PHYSICO-CHEMICAL STUDIES OF DIFFERENT SOLUTIONS OF ELECTROLYTES (NH_4Cl, $FeCl_3$ AND $NiCl_2$) IN MIXED SOLVENTS (WATER-DMSO)

By
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Submitted in partial fulfillment of the requirements for the degree of
Master of Philosophy (M. Phil.) in Chemistry

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Dedicated

To

My Parents

Abdul Mannan Khan
&
Amina Khanom

DECLARATION

I declare that the content in my M. Phil. thesis entitled "Physico-Chemical studies of different solutions of electrolytes (NH_4Cl, $FeCl_3$ and $NiCl_2$) in mixed solvents (water-DMSO)" is original and accurate to the best of my knowledge. I also declare that the materials contained in my research work have not been previously published or written by any person for any degree or diploma.

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CERTIFICATE

This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any University.

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Abstract

The volumetric, viscometric and some other related properties of DMSO in aqueous solutions and some electrolytes such as NH_4Cl, $NiCl_2$ and $FeCl_3$ in water, DMSO and mixed solvents have been measured. The apparent molal volumes, φ_v and viscosities, η of NH_4Cl, $NiCl_2$ and $FeCl_3$ in water and water-DMSO solutions were studied as a function of concentration at a wide range of temperatures of 288, 293, 298, 303, 308 and 313 K. The apparent molal volumes at infinite dilutions φ_v^0 (limiting apparent molal volume) of these electrolytes were determined by extrapolating φ_v values to the zero concentrations which is practically equal to the partial molal volume. Limiting apparent molal volume for all the three electrolytes studied showed higher values in aqueous DMSO solution then those in aqueous solution in the temperature range of 288 K to 313 K. Apparent molal volumes, φ_v is depended upon the electrolyte concentration as well as on the temperature. Apparent molal volumes showed the gradual decrease of volume with concentration except $FeCl_3$ in water and in pure DMSO solution.

The value of viscosities increase in molality of the electrolytes except NH_4Cl. No significant change of viscosity observed for NH_4Cl with increase in molality in aqueous and in 20% aqueous-DMSO solutions. The viscosities, η for all the studied electrolytes are greater in aqueous DMSO solvent system than those in water system alone indicating that electrolytes in aqueous DMSO systems are more structural than those in aqueous system. Viscosity coefficients (A and B) for the above systems were also determined for the Jones-Dole equation. B values for $NiCl_2$ and $FeCl_3$ were found to be positive that indicate these electrolytes exhibit structure making behavior in water and in water-DMSO solutions. The B value is negative in water and water-DMSO for NH_4Cl. This indicates that NH_4Cl salt behaves as a water structure breaker in aqueous and aqueous DMSO system. The coefficient A represents the solute-solute interactions coupled with size and shape effect of the solute and to some extent solute-solvent interactions. A coefficient was obtained with an irregular variation. The behaviors of three solutes in binary and ternary systems were discussed in terms of the charge, size and hydrogen bonding effect.

Contents

Page

Introduction

1.1 Chemistry of Ammonium Chloride

According to French and Spanish the name of Ammonium Chloride is Chlorure diammonium and Cloruro de amonio respectively. The Chemical Formula is NH_4Cl. It is a odorless, colorless, slightly hygroscopic crystalline solid. Molecular mass 53.49, melting point 340°C, boiling point 520°C, relative density (specific gravity) 1.53 at 20°C and sublimes at 340°C. Highly soluble in water, liquid ammonia, methanol and slightly soluble in ethanol. It is almost insoluble in acetone, diethyl ether and ethyl acetate.

In NH_4^+ sp^3 hybridization is held at nitrogen atom. Four tetrahedral shaped sp^3 hybrid orbitals are formed. Out of these orbitals one is having one lone pair electron and rest of three each one electron. Three N–H σ-bonds are formed by the overlapping between sp^3 orbital and s orbital of hydrogen. Ammonium ion (NH_4^+) is formed by addition with H^+ ion and lone pair electron of Nitrogen. At last NH_4^+ ion is combined with Chloride ion (Cl^-) by ionic band and produce NH_4Cl.

Thermal dissociation of NH_4Cl: Upon heating ammonium chloride produces pungent smelling NH_3 gas.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

If a glass dipped in concentrated HCl acid comes in contact with the ammonia gas, white fumes of NH_4Cl are formed.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(g)$ white fume.

By the reaction between ammonia and Hydrochloric acid ammonium chloride is produced. Beside this NH_4Cl is produced from the boiled mixture of $(NH_4)_2SO_4$ and Sodium Chloride.

$$NH_3 + HCl \rightarrow NH_4Cl$$

$$(NH_4)_2SO_4 + 2NaCl \rightarrow 2NH_4Cl + Na_2SO_4$$

Ammonium chloride is a stable crystalline salts of the tetrahedral NH_4^+ ion, it is soluble like alkali metal salt. Salts of strong acids are fully ionized and the solutions are slightly acidic.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \quad K \approx \propto$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_2O^+ \quad K_{25} \approx 5.5\times10^{-10}$$

Thus a 1(M) solution of NH_4Cl will have a pH ≈ 4.7. The constant for the second reaction is some times called the hydrolysis constant; however, it may equally well be considered as the acidity constant of the cationic acid NH_4^+, and the system regarded as an acid-base system in the following sense:

$$\underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{NH_{3\,(aq)}}$$

Ammonium chloride with potassium and Rubidium in solubility and except where hydrogen bonding effects are important, in structure, since the three ions are of comparable radii NH_4^+ = 1.43 Å, K^+= 1.33 Å, Rb^+=1.48 Å.

Ammonium chloride volatilize with dissociation at around 300^0C for example

$$NH_4Cl\,(s) \rightleftharpoons NH_3(g) + HCl(g) \quad \Delta H = 42.3 \text{ Kcal/mole}$$

If a mixture of a small amount of ammonium chloride and base is taken in a test tube and heat is applied a smell comes out, which is ammonia gas.

$$2NH_4Cl + CaO \longrightarrow 2NH_3\uparrow + CaCl_2 + H_2O$$

Micro-cosmic salt is produced from the mixture of NH_4Cl and disodium hydrogen phosphate (Na_2HPO_4).

$$NH_4Cl + Na_2HPO_4 \rightarrow NaNH_4PO_4 + NaCl$$

When Nessler's reagent is added to the solution of ammonium salt or ammonium Chloride then if produces a brown precipitate.

$$NH_4Cl + KOH \rightarrow KCl + NH_3 + H_2O$$

$$2KHgI_3 \rightarrow 2KI + 2HgI_2$$

$2HgI_2 \rightarrow Hg_2I_4$

$Hg_2I_4 + 2NH_3 \rightarrow NH_2[Hg_2I_3]\downarrow + NH_4I$

The ammonium and chloride ions are found naturally in the body. Ammonium chloride is rapidly absorbed from the gastrointestinal tract. It is metabolized in the liver to form urea and hydrochloric acid which are excreted in the urine, NH_4Cl is used as an electrolyte in dry-cell batteries; to make quarrying explosives; as a component of soldering flux; in zinc and tin plating; for electrolytic refining of zinc; as a hardener for formaldehyde-based adhesives; as a flame suppressant; in etching solutions; as a fertilizer; as a mordant in dyeing and printing; in the manufacture of ammonium compounds; as a rapid fixer additive in photography; in freezing mixtures; for cleaning soldering irons; in pharmaceuticals and veterinary medicine; in washing powders; for snow treatment; to manufacture dyes; in tanning; in cement for iron pipes and in bakery products.

1.2 Chemistry of Nickel (II) Chloride

According to IUPAC system the name of $NiCl_2$ is Nickel (II) chloride and it's other name Nickelous chloride. Molecular formula $NiCl_2$, density 3.55 g/cm^3, melting point 1001°C and vapour pressure 133.3 Pa at 671°C. It is monoclinic and octahedral in geometrical structure. Nickel (II) chloride is highly soluble in water and ethanol. Color of nickel chloride in hexahydrate stated is green and anhydrous nickel chloride is golden-yellow. Aqueous solution of nickel chloride is acidic.

Nickel (II) chloride anhydrous salt is yellow, but the more familiar hydrate $NiCl_2{\cdot}6H_2O$ is green. A dihydrate is also known. In general nickel (II) chloride, in various forms, is the most important source of nickel for chemical synthesis. Nickel salts are carcinogenic.

Probably the largest scale production of nickel chloride involves the extraction with hydrochloric acid of nickel matte and residues obtained from roasting refining nickel-containing ores.

$NiCl_2{\cdot}6H_2O$ is rarely prepared in the laboratory because it is inexpensive and has a long shelf-life. The hydrate can be converted to the anhydrous form upon heating in thionyl chloride or by heating under a stream of HCl gas. Simply heating the hydrates does not afford the anhydrous dichloride.

$NiCl_2 \cdot 6H_2O + 6SOCl_2 \rightarrow NiCl_2 + 6SO_2 + 12HCl$

The dehydration is accompanied by a color change from green to yellow.

Nickel Chloride is an excellent water soluble crystalline Nickel source for uses compatible with chlorides. Chloride compounds can conduct electricity when fused or dissolved in water. Chloride materials can be decomposed by electrolysis to chlorine gas and the metal. They are formed through various chlorination processes whereby at least one chlorine anion (Cl^-) is covalently bonded to the relevant metal or cation. Ultra high purity and proprietary formulations can be prepared. The chloride ion controls fluid equilibrium and pH levels in metabolic systems. They can form either inorganic or organic compounds. Nickel Chloride is generally immediately available in most volumes. High purity, submicron and nanopowder forms may be considered.

If an aqueous solution of a Nickel chloride is prepared basic with NH_4OH and then add excess solution of dimethyl glyoxime. Red color complex compound of Nickel dimethyl glyoxime is obtained which is soluble in acid but insoluble in ammonia solution (NH_4OH).

Nickel is a Block d, Group iv, Period 4 element. The electronic configuration is $[Ar]3d^8 4s^2$. The nickel atom has a radius of 149.pm and it's Vander Waals radius is 163.pm. It is extensively alloyed with iron, chromium, molybdenum, tungsten and other metals produce stainless and other anti-corrosive steel and other corrosion-resistant alloys. It is highly electronically conductive and has many applications as a result. It is the basis of the nickel hydride battery. Most recently, its conductive properties have made it an ideal component for ceramic anode formulations used in oxygen generation and solid oxide fuel cell applications. Catalytic nickel is used to hydrogenate vegetable oils. Nickel additions to glass and ceramic glazes impart a bright green.

1.3 Chemistry of Ferric Chloride

The three stable Iron (III) halides can be obtained by direct halogenations of the metal. The Chemical Formula is $FeCl_3$. It is red-brown, very hygroscopic (foaming yellow-brown liquids) and volatile. If heated in vacuum, it decomposes with loss of chloride to give the Iron (II) chloride. Iron (III) chloride has a relatively low melting point and boils at around 315 °C. The vapour consists of the dimer Fe_2Cl_6 (compare aluminium chloride) which increasingly dissociates into the monomeric $FeCl_3$ (D_{3h} point group molecular symmetry) at higher temperature, in competition with its reversible decomposition to give iron (II) chloride and chlorine gas. Ordinarily the anhydrous $FeCl_3$ is black fibrous but the hexahydrate, $FeCl_3.6H_2O$, is yellow lumps. It is deliquescent and soluble in water.

The anhydrous $FeCl_3$ is prepared by passing dry chlorine gas over red hot iron turnings by a heat proof test tube at approximately 1000°C temperatures.

$$2\ Fe(s) + 3Cl_2 \rightarrow 2FeCl_3$$

The hydrated ferric chloride is prepared by the action of dilute hydrochloric acid over Iron (III) oxide or hydroxide. The clear solution is concentrated and allowed to cool when crystals of $FeCl_3.6H_2O$ separate out.

$$Fe\ (OH)_3\ (s) + 3HCl \rightarrow FeCl_3\ (aq) + 3H_2O.$$

Solutions of iron(III) chloride are produced industrially both from iron and from ore, in a closed-loop process by:

Dissolving pure iron in a solution of iron(III) chloride

$$Fe(s) + 2\ FeCl_3(aq) \rightarrow 3\ FeCl_2(aq)$$

Dissolving iron ore in hydrocloric acid

$$Fe_3O_4(s) + 8\ HCl(aq) \rightarrow FeCl_2(aq) + 2\ FeCl_3(aq) + 4\ H_2O$$

Upgrading the iron (II) cloride with chlorine

$$2\ FeCl_2(aq) + Cl_2(g) \rightarrow 2\ FeCl_3(aq)$$

Iron (III) chloride is a moderately strong Lewis acid, forming adducts with Lewis bases.

Iron (III) chloride reacts with other chloride salts to give the yellow tetrahedral $FeCl_4^-$ ion. Salts of $FeCl_4^-$ in hydrochloric acid can be extracted into diethyl ether.

When heated with iron (III) oxide at 350 °C, iron(III) chloride gives iron oxychloride, a layered solid and intercalation host.

$$FeCl_3 + Fe_2O_3 \rightarrow 3\ FeOCl$$

In the presence of base, alkali metal alkoxides react to give the dimeric complexes:

$$2\ FeCl_3 + 6\ C_2H_5OH + 6\ NH_3 \rightarrow (Fe(OC_2H_5)_3)_2 + 6\ NH_4Cl$$

Oxalates react rapidly with aqueous iron(III) chloride to give $[Fe(C_2O_4)_3]^{3-}$. Other carboxylate salts form complexes, e.g. citrate and tartrate.

Iron (III) chloride is a mild oxidising agent for example capable of oxidising copper (I) chloride to copper (II) chloride. Reducing agents such as hydrazine convert iron (III) chloride to complexes of iron (II).

Ferric chloride is mild reducing agent, so ferric chloride is reduced to ferrous salt by the action of reducing agents like nascent hydrogen, hydrogen sulfide stannous chloride, sulfur di-oxide etc.

As the aquoion readily loses protons to form the mono and dihydroxo species, so too are halo complexes also yellow in color, readily formed,

$Fe^{3+} + Cl^- = FeCl^{2+}$ K~30

$FeCl^{2+} + Cl^- = FeCl_2^+$ K~5

$FeCl_2^+ + Cl^- = FeCl_3$ K~0.1

The nature of more concentrated aqueous solutions of $FeCl_3$ is complex. Solutions of diluted in Fe^{3+} and concentrated HCl contain mainly $FeCl_4^-$ but a higher Fe^{3+} and / or lower H^+ concentrations octahydral species such as $[FeCl_4(H_2O)_2]$ and polymers of uncertain nature arise.

Ferric Iron in aqueous solution is rather readily reduced by many reducing agents, such as I^-, as already noted. It also oxidized sulfide ion so that no ferric sulfide can be precipitated. On adding H_2S or sulfide to Fe (III) solutions, a precipitate consisting of Iron (II) sulfide and Colloidal sulfur is obtained.

Ferric salt are reduced to ferrous chloride by the nascent hydrogen produced by the action of Zn on HCl.

$$FeCl_3 \rightarrow FeCl_2 + HCl.$$

Ferric chloride is reduced by stannous chloride to produce ferrous chloride.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

In presence of acid Ferric chloride is converting into ferrous chloride by hydrazine.

$$N_2H_4 + 4FeCl_3 \rightarrow 4FeCl_3 + 4HCl + N_2$$

Aqueous solution of ammonia i.e. ammonium hydroxide reacts with $FeCl_3$ to produce brown precipitate of ferric hydroxides.

$$FeCl_3 + 3NH_4OH_{(aq)} \rightarrow Fe\ (OH)_{3(s)} + 3NH_4Cl_{(aq)}$$

Fe^{3+}(aq) solution reacts with caustic soda, caustic potash or ammonium hydroxide solution to obtain reddish brown precipitate of iron (III) hydroxide.

$$FeCl_3 + 3NaOH \rightarrow Fe\ (OH)_{3(s)} + 3NaCl$$

Fe^{3+}(aq) solution reacts with potassium hexacyanoferrate (II) solution deep blue precipitate of potassium ferro-ferricyanide is formed.

$$FeCl_3 + K_4\,[Fe(CN)_6]_{(aq)} \rightarrow KFe[Fe(CN)_6] + 3KCl$$

$Fe^{3+}_{(aq)}$ solution reacts with potassium or ammonium thiocyanate solution to the iron (III) chloride solution. The solution is blood red.

$$FeCl_3 + 3NH_4CNS \rightarrow Fe\ (CNS)_3 + 3NH_4Cl.$$

1.4 Dimethyl sulfoxide

Dimethyl sulfoxide (DMSO) is a good organic solvent. Molecular formula C_2H_6OS, molecular mass 78.13, density 1.099 g/cm^3 at 20°C. It has bad odor and is irritating to eyes and skin. The unique capability of DMSO to penetrate living tissues without causing significant damage is most probably related to its relatively polar nature, its capacity to accept hydrogen bonds, and its relatively small and compact structure. This combination of properties results in the ability of DMSO to associate with water, proteins, carbohydrates, nucleic acid, ionic substances, and other constituents of living systems.

DMSO stabilizes ice-like water clusters, and that it may therefore be capable of displacing the equilibrium between the less and more highly structured water, in favor of the latter. Since the hydration of cell constituents and the activity of water in general are not necessarily the same in the different states of water, it follows that DMSO may exert an indirect effect on biological systems by virtue of the changes that it causes in the liquid structure of water. Among the more important biological consequences of this indirect effect of DMSO, one can mention changes in the conformations and associations of proteins and other molecules. More direct biological effects caused by DMSO, without a profound change in its chemical identity, may include changes in ion-pairing equilibrium and in the specific salvation of hydrogen-bond donors.

When the alkaline hydrolysis of methyl iodide is studied in the presence of hydroxyl ion in DMSO-water, the rate of hydrolysis increases with increasing DMSO content

$$\mathrm{CH_3I + NaOH \xrightarrow{DMSO\text{-}H_2O} CH_3OH + NaI}$$

Similar results are obtained with other primary alkyl halides (iodides, bromides, chlorides). [1] The rate constants for the reaction of hydroxide ion with ring substituted benzyl chlorides in acetone-water and DMSO-water mixtures are reported as a function of both solvent composition and temperature. The reaction rate increases with increasing DMSO concentration but decreases with increasing acetone concentration. [2]

A breakthrough in the preparation of carbonyl compounds from alcohols was achieved with the development of reagents based on DMSO. [5-8] Several procedures have been developed which permit the selective oxidation of structurally diverse primary and secondary alcohols to the corresponding carbonyl compounds, i.e. aldehydes and ketones, respectively. Most of these reactions take place at room temperature or above. Nucleophilic attack occurs on the DMSO sulfur atom. Most reactions in which the nucleophilic attack takes place on sulfur are aided by prior electrophilic attack on the oxygen atom. [9-10]

The reaction of a tertiary phosphine (usually triphenylphosphine) with an alkyl halide to yield a phosphonium salt can be done in DMSO. [11] DMSO also seems to be a good solvent for these salts. In these phosphonium salts, C-H bonds are sufficiently acidic

[12] for the hydrogen to be removed by a strong base in DMSO, e.g. an organolithium compound. [13]

1.5 The phenomena of solute-solvent interaction

Elucidation of the nature of ion-solvent interaction [14] and interpretation of the thermodynamic and transport processes in terms of such parameters as effective size of the solvated ions in solutions have been two of the most difficult problems in the understanding of electrolytic solutions. This is because there is not satisfactory model to represent the various phenomena that occur in solution and the incompleteness in the understanding of the structure of the liquids in general. There are a number of evidence of solvation of ions [14] or solute molecules a number of studies have discussed the effect of solvation on the equilibrium properties of liquids.

The process of solvation and the process of dissolution are known to be close related. When ionic crystal is added to a solvent, the electrostatic force of attraction between the oppositely charged ions in the crystal have to be overcome by interposing solvent layers around each of the ions. The ability of a solvent to dissolve a crystal is reflected by the following properties, its dielectric properties, polarity, degree of self-association and its ability to solvate. Studies on the phenomena of solvation have led to the conclusions that:

(i) The ionic compounds are moderately soluble in dipolar aprotic solvents of relatively high dielectric constant but are much more soluble in water and other hydroxylic solvents like methanol. A number of inorganic salts are dissociated in acetonitrile, which is otherwise known to solvate cations and anions rather poorly. [15-17]

(ii) The dielectric constant alone is not an adequate measure of solvating ability and may even play a major role in determining the solvation of ionic species. Cations should be better solvated in solvents having atoms with an unshared electron pair like nitrogen and oxygen. The cations have been found to be strongly solvated in highly polar solvents with the negative charge localized on an oxygen atom, e.g. in sulphur-di-oxide, dimethylsulphoxide, the phosphorus oxide, pyridine-N-oxides, 2-pryidones, 2-pyrillidones, dimethyl formamides [18] etc. Potassium iodide is less soluble than sodium iodide in methanol or water, [19] but in dimethylsulphoxide or dimethyl formamide the reverse is true, which could be due to differences of cation solvation.

The anions have been found to be solvated in two ways:

(i) Small ions are mostly solvated by hydrogen bonding which is superimposed upon solvation by ion-dipole interactions, and

(ii) large ions are solvated by interaction due to mutual polarizability of the anions and the solvent superimposed upon solvation by dipole interactions. Thus while the anions are more strongly solvated in hydrogen bonding solvents than in dipolar aprotic solvents, the cations are better solvated in the latter type of solvents. [19]

The solubility of halides in various solvents generally follow the order :

iodides > bromides > chlorides > fluorides.

The alkaline halides are more soluble in hydroxylic solvents than in the dipolar aprotic solvents like acetionitrile and acetone. These are found to be more soluble in acetonitrile than in acetone. [20] Electrolytes may be divided into two categories: ionophores and ionogens. While the former are ionic in character in the crystalline state as well as in the fused state and in highly dilute solutions, the latter have molecular crystal lattice and ionise in solution only if suitable interaction occurs with the solvent molecules.

The ionophores may exist in solution as an equilibrium mixture containing ion-pairs and free ions. [21]

$$\underset{\text{solvated}}{M^+X^-} \rightleftharpoons \underset{\text{solvated}}{M^+} + \underset{\text{solvated}}{X^-}$$

The ion-pairs are of oppositely charged ions having life terms sufficiently long to be recognised as kinetic entities in solution and in which only electrostatic forces are assumed. [14] Fuoss *et al.* [22] have studied intensely the dependence of the dissociation constant, K_d, on the dielectric constant, the temperature, and the nature of the salt. It was found to be large for solvents having high dielectric constant. It has also been found to be dependent on the distance of closest approach of the ions in the ion pairs. For hydroxylic solvents, large ions have larger K_d values and lower conductance values than smaller ions, which doesn't hold for other solvents.

Interaction of the ions with the solvent molecules causes low conductance. Na^+ ion behaves as a large ion as the K_d of iodides of Bu_4N^+ and Na^+ are found to be of the same order. Small ions like Li^+, F^- have low conductance in acetone [23] but have low K_d values which has been attributed to the loss of the solvent molecules from the ion-pairs. [23] Solute-solvent interactions have been studied in large details by various methods, some important ones my be listed as follows:

(i) Study of the solute-solvent interactions through transference experiments.
(ii) The effect of solvation on the ionic conductance.
(iii) The experiments applying stoke's law and their relevance to the nature of solvation.
(iv) Polarographic measurements of solutions.
(v) The spectral results due to the presence of the ions in solutions.

H. Remy and others [24] determined the number of moles carried to the cathode in a transport process using the mathematical presentation:

$$S = t^+ n_c - t^- n_a$$

Where, S = the number of moles of solvent carried to the cathode in the transport process; t^+, t^-, are the transport numbers of cations and anions respectively, and n_c, n_a are the number of solvent molecules associated with cations and anions respectively. The number of moles of solvent carried to the cathode in the transport process (S), was determined by the transference methods and the solvation numbers of the ions, n, was then determined. The solvation number for the various ions that they determined are :

$Li^+ = 13$, $Na^+ = 7$, $K^+ = 4$, $Mg^{2+} = 12\text{-}14$, $Ca^{2+} = 8\text{-}12$, $Sr^{2+} = 8\text{-}10$, $Ba^{2+} = 5\text{-}3$.

Limiting ionic conductance of a variety of ions in a number of solvents show that generally the conductance depends on the interaction of the ion with the solvent and not on the size of the ions, Thus, such big ions as Me_4N^+, E_tNH_3+ etc. have much larger conductance values than Li^+, Na^+, K^+. This indicates that several of the cations are solvated or interact strongly with the solvent molecules. For the case of anions Robinson and Stokes [14], Pure and Sherrington [25] showed that anions and cations of comparable crystallographic size have similar conductance in the hydroxylic solvents, but that of the anions are much more conducting than cations in the dipolar aprotic solvents. A relationship between the values of the limiting equivalent ionic conductance λ_i, and the viscosity value η was advocated and utilized by Walden and others to study the solute-solvent interactions [14]. In one approach which assumes the constancy of the product $\lambda_1\eta$ the effects of variation of temperature, viscosity and variation of the solvent were studied. For large organic ions [14], the temperature co-efficient was found to be nearly constant in water as well as other non-aqueous solvents, while for the other ions it showed variations. For changing solvents, the product was found to vary widely in the case of inorganic ions which has been interpreted to be due to differences in solvation numbers of the ion in the various solvents. In another approach to this study Pure and Sherrington [25] used the relation between viscosity η_t, and limiting ionic conductance λ_1^0, to measure the radii of interaction of solvent and solute, called stoke's law radii, r. They compared the crystallographic radii of some cations and anions with the stoke's law radii in the case of dimethylamide and dimethy1-sulphoxide solvents. They found the degree of solvation to decrease from lithium to cesium and to be less for silver and ammonium ions which have nearly comparable crystallographic radii. They postulated the anions to be unsolvated in dipolar aprotic solvents as the radii obtained are of the same order as that of the crystallographic radii, and that the negative end of the dipole in the solvent molecule is unshielded while the positive end is protected by two methy1 groups, so that the cations, but not the anions are solvated by these solvents.

Using the polarographic half-wave reduction potentials ($E_{1/2}$) at the dropping mercury electrode for studying the nature of solvation of the various anions and cations in different solvents, Kolthoff and others [15] found that the cations are reduced at more negative potentials and the anions are depolarised at more positive potentials as they become more solvated. Cations were found to be more solvated in water than in acetonitrile except in case where the cations interact strongly with the solvents, e.g. Cu^+ and Ag^+ ions in acetonitrile. These are in agreement with other data that Ag(1) and Cu(1) salts are more soluble in acetonitrile than in water. Smith, Symon, Kasowers and others [26] used the U.V. and the visible spectral data to study the interactions of solvents with cations and anions. The spectral band due to the transition of electrons during the ionization of the various solutes going into solution, have been postulated to arise from the electron going into a centrosymmotric orbit. This transition has been labelled as Charge Transfer To Solvent

(CTTS). The spectral bond has been found to experience shifts due to the following changes in environment:

(i) due to change of solvent,
(ii) due to change of temperature and
(iii) due to change of electrolytes.

Smith and Symons [26] measured the change in the energy wise position of the band maxima in various solvents including ammonia, acetone dioxane and 1,3- dioxalane over a range of temperatures. According to smith and symons, the theory of CTTS would not hold if there is ion-pair formation between cation and anion or complex formation between solute and solvent. Their field of study has therefore encompassed the following:

(i) Proof that there is no complexation or ion-pair formation between acetone and iodides of alkali
(ii) The crystalline state of iodine and iodides in solution are similar
(iii) A model which explains the shifts of the spectral band and the drawbacks of this model.

Buckingham and others [27], studied the infra red spectra of various solutes in a number of solvents and observed mainly that :

(i) The frequency bands of the solutes showed shifts in deferent solvents.
(ii) The half intensity band width increased in various solvents and
(iii) The integrated intensity of the band width increased with certain solvent.

1.6 Structure of liquid water

Physical properties of water indicate that it is an anomalous liquid. Many properties of it differ essentially from the normal liquids of simpler structure [31]. The notable unique physical properties exhibited by liquid water are [32]: i) negative volume of melting, ii) density maximum in the normal liquid range (at 4°C), iii) isothermal compressibility minimum in the normal liquid range at (46°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 and vii) high mobility transport for H^+ and OH^- ions.

Liquid water possesses distinctive structural features which are roughly describable by the statement that it retains a certain degree of similarity or analogy to ice i.e., partial retention of the tetrahedrally directed hydrogen bonding involved in the crystalline structure of ice [33]. In other words, liquid water may be treated as a broken down form of the ice lattice, but with the length of the O----H----O bond increased. This view of water structure is supported strongly by the results of X-ray scattering, infrared and Raman absorption spectra. These study indicates that a considerable degree of short range order and the low co-ordination characteristic of the tetrahedrally bonded structure persist in the liquid [33]. The X-ray scattering studies indicate that the average number of nearest neighbors is 4.4 to 4.6 and that the average distance between centers is 2.92 A°. A high concentration of molecules is also found at 4.75A° 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 [34]. A distinct maximum at 1.1 A° is attributed to the closest O-H distance in the water molecule [34].

Water 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, several different configurations of which can co-exit simultaneously. Most modern theories of water take this view that water is a mixture of certain three dimensional structure [35].

For a very long time the physicist and the chemists have pondered over the possible structural arrangements responsible for unusual properties displayed by liquid water. To understand the solute water interactions, the most fundamental problem in solution chemistry, the knowledge of water structure is a prerequisite. The physico-chemical properties of aqueous solutions, in most of the cases, are interpreted in terms of the structural charges produced by solute molecules. The structural changes in the solvent may be crucial to the study of the role of water in biological system.

The various structural models, developed to describe the properties of water may generally be grouped into two categories, namely, the continuum models and the mixture models. The continuum models [36-37] treat liquid water as uniform dielectric medium where the environment about particular molecules is considered to be the same as about any other molecules, that is, behavior of all the molecules are equivalent. On the other hand, the mixture models [38-40], treat water as a mixture of short lived clusters consisting of highly hydrogen bonded molecules and non-hydrogen bonded monomers located in various interstices.

Nemethy and Scheraga [36] using statistical methods attempted to build up a molecular description of water, aqueous solutions of a polar solutes and proteins. The development of sophisticated Computing techniques has also widened the scope of this study and attempts have been made to study water-water interactions by ab-initio quantum mechanical methods [36]. Despite numerous endeavours, none of the proposed models on water structure has been unequivocally accepted. Different models although contradictory in some respect [41] can successfully explain several distinctive features of liquid water. Some author prefers continuum models, while other consider mixture models more effective for explaining the behavior of water and aqueous solutions. The mixture models are at present more favored than the continuum models.

Among the mixture models, the 'flickering Cluster" model of Frank and Wen [42], later developed by Nemethy and Schera [36], is commonly adopted in solution chemistry. Properties of dilute aqueous solutions, in terms of structural changes brought about by the solutes, can be explained more satisfactorily using this model than any other model. According to this model, the tetrahedrally hydrogen bonded clusters, referred to as bulky water, $(H_2O)_b$, are in dynamic equilibrium with the monomers, referred to as dense water, $(H_2O)_d$, as represented by [42]:

$$(H_2O)_b \rightleftharpoons (H_2O)_d$$

It is postulated [42] that the formation of hydrogen bonds in water is a co-operative phenomenon, so that, when one bond forms several other also come into existence and when one breaks whole cluster will be dissolved. This produces short lived clusters surrounded by non-hydrogen bonded monomers.

The properties of solution can be accounted for in terms of solvent-solvent, solvent-solute and solute-solute interactions. In terms of thermodynamics, the concentration dependence of a given property extra 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) **hydrophobic 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 and

(iii) **hydrophobic hydration**: where there is no direct molecular interactions, rather a restructuring of water molecules around the solute. This is observed in solutions of essentially apolar molecules such as long chain alcohols and long chain fatty acid salts.

The structure of water is profoundly influenced by the presence of solute molecules. The introduction of a solute produces changes in the properties of the liquid water, which are analogous to those brought about by temperature or pressure changes. It is generally agreed that in aqueous solutions of ions not larger than Cs^+ and I^-, the nearest neighbors water molecules are always immobilized by the direct ion-dipole interaction. This idea and related one of electrostriction have been invoked to explain the small or negative values of solute partial molal volumes, heat capacities, compressiblities etc. This idea also explains the influence or Li^+ on the viscosity of water in which it is dissolved. However, the more fluidity of 0.1m solution of CsCl than pure water demonstrates that the idea can't explain all the physico-chemical behavior of aqueous solutions. This phenomenon is interpreted by Bernal and Flower [43] that the ions were somehow breaking the water structure. On the basis of the comparison of results obtained from reanalysis of entropy of hydration by Frank and Evans [44] 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 [42] suggested a model, sketched in Figure-1.1 which shows that an ion surrounded by three concentric regions.

The innermost region (A), called the primary solvation sheath, consists of ordered co-ordinate water molecules, is immobilized by the strong ion-dipole interactions. In outermost region (C) water molecules have a normal liquid structure. The water molecules in the intermediate region (B) is more random in organization than normal water due to an approximate balance between the dielectric field of the central ion and the orienting influence of neighboring water molecules.

The solute that shifts the equilibrium to the left and increases the average life of the clusters, is termed as, "structure maker" and one which shifts the equilibrium to the right and increases the numbers of non-bonded dense monomers is called as "structure breaker". The cause of the structure breaking and making is presumably the shift in balance in the region (B) between two competing orienting influences. The low charge density has relatively weak electrostatic fields so that the region (A) is very small thereby causing a net breaks of 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 the solvent molecules are interacting, as indeed they must, then the chemistry of the solute in a solvent must be different and the presence of a solvent can modify the properties of a solute. There are several experimental procedures, which can in principle be used to obtain information on the solvation of molecules. The experimental result on various macroscopic properties provides useful information for proper understanding of specific interactions between the components and the structure of the solution. The thermodynamic and transport properties are sensitive to the solute-solvent, solute-solute and solvent-solvent interactions. In solution systems these three types of interaction are possible but solute-solute interactions are negligible at dilute solutions. The concentration dependencies of the thermodynamic properties are a measure of solute-solute interaction and in the limit of infinite dilution these parameters serve as a measure of solute-solvent 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 on solute-solvent interactions.

Many workers reported and discussed the role of water structure in water electrolyte interactions 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 to any marked extent the hydrogen bond interactions that exist in bulk water. Such ions would be classified as structure breakers, whereas the former type would be structure makers. It must, however, be borne in mind that the structure, which such ions enforce, is not the water structure characteristic of the radial distribution function, which reflects the tetrahedral hydrogen bonding pattern in water. Rather, it is a structure imposed on the water by strong ion-dipole forces. The structure in liquid produces spherically symmetric orientations of water molecules, quite incompatible with the tetrahedrally hydrogen bonded network in unperturbed water. Whereas one, two or possible 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 effect and hydrogen bnnding between water molecqles become equal and this must lead to a structural mismatch where the water molecules are structurally and dynamically highly perturbed.

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 nmr and dielectric methods. Thus in pure water at 25°C the life time Of the water molecule at a given site is 1 ps. [45] The life time of a water molecule in the hydration shells of Mn^{2+} is 25000 ps, whereas in the hydration shell of an I^- it is only marginally affected (4 ps). [45] Intermediate values have been estimated for the hydration shells of other ions, for instance Na^+ (10 ps) and Cl^- (5 ps). The diffusion 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 is observed for structure making ions, where the rotational diffusion is retarded. [45]

From such dynamic data it is also possible to estimate the approximate height of the energy barrier for rotation of water, relative to the energy barrier in pure water [35] such as for

0.54, Cl^- 0.96, F^-, Na^+ and Li^+ 2.0

In the recent past, thermodynamic studies on a number of non-polar or polar solutes with non polar side chains have been undertaken to apprehend the so called "hydrophobic effect". [46-48] Cabani [49] has critically reviewed such studies in aqueous solutions of non-electrolytes. Physico-chemical behavior of amino acids and peptides in aqueous solutions were systematically reviewed by Greenstein and Winitz [50], Lilley [51], Zamyatnim. [52] Wadi and Natarajan [53] and Ahluwalia [54] 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.

The foregoing discussions of ions in solution has established that long range (low concentration) properties can be adequately accounted for by electrostatics, taking into account only the magnitude of the ionic charge, the concentration and the dielectric permittivity of the solvent medium. This formalism breaks down at short range properties (high concentration) where specific ion-solvent effects dominate the solution behavior. This distinction is of particular importance in bio-chemistry, where, it is often found that the effects of electrolytes on certain processes are nonspecific up to the concentrations of about 0.1 molal and can be expressed in terms of the ionic strength.

Friedman and Krishnan [55] have suggested a model for ionic solutions based on the concepts of Frank and Evans [44] which enables to interpret the physico-chemical properties of solutions. It is assumed that around an ion there is a cosphere in which the solvent properties are affected by the solutes, characterized by thermodynamics of the process:

$$\text{n[solvent (bulk)]} \longrightarrow \text{n[solvent (cosphere)]}$$

Where, n is the number of solvent molecules in the cosphere. Even though it is necessary to consider the changes affecting the whole of the solvent, it can be assumed that significant effects come only from the solvent molecules directly attached to the solute particles. When two solute particles come close together for their cospheres to overlap 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 behavior represented a mutual constructive interaction as the cosphere comes close together. In this the solvent gets transferred to the cospheres from the bulk.

All these critical review of literatures show that a lot of works have been carried one viscometric, volumetric and thermodynamic properties of both aqueous and non-aqueous solution of different substances. But most of these works deal with binary system, either in aqueous or in non-aqueous system. Only a very few work appeared in the literature on ternary system containing both aqueous and non-aqueous substance a mixed solvent. As a result a series of properties of aqueous and non-aqueous solution still remains unknown. As for example, the structure of water which can explain its versatile behavior is still unknown to the scientist. Many models have been proposed but none of these can clearly and completely explain all the properties of water. These above stated facts lead us to carry out this study.

Theoretical Background

2.1 Physical Properties and chemical constitutions

In interpreting the composition, the structure of molecules and the molecular interaction in the binary and ternary systems, it is inevitable to find out the size and the shape of the molecules and the geometry of the arrangement of their constituent atoms. For this Purpose, it is indispensable to study the typical physical properties, such as absorption or emission of radiations, refractivity, light scattering, electrical polarization, magnetic susceptibility, optical rotations etc. The measurement of bulk properties like density, viscosity etc. are also important.

The various physical properties based upon the measurement of density, viscosity, surface tension, refractive index, dielectric constant etc, have been found to fall into the following four categories [56].

(i) **Purely additive properties:** An additive property is one, which for a given system, is the sum of the corresponding properties of the constituents. The only strictly additive property is mass, for the mass of a molecule is exactly equal to the sum of the masses of its constituent atoms, and similarly the mass of a mixture is the sum of the separate masses of the constituent parts. There are other molecular properties like molar volume, radioactivity etc. are large additive in nature.

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

- **(iii)** **Constitutive and additive properties:** These are additive properties, but the additive character is modified by the way in which the atom or Constituent parts of a system are linked together. Thus, atomic volume of oxygen in hydroxyl group (-OH) is 7.8 while in ketonic group (=CO). it is I2.2 The parachor, molar refraction, molecular viscosity etc. are the other example of this type.
- **(iv)** **Colligative properties:** A colligative property is one which depends primarily on the number of molecules concerned and not on their nature and magnitude. These properties are chiefly encountered in the study of dilute solutions. Lowering of vapor pressure of, elevation of boiling point, depression of freezing point and osmotic pressure of dilute solutions on the addition of non-volatile solute molecules are such properties.

2.2 Density and temperature

The density of a liquid is defined as the mass of a unit volume of the liquid. The generally accepted unit of volume is the milliliter (mL) which is defined as the volume occupied by 1g of water at the temperature of its maximum density (4°C). An increase in temperature of a liquid slightly increases 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 fly 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 the density.

2.3 Molarity and Molality

Molarity (C), is defined as the number of moles of solute per litre of solution. If n_2 is number of moles of solute and V liters is the volume of the solution then.

$$Molarity(\mathrm{C}) = \frac{\text{Number of moles of solute}}{\text{Volume of solution}}$$

$$\text{or } C = \frac{n_2}{V} \text{ --(2.1)}$$

For one mole of solute dissolved in one liter of solution, C=l i.e. molarity is one. Such a solution is called 1 molar. A solution containing two moles of solute in one liter is 2 molar and so on. As evident from expression (2.1), unit of molarity is mol liter^{-1}.

The molality (m) of a solution is refined as the number of moles of the solute per 1000 g of solvent. Mathematically,

$$Molality(\mathrm{m}) = \frac{\text{Number of moles of solute}}{\text{weight of solvent in gram}} \times 1000$$

$$\text{or,}\ \mathrm{m} = \frac{\frac{\mathrm{a}}{\mathrm{M_2}} \times 1000}{\text{Volume of solvent in mL.} \times \text{density of solvent in g cm}^{-3}}$$

$$\text{or,}\ \mathrm{m} = \frac{\frac{\mathrm{a}}{\mathrm{M_2}} \times 1000}{\mathrm{V_1} \times \rho_0}$$

$$\text{or,}\ \mathrm{m} = \frac{\mathrm{a}}{\mathrm{M_2}} \times \frac{1000}{\mathrm{V_1} \times \rho_0} \text{-----------} (2.2)$$

Where, a = weight of solute in gram.
M_2 = molecular weight of solute in gram.
V_1 = volume of solvent in mL,
ρ_0 = density of solvent in g cm^{-3}.

2.4 Molar volume of solutions

The volume in mL occupied by one gram of any substance is called its specific volume and the volume occupied by 1 mole is called the molar volume of the substance. Therefore, if ρ is the density and M be the molar mass, we have

$$\text{specific volume, (V)} = \frac{1}{\rho} mLg^{-1} \text{-----------} (2.3)$$

$$\text{and molar volume, } (\mathrm{V_m}) = \frac{M}{\rho} mLmol^{-1} \text{-----------} (2.4)$$

when two components are mixed together, there may be either a positive or a negative deviation in volume. The positive deviation in volume i.e. volume expansion has 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 has been thought of by many observers, as arising from the i) compound formation through association. ii) decrease in the intermolecular distance between the interacting molecules, iii) interstitial accommodation of smaller species in the structural network of the larger species and (iv) change in the bulk structure of either of the substance forming the mixture.

2.5 Apparent molal volume

The apparent molal volume of a solute in solution, generally denoted by is defined by φ_v the relation [58]

$$\varphi_v = \frac{V - n\overline{V}_1^0}{n_2} \text{-----}(2.5)$$

where, V is the volume of solution containing n_1 moles of solvent and n_2 moles of solute and $\overline{V}_1^0$ is the molal volume of the pure solvent at specified temperature and pressure. For binary solution, the apparent molal volume (φ_v) of an electrolyte in an aqueous solution is given by [55],

$$\varphi_v = \frac{1}{n_2}\left[\frac{n_1M_1 + n_2M_2}{\rho} - n_1\overline{V}_1^0\right] \text{-----}(2.6)$$

where, $V = \frac{n_1M_1 + n_2M_2}{\rho}$ and

n_1 and n_2 are the number of moles, M_1 and M_2 are molar masses of the solvent and solute respectively and ρ is the density of the solution. For molal concentration, $n_2 = m$, the molality and $n_1 = 55.51$, the number of moles of solvent in 1000g of solvent (water), the equation for apparent molal volume takes the form [55, 59],

$$\varphi_v = \frac{1}{m}\left[\frac{1000 + mM_2}{\rho} - \frac{1000}{\rho_0}\right]$$

$$\text{or, } \varphi_v = \left[\frac{M_2}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0}\right] \text{-----}(2.7)$$

$$\text{or, } \varphi_v = \frac{1}{\rho}\left[M_2 - \frac{1000}{m}\left(\frac{W - W_0}{W_0 - W_e}\right)\right] \text{-----}(2.8)$$

where, ρ_o and ρ are the densities of the solvent and solution and W_e, W_0 and W are the weight of empty pycnometer, weight of pycnometer with solvent and weight of pycnometer with solution respectively.

If the concentration is expressed in molarity (C), the equation (2.8) takes the form [60]:

$$\varphi_v = \left[\frac{M_2}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0}\right] \text{---(2.9)}$$

where, the relation, $C = \dfrac{m.\varphi_v.1000}{1000 + \varphi_v.m.\rho_0}$ ---(2.10)

is used for interconversion of the concentration in the two scales [60].

The concentration dependence of the apparent molal volume of electrolytes have been described by the Masson equation [63], the Redlich-Mayer equation [60] and Owen-Brinkley equation [61]. Masson [63] found that the apparent molal volume of the electrolytes vary with the square root of the molar concentration as,

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \text{---(2.22)}$$

where, S_v is the experimental slope depending on the nature of the electrolyte.

Redlich and Rosenfeld [64] predicated that a constant limiting slove S_v, should be obtained for a given electrolyte charge type if the Debye-Huckel limiting law is obeyed. By differentiating the Debye-Huckel limiting law for activity coefficients with respect to pressure, the theoretical limiting law slope S_v, could be calculated using the equation,

$$S_v = KW^{3/2} \text{---(2.23)}$$

where, the terms K and W are given by

$$K = N^2e^3\left(\frac{8\pi}{100D^3RT}\right)^{1/2}\left\{\left(\frac{\delta \ln D}{\delta\rho}\right) - \left(\frac{\beta}{3}\right)\right\} \text{---(2.24)}$$

and $W = 0.5\sum \gamma_i Z_i^2$ ---(2.25) where, β is the compressibility of the solvent, γ_i is the number of ions of the species i of valency Z_i formed by one molecule of the electrolyte and the other symbols have their usual significance [64]. For dilute solutions the limiting law for the concentration dependence of the apparent molal volume of electrolytes is given by the equation,

$$\varphi_v = \varphi_v^0 + KW^{3/2}\sqrt{C} \text{ --(2.26)}$$

and for not too low concentrations, the concentration dependence can be represented as,

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} + b_v C \text{ --(2.27)}$$

where, S_v, is the theoretical limiting law slope and b_v an empirical constant for 1:1 electrolyte, the limiting law slope at 298.15K is 1.868 cm^3. $mol^{-3/2}.L^{1/2}$.

2.5 Viscosity

Viscosity means viscous ability. It's more generalized definition is "the internal friction which opposes the relative motion of adjacent layers of a fluid." When a fluid is flowing through a cylindrical tube, layers just touching the sides of the tubes are stationary and velocities of the adjacent layers increases towards the centre of the tube, the layer in the centre of the tube having the maximum velocity. There thus exists a velocity gradient.

In case of liquid, this internal friction arises because of intermolecular fraction. Molecules is a slower moving layer try to decrease the velocity of the molecules in a faster moving layer and vice versa, with a result that some tangential force is required to maintain uniform flow. This tangential force f will depend upon two factors,

(i) area of contact 'A' between the two layers and

(ii) velocity gradient $\frac{dv}{dx}$

$$\text{Thus, } f \infty\ A\ \frac{dv}{dx}$$

$$\text{or} \quad f = \eta\ A\ \frac{dv}{dx} \text{ --(2.28)}$$

where, η is a proportionality constant, known as the coefficient of viscosity or simply viscosity of the liquid. Thus, the coefficient of viscosity may be defined as the force per unit area required to maintain unit difference in velocity between two parallel layers of liquid unit distance apart.

The reciprocal of viscosity called the fluidity (ϕ) is given by the relation.

$$\phi = \frac{1}{\eta} \text{------------------------------------(2.29)}$$

It is measure of the case with which a liquid can flow.

The C.G.S Unit of viscosity i.e. dynes sec cm^{-2} = g $cm^{-1}sec^{-1}$ is called poise, in honor of J.L.M. Poiseuille who is the pioneer in the study of viscosity. Since viscosity of liquid is usually very small, it is usually expressed in millipoise (mP) or centipoise (cP).

When a liquid flows through a narrow tube it is probable that the thin layer of liquid in contact with the wall is stationary; as a result of viscosity, therefore, the next layer will be slowed down to some extent, and this effect will continue upto the centre of the tube where the flow rate is maximum.

The rate of flow of the liquid, under a given pressure will obviously be less, the smaller the radius of the tube, and the connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation [62]. If a liquid with a coefficient of viscosity (η) flows with a uniform velocity, at a rate of V cm^3 in t seconds through a narrow tube of radius r cm, and length 1 cm under a driving pressure of p dynes cm^{-2} then [62]:

$$\eta = \frac{\pi \mathrm{Pr}^4 t}{8lv} \text{------------------------------------(2.30)}$$

This equation known as Poiseuille's equation, holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities. A small error arises in practice, because the liquid emerging from a capillary tube possesses appreciable kinetic energy and since this is not accounted for in Poiseuille's equation, a correction term is introduced. After correction for kinetic energy, the equation becomes,

$$\eta = \frac{\pi \mathrm{Pr}^4 t}{8lv} - \frac{\rho V}{8\pi lt} \text{ ----------(2.31)}$$

where, ρ represents the density of the liquid/solution. However, in practical purposes, the correction factor is generally ignored.

The driving pressure P=hg, where h is the difference in height of the surface of the two reservoirs, since the external pressure is the same at the surface of both reservoirs, g = acceleration due to gravity and = the density of liquid. Thus the equation (2.30) becomes,

$$\eta = \frac{\pi h \rho g r^4 t}{8vl} \text{ ----------(2.32)}$$

For a particular viscometer h, l, r and V are fixed, so the equation (2.32) becomes,

$$\eta = A\rho t \text{ ----------(2.33)}$$

where $A = \frac{\pi h g r^4}{8vl}$, called the calibration constant of the viscometer used. For flow of water, therefore,

$$\eta_{H_2O} = A\rho_{H_2O} t_{H_2O} \text{ ----------(2.34)}$$

$$\text{or, } A = \frac{\eta_{H_2O}}{\rho_{H_2O} t_{H_2O}} \text{ ----------(2.35)}$$

knowing the value of η_{H_2O} and ρ_{H_2O} at the experimental temperature and measuring the time of flow for water, the calibration constant A for a particular viscometer can be determined. Putting the value of and of the experimental liquid/solution and the value of viscometer constant A in equation (2.33), the coefficient of viscosity can be obtained for a liquid at a definite temperature.

2.6 Viscosity Coefficients A and B

The viscosity of a solution relative to that of the pure solvent is called relative viscosity which is a measure of the change of the viscosity of the pure solvent due to the addition of solute to the solvent. Attempts had been made to describe the variation of viscosity with solute concentration. Einstein [65] deduced from the classical principles of hydrodynamics that if the solute were composed of spherical incompressible uncharged particles, larger in comparison with the water molecules, then the viscosity of the solution could be expressed as:

$$\eta = \eta_0(1 + 2.5\theta) \text{--}(2.36)$$

where, θ denotes the volume fraction of the solute particles and η_0 is the viscosity of the solvent. This equation is proved to be valid only at low concentrations. Later, Falkenhagen and Dole [66] attacked the problem of the viscosity of electrolyte solutions and proposed that the electrical forces between ions in the solution tend to establish and maintain a preferred rearrangement and thus to 'stiffen' the solution i.e. increases its viscosity. The mathematical treatment of this effect resulted in the following limiting law for very low concentrations of electrolytes (0.01M) as,

$$\frac{\eta}{\eta_0} = \eta_{rel} = 1 + A\sqrt{C} \text{---}(2.37)$$

where, the always positives constant A is a function of solvent properties, ionic charges, mobilities and temperature. The Falkenhagen equation was of little use in calculating viscosities since the square root term is swamped by a much larger linear term expressed in the empirical equation of Jone and Dole [67] as follows,

$$\eta_{rel} = 1 + A\sqrt{C} + BC \text{--}(2.38)$$

where, A is again Falkenhagen theoretical coefficient while the empirical parameter B represents ion-solvent interaction.

The concentration dependence of viscosity of electrolytes in aqueous solutions are found to follow the Jones-Dole [67] equation up to 0.1M concentration [68].

In the concentrated solution region (up to 10M), several features of the viscosity of electrolyte solutions have been noted. For some salts a plot of the viscosity vs, the molality at fixed temperature fields a roughly exponentially increasing function. However, for other salts a pronounced minimum occurs. These latter salts fall into the category of structure breakers.

The effect of concentration on the viscosity of salt solutions in the more concentrates region and at fixed temperature, has been approached empirically in various V. J. Vand [69] extended Einstein's limiting theory to higher concentration giving.

$$\ln \eta_{rel} = \frac{2.5\theta}{1-Q\theta} \text{--} (2.39)$$

where, θ is proposed to be an interaction parameter dealing with the mutual interference between the spheres. Suryanarayna and Venkatesan [57] have observed that equation.

$$\eta_p = A'' \exp(B'' C_p) \text{--} (2.40)$$

adequately describes the variation of electrolyte viscosity throughout the high concentration range. Here η_p represents the ratio of the viscosity of the solution at a given concentration relative to that at saturation at the same temperature and C_p the ratio of the mole fraction of the solute at given concentration to that at saturation at the same temperature, A″ and B″ are experimentally determined constants.

Experimental

3.1 General Techniques

During the course of the present work a number of techniques were involved which were in general standard ones. Constant efforts for attaining the ideal conditions for the experiments were always attempted.

The thoroughly cleaned glass pieces were dried in electric oven. The smaller pieces of apparatus were dried in electric oven and stored in a desiccator, while larger pieces of apparatus were used directly from the oven.

Ostwald viscometer of British standard institution form was used for measurement of viscosity. The inside wall of the viscometer was cleaned thoroughly with warm chromic acid so that there was no obstruction in the capillary and the liquid could run clearly without leaving any drop behind. It was then rinsed thoroughly with distilled water followed by rectified spirit and finally with acetone and dried.

3.2 Analytical Techniques

3.3 Preparation and Purification of Reagents

High quality commercial reagents were employed in all the experiments, where necessary further purifications were done.

(i) Distillation of water

Water was purified by a quick-fit glass made distillation apparatus. About 1.5 L water was taken in a round bottom flux of which the capacity was 2 L. Then it was distilled in presence of $KMnO_4$. Distilled water was collected at only 100°C. Other liquids of which the temperatures were below and above the mentioned boiling point were discarded. In all the experiments double distilled water was used.

(ii) Purification of DMSO

DMSO was purified by a quick-fit glass made distillation apparatus. About 1.5 L DMSO was taken in a round bottom flux of which the capacity was 2 L. Distilled DMSO was received at its boiling point, 189°C. Other liquids of which the temperatures were below and above the mentioned boiling point were discarded.

(iii) Chemicals

Analytical grade chemicals viz., Ammonium Chloride (E-Merck, India), Nickel Chloride (E-Merck, Germany), Iron (III) Chloride (E-Merck, Germany) were used as received.

3.4 Density measurements

The densities of the solutions were determined by weighing a definite volume of the solution in a pycnometer at specified temperature. The volumes were obtained by measuring the weight of water at that temperature and using the density of water from literature. The density of solution was determined from the relation.

$$\rho = \frac{w - w_e}{v_0} \text{ --} (3.1)$$

where, ρ = density of the solution, w = weight of pycnometer with solution, w_e = weight of empty pycnometer, v_0 = volume of pycnometer.

The pycnometer was first thoroughly cleaned with warm chromic acid and then with enough distilled water. Then it was rinsed with acetone and finally dried at $85^{O}C$ for more than two hours. The weight of the dried empty pycnometer was noted after proper cooling. The pycnometer was calibrated at experimental temperature with doubly distilled water.

The solution under investigation was taken in a pycnometer upto the mark. The pycnometer was clamped carefully with stand in the thermostatic water bath maintained at the desired temperature. As the solution started to gain the temperature of the bath excess liquid overflowed through the capillary. Then it was allowed to keep in the bath for about 30 minutes to attain the thermal equilibrium. When no overflowed observed through the capillary the pycnometer was taken out from the thermostatic water bath, wiped with tissue-paper, dried and weighed in the analytical balance. The difference between the two weights (weight with solution and without solution) gave the weight of the solution in the pycnometer. The density measurement was performed for each of the solutions at the temperature 288, 293, 298, 303, 308 and 313K respectively in this way using equation (3.1).

3.5 Apparent molal volume measurements

The apparent molal volumes of the electrolyte for binary and ternary systems were determined from density measurement using the following equation. [55, 58]

$$\varphi_v = \frac{1}{\rho}\left\{M_2 - \frac{1000}{m}\left(\frac{\rho-\rho_0}{\rho_0}\right)\right\} \text{-----}(3.2)$$

where, ρ is the density of the experimental solution, M_2 and m are the molar mass and molality of the electrolytes respectively and ρ_0 is the density of the solvent. The molality 'm' of a solution were calculated from molarity 'C' using the equation.

$$m = \frac{1}{\left(\frac{\rho}{C} - \left(\frac{M_2}{1000}\right)\right)} \text{-----}(3.3)$$

where, C is the molarity, M_2 is the solute molecular weight and ρ is the density of the solution respectively.

The molarity 'C' of a solution was calculated from the following equation:

$$C = \frac{1}{M_2} \times \frac{a}{\text{vol. of solution in liter}} \text{-----}(3.4)$$

where, a = weight of the solute (electrolyte) in gm, M_2 = solute molecular weight.

Molal volume of solvent (pure water) at experimental temperature was calculated using the following equation [58].

$$\overline{V}_1^0 = \frac{\text{Molecular masses of solvent}}{\text{Density of solvent (at expl. temp.)}} \text{-----}(3.7)$$

The values of $\frac{d\varphi_v}{d\sqrt{m}}$ were obtained from the slope of the plot of φ_v against $\sqrt{m}$ by the use of Masson [63] equation and the apparent molal volume of electrolytes at infinite dilution ($\varphi_v^0 \approx \overline{V}_2^{\,0}$) were determined from the intercept of the plot, at m equal to zero.

3.6 Viscosity measurements

An open system was devised for the viscometric system. Viscosity of water, DMSO and several electrolyte solutions were measured by using the British standard Ostwald U-type viscometer. The interior of the viscometer was cleaned thoroughly with warm chromic acid and then with distilled water, so that there was no obstruction in the capillary and the liquid could run freely without leaving any drop behind. It was then rinsed with acetone and dried in and oven at about 75$^{\mathrm{O}}$C. The viscometer was then clamped vertically in the thermostatic water bath such that the upper mark of the top bulb was well below the water level. 20mL of doubly distilled water was poured into the viscometer. Then it was allowed to keep in the thermostatic bath for about 30 minutes to attain the bath temperature. With the help of a clean rubber tube attached to the narrower limb of the viscometer, the water was sucked up above the upper mark of the bulb. The water of bulb was then allowed to fall into the capillary and the time of fall between the two marks was noted with the help of stop-watch capable of reading up to 0.01 second. The reading at each temperature was repeated three or four times, in order to check the reproducibility of the flow time, the temperature being maintained at the same value. Since the accurate viscosity and density of water at different temperatures are known (from literature) calibration constant A of the viscometer for different temperature were obtained by using equation (1.35),

$$A = \frac{\eta_{H_{20}}}{\rho_{H_{20}} . t_{H_{20}}} \text{ --(3.8)}$$

Putting the values of the calibration constant, density and time of flow of the experimental solution, the viscosity of that solution was determined by using the equation (1.35).

$$\eta = A\rho t \text{ --(3.9)}$$

3.7 Coefficient A and B determinations

The coefficients A and B for the electrolyte solutions were calculated using the empirical equations of Jones-Dole [67]:

$$\eta_r = 1 + A\sqrt{C} + BC$$

$$\text{or, } \frac{\eta_r - 1}{\sqrt{C}} = A + B\sqrt{C} \text{ -- } (3.10)$$

where, η_r is the relative viscosity = $\frac{\text{Viscosity of solution}}{\text{Viscosity of solvent}}$

and C is the molar concentration.

The values of the coefficients A and B were obtained from the intercept and slope of the plot $\frac{\eta_r - 1}{\sqrt{C}}$ against $\sqrt{C}$ respectively.

Results and Discussion

The volumetric, viscometric and some other related properties of DMSO in aqueous solutions and some electrolytes such as NH_4Cl, $NiCl_2$ and $FeCl_3$ in water, DMSO and mixed solvents have been measured. The properties have been discussed in terms of water structure.

4.1 Volumetric properties of electrolyte solutions

Densities of NH_4Cl, $NiCl_2$ and $FeCl_3$ in aqueous and aqueous DMSO solutions were measured at 288, 293, 298, 303, 308 and 313 K respectively. The densities, ρ of the binary and ternary systems have been shown in Table 4.1-4.15 at different temperatures. The representative curves (Density vs molality) for all the electrolyte systems are linear in both the solvent systems (shown in Figure 4.1-4.15). The values of ρ increase with the increasing molality of the electrolytes. In pure state the density of the electrolytes has been found to be in the order of,

$$NH_4Cl < NiCl_2 \approx FeCl_3$$

The apparent molal volume (φ_v) of different electrolytes in aqueous and aqueous DMSO solutions have been determined from density data. The apparent molal volume (φ_v) data were tabulated in tables 4.1-4.15, respectively. The composition ranges for all the studied systems were same. The concentration dependence of φ_v of the chosen electrolytes in aqueous and aqueous DMSO solutions at different temperatures were shown in Figure 4.16-4.30, respectively. It appears from the figure that apparent molal volume is dependent upon the electrolyte concentration as well as on the temperature. Plot of φ_v shows gradual decrease of volume with concentration except $FeCl_3$ in water and in pure DMSO solutions (shown in Figure 4.26-4.27)

The limiting apparent molal volume (φ_v^o) which is also the partial molal volume of the electrolytes in aqueous and aqueous DMSO solutions at 288, 293, 298, 303, 308 and 313 K respectively are reported in table 4.1-4.15. The φ_v^o values of the electrolytes reflect the true volume of the solute and the volume change arising from the solute-solvent interactions. The change in the limiting apparent molal volume (φ_v^o) of the electrolytes can be explained by change in the limiting apparent molal volume (φ_v^o) of the electrolytes can be explained by considering of the charge and size of the cations and anions of the electrolytes in aqueous and in aqueous DMSO solutions. The salt NH_4Cl, $NiCl_2$ and $FeCl_3$ contains mono-, di- and trivalent dissimilar cations having same anion. The crystallographic radius of NH_4^+, Ni^{2+} and Fe^{3+} are 1.43A°, 0.72A° and 0.64A° respectively. The variation of φ_v^o in these cases, therefore, may be due to the difference in ionic radii, charge density and ion-solvent interactions respectively.

The limiting apparent molal volume φ_v^o for all the three electrolytes studied show higher values in aqueous DMSO solution than those in aqueous solution. The variation of φ_v^o with molality of DMSO can be rationalized in terms of cosphere overlap model. According to this model, the overlap of the cospheres of two similar ions or polar groups and an ion with that of a hydrophilic group, always produces positive volume change. On the other hand, the overlap of the cospheres of an ion with that of a hydrophobic groups result in a negative change. In the present ternary systems, the overlap of cospheres of DMSO-DMSO and DMSO-hydrophilic groups of Zwitterions interactions take place. The overlap of cospheres of DMSO gives positive change in volume due to the relaxation of the electrostricted water molecules from its cosphere to the bulk. The overlap of the cospheres of DMSO with those of hydrophilic groups of salts results positive changes in volume.

The positive volume change due to the overlap of the cospheres of DMSO with those of the hydrophilic groups of salts outweighs the negative volume change due to the overlap of cospheres of DMSO and hydrophobic groups of salts (negligible) giving greater φ_v^o value in DMSO, compared to that in water.

The water-water and water-DMSO interactions are assumed to be the same and do not produce considerable change in volume. An increase in the DMSO concentration increases the ion-zwitterions and also the DMSO-DMSO interaction giving rise to an increased φ_v^o value. This accounts for the increase in φ_v^o value with the increase in DMSO concentration.

The transfer volume $\varphi_{v,tr}^{o}$ is given by the equation

$$\varphi_{v,tr}^{o} = V_{DS}+V_{DD}-V_{DW}-V_{SW} \text{--} (4.1)$$

Where V_{DS} ,V_{DD}, V_{DW}, and V_{SW} are the contribution from DMSO-salt, DMSO-DMSO, DMSO –water and salt –water interactions respectively. Addition of DMSO increases contribution due to V_{DS} and V_{DD}, but decreases V_{DW} and V_{SW}, thereby overall increasing $\varphi_{v,tr}^{o}$ with the addition of DMSO. The increase of φ_{v}^{o} with increase in temperature in all cases is expected to be due to the following effects:

- i) due to increased thermal energy at higher temperature , the relaxation to the bulk of the electrostricted water molecules from the interaction regions of SO^{-} ...M^{+} results in a positive volume change.
- ii) An increase in temperature renders the salt-salt interactions relatively weaker giving rise to a small negative volume change,
- iii) A decrease in salt-water interactions causes a positive volume change and
- iv) The water-water interactions decrease with the increase in temperature giving a very small negative change in volume.

For $FeCl_3$, the φ_v increases, initially and then almost unchanged with the square root of molality in aqueous and in DMSO solutions. This is most probably due to strong solute – solute interactions at higher concentration of DMSO where the orientations of the polar groups are restricted.

4.2 Viscometric properties of electrolyte solutions

Viscosities in aqueous and in aqueous DMSO solutions of NH_4Cl, $NiCl_2$ and $FeCl_3$ have been determined at 288, 293, 298, 303, 308 and 313 K respectively. The relevant data were shown in table 4.16-4.30 and the results were represented graphically in figures 4.31-4.45 respectively. The representative curves (viscosity vs molality) for all the electrolytes systems are linear in both the solvent systems. The value of η increases with the increase in molality of the electrolytes except NH_4Cl. No significant changes of η observed for NH_4Cl with the increase in molality in aqueous and in 20% aqueous –DMSO solution (figure 4.31, 4.35). The viscosity η for all the studied electrolytes are greater in aqueous DMSO solvent system than those in water system alone indicating that electrolyte in aqueous DMSO systems are more structural than those in aqueous system. Viscosity of all the studying electrolytes increases for any particular composition and at a particular temperature in the following order:

$$NH_4Cl < NiCl_2 \approx FeCl_3$$

The sequence can be explained by the viscosity B coefficient data. The viscosity coefficient B for the chosen electrolytes in aqueous and in aqueous DMSO solutions at 288, 293, 298, 303, 308 and 313 K are shown in table 4.16-4.30. From the table it is seen that the B-coefficient for electrolytes $NiCl_2$ and $FeCl_3$ in aqueous and in aqueous DMSO solutions at all the temperatures are positive. Usually the positive value of the coefficient B corresponds to the structure making behavior of solutes. As the molecular mass of the salt is relatively large, it may show an obstructive effect, which causes bending of the streamlines around a large solute particle. In such case B coefficient will always positive irrespective of how it interact with the solvent. The negative value of the B coefficient corresponds to the structure breaking behavior of solutes. The B coefficient values of the above electrolytes in aqueous solutions are based on the fact that there exists around an ion, a region of modified solvent differing from the bulk in structure and in properties. Gurney's cosphere, Frank and Wens A, B and C zones (shown in the introduction chapter) and Nightinagle's hydrated radius are recent reflection of this idea. From the above approaches Kaminsky indicated that the observed viscosity changes result from competition between various effects occurring in the neighborhood ion. The viscosity of a dilute electrolyte solutions to that of the solvent plus the contributions from four other sources can be equated in the following manner:

$$\eta-\eta_o= \eta^*+\eta^E+\eta^A+\eta^D \text{--} (4.2)$$

where, η^* is the positive increment in the viscosity caused by coulombic interactions ,η^E is the viscosity increment arising from the size and shape of an ion which is closely related to the Einstein effect. It is always positive and normally increases with the increasing ion size, η^A is the increment due to the alignment or orientation of polar molecules by the ionic field. Since the freedom of movement of these molecules is restricted this generally results in stiffening of the solution and the increment will again be positive, η^D is the viscosity change associated with distortion of the solvent structure leading to greater fluidity. This distortion can be thought of as due to competing forces from the solvent structure in the bulk and from the ionic field and /or the oriented molecules associated with the ion. In mixed solvents the η^D is of considerable magnitude due to significant distortion in the solvent molecules present in the vicinity of ionic field.

Substituting equation (2) into the following Jone-Dole equation one obtains,

$$\eta-\eta_o=\eta_o\,(A\sqrt{C}+BC)$$

Or $$\eta^*+\eta^E+\eta^A+\eta^D=\eta_o\,(A\sqrt{C}+BC)\text{---}(4.3)$$

Eliminating the contributions due to the ionic interaction from both sides we have,

$$\eta^E+\eta^A+\eta^D = \eta_o BC \text{ --}(4.4)$$

Thus at a given concentration (C), the coefficient B can be interpreted in terms of a competition between these specialized viscosity effects.

Small and highly charged cations Ni^{2+} and Fe^{3+} strongly orient water molecules and in fact are believed to have a primary sheath of firmly attached molecules which moves with them as a kinetic entity, η^E will therefore be large because the ion plus its primary sheath can be visualized as a single particle. It is also probable that at room temperature water molecules beyond this inner layer are oriented to some extent, giving positive η^A. The sum of $\eta^E+\eta^A$ will far outweigh the decrement due to η^D because it is thought to be small for these ions as the fixed outward pointing hydrogen atoms fit reasonably well into the tetrahedral water structure. Thus in this class of ions the $\eta^E+\eta^A >> \eta^D$ and the coefficient B is fairly large and positive.

It is seen in the table 4.21-4.30 that $NiCl_2$ and $FeCl_3$ in aqueous solution have large positive B values. This indicates that these electrolytes clearly exhibit structure making behavior in water and in water DMSO solutions.

For NH_4Cl, the viscosity coefficient B is negative in a water and water DMSO (shown in table 4.16-4.21). This indicates that NH_4Cl salt behaves as a water structure breaker in aqueous and aqueous DMSO solution. The structure breaking tendency of NH_4Cl can be explained by the consideration of large size and low charge density of NH_4^+ ion. Because of the dipole –dipole repulsion between solvation shell molecules, the relatively weak electrostatic field about such ions can cause polarization, immobilization and electrostriction of water molecules only in the first layer. Beyond this layer a strong structure breaking effect persists i.e. a shift in the structure equilibrium in the direction of smaller degree of ice-likeness. Non nearest neighbor water molecules in the vicinity of these ions probably become more mobile than those in pure water. For the interaction of such ions with water the term negative hydration has been employed. In the view of Gurney there is a critical radius above which the electric field of the ion is too weak to produce order in the water. For an ion to fit into a cavity formerly occupied by a water molecule, its radius must be less than that of water molecule (1.38 A^o). This type of ions should fit into such cavity without disruption of the water structure [the primary and secondary hydration layers about this cavity]. NH_4^+ whose radius is 1.43A^0 would be expected to disrupt the primary hydration layer slightly. Furthermore this would also result in a disruption of the secondary hydration layer. This disruption should lead to a weakening of the bonds holding this water molecule together in the hydration layer. This disruption is always accompanied by structure breaking effects in aqueous solution.

The increase of B coefficient of NH_4Cl, $NiCl_2$ and $FeCl_3$ with the increase in DMSO concentration reveals that these electrolytes must be in a progressively more structured environment as DMSO molality is increased. In the ternary (H_2O+DMSO+electrolyte) solution, DMSO polar group interactions disrupt the less structured region around them and the water molecules move to the more structured bulk region, resulting in an increase in viscosity. The predominance of DMSO-polar group interactions over DMSO-hydrophobic (negligible) group interactions gives a net increased in viscosity. The DMSO-electrolytes and DMSO-DMSO interaction progressively enhance the overall structure of the solution as the molality of DMSO is increased reflecting, the increase in B coefficient value with the molality of DMSO.

The coefficient A represents the solute-solute interactions coupled with size and shape effect of the solute and to some extent solute-solvent interactions. In this study an irregular variation in values of A coefficient is found (shown in table 4.16-4.30). This irregular variation in the values of A coefficient may be due to:

i) an incomplete dissociation and ion association of electrolyte in aqueous and aqueous DMSO solvent and

ii) the size of the ions which differs in the degree of hydration or solvation.

The values of 'A' have been found to decrease with the rise of temperature. This is probably due to the greater thermal agitation and reduction of attractive forces between the ions. The increase in A value can be explained by the inter-penetration effect, which brings the ions closer together. The higher positive A values for aqueous solution of $NiCl_2$ and $FeCl_3$ were observed. This is may be due to the higher charge to radius for Ni^{2+} and Fe^{3+}.

Table 4.1: Densities (ρ) and apparent molal volume (φ_v) of NH_4Cl in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	0.99900	58	56	0.99791	63	60	0.99667	65	60
0.08060	0.28390	0.99945	50		0.99848	51		0.99723	52	
0.12120	0.34814	1.00039	43		0.99922	45		0.99817	44	
0.16190	0.40237	1.00061	44		0.99924	47		0.99863	44	
0.24390	0.49386	1.00258	39		1.00136	40		1.00003	41	
0.41010	0.64039	1.00505	38		1.00395	39		1.00268	39	

m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	0.99498	72	65	0.99364	64	61	0.99158	70	65
0.08060	0.28390	0.99572	53		0.99406	54		0.99224	54	
0.12120	0.34814	0.99640	47		0.99505	45		0.99277	49	
0.16190	0.40237	0.99697	45		0.99546	45		0.99364	45	
0.24390	0.49386	0.99823	43		0.99678	42		0.99495	42	
0.41010	0.64039	1.00086	40		0.99945	40		0.99707	41	

Table 4.2: Densities (ρ) and apparent molal volume (φ_v) of NH_4Cl in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**$\sqrt{m}$**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**
0.04020	0.20050	1.10465	420	56	1.09947	43	60	1.09541	23	60
0.08060	0.28390	1.10592	221		1.10042	36		1.09592	30	
0.12120	0.34814	1.12170	57		1.10155	32		1.09642	33	
0.16190	0.40237	1.12238	51		1.11900	51		1.11455	55	
0.24390	0.49386	1.12613	38		1.12085	24		1.11634	26	
0.41010	0.64039	1.12676	40		1.12304	0		1.11951	2	

m (mol kg^{-1})	**$\sqrt{m}$**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**
0.04020	0.20050	1.08985	29	61	1.08506	5	61	1.07967	32	65
0.08060	0.28390	1.09058	31		1.08540	18		1.08031	34	
0.12120	0.34814	1.09117	33		1.08628	22		1.08089	35	
0.16190	0.40237	1.10947	56		1.10391	62		1.10042	63	
0.24390	0.49386	1.11108	27		1.10588	31		1.10168	30	
0.41010	0.64039	1.11391	2		1.10944	6		1.10438	3	

Table 4.3: Densities (ρ) and apparent molal volume (φ_v) of NH_4Cl in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg-1)	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.10484	416	353	1.09998	32	35	1.09544	22	26
0.08060	0.28390	1.10525	227		1.10022	38		1.09613	28	
0.12120	0.34814	1.10579	164		1.10138	33		1.09625	34	
0.16190	0.40237	1.10611	133		1.10148	36		1.09681	35	
0.24390	0.49386	1.10661	103		1.10261	36		1.09814	35	
0.41010	0.64039	1.10816	77		1.10635	34		1.10282	31	

m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.09088	7	9	1.08613	28	17	1.08154	7	1
0.08060	0.28390	1.09194	17		1.08675	4		1.08253	10	
0.12120	0.34814	1.09210	26		1.08779	11		1.08319	18	
0.16190	0.40237	1.09240	30		1.08806	19		1.08311	27	
0.24390	0.49386	1.09389	31		1.08944	24		1.08403	31	
0.41010	0.64039	1.09823	29		1.09354	26		1.08753	31	

Table 4.4: Densities (ρ) and apparent molal volume (φ_v) of NH_4Cl in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	√m	288 K			293 K			298 K		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.07666	1007	850	1.07281	606	577	1.06928	579	490
0.08060	0.28390	1.07709	522		1.07356	319		1.07013	304	
0.12120	0.34814	1.07819	356		1.07406	225		1.07085	214	
0.16190	0.40237	1.07874	276		1.07494	176		1.07164	168	
0.24390	0.49386	1.07929	198		1.07581	130		1.07244	125	
0.41010	0.64039	1.08177	132		1.07826	92		1.07435	90	

m (mol kg^{-1})	√m	303 K			308 K			313 K		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.06551	551	465	1.06179	498	420	1.05877	488	419
0.08060	0.28390	1.06622	292		1.06279	262		1.05859	270	
0.12120	0.34814	1.06686	206		1.06342	186		1.05947	190	
0.16190	0.40237	1.06778	162		1.06417	148		1.06040	150	
0.24390	0.49386	1.06871	121		1.06492	112		1.06134	113	
0.41010	0.64039	1.07066	88		1.06724	82		1.06367	82	

Table 4.5: Densities (ρ) and apparent molal volume (φ_v) of NH_4Cl in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**$\sqrt{m}$**	**288 K**			**293 K**			**298 K**		
		ρ **(gcm^{-3})**	φ_v **(gcm^{-3})**	φ_v^0 **(gcm^{-3})**	ρ **(gcm^{-3})**	φ_v **(gcm^{-3})**	φ_v^0 **(gcm^{-3})**	ρ **(gcm^{-3})**	φ_v **(gcm^{-3})**	φ_v^0 **(gcm^{-3})**
0.04020	0.20050	1.02974	2062	1735	1.02796	1620	1365	1.02572	1569	1320
0.08060	0.28390	1.02997	1051		1.02793	834		1.02580	807	
0.12120	0.34814	1.03047	713		1.02848	568		1.02664	548	
0.16190	0.40237	1.03134	541		1.02919	434		1.02713	420	
0.24390	0.49386	1.03254	372		1.03058	300		1.02867	290	
0.41010	0.64039	1.03513	236		1.03306	193		1.03094	188	
m (mol kg^{-1})	**$\sqrt{m}$**	**303 K**			**308 K**			**313 K**		
		ρ **(gcm^{-3})**	φ_v **(gcm^{-3})**	φ_v^0 **(gcm^{-3})**	ρ **(gcm^{-3})**	φ_v **(gcm^{-3})**	φ_v^0 **(gcm^{-3})**	ρ **(gcm^{-3})**	φ_v **(gcm^{-3})**	φ_v^0 **(gcm^{-3})**
0.04020	0.20050	1.02321	1519	1280	1.02117	1432	1205	1.01862	1416	1195
0.08060	0.28390	1.02350	780		1.02126	739		1.01857	733	
0.12120	0.34814	1.02420	530		1.02189	504		1.01932	499	
0.16190	0.40237	1.02475	407		1.02251	386		1.01977	384	
0.24390	0.49386	1.02603	282		1.02401	268		1.02122	266	
0.41010	0.64039	1.02863	183		1.02644	175		1.02390	173	

Table 4:6: Densities (ρ) and apparent molal volume (φ_v) of $NiCl_2$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**$\sqrt{m}$**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.00323	136	120	1.00189	147	130	1.00058	151	133
0.08060	0.28390	1.00931	111		1.00799	116		1.00664	118	
0.12120	0.34814	1.01493	106		1.01354	110		1.01209	112	
0.16190	0.40237	1.02043	104		1.01896	107		1.01751	109	
0.24390	0.49386	1.02628	123		1.02564	122		1.02413	123	
0.41010	0.64039	1.04612	117		1.04581	116		1.04294	120	
m (mol kg^{-1})	**$\sqrt{m}$**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	0.99890	158	139	0.99734	156	137	0.99610	141	131
0.08060	0.28390	1.00487	123		1.00351	119		1.00148	122	
0.12120	0.34814	1.01027	115		1.00867	115		1.00624	120	
0.16190	0.40237	1.01581	111		1.01394	112		1.01181	114	
0.24390	0.49386	1.02219	125		1.02148	122		1.01865	126	
0.41010	0.64039	1.04181	119		1.03977	120		1.03719	122	

Table 4.7: Densities (ρ) and apparent molal volume (φ_v) of $NiCl_2$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**$\sqrt{m}$**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.10948	488	421	1.10526	91	89	1.10024	90	91
0.08060	0.28390	1.11608	283		1.11128	91		1.10641	89	
0.12120	0.34814	1.12044	230		1.11564	102		1.11116	98	
0.16190	0.40237	1.12481	203		1.12000	107		1.11591	103	
0.24390	0.49386	1.13427	173		1.13038	107		1.12548	106	
0.41010	0.64039	1.15655	142		1.15135	105		1.14592	106	
m (mol kg^{-1})	**$\sqrt{m}$**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.09479	94	90	1.09000	59	69	1.08471	95	99
0.08060	0.28390	1.10121	88		1.09511	84		1.08992	101	
0.12120	0.34814	1.10563	100		1.10006	94		1.09431	109	
0.16190	0.40237	1.11005	106		1.10500	98		1.09871	113	
0.24390	0.49386	1.12020	106		1.11522	101		1.10831	113	
0.41010	0.64039	1.14056	106		1.13564	103		1.12981	108	

Table 4.8: Densities (ρ) and apparent molal volume (φ_v) of $NiCl_2$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.11091	459	417	1.10603	75	96	1.10149	64	90
0.08060	0.28390	1.11141	331		1.10681	137		1.10133	142	
0.12120	0.34814	1.12019	231		1.11513	105		1.10985	107	
0.16190	0.40237	1.12784	188		1.12270	94		1.11831	90	
0.24390	0.49386	1.13292	178		1.12752	117		1.12337	114	
0.41010	0.64039	1.15142	153		1.14653	115		1.13868	121	
m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.09663	55	82	1.09236	9	59	1.08783	28	62
0.08060	0.28390	1.09679	134		1.09280	109		1.08767	125	
0.12120	0.34814	1.10523	103		1.09286	145		1.09654	93	
0.16190	0.40237	1.11369	87		1.10960	74		1.10460	81	
0.24390	0.49386	1.11903	111		1.11503	102		1.11041	106	
0.41010	0.64039	1.13819	111		1.13404	107		1.12944	109	

Table 4.9: Densities (ρ) and apparent molal volume (φ_v) of $NiCl_2$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.08179	1067	902	1.07822	660	562	1.07479	631	540
0.08060	0.28390	1.08801	575		1.08425	374		1.08086	359	
0.12120	0.34814	1.09113	433		1.08738	300		1.08389	290	
0.16190	0.40237	1.09860	339		1.09508	238		1.09151	231	
0.24390	0.49386	1.10555	273		1.10163	207		1.09810	203	
0.41010	0.64039	1.12354	210		1.11999	171		1.11646	168	

m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.07112	601	516	1.06754	544	470	1.06355	555	479
0.08060	0.28390	1.07707	345		1.07324	320		1.06962	321	
0.12120	0.34814	1.08015	281		1.07654	262		1.07276	265.	
0.16190	0.40237	1.08758	225		1.08390	211		1.07985	214	
0.24390	0.49386	1.09427	198		1.09069	189		1.08639	192	
0.41010	0.64039	1.11276	165		1.10932	159		1.10542	160	

Table 4.10: Densities (ρ) and apparent molal volume (φ_v) of $NiCl_2$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**
0.04020	0.20050	1.03305	2163	1820	1.03124	1721	1455	1.02931	1663	1410
0.08060	0.28390	1.03829	1132		1.03612	916		1.03402	889	
0.12120	0.34814	1.04303	792		1.04076	649		1.03876	631	
0.16190	0.40237	1.05050	606		1.04808	500		1.04674	482	
0.24390	0.49386	1.05604	457		1.05343	387		1.05140	378	
0.41010	0.64039	1.07345	322		1.07103	280		1.06908	274	
m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**	**ρ (gcm^{-3})**	**φ_v (gcm^{-3})**	**φ_v^0 (gcm^{-3})**
0.04020	0.20050	1.03305	2163	1820	1.03124	1721	1455	1.02931	1663	1410
0.08060	0.28390	1.03829	1132		1.03612	916		1.03402	889	
0.12120	0.34814	1.04303	792		1.04076	649		1.03876	631	
0.16190	0.40237	1.05050	606		1.04808	500		1.04674	482	
0.24390	0.49386	1.05604	457		1.05343	387		1.05140	378	
0.41010	0.64039	1.07345	322		1.07103	280		1.06908	274	

Table 4.11: Densities (ρ) and apparent molal volume (φ_v) of $FeCl_3$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	√m	288 K			293 K			298 K		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.00410	68	73	1.00276	57	64	1.00130	50	57
0.08060	0.28390	1.00977	77		1.00849	72		1.00702	69	
0.12120	0.34814	1.01538	79		1.01404	75		1.01250	72	
0.16190	0.40237	1.02061	77		1.01934	75		1.01810	75	
0.24390	0.49386	1.03151	76		1.03019	75		1.02871	74	
0.41010	0.64039	1.05286	73		1.05172	73		1.05032	72	
m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	0.99986	50	54	0.99804	45	49	0.99580	35	49
0.08060	0.28390	1.00519	64		1.00301	57		1.00236	72	
0.12120	0.34814	1.01076	70		1.00944	73		1.00737	71	
0.16190	0.40237	1.01662	74		1.01484	74		1.01267	72	
0.24390	0.49386	1.02696	73		1.02540	73		1.02344	73	
0.41010	0.64039	1.04833	71		1.04717	73		1.04454	71	

Table 4.12: Densities (ρ) and apparent molal volume (φ_v) of $FeCl_3$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.12830	139	140	1.12320	242	177	1.11734	229	170
0.08060	0.28390	1.13308	142		1.12825	51		1.12257	45	
0.12120	0.34814	1.13839	139		1.13327	12		1.12771	15	
0.16190	0.40237	1.14560	128		1.13881	41		1.13259	47	
0.24390	0.49386	1.15339	138		1.14824	76		1.14206	79	
0.41010	0.64039	1.17285	138		1.16803	100		1.16219	102	

m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.11232	237	178	1.10727	270	203	1.10222	242	177
0.08060	0.28390	1.11855	60		1.11187	59		1.10675	45	
0.12120	0.34814	1.12221	15		1.11700	6		1.11125	20	
0.16190	0.40237	1.12651	50		1.12160	41		1.11549	54	
0.24390	0.49386	1.13640	80		1.13108	76		1.12536	83	
0.41010	0.64039	1.15545	104		1.14977	103		1.14337	108	

Table 4.13: Densities (ρ) and apparent molal volume (φ_v) of $FeCl_3$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.08213	1090	1000	1.07792	697	630	1.07495	658	590
0.08060	0.28390	1.08769	609		1.08437	403		1.08076	390	
0.12120	0.34814	1.10737	349		1.10512	204		1.10216	190	
0.16190	0.40237	1.11410	287		1.11131	181		1.10824	172	
0.24390	0.49386	1.12718	226		1.12286	162		1.11919	157	
0.41010	0.64039	1.14620	192		1.14376	149		1.14061	146	

m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.07116	630	565	1.06764	572	512	1.06381	580	520
0.08060	0.28390	1.07709	375		1.07328	350		1.06924	356	
0.12120	0.34814	1.09886	177		1.09527	157		1.09149	159	
0.16190	0.40237	1.10559	158		1.10172	145		1.09843	144	
0.24390	0.49386	1.11556	152		1.11137	144		1.10821	143	
0.41010	0.64039	1.13630	144		1.13331	137		1.12920	138	

Table 4.14: Densities (ρ) and apparent molal volume (φ_v) of $FeCl_3$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.03296	2196	2050	1.03068	1766	1650	1.02866	1710	1600
0.08060	0.28390	1.03812	1165		1.03562	954		1.03346	927	
0.12120	0.34814	1.04372	818		1.04117	677		1.03949	656	
0.16190	0.40237	1.04901	646		1.04675	539		1.04497	524	
0.24390	0.49386	1.05957	474		1.05730	403		1.05500	395	
0.41010	0.64039	1.08018	336		1.07786	294		1.07579	289	

m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.02610	1661	1560	1.02401	1576	1470	1.02120	1566	1475
0.08060	0.28390	1.03103	901		1.02889	859		1.02641	851	
0.12120	0.34814	1.03740	636		1.03514	609		1.03292	601	
0.16190	0.40237	1.04228	513		1.04027	491		1.03754	488	
0.24390	0.49386	1.05289	385		1.05076	371		1.04821	369	
0.41010	0.64039	1.07347	283		1.07130	275		1.06886	274	

Table 4.15: Densities (ρ) and apparent molal volume (φ_v) of $FeCl_3$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (mol kg^{-1})	**√m**	**288 K**			**293 K**			**298 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.12824	51	55	1.12375	446	383	1.11939	464	395
0.08060	0.28390	1.13284	46		1.12863	246		1.12394	252	
0.12120	0.34814	1.13758	45		1.13375	181		1.12892	184	
0.16190	0.40237	1.14315	49		1.13924	150		1.13481	154	
0.24390	0.49386	1.15345	49		1.15021	118		1.14561	121	
0.41010	0.64039	1.17269	45		1.16927	87		1.16573	90	
m (mol kg^{-1})	**√m**	**303 K**			**308 K**			**313 K**		
		ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})	ρ (gcm^{-3})	φ_v (gcm^{-3})	φ_v^0 (gcm^{-3})
0.04020	0.20050	1.11445	475	404	1.10996	520	442	1.10538	504	430
0.08060	0.28390	1.11871	255		1.11426	278		1.11002	274	
0.12120	0.34814	1.12474	193		1.12037	210		1.11571	204	
0.16190	0.40237	1.12971	157		1.12536	169		1.12086	166	
0.24390	0.49386	1.14128	125		1.13695	134		1.13288	133	
0.41010	0.64039	1.16124	93		1.15717	99		1.15280	98	

Table 4.16: Viscosities (η), Coefficients A and B of NH_4Cl in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	**288 K**			**293 K**			**298 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.11928	0.06142	-0.09785	1.01328	0.03538	-0.05463	0.89324	0.03075	-0.01643
0.08000	1.11454			1.00052			0.89374		
0.12000	1.12608			1.00661			0.90516		
0.16000	1.11582			1.00663			0.90823		
0.24000	1.11802			1.01143			0.90155		
0.41000	1.10759			1.00600			0.89330		

m (moldm^{-3})	**303 K**			**308 K**			**313 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	0.79741	0.02850	-0.04652	0.72222	0.03106	-0.01978	0.65506	0.03745	-0.00610
0.08000	0.80319			0.72508			0.66050		
0.12000	0.80633			0.72579			0.66336		
0.16000	0.80679			0.73374			0.66895		
0.24000	0.79482			0.72706			0.65979		
0.41000	0.79432			0.72389			0.66372		

Table 4.17: Viscosities (η), Coefficients A and B of NH4Cl in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	2.17362	5.28384	-5.23343	2.00115	5.49606	-5.42659	1.81312	5.70567	-5.76184
0.08000	2.22516			2.06964			1.86692		
0.12000	2.35640			2.15196			1.92872		
0.16000	2.38403			2.21864			1.98214		
0.24000	2.51027			2.33928			2.09053		
0.41000	2.74839			2.54007			2.28041		
m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	1.61554	5.64463	-5.67794	1.46639	5.74193	-5.92123	1.32198	5.67364	-5.80281
0.08000	1.66333			1.50767			1.36034		
0.12000	1.71357			1.54718			1.39867		
0.16000	1.77398			1.59823			1.44947		
0.24000	1.87438			1.67646			1.52010		
0.41000	2.02757			1.81224			1.63908		

Table 4.18: Viscosities (η), Coefficients A and B of NH_4Cl in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	3.87603	14.24141	-17.12956	3.46495	13.92837	-16.57977	2.99634	13.44217	-15.97285
0.08000	3.90845			3.46837			3.01944		
0.12000	3.93617			3.54418			3.07275		
0.16000	3.98894			3.54183			3.07431		
0.24000	4.00881			3.67659			3.17623		
0.41000	4.31966			3.87970			3.37097		

m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	2.59563	12.94072	-15.44570	2.25409	12.23344	-14.48599	2.22467	13.15481	-16.87523
0.08000	2.65010			2.31156			2.02086		
0.12000	2.67127			2.33166			2.04721		
0.16000	2.67200			2.33225			2.03450		
0.24000	2.78237			2.41714			2.11163		
0.41000	2.88225			2.53932			2.21934		

Table 4.19: Viscosities (η), Coefficients A and B of NH_4Cl in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	3.47560	12.40377	-15.53192	3.03568	11.75890	-14.55465	2.59665	11.02921	-13.58067
0.08000	3.49210			3.06648			2.61166		
0.12000	3.51830			3.08876			2.63411		
0.16000	3.51505			3.09127			2.61018		
0.24000	3.50172			3.09640			2.66394		
0.41000	3.58555			3.19242			2.75436		

m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	2.23102	10.39468	-12.95242	1.90909	9.59340	-11.87082	1.65732	8.84854	-10.82259
0.08000	2.23252			1.92337			1.65704		
0.12000	2.24654			1.94452			1.68298		
0.16000	2.25357			1.95089			1.69676		
0.24000	2.28858			1.95726			1.71056		
0.41000	2.29276			1.98913			1.75131		

Table 4.20: Viscosities (η), Coefficients A and B of NH_4Cl in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	**288 K**			**293 K**			**298 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.59597	2.59686	-3.32214	1.45439	2.58972	-3.31365	1.27147	2.48292	-3.13929
0.08000	1.61075			1.45185			1.27157		
0.12000	1.60432			1.43017			1.27013		
0.16000	1.59846			1.43115			1.27321		
0.24000	1.59549			1.44809			1.28009		
0.41000	1.58982			1.45408			1.27295		

m (moldm^{-3})	**303 K**			**308 K**			**313 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.10774	2.28538	-2.89622	0.98403	2.13680	-2.68672	0.87636	1.99692	-2.48435
0.08000	1.12024			0.99372			0.88341		
0.12000	1.10882			0.97992			0.87933		
0.16000	1.11673			0.98532			0.88445		
0.24000	1.10104			0.98436			0.88334		
0.41000	1.11851			0.99876			0.89041		

Table 4.21: Viscosities (η), Coefficients A and B of $NiCl_2$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	**288 K**			**293 K**			**298 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.22404	0.38814	0.18424	1.03875	0.10262	0.25533	0.91531	0.07010	0.29248
0.08000	1.17320			1.04237			0.92619		
0.12000	1.21169			1.06978			0.94462		
0.16000	1.21825			1.08639			0.96047		
0.24000	1.29256			1.11818			0.98030		
0.41000	1.33402			1.17091			1.03701		
m (moldm^{-3})	**303 K**			**308 K**			**313 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	0.81615	0.02859	0.51510	0.73257	-0.00160	0.43809	0.67563	0.08915	0.19631
0.08000	0.82364			0.74481			0.67423		
0.12000	0.83595			0.75122			0.67743		
0.16000	0.84847			0.77072			0.69904		
0.24000	0.86444			0.81043			0.71918		
0.41000	0.97320			0.83558			0.74272		

Table 4.22: Viscosities (η), Coefficients A and B of NiCl$_2$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	2.36958	4.64577	0.58800	2.25309	5.21566	0.82249	1.98860	5.53640	1.50411
0.08000	2.62333			2.41908			2.15480		
0.12000	2.73559			2.51793			2.24729		
0.16000	2.96678			2.43808			2.45374		
0.24000	3.53715			3.20956			2.80114		
0.41000	5.21559			4.62427			3.90698		
m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	1.76614	5.60147	2.09642	1.59347	5.72569	2.67113	1.44386	5.87718	3.37410
0.08000	1.90227			1.70904			1.53673		
0.12000	1.98882			1.78399			1.60890		
0.16000	2.15261			1.89589			1.68161		
0.24000	2.42550			2.14931			1.90192		
0.41000	3.32443			2.88265			2.47855		

Table 4.23: Viscosities (η), Coefficients A and B of $NiCl_2$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	4.04255	13.53176	9.27298	3.60748	13.06893	9.28187	3.13001	12.56651	9.02687
0.08000	4.37901			3.68254			3.19342		
0.12000	4.70123			4.15946			3.48631		
0.16000	5.25984			4.61816			3.95605		
0.24000	5.55325			4.78848			4.15309		
0.41000	7.31294			6.30495			5.39281		
m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	2.69542	11.81705	8.38081	2.34917	11.36861	8.38227	2.06606	10.94388	8.41327
0.08000	2.71147			2.39121			2.08089		
0.12000	3.01109			2.59426			2.29368		
0.16000	3.39452			2.92086			2.52314		
0.24000	3.59183			3.11862			2.69349		
0.41000	4.60393			3.91808			3.35253		

Table 4.24: Viscosities (η), Coefficients A and B of $NiCl_2$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	**288 K**			**293 K**			**298 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	3.53258	12.01494	12.04891	3.15044	11.74962	11.80891	2.66718	10.99162	10.98621
0.08000	3.72811			3.30226			2.80761		
0.12000	3.78466			3.35136			2.86786		
0.16000	4.00033			3.55582			3.02782		
0.24000	4.14950			3.75621			3.19734		
0.41000	4.89623			4.29717			3.62847		

m (moldm^{-3})	**303 K**			**308 K**			**313 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	4.82705	23.02144	36.14087	1.96460	8.74117	8.87854	1.70179	8.87302	8.92724
0.08000	2.38337			2.06084			1.78592		
0.12000	2.43903			2.09501			1.82102		
0.16000	2.57224			1.18714			1.90316		
0.24000	2.70262			2.32763			2.01043		
0.41000	3.07130			2.83670			2.25841		

Table 4.25: Viscosities (η), Coefficients A and B of $NiCl_2$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.63486	2.56314	2.29975	1.48155	2.58593	2.44669	1.29333	2.47861	2.29221
0.08000	1.67950			1.52126			1.32922		
0.12000	1.72857			1.54070			1.35540		
0.16000	1.76547			1.57188			1.44169		
0.24000	1.88570			1.67450			1.43540		
0.41000	1.99195			1.77525			1.56029		
m (moldm^{-3})	**303 K**			**308 K**			**313 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.14082	2.32207	2.19934	0.99947	2.02138	1.59232	0.89352	1.92749	1.56712
0.08000	1.15839			1.02585			0.91668		
0.12000	1.18111			1.04507			0.92681		
0.16000	1.23451			1.07685			0.95138		
0.24000	1.25282			1.16459			1.04195		
0.41000	1.35262			1.23835			1.08325		

Table 4.26: Viscosities (η), Coefficients A and B of $FeCl_3$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	**Coefficient A**	**Coefficient B**	η (CP)	**Coefficient A**	**Coefficient B**	η (CP)	**Coefficient A**	**Coefficient B**
0.04000	1.18558	0.21183	0.40038	1.03429	0.00010	0.75809	0.91596	-0.01605	0.78318
0.08000	1.20553			1.06445			0.94523		
0.12000	1.23887			1.09740			0.96648		
0.16000	1.25328			1.11676			1.00422		
0.24000	1.32080			1.18370			1.03651		
0.41000	1.46416			1.31242			1.16968		

m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	**Coefficient A**	**Coefficient B**	η (CP)	**Coefficient A**	**Coefficient B**	η (CP)	**Coefficient A**	**Coefficient B**
0.04000	0.82214	0.00130	0.71607	0.72798	-0.09269	0.89437	0.65785	-0.02632	0.70946
0.08000	0.83699			0.75984			0.70262		
0.12000	0.86530			0.77505			0.70613		
0.16000	0.90999			0.80516			0.72006		
0.24000	0.92192			0.82404			0.74836		
0.41000	1.02840			0.94070			0.82437		

Table 4.27: Viscosities (η), Coefficients A and B of $FeCl_3$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	2.32812	4.88117	0.91791	2.15882	5.36278	1.99595	1.93310	5.62002	2.89068
0.08000	2.50461			2.31640			2.05066		
0.12000	2.69439			2.46971			2.17994		
0.16000	2.90131			2.64207			2.31526		
0.24000	3.32486			2.99835			2.59404		
0.41000	4.57181			3.99962			3.36990		

m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	1.73090	5.78454	3.64321	1.55366	5.88504	4.19798	1.41604	6.03080	4.78448
0.08000	1.82842			1.64112			1.47833		
0.12000	1.92252			1.71696			1.54619		
0.16000	2.03174			1.80838			1.61158		
0.24000	2.25778			1.97784			1.75633		
0.41000	2.84822			2.44290			2.12117		

Table 4.28: Viscosities (η), Coefficients A and B of $FeCl_3$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	**288 K**			**293 K**			**298 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	3.47560	11.43835	9.66304	3.03446	10.98375	9.27953	2.65978	11.82616	10.85459
0.08000	3.71178			3.31578			2.84653		
0.12000	4.00122			3.49990			4.05340		
0.16000	4.19977			3.68403			3.13312		
0.24000	4.52535			3.97300			3.38042		
0.41000	5.42574			4.73812			3.99359		

m (moldm^{-3})	**303 K**			**308 K**			**313 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	2.28108	10.03787	9.05473	1.98486	9.55617	8.85980	1.72687	8.90649	8.21782
0.08000	2.42442			2.10632			1.81256		
0.12000	2.53618			2.18810			1.90343		
0.16000	2.65430			2.29161			1.99451		
0.24000	2.84812			2.44490			2.11504		
0.41000	3.36610			2.85008			2.46149		

Table 4.29: Viscosities (η), Coefficients A and B of $FeCl_3$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.68777	2.78079	2.33055	1.50826	2.63739	2.17527	1.31488	2.49839	2.07348
0.08000	1.72527			1.54565			1.34848		
0.12000	1.84664			1.59942			1.38398		
0.16000	1.84867			1.64354			1.43420		
0.24000	1.94146			1.73709			1.51425		
0.41000	2.16833			1.93567			1.66366		
m (moldm^{-3})	**303 K**			**308 K**			**313 K**		
	η (CP)	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**	**η (CP)**	**Coefficient A**	**Coefficient B**
0.04000	1.14261	2.23206	1.66038	1.02287	2.16905	1.66623	0.90227	2.01711	1.45339
0.08000	1.17755			1.04467			0.93782		
0.12000	1.21444			1.08021			0.98209		
0.16000	1.25487			1.11246			0.99129		
0.24000	1.32777			1.18542			1.05496		
0.41000	1.48143			1.29924			1.16002		

Table 4.30: Viscosities (η), Coefficients A and B of $FeCl_3$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

m (moldm^{-3})	288 K			293 K			298 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	4.15564	13.32972	7.91590	3.72528	13.41912	8.85024	3.21874	13.11269	9.28709
0.08000	4.40792			3.93043			3.38936		
0.12000	4.76623			4.25091			3.64170		
0.16000	5.08578			4.50375			3.86636		
0.24000	5.95544			5.23658			4.45676		
0.41000	7.91609			6.79036			5.64207		

m (moldm^{-3})	303 K			308 K			313 K		
	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B	η (CP)	Coefficient A	Coefficient B
0.04000	2.77367	12.42335	8.95053	2.41571	11.92673	8.90130	2.11734	11.49228	9.01106
0.08000	2.91204			2.52982			2.21374		
0.12000	3.11240			2.69379			2.36222		
0.16000	3.29282			2.86979			2.47970		
0.24000	3.77459			3.27343			2.81630		
0.41000	4.80768			4.06598			3.45663		

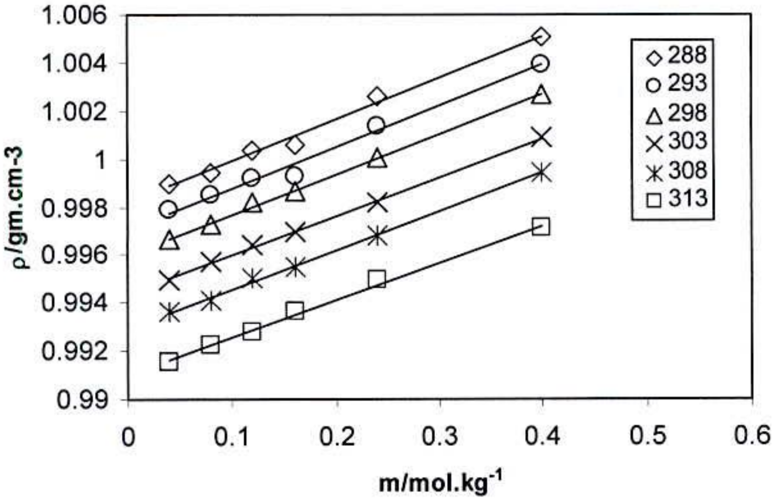

Figure- 4.1 Plots of Densities (ρ) vs molality (m) of NH_4Cl in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

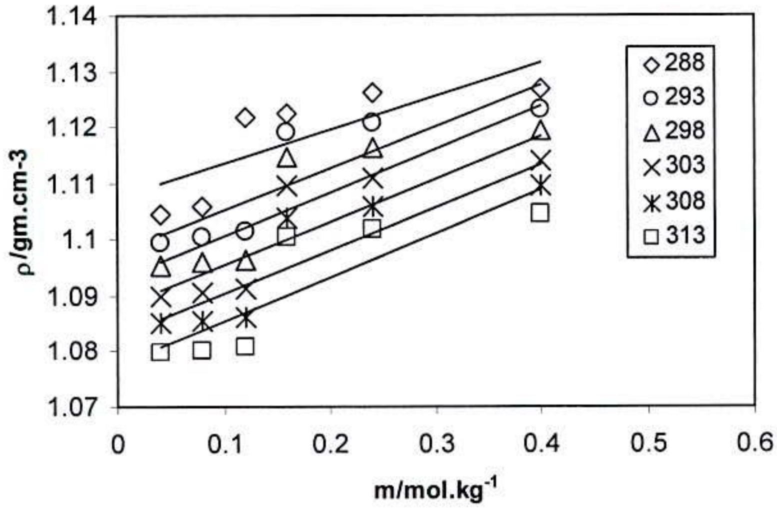

Figure- 4.2 Plots of Densities (ρ) vs molality (m) of NH_4Cl in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

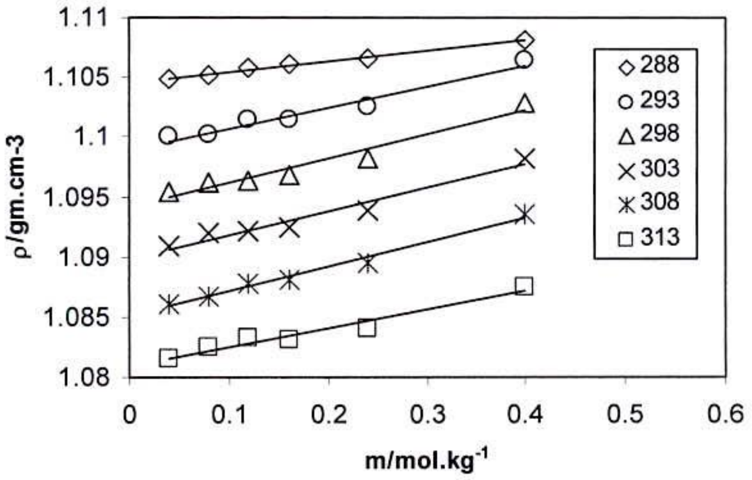

Figure- 4.3 Plots of Densities (ρ) vs molality (m) of NH_4Cl in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

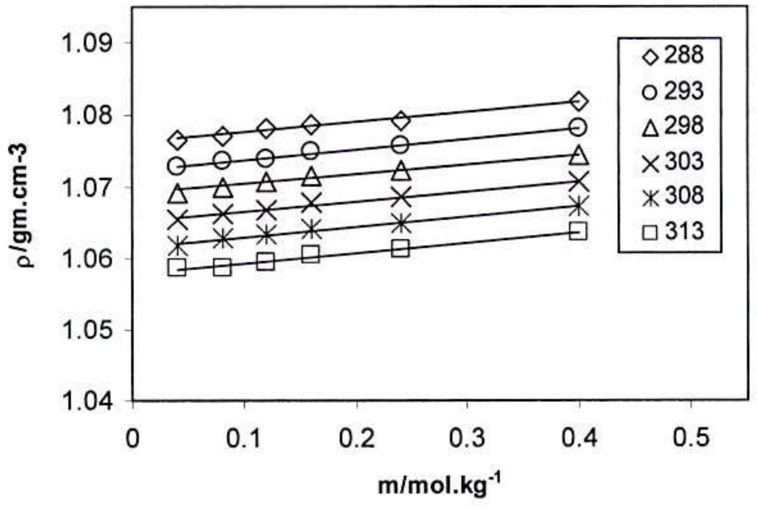

Figure- 4.4 Plots of Densities (ρ) vs molality (m) of NH_4Cl in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

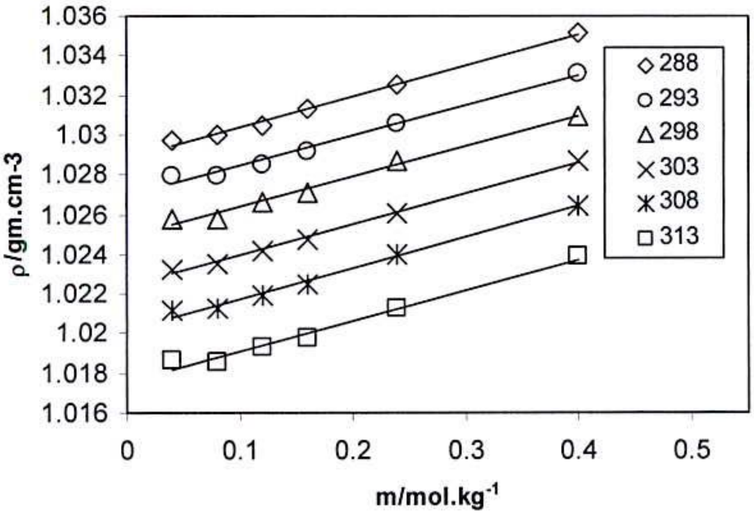

Figure- 4.5 Plots of Densities (ρ) vs molality (m) of NH_4Cl in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

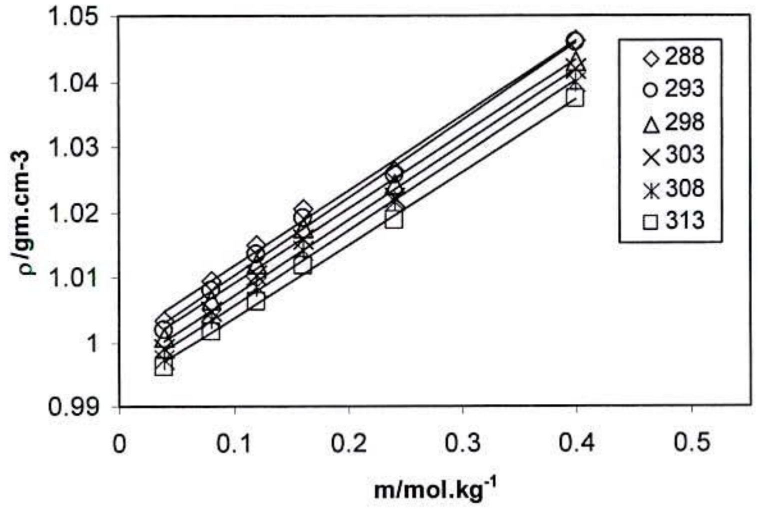

Figure- 4.6 Plots of Densities (ρ) vs molality (m) of $NiCl_2$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

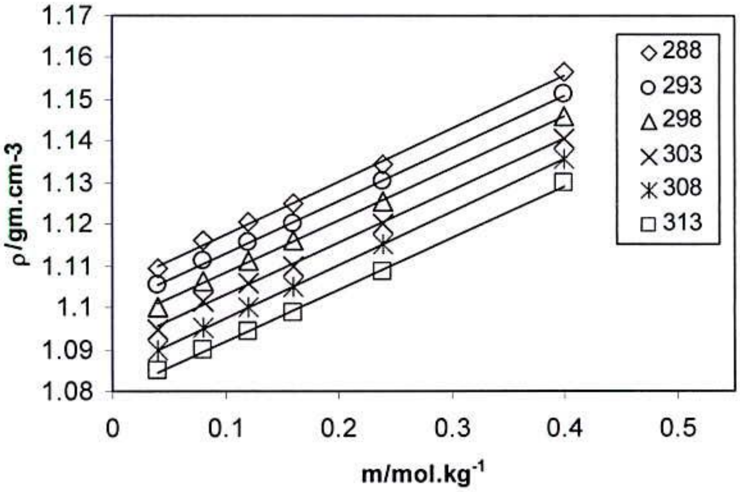

Figure- 4.7 Plots of Densities (ρ) vs molality (m) of $NiCl_2$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

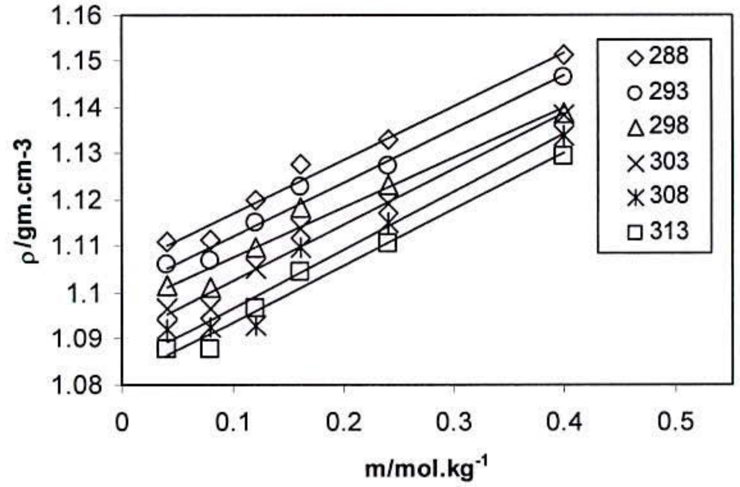

Figure- 4.8 Plots of Densities (ρ) vs molality (m) of $NiCl_2$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

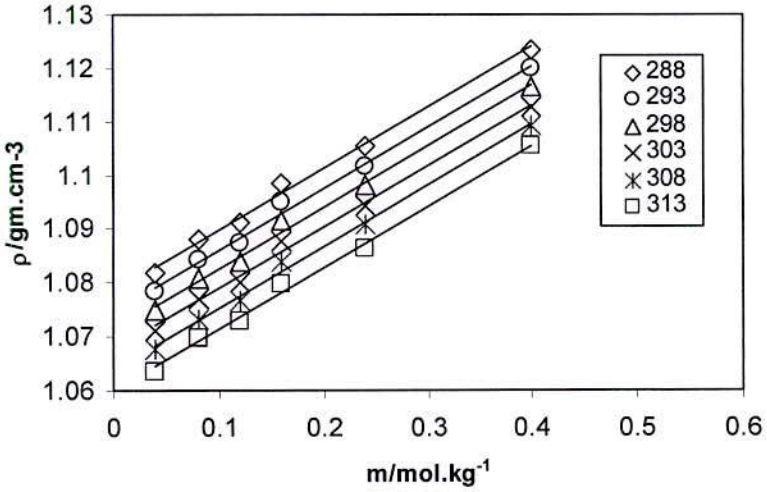

Figure- 4.9 Plots of Densities (ρ) vs molality (m) of $NiCl_2$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

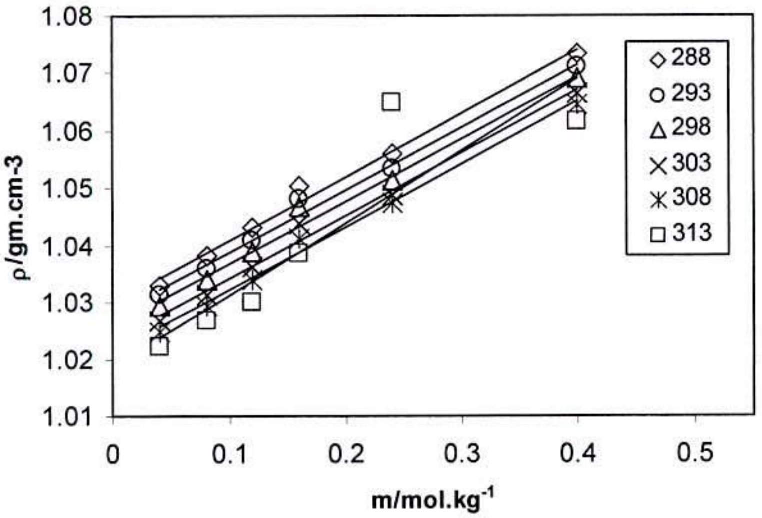

Figure- 4.10 Plots of Densities (ρ) vs molality (m) of $NiCl_2$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

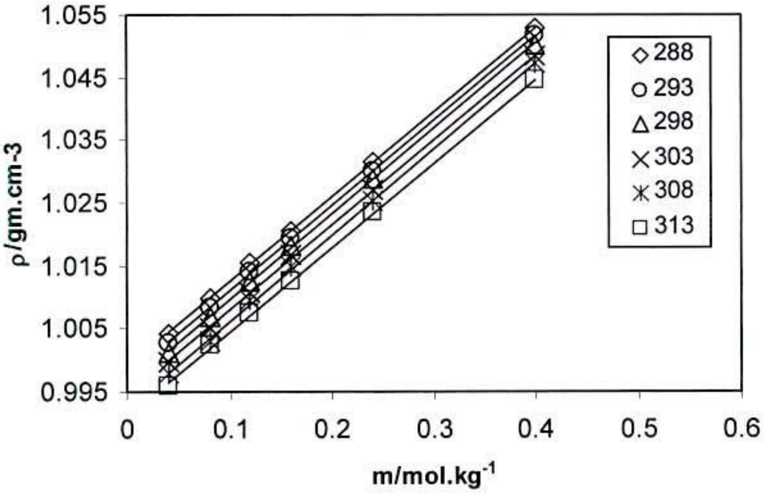

Figure- 4.11 Plots of Densities (ρ) vs molality (m) of $FeCl_3$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

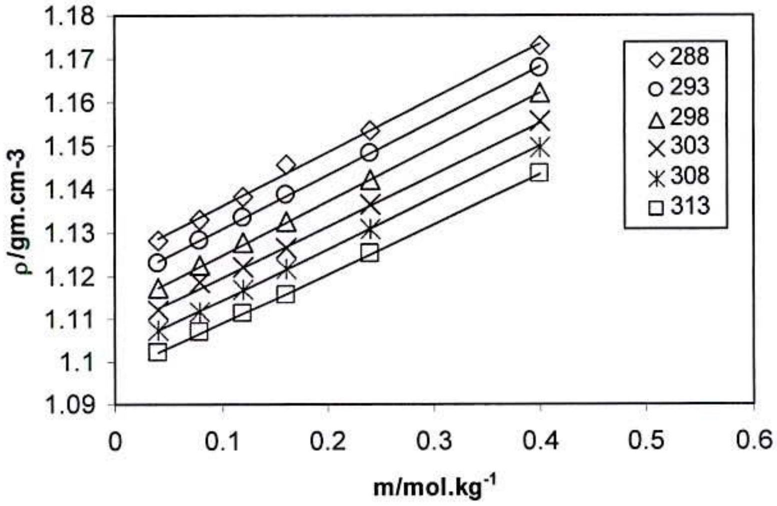

Figure- 4.12 Plots of Densities (ρ) vs molality (m) of $FeCl_3$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

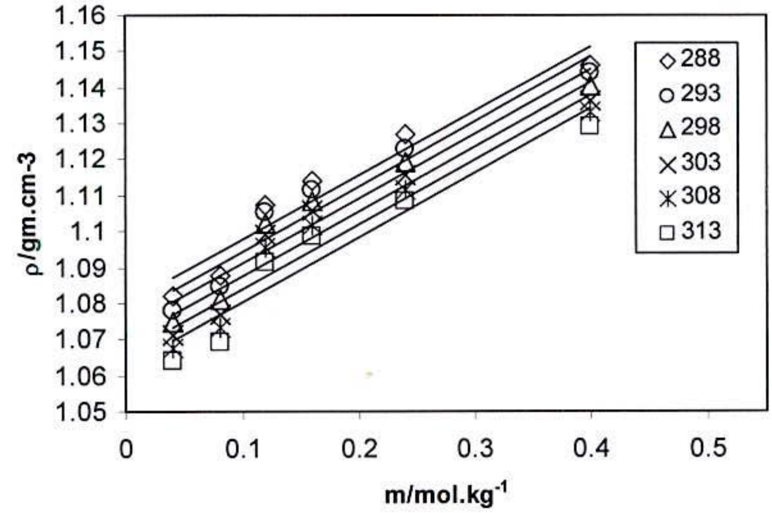

Figure- 4.13 Plots of Densities (ρ) vs molality (m) of $FeCl_3$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

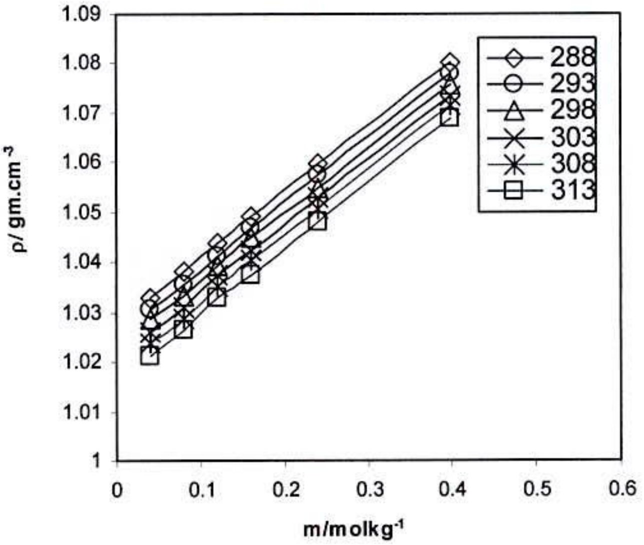

Figure- 4.14 Plots of Densities (ρ) vs molality (m) of $FeCl_3$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

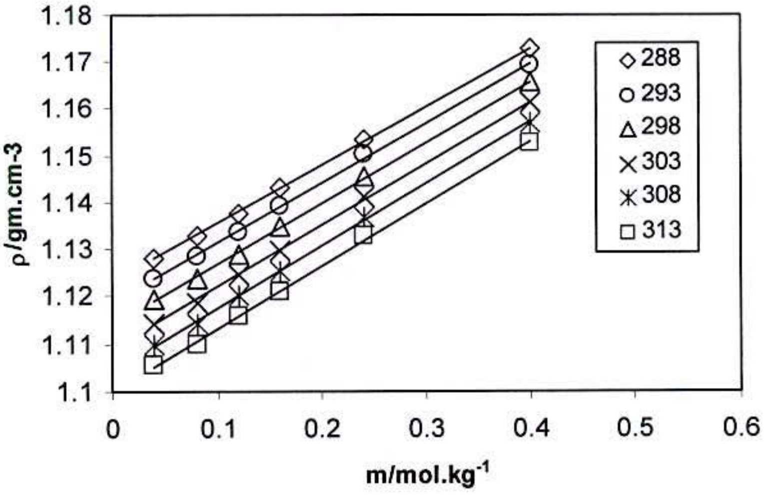

Figure- 4.15 Plots of Densities (ρ) vs molality (m) of $FeCl_3$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

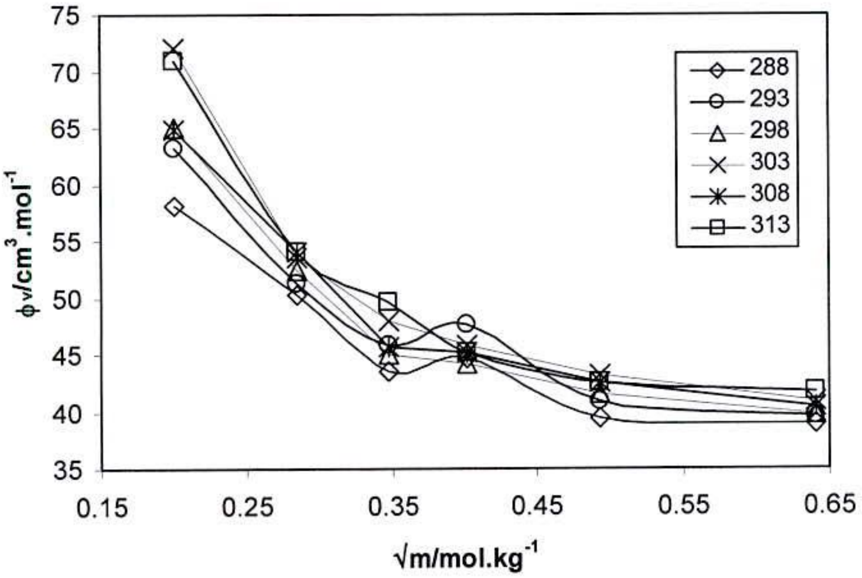

Figure- 4.16 Plots of Apparant molal volume (φ_v) vs square root of molality ($\sqrt{m}$) for NH_4-Cl in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

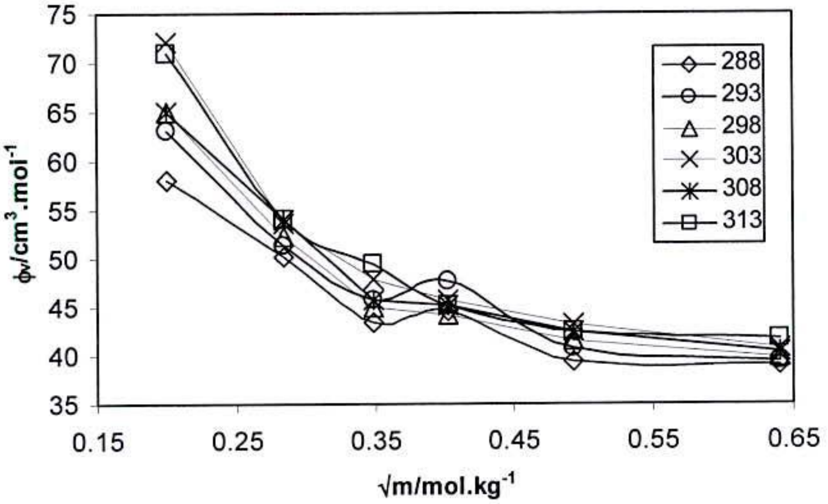

Figure- 4.17 Plots of Apparant molal volume (φ_v) vs square root of molality ($\sqrt{m}$) for NH_4-Cl in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

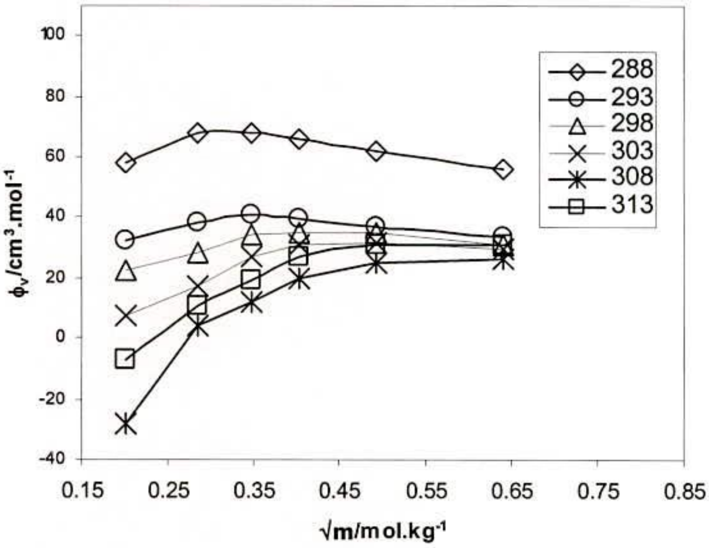

Figure- 4.18 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for NH_4-Cl in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K respectively.

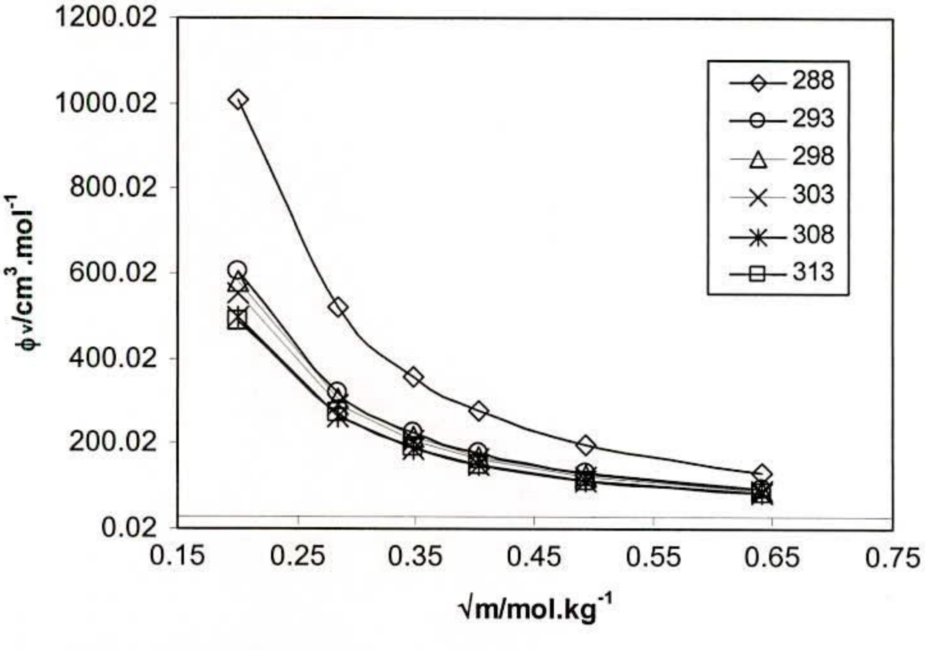

Figure- 4.19 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for NH_4-Cl in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K respectively.

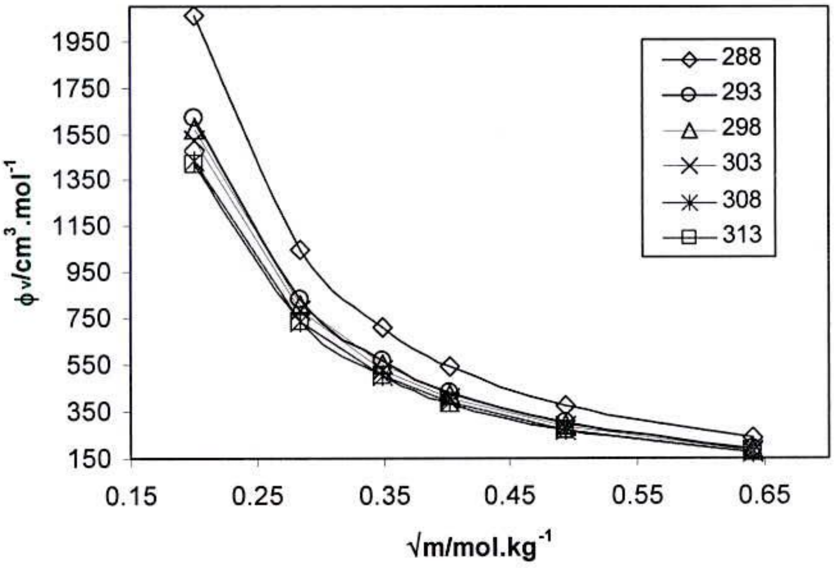

Figure- 4.20 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for NH_4-Cl in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

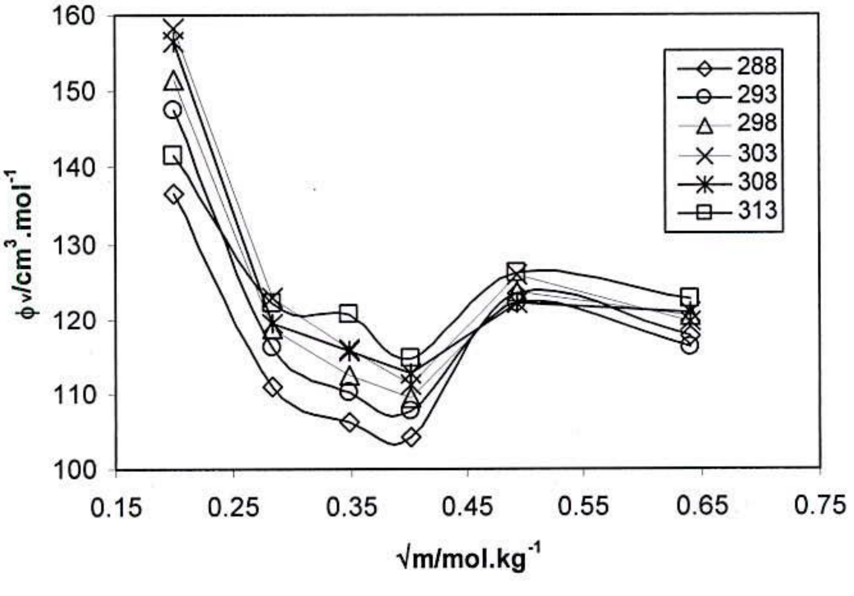

Figure- 4.21 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for $NiCl_2$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

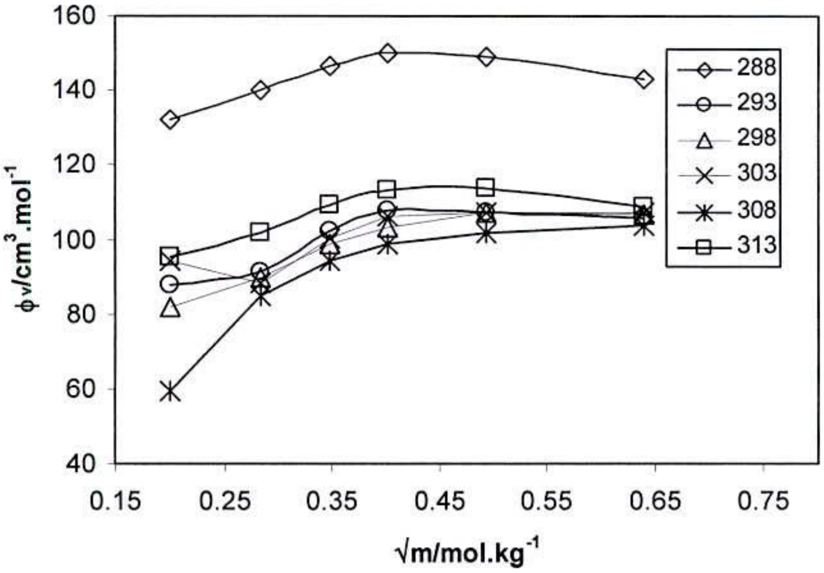

Figure- 4.22 Plots of Apparant molal volume (φ_v) vs square root of molality ($\sqrt{m}$) for $NiCl_2$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

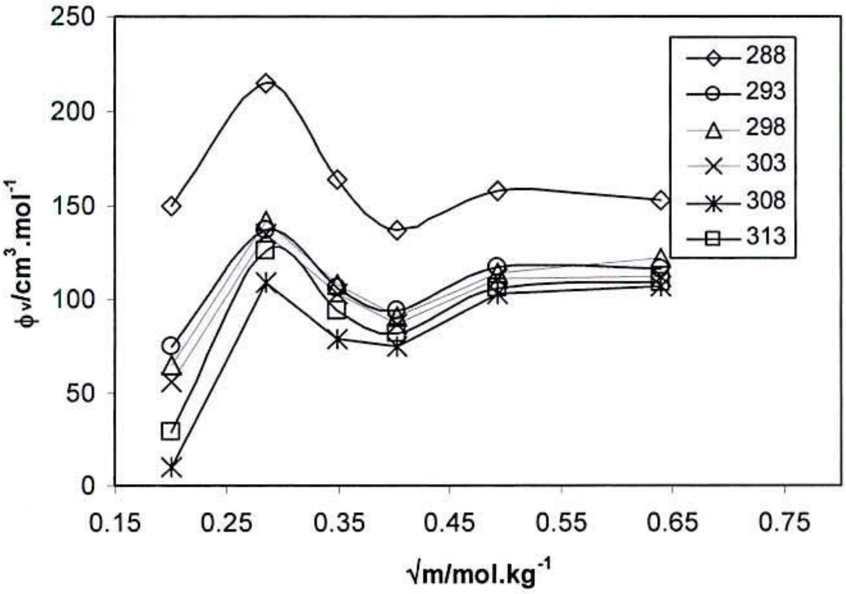

Figure- 4.23 Plots of Apparant molal volume (φ_v) vs square root of molality ($\sqrt{m}$) for $NiCl_2$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

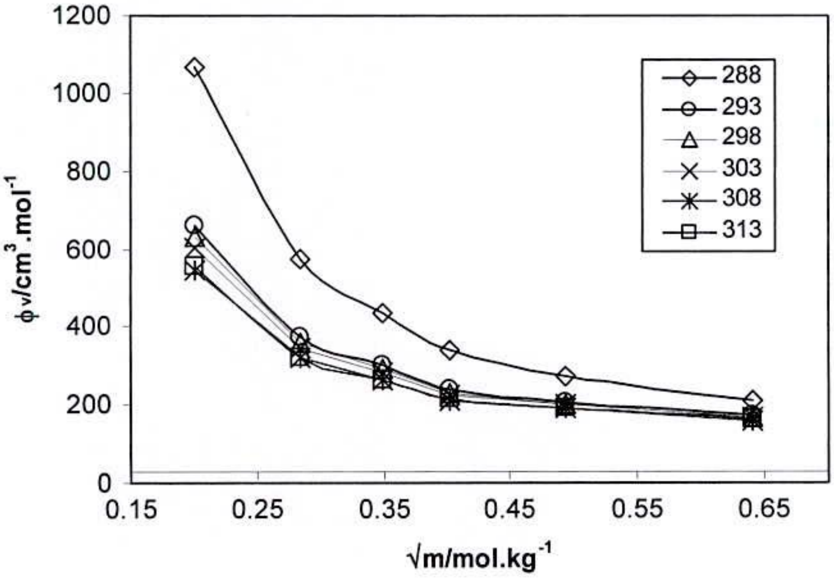

Figure- 4.24 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for $NiCl_2$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

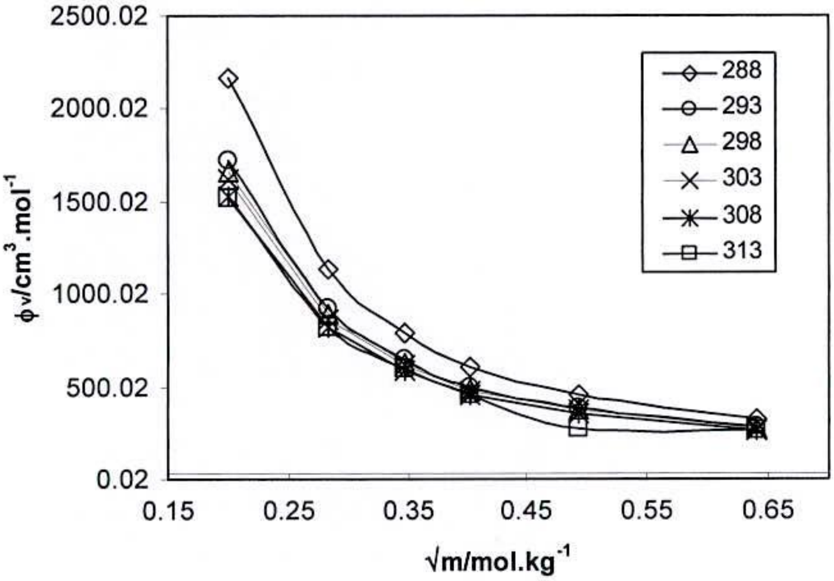

Figure- 4.25 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for $NiCl_2$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

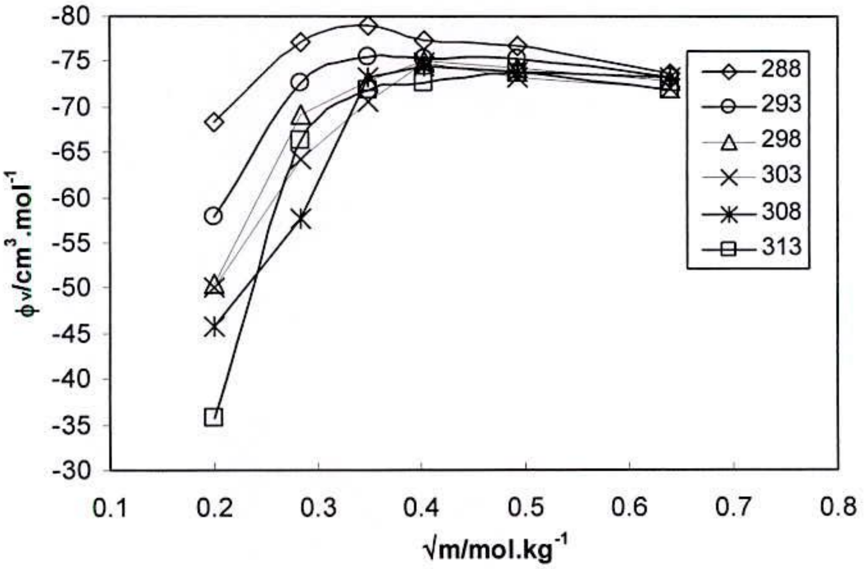

Figure- 4.26 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for $FeCl_3$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

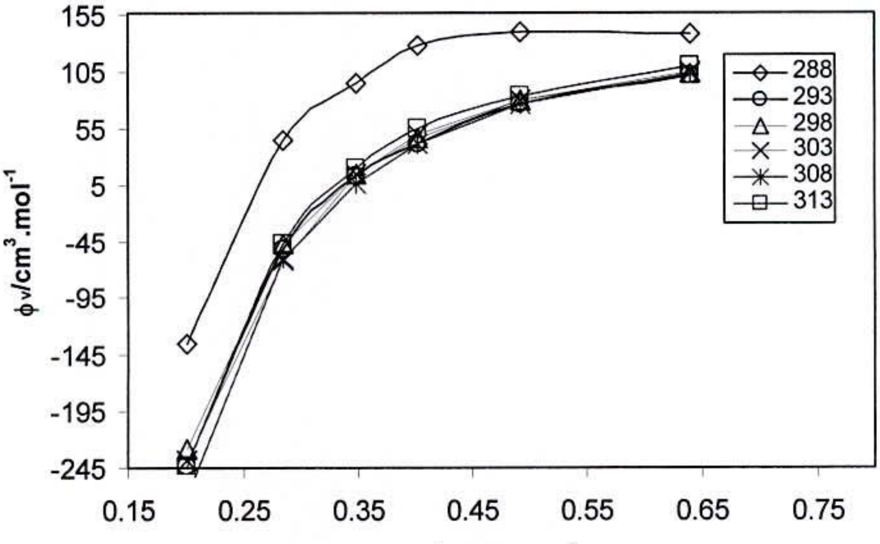

Figure- 4.27 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for $FeCl_3$ n Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

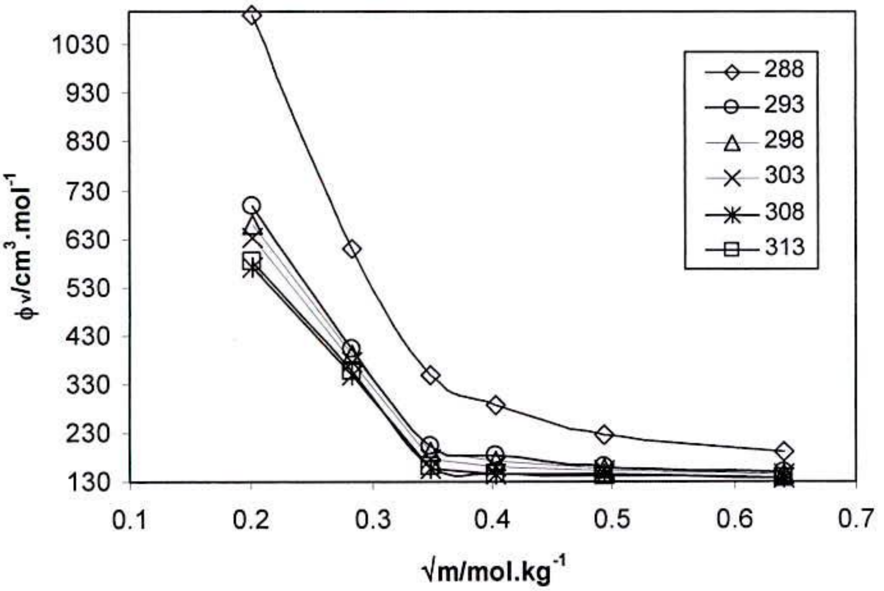

Figure- 4.28 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for $FeCl_3$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

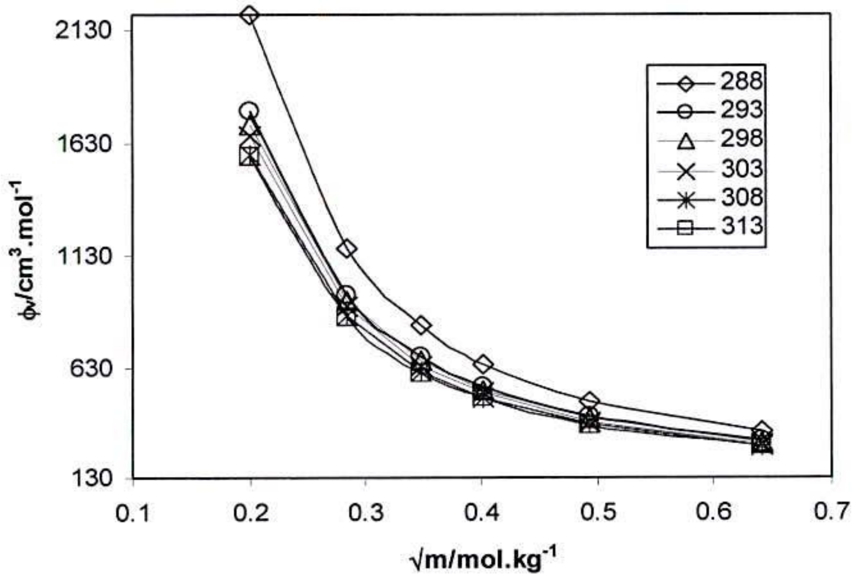

Figure- 4.29 Plots of Apparant molal volume (φ_v) vs square root of molality (√m) for $FeCl_3$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

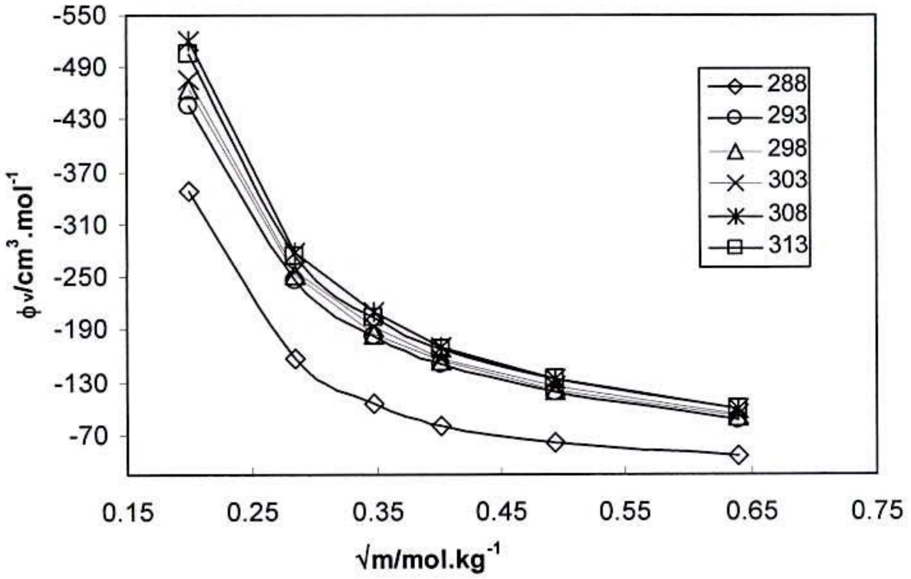

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Figure- 4.30 Plots of Apparant molal volume (φ_v) vs square root of molality ($\sqrt{m}$) for $FeCl_3$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

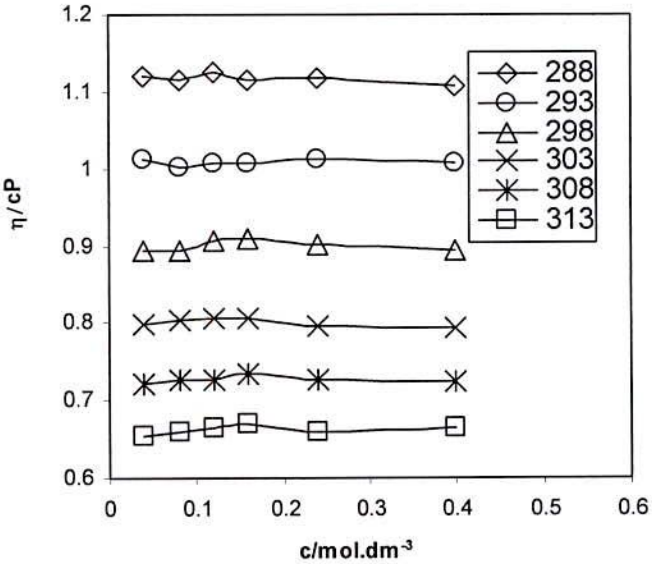

Figure- 4.31 Plots of Viscosities (η) vs molarity (c) for NH_4Cl in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

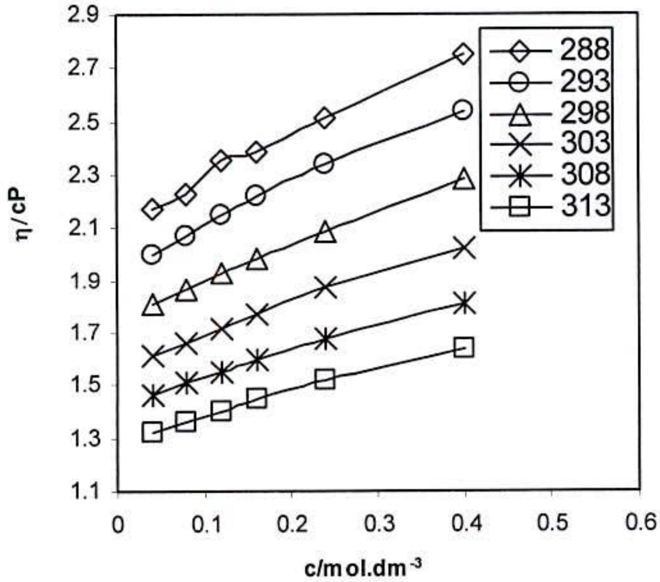

Figure- 4.32 Plots of Viscosities (η) vs molarity (c) for NH_4Cl in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

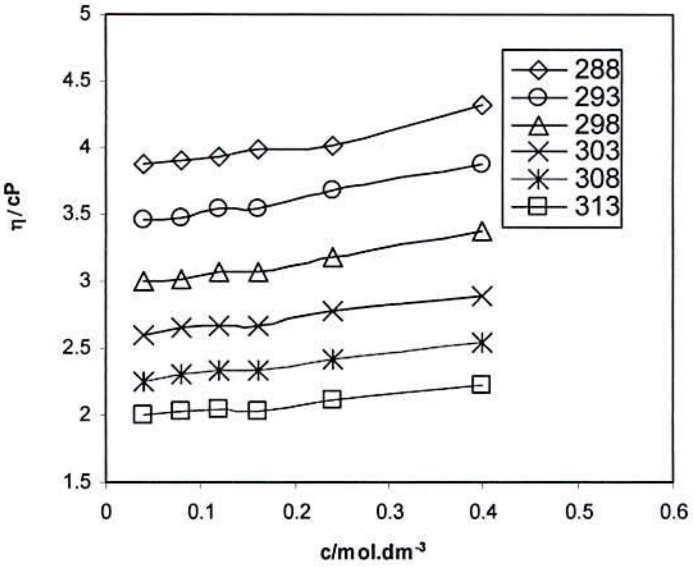

Figure- 4.33 Plots of Viscosities (η) vs molarity (c) for NH_4Cl in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

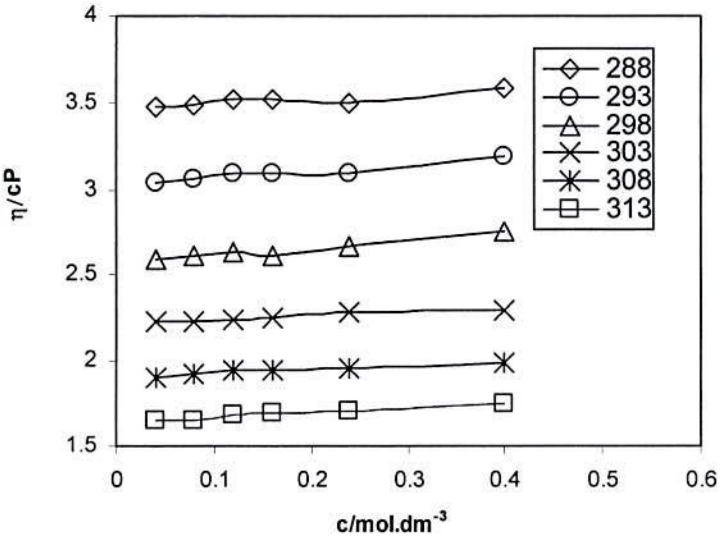

Figure- 4.34 Plots of Viscosities (η) vs molarity (c) for NH_4Cl in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

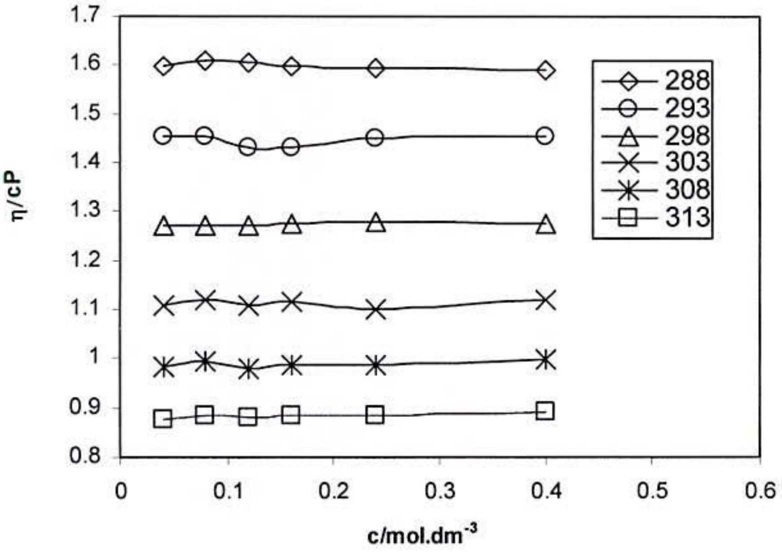

Figure- 4.35 Plots of Viscosities (η) vs molarity (c) for NH_4Cl in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

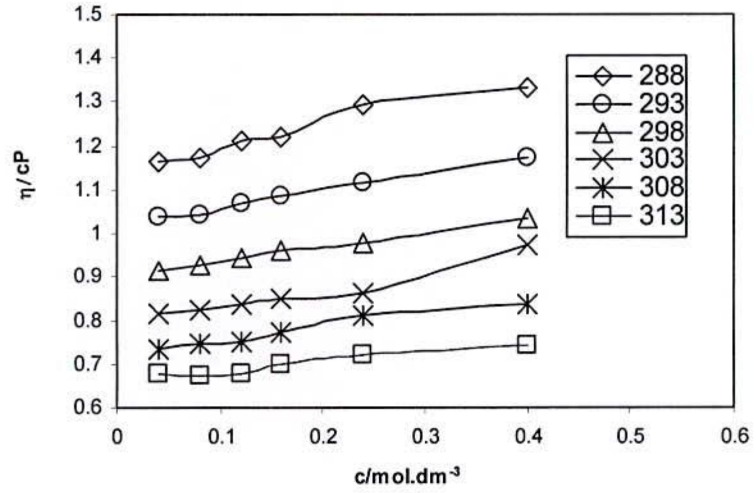

Figure- 4.36 Plots of Viscosities (η) vs molarity (c) for $NiCl_2$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

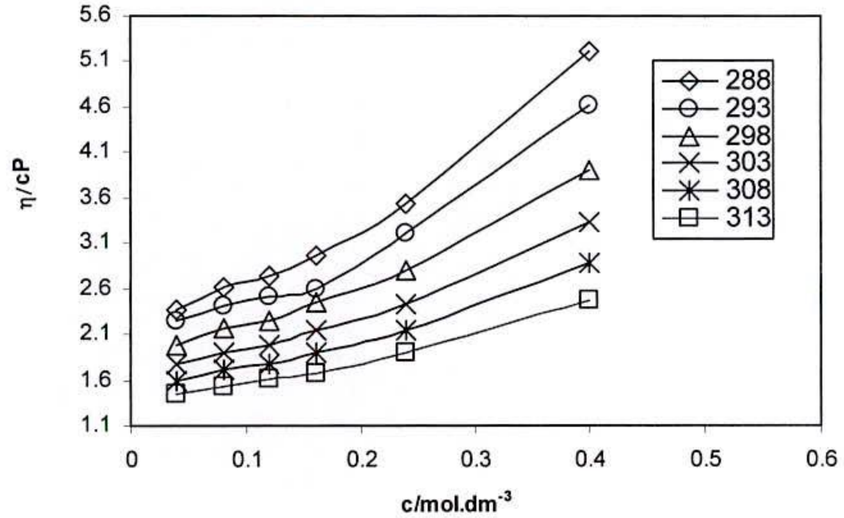

Figure- 4.37 Plots of Viscosities (η) vs molarity (c) for $NiCl_2$ in Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

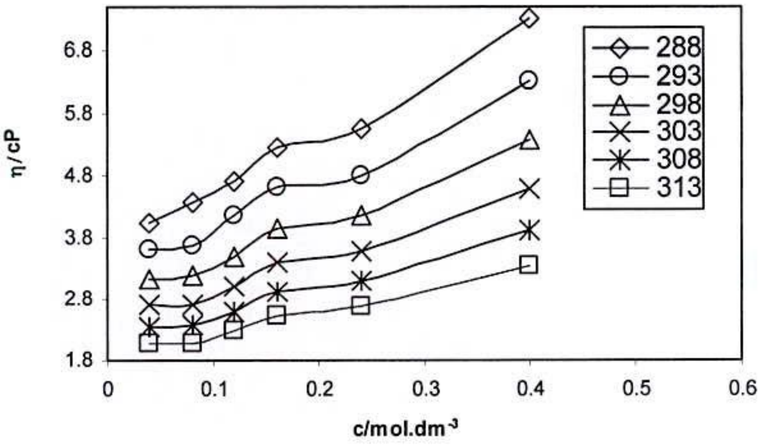

Figure- 4.38 Plots of Viscosities (η) vs molarity (c) for $NiCl_2$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

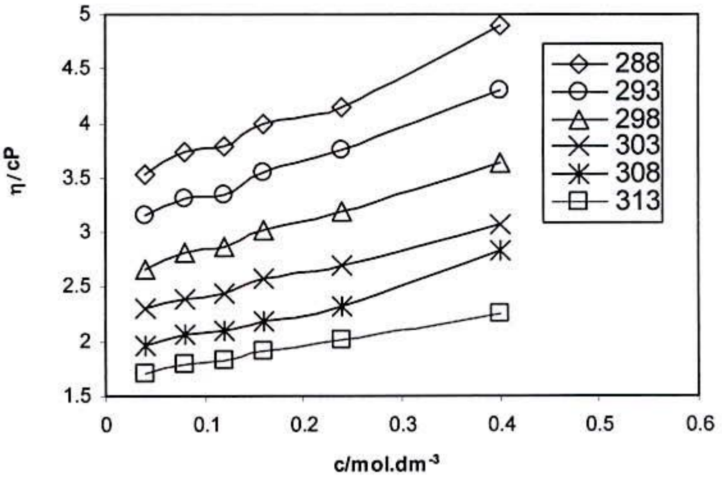

Figure- 4.39 Plots of Viscosities (η) vs molarity (c) for $NiCl_2$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

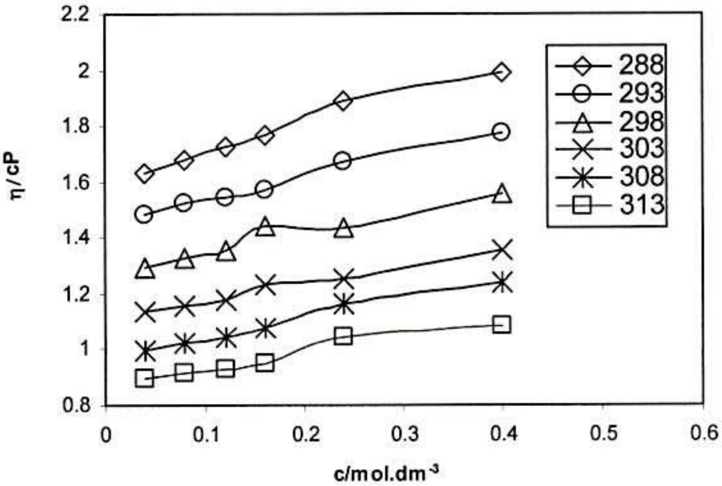

Figure- 4.40 Plots of Viscosities (η) vs molarity (c) for $NiCl_2$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

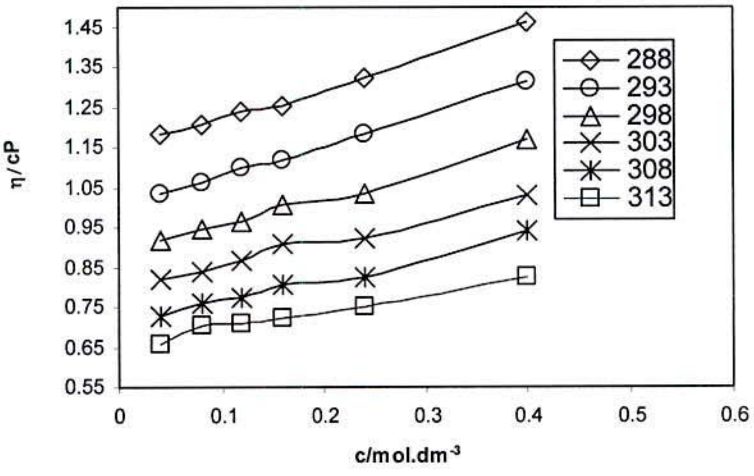

Figure- 4.41 Plots of Viscosities (η) vs molarity (c) for $FeCl_3$ in water solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

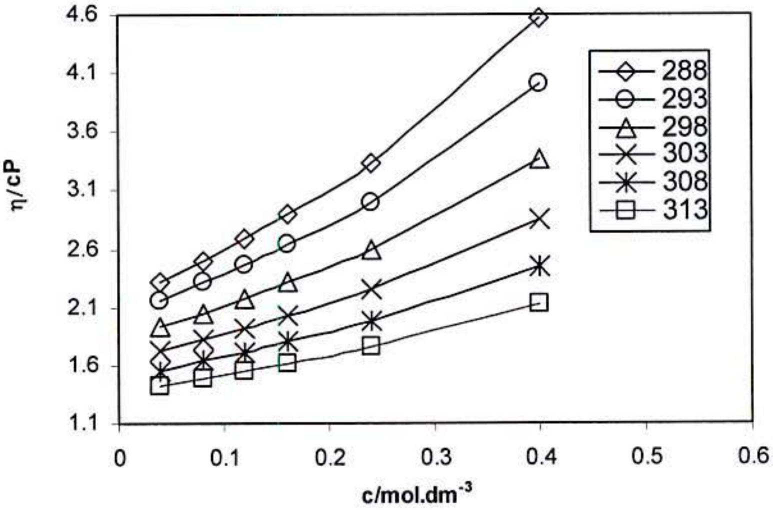

Figure- 4.42 Plots of Viscosities (η) vs molarity (c) for $FeCl_3$ n Pure DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

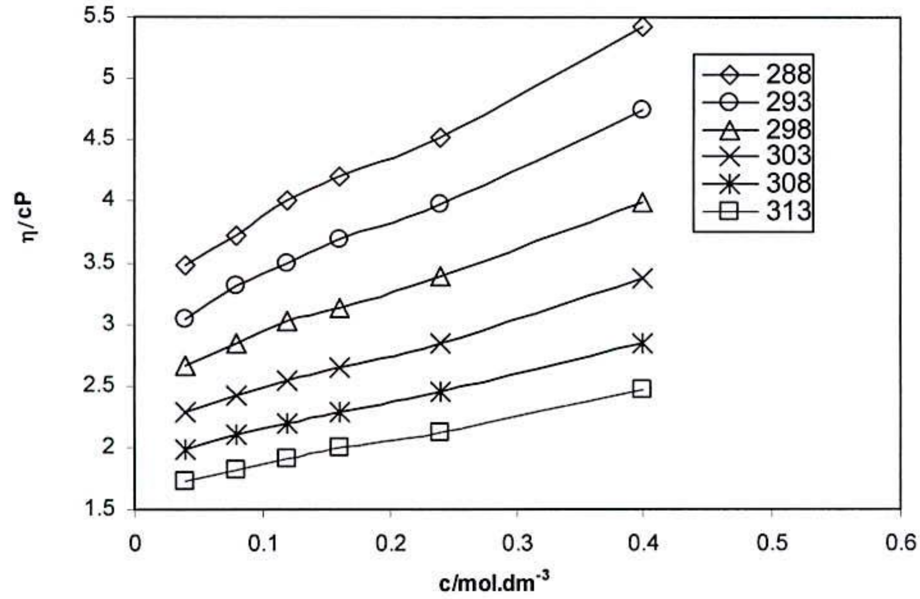

Figure- 4.43 Plots of Viscosities (η) vs molarity (c) for $FeCl_3$ in 50% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

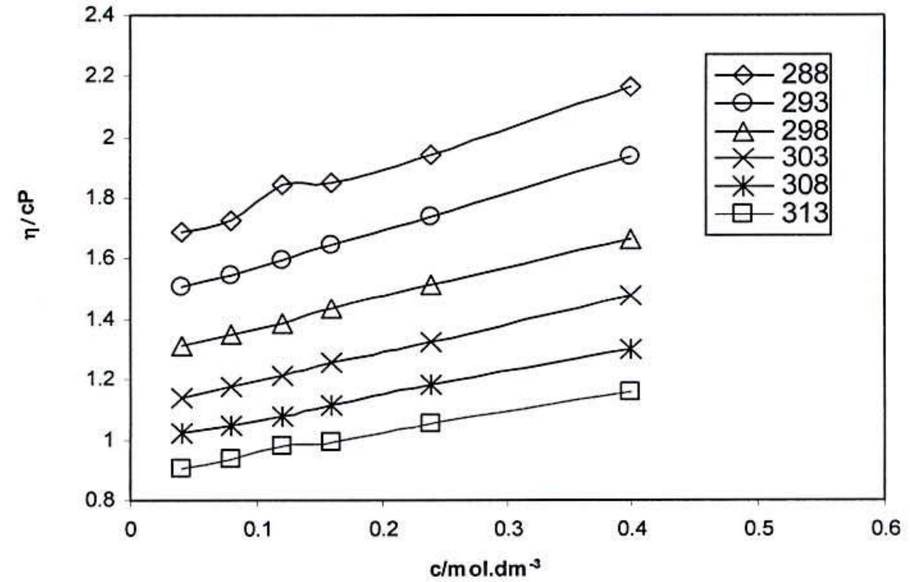

Figure- 4.44 Plots of Viscosities (η) vs molarity (c) for $FeCl_3$ in 20% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

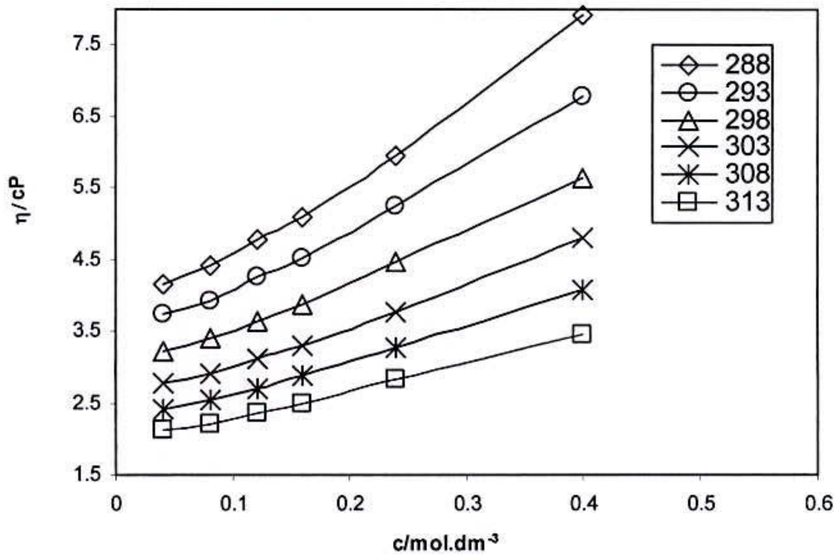

Figure- 4.45 Plots of Viscosities (η) vs molarity (c) for $FeCl_3$ in 80% DMSO solutions at 288 K, 293 K, 298 K, 303 K, 308 K and 313 K, respectively.

Conclusion

Volumetric and viscometric properties of some simple electrolytes e.g., NH_4Cl, $NiCl_2$ and $FeCl_3$ were studied in aqueous and aqueous DMSO. All the electrolytes are found to be dissolved readily in water but that of it was limited in DMSO and aqueous DMSO. Some interesting solution properties of these electrolytes were observed as follows:

(i) Both the volumetric and viscometric properties are depended upon electrolyte concentration as well as on the temperature.

(ii) The limiting apparent molal volume (φ_v^0) and the B coefficient value for all three electrolytes are greater in aqueous DMSO solutions than these in aqueous solutions indicating that these electrolytes induce aqueous DMSO solutions more structured than aqueous solutions.

(iii) $NiCl_2$ and $FeCl_3$ are more structured than NH_4Cl in aqueous and aqueous DMSO solutions. This is probably due to the higher charge to radius ratio of Ni^{+2} and Fe^{3+} than that of NH_4^+.

(iv) The apparent molal volumes, φ_v for $FeCl_3$ were found to be higher at very lower concentration then it was almost unchanged with square root of molality both in aqueous and aqueous DMSO solution.

(v) The structure making property of DMSO and electrolytes for water may take out from interaction zone of the protein enzyme, thereby inducing protein-protein interaction and hence denaturation of the protein/enzymes.

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List of the symbols and abbreviations

Symbols/Abbreviations	Explanation
DMSO	Dimethyl sulfoxide
β	Bita co-efficient
φ_v	The apparent molal volume
φ_v^0	The limiting apparent molal volume
η	Viscosity
A and B	Viscosity co-efficient
σ	sigma
Å	Amngstrung
t^+	Transport number of cation
t^-	Transport number of cation
λ_i	Ionic conductance
λ_i^0	Limiting ionic conductance
CTTS	Charge Transfer to Solvent
δ	Delta
c	Molarity
n_2	Number of moles of solute
a	weight of solute in gram
M_2	Molecular mass of solute in gram
v_1	volume of solvent in mL.
ρ_0	Density of Solvent in gm^{-3}
$\bar{v}_1^0$	Molal volume of the pure solvent
w_e	Weight of empty pycnometer
w_0	Wight of the pycnometer with solvent
w	Weight of the pycnometer