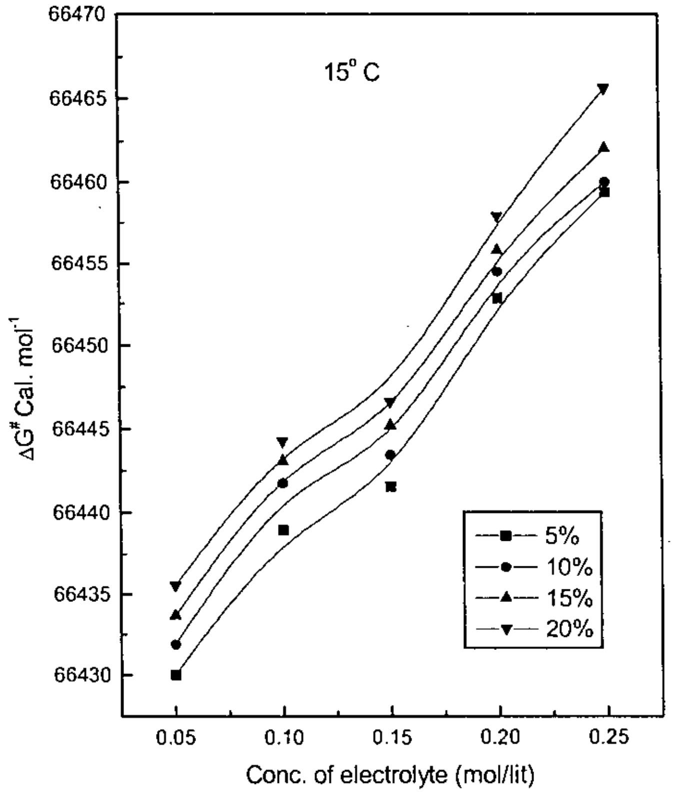


Fig. 5.132: Variation of free energy of $NiCl_2$ at different concentration of EtOH.

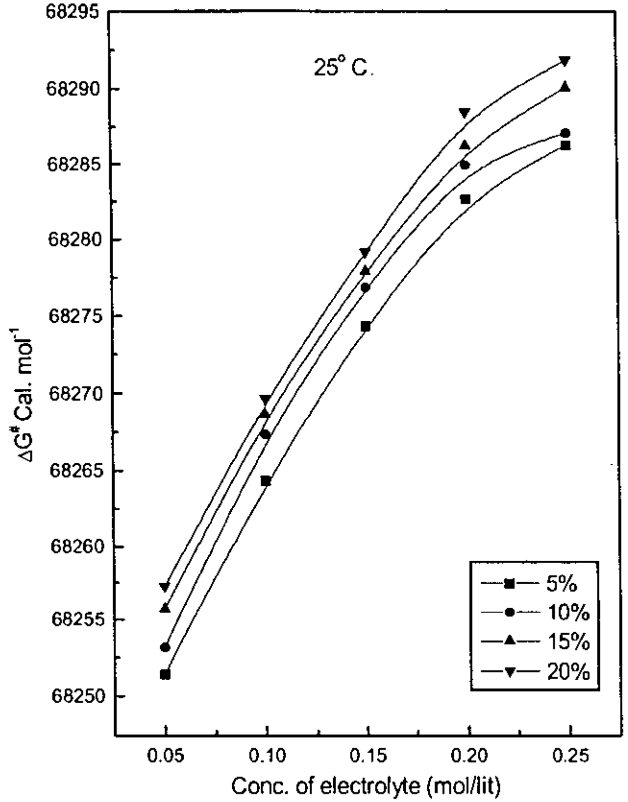


Fig. 5.133: Variation of free energy of $NiCl_2$ at different concentration of MeOH.

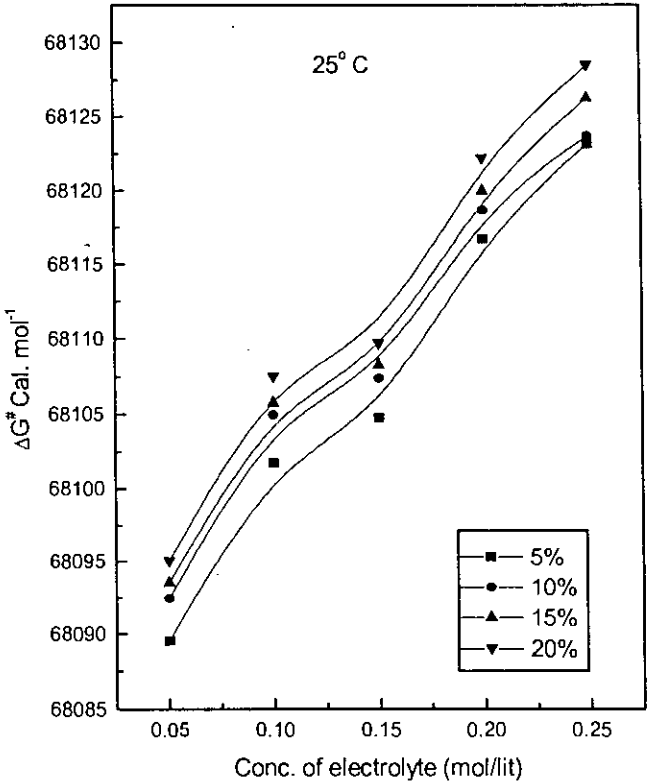


Fig. 5.134: Variation of free energy of $NiCl_2$ at different concentration of EtOH.

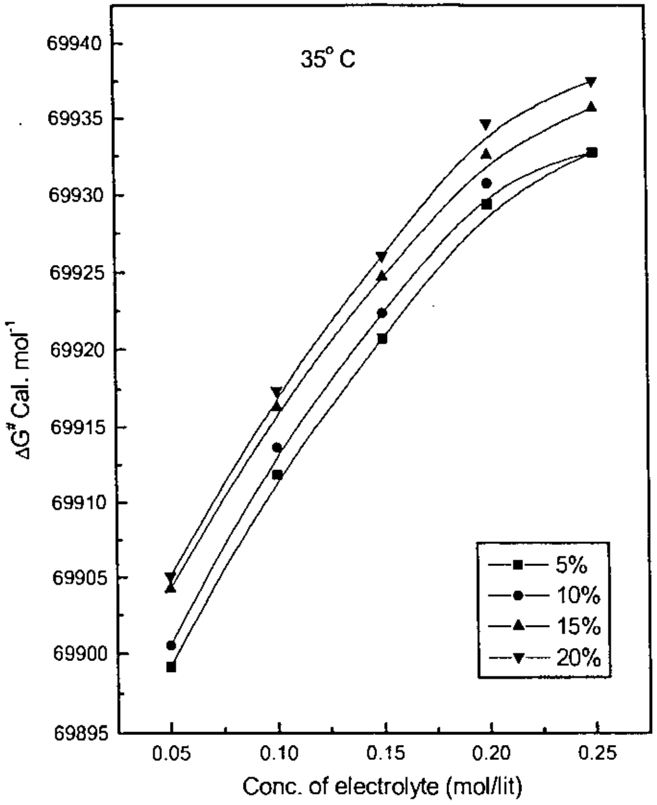


Fig. 5.135: Variation of free energy of $NiCl_2$ at different concentration of MeOH.

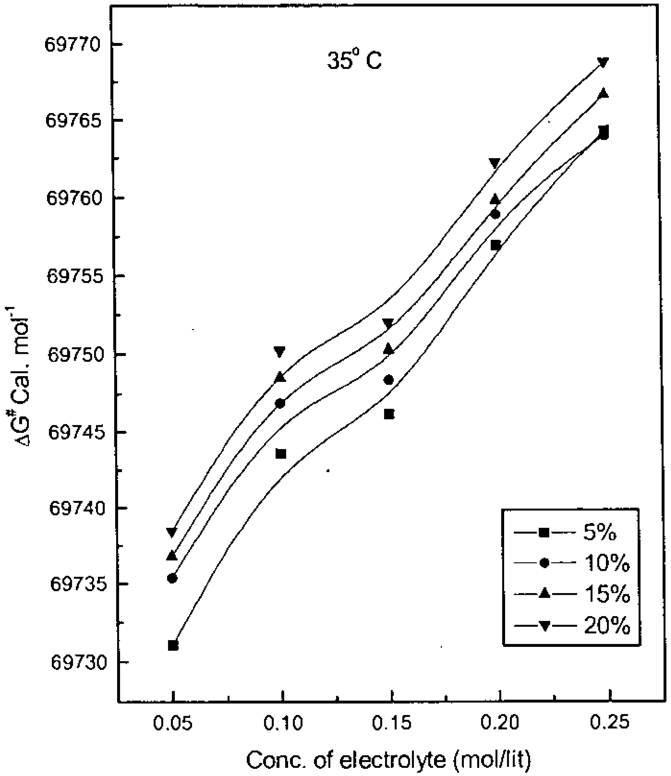


Fig. 5.136: Variation of free energy of $NiCl_2$ at different concentration of EtOH.

The values of entropy of activation of flow process were calculated using the values of enthalpy and free energy change of action by the following equation:

$$\Delta G_\eta^{\#}=\Delta H_\eta^{\#}-T\Delta S_\eta^{\#}$$

$$\text{or}\quad \Delta S_\eta^{\#}=\frac{\Delta H_\eta^{\#}-\Delta G_\eta^{\#}}{T}$$

The calculated values are presented in table 5.26-5.35. It is observed from these tables that in general the values of entropy of activation increases with increase of percentage of both the alcohol. But there is no systematic change of entropy of activation with concentration of electrolytes.

Data table: 5.26 Entropy $\Delta S_\eta^{\#}$(K.cal.mol^{-1}) of different solution of $FeCl_3$ at different temperature

Conc. of MeOH (v/v)	Concentration of $FeCl_3$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0 %	0.175	0.173	0.175	0.171	0.172
5%	0.175	0.177	0.176	0.171	0.173
10%	0.180	0.178	0.181	0.176	0.176
15%	0.180	0.175	0.179	0.167	0.176
20%	0.176	0.176	0.178	0.167	0.179

Data table:5.27 Entropy $\Delta S_\eta^{\#}$(K.cal.mol^{-1}) of different solution of $FeCl_3$ at different temperature

Conc. of EtOH (v/v)	Concentration of $FeCl_3$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	0.175	0.173	0.175	0.171	0.172
5%	0.179	0.177	0.179	0.174	0.173
10%	0.183	0.182	0.187	0.175	0.176
15%	0.182	0.179	0.181	0.171	0.179
20%	0.180	0.180	0.183	0.173	0.171

Data table:5.28 Entropy $\Delta S_{\eta}^{\#}$(K.cal.mol^{-1}) of different solution of $CoCl_3$ at different temperature

Conc. of MeOH (v/v)	Concentration of $CoCl_3$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0 %	0.168	0.169	0.179	0.169	0.168
5%	0.180	0.180	0.186	0.179	0.169
10%	0.173	0.172	0.176	0.167	0.167
15%	0.177	0.173	0.180	0.169	0.168
20%	0.179	0.181	0.185	0.182	0.169

Data table: 5.29 Entropy $\Delta S_{\eta}^{\#}$(K.cal.mol^{-1}) of different solution of $CoCl_3$ at different temperature

Conc. of EtOH (v/v)	Concentration of $CoCl_3$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	0.168	0.169	0.179	0.169	0.168
5%	0.177	0.177	0.184	0.178	0.178
10%	0.174	0.179	0.184	0.174	0.177
15%	0.182	0.180	0.185	0.174	0.167
20%	0.182	0.185	0.191	0.182	0.178

Data table: 5.30 Entropy $\Delta S_\eta^{\#}$(K.cal.mol^{-1}) of different solution of $CuCl_2$ at different temperature

Conc. of MeOH (v/v)	Concentration of $CuCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0 %	0.128	0.132	0.137	0.149	0.142
5%	0.139	0.145	0.157	0.169	0.137
10%	0.144	0.149	0.154	0.166	0.138
15%	0.150	0.146	0.156	0.165	0.136
20%	0.146	0.154	0153	0.165	0.143

Data table:5.31 Entropy $\Delta S_\eta^{\#}$(K.cal.mol^{-1}) of different solution of $CuCl_2$ at different temperature

Conc. of EtOH (v/v)	Concentration of $CuCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	0.178	0.152	0.167	0.169	0.153
5%	0.171	0.138	0.159	0.157	0.148
10%	0.154	0.155	0.146	0.152	0.163
15%	0.146	0.149	0.156	0.153	0.134
20%	0.129	0.150	0.144	0.134	0.142

Data table: 5.32 Entropy $\Delta S_{\eta}^{\#}$(K.cal.mol^{-1}) of different solution of $MgCl_2$ at different temperature

Conc. of MeOH (v/v)	Concentration of $MgCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0 %	0.151	0.155	0.163	0.156	0.154
5%	0.149	0.157	0.157	0.148	0.152
10%	0.155	0.157	0.160	0.156	0.153
15%	0.155	0.157	0.159	0.149	0.151
20%	0.151	0.154	0.158	0.146	0.153

Data table:5.33 Entropy $\Delta S_{\eta}^{\#}$(K.cal.mol^{-1}) of different solution of $MgCl_2$ at different temperature

Conc. of EtOH (v/v)	Concentration of $MgCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	0.151	0.155	0.163	0.156	0.152
5%	0.152	0.157	0.164	0.157	0.156
10%	0.158	0.161	0.165	0.159	0.162
15%	0.156	0.159	0.162	0.153	0.158
20%	0.53	0.161	0.163	0.151	0.165

Data table:5.34 Entropy $\Delta S_{\eta}^{\#}$(K.cal.mol^{-1}) of different solution of $NiCl_2$ at different temperature

Conc. Of MeOH (v/v)	Concentration of $NiCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0 %	0.168	0.171	0.173	0.167	0.171
5%	0.170	0.173	0.176	0.169	0.173
10%	0.171	0.166	0.170	0.163	0.168
15%	0.175	0.167	0.172	0.158	0.162
20%	0.171	0.174	0.176	0.164	0.159

Data table: 5.35 Entropy $\Delta S_{\eta}^{\#}$(K.cal.mol^{-1}) of different solution of $NiCl_2$ at different temperature

Conc. of EtOH (v/v)	Concentration of $NiCl_2$				
	0.05	**0.01**	**0.15**	**0.20**	**0.25**
0%	0.168	0.171	0.173	0.167	0.164
5%	0.132	0.145	0.164	0.159	0.138
10%	0.134	0.138	0.152.	0.138	0.165
15%	0.136	0.138	0.159	0.141	0.154
20%	0.134	0.147	0.163	0.145	0.132

Conclusion

From the experimental data and the theoretical interpretation of the results obtained in this investigation, the following conclusion can be drawn:

1. The excess molar volume for all solutions under study are found negative It is observed from the results that the value of V^E increases with the decrease of concentration both the alcohols (i.e., methanol & ethanol). However, after certain point it is found to increase with the increase of mole fraction of electrolytes and a minimum curvature is found in the diagram.

2. The apparent molar volumes of all solutions under study are positive and the values increase almost linearly with increase mole fraction of electrolytes both in methanol-water and also in ethanol-water system

3. The viscosity coefficients of different solutions at different temperature were experimentally determined and observed that the viscosity coefficients of different solutions decrease with increase of temperature.

4. For all electrolytic solutions the values of B-coefficients of Jone-Dole equation were found to be positive. However, the positive values of B-coefficients for trivalent cation such as Fe^{3+},Co^{3+} were found larger than those for bivalent cations such as Mg^{2+},Cu^{2+} etc. The positive values of B-coefficients indicate that the electrolytic salts taken in this study are all structure maker.

5. In this study the values of enthalpy of activation for electrolytes sequences were $FeCl_3 > CoCl_3 > CuCl_2 > MgCl_2 > NiCl_2$. The increases of enthalpy of activation correspond to the increase in intensification of structure.

6. The values of free energy of activation $\Delta G_\eta^{\#}$ for viscous flow increase with the increase of concentration of methanol or ethanol and all were positive. These results indicate that the viscous flow is not favored.

7. The calculated values of entropy of activation increases with increase of percentage of both the alcohol. But there is no systematic change

APPENDICES

Appendix-I

Part-A

Density(g/cm^3)of different solutions at different temperature.

Concentration of MeOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $FeCl_3$	0.9965	0.9947	0.9925	0.9897
	0.05 $FeCl_3$	1.0036	1.0031	1.0024	1.0003
	0.10 $FeCl_3$	1.0046	1.0043	1.0038	1.0020
	0.15 $FeCl_3$	1.0052	1.0054	1.0049	1.0033
	0.20 $FeCl_3$	1.0058	1.0054	1.0047	1.0037
	0.25 $FeCl_3$	1.0067	1.0058	1.0056	1.0048
5%	0.00 $FeCl_3$	0.9975	0.9957	0.9935	0.9908
	0.05 $FeCl_3$	1.0042	1.0035	1.0027	1.0003
	0.10 $FeCl_3$	1.0050	1.0044	1.0039	1.0021
	0.15 $FeCl_3$	1.0061	1.0056	1.0051	1.0035
	0.20 $FeCl_3$	1.0062	1.0059	1.0053	1.0042
	0.25 $FeCl_3$	1.0069	1.0068	1.0060	1.0052
10%	0.00 $FeCl_3$	0.9985	0.9967	0.9945	0.9918
	0.05 $FeCl_3$	1.0046	1.0040	1.0034	1.0014
	0.10 $FeCl_3$	1.0056	1.0047	1.0041	1.0028
	0.15 $FeCl_3$	1.0065	1.0060	1.0052	1.0041
	0.20 $FeCl_3$	1.0066	1.0061	1.0055	1.0046
	0.25 $FeCl_3$	1.0078	1.0074	1.0069	1.0060
15%	0.00 $FeCl_3$	0.9994	0.9978	0.9956	0.9928
	0.05 $FeCl_3$	1.0051	1.0045	1.0038	1.0016
	0.10 $FeCl_3$	1.0059	1.0055	1.0050	1.0032
	0.15 $FeCl_3$	1.0068	1.0064	1.0059	1.0044
	0.20 $FeCl_3$	1.0072	1.0065	1.0061	1.0048
	0.25 $FeCl_3$	1.0083	1.0074	1.0069	1.0057
20%	0.00 $FeCl_3$	0.9996	0.9988	0.9966	0.9938
	0.05 $FeCl_3$	1.0055	1.0052	1.0041	1.0032
	0.10 $FeCl_3$	1.0064	1.0055	1.0046	1.0037
	0.15 $FeCl_3$	1.0076	1.0071	1.0065	1.0058
	0.20 $FeCl_3$	1.0079	1.0075	1.0069	1.0065
	0.25 $FeCl_3$	1.0093	1.0087	1.0083	1.0075

Appendix-I
Part-B
Density (g/cm^3)of different solutions at different temperature.

Concentration of EtOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $FeCl_3$	0.9965	0.9947	0.9925	0.9897
	0.05 $FeCl_3$	1.0041	1.0034	1.0029	1.0005
	0.10 $FeCl_3$	1.0049	1.0045	1.0038	1.0019
	0.15 $FeCl_3$	1.0055	1.0055	1.0049	1.0032
	0.20 $FeCl_3$	1.0061	1.0056	1.0049	1.0039
	0.25 $FeCl_3$	1.0070	1.0060	1.0058	1.0049
5%	0.00 $FeCl_3$	0.9975	0.9957	0.9935	0.9908
	0.05 $FeCl_3$	1.0045	1.0038	1.0031	1.0007
	0.10 $FeCl_3$	1.0053	1.0046	1.0041	1.0021
	0.15 $FeCl_3$	1.0062	1.0057	1.0051	1.0034
	0.20 $FeCl_3$	1.0064	1.0061	1.0054	1.0044
	0.25 $FeCl_3$	1.0072	1.0071	1.0063	1.0054
10%	0.00 $FeCl_3$	0.9985	0.9967	0.9945	0.9918
	0.05 $FeCl_3$	1.0051	1.0042	1.0032	1.0009
	0.10 $FeCl_3$	1.0058	1.0048	1.0041	1.0024
	0.15 $FeCl_3$	1.0066	1.0061	1.0051	1.0038
	0.20 $FeCl_3$	1.0068	1.0063	1.0056	1.0044
	0.25 $FeCl_3$	1.0081	1.0076	1.0070	1.0061
15%	0.00 $FeCl_3$	0.9994	0.9978	0.9956	0.9928
	0.05 $FeCl_3$	1.0054	1.0047	1.0041	1.0023
	0.10 $FeCl_3$	1.0061	1.0057	1.0051	1.0034
	0.15 $FeCl_3$	1.0070	1.0066	1.0059	1.0044
	0.20 $FeCl_3$	1.0074	1.0067	1.0061	1.0049
	0.25 $FeCl_3$	1.0085	1.0076	1.0069	1.0057
20%	0.00 $FeCl_3$	0.9996	0.9988	0.9966	0.9938
	0.05 $FeCl_3$	1.0055	1.0052	1.0041	1.0032
	0.10 $FeCl_3$	1.0064	1.0055	1.0046	1.0037
	0.15 $FeCl_3$	1.0076	1.0071	1.0065	1.0058
	0.20 $FeCl_3$	1.0079	1.0075	1.0069	1.0065
	0.25 $FeCl_3$	1.0093	1.0087	1.0083	1.0075

Appendix-I

Part-C

Density(g/cm^3)of different solutions at different temperature.

Concentration of MeOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $CoCl_3$	0.9965	0.9947	0.9925	0.9908
	0.05 $CoCl_3$	0.9992	0.9985	0.9976	0.9957
	0.10 $CoCl_3$	1.0018	0.9996	0.9988	0.9973
	0.15 $CoCl_3$	1.0010	1.0005	1.0000	0.9988
	0.20 $CoCl_3$	1.0017	1.0009	1.0004	0.9994
	0.25 $CoCl_3$	1.0023	1.0016	1.0010	1.0003
5%	0.00 $CoCl_3$	0.9975	0.9957	0.9935	0.9938
	0.05 $CoCl_3$	0.9997	0.9988	0.998	0.9982
	0.10 $CoCl_3$	1.0006	1.0001	0.9993	0.9993
	0.15 $CoCl_3$	1.0015	1.001	1.0004	1.0007
	0.20 $CoCl_3$	1.0020	1.0013	1.0007	1.0015
	0.25 $CoCl_3$	1.0024	1.002	1.0014	1.0021
10%	0.00 $CoCl_3$	0.9985	0.9967	0.9945	0.9918
	0.05 $CoCl_3$	1.0002	0.9992	0.9984	0.9963
	0.10 $CoCl_3$	1.0011	1.0003	0.9997	0.9980
	0.15 $CoCl_3$	1.0021	1.0014	1.0005	0.9993
	0.20 $CoCl_3$	1.0025	1.0018	1.0011	0.9999
	0.25 $CoCl_3$	1.0030	1.0022	1.0017	1.0004
15%	0.00 $CoCl_3$	0.9994	0.9978	0.9956	0.9928
	0.05 $CoCl_3$	1.0003	0.9995	0.9986	0.9963
	0.10 $CoCl_3$	1.0012	1.0007	0.9997	0.9980
	0.15 $CoCl_3$	1.0021	1.0015	1.0007	0.9994
	0.20 $CoCl_3$	1.0026	1.0020	1.0014	1.0001
	0.25 $CoCl_3$	1.0037	1.0029	1.0021	1.0011
20%	0.00 $CoCl_3$	0.9996	0.9988	0.9966	0.9897
	0.05 $CoCl_3$	1.0014	1.0010	0.9999	0.9953
	0.10 $CoCl_3$	1.0022	1.0019	1.0016	0.9971
	0.15 $CoCl_3$	1.0028	1.0021	1.0015	0.9984
	0.20 $CoCl_3$	1.0033	1.0027	1.0019	0.9994
	0.25 $CoCl_3$	1.0042	1.0032	1.0027	1.0001

Appendix-I

Part-D

Density(g/cm^3)of different solutions at different temperature.

Concentration of EtOH(v/v)	Concentration of Electrolytes (mol/L)	**5°C**	**15°C**	**25°C**	**35°C**
0%	0.00 $CoCl_3$	0.9965	0.9947	0.9925	0.9897
	0.05 $CoCl_3$	0.9994	0.9989	0.9981	0.9957
	0.10 $CoCl_3$	1.0003	0.9999	0.9992	0.9973
	0.15 $CoCl_3$	1.0011	1.0008	1.0003	0.9986
	0.20 $CoCl_3$	1.0017	1.0011	1.0006	0.9995
	0.25 $CoCl_3$	1.0023	1.0016	1.0011	1.0001
5%	0.00 $CoCl_3$	0.9975	0.9957	0.9935	0.9908
	0.05 $CoCl_3$	0.9998	0.9992	0.9984	0.9962
	0.10 $CoCl_3$	1.0007	1.0003	0.9995	0.9975
	0.15 $CoCl_3$	1.0016	1.0012	1.0005	0.999
	0.20 $CoCl_3$	1.0021	1.0015	1.0009	0.9996
	0.25 $CoCl_3$	1.0024	1.0021	1.0015	1.0004
10%	0.00 $CoCl_3$	0.9985	0.9967	0.9945	0.9918
	0.05 $CoCl_3$	1.0006	0.9997	0.9988	0.9966
	0.10 $CoCl_3$	1.0015	1.0007	0.9999	0.9981
	0.15 $CoCl_3$	1.0023	1.0016	1.0006	0.9993
	0.20 $CoCl_3$	1.0027	1.0020	1.0012	1.0000
	0.25 $CoCl_3$	1.0031	1.0023	1.0017	1.0004
15%	0.00 $CoCl_3$	0.9994	0.9978	0.9956	0.9928
	0.05 $CoCl_3$	1.0010	1.0002	0.9994	0.9972
	0.10 $CoCl_3$	1.0017	1.0012	1.0002	0.9987
	0.15 $CoCl_3$	1.0025	1.0019	1.0011	1.0001
	0.20 $CoCl_3$	1.0030	1.0024	1.0017	1.0005
	0.25 $CoCl_3$	1.0041	1.0033	1.0023	1.0012
20%	0.00 $CoCl_3$	0.9996	0.9988	0.9966	0.9938
	0.05 $CoCl_3$	1.0014	1.0010	0.9999	0.9982
	0.10 $CoCl_3$	1.0022	1.0019	1.0016	0.9993
	0.15 $CoCl_3$	1.0028	1.0021	1.0015	1.0007
	0.20 $CoCl_3$	1.0033	1.0027	1.0019	1.0015
	0.25 $CoCl_3$	1.0042	1.0032	1.0027	1.0021

Appendix-I

Part-E

Density(g/cm^3)of different solutions at different temperature.

Concentration of MeOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $CuCl_2$	0.9965	0.9947	0.9925	0.9897
	0.05 $CuCl_2$	0.9998	0.9991	0.9988	0.9984
	0.10 $CuCl_2$	1.0001	0.9998	0.9992	0.9988
	0.15 $CuCl_2$	1.0004	1.0001	0.9997	0.9992
	0.20 $CuCl_2$	1.0006	1.0001	0.9998	0.9995
	0.25 $CuCl_2$	1.0009	1.0004	0.9999	0.9996
5%	0.00 $CuCl_2$	0.9975	0.9957	0.9935	0.9908
	0.05 $CuCl_2$	1.0001	0.9994	0.9991	0.9988
	0.10 $CuCl_2$	1.0004	1.0000	0.9996	0.9993
	0.15 $CuCl_2$	1.0007	1.0003	1.0000	0.9997
	0.20 $CuCl_2$	1.0010	1.0006	1.0004	1.0001
	0.25 $CuCl_2$	1.0013	1.0008	1.0005	1.0002
10%	0.00 $CuCl_2$	0.9985	0.9967	0.9945	0.9918
	0.05 $CuCl_2$	1.0004	0.9998	0.9996	0.9992
	0.10 $CuCl_2$	1.0008	1.0003	1.0000	0.9996
	0.15 $CuCl_2$	1.0011	1.0007	1.0002	1.0000
	0.20 $CuCl_2$	1.0014	1.0009	1.0005	1.0002
	0.25 $CuCl_2$	1.0016	1.0011	1.0007	1.0003
15%	0.00 $CuCl_2$	0.9994	0.9978	0.9956	0.9928
	0.05 $CuCl_2$	1.0006	1.0002	0.9999	0.9996
	0.10 $CuCl_2$	1.0010	1.0007	1.0002	0.9998
	0.15 $CuCl_2$	1.0013	1.0009	1.0006	1.0003
	0.20 $CuCl_2$	1.0019	1.0013	1.0010	1.0005
	0.25 $CuCl_2$	1.0023	1.0015	1.0013	1.0007
20%	0.00 $CuCl_2$	0.9996	0.9988	0.9966	0.9938
	0.05 $CuCl_2$	1.0004	0.9997	0.9990	0.9971
	0.10 $CuCl_2$	1.0013	1.0004	0.9995	0.9984
	0.15 $CuCl_2$	1.0015	1.0010	1.0004	0.9993
	0.20 $CuCl_2$	1.0018	1.0014	1.0008	0.9994
	0.25 $CuCl_2$	1.0022	1.0016	1.0012	1.0004

Appendix-I

Part-F

Density(g/cm^3)of different solutions at different temperature.

Concentration of EtOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $CuCl_2$	0.9965	0.9947	0.9925	0.9897
	0.05 $CuCl_2$	0.9995	0.9987	0.9983	0.9982
	0.10 $CuCl_2$	1.0003	0.9999	0.9994	0.9990
	0.15 $CuCl_2$	1.0006	1.0003	0.9998	0.9993
	0.20 $CuCl_2$	1.0009	1.0008	1.0002	0.9996
	0.25 $CuCl_2$	1.0014	1.0013	1.0007	1.0000
5%	0.00 $CuCl_2$	0.9975	0.9957	0.9935	0.9908
	0.05 $CuCl_2$	0.9999	0.9995	0.9992	0.9988
	0.10 $CuCl_2$	1.0007	1.0002	0.9997	0.9993
	0.15 $CuCl_2$	1.0008	1.0008	1.0001	0.9998
	0.20 $CuCl_2$	1.0011	1.0011	1.0007	1.0001
	0.25 $CuCl_2$	1.0015	1.0019	1.0012	1.0005
10%	0.00 $CuCl_2$	0.9985	0.9967	0.9945	0.9918
	0.05 $CuCl_2$	1.0003	0.9997	0.9992	0.9988
	0.10 $CuCl_2$	1.0010	1.0002	0.9997	0.9993
	0.15 $CuCl_2$	1.0012	1.0008	1.0002	0.9998
	0.20 $CuCl_2$	1.0018	1.0012	1.0007	1.0003
	0.25 $CuCl_2$	1.0024	1.0019	1.0013	1.0004
15%	0.00 $CuCl_2$	0.9994	0.9978	0.9956	0.9928
	0.05 $CuCl_2$	1.0006	0.9999	0.9996	0.9992
	0.10 $CuCl_2$	1.0014	1.0005	1.0002	0.9998
	0.15 $CuCl_2$	1.0017	1.0011	1.0007	1.0003
	0.20 $CuCl_2$	1.0024	1.0016	1.0011	1.0005
	0.25 $CuCl_2$	1.0029	1.0021	1.0015	1.0006
20%	0.00 $CuCl_2$	0.9996	0.9988	0.9966	0.9938
	0.05 $CuCl_2$	1.0004	0.9997	0.9990	0.9971
	0.10 $CuCl_2$	1.0013	1.0004	0.9995	0.9984
	0.15 $CuCl_2$	1.0015	1.0010	1.0004	0.9993
	0.20 $CuCl_2$	1.0018	1.0014	1.0008	0.9994
	0.25 $CuCl_2$	1.0022	1.0016	1.0012	1.0004

Appendix-I
Part-G

Density(g/cm^3)of different solutions at different temperature.

Concentration of MeOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $MgCl_2$	0.9965	0.9947	0.9925	0.9897
	0.05 $MgCl_2$	0.9991	0.9985	0.9977	0.9959
	0.10 $MgCl_2$	0.9996	0.9992	0.9987	0.9973
	0.15 $MgCl_2$	1.0000	0.9997	0.9992	0.9982
	0.20 $MgCl_2$	1.0004	1.0000	0.9996	0.9984
	0.25 $MgCl_2$	1.0006	1.0003	0.9997	0.9987
5%	0.00 $MgCl_2$	0.9975	0.9957	0.9935	0.9908
	0.05 $MgCl_2$	0.9996	0.9986	0.9979	0.9958
	0.10 $MgCl_2$	1.0001	0.9995	0.9989	0.9974
	0.15 $MgCl_2$	1.0006	1.0001	0.9994	0.9983
	0.20 $MgCl_2$	1.0011	1.0007	1.0000	0.9991
	0.25 $MgCl_2$	1.0013	1.0010	1.0003	0.9996
10%	0.00 $MgCl_2$	0.9985	0.9967	0.9945	0.9918
	0.05 $MgCl_2$	0.9998	0.999	0.9983	0.9963
	0.10 $MgCl_2$	1.0005	0.9998	0.9994	0.9980
	0.15 $MgCl_2$	1.0011	1.0005	1.0000	0.9990
	0.20 $MgCl_2$	1.0015	1.0010	1.0005	0.9994
	0.25 $MgCl_2$	1.0019	1.0016	1.0011	1.0004
15%	0.00 $MgCl_2$	0.9994	0.9978	0.9956	0.9928
	0.05 $MgCl_2$	1.0003	0.9996	0.9989	0.9969
	0.10 $MgCl_2$	1.0011	1.0004	0.9996	0.9981
	0.15 $MgCl_2$	1.0014	1.0009	1.0002	0.9991
	0.20 $MgCl_2$	1.0017	1.0013	1.0005	0.9995
	0.25 $MgCl_2$	1.0019	1.0015	1.0008	0.9999
20%	0.00 $MgCl_2$	0.9996	0.9988	0.9966	0.9938
	0.05 $MgCl_2$	1.0007	0.9999	0.9993	0.9973
	0.10 $MgCl_2$	1.0016	1.0008	0.9999	0.9987
	0.15 $MgCl_2$	1.0018	1.0013	1.0007	0.9996
	0.20 $MgCl_2$	1.0022	1.0017	1.0011	0.9999
	0.25 $MgCl_2$	1.0025	1.0019	1.0015	1.0007

Appendix-I

Part-H

Density(g/cm^3)of different solutions at different temperature.

Concentration of EtOH(v/v)	Concentration. of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $MgCl_2$	0.9960	0.9941	0.9921	0.9895
	0.05 $MgCl_2$	0.9995	0.9991	0.9984	0.9963
	0.10 $MgCl_2$	1.0000	0.9997	0.9992	0.9974
	0.15 $MgCl_2$	1.0003	1.0000	0.9996	0.9984
	0.20 $MgCl_2$	1.0006	1.0003	0.9999	0.9986
	0.25 $MgCl_2$	1.0008	1.0006	0.9999	0.9990
5%	0.00 $MgCl_2$	0.9996	0.9951	0.9929	0.9901
	0.05 $MgCl_2$	1.0007	0.9993	0.9985	0.9965
	0.10 $MgCl_2$	1.0016	1.0000	0.9993	0.9978
	0.15 $MgCl_2$	1.0018	1.0005	0.9998	0.9987
	0.20 $MgCl_2$	1.0022	1.0009	1.0003	0.9994
	0.25 $MgCl_2$	1.0025	1.0012	1.0005	0.9998
10%	0.00 $MgCl_2$	0.9980	0.9962	0.9940	0.9912
	0.05 $MgCl_2$	1.0001	0.9998	0.9991	0.9970
	0.10 $MgCl_2$	1.0007	1.0004	0.9999	0.9984
	0.15 $MgCl_2$	1.0013	1.001	1.0004	0.9993
	0.20 $MgCl_2$	1.0017	1.0013	1.0009	0.9997
	0.25 $MgCl_2$	1.0021	1.0018	1.0012	1.0005
15%	0.00 $MgCl_2$	0.9970	0.9974	0.9951	0.9923
	0.05 $MgCl_2$	1.0001	0.9996	0.9988	0.9969
	0.10 $MgCl_2$	1.0005	1.0004	0.9995	0.9981
	0.15 $MgCl_2$	1.0009	1.0009	1.0001	0.9990
	0.20 $MgCl_2$	1.0012	1.0014	1.0005	0.9995
	0.25 $MgCl_2$	1.0014	1.0017	1.0009	1.0000
20%	0.00 $MgCl_2$	0.9991	0.9988	0.9966	0.9938
	0.05 $MgCl_2$	1.0003	0.9999	0.9993	0.9973
	0.10 $MgCl_2$	1.0011	1.0008	0.9999	0.9987
	0.15 $MgCl_2$	1.0014	1.0013	1.0007	0.9996
	0.20 $MgCl_2$	1.0018	1.0017	1.0011	0.9999
	0.25 $MgCl_2$	1.0021	1.0019	1.0015	1.0007

Appendix – 1
Part -I

Density (g/cm^3) of different solutions at different temperature

Concentration of MeOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $HgCl_2$	0.9965	0.9947	0.9925	0.9897
	0.05 $HgCl_2$	0.9996	0.9989	0.9981	0.9972
5%	0.00 $HgCl_2$	0.9975	0.9957	0.9935	0.9908
	0.05 $HgCl_2$	1.0001	0.9992	0.9987	0.9981
10%	0.00 $HgCl_2$	0.9985	0.9967	0.9945	0.9918
	0.05 $HgCl_2$	1.0004	0.9996	0.9993	0.9983
15%	0.00 $HgCl_2$	0.9994	0.9978	0.9956	0.9928
	0.05 $HgCl_2$	1.0009	1.0002	0.9998	0.9987
20%	0.00 $HgCl_2$	0.9996	0.9988	0.9966	0.9938
	0.05 $HgCl_2$	1.0014	1.0006	1.0002	0.9992

Appendix –I
Part -J

Density (g/cm^3) of different solutions at different temperature

Concentration of EtOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $HgCl_2$	0.9965	0.9947	0.9925	0.9897
	0.05 $HgCl_2$	0.9998	0.9992	0.9983	0.9974
5%	0.00 $HgCl_2$	0.9975	0.9957	0.9935	0.9908
	0.05 $HgCl_2$	1.0003	0.9994	0.9989	0.9983
10%	0.00 $HgCl_2$	0.9985	0.9967	0.9945	0.9918
	0.05 $HgCl_2$	1.0006	0.9998	0.9993	0.9985
15%	0.00 $HgCl_2$	0.9994	0.9978	0.9956	0.9928
	0.05 $HgCl_2$	1.0011	1.0004	1.0000	0.9989
20%	0.00 $HgCl_2$	0.9996	0.9988	0.9966	0.9938
	0.05 $HgCl_2$	1.0016	1.0008	1.0004	0.9994

Appendix-I

Part-K

Density(g/cm^3)of different solutions at different temperature.

Concentration of MeOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $NiCl_2$	0.9965	0.9947	0.9925	0.9897
	0.05 $NiCl_2$	0.9988	0.9981	0.9974	0.9953
	0.10 $NiCl_2$	0.9996	0.9990	0.9983	0.9968
	0.15 $NiCl_2$	1.0002	0.9997	0.9991	0.9979
	0.20 $NiCl_2$	1.0008	1.0000	0.9994	0.9984
	0.25 $NiCl_2$	1.0013	1.0006	1.0002	0.9995
5%	0.00 $NiCl_2$	0.9975	0.9957	0.9935	0.9928
	0.05 $NiCl_2$	0.9995	0.9987	0.9978	0.997
	0.10 $NiCl_2$	1.0002	0.9996	0.9988	0.9984
	0.15 $NiCl_2$	1.0008	1.0004	0.9995	0.9996
	0.20 $NiCl_2$	1.0013	1.0008	1.0000	1.0001
	0.25 $NiCl_2$	1.0017	1.0012	1.0005	1.0008
10%	0.00 $NiCl_2$	0.9985	0.9967	0.9945	0.9918
	0.05 $NiCl_2$	0.9998	0.9989	0.9982	0.9962
	0.10 $NiCl_2$	1.0003	0.9996	0.999	0.9975
	0.15 $NiCl_2$	1.0009	1.0002	0.9996	0.9986
	0.20 $NiCl_2$	1.0013	1.0008	1.0000	0.9985
	0.25 $NiCl_2$	1.0020	1.0011	1.0008	0.9999
15%	0.00 $NiCl_2$	0.9994	0.9978	0.9956	0.9908
	0.05 $NiCl_2$	1.0004	0.9997	0.9989	0.9957
	0.10 $NiCl_2$	1.0011	1.0006	0.9998	0.9972
	0.15 $NiCl_2$	1.0017	1.0011	1.0005	0.9982
	0.20 $NiCl_2$	1.0025	1.0018	1.0011	0.9990
	0.25 $NiCl_2$	1.0030	1.0021	1.0019	0.9998
20%	0.00 $NiCl_2$	0.9996	0.9988	0.9966	0.9938
	0.05 $NiCl_2$	1.0008	1.0000	0.9994	0.9974
	0.10 $NiCl_2$	1.0017	1.0009	0.9999	0.9988
	0.15 $NiCl_2$	1.0019	1.0014	1.0008	0.9997
	0.20 $NiCl_2$	1.0023	1.0018	1.0012	0.9999
	0.25 $NiCl_2$	1.0026	1.0019	1.0016	1.0008

Appendix-I

Part-L

Density(g/cm^3)of different solutions at different temperature.

Concentration of EtOH(v/v)	Concentration of Electrolytes (mol/L)	5°C	15°C	25°C	35°C
0%	0.00 $NiCl_2$	0.9965	0.9947	0.9925	0.9897
	0.05 $NiCl_2$	0.9991	0.9985	0.9979	0.9959
	0.10 $NiCl_2$	0.9998	0.9993	0.9986	0.9971
	0.15 $NiCl_2$	1.0004	0.9999	0.9993	0.9981
	0.20 $NiCl_2$	1.0009	1.0002	0.9996	0.9986
	0.25 $NiCl_2$	1.0013	1.0007	1.0003	0.9996
5%	0.00 $NiCl_2$	0.9975	0.9957	0.9935	0.9908
	0.05 $NiCl_2$	0.9996	0.9991	0.9982	0.9962
	0.10 $NiCl_2$	1.0005	0.9999	0.9991	0.9976
	0.15 $NiCl_2$	1.0011	1.0007	0.9997	0.9985
	0.20 $NiCl_2$	1.0014	1.0010	1.0002	0.9992
	0.25 $NiCl_2$	1.0017	1.0013	1.0007	1.0000
10%	0.00 $NiCl_2$	0.9985	0.9967	0.9945	0.9918
	0.05 $NiCl_2$	1.0001	0.9993	0.9985	0.9964
	0.10 $NiCl_2$	1.0005	0.9998	0.9992	0.9978
	0.15 $NiCl_2$	1.0011	1.0004	0.9997	0.9987
	0.20 $NiCl_2$	1.0014	1.0009	1.0001	0.9992
	0.25 $NiCl_2$	1.0021	1.0012	1.0005	1.0000
15%	0.00 $NiCl_2$	0.9994	0.9978	0.9956	0.9928
	0.05 $NiCl_2$	1.0008	1.0001	0.9992	0.9973
	0.10 $NiCl_2$	1.0014	1.0009	1.0003	0.9989
	0.15 $NiCl_2$	1.0019	1.0014	1.0009	0.9999
	0.20 $NiCl_2$	1.0026	1.0020	1.0013	1.0003
	0.25 $NiCl_2$	1.0031	1.0025	1.0020	1.0010
20%	0.00 $NiCl_2$	0.9996	0.9988	0.9966	0.9938
	0.05 $NiCl_2$	1.0008	1.0000	0.9994	0.9974
	0.10 $NiCl_2$	1.0017	1.0009	0.9999	0.9988
	0.15 $NiCl_2$	1.0019	1.0014	1.0008	0.9997
	0.20 $NiCl_2$	1.0023	1.0018	1.0012	0.9999
	0.25 $NiCl_2$	1.0026	1.0019	1.0016	1.0008

Appendix-II

Part- A

Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes ($FeCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	-0.00655	-0.17278	-0.11521	-0.10594
	0.05	-0.01884	-0.01937	-0.02334	-0.02740
	0.10	-0.02074	-0.02185	-0.02436	-0.03209
	0.15	-0.02250	-0.02733	-0.02852	-0.03750
	0.20	-0.01804	-0.01972	-0.02327	-0.02692
	0.25	-0.00532	-0.01346	-0.01671	-0.01698
15°C	0.00	-0.00885	-0.18353	-0.12683	-0.11302
	0.05	-0.01458	-0.01496	-0.01925	-0.02079
	0.10	-0.01624	-0.01985	-0.02289	-0.02421
	0.15	-0.01720	-0.02184	-0.02852	-0.03396
	0.20	-0.01413	-0.02002	-0.02183	-0.02762
	0.25	-0.00773	-0.01287	-0.01340	-0.01489
25°C	0.00	-0.01033	-0.18675	-0.12996	-0.11766
	0.05	-0.01578	-0.01762	-0.02062	-0.02133
	0.10	-0.01912	-0.0202	-0.02365	-0.02684
	0.15	-0.02098	-0.02896	-0.03342	-0.03734
	0.20	-0.01218	-0.01675	-0.01717	-0.02382
	0.25	-0.00515	-0.00785	-0.00810	-0.01554
35°C	0.00	-0.01174	-0.18828	-0.13736	-0.12885
	0.05	-0.01134	-0.01677	-0.01928	-0.02135
	0.10	-0.01915	-0.02225	-0.02736	-0.02957
	0.15	-0.02100	-0.02826	-0.03345	-0.03904
	0.20	-0.01367	-0.01615	-0.01952	-0.02069
	0.25	-0.00119	-0.00503	-0.00955	-0.01703

Appendix-II

Part -B

Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Concentration of Electrolytes ($FeCl_3$)in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	-0.01418	-0.18273	-0.12583	-0.11496
	0.05	-0.02269	-0.02665	-0.02840	-0.02995
	0.10	-0.02578	-0.03166	-0.04270	-0.04862
	0.15	-0.02620	-0.03706	-0.04788	-0.04972
	0.20	-0.01791	-0.02687	-0.02721	-0.03103
	0.25	-0.00692	-0.01550	-0.02231	-0.02959
15°C	0.00	-0.01651	-0.19353	-0.13965	-0.12666
	0.05	-0.01703	-0.01899	-0.02233	-0.02362
	0.10	-0.01852	-0.02071	-0.02593	-0.03503
	0.15	-0.02242	-0.02579	-0.02890	-0.03773
	0.20	-0.01538	-0.02012	-0.02392	-0.02673
	0.25	-0.01066	-0.01471	-0.02111	-0.02201
25°C	0.00	-0.01803	-0.19881	-0.14287	-0.13370
	0.05	-0.0191	-0.02173	-0.02692	-0.03021
	0.10	-0.02378	-0.02559	-0.03124	-0.03871
	0.15	-0.03256	-0.03873	-0.03963	-0.04932
	0.20	-0.01943	-0.02387	-0.02637	-0.03324
	0.25	-0.00555	-0.00981	-0.02026	-0.02812
35°C	0.00	-0.01949	-0.20652	-0.15473	-0.14507
	0.05	-0.02089	-0.02265	-0.02507	-0.03545
	0.10	-0.02818	-0.02931	-0.03138	-0.03875
	0.15	-0.0326	-0.03393	-0.03632	-0.04703
	0.20	-0.02094	-0.02473	-0.02552	-0.03165
	0.25	-0.00161	-0.00839	-0.01058	-0.02967

Appendix-II

Part -C

Values of excess molar volume, V_m^E (cm^3.mole^{-1}) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes($CoCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	-0.00655	-0.17278	-0.11521	-0.10594
	0.05	-0.01971	-0.02192	-0.02447	-0.02641
	0.10	-0.02325	-0.02532	-0.02874	-0.02885
	0.15	-0.02572	-0.02791	-0.03142	-0.03658
	0.20	-0.01130	-0.01718	-0.02291	-0.02749
	0.25	-0.00314	-0.00699	-0.01384	-0.01628
15°C	0.00	-0.00885	-0.18353	-0.12683	-0.11302
	0.05	-0.01312	-0.01385	-0.01675	-0.02269
	0.10	-0.01393	-0.01481	-0.01682	-0.02420
	0.15	-0.01600	-0.01815	-0.02240	-0.02764
	0.20	-0.01013	-0.01024	-0.01268	-0.01972
	0.25	-0.00229	-0.00441	-0.00884	-0.02125
25°C	0.00	-0.01033	-0.18675	-0.12996	-0.11766
	0.05	-0.01329	-0.01565	-0.01813	-0.01861
	0.10	-0.01452	-0.01820	-0.02230	-0.02422
	0.15	-0.01758	-0.01977	-0.02327	-0.02600
	0.20	-0.01426	-0.01475	-0.01662	-0.01900
	0.25	-0.00590	-0.01123	-0.01135	-0.01833
35°C	0.00	-0.01174	-0.18828	-0.13736	-0.12885
	0.05	-0.01779	-0.01965	-0.02042	-0.02798
	0.10	-0.01893	-0.02264	-0.02577	-0.03777
	0.15	-0.02170	-0.02798	-0.03065	-0.03925
	0.20	-0.01827	-0.02119	-0.02757	-0.03071
	0.25	-0.01135	-0.01384	-0.01531	-0.01780

Appendix-II

Part- D

Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solution at different temperature.

Temp. (°C)	Concentration of Electrolytes ($CoCl_3$)in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	-0.01418	-0.18273	-0.12583	-0.11496
	0.05	-0.09834	-0.10425	-0.11077	-0.12630
	0.10	-0.10355	-0.11654	-0.12198	-0.13257
	0.15	-0.12325	-0.12905	-0.12613	-0.15795
	0.20	-0.08718	-0.10420	-0.1076	-0.11365
	0.25	-0.07156	-0.08485	-0.10035	-0.10113
15°C	0.00	-0.01651	-0.19353	-0.13965	-0.12666
	0.05	-0.01562	-0.03066	-0.03606	-0.03885
	0.10	-0.01630	-0.03354	-0.03801	-0.03994
	0.15	-0.02133	-0.03938	-0.04026	-0.04330
	0.20	-0.01957	-0.03134	-0.03607	-0.03950
	0.25	-0.01708	-0.02288	-0.02117	-0.02869
25°C	0.00	-0.01803	-0.19881	-0.14287	-0.13370
	0.05	-0.02913	-0.02932	-0.03100	-0.03422
	0.10	-0.03239	-0.03255	-0.03452	-0.03633
	0.15	-0.03490	-0.03532	-0.04106	-0.04400
	0.20	-0.02155	-0.02198	-0.03297	-0.03568
	0.25	-0.01446	-0.02147	-0.0236	-0.03098
35°C	0.00	-0.01949	-0.20652	-0.15473	-0.14507
	0.05	-0.03054	-0.03203	-0.03287	-0.03593
	0.10	-0.03682	-0.03874	-0.03903	-0.03819
	0.15	-0.03904	-0.03946	-0.04518	-0.04749
	0.20	-0.03250	-0.03687	-0.04078	-0.04179
	0.25	-0.02812	-0.03372	-0.03823	-0.04012

Appendix-II

Part- E

Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes ($CuCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	-0.00655	-0.17278	-0.11521	-0.10594
	0.05	-0.10043	-0.10553	-0.11045	-0.12483
	0.10	-0.10250	-0.11815	-0.11872	-0.12632
	0.15	-0.11943	-0.12377	-0.12638	-0.13769
	0.20	-0.07455	-0.09593	-0.10075	-0.10695
	0.25	-0.06245	-0.07383	-0.08449	-0.08498
15°C	0.00	-0.00885	-0.18353	-0.12683	-0.11302
	0.05	-0.10043	-0.10553	-0.11045	-0.12483
	0.10	-0.1025	-0.11815	-0.11872	-0.12632
	0.15	-0.11943	-0.12377	-0.12638	-0.13769
	0.20	-0.07455	-0.09593	-0.10075	-0.10695
	0.25	-0.06245	-0.07383	-0.08449	-0.08498
25°C	0.00	-0.01033	-0.18675	-0.12996	-0.11766
	0.05	-0.08313	-0.09398	-0.09559	-0.11211
	0.10	-0.09918	-0.10065	-0.11515	-0.12140
	0.15	-0.10466	-0.11378	-0.12604	-0.13110
	0.20	-0.0805	-0.09216	-0.09485	-0.11843
	0.25	-0.06762	-0.08911	-0.08950	-0.09263
35°C	0.00	-0.01174	-0.18828	-0.13736	-0.12885
	0.05	-0.06587	-0.07225	-0.07940	-0.08937
	0.10	-0.08501	-0.09938	-0.10170	-0.10638
	0.15	-0.10324	-0.11744	-0.11881	-0.12266
	0.20	-0.07254	-0.07641	-0.07703	-0.08391
	0.25	-0.05516	-0.06283	-0.06900	-0.07350

Appendix-II

Part- F

Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Concentration of Electrolytes ($CuCl_2$)in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	-0.01418	-0.18273	-0.12583	-0.11496
	0.05	-0.09834	-0.10425	-0.11077	-0.12630
	0.10	-0.10355	-0.11654	-0.12198	-0.13257
	0.15	-0.12325	-0.12905	-0.13133	-0.15795
	0.20	-0.08718	-0.10420	-0.10760	-0.11365
	0.25	-0.07156	-0.08485	-0.10035	-0.10113
15°C	0.00	-0.01651	-0.19353	-0.13965	-0.12666
	0.05	-0.09719	-0.10077	-0.11019	-0.12834
	0.10	-0.10031	-0.11523	-0.12038	-0.13014
	0.15	-0.11337	-0.13099	-0.13089	-0.15920
	0.20	-0.10332	-0.10767	-0.11548	-0.11866
	0.25	-0.01085	-0.09382	-0.10629	-0.11002
25°C	0.00	-0.01803	-0.19881	-0.14287	-0.13370
	0.05	-0.08680	-0.09249	-0.09366	-0.11316
	0.10	-0.10835	-0.11075	-0.11590	-0.12244
	0.15	-0.11625	-0.12915	-0.12907	-0.13477
	0.20	-0.09442	-0.10026	-0.10644	-0.11840
	0.25	-0.09101	-0.10003	-0.10954	-0.11591
35°C	0.00	-0.01949	-0.20652	-0.15473	-0.14507
	0.05	-0.06645	-0.06922	-0.07327	-0.09169
	0.10	-0.09402	-0.09849	-0.10220	-0.10805
	0.15	-0.10972	-0.11377	-0.11817	-0.12261
	0.20	-0.07396	-0.07944	-0.08474	-0.09773
	0.25	-0.06414	-0.06786	-0.07278	-0.09085

Appendix-II

Part- G

Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes ($MgCl_2$)in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	-0.00655	-0.17278	-0.11521	-0.10594
	0.05	-0.01673	-0.01755	-0.01885	-0.01900
	0.10	-0.01897	-0.02178	-0.02256	-0.02354
	0.15	-0.02260	-0.02551	-0.02560	-0.02996
	0.20	-0.01267	-0.01721	-0.02216	-0.02672
	0.25	-0.00810	-0.01361	-0.01942	-0.02454
15°C	0.00	-0.00885	-0.18353	-0.12683	-0.11302
	0.05	-0.01849	-0.01858	-0.02047	-0.02462
	0.10	-0.02063	-0.02213	-0.02744	-0.02886
	0.15	-0.02876	-0.03175	-0.03495	-0.03939
	0.20	-0.01818	-0.02276	-0.02775	-0.02831
	0.25	-0.01635	-0.01810	-0.01943	-0.02373
25°C	0.00	-0.01033	-0.18675	-0.12996	-0.11766
	0.05	-0.01822	-0.02038	-0.02150	-0.02261
	0.10	-0.02028	-0.02722	-0.02746	-0.03119
	0.15	-0.02272	-0.03033	-0.03377	-0.03502
	0.20	-0.01563	-0.01874	-0.01967	-0.02180
	0.25	-0.01131	-0.01222	-0.01583	-0.01593
35°C	0.00	-0.01174	-0.18828	-0.13736	-0.12885
	0.05	-0.01593	-0.01811	-0.02050	-0.02161
	0.10	-0.01882	-0.02149	-0.02372	-0.02662
	0.15	-0.02128	-0.02268	-0.02772	-0.03200
	0.20	-0.01602	-0.01875	-0.02122	-0.02406
	0.25	-0.01317	-0.01729	-0.02090	-0.02396

Appendix-II

Part-H

Values of excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes ($MgCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	-0.01418	-0.18273	-0.12583	-0.11496
	0.05	-0.02754	-0.02877	-0.03716	-0.03777
	0.10	-0.02938	-0.03269	-0.03750	-0.04420
	0.15	-0.03354	-0.03697	-0.04100	-0.05808
	0.20	-0.02776	-0.03286	-0.03605	-0.04489
	0.25	-0.02095	-0.0234	-0.02488	-0.02736
15°C	0.00	-0.01651	-0.19353	-0.13965	-0.12666
	0.05	-0.02275	-0.02416	-0.02550	-0.02977
	0.10	-0.02904	-0.02929	-0.02941	-0.03023
	0.15	-0.03209	-0.03396	-0.03466	-0.03777
	0.20	-0.02374	-0.02731	-0.02889	-0.03277
	0.25	-0.01769	-0.01849	-0.02049	-0.02283
25°C	0.00	-0.01803	-0.19881	-0.14287	-0.13370
	0.05	-0.02124	-0.02317	-0.02654	-0.02980
	0.10	-0.02431	-0.02697	-0.02943	-0.03270
	0.15	-0.02776	-0.03257	-0.03360	-0.03952
	0.20	-0.02162	-0.02329	-0.02643	-0.02874
	0.25	-0.01179	-0.01774	-0.02345	-0.02387
35°C	0.00	-0.01949	-0.20652	-0.15473	-0.14507
	0.05	-0.02174	-0.02274	-0.02469	-0.02779
	0.10	-0.02362	-0.02668	-0.02971	-0.03008
	0.15	-0.02633	-0.03118	-0.03361	-0.03824
	0.20	-0.01651	-0.02078	-0.02487	-0.02715
	0.25	-0.01370	-0.01775	-0.02052	-0.02188

Appendix-II

Part- I

Values of excess molar volume V_m^E($cm^3.mole^{-1}$) of different Solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($HgCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	-0.00655	-0.17278	-0.11521	-0.10594
	0.05	-0.05280	-0.08360	-0.0516	-0.0418
15°C	0.00	-0.00885	-0.18353	-0.12683	-0.11302
	0.05	-0.05550	-0.08180	-0.05030	-0.04130
25°C	0.00	-0.01033	-0.18675	-0.12996	-0.11766
	0.05	-0. 0538	-0.07210	-0.04620	-0.03440
35°C	0.00	-0.01174	-0.18828	-0.13736	-0.12885
	0.05	-0.04940	-0.05920	-0.05080	-0.03390

Appendix-II

Part -J

Values of excess molar volume V_m^E($cm^3.mole^{-1}$) of different Solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($HgCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	-0.01418	-0.18273	-0.12583	-0.11496
	0.05	-0.05450	-0.08040	-0.04830	-0.03660
15°C	0.00	-0.01651	-0.19353	-0.13965	-0.12666
	0.05	-0.04620	-0.07910	-0.0579	-0.03930
25°C	0.00	-0.01803	-0.19881	-0.14287	-0.13370
	0.05	-0.03030	-0.07920	-0.0502	-0.03330
35°C	0.00	-0.01949	-0.20652	-0.15473	-0.14507
	0.05	-0.03340	-0.07920	-0.05020	-0.02780

Appendix-II

Part- K

Values of Excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($NiCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	-0.00655	-0.17278	-0.11521	-0.10594
	0.05	-0.10168	-0.11395	-0.11911	-0.12151
	0.10	-0.10421	-0.11595	-0.12669	-0.12825
	0.15	-0.10448	-0.12157	-0.13423	-0.13589
	0.20	-0.09118	-0.10431	-0.11775	-0.11942
	0.25	-0.08438	-0.08978	-0.10707	-0.11181
15°C	0.00	-0.00885	-0.18353	-0.12683	-0.11302
	0.05	-0.09536	0.108140	-0.1192	-0.12579
	0.10	-0.10496	-0.11239	-0.12063	-0.13600
	0.15	-0.11001	-0.12007	-0.12952	-0.13950
	0.20	-0.09009	-0.09819	-0.10542	-0.12104
	0.25	-0.08617	-0.09401	-0.10111	-0.10888
25°C	0.00	-0.01033	-0.18675	-0.12996	-0.11766
	0.05	-0.09658	-0.10707	-0.10917	-0.10960
	0.10	-0.10038	-0.11113	-0.11707	-0.12498
	0.15	-0.11323	-0.12176	-0.12739	-0.13614
	0.20	-0.09311	-0.10274	-0.10384	-0.10548
	0.25	-0.06462	-0.08100	-0.08236	-0.09437
35°C	0.00	-0.01174	-0.18828	-0.13736	-0.12885
	0.05	-0.09434	-0.10715	-0.11106	-0.11710
	0.10	-0.09908	-0.11388	-0.12936	-0.13269
	0.15	-0.10873	-0.12501	-0.13424	-0.13601
	0.20	-0.08674	-0.10134	-0.10559	-0.10872
	0.25	-0.07603	-0.09029	-0.09416	-0.10031

Appendix-II

Part- L

Values of Excess molar volume, V_m^E ($cm^3.mole^{-1}$) of different solution at different temperature.

Temp. (°C)	Concentration of Electrolytes ($NiCl_2$)in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	-0.01418	-0.18273	-0.12583	-0.11496
	0.05	-0.10247	-0.11272	-0.12333	-0.13276
	0.10	-0.10476	-0.11751	-0.12892	-0.13328
	0.15	-0.10770	-0.12586	-0.13281	-0.13345
	0.20	-0.09701	-0.11113	-0.11649	-0.12363
	0.25	-0.09286	-0.09476	-0.10615	-0.11029
15°C	0.00	-0.01651	-0.19353	-0.13965	-0.12666
	0.05	-0.10371	-0.10686	-0.10882	-0.10982
	0.10	-0.10717	-0.10978	-0.11680	-0.11967
	0.15	-0.10973	-0.11922	-0.12114	-0.12482
	0.20	-0.09737	-0.10500	-0.10876	-0.10965
	0.25	-0.10323	-0.10357	-0.10616	-0.10634
25°C	0.00	-0.01803	-0.19881	-0.14287	-0.13370
	0.05	-0.10617	-0.10876	-0.11679	-0.11727
	0.10	-0.11328	-0.11667	-0.12152	-0.12991
	0.15	-0.11928	-0.12094	-0.12947	-0.13893
	0.20	-0.10635	-0.10961	-0.11195	-0.11616
	0.25	-0.08725	-0.09781	-0.10189	-0.10778
35°C	0.00	-0.01949	-0.20652	-0.15473	-0.14507
	0.05	-0.10979	-0.11066	-0.11802	-0.12077
	0.10	-0.11200	-0.11716	-0.12218	-0.12713
	0.15	-0.12492	-0.12586	-0.12787	-0.13017
	0.20	-0.10618	-0.10972	-0.11205	-0.12098
	0.25	-0.09871	-0.10117	-0.10343	-0.10789

Appendix- III

Part- A

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes($FeCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	39.707251	48.077783	64.635163	79.188382
	0.05	244.15529	244.30798	244.37347	244.46085
	0.10	244.94954	245.12533	245.21332	245.30138
	0.15	245.85636	246.65921	246.74843	246.83771
	0.20	246.67726	247.35879	247.97439	248.10981
	0.25	247.54477	248.53003	248.66613	249.27431
15°C	0.00	40.193975	49.385000	64.989214	79.342613
	0.05	244.22071	244.35164	244.46085	244.54830
	0.10	245.03741	245.21332	245.32340	245.41153
	0.15	245.96710	246.72612	246.86004	247.62096
	0.20	246.81116	247.44857	247.56088	247.65081
	0.25	247.65721	248.17261	248.30827	248.91604
25°C	0.00	40.261895	49.703597	65.128095	79.897186
	0.05	244.30798	244.39531	244.46085	244.54830
	0.10	245.10335	245.21332	245.32340	245.41153
	0.15	246.05577	246.72612	246.86004	247.62096
	0.20	246.46398	247.44857	247.56088	247.65081
	0.25	247.05326	248.17261	248.30827	248.48939
35°C	0.00	40.408192	49.907641	65.308384	80.288923
	0.05	244.39531	244.57017	244.65768	246.64725
	0.10	245.19132	245.27936	245.38949	247.51380
	0.15	245.42937	246.83771	246.94940	247.71093
	0.20	245.50066	247.03464	247.16892	247.74080
	0.25	245.86488	248.71153	249.60931	251.78832

Appendix- III
Part- B

Values of apparent molar volume, ϕ_v ($cm^3.g^{-1}$) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes $FeCl_3$ in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	53.409239	61.643275	78.962044	93.174424
	0.05	246.11351	246.20230	246.26894	246.33562
	0.10	246.95355	247.02064	247.13255	247.22215
	0.15	247.14970	247.93102	248.69094	248.75907
	0.20	247.63647	248.27389	248.88981	249.00358
	0.25	248.30352	249.73738	250.23168	250.36983
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	248.18270	248.31840	248.36367	248.45425
	0.10	249.04783	250.18787	250.25690	250.34900
	0.15	250.65296	251.43804	251.53109	251.57764
	0.20	251.42536	252.04443	252.13796	252.20815
	0.25	251.86466	252.78672	253.28369	253.78131
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	248.25053	248.40895	248.47690	248.54489
	0.10	249.13897	250.25690	250.34900	250.41812
	0.15	250.74538	250.83788	250.90729	250.97674
	0.20	250.99247	251.61150	251.65808	251.72799
	0.25	251.53209	252.05151	252.12165	252.19183
35°C	0.00	53.751890	62.307994	79.478060	94.103813
	0.05	248.31840	248.47690	248.54489	248.63560
	0.10	250.23389	250.30294	250.44116	251.53952
	0.15	250.81475	250.88415	250.97674	251.76401
	0.20	251.58822	251.70468	251.77461	251.84458
	0.25	251.60192	251.71839	251.81164	252.16204

Appendix- III
Part -C

Values of apparent molar volume, ϕ_v ($cm^3.g^{-1}$) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($CoCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	39.707251	48.077783	64.635163	79.188382
	0.05	215.83825	215.97395	216.03216	216.10981
	0.10	216.70017	216.85665	216.93498	217.01335
	0.15	216.97362	217.07166	217.15016	217.89960
	0.20	216.98253	217.64242	217.72138	218.32392
	0.25	217.78799	217.90664	218.02541	218.56772
15°C	0.00	40.193975	49.385000	64.989214	79.342613
	0.05	215.89639	216.01275	216.10981	216.18752
	0.10	216.77839	216.93498	217.03296	217.11141
	0.15	217.07166	217.13053	217.24836	217.30732
	0.20	217.60297	218.20480	218.30406	218.40340
	0.25	218.26945	218.34891	218.46821	218.62747
25°C	0.00	40.261895	49.703597	65.128095	79.897186
	0.05	215.97395	216.05156	216.10981	216.18752
	0.10	216.83708	216.93498	217.03296	217.11141
	0.15	217.15016	217.80074	218.63011	218.68990
	0.20	217.25730	218.20480	218.30406	218.90748
	0.25	217.68150	218.77147	218.93124	219.03122
35°C	0.00	40.408192	49.907641	65.308384	80.288923
	0.05	216.05156	216.20696	216.28474	216.28474
	0.10	216.91539	216.99375	217.09179	217.15065
	0.15	217.20907	217.22871	217.32698	217.38598
	0.20	217.33594	217.82015	217.93879	218.50284
	0.25	218.18397	218.46821	218.99122	219.13128

Appendix- III
Part- D

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes($CoCl_3$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	53.409000	61.643000	78.962000	93.174000
	0.05	214.70253	215.85763	215.91577	215.97395
	0.10	216.62202	216.71972	216.81751	217.91970
	0.15	216.83651	216.97362	217.72173	217.78098
	0.20	217.34686	217.50440	218.64805	218.72781
	0.25	218.43273	219.11399	219.17409	219.65712
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	215.81888	215.93516	215.97395	216.05156
	0.10	216.70017	216.79795	216.85665	216.93498
	0.15	216.93443	217.01283	217.09128	217.82051
	0.20	217.00214	217.58325	217.66216	217.74112
	0.25	217.80776	217.88685	217.96601	218.50800
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	215.87701	216.01275	216.07098	216.12924
	0.10	216.77839	216.85665	216.93498	216.99375
	0.15	217.03244	217.09128	217.15016	217.18943
	0.20	217.60297	217.62270	217.70163	217.72138
	0.25	217.92642	217.94621	218.04522	218.06503
35°C	0.00	53.751890	62.307994	79.478060	94.103813
	0.05	215.93516	216.07098	216.12924	216.20696
	0.10	216.83708	216.89581	217.01335	218.09792
	0.15	217.76123	217.82051	217.89960	219.36132
	0.20	218.18496	218.28420	219.37130	219.97588
	0.25	218.83136	218.85133	219.81830	220.32299

Appendix - III
Part - D

Values of apparent molar volume, ϕ_v ($cm^3.g^{-1}$) of different solutions at different temperature.

Temp. (°C)	Conc. of Electrolytes($CoCl_3$) in mol/L	% of EtOH			
		5	**10**	**15**	**20**
5°C	0.00	53.409000	61.643000	78.962000	93.174000
	0.05	214.70253	215.85763	215.91577	215.97395
	0.10	216.62202	216.71972	216.81751	217.91970
	0.15	216.83651	216.97362	217.72173	217.78098
	0.20	217.34686	217.50440	218.64805	218.72781
	0.25	218.43273	219.11399	219.17409	219.65712
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	215.81888	215.93516	215.97395	216.05156
	0.10	216.70017	216.79795	216.85665	216.93498
	0.15	216.93443	217.01283	217.09128	217.82051
	0.20	217.00214	217.58325	217.66216	217.74112
	0.25	217.80776	217.88685	217.96601	218.50800
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	215.87701	216.01275	216.07098	216.12924
	0.10	216.77839	216.85665	216.93498	216.99375
	0.15	217.03244	217.09128	217.15016	217.18943
	0.20	217.60297	217.62270	217.70163	217.72138
	0.25	217.92642	217.94621	218.04522	218.06503
35°C	0.00	53.751890	62.307994	79.478060	94.103813
	0.05	215.93516	216.07098	216.12924	216.20696
	0.10	216.83708	216.89581	217.01335	218.09792
	0.15	217.76123	217.82051	217.89960	219.36132
	0.20	218.18496	218.28420	219.37130	219.97588
	0.25	218.83136	218.85133	219.81830	220.32299

Appendix-III
Part-E

Values of apparent molar volume, ϕ_v ($cm^3.g^{-1}$) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($CuCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	39.707251	48.077783	64.635163	79.188382
	0.05	129.87516	131.89501	133.91062	135.93195
	0.10	134.18400	135.21187	136.23085	137.25160
	0.15	135.84937	136.53750	137.22378	138.58211
	0.20	144.94546	146.50331	147.54111	149.59967
	0.25	149.79058	150.23417	151.08789	151.94384
15°C	0	40.193975	49.385000	64.989214	79.342613
	0.05	131.88640	133.90807	135.93195	137.95686
	0.1	135.20044	137.23862	138.26381	139.28754
	0.15	138.55722	139.24180	139.93876	140.62557
	0.2	147.50893	149.56510	150.61287	151.15280
	0.25	150.62467	151.46622	152.32202	152.37265
25°C	0.00	40.261895	49.703597	65.128095	79.897186
	0.05	135.91134	137.93349	139.95548	141.98441
	0.10	136.21558	138.24658	139.27298	142.31865
	0.15	137.22378	140.58606	141.28883	143.32839
	0.20	140.94894	142.97599	147.55719	148.60870
	0.25	142.93893	146.58692	151.51559	152.77640
35°C	0.00	40.408192	49.907641	65.308384	80.288923
	0.05	137.93349	139.97417	139.98910	139.98910
	0.10	138.24313	140.27466	141.30404	141.30808
	0.15	139.25655	141.28475	141.98092	141.98934
	0.20	141.98151	144.51464	147.09031	148.12078
	0.25	143.36508	148.23135	152.35367	153.21899

Appendix-III
Part-F

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($CuCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	53.409239	61.643275	78.962044	93.174424
	0.05	131.87343	133.88765	137.91004	137.92010
	0.10	134.17866	137.20278	138.22586	139.24744
	0.15	137.85295	138.5394	139.22334	140.5821
	0.20	146.44645	149.01094	149.54204	151.09825
	0.25	149.76715	150.21637	151.46005	152.72512
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	133.88252	135.90543	137.9201	137.93349
	0.10	134.18400	138.22240	139.24014	140.26311
	0.15	138.53227	139.21964	140.58606	143.29252
	0.20	147.48746	149.54204	150.07403	151.11644
	0.25	150.62467	151.05134	151.48474	153.97385
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	133.89021	135.91723	137.93683	139.95922
	0.10	135.20044	138.23277	139.25475	140.27466
	0.15	139.21964	139.23442	140.59397	141.28066
	0.20	147.50893	150.07403	151.61375	151.63223
	0.25	151.05743	151.49091	152.32835	152.34734
35°C	0.00	53.751890	62.307994	79.478060	94.103813
	0.05	135.90543	137.93683	139.95922	141.98855
	0.10	137.22235	139.24744	140.2785	142.31017
	0.15	141.25204	141.26432	141.95563	143.32391
	0.20	149.55934	150.60691	151.13463	152.17337
	0.25	152.71230	152.74435	152.76999	153.60992

Appendix-III
Part-G

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($MgCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	39.707251	48.077783	64.635163	79.188382
	0.05	171.14356	171.24089	171.28264	171.33833
	0.10	171.94198	172.05452	172.11085	172.16721
	0.15	172.13020	172.88477	173.62650	173.68408
	0.20	175.18127	175.28428	175.34319	176.98812
	0.25	176.14659	177.07119	177.16173	178.53943
15°C	0.00	40.193975	49.385000	64.989214	79.342613
	0.05	171.18526	171.26872	171.33833	171.39405
	0.10	171.99823	172.11085	172.18130	172.23771
	0.15	172.20071	172.92751	173.69848	173.74169
	0.20	176.30483	176.37950	176.97306	177.55265
	0.25	177.05611	177.11645	178.04401	178.58555
25°C	0.00	40.261895	49.703597	65.128095	79.897186
	0.05	171.24089	171.29656	173.36088	173.41823
	0.10	172.04045	173.12965	174.22115	174.27919
	0.15	173.62650	174.98172	175.75556	175.80001
	0.20	176.94295	177.93474	178.01102	179.11131
	0.25	177.64067	181.29967	181.39526	181.52288
35°C	0.00	40.408192	49.907641	65.308384	80.288923
	0.05	171.29656	171.40799	171.46376	171.57540
	0.10	172.09676	172.16721	173.24404	174.30822
	0.15	174.35496	175.74075	177.87480	177.92051
	0.20	177.00318	177.53748	179.66224	179.69343
	0.25	177.71665	177.73186	181.47500	181.97493

Appendix-III
Part-H

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($MgCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	53.409239	61.643275	78.962044	93.174424
	0.05	171.08798	173.17476	173.21768	173.26062
	0.10	173.94598	173.98938	174.06174	175.13848
	0.15	174.12273	174.86451	175.59277	175.63714
	0.20	176.67243	177.26487	177.32538	177.40108
	0.25	177.33735	177.86093	178.74247	178.83502
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	171.14356	173.23199	173.26062	173.31790
	0.10	173.97491	174.04726	174.09070	174.14866
	0.15	174.15172	174.8938	176.33695	177.05224
	0.20	176.74749	176.80759	177.90424	177.96524
	0.25	177.44340	178.74247	179.22252	179.71897
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	173.18906	173.28925	173.33222	173.37522
	0.10	174.03279	174.09070	174.14866	174.19215
	0.15	174.20975	174.95241	174.99638	175.04039
	0.20	176.80759	177.38593	177.93474	178.49943
	0.25	177.50405	177.56475	178.02874	178.49334
35°C	0.00	53.751890	62.307994	79.47806	94.103813
	0.05	173.23199	173.33222	173.37522	173.43257
	0.10	174.07622	174.11968	174.20665	174.25016
	0.15	174.93775	174.98172	175.04039	176.47144
	0.200	176.85269	176.92790	176.97306	177.01824
	0.25	178.38588	178.46262	178.52407	178.98946

Appendix-III
Part-I

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes (HgCl2) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	39.707251	48.077783	64.635163	79.188382
	0.05	199.83670	276.43420	312.98680	325.29120
15°C	0.0	40.193975	49.38500	64.989214	79.342613
	0.05	199.84310	278.4929	313.08540	327.43690
25°C	0.00	40.261895	49.703597	65.128095	79.897186
	0.05	201.85950	286.63150	319.18650	333.55140
35°C	0.00	40.408192	49.907641	65.308384	80.288923
	0.05	203.87950	290.84710	311.27090	335.67790

Appendix-III
Part-J

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($HgCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	53.409239	61.643275	78.962044	93.174424
	0.05	201.83420	284.41550	320.95840	335.27010
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	207.724600	285.943100	316.042500	336.205200
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	209.78880	286.05770	320.20840	338.34440
35°C	0.00	53.751890	62.307994	79.47806	94.103813
	0.05	209.85180	286.14370	320.3047	338.48000

Appendix-III
Part-K

Values of apparent molar volume, ϕ_v ($cm^3.g^{-1}$) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes($NiCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	39.707251	48.077783	64.635163	79.188382
	0.05	133.91100	133.92192	133.92657	135.94290
	0.10	181.54182	181.63043	181.67476	182.73571
	0.15	193.26539	194.01584	194.07008	195.49366
	0.20	204.11673	204.22584	204.28823	204.38188
	0.25	207.25612	207.77225	207.87012	208.42084
15°C	0.00	40.193975	49.385000	64.989214	79.342613
	0.05	135.92146	135.93318	135.94290	135.95064
	0.10	182.60030	182.69056	182.74699	182.79216
	0.15	193.33247	194.05651	195.50750	195.54904
	0.20	204.21024	204.28823	205.40534	205.46864
	0.25	207.33719	207.82117	208.33876	208.47012
25°C	0.00	40.261895	49.703597	65.128095	79.897186
	0.05	135.92928	135.93708	139.96443	139.98629
	0.10	183.64913	184.72276	184.78123	184.82801
	0.15	196.12262	196.79297	196.87764	196.91999
	0.20	204.33505	204.80720	205.40534	205.98875
	0.25	207.51575	207.82117	208.33876	209.31104
35°C	0.0	40.408192	49.907641	65.308384	80.288923
	0.05	133.92811	133.94040	135.96026	146.02730
	0.100	185.72728	185.77485	186.85257	186.88889
	0.15	198.21954	199.60488	199.6782	200.40900
	0.20	206.47689	208.00485	208.10291	209.17780
	0.25	208.00076	210.84162	210.96004	211.02776

Appendix-III
Part-L

Values of apparent molar volume, ϕ_v (cm^3.g^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($NiCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	53.409239	61.643275	78.962044	93.174424
	0.05	137.91818	139.93970	141.95377	143.97693
	0.10	183.56878	187.68654	188.73962	189.80682
	0.15	196.65200	196.70837	198.83223	198.86126
	0.20	205.68644	206.26868	206.33270	206.91635
	0.25	206.88625	206.91852	206.99923	207.08001
15°C	0.00	53.482301	61.736346	79.097659	93.471038
	0.05	137.91818	137.93234	141.95377	143.97693
	0.10	183.56878	187.68654	188.73962	189.80682
	0.15	196.65200	196.70837	198.83223	198.86126
	0.20	205.68644	205.75002	206.33270	206.39676
	0.25	206.88625	206.93466	206.99923	207.08001
25°C	0.00	53.567790	61.845271	79.256417	93.671552
	0.05	137.92527	139.95071	141.96951	143.99110
	0.10	183.61469	184.67601	185.73917	188.82711
	0.15	196.70837	197.44895	198.17640	200.96145
	0.20	205.75002	206.33270	206.88411	207.97218
	0.25	207.78855	207.83749	208.32235	208.79151
35°C	0.00	53.751890	62.307994	79.4780600	94.103813
	0.05	139.93970	141.96951	143.99110	144.00525
	0.10	184.66433	185.71539	186.80417	187.85870
	0.15	196.75066	197.47743	198.21954	199.64887
	0.20	205.79772	206.39676	206.44483	207.01314
	0.25	207.83749	208.33876	209.24468	210.13554

Appendix- IV

Part-A

Viscosity (C.P) of different solutions at different temperature

Conc.of MeOH (v/v)	Conc. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $FeCl_3$	1.1955	1.0067	0.8899	0.7189
	0.05 ”	1.9136	1.9123	1.9111	1.9101
	0.10 ”	1.9218	1.9202	1.9194	1.9184
	0.15 ”	1.9297	1.9285	1.9274	1.9264
	0.20 ”	1.9353	1.9342	1.9331	1.9321
	0.25 ”	1.9417	1.9405	1.9394	1.9384
5%	0.00 $FeCl_3$	1.2065	1.1875	0.9866	0.7526
	0.05 ”	1.9144	1.9134	1.9123	1.9114
	0.10 ”	1.9226	1.9216	1.9206	1.9197
	0.15 ”	1.9305	1.9296	1.9286	1.9277
	0.20 ”	1.9361	1.9353	1.9343	1.9334
	0.25 ”	1.9425	1.9416	1.9406	1.9397
10%	0.00 $FeCl_3$	1.2074	1.1882	0.9876	0.7638
	0.05 ”	1.915	1.9139	1.9128	1.912
	0.10 ”	1.9232	1.9221	1.9211	1.9203
	0.15 ”	1.9311	1.9301	1.9291	1.9283
	0.20 ”	1.9367	1.9358	1.9348	1.934
	0.25 ”	1.9431	1.9421	1.9411	1.9403
15%	0.00 $FeCl_3$	1.2086	1.1895	0.9885	0.7742
	0.05 ”	1.9156	1.9144	1.9133	1.9126
	0.10 ”	1.9238	1.9226	1.9216	1.9209
	0.15 ”	1.9317	1.9306	1.9296	1.9289
	0.20 ”	1.9373	1.9363	1.9353	1.9346
	0.25 ”	1.9437	1.9426	1.9416	1.9409
20%	0.00 $FeCl_3$	1.2089	1.1906	0.9885	0.7785
	0.05 ”	1.9162	1.9149	1.9133	1.9132
	0.10 ”	1.9244	1.9231	1.9216	1.9215
	0.15 ”	1.9323	1.9311	1.9296	1.9295
	0.20 ”	1.9379	1.9368	1.9353	1.9352
	0.25 ”	1.9443	1.9431	1.9416	1.9415

Appendix-IV

Part-B

Viscosity (C.P) of different solutions at different temperature.

Conc. Of EtOH (v/v)	Conc. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 FeCl$_3$	1.1955	1.0067	0.8899	0.7189
	0.05 ’’	1.9136	1.9123	1.9111	1.9101
	0.10 ’’	1.9218	1.9205	1.9194	1.9184
	0.15 ’’	1.9297	1.9285	1.9274	1.9264
	0.20 ’’	1.9353	1.9342	1.9331	1.9321
	0.25 ’’	1.9417	1.9405	1.9394	1.9384
5%	0.00 FeCl$_3$	1.2055	1.1864	0.9855	0.7511
	0.05 ’’	1.9142	1.9130	1.9119	1.9110
	0.10 ’’	1.9224	1.9212	1.9202	1.9193
	0.15 ’’	1.9303	1.9292	1.9282	1.9273
	0.20 ’’	1.9359	1.9349	1.9339	1.9330
	0.25 ’’	1.9423	1.9412	1.9402	1.9393
10%	0.00 FeCl$_3$	1.2068	1.1876	0.9868	0.7623
	0.05 ’’	1.9146	1.9134	1.9123	1.9114
	0.10 ’’	1.9228	1.9216	1.9206	1.9197
	0.15 ’’	1.9307	1.9296	1.9286	1.9277
	0.20 ’’	1.9363	1.9353	1.9343	1.9334
	0.25 ’’	1.9427	1.9416	1.9406	1.9397
15%	0.00 FeCl$_3$	1.2079	1.1886	0.9874	0.7736
	0.05 ’’	1.9150	1.9138	1.9127	1.9118
	0.10 ’’	1.9232	1.9220	1.9210	1.9201
	0.15 ’’	1.9311	1.9300	1.9290	1.9281
	0.20 ’’	1.9367	1.9357	1.9347	1.9338
	0.25 ’’	1.9431	1.9420	1.9410	1.9401
20%	0.00 FeCl$_3$	1.2081	1.1893	0.9962	0.7768
	0.05 ’’	1.9154	1.9142	1.9131	1.9122
	0.10 ’’	1.9236	1.9224	1.9214	1.9205
	0.15 ’’	1.9315	1.9304	1.9294	1.9285
	0.20 ’’	1.9371	1.9361	1.9351	1.9342
	0.25 ’’	1.9435	1.9424	1.9414	1.9405

Appendix- IV

Part-C

Viscosity (C.P) of different solutions at different temperature

Conc.of MeOH (v/v)	Conc. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $CoCl_3$	1.1955	1.0067	0.8899	0.7189
	0.05 ’’	1.7447	1.7436	1.7424	1.7415
	0.10 ’’	1.7537	1.7526	1.7514	1.7505
	0.15 ’’	1.7613	1.7603	1.7591	1.7582
	0.20 ’’	1.7698	1.7681	1.7669	1.7660
	0.25 ’’	1.7743	1.7731	1.7719	1.7710
5%	0.00 $CoCl_3$	1.2065	1.1875	0.9866	0.7526
	0.05 ’’	1.7458	1.7448	1.7437	1.7429
	0.10 ’’	1.7548	1.7538	1.7527	1.7519
	0.15 ’’	1.7624	1.7615	1.7604	1.7596
	0.20 ’’	1.7709	1.7693	1.7682	1.7674
	0.25 ’’	1.7754	1.7743	1.7732	1.7724
10%	0.00 $CoCl_3$	1.2074	1.1882	0.9876	0.7638
	0.05 ’’	1.7464	1.7454	1.7443	1.7436
	0.10 ’’	1.7554	1.7544	1.7533	1.7526
	0.15 ’’	1.7630	1.7621	1.7610	1.7603
	0.20 ’’	1.7715	1.7699	1.7688	1.7681
	0.25 ’’	1.7760	1.7749	1.7738	1.7731
15%	0.00 $CoCl_3$	1.2086	1.1895	0.9885	0.7742
	0.05 ’’	1.7470	1.746	1.7449	1.7443
	0.10 ’’	1.7560	1.755	1.7539	1.7533
	0.15 ’’	1.7636	1.7627	1.7616	1.7610
	0.20 ’’	1.7721	1.7705	1.7694	1.7688
	0.25 ’’	1.7766	1.7755	1.7744	1.7738
20%	0.00 $CoCl_3$	1.2089	1.1906	0.9975	0.7738
	0.05 ’’	1.7476	1.7466	1.7455	1.7450
	0.10 ’’	1.7566	1.7556	1.7545	1.7540
	0.15 ’’	1.7642	1.7633	1.7622	1.7617
	0.20 ’’	1.7727	1.7711	1.7700	1.7695
	0.25 ’’	1.7772	1.7761	1.7750	1.7745

Appendix- IV

Part-D

Viscosity (C.P) of different solutions at different temperature.

Conc. Of EtOH (v/v)	Conc. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $CoCl_3$	1.1955	1.0067	0.8899	0.7189
	0.05 ,,	1.7447	1.7436	1.7424	1.7415
	0.10 ,,	1.7537	1.7526	1.7514	1.7505
	0.15 ,,	1.7613	1.7603	1.7591	1.7582
	0.20 ,,	1.7698	1.7681	1.7669	1.7660
	0.25 ,,	1.7743	1.7731	1.7719	1.7710
5%	0.00 $CoCl_3$	1.2055	1.1864	0.9855	0.7511
	0.05 ,,	1.7454	1.7444	1.7433	1.7425
	0.10 ,,	1.7544	1.7534	1.7523	1.7515
	0.15 ,,	1.762	1.7611	1.7600	1.7592
	0.20 ,,	1.7705	1.7689	1.7678	1.7670
	0.25 ,,	1.7750	1.7739	1.7728	1.7720
10%	0.00 $CoCl_3$	1.2068	1.1876	0.9868	0.7623
	0.05 ,,	1.7460	1.7450	1.7439	1.7432
	0.10 ,,	1.7550	1.7540	1.7529	1.7522
	0.15 ,,	1.7626	1.7617	1.7606	1.7599
	0.20 ,,	1.7711	1.7695	1.7684	1.7677
	0.25 ,,	1.7756	1.7745	1.7734	1.7727
15%	0.00 $CoCl_3$	1.2079	1.1886	0.9874	0.7736
	0.05 ,,	1.7465	1.7456	1.7445	1.7439
	0.10 ,,	1.7555	1.7546	1.7535	1.7529
	0.15 ,,	1.7631	1.7623	1.7612	1.7606
	0.20 ,,	1.7716	1.7701	1.7690	1.7684
	0.25 ,,	1.7761	1.7751	1.7740	1.7734
20%	0.00 $CoCl_3$	1.2081	1.1893	0.9962	0.7768
	0.05 ,,	1.7470	1.7462	1.7451	1.7446
	0.10 ,,	1.7560	1.7552	1.7541	1.7536
	0.15 ,,	1.7636	1.7629	1.7618	1.7613
	0.20 ,,	1.7721	1.7707	1.7696	1.7691
	0.25 ,,	1.7766	1.7757	1.7746	1.7741

Appendix- IV

Part-E

Viscosity (C.P) of different solutions at different temperature

Conc. Of MeOH (v/v)	Conc. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $CuCl_2$	1.1955	1.0067	0.8899	0.7189
	0.05 ’’	1.9136	1.9123	1.9111	1.9101
	0.10 ’’	1.9218	1.9205	1.9194	1.9184
	0.15 ’’	1.9297	1.9285	1.9274	1.9264
	0.20 ’’	1.9353	1.9342	1.9331	1.9321
	0.25 ’’	1.9417	1.9405	1.9394	1.9384
5%	0.00 $CuCl_2$	1.2065	1.1875	0.9866	0.7526
	0.05 ’’	1.9144	1.9134	1.9123	1.9114
	0.10 ’’	1.9226	1.9216	1.9206	1.9197
	0.15 ’’	1.9305	1.9296	1.9286	1.9277
	0.20 ’’	1.9361	1.9353	1.9343	1.9334
	0.25 ’’	1.9425	1.9416	1.9406	1.9397
10%	0.00 $CuCl_2$	1.2074	1.1882	0.9876	0.7638
	0.05 ’’	1.9150	1.9139	1.9128	1.9120
	0.10 ’’	1.9232	1.9221	1.9211	1.9203
	0.15 ’’	1.9311	1.9301	1.9291	1.9283
	0.20 ’’	1.9376	1.9358	1.9348	1.9340
	0.25 ’’	1.9431	1.9421	1.9411	1.9403
15%	0.00 $CuCl_2$	1.2086	1.1895	0.9885	0.7742
	0.05 ’’	1.9156	1.9144	1.9133	1.9126
	0.10 ’’	1.9238	1.9226	1.9216	1.9209
	0.15 ’’	1.9317	1.9306	1.9296	1.9289
	0.20 ’’	1.9373	1.9363	1.9353	1.9346
	0.25 ’’	1.9437	1.9426	1.9416	1.9409
20%	0.00 $CuCl_2$	1.2089	1.1906	0.9975	0.7785
	0.05 ’’	1.9162	1.9149	1.9138	1.9132
	0.10 ’’	1.9244	1.9231	1.9221	1.9215
	0.15 ’’	1.9323	1.9311	1.9301	1.9295
	0.20 ’’	1.9379	1.9368	1.9358	1.9352
	0.25 ’’	1.9443	1.9431	1.9421	1.9415

Appendix- IV
Part-F

Viscosity (C.P) of different solutions at different temperature

Conc. Of EtOH (v/v)	Conc. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $CuCl_2$	1.1955	1.0067	0.8899	0.7189
	0.05 ”	1.9136	1.9123	1.9111	1.9101
	0.10 ”	1.9218	1.9205	1.9194	1.9184
	0.15 ”	1.9297	1.9285	1.9274	1.9264
	0.20 ”	1.9353	1.9342	1.9331	1.9321
	0.25 ”	1.9417	1.9405	1.9394	1.9384
5%	0.00 $CuCl_2$	1.2055	1.1864	0.9855	0.7511
	0.05 ”	1.9142	1.9130	1.9119	1.9110
	0.10 ”	1.9224	1.9212	1.9202	1.9193
	0.15 ”	1.9303	1.9292	1.9282	1.9273
	0.20 ”	1.9359	1.9349	1.9339	1.9330
	0.25 ”	1.9423	1.9412	1.9402	1.9393
10%	0.00 $CuCl_2$	1.2068	1.1876	0.9868	0.7623
	0.05 ”	1.9146	1.9134	1.9123	1.9114
	0.10 ”	1.9228	1.9216	1.9206	1.9197
	0.15 ”	1.9307	1.9296	1.9286	1.9277
	0.20 ”	1.9363	1.9353	1.9343	1.9334
	0.25 ”	1.9427	1.9416	1.9406	1.9397
15%	0.00 $CuCl_2$	1.2079	1.1886	0.9874	0.7736
	0.05 ”	1.9150	1.9138	1.9127	1.9118
	0.10 ”	1.9232	1.9220	1.9210	1.9201
	0.15 ”	1.9311	1.9300	1.9290	1.9281
	0.20 ”	1.9367	1.9357	1.9347	1.9338
	0.25 ”	1.9431	1.9420	1.9410	1.9401
20%	0.00 $CuCl_2$	1.2081	1.1893	0.9962	0.7768
	0.05 ”	1.9154	1.9142	1.9131	1.9122
	0.10 ”	1.9236	1.9224	1.9214	1.9205
	0.15 ”	1.9315	1.9304	1.9294	1.9285
	0.20 ”	1.9371	1.9361	1.9351	1.9342
	0.25 ”	1.9435	1.9424	1.9414	1.9405

Appendix- IV

Part-G

Viscosity (C.P) of different solutions at different temperature

Conc. of MeOH (v/v)	Con. of Electrolytes in mol/L		5°C	15°C	25°C	35°C
0%	0.00	$MgCl_2$	1.1955	1.0067	0.8899	0.7189
	0.05	”	1.8649	1.8652	1.8642	1.8629
	0.10	”	1.8783	1.8771	1.8762	1.8751
	0.15	”	1.8877	1.8866	1.8855	1.8839
	0.20	”	1.8943	1.8932	1.8922	1.8910
	0.25	”	1.8988	1.8976	1.8965	1.8952
5%	0.00	$MgCl_2$	1.2065	1.1875	0.9866	0.7526
	0.05	”	1.8662	1.8666	1.8657	1.8645
	0.10	”	1.8796	1.8785	1.8777	1.8767
	0.15	”	1.8890	1.8880	1.8870	1.8855
	0.20	”	1.8956	1.8946	1.8937	1.8926
	0.25	”	1.9001	1.8990	1.8980	1.8968
10%	0.00	$MgCl_2$	1.2074	1.1882	0.9876	0.7638
	0.05	”	1.8668	1.8672	1.8663	1.8651
	0.10	”	1.8802	1.8791	1.8783	1.8773
	0.15	”	1.8896	1.8886	1.8876	1.8861
	0.20	”	1.8962	1.8952	1.8943	1.8932
	0.25	”	1.9007	1.8996	1.8986	1.8974
15%	0.00	$MgCl_2$	1.2086	1.1895	0.9885	0.7742
	0.05	”	1.8674	1.8678	1.8669	1.8657
	0.10	”	1.8808	1.8797	1.8789	1.8779
	0.15	”	1.8902	1.8892	1.8882	1.8867
	0.20	”	1.8968	1.8958	1.8949	1.8938
	0.25	”	1.9013	1.9002	1.8992	1.8980
20%	0.00	$MgCl_2$	1.2089	1.1906	0.9975	0.7785
	0.05	”	1.868	1.8684	1.8675	1.8663
	0.10	”	1.8814	1.8803	1.8795	1.8785
	0.15	”	1.8908	1.8898	1.8888	1.8873
	0.20	”	1.8974	1.8964	1.8955	1.8944
	0.25	”	1.9019	1.9008	1.8998	1.8986

Appendix- IV

Part-H

Viscosity (C.P) of different solutions at different temperature

Conc. Of EtOH (v/v)	Conc. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $MgCl_2$	1.1955	1.0067	0.8899	0.7189
	0.05 ’’	1.8649	1.8652	1.8642	1.8629
	0.10 ’’	1.8783	1.8771	1.8762	1.8751
	0.15 ’’	1.8877	1.8866	1.8855	1.8839
	0.20 ’’	1.8943	1.8932	1.8922	1.8910
	0.25 ’’	1.8988	1.8976	1.8965	1.8952
5%	0.00 $MgCl_2$	1.2055	1.1864	0.9855	0.7511
	0.05 ’’	1.8656	1.8660	1.8651	1.8639
	0.10 ’’	1.8790	1.8779	1.8771	1.8761
	0.15 ’’	1.8884	1.8874	1.8864	1.8849
	0.20 ’’	1.8950	1.8940	1.8931	1.8920
	0.25 ’’	1.8995	1.8984	1.8974	1.8962
10%	0.00 $MgCl_2$	1.2068	1.1876	0.9868	0.7623
	0.05 ’’	1.8662	1.8666	1.8657	1.8645
	0.10 ’’	1.8796	1.8785	1.8777	1.8767
	0.15 ’’	1.8890	1.8880	1.8870	1.8855
	0.20 ’’	1.8956	1.8946	1.8937	1.8926
	0.25 ’’	1.9001	1.8990	1.8980	1.8968
15%	0.00 $MgCl_2$	1.2079	1.1886	0.9874	0.7736
	0.05 ’’	1.8668	1.8672	1.8663	1.8651
	0.10 ’’	1.8802	1.8791	1.8783	1.8773
	0.15 ’’	1.8896	1.8886	1.8876	1.8861
	0.20 ’’	1.8962	1.8952	1.8943	1.8932
	0.25 ’’	1.9007	1.8996	1.8986	1.8974
20%	0.00 $MgCl_2$	1.2081	1.1893	0.9962	0.7768
	0.05 ’’	1.8674	1.8678	1.8669	1.8657
	0.10 ’’	1.8808	1.8797	1.8789	1.8779
	0.15 ’’	1.8902	1.8892	1.8882	1.8867
	0.20 ’’	1.8968	1.8958	1.8949	1.8938
	0.25 ’’	1.9013	1.9002	1.8992	1.8980

Appendix- IV

Part-I

Viscosity (C.P) of different solutions at different temperature

Conc. of MeOH(v/v)	Con. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $HgCl_2$	1.0009	0.9766	0.8899	0.7189
	0.05 ,,	1.1894	1.1884	1.1875	1.1863
5%	0.00 $HgCl_2$	1.1583	1.1566	1.1555	1.1547
	0.05 ,,	1.1896	1.1887	1.1878	1.1867
10%	0.00 $HgCl_2$	1.1593	1.1583	1.1595	1.1561
	0.05 ,,	1.1905	1.1898	1.1889	1.1877
15%	0.00 $HgCl_2$	1.1616	1.1605	1.1597	1.1583
	0.05 ,,	1.1911	1.1903	1.1894	1.1856
20%	0.00 $HgCl_2$	1.1631	1.1617	1.1605	1.1598
	0.05 ,,	1.192	1.191	1.1902	1.1892

Appendix-IV

Part-J

Viscosity (C.P) of different solutions at different temperature

Conc. of EtOH(v/v)	Con. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $HgCl_2$	1.0009	0.9766	0.8899	0.7189
	0.05 ,,	1.1894	1.1884	1.1875	1.1863
5%	0.00 $HgCl_2$	1.1587	1.1572	1.1561	1.1552
	0.05 ,,	1.1901	1.1891	1.1881	1.1869
10%	0.00 $HgCl_2$	1.1599	1.1588	1.1576	1.1564
	0.05 ,,	1.1910	1.1903	1.1893	1.1881
15%	0.00 $HgCl_2$	1.1621	1.1611	1.1600	1.1589
	0.05 ,,	1.1916	1.1911	1.1901	1.1891
20%	0.00 $HgCl_2$	1.1635	1.1621	1.1611	1.1601
	0.05 ,,	1.1924	1.1914	1.1906	1.1897

Appendix- IV

Part-K

Viscosity (C.P) of different solutions at different temperature

Conc.of MeOH(v/v)	Con. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 $NiCl_2$	1.1955	1.0067	0.8899	0.7189
	0.05 ”	1.7511	1.7494	1.7462	1.7451
	0.10 ”	1.7586	1.7577	1.7566	1.7555
	0.15 ”	1.7620	1.7612	1.7601	1.7590
	0.20 ”	1.7705	1.7697	1.7690	1.7673
	0.25 ”	1.7770	1.7761	1.7751	1.7738
5%	0.00 $NiCl_2$	1.2055	1.1864	0.9855	0.7511
	0.05 ”	1.7516	1.7503	1.7472	1.7462
	0.10 ”	1.7591	1.7586	1.7576	1.7566
	0.15 ”	1.7625	1.7621	1.7611	1.7601
	0.20 ”	1.7710	1.7706	1.7700	1.7684
	0.25 ”	1.7775	1.7770	1.7761	1.7749
10%	0.00 $NiCl_2$	1.2068	1.1876	0.9868	0.7623
	0.05 ”	1.7521	1.7508	1.7477	1.7467
	0.10 ”	1.7596	1.7591	1.7616	1.7572
	0.15 ”	1.7630	1.7626	1.7705	1.7607
	0.20 ”	1.7715	1.7711	1.7766	1.7690
	0.25 ”	1.7780	1.7775	1.7766	1.7755
15%	0.00 $NiCl_2$	1.2079	1.1886	0.9874	0.7736
	0.05 ”	1.7526	1.7514	1.7483	1.7473
	0.10 ”	1.7601	1.7597	1.7587	1.7578
	0.15 ”	1.7635	1.7632	1.7622	1.7613
	0.20 ”	1.772	1.7717	1.7711	1.7696
	0.25 ”	1.7785	1.7781	1.7772	1.7761
20%	0.00 $NiCl_2$	1.2081	1.1893	0.9962	0.7768
	0.05 ”	1.7533	1.7519	1.7489	1.7480
	0.10 ”	1.7608	1.7602	1.7593	1.7585
	0.15 ”	1.7642	1.7637	1.7628	1.7620
	0.20 ”	1.7727	1.7722	1.7717	1.7703
	0.25 ”	1.7792	1.7786	1.7778	1.7768

Appendix- IV
Part-L

Viscosity (C.P) of different solutions at different temperature

Conc. Of EtOH(v/v)	Con. of Electrolytes in mol/L	5°C	15°C	25°C	35°C
0%	0.00 NiCl$_2$	1.1955	1.0067	0.8899	0.7189
	0.05 ”	1.7511	1.7494	1.7462	1.7451
	0.10 ”	1.7586	1.7577	1.7566	1.7555
	0.15 ”	1.7620	1.7612	1.7601	1.7590
	0.20 ”	1.7705	1.7697	1.7690	1.7673
	0.25 ”	1.7770	1.7761	1.7751	1.7738
5%	0.00 NiCl$_2$	1.2065	1.1875	0.9866	0.7526
	0.05 ”	1.7521	1.7508	1.7477	1.7467
	0.10 ”	1.7596	1.7591	1.7581	1.7572
	0.15 ”	1.7630	1.7626	1.7616	1.7607
	0.20 ”	1.7715	1.7711	1.7705	1.7690
	0.25 ”	1.778	1.7775	1.7765	1.7755
10%	0.00 NiCl$_2$	1.2074	1.1882	0.9876	0.7638
	0.05 ”	1.7526	1.7513	1.7482	1.7472
	0.10 ”	1.7601	1.7596	1.7586	1.7577
	0.15 ”	1.7635	1.7631	1.7621	1.7612
	0.20 ”	1.7720	1.7716	1.7710	1.7695
	0.25 ”	1.7785	1.7780	1.7771	1.7760
15%	0.00 NiCl$_2$	1.2086	1.1895	0.9885	0.7742
	0.05 ”	1.7532	1.7519	1.7488	1.7478
	0.10 ”	1.7607	1.7602	1.7592	1.7583
	0.15 ”	1.7410	1.7637	1.7627	1.7618
	0.20 ”	1.7726	1.7722	1.7716	1.7701
	0.25 ”	1.7791	1.7786	1.7777	1.7766
20%	0.00 NiCl$_2$	1.2089	1.1906	0.9975	0.7785
	0.05 ”	1.7539	1.7526	1.7495	1.7486
	0.10 ”	1.7614	1.7609	1.7599	1.7591
	0.15 ”	1.7648	1.7644	1.7634	1.7626
	0.20 ”	1.7733	1.7729	1.7723	1.7709
	0.25 ”	1.7798	1.7793	1.7784	1.7772

Appendix-V

Part-A

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($FeCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	66.63	66.63	66.64	66.64
	0.10	66.65	66.65	66.65	66.65
	0.15	66.66	66.66	66.66	66.66
	0.20	66.66	66.67	66.67	66.67
	0.25	66.67	66.67	66.67	66.67
15°C	0.00	66.40	68.49	70.23	71.94
	0.05	68.38	68..38	68.38	68.39
	0.10	68.39	68.4.0	68.40	68.40
	0.15	68.40	68.41	68.41	68.41
	0.20	68.41	68.41	68.42	68.42
	0.25	68.42	68.42	68.42	68.42
25°C	0.00	66.78	68.53	70.27	71.99
	0.05	70.11	70.11	70.12	70.12
	0.10	70.13	70.13	70.13	70.13
	0.15	70.14	70.14	70.14	70.14
	0.20	70.14	70.15	70.15	70.15
	0.25	70.15	70.15	70.15	70.15
35°C	0.00	66.81	68.57	70.31	72.03
	0.05	71.82	71.82	71.83	71.83
	0.10	71.83	71.84	71.84	71.84
	0.15	71.84	71.85	71.85	71.85
	0.20	71.85	71.86	71.86	71.86
	0.25	71.86	71.86	71.86	71.86

Appendix-V

Part-B

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($FeCl_3$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.90	64.90	64.91	64.91
	0.10	64.92	64.92	64.92	64.92
	0.15	64.93	64.93	64.93	64.93
	0.20	64.93	64.94	64.94	64.94
	0.25	64.43	64.94	64.94	64.94
15°C	0.00	66.73	68.49	70.22	71.95
	0.05	66.59	66.59	66.59	66.59
	0.10	66.60	66.61	66.61	66.61
	0.15	66.61	66.62	66.62	66.62
	0.20	66.62	66.62	66.62	66.63
	0.25	66.62	66.63	66.63	66.63
25°C	0.00	66.78	68.53	70.28	72.00
	0.05	68.26	68.26	68.26	68.26
	0.10	68.27	68.27	68.28	68.28
	0.15	68.28	68.29	68.29	68.29
	0.20	68..25	68.29	68.29	68.30
	0.25	68.29	68.30	68.30	68.30
35°C	0.00	66.81	68.57	70.30	72.04
	0.05	69.91	69.91	69.14	69.91
	0.10	69.92	69.92	69.92	69.92
	0.15	69.93	69.93	69.93	69.93
	0.20	69.94	69.94	69.94	69.94
	0.25	69.94	69.94	69.94	69.95

Appendix-V

Part-C

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($CoCl_3$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.75	64.75	64.75	64.75
	0.10	64.76	64.76	64.76	64.77
	0.15	64.77	64.77	64.77	64.77
	0.20	64.78	64.78	64.78	64.78
	0.25	64.78	64.79	64.79	64.79
15°C	0.00	66.74	68.49	70.23	71.94
	0.05	66.43	66.43	66.43	66.43
	0.10	66.44	66.44	66.44	66.45
	0.15	66.45	66.45	66.45	66.46
	0.20	66.46	66.46	66.46	66.46
	0.25	66.47	66.47	66.47	66.47
25°C	0.00	66.78	68.53	70.27	71.99
	0.05	68.09	68.09	68.10	68.10
	0.10	68.10	68.10	68.11	68.11
	0.15	68.11	68.11	68.11	68.12
	0.20	68.12	68.12	68.13	68.13
	0.25	68.13	68.13	68.13	68.14
35°C	0.00	66.81	68.57	70.31	72.03
	0.05	69.74	69.74	69.74	69.74
	0.10	69.75	69.75	69.75	69.75
	0.15	69.76	69.76	69.76	69.76
	0.20	69.77	69.77	69.77	69.77
	0.25	69.77	69.77	69.77	69.78

Appendix-V

Part-D

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($CoCl_3$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.75	64.75	64.75	64.76
	0.10	64.76	64.76	64.76	64.77
	0.15	64.77	64.77	64.77	64.78
	0.20	64.78	64.78	64.78	64.79
	0.25	64.79	64.79	64.79	64.79
15°C	0.00	66.73	68.49	70.22	71.95
	0.05	66.43	66.36	66.43	66.43
	0.10	66.44	66.44	66.44	66.45
	0.15	66.45	66.45	66.45	66.46
	0.20	66.46	66.46	66.46	66.46
	0.25	66.47	66.47	66.47	66.47
25°C	0.00	66.78	68.53	70.28	72.00
	0.05	68.09	68.09	68.10	68.10
	0.10	68.10	68.10	68.11	68.11
	0.15	68.11	68.11	68.12	68.12
	0.20	68.12	68.12	68.13	68.13
	0.25	68.13	68.13	68.13	68.14
35°C	0.00	66.81	68.57	70.30	72.04
	0.05	69.74	69.74	69.74	69.74
	0.10	69.75	69.75	69.75	69.75
	0.15	69.76	69.76	69.76	69.76
	0.20	69.77	69.77	69.77	69.77
	0.25	69.77	69.77	69.77	69.78

Appendix-V

Part-E

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($CuCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.96	64.96	64.96	64.97
	0.10	64.97	64.97	64.97	64.97
	0.15	64.98	64.98	64.98	64.98
	0.20	64..98	64.99	64.99	64.99
	.25	64.99	64.99	64.99	65.00
15°C	0.00	66.74	68.49	70.23	71.94
	0.05	66.65	66.65	66.65	66.65
	0.10	66.66	66.66	66.66	66.66
	0.15	66.67	66.67	66.67	66.67
	0.20	66.67	66.67	66.67	66.68
	0.25	66.68	66.68	66.68	66.68
25°C	0.00	66.78	68.53	70.27	71.99
	0.05	68.32	68.32	68.32	68.32
	0.10	68.33	68.33	68.33	68.33
	0.15	68.34	68.34	68.34	68.34
	0.20	68.34	68.34	68.34	68.35
	0.25	68.35	68.35	68.35	68.35
35°C	0.00	66.81	68.57	70.31	72.03
	0.05	69.96	69.97	69.97	69.97
	0.10	69.97	69.98	69.98	69.98
	0.15	69.98	69.99	69.99	69.99
	0.20	69.99	69.99	69.99	69.99
	0.25	70.00	70.00	70.00	70.00

Appendix-V

Part-F

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($CuCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.96	64.96	64.96	64.97
	0.10	64.97	64.97	64.97	64.98
	0.15	64.98	64.98	64.98	64.98
	0.20	64.99	64.99	64.99	64.99
	0.25	64.99	64.99	65.00	65.00
15°C	0.00	66.73	68.49	70.22	71.95
	0.05	66.65	66.65	66.65	66.65
	0.10	66.66	66.66	66.66	66.66
	0.15	66.67	66.67	66.67	66.67
	0.20	66.67	66.68	66.68	66.68
	0.25	66.68	66.68	66.68	66.68
25°C	0.00	66.78	68.53	70.28	72.00
	0.05	68.32	68.32	68.32	68.32
	0.10	68.33	68.33	68.33	68.37
	0.15	68.34	68.34	68.34	68.34
	0.20	68.34	68..35	68.35	68.35
	0.25	68.35	68.35	68.35	68.36
35°C	0.00	66.81	68.57	70.30	72.04
	0.05	69.96	69.96	69.97	69.97
	0.10	69.97	69.97	69.98	69.98
	0.15	69.98	69.98	69.99	69.99
	0.20	69.99	69.99	70.00	70.00
	0.25	70.00	70.00	70.01	70.01

Appendix-V

Part-G

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($MgCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.66	64.67	64.67	64.67
	0.10	64.68	64.68	64.68	64.68
	0.15	64.69	64.69	64.69	64.69
	0.20	64.69	64.69	64.70	64.70
	0.25	64.70	64.70	64.71	64.71
15°C	0.00	66.74	68.49	70.23	71.94
	0.05	66.35	66.34	66.34	66.34
	0.10	66.36	66.36	66.36	66.36
	0.15	66.37	66.37	66.37	66.36
	0.20	66.38	66.37	66.37	66.37
	0.25	66.38	66.38	66.38	66.37
25°C	0.00	66.78	68.53	70.27	71.99
	0.05	68.01	68.00	68.00	68.01
	0.10	68.02	68.02	68.02	68.02
	0.15	68.02	68.03	68.03	68.03
	0.20	68.03	68.03	68.03	68.04
	0.25	68.04	68.04	68.04	68.04
35°C	0.00	66.81	68.57	70.31	72.03
	0.05	69..64	69.64	69.65	69.65
	0.10	6966	69.66	69.66	69.66
	0.15	69.67	69.66	69.67	69.67
	0.20	69.67	69.67	69.67	69.67
	0.25	69.67	69.67	69.68	69.68

Appendix-V

Part-H

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($MgCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.66	64.67	64.67	64.67
	0.10	64.68	64.68	64.68	64.69
	0.15	64.69	64.69	64.69	64.69
	0.20	64.69	64.69	64.70	64.70
	0.25	64.70	64.70	64.70	64.71
15°C	0.00	66.73	68.49	70.22	71.95
	0.05	66.34	66.34	66.34	66.35
	0.10	66.36	66.36	66.36	66.36
	0.15	66.36	66.37	66.37	66.37
	0.20	66.37	66.37	66.37	66.38
	0.25	66.37	66.38	66.38	66.38
25°C	0.00	66.78	68.53	70.28	72.00
	0.05	68.00	68.00	68.00	68.01
	0.10	68.02	68.02	68.02	68.02
	0.15	68.02	68.03	68.03	68.03
	0.20	68.03	68.03	68.03	68.04
	0.25	68.03	68.04	68.04	68.04
35°C	0.00	66.81	68.57	70.30	72.04
	0.05	69.64	69.64	69.64	69.65
	0.10	69.65	69.66	69.66	69.66
	0.15	69.66	69.67	69.67	69.67
	0.20	69.67	69.67	69.67	69.67
	0.25	69..67	69.68	69.68	69.68

Appendix-V

Part-I

Values of free energy of activation, $\Delta G_\eta^{\#}$ (Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($HgCl_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	63.91	63.91	65.50	65.05
15°C	0.00	66.74	68.49	70.23	71.94
	0.05	67.10	67.10	68.80	68.70
25°C	0.00	66.78	68.53	70.27	71.99
	0.05	63.90	63.90	65.50	65.50
35°C	0.00	66.81	68.57	70.31	72.03
	0.05	67.10	67.10	68.80	68.70

Appendix-V

Part-J

Values of free energy of activation, $\Delta G_\eta^{\#}$ (K.Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($HgCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	63.90	63.90	65.50	65.50
15°C	0.00	66.73	68.49	70.22	71.95
	0.05	67.10	67.10	68.70	68.70
25°C	0.00	66.78	68.53	70.28	72.00
	0.05	63.90	63.90	65.50	65.50
35°C	0.00	66.81	68.57	70.30	72.04
	0.05	67.10	67.10	68.70	68.80

Appendix-V

Part-K

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes(NiCl$_2$) in mol/L	% of MeOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.89	64.89	64.90	64.90
	0.10	64.91	64.91	64.91	64.91
	0.15	64.92	64.92	64.92	64.92
	0.20	64.92	64.93	64.93	64.93
	0.25	64.93	64.93	64.93	64.93
15°C	0.00	66.74	68.49	70.23	71.94
	0.05	66.58	66.58	66.58	66.58
	0.10	66.59	66.59	66.60	66.60
	0.15	66.60	66.60	66.60	66.61
	0.20	66.61	66.61	66.61	66.61
	0.25	66.61	66.61	66.62	66.62
25°C	0.00	66.78	68.53	70.27	71.99
	0.05	68.25	68.25	68.25	68.25
	0.10	68.26	68.26	68.26	68.26
	0.15	68.27	68.27	68.27	68.27
	0.20	68.28	68.28	68.28	68.28
	0.25	68.28	68.28	68.29	68.29
35°C	0.00	66.81	68.57	70.31	72.03
	0.05	69.89	69.90	69.90	69.90
	0.10	69.91	69.91	69.91	69.91
	0.15	69.92	69.92	69.92	69.92
	0.20	69.92	69.93	69.93	69.93
	0.25	69.93	69.93	69.93	69.93

Appendix-V

Part-L

Values of free energy of activation, $\Delta G_{\eta}^{\#}$ (Cal.mol^{-1}) of different solution at different temperature.

Temp. (°C)	Conc. of Electrolytes ($NiCl_2$) in mol/L	% of EtOH			
		5	10	15	20
5°C	0.00	66.71	68.46	70.19	71.91
	0.05	64.75	64.75	64.75	64.75
	0.10	64.75	64.60	64.76	64.76
	0.15	64.76	64.76	64.76	64.76
	0.20	64.77	64.77	64.77	64.77
	0.25	64.77	64.77	64.78	64.78
15°C	0.00	66.73	68.49	70.22	71.95
	0.05	66.43	66.43	66.43	66.43
	0.10	66.43	66.44	66.44	66.44
	0.15	66.44	66.44	66.44	66.44
	0.20	66.45	66.45	66.45	66.45
	0.25	66.45	66.46	66.46	66.46
25°C	0.00	66.78	68.53	70.28	72.00
	0.05	68.08	68.09	68.09	68.09
	0.10	68.10	68.10	68.10	68.10
	0.15	68.10	68.10	68.10	68.10
	0.20	68.11	68.11	68.11	68.12
	0.25	68.12	68.12	68.12	68.12
35°C	0.00	66.81	68.57	70.30	72.04
	0.05	69.73	69.73	69.73	69.73
	0.10	69.74	69.74	69.74	69.75
	0.15	69.74	69.74	69.75	69.75
	0.20	69.75	69.75	69.75	69.76
	0.25	69.76	69.76	69.76	69.76

References

1. D. Eisenberg, W. Kanzmann, Structure and Properties of Water, Clarendon Press, Oxford (1969).

5. A. Fraliello and D.P. Miller, Physics, 11, 1, 37-47 (1966).

2. H. Frank, Science 169, 635 (1970).

6. R.G. Bruant, Ann. Rev. Phys, Chem, 29, 167-188 (1978).

7. A. Fratiello, R.E. Lee, D.P. Miller and V.M. Nishida, Molecular Physics 13.4. 349-359 (1967).

3. R. Harne, Marine Chemistry, Willey, New York (1969).

4. J. Kareanan, Water and Solute Water Interaction, Holden Day Inc., California (1964).

8. J.A. Jackson, J.F. Lemons and H. Taube, J. Chem. Phys. 32, 2, 553-555 (1960).

9. 1. Koltz, Water, Its Fitness as a Molecular Environment on in Membrances Ion Transport, Vol I, Chap-4, Ed. Bitter, willey Interscience, New York (1970).

10. H.G. Hertz, M. Holz, R. Klute, G. Stalidis and H. Vers, Berichte der Bunsen Gessellschaft, 78, 1, 24-35 (1974).

11. S. Ando, I. Ando, A. Shoji and T. Ozaki, J. Am. Chem. Soc., 110, 3380-3386 (1988).

12. K. Beshah, E.T. Objiniezak and R.G. Griffin, J. Chem. Phys. 86, 9, 4730-4736 (1987).

13. H. Herrman, H.G. Hertz and R. Maurer, Chimia Forchung, 39, 2-3, 61-63 (1985).

14. V.G. Kunze, A.E. Bert, H. Langund, B. Phillip, Z. Phys. Chemie, Leipzig, 1, 5, 49-58 (1985).

15. A.L.V. Geet, J. Am. Chem. Soc., 94, 16, 5583-5587 (1971).

16. A. Fratiello, R.E. Lee, V.M. Nishida and R.E. Shuster, J. Chem. Phys., 48.8, 3705-3711 (1967).

17. J. Bernal, R. Fowler, J. Chem. Phys. 1, 515 (1973).

18. J. Bernal, Proc. Roy. Soc. A. 280, 299 (1964).

19. J.L. Jones and J. Pople, Proc. Roy. Soc., A. 205, 155 (1955).

20. H.S. Frank, W.Y. Wen, Discuss, Faraday Soc., 24, 133 (1957).

21. V. Vand, W. Senior, J. Chem. Phys. 43, 1869 (1969).

22. G.E. Walrafen, Hydrogen Bonded Solvent System, Ed. A. Convington, P. Jones and Taylor Francis, London (1968).

23. F. Frank, Physico-Chemical Process in Mixed Aqueous Solvents, Heinemann, London (1967).

24. Fratiello and D.P. Miller, Phys., 11, 1, 37-47 (1966).

25. Felix Franks, "Water", A Comprehensive Treaties, 1, Plenum Press, New York, 9 (1972)

26. W. K. Rontgen, Am. Phy., 45,91 (1892)

27. R.W. Gurney, "*Ionic Process in Solution*", Mc Graw Hill, New York (1953).

28. M. Tanfard and H. A. Levy, J. Am. Chem. Soc., 84, 3965 (1962)

29. J .L. Ravanan, Water and Solute-Water Interaction, Holden Day. Inc., (1964).

30. T.T. Wall and D.F. Herning, J. Chem. Phys., 43, 2079 (1965).

31. M. Falk and T.A. Fard, Can. J. Chem. 44, 1699 (1966).

32. E.U. Frank and K. Roth, Discuss, Faraday Soc., 43, 108 (1967).

33. J.D. Bernal and R.H. Fowler, J.Chem. Phys., 1, 515 (1933)

34. H.S. Frank and M. Evans, J. Chem. Phys. 13, 507 (1945) Disc. Faraday Soc., 24, 133 (1957).

35. G.Jones and M.Dole, J.Am. Chem. Soc., 51,2950 (1929)

36. Felix, Franks, "*Water*" The Royal Society O Chemistry, 66 (1983)

37. R.H. Stokes and R Mills, "*Viscosity of Electrolytes and Related Properties*" Pergamon Press, London, 33-45 (1965)

38. F. Frank, M. Pedley and D.S. Reid, J. Chem. Soc., Faraday Trans. 72, 197 (1976)

39. F. Franks. J. Chem. Soc., Faraday Trans. 73, 830 (1977)

40. F. Frank, H.T. Smith, Trans Faraday. Soc., 64, 2962 (1968)

41. D. England and N. J. Crawther Faraday Symp. Chem. Soc., 17,141 (1982)

42. S. Cabani, in "*Advance in solution Chemistry*". Eds. I. Bretini L. Lunajji and A. Dei. Plenum Press (1981)

43. J. P. Greenstein and M. Winitj, "*Chemistry of the Amino Acids*". Weley-Interscience (1961).

44. T. H. Lilley, in "*Chemistry and Bio-Chemistry of Amino Acids*", Ed. G.C. Berrett, Chapman Hall, London, Chp.,21(1985)

45. A. A. Zamyatnin, Ann Rev. Biophys. Bio., 13, 145 (1984)

46. R. K. Wadi and M. Nataranjan, J. Scient, Ind. Res., 43, 380 (1984)

47. Y. C. Ahluwalia, J. Indian Chem. Soc., 63, 727 (1986)

48. B. S. Lark, K. Bala and A. S. Bhui, J. Chem. Sci., 7, 35 (1981)

49. H. L. Friedman and C. V. Krisman, in "*Water*" A Comprehensive Trestise, Ed. F. Franks, Plenum Press, New York (1973)

50. G. Nemethy and H.A. Scheraga, J. Chem. Phys., 36, 3382 (1962)

51. D. E. Goldsack and R. Franchetto, Can. J. Chem., 55,1062-1072 (1977)

52. S. Glasstone, K. Laider and H. Eyring, Theory of Rate Porcess, Mc Graw Hill, New York (1941).

53. Flory, P.J., Am. Chem. Soc., 87, 1838 (1965)

54. Abu, A. and Flory, P.J., J. Am. Chem. Soc., 87, 1838 (1965)

55. M. Azhar Ali and M. L. Lakhanpal and Raviprashar. Journal of the Bangladesh Chemical Soc., 4(2), 175-181(1991)

56. Kaur, H.; Sarma, N.S.; Mahl, B.S.: Khamura. J.R.; Bender, M.; Heintz, A Fluid Phase Equilib., 67, 241 (1991) ✓

57. Chaudhari, S. X. Katti, S.S. (Nolt. Chem. Lab., Pure, 411008 India) J. Chem. Thermodyn., 21(6), 667-71 (1989)

58. Dewan, R. K., Gupta, C. M., Mehta S. K. (Dep. Chem., Panjab University, Chandigarh, 160014 India) J. Phys. Chem. (Manich) 106 (1-2)221-8 (Eng.) Chemical Abs.111, 141724p(1989)

59. Treszczanowiez, T., Lu, B. C.-Y, Benson, G.C.(Institute Chemi. Fizycznej, Polska Academia Nauk, 10-224, Warsaw, Pol.) Int. Data Ser., Sel. Chemical Abstarts. 128, No, 22, 27581w (1998) ✓

60. Bharati Bhattacharjee and S. N. Bhat, J. Indian Chem. Soc., 76, 89- 94 (1999) ✓

61. C. Holszky, C. Sucin, D. Sandulescu, Rev. Romaine de Chimie, 19, 5 (1974)

62. Satwinder P. Sing and O. P. Yadev., J, Indian Chem. Soc., 75, 443-446 (1998)

63. T. L. Broad water and L. Kay, J. Phy. Chem. 74, 21, 3802-3812(1970)

64. J. Gangopadhy and S. C. Lahiri., J. Indian. Chem. Soc., Vol. 75, 223-228 (1998)

65. N.M. Murthy and S.V. Subrahmanyam, Cand. J. Indian Chem., 58, 1527-1532 (1980).

66. U. R. Kapadi. D. G. Hundiwale, N.B. Patil and M. K. Lande, J. Indian Chem. Soc., 77, 319-321 (2000). ✓

67. N.M. Murthy and S.V. Subrahmanyam., Indian Journal of Pure and Applied Physics, 15, 485-489 (1977).

68. (Ms) Dimple Agarwal and Mukhtar Sing., J. Indian Chem. Soc., 81, 850-859 (2004). ✓

69. N. C. Day, H.K. Saikia and L Haque. Can. J. Chem., 58, 1542-1545 (1980).

70. M. M. Huque and D. Sandlenscu, Rev. Roumaine de Chimia, 29, 415-421 (1984).

71. Amalendu Pal and Suresh Kumärtz, J. Indian Chem. Soc., 81, 1019-1024 (2004). ✓

72. S. V. Subrahmanyam C.V. Ragavan, et. al., Acusticam., 13, 11(1963).

73. S. V. Subrahmanyam C.V. Ragavan, et. al., Acusticam., 28, 215(1973)

74. (Ms) Gunjan Maheswary and Mukhtar Sing, J. Indian Chem. Soc., 79, 659-664(2002).

75. R. H. Stokes and R. Mills, Viscosity of Electrolytes and Properties, Pergamon Press., (1971).

76. R. W. Gurney, Ionic Process in Solution, Mc Graw Hill., (1953)

77. Anwar Ali, Soghra Hyder, Shahla Khan and Saba Sabir, J. Indian Chem. Soc., 81, 860-864 (2004).

78. M.A. Rashid, Rhes. Studies on Aqueous Solution etc., unpublished M. Phil Thesis, BUET, Dhaka (1991).

79. M.M. Huque and Mrs. S.T. Saad, J. Bang. Aca. of Sci. 12(l), 81-88 (1988).

80. P. S. Nikam, H. R. Ansari and Mehdi Hasan., J. Indian Chem. Soc., 79, 344-346(1999).

81. Singh, P. Ramesh, C.R.P. Sinha and B. Singh (1986), J. Chem. Eng. data 31(2) 107-111 Chem. Abstr., 104, 95975Z (1986).

82. M. L. Parmer and D. K. Dhiman., J. Indian Chem. Soc., 79, 729-731 (2002).

83. Sakurai, Masao and T. Nakagawa, 1984, J. Chem. Thermodyn. 16(2) 171-4, Chem. Abstr. 100, 215893n (1984).

84. H. N. Solimo, R. Riggio, F. Doualio, M. Katz, Can. J. Chem. 53(9), 1258 (1975), Chem. Abstr. 83(4), 85735e (1975).

85. Man Singh., J. Indian Chem. Soc., 82, 295-301 (2005).

86. F.H. Jumean, J. Ind. Chem. Soc. 68, 4, 197-200 (April 1991).

87. F.H. Jumean and M.I. Qaderi, J. Indian Chem. Soc., 68, 9, 502-505 (1991).

88. M. Monimul Huque and Md. Nizam Uddin, J. Indian Chem. Soc., 82, 333-336 (2005).

89. Tito Tomicic, Javwnovic Kolar, Javanka, Fac, Trchnol, Zagreb, Yugoslavia, Hem. Ind., 29(9), 397-400(1975).

90. P. S. Nikam, R. P. Shewale, A. B. Sawant and Mehdi Hasan, J. Indian Chem. Soc., 82, 36-38. (2005). ✓

91. Shiro Kurolowa and Mato Nakamura (Tokyo Univ.), Kobumshi Kagaku., 22(243), 394-404(1965).

92. Kamal K. Mandal and Priyanathe Haldar., J. Chem. Indian Soc., 77, 201-203(2000).

93. Jan Wozniak: (Ins. Bio. Farm. Akad. Med., Warsow, Pol). Rocz. Panstw. Zakl. Hig., 23(1) 117-27 (1972)

94. B. Nagendra Prasad, N. Surendra Babu, M. C. X. Subha and K. Chowdori Rao, J. Indian Chem. Soc., 77, 8-10 (2000).

95. Sepulveda Luis, Gamboa, consuelo [Fac. Cienc. Univ. Chile. Santiago Chile] J. Colloid Interface Sci., 118(1), 87-90 (1987)

96. Reena Gupta and Mukhtar Sing, J. Indian Chem. Soc., 81, 561-569 (2004).

97. R.A. Horne, Water and Solute-Water Interaction, Holden Day Inc., (1964).

98. O.Y. Samoilov, Structure of Aqueous Electrolyte Solutions and Hydration of Ions, Consultant Bureau (1965).

99. J.C. Ahiuwalia and C.N. Rao, J. Sci. Indi. Res. India, 30, 453 (1971).

100. R.L. Kay, T. vitreccio, C. Zawoyski and D.F. Evans, J. Phys. Chem., 70, 2336 (1967).

101. P. S. Nikam, and Mehdi Hasan, J. Indian Chem. Soc., 69, 6, 300-302 (1988).

102. J.S. Sandhu and Gurbir Singh, J. Indian Chem. Soc. LXV (1988).

103. Cruickshank, J.B. and Everett, D.H.; Chem Soc. Ann. Rep., 50, 80 (1953).

104. Rice, O. K. Chemical Rev., 44, 69 (1949).

105. Scatchard, G., Chemical Rev., 44, 7 (1949).

106. Stokes, R. H. and Marsh, K. H. Ann. Rev. Phys, Chem., 23, 65 (1972).

107. D.P. Shoemaker, C. W. Garland, J. I. Steinfeld and J. W. Nibler, Experiments in Physical Chemistry, Fourth. Edition, U.S.A., 164-167 (1981).

108. R. C. Das, B. Behera, Experiments in Physical Chemistry, First Edition., 30-31 (1994).

109. A.J. Batschiusk, Phys.Chem., 48, 643 (1913).

110. A.K. Doiolitte, J. App. Phys., 22, 1471 (1959).

111. M.H. Cohen and D. Tuenbule, J. Chem. Phys., 30, 1164 (1989).

112. F. Boche, J. Chem. Phys., 30, 748 (1959).

113. P. Mc Cedo and T.A. Litovitz, J. Chem. Phys., 42, 245 (1965).

114. M.L. William, R.F. Landel, J.D. Ferry, J. Am. Chem. Soc., 77, 3701 (1955).

115. E. Gutenberg, Z. Physik. Chem., 123, 199 (1926).

116. T.H. Gronwell, V.K. Lamer and K. Sandved, Z. Physik., 29, 258 (1928).

117. R. Robinson and R. Stokes, Electrolytes Solution, 2nd Edition, Butter worth, London (1954).

118. S.C. Paul and P.K. Chakrobarty , Degree Physical Chemistry, Eighth Edition, 156 & 363 (1994).

119 J.S.Sandhu, P. Kaur and Urmil Kashyap, J.Ind.Chem. Soc. LXIII, 729-734 (1986)

120. Weisberger,A.,Physical methods of organic chemistry Ist Part, Interscience publisher Inc. New York (1949).

121. Shikder ,N. U., An M.Phil Thesis, Chemistry Department, BUET, Dhaka, (1994)

122. R. Furth, Porc. Cambridge Phil, Soc., 252, 276 & 281(194[illegible])