

**ION ASSOCIATION AND SOLVATION OF ALKALI
METAL AND TETRAALKYLMONIUM IONS IN
N,N-DIMETHYLACETAMIDE AND AMIDE-WATER
MIXED SOLVENTS**

**THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF
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CHAPTER I

SCOPE AND OBJECT OF THE WORK

Fundamental research on non-aqueous electrolyte solutions has catalysed their wide technical applications in many fields. Non-aqueous electrolyte solutions are actually competing with other ion conductors, especially at ambient and at low temperatures, due to their high flexibility based on the choice of numerous solvents, additives and electrolytes with widely varying properties. High-energy primary and secondary batteries, wet double-layer capacitors and supercapacitors, electrodeposition and electroplating are some devices and processes for which the use of non-aqueous electrolyte solutions has brought the biggest success.¹⁻⁴ Other fields where non-aqueous electrolyte solutions are broadly used include electrochromic displays and smart windows, photochemical cells, electromachining, etching, polishing and electrosynthesis. In spite of wide technical applications, our understanding of these systems at a quantitative level is still not clear. The main reason for this is the absence of detailed information about the nature and strength of ion-molecular interactions and their influence on structural and dynamic properties of non-aqueous electrolyte solutions.

Apart from this, there lies a close resemblance of certain non-aqueous solvents with some biomolecules which help building up the larger part of the animal body. In particular solvents like tertiary amides offer great interest for biochemists because they are related to structural problems in molecular biology.⁵ The results obtained from the study of different electrolytes in these solvents help

us to understand the role and nature of interaction of biological macromolecules in living organism.

The proper understanding of ion-solvent interactions at a quantitative level is required for analyzing the different phenomena associated with non-aqueous solution chemistry.⁶⁻⁸ An extensive study in aqueous, non-aqueous and mixed solvents makes one thing clear that due to the presence of ion-solvent interaction majority of solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, like water, is substantially modified by the presence of solutes.^{9,10}

In this context, it is apparent that the real understanding of the ion-solvent interactions is a difficult task as the aspect embraces a wide range of topics. But this dissertation would like to concentrate on the measurements of transpsort properties like viscosity and conductivity, spectroscopic properties like FT-Raman and FTIR along with such thermodynamic properties as apparent and partial molar volumes and apparent molar adiabatic compressibility.

1.1 CHOICE OF THE SOLVENTS USED

Solvents containing the amide functional group constitute an important tool in the interpretation of complex molecules of biological interest because they possess the very common in nature donor – acceptor – CO-NH – peptide bond and also display the property of self-association by the H-bond.⁵

N,N-dimethylacetamide (DMA), one of the members of tertiary amide series has drawn much attention as a solvent medium for various biochemical and electrochemical investigations in recent years.⁵ It is a dipolar aprotic solvent with dielectric constant of 37.78 at 298.15K.¹¹ It also has unique solvating properties associated with its hydrogen-bonding network.⁵ We have done a series of investigations on N,N-dimethylacetamide to study the structure of ions and their mutual and specific interactions with solvent molecules by studying the transport and thermodynamic properties of some selected electrolytes in this medium.

In our investigations we have included one unsubstituted amide formamide (FA) and a disubstituted amide N,N-dimethylformamide (DMF) as an organic component for the binary mixture with DMA. Formamide has a relatively high dielectric constant ($\epsilon = 109.5$ at 298.15K)¹¹. It is a dipolar protic solvent with a dipole moment of 3.73D at 298.15K.¹¹ On the other hand, DMF is a dipolar aprotic solvent with a quite large dipole moment ($\mu = 3.28D$ at 298.15K)¹¹ and a moderately high dielectric constant ($\epsilon = 37.5$ at 298.15K)¹¹. Due to the large dipole moment DMF has high solvating power with respect to a lot of organic and inorganic substances and is also miscible with almost all common polar and non-polar solvents. 2-ethoxyethanol, commercially known as 'cellosolve' is also used as a component for the binary mixture with DMA. The cellosolves can also form intramolecularly hydrogen-bonded five membered ring monomers.¹² The solvent has a density 0.9252 g.cm⁻³ and a refractive index 1.4057 at 298.15K.¹³ In view of its

property and structure, the 2-ethoxyethanol is often regarded as ‘quasi-aprotic’ solvent.¹² More information about these solvents are given in the chapters.

1.2 SCOPE OF THE WORK

The object of the present work is therefore to elucidate the nature of various interactions of some common alkali and tetraalkylammonium salts in N,N-dimethylacetamide from volumetric, viscometric, conductometric, interferometric, FTIR and FT-Raman spectral measurements. Conductometric measurements of some alkali metal salts also have been done in aqueous binary mixture of N,N-dimethylacetamide. The available data have been utilized to examine the solvation phenomena of ions and ion-pairs in this non-aqueous solvent and its aqueous binary mixtures. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity.

Our further objective is to study the interaction between N,N-dimethylacetamide (DMA) and a protic solvent, formamide (FA), as well as dipolar aprotic solvent, N,N-dimethylformamide (DMF) and a quasi-aprotic solvent 2-ethoxyethanol (EE).

1.3 METHODS OF INVESTIGATIONS

The phenomenon of ion-solvent interactions and solvation is intriguing. It is desirable to attack this problem using different experimental techniques. We have, therefore, employed five important methods, namely, conductometry, viscometry,

densitometry, ultrasonic interferometry and spectrophotometry to probe the problem of solvation phenomena.

Thermodynamic properties, like partial molar volumes obtained from density measurements, are generally convenient parameters for interpreting solute-solvent and solute-solute interactions in solution. The compressibility, a second derivative of Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information in such cases where partial molar volume data alone cannot provide an unequivocal interpretation of these interactions.

The change in solvent viscosity by the addition of electrolyte solutions is attributed to interionic and ion-solvent effects. The B-coefficients are also separated into ionic components by the "reference electrolyte" method and from the temperature dependence of ionic values, a satisfactory interpretation of ion-solvent interactions such as the effects of solvation, structure breaking or structure making, polarization, etc, may be given.¹⁴

The transport properties in most cases are studied using the conductance data, especially the conductance at infinite dilution. Conductance data obtained as a function of concentration can be used to study the ion-association with the help of appropriate equations.

1.4 A SUMMARY OF THE WORK DONE

This dissertation consists of nine chapters, including the present one which is chapter I.

Chapter II gives a general background to the area of the present work. It presents a brief review of significant works done earlier in the field of solvation phenomena and ion-solvent interactions. Beginning with a short note on the importance of solution chemistry, it discusses viscosity and conductance studies, ion association together with single-ion conductance values, apparent and partial molar volumes and also ultrasonic velocity measurements, in more detail. It also contains a brief note on the recent research in these areas and ends with an account of the notable earlier works done on the solvents investigated, namely, N,N-dimethylacetamide, formamide, N,N-dimethylformamide and 2-ethoxyethanol.

Chapter III details the information about the various chemicals used, their methods of preparation and purification, and a brief description of the experimental techniques employed.

Chapter IV presents the conductance, density and ultrasonic sound velocity measurements and FT-Raman, FTIR spectral analysis of alkali metal salts in pure DMA at 298.15 K. The conductance data have been analysed by the 1978 Fuoss conductance equation. From the density and ultrasonic sound velocity measurements apparent molar volumes (ϕ_v) and limiting apparent molar volume (ϕ_v°), apparent molar adiabatic compressibility (ϕ_k) and its limiting value (ϕ_k°) have

been calculated. The results are interpreted in terms of ionic association of these salts and electrostriction of the solvent molecules and their influence on the compressibility of the medium.

Chapter V deals with the electrical conductances and viscosities of some tetraalkylammonium and alkali metal salts in pure DMA at 298.15K. The viscosity data have been analysed by the Jones-Dole equation to evaluate the viscosity B-coefficients of the electrolytes. The densities and ultrasonic sound velocities of the salts and solvent have been mentioned at 298.15K. Apparent molar volumes (ϕ_v) and apparent molar adiabatic compressibilities (ϕ_k) are derived from these data supplemented by their densities and sound velocities. The limiting values ϕ_v° and ϕ_k° and the experimental slopes S_v and S_k have been interpreted in terms of ion-solvent and ion-ion interactions respectively. Use has been made of the non-thermodynamic, so called extrapolation method to split the limiting apparent molar volumes into ionic contributions.

Chapter VI describes the studies on the conductances of alkali metal salts in aqueous binary mixture of DMA at 25°C. The data have been analysed by the 1978 Fuoss conductance equation and the characteristic parameters Λ° , K_A and R have been evaluated. The single-ion conductances have been determined using the "reference electrolyte" method.

Chapter VII describes conductivity, viscosity, density and ultrasonic sound velocity measurement of some tetraalkylammonium salts in aqueous binary mixture

of DMA at 298.15K. Various thermodynamic parameters derived from these measurements are interpreted in terms of ion-ion and ion-solvent interactions.

Chapter VIII analyses the excess molar volumes, viscosity deviations of N,N-dimethylacetamide and formamide, on the one hand, and, of N,N-dimethylacetamide and N,N-dimethylformamide, on the other. The chapter also includes isentropic compressibility, density, viscosity, intermolecular free length, acoustic impedance molar sound speed and some of their respective excess properties in the binary mixtures of N,N-dimethylacetamide with 2-ethoxyethanol. The data obtained are interpreted in terms of specific/general interactions between the solvent molecules.

Chapter IX contains some concluding remarks.

References :

1. (a) Y.Marcus, *Ion Solvation*, Wiley-Interscience, Chichester, 1986.
(b) Y. Marcus, *Ion Properties*, Dekker, New York, 1997.
2. A. Marquez, A. Vargas and P.B.Balbuena, *J. Electrochem. Soc.*, **45**, 3328, 1998.
3. A.F.D.Namor, M.A.L.Tanaco, M.Salomon and J.C.Y.Ng, *J.Phys.Chem.*, **98**, 11796, 1994.
4. Y.Matsuda and H.Satake, *J.Electroanal. Chem.*, **127**, 877, 1980.
5. B.Garcia, R.Alcalde and J.M.Leal, *J.Phys. Chem.*, **101**, 7991, 1997.
6. O.Popovych and R.P.T.Tomkins, Nonaqueous Solution Chemistry, Wiley-Interscience, New York, 1981.
7. A. Chandra and B.Bagchi, *J.Phys.Chem. B.*, **104**, 9067, 2000.
8. G.Atkinson, R. Garnsey and M.J.Taft, in Hydrogen Bonded Solvent Systems, Eds. A.K.Covington and P. Jones, Taylor and Francis Ltd., London, 1968.
9. R.G.Bates, *J.Electroanal. Chem.*, **29**, 1, 1971.
10. K. Gunaseelan, S.Dev and K.Ismail, *Ind.J.Chem.*, **39A**, 761, 2000.
11. Physical Chemistry of Organic Solvent Systems, Eds. A.K.Covington and T.Dickinson, Plenum Press, New York, 1973, p.4.
12. H. Piekarski and M. Tkaczyk, *J. Chem. Soc. Faraday Trans.*, **91**, 2299, 1995.
13. M.I.Aralaguppi, C.V.Jadar and T.M.Aminabhavi, J.D.Ortego, S.C.Mehrotra, *J.Chem.Eng. Data*, **42**, 301, 1997.
14. B.Das and D.K.Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470, 1992.

CHAPTER II

GENERAL INTRODUCTION

2.1 THE IMPORTANCE OF SOLUTION CHEMISTRY

One of the interesting facts of solution chemistry is that the exact structure of the solvent molecule in a solution is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an extent whereas the solute molecules are also modified. The interactions between solute and solute, solute and solvent, and solvent and solvent molecules and the resulting ion-solvation becomes predominant. The assessment of ion pairing in these systems is important because of its effect on the ionic conductivity and hence the mobility of the ions in solution. This explains the spurt in research in solution chemistry to elucidate the exact nature of these interactions through experimental studies involving conductometry, viscometry, densitometry, spectroscopy, ultrasonic interferometry and other suitable methods and to interpret the experimental data collected.¹⁻⁸

The behaviour of electrolytes in solution depends mainly on ion-ion and ion-solvent interactions. The former interaction, in general, is stronger than the latter. Ion-ion interaction in dilute electrolyte solutions is now theoretically well understood, but the ion-solvent interaction or ion-solvation still remains a complex process.

In the last few decades, considerable emphasis has been placed on research in the behaviour of electrolytes in non-aqueous and mixed solvents to investigate the

ion-ion (solute-solute) and ion-solvent interactions under varied conditions. Different sequences of solubility, differences in solvating power and possibilities of chemical or electrochemical reactions unfamiliar in aqueous chemistry have opened new vistas for physical chemists and interest in these organic solvents transcends traditional boundaries of inorganic, organic, physical, analytical and electrochemistry.⁹

In ion-solvation studies, broadly three types of approaches have been made to estimate the extent of solvation. The first is the solvational approach involving the studies of viscosity, conductance, etc., of electrolytes and the derivation of various factors associated with ionic solvation,^{10,11} the second is the thermodynamic approach by measuring the free energies, enthalpies and entropies of solvation of ions from which factors associated with solvation can be elucidated,^{12,13} and the third is to use spectroscopic measurements where the spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature.¹⁴⁻¹⁶

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation is intimately related to the studies of viscosities, conductances, ultrasonic velocities and spectroscopic properties of some important electrolytes in N,N-dimethylacetamide and its aqueous binary mixture. It also includes the study of excess properties of the binary mixtures of N,N-dimethylacetamide (DMA) with formamide (FA), N,N-dimethylformamide(DMF) and 2-ethoxyethanol (EE) at three different temperatures.

2.2 VISCOSITY

Although viscosity is not a thermodynamic property, together with the partial molal volume V_2 , it gives much information regarding the ion-solvent interactions, structures of electrolytic solutions and solvation. Jones and Dole¹⁷ suggested the first quantitative empirical relation correlating the relative viscosities (η_r) of the electrolytes and their molar concentrations (c) :

$$\eta_r = 1 + Ac^{\frac{1}{2}} + Bc \quad (1)$$

The equation reduces to

$$(\eta_r - 1)/c^{\frac{1}{2}} = A + B c^{\frac{1}{2}} \quad (2)$$

where A and B are constants specific to ion-ion and ion-solvent interactions respectively. The equation is equally applicable to aqueous and non-aqueous systems where there is no ion-association. The term $A c^{\frac{1}{2}}$, arose from the long range coulombic forces between the ions. The significance of the term has since been realized due to the development of Debye-Hückel theory¹⁸ of interionic attractions, Falkenhagen's theoretical calculations of 'A' using the equilibrium theory^{19,20} and the theory of irreversible processes in electrolytes developed by Onsager and Fuoss.²¹

For associated electrolytes the viscosity data have been analyzed by the following equation²²

$$\eta_r = 1 + A(\alpha c)^{\frac{1}{2}} + B\alpha c + B'(1 - \alpha)c \quad (3)$$

Here A, B and B' are the characteristic constants and α is the degree of dissociation of the ion pair.

Eq. (3) can be rearranged to give

$$[\eta_r - 1 - A(\alpha c)^{1/2}] / \alpha c = B + B' (1-\alpha)/\alpha \quad (4)$$

The values of α were calculated from the conductance data using the equations described in the literature.²²

The 'A' coefficient depends on the ion-ion interactions and can be calculated using the Falkenhagen-Vernon equation.²⁰

$$A_{\text{theo}} = \frac{0.2577 \Lambda^\circ}{\eta_0 (\epsilon T)^{1/2} \lambda_+^\circ \lambda_-^\circ} \left[1 - 0.6863 \left(\frac{\lambda_+^\circ - \lambda_-^\circ}{\Lambda^\circ} \right)^2 \right] \quad (5)$$

where Λ° , λ_+° and λ_-° are the limiting conductances of the electrolyte, cation and anion respectively, at temperature T, ϵ is the dielectric constant and η_0 is the viscosity of the solvent. For most solutions this equation is valid upto 0.1M.^{23,24}

2.2.1 Division of B-Coefficients into Ionic Values

In order to identify the separate contributions of cations and anions to the total solute-solvent interactions, the B-coefficients as determined by Jones-Dole's equation has to be resolved into ionic components. For this Cox and Wolfenden,²⁵ Gurney,²⁶ Sacco *et al.*²⁷ Tuan and Fuoss,²⁸ and several authors used different approximations and assumptions for different systems. For example, Sacco *et al.*²⁷

proposed the widely used 'reference electrolyte' method. Thus, for Ph_4PBPh_4 in water, we have,

$$B_{\text{BPh}_4} = B_{\text{PPH}_4^+} = B_{\text{Ph}_4\text{PBPh}_4} / 2 \quad (6)$$

$B_{\text{Ph}_4\text{PBPh}_4}$ is obtained from,

$$B_{\text{Ph}_4\text{PBPh}_4} = B_{\text{NaBPh}_4} + B_{\text{Ph}_4\text{PBr}} - B_{\text{NaBr}} \quad (7)$$

(since Ph_4PBPh_4 is scarcely soluble in water). These values are in good agreement with those obtained by other methods.

However, according to Krumgalz²⁹ it is impossible to select any two ions for which $\lambda_+^\circ = \lambda_-^\circ$ in all solvents and at proper temperatures. Also, even if the mobilities of some ions are equal at infinite dilution, they are not necessarily equal at moderate concentrations. Further, equality of ionic dimensions does not necessarily imply equality of B-coefficients of these ions, as they are likely to be solvent and ion-structure dependent.

Krumgalz proposed a method³⁰ based on the fact that the large tetraalkyl-ammonium ions are not solvated in organic solvents. So, the ionic B-values for large R_4N^+ ions (where $\text{R} \geq \text{Bu}$) in organic solvents are proportional to their ionic dimensions.

$$B_{\text{R}_4\text{NX}} = a + b r^3_{\text{R}_4\text{N}^+} \quad (8)$$

where, $a = B_x^-$ and b is a constant independent of temperature and solvent nature. Extrapolation of the plot of B_{R_4NX} ($R > \text{Pr or Bu}$) against $r^3_{R_4N^+}$ to zero cation dimension gives B_x^- directly in the proper solvent from which other ionic B-values can be calculated.

Ionic B-values can also be calculated from the following equations :

$$B_{R_4N^+} - B_{R'_4N^+} = B_{R_4NX} - B_{R'_4NX} \quad (9)$$

and

$$B_{R_4N^+}/B_{R'_4N^+} = r^3_{R_4N^+}/r^3_{R'_4N^+} \quad (10)$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductance data.³¹

On similar reasoning, Gill and Sharma³² used Bu_4NBPh_4 as the reference electrolyte and proposed the equation.

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \frac{r^3_{\text{Ph}_4\text{B}^-}}{r^3_{\text{Bu}_4\text{N}^+}} = \left[\frac{5.35}{5.00} \right]^3 \quad (11)$$

and

$$B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{N}^+} + B_{\text{Ph}_4\text{B}^-} \quad (12)$$

because the ionic radii of Bu_4N^+ (5.00 Å) and of Ph_4B^- (5.35 Å) have been found to remain constant in different non-aqueous and mixed non-aqueous solvents. Lawrence and Sacco^{33,34} used Bu_4NBBu_4 and Ph_4PBPh_4 as reference electrolytes because these cations and anions are symmetrically shaped and have almost equal van der Waals volumes. Their results and the conclusions of Thomson *et al*³⁵ agreed well with the reported values.

It is obvious that most of these methods are based on certain approximations and anomalous results may arise unless proper mathematical theories are developed to calculate B-values.

2.2.2 Thermodynamics of Viscous Flow

Feakins *et al*³⁶ suggested the following expression

$$B = \frac{\bar{V}_1^\circ - \bar{V}_2^\circ}{1000} + \frac{\bar{V}_1^\circ}{1000} \left[\frac{\Delta\mu_2^{\circ\#} - \Delta\mu_1^{\circ\#}}{RT} \right] \quad (13)$$

where \bar{V}_1° and \bar{V}_2° are the partial molal volumes of the solvent and solute respectively, $\Delta\mu_1^{\circ\#}$ is the free energy of activation for viscous flow per mole of the solvent and $\Delta\mu_2^{\circ\#}$ is the contribution per mole of solute to the free energy of activation for the viscous flow of the solution.

2.2.3 Effects of Shape and Size

Stokes and Mills²³ regarded the ions in solution as rigid spheres suspended in a continuum and proposed an equation for relative viscosity as

$$\eta/\eta_0 = 1 + 2.5 \phi \quad (14)$$

where ϕ is the volume of the fraction occupied by the particles. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monatomic cation). Thus combining the above equation with Jones-Dole equation (1), we have

$$2.5 \phi = Ac^{1/2} + Bc \quad (15)$$

Neglecting $Ac^{1/2}$ in comparison with Bc , and substituting $\phi = c\bar{V}_i$ where \bar{V}_i is the partial molal volume of the solute, we get

$$2.5 \bar{V}_i = B \quad (16)$$

Assuming that the ions behave like rigid spheres with effective radii R_{\pm} , moving in a continuum, B_{\pm} , can be equated to

$$B_{\pm} = 2.5 V_{\pm} = 2.5 \times 4/3 \pi (R_{\pm}^3 N/1000) \quad (17)$$

R_{\pm} calculated using eqn (17) should be close to crystallographic radii or corrected Stokes' radii if the ions are scarcely solvated and behave as spherical entities. But R_{\pm} values of the ions, which are higher than the crystallographic radii indicate solvation.

The number (n) of solvent molecules bound to the ion in the primary solvation shell can be calculated by comparing the Jones-Dole equation with that of Einstein³⁷

$$B_{\pm} = 2.5 (V_i + n V_s) / 1000 \quad (18)$$

Where V_i is the bare ion molar volume and V_s the molar volume of the solvent. The above equation has been used by a number of workers³⁸⁻⁴¹ to study the nature of solvation.

2.3 CONDUCTANCE

Conductance measurement is one of the most accurate and widely used physical methods for investigating the electrolytic solutions.^{42,43} Together with transference number determination, it provides an excellent method for obtaining single ion values. In conjunction with viscosity measurements, conductance data give much information regarding ion-ion and ion-solvent interaction.

Onsager⁴⁴ was the first to successfully apply Debye-Hückel theory of interionic associations. Subsequently, Pitts,⁴⁵ and Fuoss and Onsager^{46,47} independently worked to account for both long and short range interactions. As Pitts' values differed considerably from Fuoss and Onsager's values, Fuoss and Hsia⁴⁸ modified the original Fuoss-Onsager equation. The modified Fuoss-Onsager equation is of the form⁴³

$$\Lambda = \Lambda^o - \frac{\alpha \Lambda^o c^{1/2}}{(1 + \kappa a)} - \frac{\beta c^{1/2}}{(1 + \kappa a)^2} + G(\kappa a) \quad (19)$$

where $G(\kappa a)$ is a complicated function of the variable. The simplified form

$$\Lambda = \Lambda^o - Sc^{1/2} + E c \ln c + J_1 c - J_2 c^{3/2} \quad (20)$$

is generally employed in the analysis of experimental results. Fuoss and Accascina⁴⁶ made further correction of equation(20) taking into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation is

$$\Lambda = \Lambda^o - Sc^{1/2} + E c \ln c + J_1 c - J_2 c^{3/2} - BA^o c \quad (21)$$

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In most cases, however, J_2 is made zero, but this leads to a systematic deviation of the experimental data from the theoretical equations.

2.3.1 Ion - Association

The plot Λ versus $c^{1/2}$ (limiting Onsager equation) is used to determine the dissociation or association of electrolytes. If $\Lambda^{\circ}_{(\text{expt})} > \Lambda^{\circ}_{(\text{theo})}$, the electrolyte may be regarded as completely dissociated but if $\Lambda^{\circ}_{(\text{expt})} < \Lambda^{\circ}_{(\text{theo})}$, the electrolytes may be regarded as associated. The difference between $\Lambda^{\circ}_{(\text{expt})}$ and $\Lambda^{\circ}_{(\text{theo})}$ would be considerable with increasing association.⁴⁹

For strongly associated electrolytes, association constants K_A and Λ° were determined using the Fuoss-Kraus equation⁵⁰ or Shedlovsky's equation.^{51,52}

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda^{\circ}} + \frac{K_A}{(\Lambda^{\circ})^2} \times \frac{c\gamma_{\pm}^2 \Lambda}{T(z)} \quad (22)$$

where, $T(z) = F(z)$ (Fuoss-Kraus) and $1/T(z) = S(z)$ (Shedlovsky)

$$F(z) = 1 - z(1 - z(1 - z(1 - \dots)^{-1/2})^{-1/2})^{-1/2} \quad (23)$$

and

$$S(z) = 1 + z + z^2/2 + z^3/8 + \dots \quad (24)$$

The plot of $T(z) / \Lambda$ against $c\gamma_{\pm}^2 \Lambda / T(z)$ should be a straight line having an intercept of $1/\Lambda^{\circ}$ and a slope of $K_A / (\Lambda^{\circ})^2$. When K_A is large, there will be considerable uncertainty in the values of Λ° and K_A determined from equation.(22)

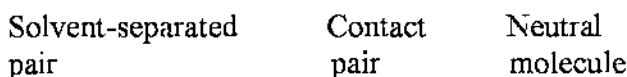
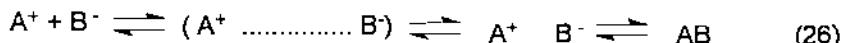
The Fuoss-Hsia conductance equation for associated electrolytes is given as

$$\Lambda = \Lambda^o - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda \gamma_{\pm}^{-2} (\alpha c) \quad (25)$$

The equation was modified by Justice.⁵³

2.3.2 Ion-size Parameter and Ionic Association

In 1978, Fuoss put forward a new conductance equation⁵⁴ replacing the one he had formulated three years earlier. He classified the ions of electrolytic solutions into three categories; (i) those which find an ion of opposite charge in the first shell of the nearest neighbours (contact pairs) with $r_{ij} = a$, (ii) those with overlapping Gurney co-spheres (solvent separated pairs); and (iii) those which find no other unpaired ion in a surrounding sphere of radius R, where R is the diameter of the co-sphere (unpaired ions). Thermal motion and forces establish a steady state, represented by the equilibria



From this equation Fuoss derived an expression for the association constant or conductometric pairing constant

$$K_A = K_R (1 + K_s) \quad (27)$$

where, K_R describes the formation and separation of solvent-separated pairs by diffusion, in and out of the spheres of diameter R around the cations (calculated using the continuum theory), K_s is a constant describing the specific short range ion-solvent and ion-ion interactions by which contact pairs form and dissociate.

The details of the calculations are presented in the 1978 paper. The shortcomings of the previous papers have been rectified in the new set of equations that are more general than the previous ones and can be used in higher concentration regions (0.1 N in aqueous solutions).

For a given set of conductivity values (c_j , Λ_j , $j = 1, \dots, n$), three adjustable parameters, the limiting molar conductivity (Λ°), association constant (K_A), and the co-sphere diameter (R), are derived from the following set of equations :

$$\Lambda = p[\Lambda^\circ (1 + R_x) + E_L] \quad (28)$$

$$p = 1 - \alpha(1 - \gamma) \quad (29)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (30)$$

$$- \ln f = \beta k / 2(I + kR) \quad (31)$$

$$\beta = e^2 / D k_B T \quad (32)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_s) \quad (33)$$

Where R_x is the relaxation field effect, E_L is the electrophoretic countercurrent, k^{-1} is the radius of the ion atmosphere, D is the dielectric constant of the solvent, e is the electron charge, k_B is the Boltzmann constant, γ is the fraction of solute present as unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The computations can be performed on a computer using the programme suggested by Fuoss.

2.3.3 Limiting Ionic Equivalent Conductances

The limiting equivalent conductance (Λ°) can be divided into ionic components using the experimentally determined transport number of ions (t_{\pm}) as follows :

$$\lambda_{\pm}^{\circ} = t_{\pm} \Lambda^{\circ} \text{ and } \lambda_{\mp}^{\circ} = t_{\mp} \Lambda^{\circ} \quad (34)$$

However, accurate transference number determinations are limited to only a few solvents. Hence, various attempts were made to develop indirect methods to obtain the limiting ionic equivalent conductance in ionic solvents for which experimental transference numbers are not yet available. These methods have been well described by Walden,⁵⁵ Fuoss,⁵⁶ and Gill.⁵⁷

Krumgalz,⁵⁸ suggested a new method based on the fact, confirmed by NMR studies, that the large tetraalkyl (aryl) onium ions are not solvated in organic solvents, in the kinetic sense, due to the extremely weak electrostatic interactions between the solvent molecules and the large ions with low surface charge density.

From the consideration of the motion of a solvated ion in an electrostatic field as a whole, it is possible to calculate the radius of the moving particle by the Stokes' equation

$$r_s = |Z| F^2 / (A \pi N \eta_0 \lambda_{\pm}^{\circ}) \quad (35)$$

where A is a coefficient varying from 6 (in the case of perfect sticking) to 4 (in the case of perfect slipping). Since the r_s values, the real dimensions of the non-solvated tetraalkyl(aryl) onium ions must be constant, we have

$$\lambda_{\pm}^{\circ} \eta_0 = \text{constant} \quad (36)$$

This relation has been tested using the λ_{\pm}° values determined with precise transference numbers. The product becomes constant and independent of the

chemical nature of the organic solvents for the I-Am₄B⁻, Ph₄As⁺, Ph₄B⁻ ions and for tetraalkylammonium cations starting from Et₄N⁺. The relation can also be well utilized to determine λ_{\pm}° values of ions in other organic solvents from the determined Λ° values

We have used Bu₄NBPh₄ as the 'reference electrolyte', but instead of equal division, we divided the Λ° values using a method similar to that proposed by Krumgalz²⁹ for division of B-values

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B}^-)} = \frac{r(\text{Ph}_4\text{B}^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (37)$$

The r values have been taken from the works of Gill *et al*⁵⁷

The values calculated by this method seem to be correct in different organic and mixed organic solvents. However, in aqueous binary mixtures, the solvation pattern may be different and the validity of this equation may be questioned.

Recently, Gill *et al*⁵⁹ proposed the following equation

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B}^-)} = \frac{5.35 - (0.0103\epsilon_0 + r_y)}{5.00 - (0.0103\epsilon_0 + r_y)} \quad (38)$$

and the ratio is close to 1.07 as used by us.

2.3.4 Solvation Number

An ion has an electric field or force around it which fades out into a negligible value after a short distance (~10 Å). In other words there is an effective volume within which its influence operates. The solvent molecules within this

volume may be said to be interacting with the ion, resulting in the solvation of the ion. These interactions result in the orientation of the solvent molecules towards the ion. The number of solvent molecules that are involved in the solvation of the ion is called solvation number. If the solvent is water, this is called hydration number.⁶⁰

Depending upon the distance from the ion, we can classify two solvation regions : primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion.

If the limiting conductance of the ion i of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law. The volume of the solvation shell is given by the equation

$$V_s^s = 4/3 \pi (r_s^3 - r_c^3) \quad (39)$$

Where r_c is the crystallographic radius of the ion. The solvation number n_s would then be obtained from

$$n_s = V_s^s / \bar{V}_o \quad (40)$$

Assuming Stokes' relation to hold good, the ionic solvated volume can be obtained, because of the packing effects,⁶¹ from

$$V_s^o \approx 4.35 r_s^3 \quad (41)$$

where V_s° is expressed in mol/mole and r_s in angstroms. However, this method is not applicable to ions of medium size though a number of empirical⁶² and theoretical corrections^{63,64} have been suggested in order to apply it to most of the ions.

2.3.5 Stokes' Law and Walden's Rule

The limiting conductance λ_i° of a spherical ion of radius R_i moving in a solvent of dielectric continuum can be written, according to Stokes' hydrodynamics, as

$$\lambda_i^{\circ} = 0.819 |Z_i| / \eta_i R_i \quad (42)$$

If the radius R_i is assumed to be the same in every organic solvent, as would be the case of bulky organic ions, we get

$$\lambda_i^{\circ} \eta_o = 0.819 |Z_i| / R_i = \text{constant} \quad (43)$$

This is known as the Walden rule.⁶⁵ The effective radii obtained using this equation can be used to estimate the solvation numbers. However, Stokes' radii failed to give the effective size of the solvated ions for small ions.

2.3.6 Recent Conductivity Equations

In 1986, Papadopoulos⁶⁶ analysed some conductance data using the Lee-Wheaton⁶⁷ conductance equation and compared the values with those obtained by Kay and his co-workers.⁶⁸ From 1992 to 1995, Blum, Turq and co-workers⁶⁹⁻⁷¹ have developed a mean spherical approximation (MSA) version of conductivity

equations. Their theory starts from the same continuity and hydrodynamics equations used in the more classical treatments; however, an important difference consists in the use of the MSA expressions for the equilibrium and structural properties of the electrolyte solutions. Although the differences in the derivation of the classical and MSA conductivity theories seem relatively small, it has been claimed that the performance of the MSA equation is good over a much wider concentration range than that covered by the classical equations. However, no thorough study of the performance of the new equations at the level of the experimental uncertainty of conductivity measurement is yet available in the literature, with the exception of a very recent study by Bianchi *et al.*⁷² They compared the results obtained, using the old and new equations in order to evaluate their capacity to describe the conductivity of different electrolyte solution. Their investigation too is limited to only three aqueous salt solutions and the picture is consistent showing a better performance for the classical equations as far as the system electrolytes are concerned.

In 2000, Chandra and Bagchi⁷³ have evolved a new microscopic approach to ionic conductance and viscosity based on mode coupling theory. Their study gives microscopic expressions of conductance and viscosity in terms of static and dynamic structure factors of the charge and number densities of the electrolyte solution. They claim that their new equation is applicable at low as well as at high concentrations and it describes the crossover from low to high concentration smoothly. Debye, Hückel, Onsager and Falkenhagen expressions can be derived

from this self-consistent theory at the limiting, very low ion concentration. For conductance the agreement seems to be satisfactory up to 1 M concentration.

2.4 APPARENT AND PARTIAL MOLAR VOLUMES

Fundamental properties such as enthalpy, entropy and Gibbs energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these properties in terms of molecular phenomena is generally difficult. Sometimes, higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. For example, the partial molar volume, the pressure derivative of partial molal Gibbs energy, is a useful parameter for interpreting solute-solvent interactions. Various concepts regarding molecular processes in solutions such as, electrostriction,⁷⁴⁻⁷⁶ hydrophobic hydration,⁷⁷ micellization⁷⁸ and cosphere overlap during solute-solute interactions.^{26,79} have to a large extent been derived and interpreted from the partial molar volume data of many compounds.

The apparent molar volumes, ϕ_v , of the solutes can be calculated using the following equation

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0) / c\rho_0 \quad (44)$$

where M is the molecular weight of the solute, ρ_0 and ρ are the densities of the solvent and solution respectively and c is the molarity of the solution. The partial molar volume, \bar{V}_2 , can be obtained from the equation

$$\bar{V}_2 = \phi_v + \frac{1000 - c\phi_v}{2000 + c^{3/2}(d\phi_v/dc^{1/2})} c^{1/2} \frac{d\phi_v}{dc^{1/2}} \quad (45)$$

Masson⁸⁰ found that ϕ_v varies with the square root of the molar concentration by the linear equation.

$$\phi_v = \phi_v^0 + S^*_v \sqrt{c} \quad (46)$$

where ϕ_v^0 is the apparent molar volume at infinite dilution (equal to the partial molar volume at infinite dilution) and S^*_v is the experimental slope. Redlich and Meyer⁸¹ have shown that an equation of the form of (46) cannot be any more than a limiting law where for a given solvent and temperature, the slope S^*_v should depend only upon the valence type. They suggested the equation

$$\phi_v = \phi_v^0 + S_v \sqrt{c} + b_v c \quad (47)$$

where $S_v = K_w^{3/2}$, is the theoretical slope based on molar concentration, including the valence factor where

$$w = 0.5 \sum v_i Z_i^2 \quad (48)$$

and

$$K = N^2 e^3 (8\pi / 1000 \epsilon^3 R T)^{1/2} [\partial \ln \epsilon / \partial P]_T - \beta / 3 \quad (49)$$

In equation (49), β is the compressibility of the solvent and the other terms have their usual significance.

The Redlich-Meyer's extrapolation equation⁸¹ adequately represents the concentration dependence of many 1:1 and 2:1 electrolytes in dilute solutions; however, studies⁸² on some 2:1, 3:1 and 4:1 electrolytes show deviations from this equation. Thus, for poly-valent electrolytes, the more complete Owen-Brinkley equation⁸³ can be used to aid in the extrapolation to infinite dilution and to

adequately represent the concentration dependency of ϕ . The Owen-Brinkley equation⁸³ which includes the ion-size parameter, a (cm), is given by

$$\phi_v = \phi_v^0 + S_v \tau(\kappa a) \sqrt{c} + 0.5 W_v \theta(\kappa a) c + 0.5 K_v c \quad (50)$$

where the symbols have their usual significance. However, this equation is not widely used for non-aqueous solutions.

Recently, the Pitzer formalism has been used by Pogue and Atkinson⁸⁴ and Krumgalz *et al.*⁸⁵ to fit the apparent molal volume data. The Pitzer equation for the apparent molar volume of a single salt $Mv_M Xv_X$ is

$$\phi_v = \phi_v^0 + v |Z_M Z_X| A_v / 2 b \ln(1 + b \sqrt{I}) + 2 v_M v_X RT [m^o B_{MX}^v m^2 (v_M v_X)^{1/2} C_{MX}^v] \quad (51)$$

where the symbols have their usual significance.

2.4.1 Ionic Limiting Partial Molar Volumes

Most of the existing ionic limiting partial molar volumes in organic solvents were obtained by the application of methods developed for aqueous solutions. For some time, the method of Conway *et al.*⁸⁶ was widely used. They plotted the limiting partial molar volume, $\bar{V}_{R_4 N X}^o$ for a series of homologous tetraalkylammonium chlorides, bromides and iodides with a halide ion in common,

of the formula weight of the cation $M_{R_4 N}^+$, and obtained straight-line graphs for each series. Their results were claimed to fit the equation.

$$\bar{V}_{R_4 N X}^o = \bar{V}_{X^-}^o + b M_{R_4 N}^+ \quad (52)$$

and the extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the halide ions, V_x^0 . Uosaki *et al*⁸⁷ and later Krumgalz⁸⁸ applied the same method to non-aqueous electrolyte solutions in a wide temperature range. In our laboratory too we have used this method for the division of partial molar volumes into the ionic components in 2-methoxyethanol.^{89,90}

2.5 ULTRASONIC VELOCITY

In the last two decades there have been a number of studies on the ultrasonic velocities and isentropic compressibilities of liquids, solutions and liquid mixtures⁹¹ because these data provide useful information about molecular interactions, association and dissociation. Various parameters like molar isentropic and isothermal compressibilities, apparent molal compressibility, isentropic compressibility, deviation in isentropic compressibility from ideality, etc. can very well be evaluated and studied from the measurement of ultrasonic speeds in solutions. Isentropic compressibilities play a vital role in characterization of binary liquid mixtures.

2.5.1 Apparent Molal Isentropic Compressibility

The apparent molal isentropic compressibility, the second derivative of the Gibbs energy, is also a sensitive indicator of molecular interactions and can provide useful information about these, particularly in cases where partial molal volume data alone fail to provide an unequivocal interpretation of the interactions.⁹²⁻⁹⁶ The isentropic compressibility (κ_s) values are calculated using the Laplace equation

$$\kappa_s = 1 / (u^2 \rho) \quad (53)$$

where u is the sound velocity in solution and ρ is the solution density. The apparent molal isentropic compressibility (κ_ϕ) of the liquid solution is calculated using the relation

$$\kappa_\phi = [(1000/m\rho\rho_0)(\kappa_s\rho_0 - \kappa_s^\circ\rho)] + \kappa_s M/\rho_0 \quad (54)$$

where m is the molality of the solution; κ_s° and κ_s are the compressibility coefficients of the solvent and solution respectively.

Plotting of κ_ϕ against the square-root of the molal concentration of solutes and extrapolation to zero molal concentration gives the limiting apparent molal isentropic compressibility(κ_ϕ°) according to the equation.^{92,96}

$$\kappa_\phi = \kappa_\phi^\circ + S_k \sqrt{m} \quad (55)$$

where S_k is the experimental slope.

The limiting molal isentropic compressibility (κ_ϕ°) and the experimental slope (S_k) can be interpreted in terms of solute-solvent and solute-solute interactions, respectively. It is well established that the solutes causing electrostriction lead to a decrease in the compressibility of the solution.^{97,98} This is reflected by the negative values of κ_ϕ° of electrolyte solutions. Hydrophobic solutes often show negative compressibilities due to the ordering induced by them in the water structure.^{78,97} The compressibility of hydrogen-bonded structure, however, varies depending on the nature of H-bonds involved,⁹⁷ the poor fit of the solute

molecules⁹⁹ as well as the possibility of flexible H-bond formation causing a more compressible environment (and hence a positive κ_ϕ° value) in the aqueous medium. Positive κ_ϕ° values have been reported in aqueous non-electrolytes¹⁰⁰ and non-electrolyte – non-electrolyte solutions.¹⁰¹

2.6 SOME RECENT TRENDS IN SOLVATION MODELS

The last decade (1990-2000) witnessed some interesting trends in development of some solvation models and computer software. Based on a vast collection of experimental free energy of solvation data, Cramer, Truhlar and co-workers constructed a series of solvation models (SM1 – SM5 series) to predict and calculate the free energy of solvation of a chemical compound.¹⁰²⁻¹⁰⁶ These models are applicable to virtually any substance composed of H, C, N, O, F, P, S, Cl, Br and / or I. The only input data required are molecular formula, geometry, refractive index, surface tension, Abraham's α (acidity parameter) and β (basicity parameter) values, and, in the latest models, the dielectric constants. Many of these parameters for a number of compounds are available in the internet.¹⁰⁷

The advantage of models like SM5 series is that they can be used to predict the free energy of self-solvation to better than 1 kcal/mol. They can also be used to predict the vapour pressure at 298.15K with useful accuracy. They are especially useful when other methods are not available. One can also analyse factors like, electrostatics, dispersion, hydrogen bonding, etc, using these tools. They are also relatively inexpensive and available in easy to use computer codes.

Galindo *et al*^{108,109} have developed Statistical Associating Fluid Theory for Variable Range (SAFT-VR) to model the thermodynamics and phase equilibria of electrolyte aqueous solutions. The water molecules are modeled as hard spheres with four short range attractive sites to account for the hydrogen-bond interactions. The electrolyte is modeled as two hard spheres of different diameter to describe the anion and cation. The Debye-Hückel and mean spherical approximations are used to describe the interactions. Good agreement with experimental data is found for a number of aqueous electrolyte solutions. The relative permittivity takes values very close to unity, especially in the case in which the mean spherical approximation is used, indicating a good description of the solvent. Bosch *et al*¹¹⁰ have compared several Preferential Solvation Models especially for describing the polarity of dipolar hydrogen bond acceptor – cosolvent mixtures.

2.7 A BRIEF LITERATURE SURVEY OF THE SOLVENTS USED FOR THIS INVESTIGATION

2.7.1 N,N-Dimethylacetamide (DMA)

N,N-Dimethylacetamide has a liquid range of 253.15 to 438.15K and a dielectric constant of 37.78 at 298.15K.⁹ It is miscible with water and is generally similar in its properties to N,N-dimethylformamide (DMF). It is a dipolar aprotic solvent and due to the presence of the two methyl groups attached to the nitrogen, it is more electron donating. Its ability to solvate cations is greater than that of DMF, acetone, acetonitrile and benzonitrile.¹¹¹

Solubilities of several alkali and alkaline earth metal halides and transition metal halides in DMA were measured by Pistoia and Scrosati.¹¹² The solubilities increase in the order Cl<Br<I. Alexander *et al*¹¹³ reported solubility product values for numerous silver salts in DMA. The solubilities of silver halides show the same trend as in water. Cations, particularly small cations (Ag^+ and K^+) and even large ones like trans- and cis- $[\text{CoCl}_2(\text{en})_2]^+$ which possess H-bond donor sites, are substantially better solvated in strongly dipolar aprotic solvents like DMA. Sears *et al*¹¹⁴ measured the conductances of some alkali and tetraalkylammonium salts in pure DMA at 298.15K. Large polarisable anions, like picrate, perchlorate, AgCl_2^- are better solvated by the strong dipolar solvents, presumably through dipole-induced dipole interactions.¹¹⁵

Studies on binary mixtures of DMA have also been reported in the literature, mostly as a comparative study of different amides. Gomaa¹¹⁶ and also Pal *et al*¹¹⁷ investigated the interactions of DMF and DMA with water. Conductance measurements of some tetraalkylammonium bromides in DMA + water binary mixtures have also been reported by Ramanamurti *et al*¹¹⁸

2.7.2 Formamide

Formamide has received considerable attention as a solvent for various electrochemical study, mainly because it is an example of a solvent with a higher dielectric constant ($\epsilon = 109.5$ at 298.15K)⁹ than water and thus can dissolve many electrolytes. The oxygen and nitrogen atoms within a formamide molecule are

negatively charged and the carbon and hydrogen atoms have partially positive charges and has a dipole moment(μ) of about 3.68D at 298.15K⁹. Formamide molecules in their liquid state are strongly self-associated through extensive networks of hydrogen bonds.¹¹⁹ The molecular and liquid structures of formamide have been studied by means of X-ray diffraction.¹²⁰ From the X-ray diffraction experiment we know that liquid formamide mainly consists of chain-like hydrogen bonded structure combining through $-\text{NH}_2 \dots \text{O} = \text{CH}-$ interactions. However, the stable ring structure existing in the solid state may be rather unfavourable to give the high dielectric constant of formamide and high solubilities of electrolytes in it in the liquid phase. Spiro¹²¹ combined the value obtained for the limiting transference number, using moving boundary method with the data for the limiting equivalent conductance to generate a set of individual ionic conductances for a variety of ions in formamide.

Formamide along with other amides is also used as one of the component in the binary mixture with different alcohols and water. Ali *et al*¹¹⁹ reported the thermodynamic properties of formamide + ethanol binary mixtures as a function of concentration and temperature. Leal and co-workers¹²² investigated the thermodynamic properties of the aqueous binary mixtures of different amides including formamide also and the results were used to make a comparison with amide – alcohol mixtures. The changes in dielectric constant of formamide with respect to concentration in its aqueous binary mixture was measured by Rohdewald *et al.*¹²³

2.7.3 N,N-Dimethylformamide (DMF)

N,N-Dimethylformamide (DMF) is an aprotic, protophylic and a potentially basic medium. Owing to its easy miscibility with almost all common polar and non polar solvents and high solvating power DMF is largely utilized in analytical and electrochemical applications. DMF has a quite large dipole moment ($\mu = 3.28\text{D}$ at 25°C)⁹ and a moderately high dielectric constant ($\epsilon = 37.5$ at 25°C)⁹. The striking tendency to provide hydrogen bonds via acceptor sites – C (= O) – N =, makes DMF a powerful breaker of polymerized structure of hydroxy compounds.¹²⁴ Raman and infrared spectra of liquid DMF have been recorded by Fini and Mirone,¹²⁵ X-ray diffraction¹²⁶ and NMR¹²⁷⁻¹³⁰ study of liquid DMF indicates that there is no significant interactions, only a weak hydrogen bonded interaction existed between DMF molecules.

Several papers have been published on the measurements of transport and thermodynamic properties in pure DMF and also its binary mixture with other organic solvents. Physicochemical Data of pure DMF and its aqueous binary mixture have been reported by Rohdewald *et al.*¹²³ Excess properties of aqueous binary mixtures of a series of amides including N,N-dimethylformamide were calculated from density and viscosity measurements.¹²²

2.7.4 2-Ethoxyethanol (EE)

2-Ethoxyethanol is a bifunctional, versatile organic liquid commonly known as ‘cellosolve’¹³¹ and is widely used in chemical industries as a solvent for

lacquers, oils, resins, dyes and as an antifreeze for explosives.¹³² They can be considered to be ethylene glycol derivatives obtained by the replacement of one of the hydroxy groups by an alkoxy group. Generally the 'cellosolves' are self associated through intramolecular hydrogen bond formation and further it exists as a five membered ring monomers also.¹³³⁻¹³⁵ The physical properties of 2-ethoxyethanol are obtained from the literature.^{132,136} Thermochemical properties of aqueous binary mixture of 2-ethoxyethanol along with other alkanols have been reported in the literature.¹³¹ Density, refractive index, speed of sound and their related excess properties in the binary mixtures of 2-ethoxyethanol with a number of important industrial liquids that find applications in a variety of areas have also been reported.¹³²

In this dissertation we have devoted our attention to the study of transport and thermodynamic properties of some selected alkali-metal and tetraalkaliammonium salts in DMA and aqueous binary mixture of DMA and the excess properties of non-aqueous binary mixtures of DMA with formamide, dimethylformamide and 2-ethoxy ethanol.

The results have been described in subsequent chapters.

References

1. Y. Marcus, *Introduction to Liquid State Chemistry*, Wiley-Interscience, New York, 1997.
2. G.A.Krestov, *Thermodynamics of Solvation*, Ellis Horwood, Chichester, 1991.
3. J.Padova, in *Water and Aqueous Solutions*, Ed. R.A.Horne, Wiley-Interscience, New York, 1972, chapter 4.
4. R. Fernandez-Prini, H.Corti and M. Japas, *High Temperature Aqueous Solutions: Thermodynamic Properties*, C.R.C. Press, Boca Raton, Florida, 1992.
5. V.N.Afanasyev and I.E.Korolev, *Thermodynamics of Electrolyte Solutions*, Institute of Non-Aqueous Solution Chemistry, Ivarovo, Russia, 1992.
6. J.Barthel, H-J. Gores, G.Schmeer and R. Water, in *Non-aqueous Electrolyte Solutions in Chemistry and Modern Technology*, Topics in Current Chemistry, Vol.3, Springer Verlag, Berlin-Heidelberg, New York, 1983.
7. O. Popovych and R.P.T.Tomkins, *Nonaqueous Solution Chemistry*, Wiley-Interscience, New York, 1981.
8. J.Berthel, R. Buchner, C.G.Hölzl, M. Münsterer, *Z.Phys.Chem.*, **214**, 1213, 2000.
9. *Physical Chemistry of Organic Solvent Systems*, Eds. A.K.Covington and T. Dickinson, Plenum Press, New York, 1973, Chapter I.
10. J.D.Pandey and A.Yasmin, *Proc.Ind.Acad.Sci.*, **109**, 289, 1997.
11. J.D.Pandey, Y. Akhtar and A.K.Sharma, *Ind. J. Chem.*, **37A**, 1094, 1998.

12. F. Comelli, R.Francesconi and C. Castellari, *J. Chem. Eng. Data*, **44**, 739, 1999.
13. J.I.Kim, *J. Phys. Chem.*, **82**, 191, 1978.
14. D.E.Irish, in Ref. 9, Chapter 4.
15. W.Kemp, *Organic Spectroscopy*, 3rd (ELBS) ed., Macmillan Press, Hampshire, U. K., 1993.
16. J.Barthel, R. Buchner, E. Wismeth, *J. Solution Chem.*, **29**, 953, 2000.
17. G. Jones and M. Dole, *J. Amer. Chem. Soc.*, **51**, 2950, 1929.
18. P. Debye and E. Hückel, *Z. Phys.*, **24**, 185, 1923.
19. H. Falkenhagen, *Z. Phys.*, **32**, 745, 1931.
20. H.Falkenhagen and E.L.Vernon, *Phil. Mag.*, **14**, 537, 1932.
21. L.Onsager and R.M.Fuoss, *J.Phys.Chem.*, **36**, 2689, 1932.
22. J. Crudden, G. M. Delaney, D. Feakins, P. J. O'Reilley and W.E.Waghorne, K.G.Lawrence, *J.Chem.Soc., Faraday Trans.*, **1**, **82**, 2195, 1986.
23. R.H.Stokes and R. Mills, *Viscosities of Electrolytes and Related Properties*, Pergamon Press Ltd., 1965.
24. H. Donald, B. Jenkins and Y. Marcus, *Chem. Rev.*, **95**, 2695, 1995.
25. W.M.Cox and J.H.Wolfenden, *Proc. Roy. Soc. London*, **145A**, 475, 1934.
26. R.W.Gurney, *Ionic Processes in Solution*, McGraw Hill, New York, 1954.
27. A. Sacco, A. D.Giglio and A. Dell' Atti, *J.Chem.Soc., Faraday Trans.*, **1**, **77**, 2693, 1981.
28. D.F.Tuan and R.M.Fuoss, *J.Phys.Chem.*, **67**, 1343, 1963.
29. B.S.Krumgalz, *J.Chem. Soc., Faraday Trans.*, **I**, **76**, 1275, 1980.
30. B.S.Krumgalz, *Russ. J.Phys. Chem.*, **46**, 858, 1972, **47**, 528, 1973.

31. B.S.Krumgalz, *Russ. J.Phys. Chem.*, **45**, 1448, 1971.
32. D.S.Gill and A.N.Sharma, *J.Chem.Soc., Faraday Trans., I*, **78**, 475, 1982.
33. K.G.Lawrence and A. Sacco, *J.Chem.Soc., Faraday Trans., I*, **79**, 615, 1983.
34. A. Sacco, M.D.Monica, A.D.Giglio and K.G.Lawrence, *J.Chem.Soc., Faraday Trans., I*, **79**, 2631, 1983.
35. P.T.Thomson, B. Fischer and R.H.Wood, *J.Soln. Chem.*, **11**, 1, 1982.
36. D. Feakins, D.J.Freemanle and K.G.Lawrence, *J.Chem.Soc., Faraday Trans., I*, **70**, 795, 1974.
37. D. Feakins and K.G.Lawrence, *J.Chem. Soc., A*, 212, 1966.
38. R.T.M.Bicknell, K.G.Lawrence, M.A.Scley, D. Feakins and L.Werblan, *J.Chem.Soc., Faraday Trans., I*, **72**, 307, 1976.
39. D. Feakins, W.E.Waghorne and K.G.Lawrence, *J.Chem.Soc., Faraday Trans., I*, **82**, 563, 1986.
40. D. Nandi and D.K.Hazra, *J.Chem.Soc., Faraday Trans., I*, **85**, 4227 , 1989.
41. B. Das and D.K.Hazra, *Bull. Chem. Soc. Jpn.* **65**, 3470, 1992.
42. A.P.Abbott and C.A.Eardley, *J.Phys.Chem. B.*, **104**, 9351, 2000.
43. R.Fernandez-Prini, in Ref. 9, Chapter 5.
44. L. Onsager , *Z. Phys.*, **28**, 277, 1927.
45. E.Pitts, *Proc. Roy. Soc., 217A*, 43, 1953.
46. R.M.Fuoss and F. Accascina, *Electrolytic Conductance*, Interscience, New York, 1959.
47. R.M.Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 663, 1957.

48. R.M.Fuoss and K.L.Hsia, *Proc. Natl.Acad.Sci.*, **59**, 1550, 1967, *J.Am.Chem.Soc.*, **90**, 3055, 1968.
49. D.E.Arrington and E. Grinswold, *J.Phys.Chem.*, **74**, 123, 1970.
50. R.M.Fuoss and C.A.Kraus, *J.Am.Chem. Soc.*, **55**, 476, 1933.
51. T. Shedlovsky, *J.Franklin Inst.*, **225**, 739, 1938.
52. R.M.Fuoss and T.Shedlovsky, *J.Am.Chem.Soc.*, **71**, 1496, 1949.
53. J.C.Justice, R.Bury and C.Treiner, *J.Chim.Phys.*, **65**, 1707, 1968.
54. R.M.Fuoss, *J.Phys.Chem.*, **49**, 525, 1975; **82**, 2427, 1978 .
55. P.Walden, H.Ulich and G. Busch, *Z.Phys.Chem.*, **123**, 429, 1926.
56. A.D.' Aprano and R.M.Fuoss, *J.Soln.Chem.*, **4**, 175, 1975.
57. D.S.Gill and M.B.Sekhri, *J.Chem.Soc., Faraday Trans.*, I, **78**, 119, 1982.
58. B.S.Krumgalz, *J.Chem.Soc., Faraday Trans.*, I, **79**, 571, 1983; **81**, 241, 1985.
59. D.S.Gill, N.Kumari and M.S. Chauhan, *J.Chem.Soc., Faraday Trans.*, I, **81**, 687, 1985.
60. J.O'M. Bockris and A.K.N.Reddy, *Modern Electrochemistry*, Vol. 1, Plenum Press, New York, 1971.
61. R.H.Stokes and R.A. Robinson, *Trans. Faraday Soc.*, **53**, 301, 1957.
62. R.T.M. Bicknell, K.G.Lawrence and D.Feakins, *J.Chem.Soc., Faraday Trans.*, I, **76**, 637, 1980.
63. R. Zwanzig, *J.Chem.Phys.*, **38**, 1603, 1605, 1963.
64. E. J.Passeron, *J.Phys.Chem.*, **68**, 2728, 1964.
65. P.Walden, *Z.Phys.Chem.*, **55**, 207, 1906

66. N.Papadopoulos, G. Ritzoulis and D. Jannakoudakis, *Anali di Chimica*, **76**, 307, 1986.
67. W.Lee and R.Wheaton, *J.Chem.Soc., Faraday Trans., II*, **74**, 743, 1456, 1978.
68. R.L.Kay, C.Zawoyski and D.F.Evans, *J.Phys.Chem.* **70**, 2336, 1966.
69. O. Bernard, W.Kunz, P. Turq and L. Blum, *J.Phys.Chem.*, **96**, 3833, 1992.
70. P. Turq, L. Blum, O. Bernard and W.Kunz, *J. Phys. Chem.* **99**, 822, 1995.
71. S.Durand-Vidal, P.Turq and O.Bernard, *J. Phys. Chem.*, **100**, 17345, 1996.
72. H.L.Bianchi, I. Dujovne and R. Fernandez-Prini, *J. Soln.Chem.*, **29**, 237, 2000.
73. A. Chandra and B.Bagchi, *J. Phys.Chem. B.*, **104**, 9067, 2000.
74. P.J.Victor, B. Das and D.K.Hazra, *J.Phys.Chem. A.*, **105**, 5960, 2001.
75. P.J.Victor, P.K.Muhuri, B.Das and D.K.Hazra, *J.Phys.Chem. B*, **103**, 11227, 1999.
76. P.J.Victor, B.Das and D.K.Hazra, *J. Soln. Chem.*, **30**, 435, 2001.
77. C. Tanford, *Hydrophobic Effect : Formation of Micelles and Biological Membranes*, 2nd edn., Wiley-Interscience, New York, 1980.
78. E.Vikingstad, *Aggregation Process in Solutions*, Eds. E. Wyn-Jones and J. Gormally, Elsevier, Amsterdam, 1983, pp. 100-117.
79. J.E.Desnoyers, M. Arel, G. Perron and C.Jolicoeur, *J. Phys. Chem.*, **73**, 3347, 1969.
80. D.O.Masson, *Phil. Mag.* **8**, 218, 1929.
81. O.Redlich and D.M.Meyer, *Chem.Rev.*, **64**, 221, 1964.
82. L.A.Dunn, *Trans. Faraday Soc.*, **64**, 2951, 1968.

83. B.B.Owen and S.R.Brinkley, Jr., *Ann. N.Y.Acad. Sci.*, **51**, 753, 1949.
84. R.Pogue and G.Atkinson, *J.Chem.Eng.Data*, **33**, 1988, 370.
85. B.S.Krumgalz, R. Pogorelski, A. Sokolov and K.S.Pitzer, *J. Phys. Chem. Ref. Data*, **29**, 1123, 2000.
86. B.E.Conway, R.E.Verral and J.E.Desnoyers, *Trans. Faraday Soc.*, **62**, 2738, 1966.
87. K.Uosaki, Y.Kondo and N. Tokura, *Bull. Chem. Soc. Jpn.*, **45**, 871, 1972.
88. B.S.Krumgalz, *J.Chem.Soc., Faraday Trans.*, **1**, **76**, 1887, 1980.
89. B.Das and D.K.Hazra, *J.Chem.Eng.Data*, **36**, 403, 1991.
90. B.Das and D.K.Hazra, *Bull. Chem.Soc.Jpn.*, **68**, 734, 1995.
91. G.Douheret and M.I.Davis, *Chem. Soc. Rev.*, **22**, 43, 1993.
92. B.Das, P.K.Muhuri and D.K.Hazra, *Acoustics Letters*, **18**, 69, 1994.
93. N.Rohman and S. Mohiuddin, *J.Chem. Soc. Faraday Trans.*, **93**, 2053, 1997.
94. M.V.Kaulgud and K.S.Mohan Rao, *Ind. J. Chem.*, **27A**, 12, 1988.
95. A.Kumar, *J.Am.Chem.Soc.*, **115**, 9243, 1993.
96. M.Iqbal and R.E.Verral, *Can. J. Chem.*, **67**, 727, 1989.
97. B.E.Conway and R.E.Verral, *J.Phys.Chem.*, **70**, 3952, 1966.
98. K.Gekko and H.Noguchi, *J.Phys.Chem.*, **83**, 2706, 1979.
99. L.G.Hepler, *Can. J. Chem.*, **47**, 4613, 1969.
100. M.V. Kaulgud and K.J.Patil, *J.Phys. Chem.*, **80**, 138, 1976.
101. K.J.Patil, G.R.Mehta and R.K.Candewar, *Ind. J.Chem.*, **25A**, 1147, 1986.
102. C.J.Cramer and D.G.Truhlar, *J.Am.Chem.Soc.*, **113**, 8305, 1991.

103. D.J.Giesen, J.W.Storer, C.J.Cramer and D.G.Truhlar, *J.Am.Chem.Soc.*, **117**, 1057, 1995.
104. C.J.Cramer and D.G.Truhlar, *J.Org.Chem.*, **61**, 8720, 1996, erratum, **101**, 309, 1999.
105. G.D.Hawkins, C.J.Cramer and D.G.Truhlar, *J.Phys.Chem., B*, **101**, 7147, 1997.
106. G.D.Hawkins, C.J.Cramer and D.G.Truhlar, *J.Phys.Chem., B*, **102**, 3257, 1998.
107. P.Winget, G.D.Hawkins, C.J.Cramer and D.G.Truhlar, *J.Phys.Chem., B*, **104**, 4726, 2000.
108. A. Gil-Villegas, A. Galindo, P. J. Whitehead, S.J.Mills, G. Jackson and A.N.Burgess, *J. Chem. Phys.*, **106**, 4168, 1997.
109. A. Galindo, L.A.Davies, A.Gil-Villegas and G.Jackson, *Mol.Phys.*, **93**, 241, 1998.
110. M.Roses, C. Rafols, J.Ortega and E.Bosch, *J.Chem.Soc., Perkin Trans.*, **2**, 1607, 1995.
111. A.J.Parker, *Quart. Rev.*, **16**, 162, 1962.
112. G.Pistoia and B.Scrosati, *Ric. Sci.*, **37**, 1173, 1967.
113. R.Alexander, E.C.F.Ko, Y.C.Mac and A.J.Parker, *J.Am.Chem. Soc.*, **89**, 3703, 1967.
114. G.R.Lester, T.A.Gover and P.G.Sears, *J. Phys. Chem.*, **60**, 1076, 1956.
115. D.W.Watts in Physical Chemistry of Organic Solvent Systems, Eds. A.K.Covington and T.Dickinson, (Plenum Press, New York), 1973, p. 689.
116. A.E.Gomaa, *Ind. J.Techn.*, **26**, 461, 1988.
117. A.Pal, Y.P.Singh and W.Singh, *Ind. J. Chem.*, **33A**, 1083, 1994.

118. L. Bahadur and M.V.Ramanamurti., *J.Chem.Soc., Faraday Trans., I*, **76**, 1409, 1980.
119. A. Ali and A.K.Nain, *Ind. J.Chem.*, **35A**, 751, 1996.
120. H.Ohtaki, A.Funaki, B.M.Rode and G.J.Reibnegger, *Bull. Chem. Soc. Jpn.*, **56**, 2116, 1983.
121. J.M.Notley and M.Spiro, *J.Phys.Chem.*, **70**, 1502, 1966.
122. B.Garcia, R.Alcalde and J.M.Leal, *J.Phys.Chem., B*, **101**, 7991, 1997.
123. P.Rohdewald and M. Moldner, *J.Phys.Chem.*, **77**, 373, 1973.
124. F.Corradiini, L.Marcheselli, A.Marchetti, M. Tagliazucchi, L.Tassi and G.Tosi, *Bull.Chem.Soc.Jpn.*, **65**, 503, 1992.
125. G.Fini and P.Mirone, *J.Chem.Soc.,Faraday Trans., 2*, **70**, 1776, 1974.
126. H.Ohtaki, S.Itoh, T.Yamaguchi, S.Ishiguro and B.M.Rode, *Bull. Chem. Soc. Jpn.*, **56**, 3406, 1983.
127. A.G.Whittaker and S.Siegel, *J.Chem.Phys.*, **42**, 3320, 1965.
128. R.C.Neuman, Jr., W.Suider and V.Jonas, *J.Phys.Chem.*, **72**, 2469, 1968.
129. W.T.Raynes and M.A.Raza, *Mol.Phys.*, **20**, 339, 1971.
130. H.J.Bittrich and D.Kirsch, *Z.Phys.Chem. (Leipzig)*, **257**, 403, 1976.
131. H.Piekarski and M.Tkaczyk, *J.Chem.Soc., Faraday Trans.*, **91**, 2299, 1995.

132. M.I.Aralaguppi, C.V.Jadar and T.M.Aminabhavi, J.D.Ortego,
S.C.Mehrotra, *J.Chem.Eng.Data*, **42**, 301, 1997.
133. S.Prabhumirashi, *J.Chem.Soc.Faraday Trans.*, **174(2)**, 1567, 1978.
134. H.Takeuchi and M.Tasumi, *Chem.Phys.*, **77**, 21, 1983.
135. P.Buckley and M.Brochu, *Can. J. Chem.*, **50**, 1149, 1972.
136. G.Douheret and A.Pal, *J. Chem. Eng. Data*, **33**, 40, 1988.

CHAPTER III

EXPERIMENTAL SECTION

CHEMICALS USED : THEIR SOURCES AND PURIFICATION

3.1.1 Electrolytes

The salts were of Fluka's purum or puriss grade. Lithium chloride (LiCl), lithium bromide (LiBr), lithium iodide (LiI), lithium tetrafluoroborate (LiBF_4) and lithium hexafluoroarsenate (LiAsF_6) were dried under vacuum at high temperature for 48 hours and were used without further purification. Lithium perchlorate (LiClO_4) was recrystallized three times from conductivity water and then dried under vacuum for several days.¹

Tetraalkylammonium salts were purified in the manner given in the literature.^{2,3} Generally these salts were purified by recrystallization. Higher tetraalkyl homologues were recrystallized second time to ensure the highest purity. The crystallized salts were dried in vacuum and stored in glass bottles in darkened dessicator over fused CaCl_2 .

Tetraethylammonium bromide (Et_4NBr) was recrystallized from methanol and dried at 363K for 24 hours.

Tetrapropylammonium bromide (Pr_4NBr) was taken in a minimum volume of methanol, reprecipitated from dry ether and dried at 363K for 48 hours.

Tetrabutylammonium bromide (Bu_4NBr) was taken in a minimum volume of acetone. Ether was added to the solution till the commencement of precipitation. The

solution was then cooled and the resulting crystals were filtered. After a preliminary drying, the salt was finally ground in a mortar and dried at 333K for 48 hours.

Tetrapentylammonium bromide (Pen_4NBr) was recrystallized from acetone + ether mixtures and dried in vacuo at 333K for 48 hours.

Tetrahexylammonium bromide (Hex_4NBr) and tetraheptylammonium bromide (Hep_4NBr) were washed with ether and dried in vacuo at room temperature for 48 hours.

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by precipitation from tetrabutylammonium bromide (Bu_4NBr) and sodium tetraphenylborate (NaBPh_4) in water and the precipitate was washed five times by water. The bulky white precipitate was dried in vacuo at 353K for 48 hours.⁴

Sodium tetraphenylborate (NaBPh_4) was recrystallized three times from acetone and dried in vacuo at 353K for 72 hours.

Potassium tetraphenylborate (KBPh_4) was prepared by mixing equimolar aqueous solutions of potassium nitrate (KNO_3) and sodium tetraphenylborate (NaBPh_4). The product was recrystallized from 30 mass percentage aqueous acetone and dried in vacuo for several weeks.

The alkali-metal bromides – sodium bromide (NaBr), potassium bromide (KBr), rubidium bromide (RbBr) and cesium bromide (CsBr) were dried in vacuo for a long time immediately prior to use and were used without further purification.

3.1.2 Solvents

N,N-Dimethylacetamide (DMA, E.Merck, India, >99.5%) was shaken well with charged CaO (A.R.BDH) for 1-2 hours, decanted, and distilled twice⁵ and the middle fraction was collected and used. Its density (0.93644 g cm⁻³) and viscosity (0.9330 mPa-s) at 298.15K, compared well with the literature values which are 0.9366 g cm⁻³ and 0.919 mPa - s respectively.⁶ The relative permittivity of N,N-dimethylacetamide ($\epsilon = 37.78$) at 298.15K was taken from the literature.⁶

Formamide (E. Merck, Germany, > 99%) was dried over freshly ignited quicklime for several hours and then distilled over reduced pressure and the purified solvent had a density 1.1254g.cm⁻³ and viscosity 2.9527 mPa-s at 298.15K.⁶

N,N-Dimethylformamide (E Merck, India) was kept overnight with phosphorous pentoxide, decanted and distilled over nitrogen. The purified solvent had a density of 0.94362 g cm⁻³ and viscosity 0.80240 mPa-s at 298.15K . All these values are in good agreement with the literature values.⁶

2-Ethoxyethanol (E.Merck, India) was kept overnight with anhydrous K₂CO₃, decanted and distilled in an all glass distillation set and the middle fraction was collected. The purified solvent had a density 0.9252 g. cm⁻³ and a viscosity 1.8243 mPa-s at 298.15K⁷.

3.2 EXPERIMENTAL TECHNIQUES

3.2.1 Density Measurements

Densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 35 and 45°C with doubly distilled water. Measurements were made using a single pan Mettler balance with an accuracy of ±0.00001 g. The measurements were carried out in a thermostatic water bath maintained with an accuracy of ±0.01°C of the desired temperature.⁸ The reproducibility of density measurements was ± 3 × 10⁻⁵ gm cm⁻³.

3.2.2 Viscosity Measurements

The kinematic viscosities were measured by means of a suspended-level Ubbelohde⁹ viscometer with a flow time of about 539s for distilled water at 25°C. The time of efflux was measured with a stop watch capable of recording 0.1s. The viscometer was always kept in a vertical position in a water thermostat. The viscometer needed no correction for kinetic energy. The kinematic viscosity (ν) and the absolute viscosity (η) are given by the following equations :

$$\nu = ct - k/t \quad (1)$$

$$\eta = \nu \rho \quad (2)$$

where, t is the efflux time, ρ is the density and c and k are the characteristic constants of the viscometer. The values of the constants c and k , determined by

using water and benzene as the calibration liquids at 25, 35 and 45°C were found to be $1.648 \times 10^{-5} \text{ cm}^2\text{s}^2$ and -0.02331647 cm^2 respectively. The precision of the viscosity measurements was 0.05%. In all cases experiments were performed in at least five replicates and the results were averaged.

Relative viscosities (η_r) were obtained using the equation :

$$\eta_r = \eta / \eta_o = \rho t / \rho_o t_o \quad (3)$$

where, η , η_o , ρ , ρ_o and t , t_o are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic water bath maintained within an accuracy of $\pm 0.01^\circ\text{C}$ of the desired temperature.

3.2.3 Conductance Measurements

Conductance measurements were carried out with a Philips Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell of cell constant 1.14 cm^{-1} and having an accuracy of 0.1%. The instrument was calibrated using standard KCl solutions. The cell was calibrated by the method of Lind and co-workers.¹⁰ the conductivity cell was sealed to the side of a 500 cm^3 conical flask closed by a ground glass fitted with a side arm through which dry and pure nitrogen was passed to prevent admission of air into the cell when solvent or solution was added. The measurements were made in an oil bath maintained at the required temperatures $\pm 0.005^\circ\text{C}$ by means of a mercury in glass thermoregulator.^{11,12}

Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured as described above. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent at all temperatures.

3.2.4 Ultrasonic Velocity Measurements

Sound velocities were measured,^{13,14} with an accuracy of $\pm 0.3\%$ using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at 4 MHz, which was calibrated with water, methanol, and benzene at each temperature. The temperature stability was maintained at $\pm 0.01^\circ\text{C}$ by circulating thermostated water around the cell by a circulating pump.

The principle used in the measurement of the sound velocity (u) is based on the accurate determination of the wave length (λ) in the medium. Ultrasonic waves of known frequency (v) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wave length, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wavelength ($\lambda/2$) or integral multiple of it, anode current again becomes maximum.

From the knowledge of the wave length (λ), the velocity (u) can be obtained by the relation :

$$\text{Velocity (u)} = \text{Wave length} (\lambda) \times \text{Frequency} (v) \quad (4)$$

Isentropic compressibility (k_s) can then be calculated by the following formula :

$$k_s = 1 / (u^2 \rho) \quad (5)$$

Where ρ is the density of the experimental liquid.

The ultrasonic interferometer consists of the following two parts : (i) the high frequency generator, and (ii) the measuring cell. The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The cell is filled with the experimental liquid before switching on the generator. The ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal.

The micrometer is slowly moved till the anode current on the high frequency generator shows a maximum. A number of maximum readings of anode current are passed on and their number (n) is counted. The total distance (r) thus moved by the micrometer gives the value of wavelength (λ) with the following relation :

$$r = n \times \lambda / 2 \quad (6)$$

3.2.5 Spectroscopic Measurements

The FTIR spectra in the region 4000-500 cm⁻¹ were recorded on a Bomen d-8.02 FTIR Spectrophotometer using potassium bromide window in a capillary cell construction. For each sample, fifty scans were accumulated and the results averaged. The spectra were recorded by the Regional Sophisticated Instrumentation centre, North Eastern Hill University, Shillong. All spectra were scanned atleast twice to ensure repeatability. The wave number resolution in spectral acquisition was 1 cm⁻¹. The FT Raman spectra were recorded by the Regional sophisticated Instrumentation centre, Indian Institute of Technology, Madras. The samples were excited at 1064 nm using a Nd : YAG laser and Brucker IFS 66V optical bench with an FRA 106 Raman module attached to it. Laser power was set at 200 mw, and 250 (averaged) scans were accumulated with a resolution of 2 cm⁻¹.

References

1. H.L.Friedman, *J.Phys.Chem.*, **71**, 1723, 1967.
2. B. E.Conway, R.E.Verral and J.E.Desnoyers, *Trans. Faraday Soc.*, **62**, 2738, 1966.
3. D.F.Evans, C.Zawoyski and R.L.Kay, *J. Phys. Chem.*, **69**, 3878, 1965.
4. M.Castagnolo, A. Sacco and A.D.Giglio, *J.Chem.Soc., Faraday Trans.*, **1**, **80**, 2669, 1984.
5. D.Das, B.Das & D.K.Hazra, *J.Soln. Chem.*, **31**, 425, 2002.
6. Physical Chemistry of Organic Solvent Systems, Eds. A.K.Covington and T. Dickinson, Plenum Press, New York, 1973, p.4.
7. M.I.Aralaguppi, C.V.Jadar and T.M.Aminabhavi., *J.Chem.Eng. Data*, **42**, 301, 1997.
8. S.K.Ghosh and D.K.Hazra, *Ind.J.Chem.*, **29A**, 656, 1990.
9. J.R.Suindells, J.R.Coe Jr. and T.B.Godfrey, *J.Res.Natd.Bur.Stand.*, **48**, 1, 1952.
10. J.E.Lind Jr, J.J.Zwolenik and R.M.Fuoss, *J.Chem. Soc.*, **81**, 1557, 1959.
11. P.K.Muhuri and D.K.Hazra, *J.Chem.Soc.Faraday Trans.*, **87**, 3511, 1991.
12. P.K.Muhuri and D.K.Hazra, *Z.Naturforsch*, **48a**, 523, 1993.
13. P.J.Victor, P.K.Muhuri, B.Das and D.K.Hazra, *J.Phys.Chem., B*, **103**, 11227, 1999.
14. B. Das, P.K.Muhuri and D.K.Hazra, *Acoust. Lett.*, **18**, 69, 1994.

CHAPTER IV

SECTION A

Conductance of Some 1:1 Electrolytes in N,N-Dimethylacetamide at 298.15K.

Lithium has been used for many years as an anode material for nonaqueous batteries.¹ In such systems, the choice of electrolyte solution and optimization of its salt concentration are two important factors. An electrolyte possessing high specific conductivity and, hence, minimal ion-ion interaction is required to maintain the cell at low resistance. Knowledge of the state of association of the electrolytes and their interaction with solvent molecules is essential for the optimal choice of solvent and electrolyte.

Recently, we have initiated a comprehensive program to study Li⁺ ion solvation in different nonaqueous solvents from the measurements of various transport, thermodynamic and spectroscopic properties.²⁻⁹ In this section, an attempt is made to unravel the nature of various types of interactions prevailing in solutions of some lithium salts — lithium chloride LiCl, lithium bromide LiBr, lithium iodide LiI, lithium perchlorate LiClO₄, lithium tetrafluoroborate LiBF₄, and lithium hexafluoroarsenate LiAsF₆ in N,N-Dimethylacetamide — from precise conductivity measurements. Conductance measurements have also been performed on two other electrolytes, tetrabutylammonium bromide Bu₄NBr, and tetrabutylammonium tetraphenylborate Bu₄NBPh₄, in order to obtain the limiting single-ion conductivities in this solvent medium.

EXPERIMENTAL

N,N-Dimethylacetamide (E.Merck, India, > 99.5%) was distilled twice in an all-glass distillation set immediately before use and the middle fraction collected. The purified solvent had a density of $0.93652 \text{ g}\cdot\text{cm}^{-3}$, a coefficient of viscosity of $0.9330 \text{ mPa}\cdot\text{s}$, and a specific conductance of about $1.01 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at 298.15K. These values are in good agreement with literature values.¹⁰

The salts were of Fluka's purum or puriss grade.

To avoid moisture pick up, all solutions were prepared in a dehumidified room with utmost care. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Correction was made for the specific conductance of the solvent.

The details of the experimental procedure have been described in Chapter-III.

RESULTS AND DISCUSSION

The measured molar conductance, Λ , of electrolyte solutions, as a function of molar concentration c at 298.15K are given in Table I,

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation.^{11,12} For a given set of conductivity values (c_j , Λ_j , $j = 1 \dots, n$) three adjustable parameters, the limiting molar conductivity Λ° , association

constant K_a and the cosphere diameter R are derived from the following set of equations :

$$\Lambda = \rho [\Lambda^0 (1 + R_x) + E_L] \quad (1)$$

$$\rho = 1 - \alpha (1 - \gamma) \quad (2)$$

$$\gamma = 1 - K_a c \gamma^2 f^2 \quad (3)$$

$$-lnf = \beta k/2 (1 + K_R) \quad (4)$$

$$\beta = e^2/\epsilon K_B T \quad (5)$$

$$K_a = K_R / (1 - \alpha) = K_R (1 + K_S) \quad (6)$$

Where R_x is the relaxation field effect, E_L is the electrophoretic countercurrent, ϵ is the relative permittivity of the solvent, e is the electronic charge, K_B is the Boltzmann constant, γ is the fraction of solute present as an unpaired ion, c is the molarity of the solution, f is the activity coefficient, T is the temperature in absolute scale, and β is twice the Bjerrum distance. The initial Λ^0 values for the iteration procedure were obtained from the Shedlovsky extrapolation¹³ of the data. Input for the program is the set ($C_j, \Lambda_j, j = 1, \dots, n$), n , ϵ , η , T , initial value of Λ^0 , and an instruction to cover a preselected range of R values.

In practice, calculations are made by finding the values of Λ^0 and σ , which minimize the standard deviation, σ ,

$$\sigma^2 = \sum_{j=1}^n [\Lambda_j(\text{calc}) - \Lambda_j^0(\text{obs})]^2 / (n - 2) \quad (7)$$

for a sequence of R values and then plotting σ against R; the best-fit R corresponds to the minimum in σ vs. R curve. However, since a rough scan using unit increment of R values from 4 to 20 gave no significant minima in the $\sigma(\%)$ vs R curves, the R value was assumed to be $R = a + d$, where a is the sum of the ionic crystallographic radii and d is given by¹²

$$d = 1.183 (M/\rho_0)^{1/3} \quad (8)$$

where M is the molecular weight of the solvent and ρ_0 its density.

The values of Λ^0 , Ka and R obtained by this procedure are reported in Table II.

The association constants Ka of these electrolytes (cf., Table II) indicate that these salts are slightly associated in N,N-dimethylacetamide. This implies that a preponderant portion of each salt remains dissociated in this solvent medium. The Ka values of the lithium salts are, in general, found to decrease with increasing size of the anion; LiAsF₆ is, however, an exception, which has the highest Ka value though the crystallographic radius of AsF₆⁻ ion is maximum among the anions investigated.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components. In the absence of accurate transport number data for these systems, we have used the "reference electrolyte" method for the division of Λ^0 into their ionic components. Bu₄NBPh₄ has been used as the

"reference electrolyte."¹⁴ Bu₄NBPh₄ was also used as the reference electrolyte by Fuoss and Hirsch¹⁵ to evaluate the limiting ionic conductances in several organic solvents. We have divided the λ° values of Bu₄NBPh₄ into ionic components using a method similar to that proposed by Krumgalz¹⁶.

$$\lambda^\circ(\text{Bu}_4\text{N}^+) / \lambda^\circ(\text{Ph}_4\text{B}^-) = r(\text{Ph}_4\text{B}^-) / r(\text{Bu}_4\text{N}^+) = 5.35/5.00 = 1.07 \quad (9)$$

The r values have been taken from the works of Gill et al.^{17,18} The limiting ion conductances calculated from the above equation are recorded in Table III.

It is seen from Table III that for the halide ions, the λ° values decrease in the following order : Cl⁻ > Br⁻ > I⁻ i.e. the limiting ionic conductivity values decrease with increasing size of these anions.

This is also found to be true for the molecular anions, i.e., the λ° values of these ions decrease in the order BF₄⁻ > ClO₄⁻ > AsF₆⁻ > Ph₄B⁻.

This observation indicates that all these anions remain unsolvated in N,N-dimethylacetamide solutions. Had these ions been solvated in N,N-dimethylacetamide, their limiting ionic conductivity values would have been in the reverse order, since the smaller ions with higher surface charge density could associate a greater number of solvent molecules to form a larger solvodynamic entity with lower mobility which is not observed here.

The starting point for most evaluations of ionic conductances is Stokes' law that contends that the limiting Walden product (the limiting ionic conductance - solvent viscosity product) for any singly charged, spherical ion is a function only of

the ionic radius and, thus, under normal conditions, is a constant. In Table III we have collected the Stokes' radii (r_s) of the ions in N,N-dimethylacetamide. For lithium ion, the Stokes' radius is much higher than its crystallographic radius, suggesting that this ion is significantly solvated in this solvent medium. The Stokes' radii of the other ions are, however, found to be either very close to or smaller than their corresponding crystallographic radii. This observation indicates that these ions are scarcely solvated in N,N-dimethylacetamide solutions. This also supports our earlier contention derived from the order of the limiting ionic conductivity values.

It may thus be concluded that all these lithium salts remain slightly associated in N,N-dimethylacetamide solutions apparently due to the medium relative permittivity of the solvent. Lithium ion is found to be significantly solvated in this solvent medium, while the other ions remain scarcely solvated.

SECTION B

A STUDY ON VOLUMETRIC AND COMPRESSIBILITY PROPERTIES OF SOME LITHIUM SALTS IN N,N-DIMETHYLACETAMIDE AT 298.15 K

Proteins belong to an important family of biomolecules which make up a large part of the animal body. The most sensitive part of protein molecules are their amide or peptide linkages i.e.-CO – N < groupings. Due to the close resemblance with proteins, amides can act as a reasonable model to investigate the different structural problems in molecular biology. The study of thermodynamic properties gives a very interesting opportunity to closely follow the nature of interactions of solutes with solvent. The volumetric property is a useful parameter for interpreting solute-solvent interactions in solution. Various concepts regarding molecular processes in solutions such as electrostriction, hydrophobic hydration, micellization and co-sphere overlap during solute-solvent interactions^{19,20} have to some extent been derived from the partial molar volume data of diverse compounds. In recent years^{21,22} along with partial molar volume data the ultrasonic velocity studies in many of the non-aqueous electrolyte solutions have led to shed light on the molecular interactions in the solvation process. This paper presents the results of a comprehensive study of the apparent molar volumes and adiabatic compressibilities of some lithium salts e.g. LiCl, LiBr, LiI, LiClO₄, LiBF₄ in a tertiary amide N,N-dimethylacetamide in order to examine the ion-ion and ion-solvent interactions in this medium. The solvent is miscible with water and is generally similar in its

properties to N,N-dimethylformamide. Due to the presence of third methyl group in N,N-dimethylacetamide, it is electron donating and its ability to solvate cations is greater than that of dimethylformamide, acetone, acetonitrile and benzonitrile.²³ The importance of this solvent also lies in the fact that it has a similarity with basic peptide structure of proteins.

EXPERIMENTAL

N,N-dimethylacetamide (E.Merck, India, > 99.5%) was distilled twice in an all-glass distillation set immediately before use and the middle fraction was collected. The purified solvent had an ultrasonic sound velocity of 1463 ms⁻¹ at 298.15K. The details of the experimental procedure have been described in chapter III.

RESULTS AND DISCUSSION

The apparent molar volumes (ϕ_v) were calculated from the densities of the solutions using the equation

$$\phi_v = M/\rho_o - 1000(\rho - \rho_o)/c\rho_o \quad (10)$$

where, c is the molarity of the electrolyte solution, M is the molecular weight of the solute and ρ and ρ_o are the densities of the solution and solvent respectively.

The molar concentrations, densities and the apparent molar volumes of the various electrolyte solutions in N,N-dimethylacetamide at 298.15K are given in Table IV.

From the ϕ_v data, ϕ_v versus \sqrt{c} curves have been drawn and the plots were found to be linear in all the cases with positive slopes. Obviously, the Masson's empirical relation namely,

$$\phi_v = \phi_v^\circ + S_v \sqrt{c} \quad (11)$$

is applicable at this temperature and concentration range studied here. The limiting apparent molar volumes, ϕ_v° (equal to partial molar volumes at infinite dilution, $\phi_v^\circ = \bar{V}_2^\circ$) are obtained by the least-squares fitting of ϕ_v values to the above equation and these values along with the experimental S_v^* values have been reported in Table V.

From Table V we see that the S_v^* values are positive for all these lithium salts in N,N-dimethylacetamide, indicating appreciable ion-ion interactions in this solvent medium. The ϕ_v° values are also large and positive and increase with increase in size of the anions. This is in agreement with earlier findings in several non-aqueous solvents as well as in water and heavy water.²⁵ The calculations of the ionic limiting partial molar volumes have been done following the method of Conway et al.²⁶ The \bar{V}_2° values for the tetraalkylammonium bromides in N,N-dimethylacetamide at 298.15K were plotted against the formula weight of the corresponding tetraalkylammonium ions. An excellent linear relationship was observed for all the salts examined and therefore the results fitted eq. (12).

$$\bar{V}_2^\circ R_4 N X = \bar{V}_2^\circ x^- + b M_{R_4 N^+} \quad (12)$$

and extrapolation to zero cationic formula weight gave the limiting partial molar volumes of the bromide ion ($-9.79 \text{ cm}^3 \text{ mol}^{-1}$). Such values have been obtained for this anion in 2-methoxyethanol²⁷ and 1,2-dimethoxy ethane.²⁸ The values for the cation and other anions have been computed from this anionic value by additive procedures and were found to be 26.34 , -2.87 , -3.31 , -3.94 and $-18.54 (\text{cm}^3 \text{ mol}^{-1})$ for Li^+ , ClO_4^- , I^- , BF_4^- and Cl^- respectively.

In general, the smallest anion (Cl^- , crystallographic radius 0.18 nm) with maximum surface charge density upon it, is expected to be the least mobile because of its heavy solvation. This is exactly the opposite to what we observe in the present solvent medium. Electrostatic solvation of these ions must decrease with increase in size going from chloride to iodide ion. However, the opposite trend observed could be explained that with increase in size and hence with increasing co-ordination number of the anions, more and more solvent molecules can fit in their first co-ordination shells^{29,30} thus increasing the intrinsic size of these ions going from chloride to iodide ion.

Adiabatic compressibility coefficient, β , were derived from the relation,

$$\beta = 1/u^2 d \quad (13)$$

where, u is the velocity of sound and d is the density of the solution. The apparent molar adiabatic compressibility (ϕ_k) of the liquid solutions were calculated from the relation,

$$\phi_k = \frac{1000}{cd_o} (d_o\beta - d\beta_o) + \beta_o \frac{M}{d_o} \quad (14)$$

where, β_0 , and β are the compressibility coefficients of the solvent and solution respectively. The molar concentration (c), sound velocity (u), adiabatic compressibility (ϕ_k) for all the lithium salts in N,N-dimethylacetamide have been reported in Table IV.

From Table IV it can be seen that the sound velocity increases with increase in concentration of the salt solution and these values are less than that of the pure solvent. This can be attributed to two effects³¹; (i) a decrease in compressibility caused by the introduction of incompressible ions; and (ii) a change of solvent structure around the ion.

The contribution of (i) is generally larger and depends more on concentration than on the kind of ions. Adiabatic compressibility decreases with increase in concentration for all the electrolytes studied. The addition of electrolyte lowers the compressibility of the solvent due to the orientation of the solvent molecules around the ion, which normally increases the internal pressure. In the presence of an ionized solute, the solvent molecules in the solutions behave as though subjected to a constant effective pressure in addition to atmospheric pressure. This effective pressure arises from the forces of attraction between ions and solvent dipoles and increases with the charge density on the ions.

The concentration dependence of apparent molar adiabatic compressibility is given by,

$$\phi_k = \phi^{\circ}_k + S_k \sqrt{c} \quad (15)$$

where S_k is an experimentally determined slope and ϕ°_k is the limiting apparent molar adiabatic compressibility. The ϕ°_k values for LiCl, LiBr, LiI, LiClO₄ and LiBF₄ are -72.77 ± 0.01 , -92.31 ± 0.05 , -116.17 ± 0.01 , -113.02 ± 0.01 and -91.93 ± 0.01 ($10^{15} \text{ m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$) respectively. Such negative ϕ°_k values for alkali metal salts have also been reported in 2-methoxyethanol.²⁷

It is seen that all the Li salts studied have negative limiting apparent molar adiabatic compressibilities (ϕ°_k) which become more negative with increase in size of the anion. Negative ϕ°_k values of the salts are interpreted in terms of loss of compressibility of the N,N-dimethylacetamide due to electrostrictive forces in the vicinity of the ions. Here the lithium ion being the common cation, the loss of compressibility due to cation is the same in all cases, the anions are evidently making the difference.

In order to gain more insight regarding ion-solvent interaction, we have divided the ϕ°_k values into their ionic contributions in the same way as done for ϕ°_v values. Thus, the intercept in the plot of apparent molar adiabatic compressibilities of R₄N⁺ ions versus cation formula weights is the ionic apparent molar adiabatic compressibility of the Br⁻ ion. Individual ionic compressibilities of Cl⁻, BF₄⁻, Br⁻, ClO₄⁻, I⁻ and Li⁺ are -199.45 , -218.62 , -219 , -239.70 , -242.85 and 126.68 ($10^{15} \text{ m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$) respectively. The results show that ionic apparent molar adiabatic compressibility value for Li⁺ ion is large positive whereas those for the anions are

large negative. As oxygen atom is more electronegative than nitrogen atom, so oxygen has a greater tendency to pull the lone pair of electrons on nitrogen atom through the intervening carbon atom. This leads to the development of a positive centre on nitrogen and a negative one on oxygen atom. The electron rich oxygen atom tends to form a co-ordinate bond with the lithium ion and thus the cation forms a kinetic entity with the solvent which is compressible to a great extent thus causing a greater degree of disorder in the solvent structure. The negative compressibility of these anions are obviously due to the electrostriction of solvent molecules around these ions arising from their relatively high charge density values. The extent of electrostriction is maximum in the case of the Cl^- ion, and this will decrease gradually with increase in size of the anions. This explains the observed trend in the ionic ϕ_k^0 values : $\text{Cl}^- > \text{Br}^- > \text{I}^-$.

The investigation thus indicates that the lithium salts studied here exhibit appreciable ion-ion interaction in N,N-dimethylacetamide and comparatively larger size anions show greater electrostatic solvation in this medium in contrast to electrostriction effect where smaller size anions predominate over others.

SECTION C

SPECTRAL MEASUREMENTS OF SOME LITHIUM SALTS IN N,N-DIMETHYLACETAMIDE

In this section we have investigated the behaviour of some lithium salts e.g., lithium chloride (LiCl), lithium bromide (LiBr), lithium iodide (LiI), lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4), and lithium hexafluoroarsenate (LiAsF_6) in a tertiary amide, N,N-dimethylacetamide (DMA) using FTIR and FT Raman measurements and the results are reported here.

Experimental

The details of the experimental procedure have been described earlier in chapter III.

Results and Discussion

The FTIR and the FT-Raman spectra of pure solvent N,N-dimethylacetamide and the spectra of the salt solutions are reproduced in figures 1 to 14.

The observed frequencies of the principal infrared and Raman bands are given in Table VI and VII. Some published data on the ordinary infrared spectrum of the pure solvent are available³² and our results are found to be in good agreement with those.

A comparison of the infrared and Raman spectra clearly indicates that these two techniques are complementary — the strong peaks in infrared spectra appear as weak signals in Raman spectra and the converse being also true.

Most of the infrared bands of N,N-dimethylacetamide are almost unaffected by the presence of these solutes. All the Raman peaks do not show any appreciable shifts in salt solutions. This may be ascribed to the simultaneous control of the opposing effects induced by the solutes which are almost of equal magnitude. There is no evidence for the "spectroscopically free" anion, X^- ($X = Cl, Br, I, BF_4, AsF_6$), in the lithium salt solutions as no new peak characteristic of the anions appeared for the salt solution (a very weak peak at 931.5 cm^{-1} appeared only for ClO_4^- ion in the Raman spectrum presumably due to very high concentration). This suggests possible absence of the free anions or solvent-separated ion-pair M^+SX^- (S is the solvent molecule) and/or to the solvent, separated dimer, spectroscopically indistinguishable from each other. The association constants (K_A) of these electrolytes (in Section A) indicate that these salts are slightly associated in N,N-dimethylacetamide. This implies that a preponderant portion of each salt remains dissociated in this solvent medium. The absence of any characteristic infrared and Raman peak in the salt solutions infers that the free ions must be significantly solvated by the solvent molecules to render them spectroscopically undetectable.^{8,9} The absence of any new peak also eliminates the probability of formation of contact ion-pair in solution.^{33,34}

The most intense infrared bands involving the nitrogen and oxygen atoms of N,N-dimethylacetamide molecules exhibit almost parallel shifts in each salt solution (cf. Table VI). This suggests that the perturbations, if any, in the environments of these atoms (viz., nitrogen, and oxygen) of the solvent molecules caused by the solute species would be almost of the same order. The Raman peaks, however, do not show any appreciable shifts in the electrolyte solutions.

Thus we find that for all these lithium salts in N,N-dimethylacetamide, the corresponding cation and anion are significantly solvated in this medium.

References

1. A.M.Christie and C.A.Vincent, *J.Phys.Chem.*, **100**, 4618, 1996.
2. D.Nandi, S.Das and D.K.Hazra, *J.Chem.Soc., Faraday Trans.*, **85**, 1531, 1989.
3. D.Nandi and D.K.Hazra, *J.Chem.Soc., Faraday Trans.*, **85**, 4227, 1989.
4. P.K.Muhuri and D.K.Hazra, *J.Chem.Soc., Faraday Trans.*, **87**, 3511, 1991.
5. P.K.Muhuri and D.K.Hazra, *Z.Naturforsch.*, **48a**, 523, 1993.
6. B.Das, P.K.Muhuri and D.K.Hazra, *Acoust. Lett.*, **18**, 69, 1994.
7. B. Das and D.K.Hazra, *J. Phys. Chem.*, **99**, 269, 1995.
8. P.K.Muhuri, B.Das and D.K.Hazra, *J.Phys.Chem.*, **B,101**, 3329, 1997.
9. P.J.Victor, P.K.Muhuri, B.Das and D.K.Hazra, *J. Phys. Chem.*, **B,104**, 5350, 2000.
10. A.K.Covington and T.Dickinson, Physical Chemistry of Organic Solvent Systems, Eds. (Plenum Press, New York) 1973, Chap. 1.
11. R.M.Fuoss, *Proc.Natl.Acad.Sci. U.S.A.* **75**, 16, 1978.
12. R.M.Fuoss, *J.Phys. Chem.*, **82**, 2427, 1978.
13. R.M.Fuoss and T.Shedlovsky, *J. Amer. Chem. Soc.*, **71**, 1496, 1949.
14. B.S.Krumgalz, *J.Chem.Soc., Faraday Trans.*, **1,79**, 571, 1983.
15. R.M.Fuoss and E.Hirsch, *J.Amer. Chem. Soc.*, **82**, 1013, 1960.

16. B.S.Krumgalz, *J.Chem.Soc., Faraday Trans.*, 1, **76**, 1275, 1980.
17. D.S.Gill, *Electrochim. Acta*, **24**, 701, 1979.
18. D.S.Gill and M.B.Sekhri, *J.Chem.Soc., Faraday Trans.*, 1, **78**, 119, 1982.
19. R.W.Gurney, *Ionic Processes in Solutions* (McGraw Hill, New York), 1954.
20. J.E.Desnoyers, M.Arel, G. Perron and C. Jolicoeur, *J.Phys.Chem.*, **73**, 3347, 1969.
21. P.J.Victor, B. Das and D.K.Hazra, *J. Solution Chem.*, **30**, 435, 2001.
22. P.J.Victor, B.Das and D.K.Hazra, *J. Phys. Chem. A.*, **105**, 5960, 2001.
23. A.J.Parker, *Quart Rev.*, **16**, 162, 1962.
24. D.O.Masson, *Philos Mag.*, **8**, 218, 1929.
25. B.S.Krumgalz, *J.Chem.Soc., Faraday Trans.*, 1, **76**, 1887, 1980.
26. B.E.Conway, R.E.Verral and J.E.Desnoyers, *Trans Faraday Soc.*, **62**, 2738, 1966.
27. B. Das and D.K.Hazra, *J. Chem. Eng. Data.*, **36**, 403, 1991.
28. P.K.Muhuri, B. Das and D.K.Hazra, *Ind. J. Chem.*, **35A**, 288, 1996.
29. R.Zana, G.Perron and J.E.Desnoyers, *J. Soln. Chem.*, **9**, 59, 1980.
30. I. Davidson, G.Perron and J.E.Desnoyers, *Can. J. Chem.*, **59**, 2212, 1981.
31. F. Hirata and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **45**, 2715, 1972.

32. V.V.Chalapathi and K.V.Ramiah, *Proc. Ind. Acad. Sci.*, **68A**, 109, 1968.
33. S. Cheng, M.W.Sevensen and P.P.Schmidt, *J. Phys. Chem.*, **91**, 3047, 1987.
34. Z. Deng and D.E. Irish, *Can. J. Chem.*, **69**, 1766, 1991.

Table 1 : Equivalent Conductances and Corresponding Molarities of Electrolytes in N,N-Dimethylacetamide at 298.15K

$10^4 c$ mol-dm $^{-3}$	Λ S-cm $^2\text{-mol}^{-1}$	$10^4 c$ mol-dm $^{-3}$	Λ S-cm $^2\text{-mol}^{-1}$
	LiCl		LiBr
149.961	50.67	150.418	51.70
138.853	51.36	140.390	52.33
127.745	52.12	130.362	52.90
116.636	52.90	120.334	53.58
105.528	53.73	110.307	54.19
94.420	54.59	100.278	54.70
83.312	55.56	90.251	55.18
72.204	56.52	80.223	55.48
61.095	57.59	70.493	55.84
		60.715	57.60
	LiI		LiClO₄
129.606	41.34	141.250	47.70
120.180	41.75	131.987	48.09
109.969	42.35	122.725	48.46
99.757	42.88	113.463	48.89
89.546	43.30	104.201	49.23
78.549	43.89	94.938	49.68
69.909	44.45	85.676	50.15
59.691	45.02	76.414	50.61
52.766	45.43	67.151	51.10
47.032	45.87	57.889	51.69
			Contd...

$10^4 c$ $\text{mol}\cdot\text{dm}^{-3}$	Λ $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$10^4 c$ $\text{mol}\cdot\text{dm}^{-3}$	Λ $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
LiBF₄		LiAsF₆	
140.241	51.34	149.511	30.63
129.810	51.85	139.543	31.01
120.538	52.44	129.576	31.51
110.107	52.96	119.608	31.89
99.675	53.59	109.641	32.37
90.403	54.22	99.674	32.90
79.972	54.91	89.707	33.39
69.541	55.67	79.739	33.93
49.837	57.22		
Bu₄NBr		Bu₄NBPh₄	
138.937	47.52	163.589	34.20
129.013	48.22	154.471	34.66
119.089	49.00	139.353	35.06
109.165	49.71	127.236	35.54
99.241	50.54	115.118	36.05
89.317	51.49	103.000	36.52
79.393	52.39	90.883	37.09
69.469	53.35	78.765	37.62
59.545	54.42	66.647	38.25

Table II. Conductivity Parameters of Electrolytes in N,N-dimethylacetamide at 298.15K^a

Salt	Λ°	K_a	R	$\sigma\%$
LiCl	69.79 ± 0.20	45.76 ± 0.82	7.93	0.10
LiBr	67.35 ± 0.26	33.14 ± 0.96	8.09	0.15
LiI	51.97 ± 0.15	30.09 ± 0.78	8.33	0.15
LiClO ₄	58.16 ± 0.06	22.33 ± 0.23	8.14	0.05
LiBF ₄	65.08 ± 0.12	30.03 ± 0.46	8.31	0.09
LiAsF ₆	43.26 ± 0.19	52.05 ± 1.28	9.26	0.09
Bu ₄ NBPh ₄	44.47 ± 0.09	30.97 ± 0.44	14.50	0.08
Bu ₄ NBr	69.27 ± 0.20	45.63 ± 0.88	12.10	0.08

^aUnits ; Λ° , S-cm²-mol⁻¹; K_a , dm³-mol⁻¹; R, Å.

**Table III . Limiting Ionic Conductances and Ionic Stokes' Radii
in N,N-Dimethylacetamide at 298.15K^a**

Ion	λ°_{\pm}	r_s	Ion	λ°_{\pm}	r_s
Li^+	21.07	3.18	ClO_4^-	37.09	1.81
Bu_4N^+	22.99	2.81	BF_4^-	44.01	1.52
Cl^-	48.72	1.37	AsF_6^-	22.19	3.02
Br^-	46.28	1.45	Ph_4B^-	21.48	3.12
I^-	30.09	2.23			

^aUnits ; λ°_{\pm} , S-cm²-mol⁻¹ ; r_s , Å

Table IV : Concentration (c), density (ρ), apparent molar volume (ϕ_v), sound velocity (u), adiabatic compressibility coefficient (β), and apparent molar adiabatic compressibility (ϕ_k) of some lithium salts in N,N-dimethylacetamide at 25°C.

Salt	c (mol dm ⁻³)	ρ (g cm ⁻³)	ϕ_v (cm ³ mol ⁻¹)	u (ms ⁻¹)	$\beta \times 10^{13}$ (pa ⁻¹)	$\phi_k \times 10^{15}$ (m ³ mol ⁻¹ pa ⁻¹)
LiCl	0.18156	0.94144	18.56	1479.0	48.56	-63.00
	0.15008	0.94079	17.58	1476.0	48.79	-63.92
	0.11016	0.93990	16.17	1472.5	49.07	-65.18
	0.07988	0.93916	14.95	1469.8	49.29	-66.31
	0.05023	0.93839	13.47	1467.2	49.50	-67.64
	0.01997	0.93753	11.36	1464.5	49.73	-69.53
LiBr	0.18132	0.94917	26.38	1478.1	48.22	-70.75
	0.14992	0.94734	25.53	1475.9	48.46	-72.79
	0.11003	0.94497	24.18	1472.9	48.77	-75.55
	0.07981	0.94311	23.13	1470.6	49.02	-78.01
	0.05016	0.94125	21.60	1468.3	49.28	-81.04
	0.01994	0.93927	19.88	1465.8	49.55	-85.15
LiI	0.18023	0.95626	32.14	1478.6	47.83	-90.93
	0.14900	0.95313	31.37	1476.3	48.14	-93.21
	0.10936	0.94911	30.20	1473.2	48.54	-96.50
	0.07930	0.94602	29.10	1470.9	48.86	-99.41
	0.04986	0.94294	27.88	1468.5	49.18	-102.90
	0.01983	0.93974	26.03	1465.9	49.52	-107.80
LiClO ₄	0.17464	0.95008	31.91	1476.7	48.27	-80.05
	0.14436	0.94787	31.12	1474.5	48.52	-83.04
	0.10595	0.94501	30.04	1471.6	48.86	-87.33
	0.07684	0.94281	28.96	1469.3	49.13	-91.14
	0.04831	0.94060	27.83	1466.8	49.41	-95.66
	0.01921	0.93829	26.32	1464.0	49.72	-102.10
LiBF ₄	0.18844	0.94929	31.62	1478.0	48.22	-65.42
	0.15579	0.94732	30.78	1476.0	48.45	-67.83
	0.11431	0.94476	29.54	1473.2	48.76	-71.28
	0.08290	0.94277	28.46	1471.0	49.01	-74.35
	0.05212	0.94076	27.34	1468.8	49.27	-77.99
	0.02074	0.93866	25.42	1466.3	49.55	-83.14

Table V : Limiting apparent molar volume (ϕ_v^0) and experimental slopes (S_v^*) of lithium salts in N,N-dimethylacetamide at 298.15K

Salt	ϕ_v^0 ($\text{cm}^3 \text{mol}^{-1}$)	S_v^* ($\text{cm}^3 \text{L}^{1/2} \text{mol}^{-3/2}$)	$\sigma\%$
LiCl	$7.80 \pm .10$	25.25 ± 0.49	.026
LiBr	$16.55 \pm .05$	$23.11 \pm .15$.024
LiI	$23.03 \pm .05$	$21.57 \pm .27$.022
LiClO ₄	$23.47 \pm .08$	$20.12 \pm .25$.020
LiBF ₄	$22.40 \pm .08$	$21.20 \pm .25$.022

Table VI : Summary of FTIR spectra of salt solutions in N,N-Dimethylacetamide

DMA	LiCl	LiBr	LiI	LiClO ₄	LiBF ₄	LiAsF ₆
595.1(s)	593.4(s)	591.5(vs)	590.7(vs)	590.3(vs)	590.3(vs)	590.3(vs)
737.2(vw)	730.8(vw)	730.8(vw)	730.8(vw)	730.8(vw)	730.8(vw)	730.8(vw)
1019.7(s)	1017.9(s)	1014.9(vs)	1014.3(vs)	1013.6(vs)	1013.2(s)	1013.2(vs)
1056.5(w)	1056.5(w)	1056.5(w)	1056.5(w)	1056.5(w)	1056.5(w)	1056.5(w)
1191.9(m)	1190.0(s)	1188.5(s)	1188.5(s)	1188.3(s)	1187.4(S)	1189.5(S)
1264.6(m)	1264.5(s)	1265.4(s)	1264.7(s)	1265.6(s)	1264.1(s)	1263.8(s)
1365.0(w)	1360.6(m)	1358.7(m)	1358.2(m)	1357.4(m)	1357.2(m)	1357.2(m)
1402.6(m)	1401.5(s)	1398.1(s)	1397.4(s)	1396.5(s)	1394.9(s)	1394.8(s)
1626.4(vs)	1629.5(vs)	1628.5(vs)	1629.5(vs)	1635.0(vs)	1625.9(vs)	1619.8(vs)
2938.6(w)	2938.0(m)	2933.0(m)	2932.8(m)	2933.8(m)	2925.4(m)	2925.1(m)
3003.0(m)	3015.3(m)	3015.3(m)	3015.3(m)	3009.1(m)	3009.1(m)	3009.1(m)
3427.7(s)	3440.9(s)	3472.6(s)	3466.1(s)	3472.2(s)	3462.3(s)	3461.6(s)

^aw = weak, m = medium, s= strong, vs = very strong.

Table VII : Summary of Raman spectra of salt solution in N,N-Dimethylacetamide

DMA	LiCl	LiBr	LiI	LiClO ₄	LiBF ₄	LiAsF ₆
590.5(m)	540.9(m)	590.9(m)	591.8(m)	591.0(m)	590.9(m)	590.5(m)
737.0(vs)	737.6(vs)	738.4(vs)	739.0(vs)	738.2(vs)	737.4(vs)	737.1(vs)
1012.1(w)	1015.3(w)	1016.4(vw)	1015.1(w)	1013.6(w)	1013.4(vw)	1013.9(vw)
1014.0(m)	1416.2(m)	1420.6(m)	1418.1(m)	1420.0(m)	1415.9(m)	1412.8(m)
1636.7(m)	1639.3(m)	1641.0(m)	1637.9(m)	1619.8(m)	1637.7(m)	1636.8(m)
2930.8(vs)	2930.6(vs)	2930.9(vs)	2931.1(vs)	2932.3(vs)	2932.0(vs)	2930.9(vs)

^aw = weak, m = medium, s= strong, vs= very strong

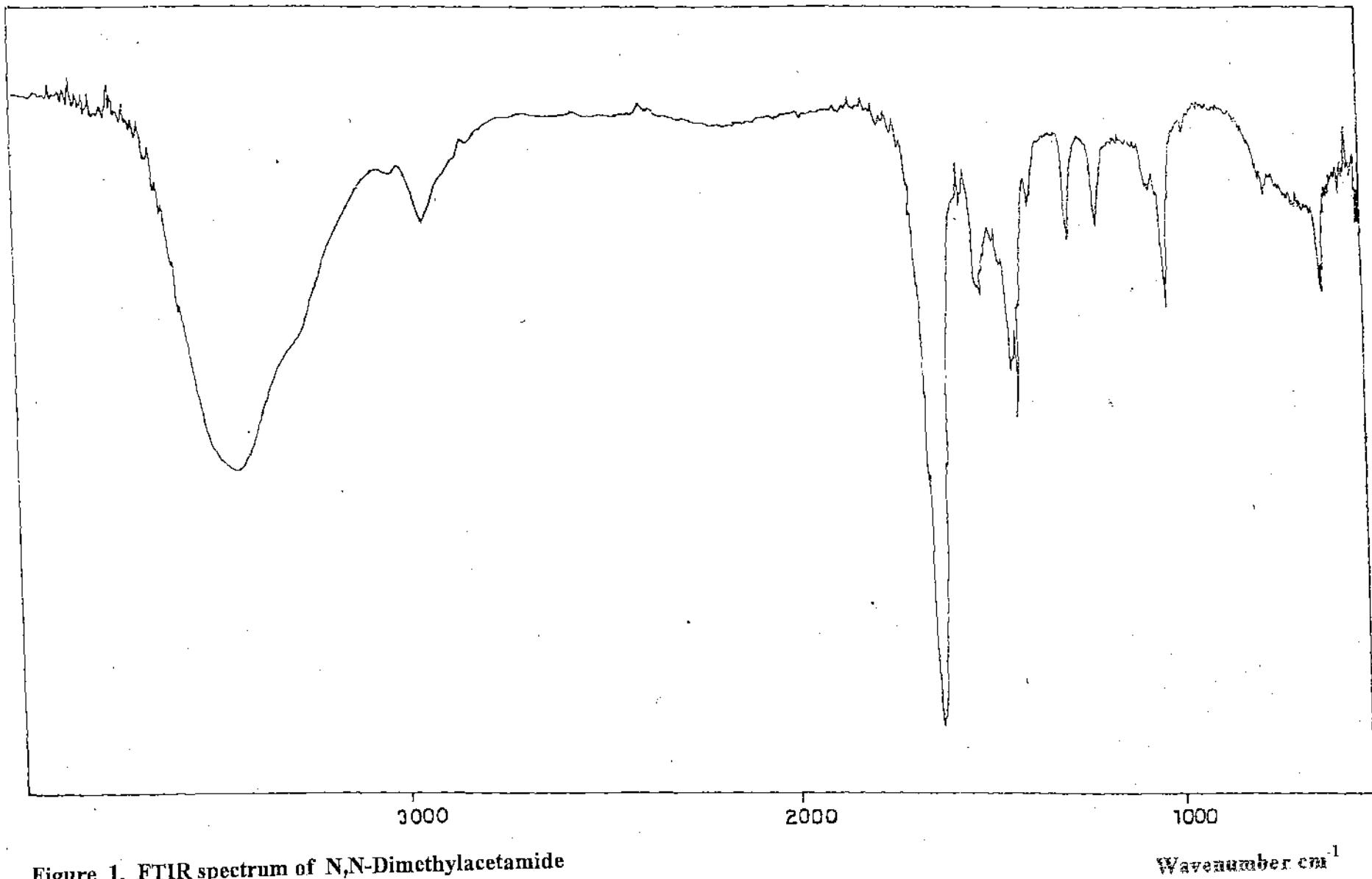


Figure 1. FTIR spectrum of N,N-Dimethylacetamide

Wavenumber cm^{-1}

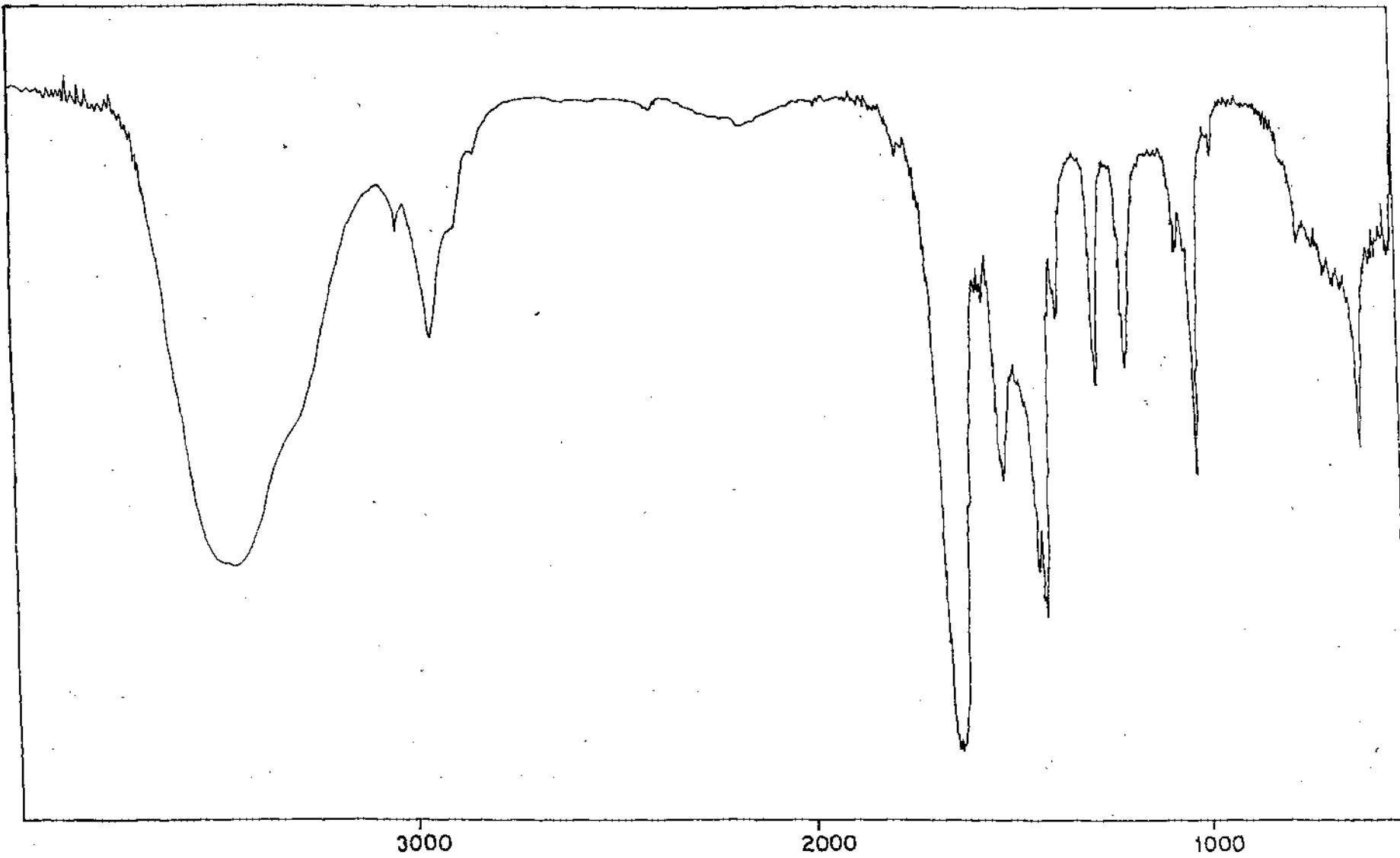


Figure 2. FTIR spectrum of LiCl in N,N-Dimethylacetamide

Wavenumber cm⁻¹

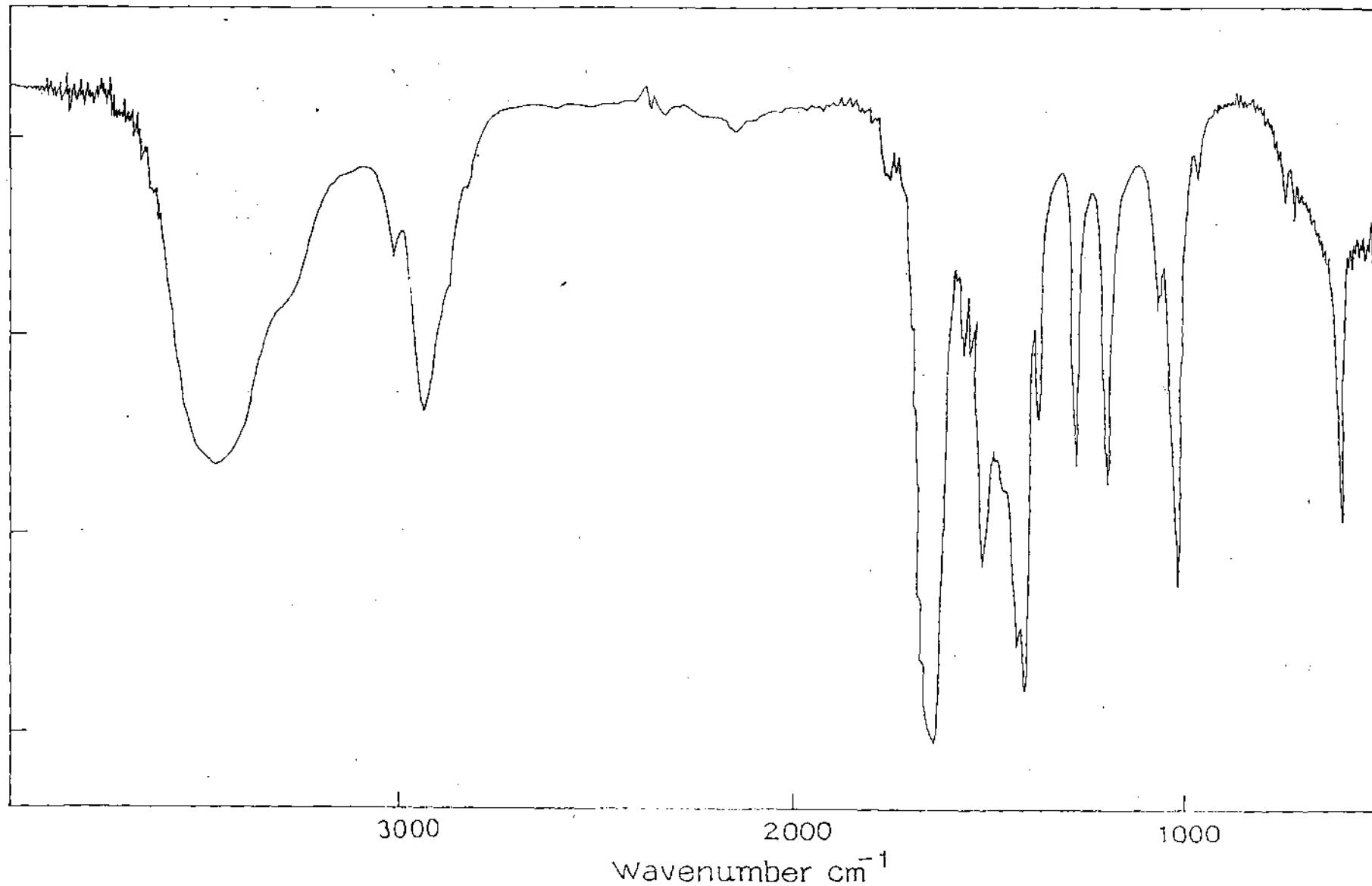


Figure 3. FTIR spectrum of LiBr in N,N-Dimethylacetamide

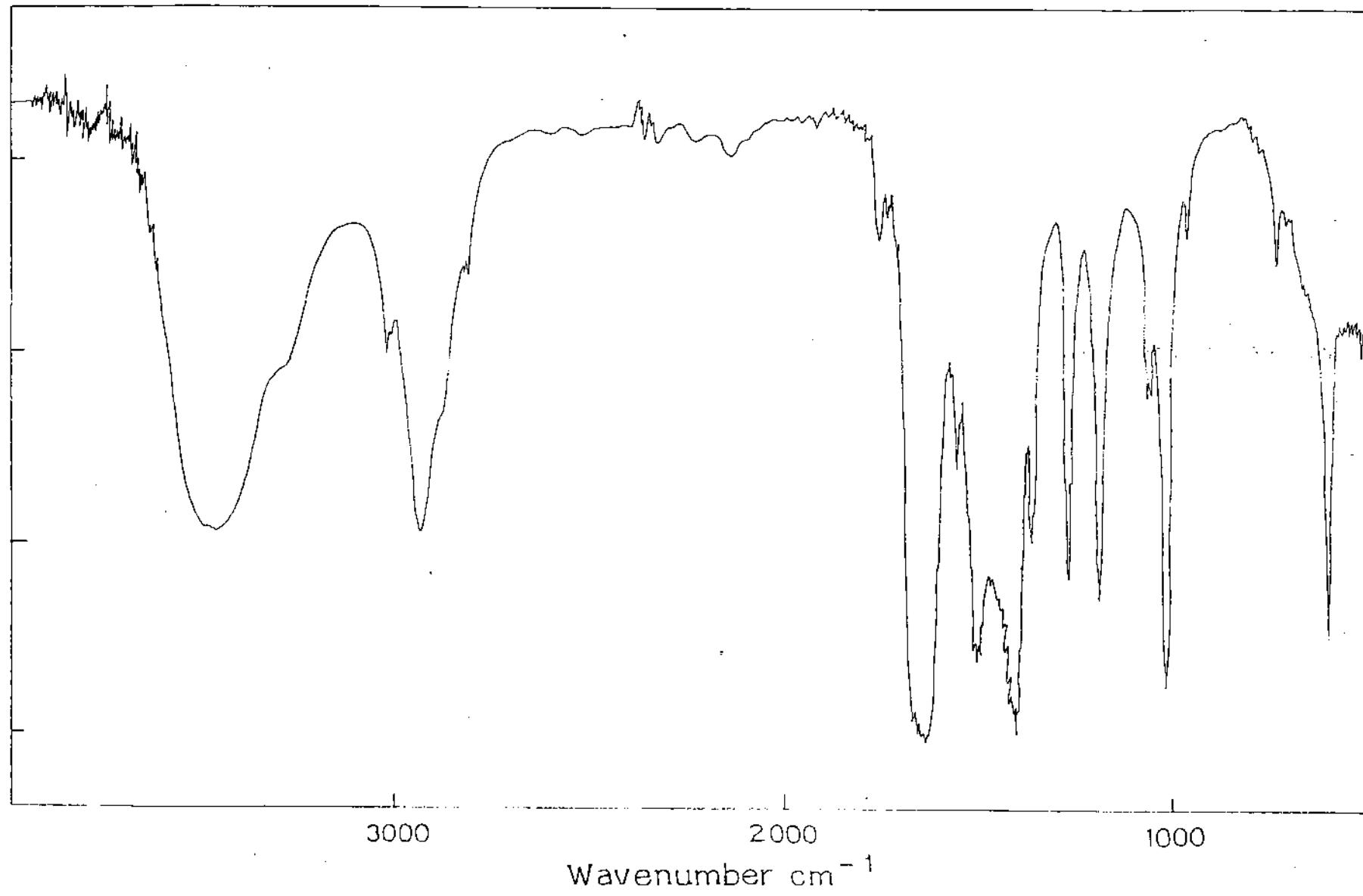


Figure 4. FTIR spectrum of LiI in N,N-Dimethylacetamide

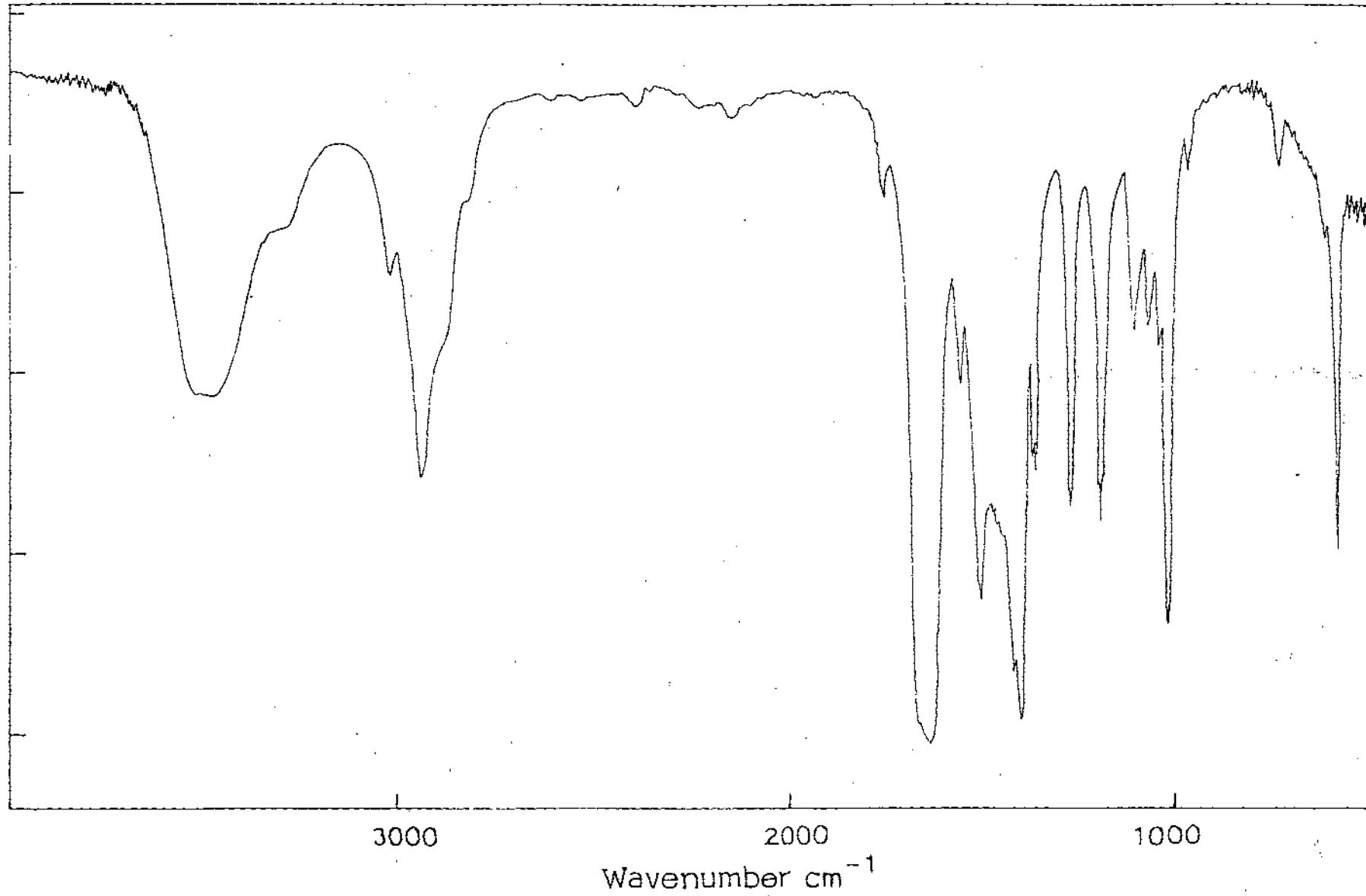


Figure 5. FTIR spectrum of LiClO_4 in N,N -Dimethylacetamide

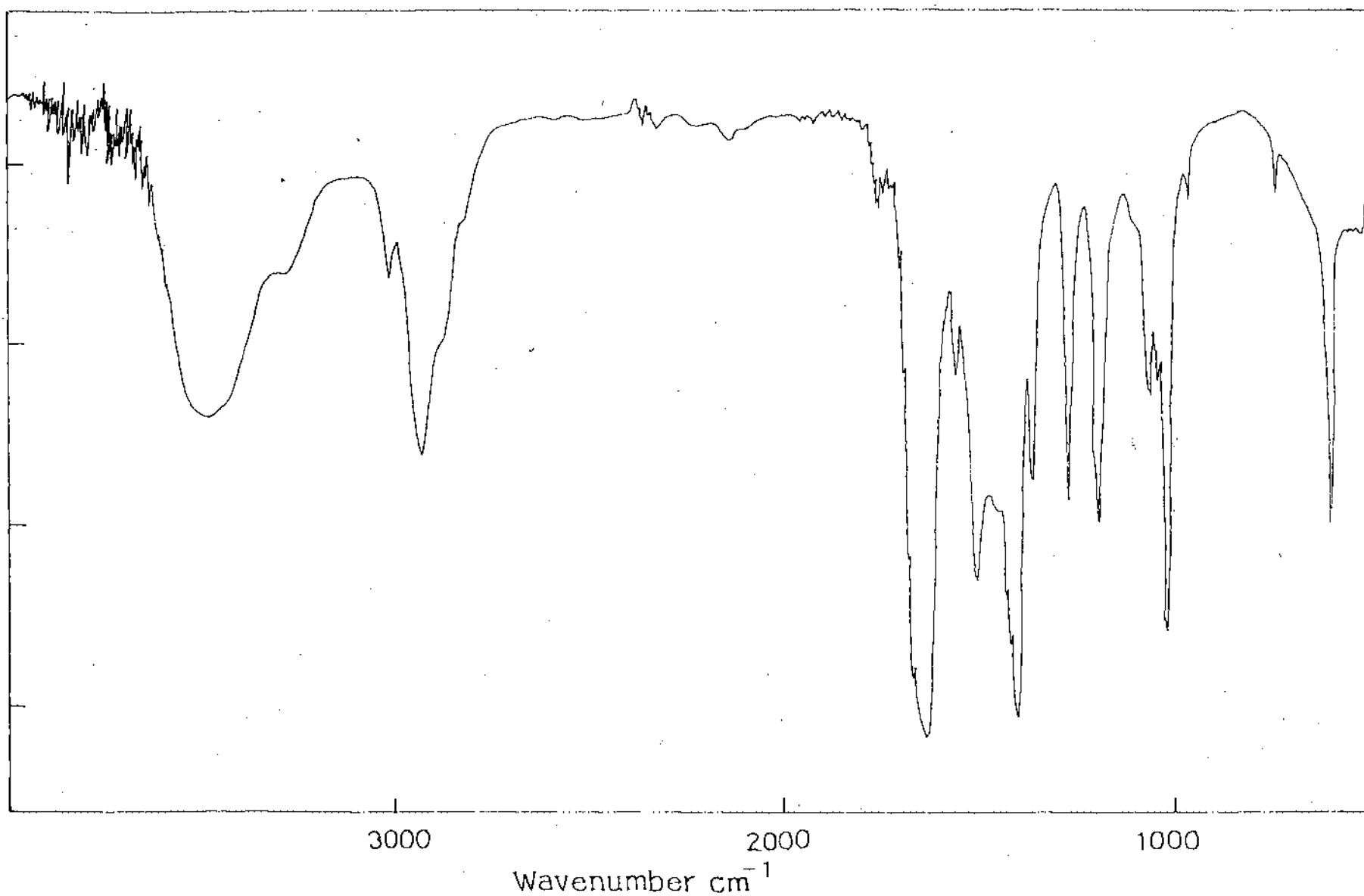


Figure 6. FTIR spectrum of LiBF₄ in N,N-Dimethylacetamide

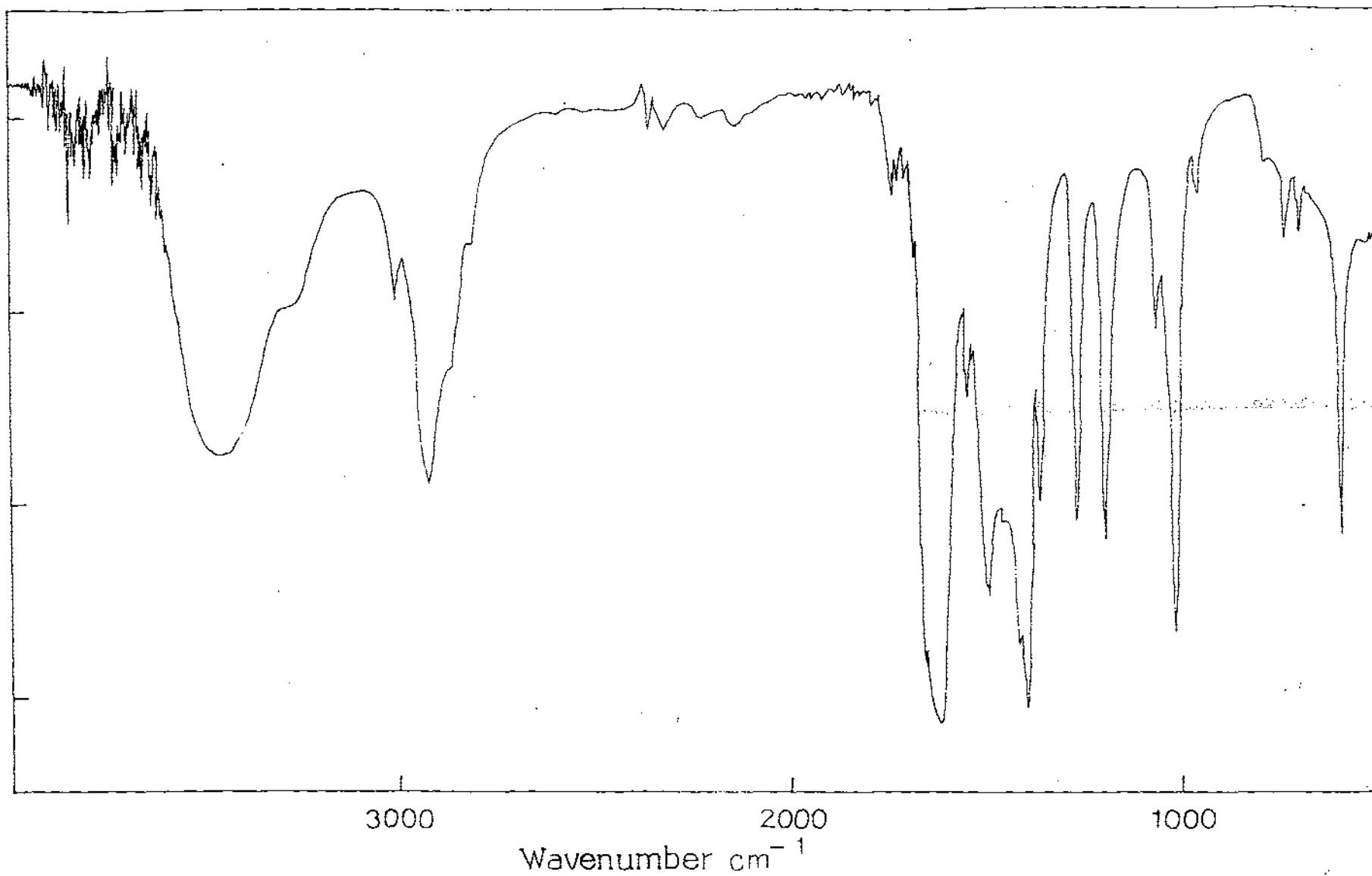


Figure 7. FTIR spectrum of LiAsF_6 in N,N -Dimethylacetamide

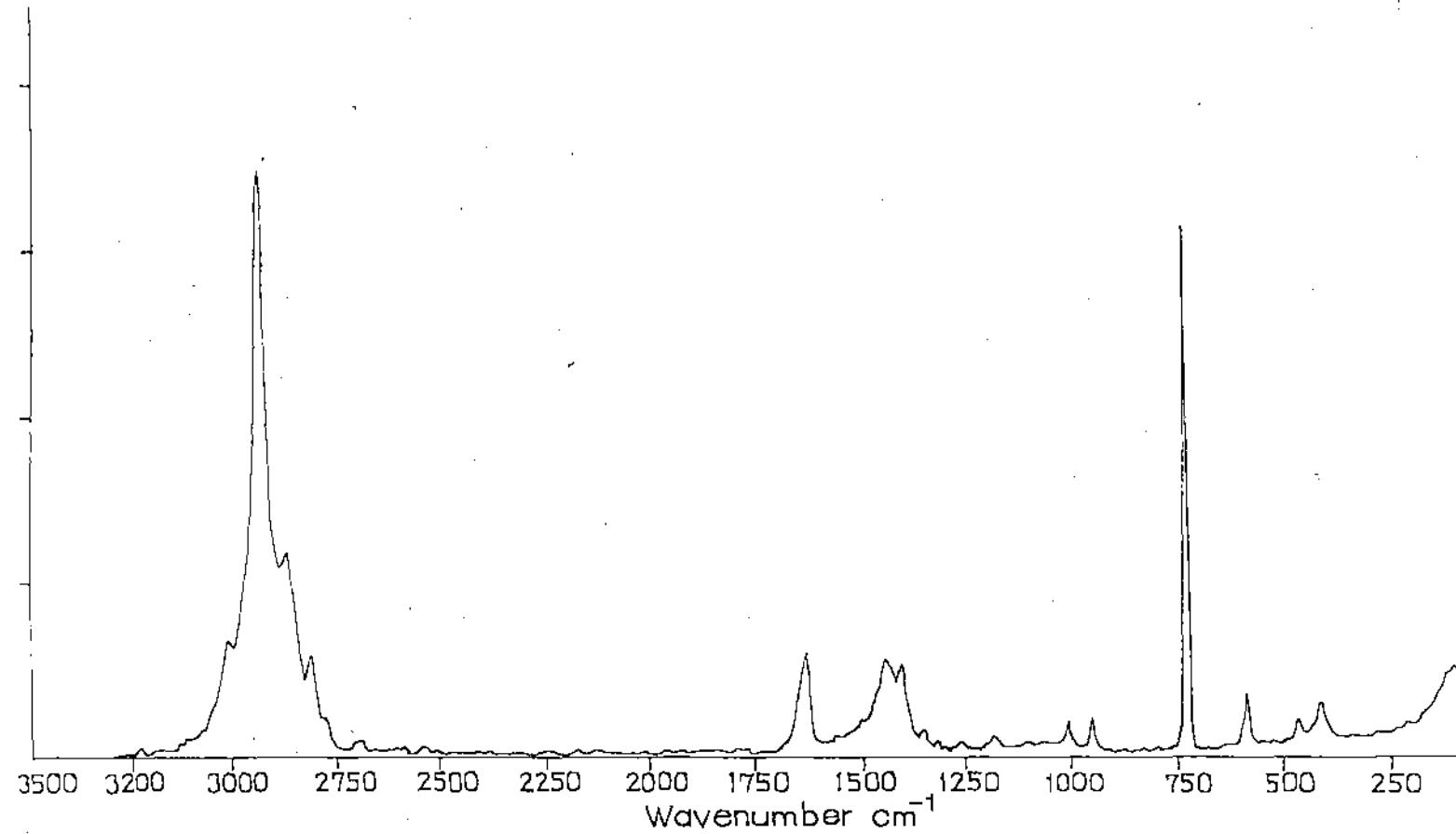


Figure 8. FT-Raman spectrum of N,N-dimethylacetamide

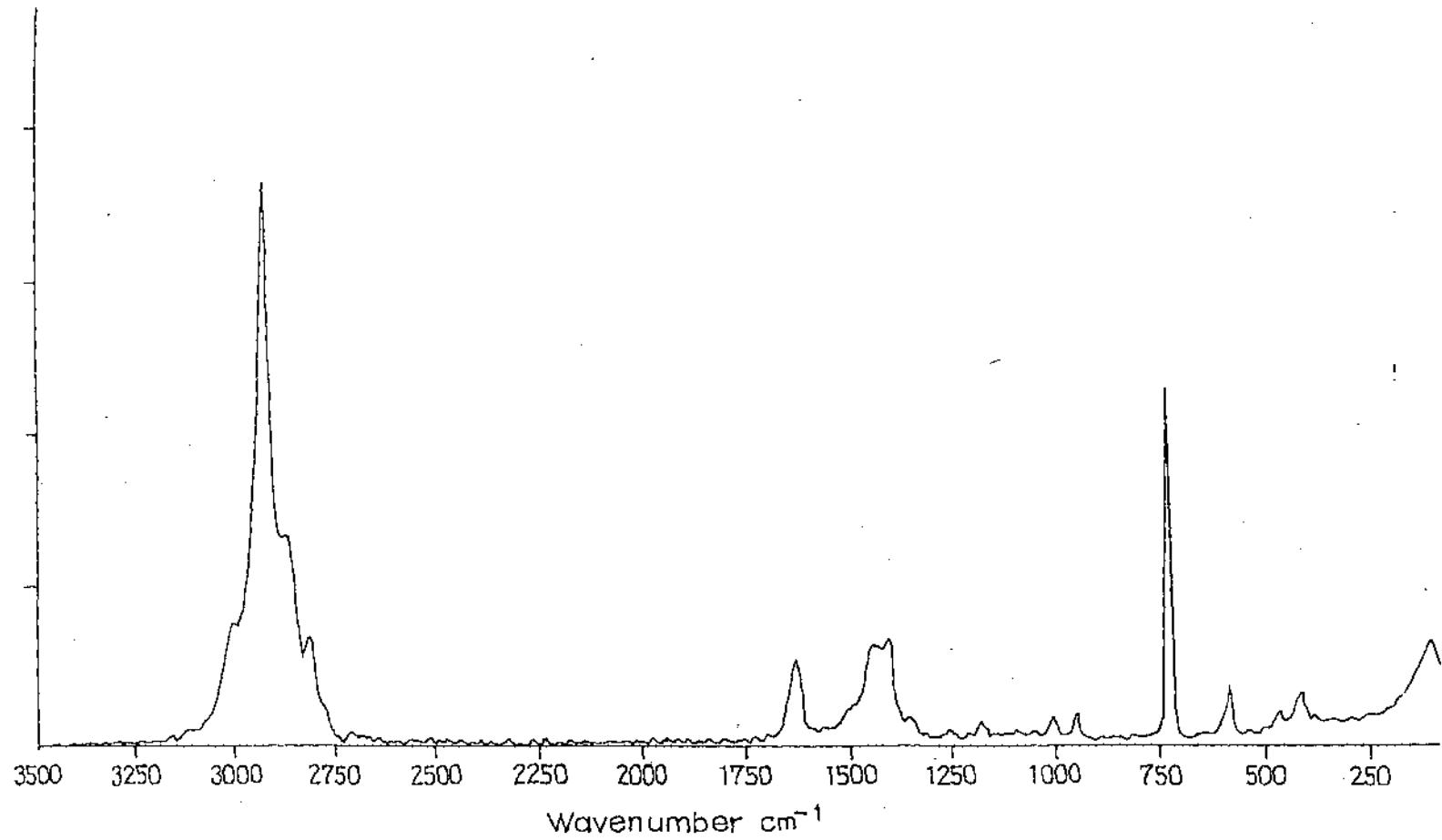


Figure 9. FT-Raman spectrum of LiCl in N,N-dimethylacetamide (C \sim 1M)

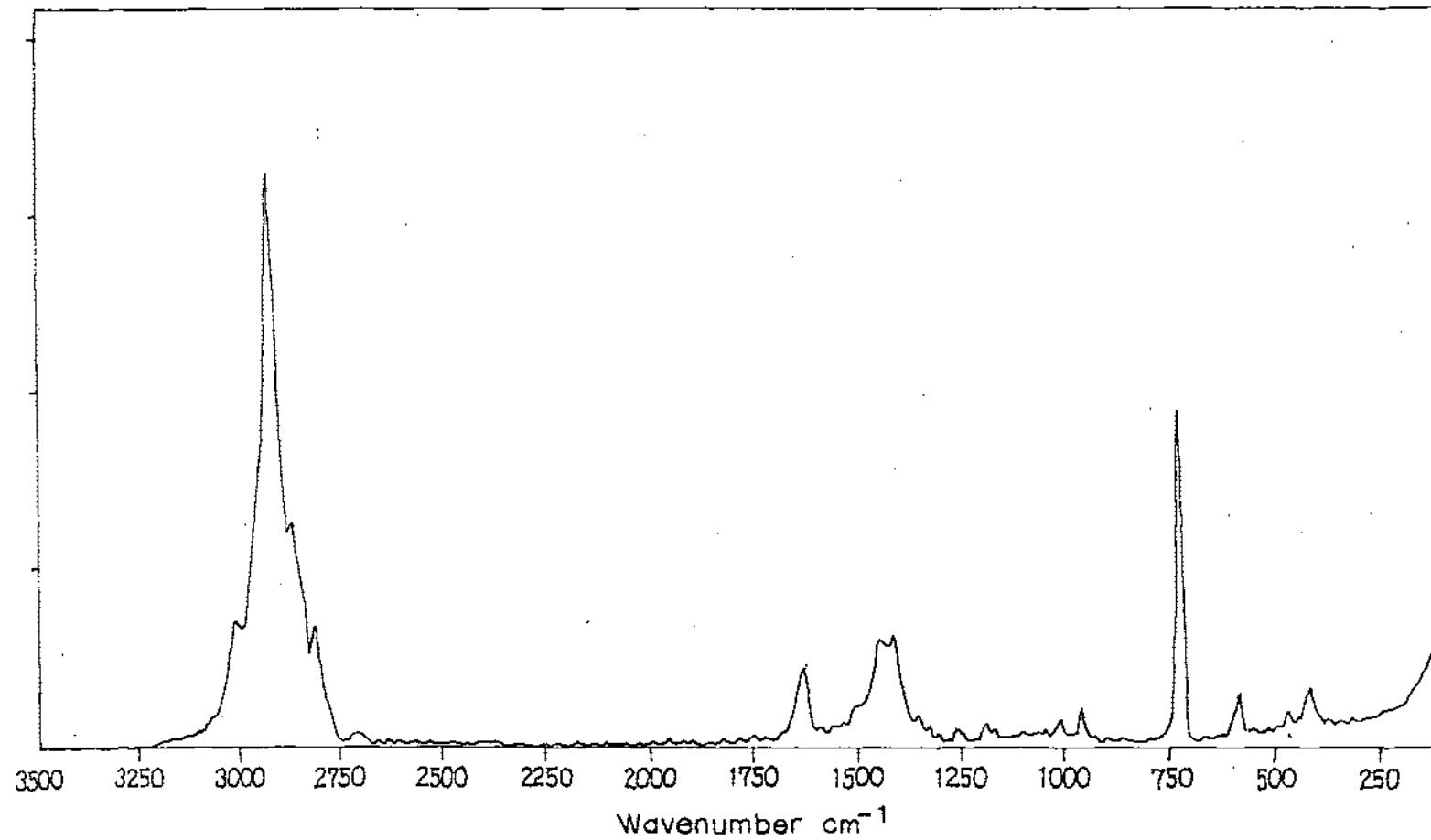


Figure 10. FT-Raman spectrum of LiBr in N,N-dimethylacetamide (C=~1M)

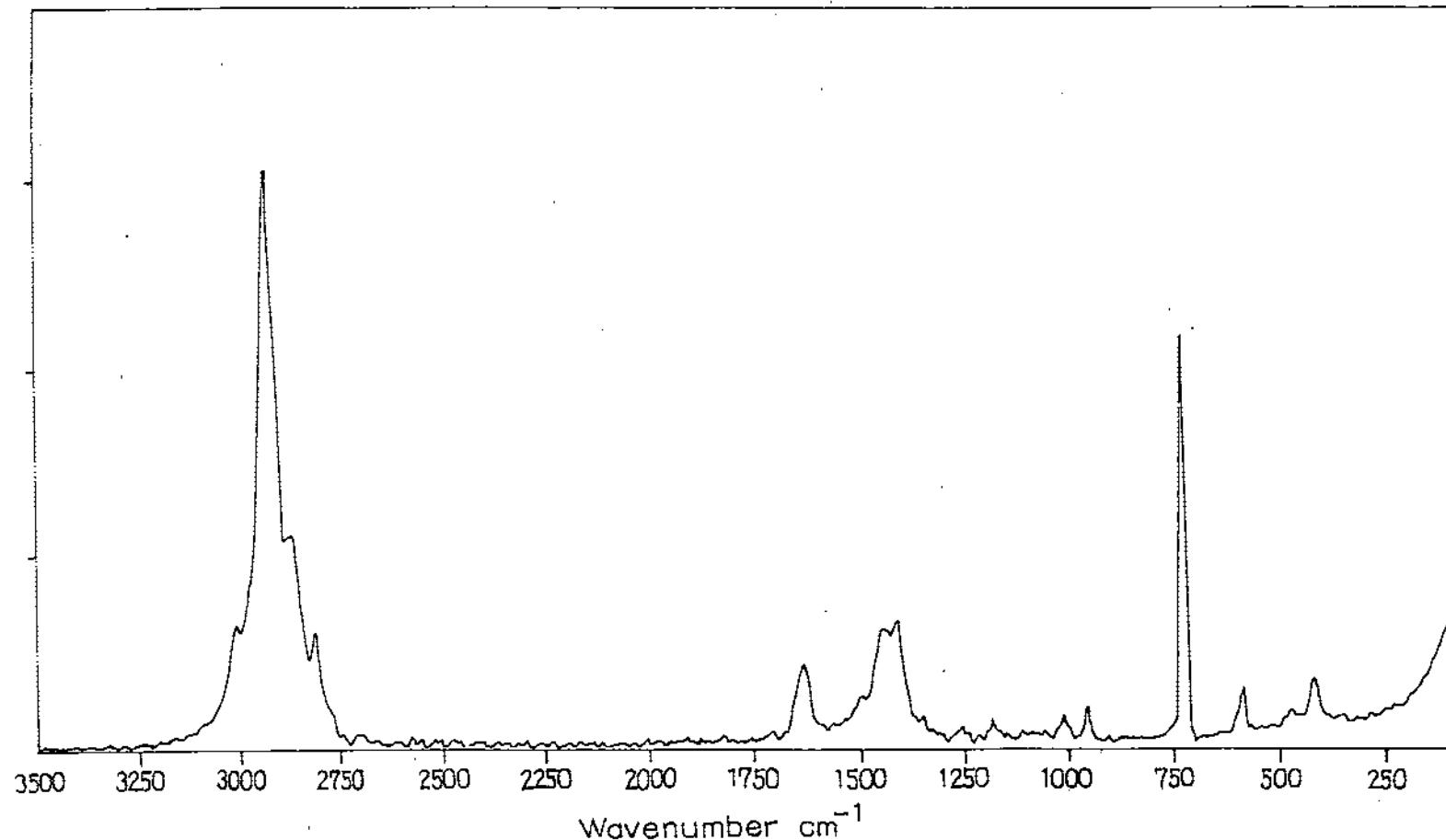


Figure 11. FT-Raman spectrum of LiI in N,N-dimethylacetamide (C=~1M)

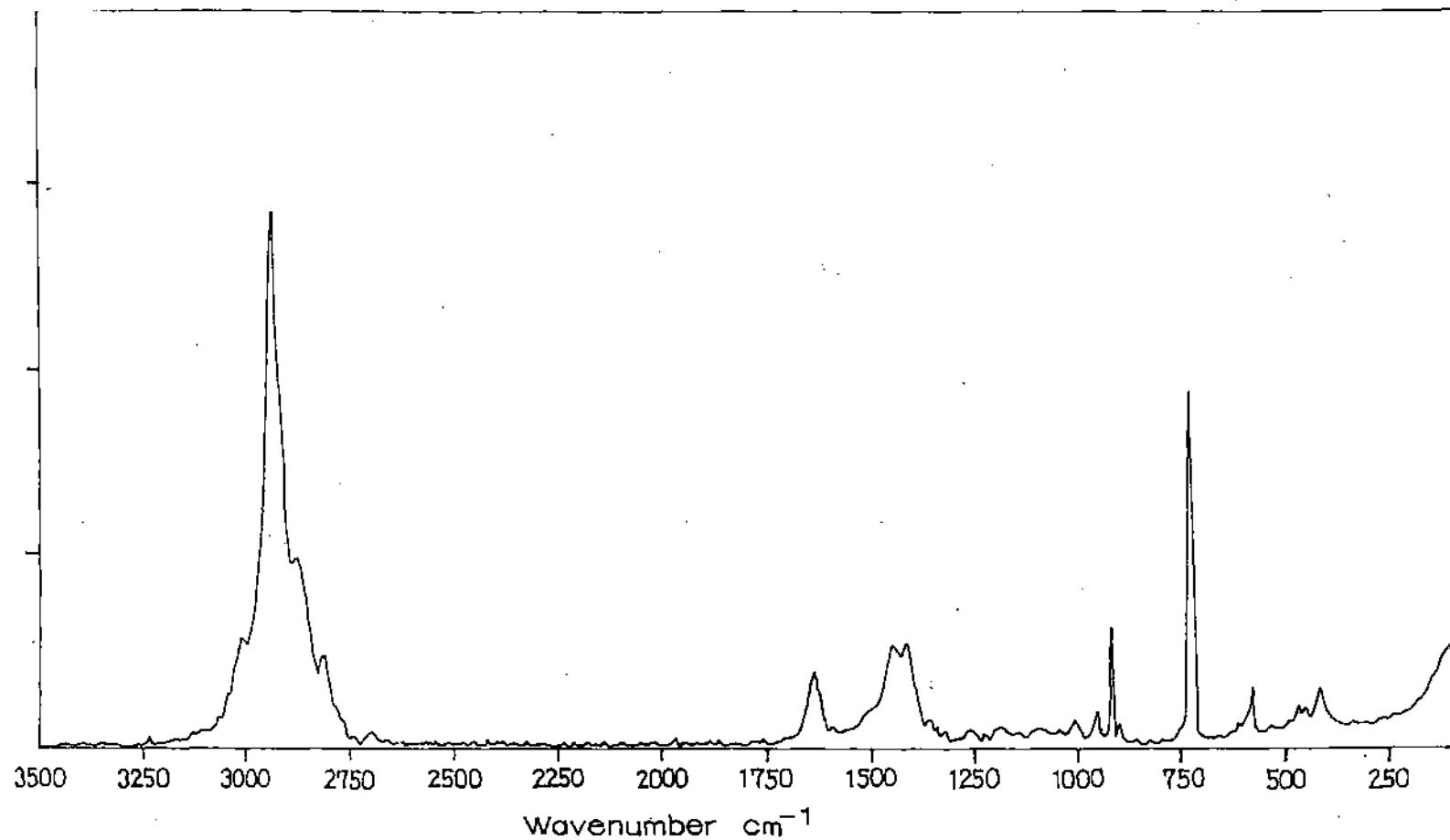


Figure 12. FT-Raman spectrum of LiClO₄ in N,N-dimethylacetamide(C=~1M)

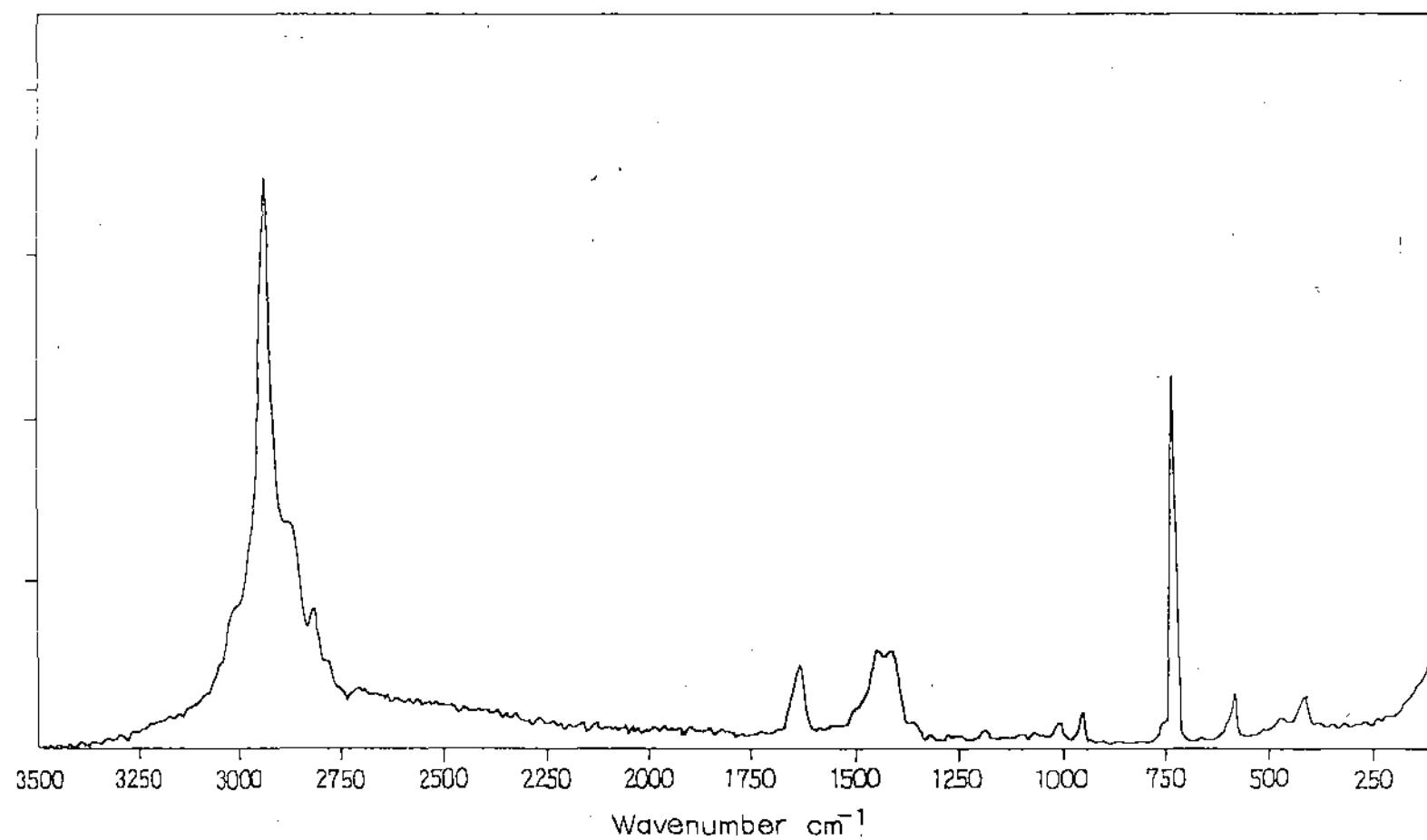


Figure 13. FT-Raman spectrum of LiBF₄ in N,N-dimethylacetamide (C = ~ .7M)

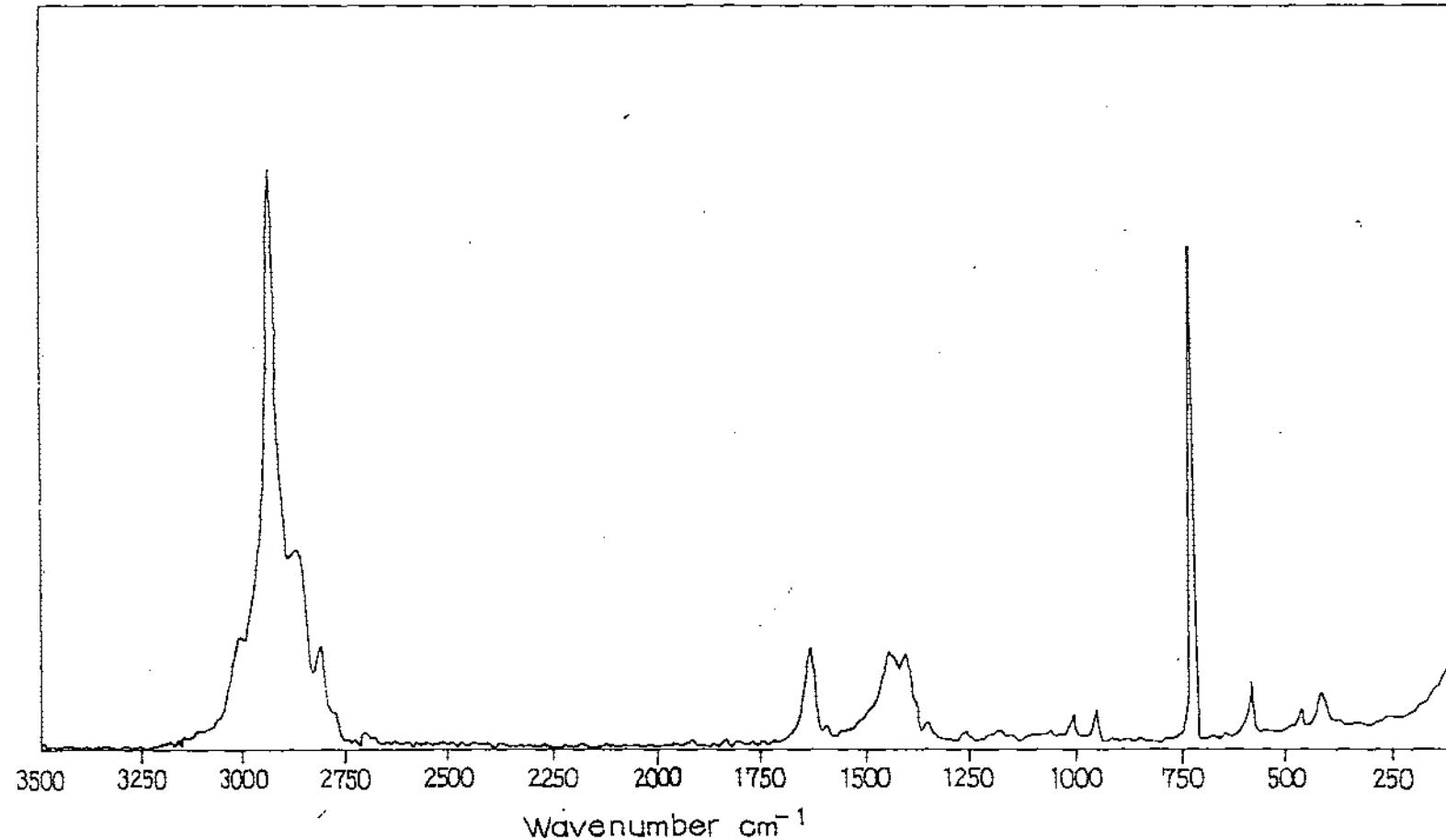


Figure 14. FT-Raman spectrum of LiAsF₆ in N,N-dimethylacetamide (C=.04M)

CHAPTER V

SECTION A

ELECTRICAL CONDUCTANCE OF SOME TETRAALKYLAMMONIUM AND ALKALI SALTS IN N,N-DIMETHYLACETAMIDE AT 298.15K

Studies of the transport properties of electrolytes in different solvent media are of great importance to obtain information on the behaviour of ions in solution. The conductometric method is well-suited to investigate the ion-solvent and ion-ion interactions in electrolyte solutions.^{1,2} Recently, we have studied the solvation and association behaviour of several 1:1 electrolytes in different non aqueous solvents from the measurements of various transport, thermodynamic, and spectroscopic properties.³⁻⁹ In this section we report the conductance studies of some selected tetraalkylammonium bromides and some other alkali metal salts e.g., of tetraethylammonium bromide (Et_4NBr), tetrapropylammonium bromide (Pr_4NBr), tetrapentylammonium bromide (Pen_4NBr), tetrahexylammonium bromide (Hex_4NBr), tetraheptylammonium bromide (Hep_4NBr), tetraoctylammonium bromide (Oct_4NBr), sodium tetraphenylborate (NaBPh_4) and potassium tetraphenylborate (KBPh_4) in N,N-dimethylacetamide to unravel the nature of various types of interactions prevailing in these solutions.

EXPERIMENTAL

The purification of salts and solvent and solution preparation have been described in chapter III. The conductance measurement has also been described in chapter III. Solutions were prepared by mass for the conductance runs, the molalities being converted to molarities by the use of densities measured with an Ostwald-Sprengel type pycnometer of about 25 cm³ capacity. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent.

RESULTS AND DISCUSSION

The measured molar conductance (Λ) of electrolyte solutions as a function of molar concentration (c) at 298.15K are given in Table 1.

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration as described earlier (chapter IV).

Calculations are made by finding the values of Λ° and σ which minimize the standard deviation, σ ,

$$\sigma^2 = \sum_{j=1}^n [\Lambda_j (\text{calcd}) - \Lambda_j^{\circ} (\text{obsd})]^2 / (n - 2) \quad (1)$$

for a sequence of R values and then plotting σ against R; the best fit R corresponds to the minimum in σ vs. R curve. However, since a rough scan using unit increment of R values from 4 to 20 gave no significant minima in the $\sigma(\%)$ vs. R curves, the R

value was assumed to be $R = a + d$, where a is the sum of the ionic crystallographic radii and d is given by

$$d = 1.183 (M / \rho_0)^{1/3} \quad (2)$$

where M is the molecular weight of the solvent and ρ_0 its density.

The values of Λ^0 , K_A , and R obtained by this procedure are reported in Table II.

Table II shows that the limiting equivalent conductivities (Λ^0) values of tetraalkylammonium bromides decrease with increasing length of the alkyl chain. This is in agreement with earlier findings in several pure and mixed solvents.^{1,5,10,11}

The association constants (K_A) of these electrolytes (cf. Table II) indicate that these salts are slightly associated in N,N-dimethylacetamide. This implies that a preponderant portion of each salt remains dissociated in this solvent medium. For all these tetraalkylammonium bromide salts the association constants are found to be very close to each other thus indicating these salts are almost similarly associated at any given concentration. Furthermore, the process of ionic association of these electrolytes do not exhibit the simple dependence upon ionic size predicted by electrostatic theory.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components. In the absence of accurate transport

number data in this solvent medium, we have earlier used the "reference electrolyte" method with tetrabutylammonium tetraphenylborate (Bu_4NBPb_4) as the "reference electrolyte" for the division of Λ° into their ionic components. The limiting ion conductances (λ°_\pm) were estimated by using $\lambda^\circ_{Bu_4N^+} = 22.99$ from our previous work. (Chapter IV, Section A). The λ°_\pm values thus obtained are presented in Table III.

The Walden products ($\lambda^\circ \pm \eta_0$) of the ions are also included in Table III. Walden products are usually employed to discuss the interactions of the ions with the solvent medium. From this table, we see that for the tetraalkylammonium ions Walden product decreases from the tetraethylammonium to tetraoctylammonium ion and for the electrolyte taken as a whole it follows the same sequence. This points out that the electrostatic ion-solvent interaction is very weak in these cases. On the other hand, the alkali-metal ions are small enough to possess high charge density, resulting in strong ion-solvent interactions.¹²

The starting point for most evaluations of ionic conductances is Stokes' law that contents that the limiting Walden product (the limiting ionic conductance - solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant. In Table III we have collected the Stokes' radii (r_s) of the ions in N,N-dimethylacetamide. For sodium and potassium ions, the Stokes' radii are much higher than their crystallographic radii suggesting that these ions are significantly solvated in this

solvent medium. The Stokes' radii of the tetraalkylammonium ions are, however, found to be either very close to or smaller than their corresponding crystallographic radii. This observation indicates that these ions are scarcely solvated in N,N-dimethylacetamide solutions. This also supports our earlier contention derived from the Walden products of these ions that the electrostatic ion-solvent interaction is very weak in these cases.

It may thus be concluded that all these tetraalkylammonium bromide salts and the two investigated alkali-metal salts remain slightly associated in N,N-dimethylacetamide solutions apparently due to the medium relative permittivity of the solvent. Sodium and potassium ions are found to be significantly solvated in this solvent medium while the tetraalkylammonium ions remain scarcely solvated.

SECTION B

VISCOSITIES OF SOME TETRAALKYLMONIUM AND ALKALI SALTS IN N,N-DIMETHYLACETAMIDE AT 298.15K

In previous section we have reported the results of conductance measurements on a number of tetraalkylammonium and alkali-metal salts e.g., tetrapropylammonium bromide (Pr_4NBr), tetrabutylammonium bromide (Bu_4NBr), tetrapentylammonium bromide (Pen_4NBr), tetrahexylammonium bromide (Hex_4NBr), tetraheptylammonium bromide (Hep_4NBr), tetraoctylammonium bromide (Oct_4NBr), tetrabutylammonium tetraphenylborate (Bu_4NBPh_4), sodium tetraphenylborate (NaBPh_4), and potassium tetraphenylborate (KBPh_4) in N,N-dimethylacetamide at 298.15K. We have now extended this work to study the viscometric behaviour of these electrolyte solutions since viscometry is well-suited to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles.¹³

EXPERIMENTAL

The kinematic viscosities were measured at $298.15 \pm 0.01\text{K}$ using a suspended Ubbelohde-type viscometer with a precision of 0.05%. the kinematic viscosities were then converted into absolute viscosities by multiplying the former with the density values measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The details of the experimental procedure have been described in chapter

III. The solutions were prepared by mass for the viscosity runs, the molalities being converted to molarities by the use of densities. In all cases the experiments were performed at least in five replicates for each solution and the results were averaged. Several independent solutions were prepared and the runs were performed to ensure the reproducibility of the results.

RESULTS AND DISCUSSION

The measured relative viscosities (η_r) and densities (ρ) of electrolyte solutions as functions of molar concentrations (c) at 298.15K are given in Table IV.

The relative viscosities of the electrolytes in solution are generally analysed by the Jones-Dole equation,¹⁴

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (3)$$

Where A and B, the characteristic parameters for salt and solvent, depend on ion-ion and ion-solvent interactions, respectively.

As the electrolytes investigated here are found to be somewhat associated from our earlier conductivity measurements, the viscosity data have been analyzed by the following equation.¹⁵

$$\eta_r = 1 + A(\alpha c)^{1/2} + B\alpha c + B'(1-\alpha)c \quad (4)$$

Here A, B, and B' are the characteristic constants and α is the degree of dissociation of the ion pair.

Eq(4) can be rearranged to give

$$[\eta_r - 1 - A(\alpha c)^{1/2}] / \alpha c = B + B' (1 - \alpha) / \alpha \quad (5)$$

For the evaluation of B coefficients from eq.(5), the method suggested earlier by us¹⁶ was followed. The values of α were calculated from the conductance data of previous section using the equations described in the literature.¹⁵ The A values were calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using the Falkenhagen and Vernon equation.¹⁷

$$A = \frac{0.2577 \Lambda^\circ}{\eta_0(\varepsilon T)^{1/2} \lambda_+^\circ \lambda_-^\circ} \left[1 - 0.6863 \left(\frac{\lambda_+^\circ - \lambda_-^\circ}{\Lambda^\circ} \right)^2 \right] \quad (6)$$

where η_0 is the coefficient of viscosity of the solvent, ε is its relative permittivity, T is the temperature in absolute scale, and Λ° , λ_+° and λ_-° are the limiting equivalent conductivities of the electrolyte, cation, and anion respectively. The values of the A coefficients thus obtained are recorded in Table II. These have been used for the analysis of the data. The viscosity B coefficients have also been included in Table V.

The viscosity data have also been analyzed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions, as suggested by Feakins et.al.¹⁸

$$B = \frac{\bar{V}_1^\circ - \bar{V}_2^\circ}{1000} + \frac{\bar{V}_1^\circ}{1000} \left[\frac{\Delta\mu_2^{\circ\#} - \Delta\mu_1^{\circ\#}}{RT} \right] \quad (7)$$

In the above equation \bar{V}_1° and \bar{V}_2° are the partial molar volumes of the solvent and solute, respectively. $\Delta\mu_2^{\circ\#}$ the contribution per mole of solute to the free energy of activation for viscous flow of the solution, has been determined from the above relationship and is reported in Table V. the free energy of activation per mole of the pure solvent, $\Delta\mu_1^{\circ\#}$ is given by the equation,¹⁹

$$\Delta\mu_1^{\circ\#} = \Delta G_1^{\circ\#} = RT \ln \left[\eta_0 \bar{V}_1^\circ / \eta N \right] \quad (8)$$

where N is the Avogadro's number and the other symbols have their usual significance.

The activation parameters for viscous flow for the electrolytes obtained from equation (7) are given table V.

The viscosity β coefficients shown in Table V are large and positive for all the electrolytes studied. The B values for the tetraalkylammonium bromides increase regularly as we go from tetrapropylammonium bromide through tetraoctylammonium bromide. From this table we see that $\Delta\mu_2^{\circ\#}$ values for all the electrolytes are also large and positive, and they follow the same pattern as the B values.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the viscosity B coefficients of

the electrolytes into their ionic components. The ionic B values were calculated using tetrabutylammonium tetraphenylborate ($Bu_4N\text{BPh}_4$) as the "reference electrolyte" from the following equations.^{20,21}

$$B(Bu_4\text{NBPh}_4) = B(Bu_4\text{N}^+) + B(\text{Ph}_4\text{B}^-) \quad (9)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \frac{r^3_{\text{Ph}_4\text{B}^-}}{r^3_{\text{Bu}_4\text{N}^+}} = \left[\frac{5.35}{5.00} \right]^3 \quad (10)$$

The r -values for the $Bu_4\text{N}^+$ and Ph_4B^- ions were taken from the literature²¹

The ionic B coefficients obtained from the above relationships are given in the Table VI. This table shows that the viscosity B coefficients for all cations and anions are positive and are also very high with the exception of bromide ion. The observed order of the ionic B values for the tetraalkylammonium ions, $\text{Oct}_4\text{N}^+ > \text{Hep}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+$, shows that the obstruction of the solvent viscous flow increases with an increase of size of these species in solution. In case of Br^- ion, it might be that the viscosity of the solvent is very little modified by its presence in solution resulting in a very low viscosity B coefficient for this ion. The other anion, Ph_4B^- , however, is found to be very efficient in modifying the solvent viscosity as manifested by its large and positive viscosity B value. Among the two alkali metal ions investigated, K^+ ion is found to cause greater obstruction of the solvent viscous flow compared to the Na^+ ion in N, N-dimethylacetamide.

The ionic free energies of activation for viscous flow, $\Delta\mu_2^{\text{OH}}(\text{ion})$ based on the division of tetrabutylammonium tetraphenylborate have been presented in Table VI. The values of $\Delta\mu_2^{\text{OH}}$ for tetraalkylammonium ions in N,N-dimethylacetamide decrease in the order $\text{Oct}_4\text{N}^+ > \text{Hep}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+$, those for the alkali metal ions decrease in order $\text{K}^+ > \text{Na}^+$, and those for anions in the order $\text{Ph}_4\text{B}^- > \text{Br}^-$. However, these values are always found to be positive, and hence the formation of the transition state is made less favourable in the presence of these ions.

The ionic viscosity B-coefficients have also been analyzed on the basis of Einstein's equation²²

$$B_{\pm} = 2.5 \frac{4}{3} \pi \frac{R_{\pm}^3 N}{1000} \quad (11)$$

where R_{\pm} is the radius of the ion assumed to be rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The values of R_{\pm} are shown in Table VI.

A comparison of the R_{\pm} value with the sum of the ionic crystallographic radius and the radius of the solvent molecule can provide important information regarding the solvation of ions in solution. With the exception of Na^+ and K^+ ions, the R values for the other ions are always found to be much less than the sum of the radii of the ion²³ and the solvent molecule ($r_{\text{solvent}} = 2.78^{\circ}\text{A}$). This indicates that the bromide, tetraphenylborate, and tetraalkylammonium ions are only scarcely solvated in N,N-dimethylacetamide. For Na^+ and K^+ ions, however, the R_{\pm} values are found

to be much higher than the sum of the radii of the ion³ and the solvent molecule which clearly demonstrates that these alkali-metal ions are significantly solvated in this solvent medium.

It may thus be concluded that the bromide, tetraphenylborate, and tetraalkylammonium ions remain only scarcely solvated in N,N-dimethylacetamide. The sodium and potassium ions, on the other hand, are found to be significantly solvated in this medium. The viscosity of the solvent is greatly modified by the presence of all the ions investigated here with the exception of the bromide ion.

SECTION C

ULTRASONIC VELOCITIES AND ISENTROPIC COMPRESSIBILITIES OF SOME SYMMETRICAL TETRAALKYLAMMONIUM SALTS IN N,N-DIMETHYLACETAMIDE AT 298.15K.

In previous section of this chapter we have described the results of conductance and viscosity measurements on a number of tetraalkylammonium salts. Here we described the findings of the compressibility behaviour of this electrolyte solutions to unravel the nature of various types of interactions prevailing in these solutions.

EXPERIMENTAL

The purification of salts and solvent have been described earlier. For the preparation of the solutions of each salt, a different batch of solvent was used and the properties of the pure solvent used in each case is recorded in Table VII.

The velocities of sound were measured with an accuracy of 0.3%, using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 4 MHz. The details of experimental procedure have been given in chapter III.

RESULTS AND DISCUSSION

Adiabatic compressibility coefficients were derived from the following equation –

$$\kappa_s = 1/u^2 \rho \quad (12)$$

where ρ is the density and u is the velocity of sound in the solution. The apparent molar isentropic compressibility κ_ϕ of the electrolyte solutions was calculated from

$$\kappa_\phi = \frac{1000}{m \rho \rho_0} (\kappa_s \rho_0 - \kappa_s^\circ \rho) + \kappa_s^\circ \frac{M}{\rho_0} \quad (13)$$

where m is the molal concentration of the solution and the other symbols have their usual significance.

The molality m , the density ρ , the sound velocity u and the apparent molar isentropic compressibility κ_ϕ of the electrolyte solutions at 298.15K are given in Table VII.

The limiting apparent molar isentropic compressibilities κ_ϕ° were obtained^{3,4} by extrapolating the linear plots of κ_ϕ versus the square root of the molal concentration of the solutes to zero concentration by the method of least-squares :

$$\kappa_\phi = \kappa_\phi^\circ + S_k \sqrt{m} \quad (14)$$

where S_k is the experimental slope. The κ_ϕ° and S_k values are listed in Table VIII. The limiting apparent molar isentropic compressibilities (κ_ϕ°) of the electrolytes investigated here are found to increase in the order :

$\text{Pr}_4\text{NBr} < \text{Bu}_4\text{NBr} < \text{Pen}_4\text{NBr} < \text{Hex}_4\text{NBr} < \text{Hep}_4\text{NBr} < \text{Oct}_4\text{NBr}$. It is also interesting to note that the κ_ϕ° values of Pr_4NBr , Bu_4NBr , Pen_4NBr are negative while those of the next three higher homologues are found to be positive.

The negative κ_ϕ° values of the electrolytes can be interpreted in terms of loss of compressibility of the solvent N,N-dimethylacetamide due to the presence of these solutes in solution. The positive κ_ϕ° values, on the other hand, indicates an increase in the compressibility of the solution compared to the pure solvent.

Several factors may contribute to the compressibility of the solution and we will now examine the important factors in order to elucidate the effects of the solutes on the solvent structure and their role as compressibility.

The bromide has been shown to remain unsolvated in N,N-dimethylacetamide from our earlier conductivity and viscosity study. Moreover, it is not a molecular ion, thus ruling out the possibility to have intrinsic compressibility. This ion, therefore, does not influence the compressibility of the medium.

Most of the interpretations of κ_ϕ° in terms of solvation effects²⁴⁻²⁶ assume that κ_ϕ° of unsolvated ions is negligible, although Conway and Verral recognized that large organic ions could have some intrinsic compressibility due to the

intermolecular free space which makes the solution more compressible. This could be expected for the unsolvated tetraalkylammonium ions in our study also.

Another effect that is possible for large organic ions is the penetration of the solvent molecules into the intramolecular free space. This is the result of the interaction of the positively charged nitrogen central atom of the tetraalkylammonium ions with the neighbouring solvent molecules. This is essentially an electrostriction effect and causes constriction in the solution volumes, resulting in a more compact and, hence, a less compressible medium.

In view of the above factors, it can be concluded that since bromide ion has no effect on the compressibility of the solution, the interplay of the other two factors actually controls the compressibility of the solution.

The negative κ_f^0 values for Pr_4NBr , Bu_4NBr , and Pen_4NBr solutions can be attributed to the predominance of the effect of the intrinsic compressibility of the tetraalkylammonium ions over the penetration effect.

Hex_4NBr , Hep_4NBr and Oct_4NBr , on the other hand, the penetration effect overrides the effect of intrinsic compressibility of these ions.

In order to investigate the behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting apparent molar isentropic compressibilities into their ionic components. However, there are no reliable methods for the division of κ_f^0 values into ionic contributions. Miller²⁷ has suggested dividing the limiting partial molar volumes of $\text{Ph}_4\text{As}^+\text{Ph}_4\text{B}^-$ into ionic

components, but such a method cannot be used here since we do not know the ratio of the compressibilities of the pure (solid as gaseous) ions. The extrapolation method as suggested by Conway *et.al*¹⁸ can also not be used for the division of κ_ϕ° values since the variation of the limiting apparent molar isentropic compressibilities of these salts with the formula weight of the tetraalkylammonium ions is not linear. The method²⁹ used for acetonitrile, which assumes $\kappa_\phi^\circ(\text{Ph}_4\text{B}^-) = 0$ is also not appropriate as the Ph_4B^- ion is large ($r = 0.535 \text{ nm}$), and therefore, its intrinsic compressibility contribution cannot be taken as zero.

Under these circumstances and also in view of the compressibility behaviour of bromide in N,N-dimethylacetamide as discussed above, the choice of $\kappa_\phi^\circ(\text{Br}^-) = 0$ seems to be the best at the moment. Ionic κ_ϕ° values based on this assumption are given in Table VIII which seem to fit quite well with the discussion made above on the basis of the κ_ϕ° values of the electrolytes as a whole.

References

1. R.Fernandez - Prini, in *Physical Chemistry of Organic Solvent Systems*, A. K.Covington and T.Dickinson, eds. (Wiley, New York, 1973).
2. E.Renard and J.C.Justice, *J.Solution Chem.*, **3**, 634, 1974.
3. B.Das and D.K.Hazra, *J.Phys.Chem.*, **99**, 269, 1995.
4. P.K.Muhuri, B. Das and D.K.Hazra, *J. Phys. Chem.*, **101**, 3329, 1997.
5. B.Das and D.K.Hazra, *J. Solution. Chem.*, **27**, 1021, 1998.
6. P.J.Victor, P.K.Muhuri, B. Das and D.K.Hazra, *J. Phys.Chem.*, B **103**, 11227, 1999.
7. P.J.Victor, P.K.Muhuri, B. Das and D.K.Hazra, *J. Phys.Chem.*, B, **104**, 5350, 2000.
8. P.J.Victor, B. Das and D.K.Hazra, *J. Solution Chem.*, **30**, 435, 2000.
9. P.J.Victor, B. Das and D.K.Hazra, *J. Phys. Chem.*, A, **105**, 5960, 2001.
10. B.Das and D.K.Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470, 1992.
11. N. Islam, S.B.A. Zaidi and A.A.Anvari, *Bull. Chem. Soc. Jpn.*, **62**, 309, 1989.
12. M.L.Jansen and H.I.Yeager, *J. Phys. Chem.*, **77**, 3089, 1973.
13. H.D.B.Jenkins and Y. Marcus, *Chem. Rev.*, **95**, 2695, 1995.
14. G. Jones and M.Dole, *J. Am. Chem. Soc.*, **51**, 2950, 1929.

15. J. Crudden, G.M.Delaney, D. Feakins, P.J.O'Reilley, W.E.Waghorne and K.G.Lawrence, *J. Chem. Soc. Faraday Trans.*, **1**, **82**, 2195, 1986.
16. B. Das and D.K. Hazra, *Bull. Chem.Soc. Jpn.*, **65**, 3470, 1992.
17. H.Falkenhagen and E.L.Vernon, *Phys. Z.*, **33**, 140, 1932.
18. D. Feakins, D. J. Freemantle and K.G. Lawrence, *J.Chem.Soc. Faraday Trans.*, **1**, **70**, 795, 1974.
19. S.Glasstone, K.J.Laidler and H.Erying, *The Theory of Rate Process*, MacGraw- Hill, New York, 1941.
20. D.F.Tuan and R.M.Fuoss, *J. Phys.Chem.*, **67**, 1343, 1963.
21. D.S.Gill and M.B.Sekhri, *J.Chem.Soc. Faraday Trans.*, **1**, **78**, 475, 1982.
22. A. Einstein, *Ann. Phys.*, **19**, 289, 1906.
23. P.K.Muhuri and D.K.Hazra, *J. Chem.Soc. Faraday Trans.*, **1**, **87**, 3511, 1991.
24. J.G.Matheisan and B.E.Conway, *J. Solution Chem.*, **3**, 455, 1973 ; see also *J.Chem.Soc. Faraday Trans.*, **1**, **70**, 752, 1974.
25. F.J.Millero, G.K.Ward and P.V.Chetrikin, *J.Account. Soc. Amer.*, **61**, **1492**, 1977.
26. B.E.Conway and R.E.Verral, *J.Phys.Chem.*, **70**, 3952, 1966.
27. F.J.Millero, *J.Phys.Chem.*, **75**, 280, 1971.

28. R.E.Conway, R.E.Verral and J.E.Desnoyers, *Trans. Faraday Soc.*, **62**, 2738, 1966.
29. I. Davidson, G. Perran and J.E.Desnoyers, *Can. J. Chem.*, **59**, 2212, 1981.

Table 1 : Equivalent Conductances and corresponding Molarities of Electrolytes in N,N-Dimethylacetamide at 298.15 K.

$10^4 c$ $\text{mol}\cdot\text{dm}^{-3}$	Λ $\text{s}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$10^4 C$ $\text{mol}\cdot\text{dm}^{-3}$	Λ $\text{s}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
Et ₄ NBr		Pr ₄ NBr	
135.258	56.48	140.322	50.33
125.930	57.19	130.64	51.08
116.602	58.01	120.967	51.88
107.273	58.78	111.290	52.66
97.945	59.62	101.613	53.49
88.617	60.47	91.935	54.45
79.289	61.40	82.258	55.31
69.961	62.39	72.580	56.38
Pen ₄ NBr		Hex ₄ NBr	
130.642	45.38	135.722	44.12
120.593	46.09	126.028	44.73
110.543	46.77	116.333	45.49
100.494	47.21	106.639	46.20
90.445	48.30	96.944	46.92
80.395	49.12	87.250	47.69
70.346	50.57	77.554	48.54
60.296	50.98	67.861	49.44
50.247	51.98	58.166	50.38

Contd...

$10^4 c$ mol-dm ⁻³	Λ s-cm ² -mol ⁻¹	$10^4 C$ mol-dm ⁻³	Λ s-cm ² -mol ⁻¹
Hep ₄ NBr			
140.779	42.88	128.189	44.76
130.723	43.54	119.033	45.34
120.668	44.23	109.176	45.95
110.612	44.91	100.720	46.17
100.556	45.33	91.564	47.33
90.501	46.55	82.407	48.14
80.445	47.43	73.251	48.80
70.389	48.36	64.095	49.63
60.334	49.32	54.938	50.49
49.837	57.22		
NaBPh ₄			
140.479	36.84	138.328	35.65
130.444	37.28	128.788	36.06
120.410	37.80	119.284	36.55
110.376	38.31	109.708	36.98
100.342	38.82	100.169	37.38
90.308	39.42	90.629	38.02
80.273	40.01	81.009	38.52
70.239	40.66	71.549	39.17
60.205	41.34		

Table II : Conductivity Parameters of Electrolytes in N,N-Dimethylacetamide at 298.15K.

Salt	Λ° $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	K_A $\text{dm}^3\cdot\text{mol}^{-1}$	R $^\circ\text{A}$	$\sigma\%$
Et ₄ NBr	76.98±0.20	47.78 ± 0.76	11.16	0.06
Pr ₄ NBr	72.03±0.27	58.31±1.13	11.68	0.08
Bu ₄ NBr	69.27±0.20	45.63±0.88	12.10	0.08
Pen ₄ NBr	62.30±0.66	51.03±3.29	12.45	0.28
Hex ₄ NBr	61.69±0.21	53.64±1.04	12.76	0.10
Hep ₄ NBr	61.35±0.46	58.15±2.33	13.04	0.21
Oct ₄ NBr	61.32±0.53	51.60±2.74	13.20	0.27
NaBPh ₄	49.27±0.09	41.80±0.50	11.33	0.06
KBPh ₄	48.38±0.18	44.64±1.07	11.65	0.09
Bu ₄ NBPh ₄	44.47±0.09	30.97±0.44	14.50	0.08

Table III. Limiting Ionic Conductances and Ionic Stokes' Radii in N,N-Dimethylacetamide at 298.15K

Ion	λ_{\pm}° S-cm ² -mol ⁻¹	r _s °A	ion	λ_{\pm}° S-cm ² -mol ⁻¹	r _s °A
Et ₄ N ⁺	30.70	2.18	Hep ₄ N ⁺	15.07	4.43
Pr ₄ N ⁺	25.75	2.60	Oct ₄ N ⁺	15.03	4.46
Bu ₄ N ⁺	22.99	2.91	Na ⁺	27.79	2.41
Pen ₄ N ⁺	16.02	4.18	K ⁺	26.90	2.49
Hex ₄ N ⁺	15.41	4.34	Br ⁻	46.28	1.45

Table IV : Molar Concentration(c), Densities(ρ) and Relative Viscosities (η_r) of Some Tetraalkylammonium and Alkali-Metal Salts in N,N-Dimethylacetamide at 298.15

c mol-dm ⁻³	ρ g-cm ⁻³	η_r	c mol-dm ⁻³	ρ g-cm ⁻³	η_r
Pr₄NBr					
0.01205	0.93749	1.0132	0.01322	0.93768	1.0163
0.02789	0.93876	1.0291	0.03247	0.93871	1.0381
0.04946	0.94033	1.0503	0.05727	0.93987	1.0659
0.07420	0.94211	1.0745	0.07930	0.94076	1.0904
0.09897	0.94388	1.0985	0.10131	0.94155	1.1147
0.11155	0.94478	1.1107	0.12773	0.94240	1.1439
Pen₄NBr					
0.01887	0.93813	1.0247	0.01184	0.93712	1.0187
0.05031	0.94003	1.0626	0.03154	0.93802	1.0459
0.08180	0.94184	1.1000	0.05126	0.93888	1.0724
0.11010	0.94340	1.1334	0.07096	0.93971	1.0986
0.15100	0.94556	1.1814	0.09066	0.94050	1.0247
0.22015	0.94902	1.2623	0.11431	0.94143	1.1557
Hep₄NBr					
0.01930	0.93715	1.0342	0.01142	0.93676	1.1903
0.03858	0.93814	1.0635	0.03045	0.93770	1.1571
0.06003	0.93918	1.0952	0.04951	0.93858	1.1234
0.07930	0.94010	1.1232	0.06854	0.93942	1.0923
0.09860	0.94098	1.1511	0.08952	0.94032	1.0600
0.12001	0.94193	1.1817	0.11042	0.94118	1.0235

Contd...

c mol-dm ⁻³	ρ g-cm ⁻³	η _r	c mol-dm ⁻³	ρ g-cm ⁻³	η _r
Bu₄NBPh₄					
0.00957	0.93680	1.0229	0.01115	0.93838	1.0228
0.02152	0.93739	1.0501	0.02972	0.94030	1.0566
0.04068	0.93816	1.0887	0.04831	0.94203	1.0889
0.05006	0.93848	1.1072	0.06687	0.94361	1.1207
0.05978	0.93878	1.1261	0.08550	0.94508	1.1525
0.08369	0.93938	1.1724	0.10778	0.94670	1.1902
KBPh₄					
0.00714	0.93768	1.0166			
0.00919	0.93791	1.0208			
0.01533	0.93860	1.0332			
0.02133	0.93924	1.0447			
0.02553	0.93965	1.0526			
0.03576	0.94062	1.0716			

Table V. Theoretical A-Coefficients, the Viscosity B-Coefficients and the Free Energies of Activation for Viscous Flow of Electrolytes in N,N-Dimethylacetamide at 298.15K

Electrolyte	A $\text{dm}^{3/2}\text{-mol}^{1/2}$;	B $\text{dm}^3\text{-mol}^{-1}$;	$\Delta\mu_2^{0\#}$ $\text{kJ}\text{-mol}^{-1}$
Pr ₄ NBr	0.0150	0.988	43.33
Bu ₄ NBr	0.0158	1.117	49.73
Pen ₄ NBr	0.0186	1.217	53.12
Hex ₄ NBr	0.0189	1.491	62.41
Hep ₄ NBr	0.0191	1.854	73.62
Oct ₄ NBr	0.0192	2.121	82.41
Bu ₄ NBPh ₄	0.0238	2.311	88.12
NaBPh ₄	0.0215	1.947	70.46
KBPh ₄	0.0219	2.220	77.62

Table VI : Ionic Viscosity B-coefficients, Ionic Free Energies of Activation for Viscous Flow and Ionic Radii in N,N-Dimethylacetamide at 298.15K.

Ion	B_{\pm} dm³-mol⁻¹	$\Delta\mu_2^{0\#}$ (ion), kJ-mol⁻¹	R_{\pm} °A.
Pr ₄ N ⁺	0.910	33.20	5.24
Bu ₄ N ⁺	1.039	39.60	5.48
Pen ₄ N ⁺	1.139	42.99	5.65
Hex ₄ N ⁺	1.413	52.28	6.07
Hep ₄ N ⁺	1.776	63.49	6.55
Oct ₄ N ⁺	2.043	72.28	6.87
Na ⁺	0.675	21.94	4.74
K ⁺	0.948	29.10	5.32
Ph ₄ B ⁻	1.272	48.52	5.86
Br ⁻	0.078	10.13	2.31

Table VII : Concentration (c), density(ρ), ultrasonic velocity (U) and apparent molar isentropic compressibility (κ_f) of the electrolyte solutions in N,N-dimethylacetamide at 298.15K.

C/mol.dm ⁻³	$\rho/\text{g cm}^{-3}$	u/cm.s ⁻¹	$\kappa_f \times 10^{10}$ cm ³ .mol ⁻¹ .bar ⁻¹	c/mol.dm ⁻³	$\rho/\text{g.cm}^{-3}$	U/cm.s ⁻¹	$\kappa_f \times 10^{10}$ cm ³ .mol ⁻¹ .bar ⁻¹
Pr ₄ NBr							
0.00000	0.93670	1460.35	-	0.00000	0.93686	1459.50	-
0.02789	0.93876	1465.82	-69.99	0.01322	0.93768	1461.87	-16.58
0.04946	0.94033	1468.44	-46.74	0.03247	0.93871	1464.42	8.27
0.07420	0.94211	1470.27	-25.64	0.05727	0.93987	1466.69	30.96
0.09897	0.94388	1471.07	-7.81	0.07930	0.94076	1468.02	47.10
0.11155	0.94478	1471.13	0.31	0.10131	0.94155	1468.80	60.87
				0.12773	0.94240	1469.03	75.68
Pen ₄ NBr							
0.00000	0.93692	1461.09	-	0.00000	0.93654	1459.50	-
0.01887	0.93813	1464.26	22.55	0.01184	0.93712	1461.62	57.65
0.05031	0.94003	1468.05	43.73	0.03154	0.93802	1464.32	78.28
0.08180	0.94184	1470.82	58.60	0.05126	0.93888	1466.43	92.90
0.11010	0.94340	1472.45	70.63	0.07096	0.93971	1467.86	104.92
0.15100	0.94556	1474.09	84.00	0.09066	0.94050	1469.02	115.23
0.22015	0.94902	1474.43	103.57	0.11431	0.94143	1469.79	126.43
Hep ₄ NBr							
0.00000	0.93610	1456.48	-	0.00000	0.93617	1458.54	-
0.01930	0.93715	1459.63	93.26	0.01142	0.93677	1460.87	98.93
0.03858	0.93814	1462.01	109.04	0.03045	0.93770	1463.98	117.86
0.06003	0.93918	1464.05	122.06	0.04951	0.93858	1466.58	131.30
0.07930	0.94010	1465.40	133.06	0.06854	0.93943	1468.68	142.30
0.09860	0.94098	1466.40	142.32	0.08952	0.94032	1470.58	152.78
0.12001	0.94193	1466.99	152.27	0.11042	0.94118	1472.08	162.04

Table VIII : Limiting Apparent Molar Isentropic Compressibilities (κ_ϕ^0), the Experimental Slopes (S_k) and the Standard Deviations for the Electrolyte Solutions in N,n-Dimethylacetamide at 298.15K.

Electrolyte	$10^{10}(\kappa_\phi^0)/$ $\text{cm}^3\text{-mol}^{-1}\text{-bar}^{-1}$	$10^{10}S_k$ $\text{cm}^3\text{-mol}^{-3/2}\text{-kg}^{1/2}\text{-bar}^{-1}$	σ
Pr ₄ NBr	-140.37±0.09	421.23	0.29
Bu ₄ NBr	-60.33±0.18	380.93	0.34
Pen ₄ NBr	-11.07±0.39	244.65	0.29
Hex ₄ NBr	25.00±0.12	299.90	0.25
Hep ₄ NBr	53.37±0.89	283.66	0.22
Oct ₄ NBr	69.00±0.01	280.00	0.23

CHAPTER VI

ELECTRICAL CONDUCTANCES OF SOME ALKALI-METAL SALTS IN N,N-DIMETHYLACETAMIDE-WATER MIXTURE AT 298.15K

Studies of the transport properties of electrolytes in different solvent media are of great importance to obtain information on the behaviour of ions in solution. The conductometric method is well-suited to investigate the ion-solvent and ion-ion interactions in electrolyte solutions.^{1,2} In previous chapters, we have reported the conductances of a number of alkali-metal and tetraalkylammonium salts in the pure solvent *N,N*-dimethylacetamide at 298.15K. Now, we have extended the work to study the conductometric behaviour of some alkali-metal salts in *N,N*-dimethylacetamide + water (50% v/v) in an attempt to unravel the nature of various types of interactions prevailing in aquo-organic mixtures.

Experimental

Triply distilled water with a specific conductance of less than 10^{-6} S.cm⁻¹ at 298.15K was used for the preparation of the mixed solvent. The mixed solvent system (50% *N,N*-dimethylacetamide + water v/v) had a density of 0.99877 g.cm⁻³ and a coefficient of viscosity of 0.03318 mPa.s at 298.15K.

The salts were of Fluka's purum or puriss grade. Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent.

The relative permittivity of *N,N*-dimethylacetamide + water (50% v/v) mixture ($\epsilon = 59.92$) at 298.15K was obtained using the equations as described in the literature.³

Results and Discussion

The measured molar conductance (Λ) of electrolyte solutions as a function of molar concentration (c) at 298.15K are given in Table 1.

The conductance data have been analyzed by the 1978 Fuoss conductance-concentration equation as described earlier.

The calculations are made by finding the values of Λ^0 and σ which minimize the standard deviation, σ ,

$$\sigma^2 = \sum_{j=1}^n [\Lambda_j(\text{calcd}) - \Lambda_j^0(\text{obsd})]^2 / (n - 2) \quad (1)$$

for a sequence of R values and then plotting σ against R ; the best-fit R corresponds to the minimum in σ vs. R curve.

The values of Λ^0 , K_A and R obtained by this procedure are reported in Table 2.

The association constants (K_A) of these electrolytes (*cf.* Table 2) - which are always less than 10 - indicate that these salts are completely dissociated in *N,N*-dimethylacetamide. This implies that these salts remain essentially in the form of free ions in this solvent medium. A comparison of the available association constant

values in pure *N,N*-dimethylacetamide with those obtained in the *N,N*-dimethylacetamide + water system in the present study reveals that the addition of water to pure *N,N*-dimethylacetamide results in a lower level of ionic association. This may be attributed to the increased relative permittivity of the mixed solvent medium compared to the pure *N,N*-dimethylacetamide.

In order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components. In the absence of accurate transport number data for these systems, we have used the "reference electrolyte" method for the division of Λ^0 into their ionic components. Tetrabutylammonium tetraphenylborate (Bu_4NBP_4) has been used as the "reference electrolyte"⁴ Bu_4NBP_4 was used as the "reference electrolyte" also by Fuoss and Hirsch⁵ to evaluate the limiting ionic conductances in several organic solvents. We have divided the Λ^0 values of Bu_4NBP_4 into ionic components using a method similar to that proposed by Krumgalz⁶ for division of viscosity B coefficients :

$$\Lambda^0(Bu_4NBP_4) = \lambda^0(Bu_4N^+) + \lambda^0(Ph_4B^-) \quad (2)$$

$$\frac{\lambda^0(Bu_4N^+)}{\lambda^0(Ph_4B^-)} = \frac{r(Ph_4B^-)}{r(Bu_4N^+)} = \frac{5.35}{5.00} \quad (3)$$

The r values have been taken from the works of Gill *et al.*⁷ The relevant limiting molar conductance of the electrolyte tetrabutylammonium tetraphenylborate

Bu_4NBPh_4 was obtained from the limiting molar conductivity values of Bu_4NBr , NaBPh_4 and NaBr by the method of additivity. The limiting ion conductances calculated from the above equations are recorded in Table 3.

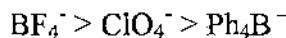
The limiting ionic equivalent conductivities of the alkali-metal and halide ions in the present solvent system are substantially lower than those observed in aqueous solutions.⁸ It is generally accepted that the alkali-metal and halide ions possess an excess mobility in aqueous medium owing to their ability to break the hydrogen bonds in their immediate vicinity and thereby reduce the local viscosity.⁹

It is seen from Table 3 that for the halide ions, the λ^0 values decrease in the following order:



i.e., the limiting ionic conductivity values decrease with increasing size of these anions.

This is also found to be true for the molecular anions, i.e., the λ^0 values of these ions decrease in the order:



This observations indicate that all these anions remain unsolvated in *N,N*-dimethylacetamide + water solvent system investigated here. Had these ions been solvated in the mixed solvent medium, their limiting ionic conductivity values would have been in the reverse order since the smaller ions with higher surface

charge density could associate greater number of solvent molecules to form a bigger solvodynamic entity with lower mobility. This is, obviously, not the case here.

The starting point for most evaluations of ionic conductances is Stokes' law that contents that the limiting Walden product (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant. In Table 3 we have collected the Stokes' radii (r_s) of the ions in *N,N*-dimethylacetamide + water solvent system. For lithium ion, the Stokes' radius is much higher than its crystallographic radius suggesting that this ion is significantly solvated in this solvent medium. The Stokes' radii of the other ions are, however, found to be either very close to or smaller than their corresponding crystallographic radii¹⁰. This observation indicates that these ions are scarcely solvated in the mixed solvent medium. This also supports our earlier contention derived from the order of the limiting ionic conductivity values (*cf.* the preceding paragraph). Similar behaviour has also been observed in pure *N,N*-dimethylacetamide solutions.¹¹

It may thus be concluded that all these alkali-metal salts, essentially dissociated in *N,N*-dimethylacetamide + water solvent system apparently due to the high relative permittivity of the solvent medium. Lithium ion is found to be significantly solvated in this solvent medium while the other ions remain scarcely solvated.

References

1. R. Fernandez-Prini, in: *Physical Chemistry of Organic Solvent Systems*, A.K. Covington and T. Dickinson, eds., (Wiley, New York ,1973).
2. E. Renard and J. C. Justice, *J. Solution Chem.*, **3**, 634, 1974.
3. M Pal and S. Bagchi, *J. Chem. Soc., Faraday Trans.*, **1**, **81**, 1961, 1985.
4. B. S. Krumgalz, *J. Chem. Soc., Faraday Trans.*, **1**, **79**, 571, 1983.
5. R. M. Fuoss and E. Hirsch, *J. Am. Chem. Soc.*, **82** , 1013, 1960.
6. B. S. Krumgalz, *J. Chem. Soc., Faraday Trans.*, **1**, **76**, 315, 1980.
7. D. S. Gill and M. B. Sekhri, *J. Chem. Soc., Faraday Trans.*, **1**, **78** , 119, 1982.
8. R. A. Robinson and R. H. Stokes, in: *Electrolyte Solutions*, Second Edition (Butterworths, London , 1959).
9. R.L.Kay and D.F.Evans, *J.Phys. Chem.*, **70**, 2325,1966.
10. Y. Marcus, *Ion Solvation*, Wiley, New York , 1985.
11. D. Das, B. Das, and D. K. Hazra, *J. Solution Chem.*, **31**, 425, 2002.

Table 1. Equivalent Conductances and Corresponding Molarities of Electrolytes in N,N-Dimethylacetamide + Water (50% v/v) at 298.15K

10^4 c/ mol.dm $^{-3}$	Λ / S.cm 2 .mol $^{-1}$	10^4 c/ mol.dm $^{-3}$	Λ / S.cm 2 .mol $^{-1}$
LiCl			LiBr
512.95	22.41	470.01	21.01
477.58	22.61	437.59	21.17
442.20	22.79	405.18	21.29
406.83	22.99	372.76	21.43
371.45	23.19	340.35	21.60
336.07	23.40	307.93	21.76
300.70	23.60	275.52	21.93
265.32	23.86	243.10	22.10
LiI			LiClO_4
444.92	17.75	433.95	19.18
414.24	17.85	404.02	19.30
383.55	17.93	374.09	19.41
352.87	18.02	344.17	19.54
322.18	18.12	314.24	19.68
291.50	18.22	284.31	19.83
260.82	18.32	254.38	20.00
230.13	18.47	224.46	20.12

Contd...

$10^4 \text{ c/mol} \cdot \text{dm}^{-3}$	$\Lambda / \text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$10^4 \text{ c/mol} \cdot \text{dm}^{-3}$	$\Lambda / \text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
LiBF_4		NaBr	
420.05	21.85	438.72	31.41
391.09	21.98	406.60	31.59
362.12	22.13	376.48	31.78
333.15	22.24	346.36	31.95
304.18	22.39	316.24	32.14
275.21	22.56	286.12	32.33
246.24	22.70	256.01	32.55
217.27	22.88	225.89	32.78
KBr		RbBr	
437.36	35.34	472.68	36.01
407.20	35.48	440.08	36.12
377.03	35.59	407.48	36.22
346.87	35.70	374.88	36.35
316.71	35.82	342.29	36.47
286.55	35.99	309.69	36.60
256.38	36.10	277.09	36.71
226.22	36.26	244.49	36.85

contd...

10^4 c/ mol.dm $^{-3}$	$\Lambda/\text{S.cm}^2.\text{mol}^{-1}$	10^4 c/ mol.dm $^{-3}$	$\Lambda/\text{S.cm}^2.\text{mol}^{-1}$
CsBr			NaBPh ₄
432.99	35.06	436.50	20.00
403.13	35.22	406.40	20.10
373.27	35.41	376.29	20.20
343.40	35.59	346.19	20.29
313.54	35.79	316.09	20.40
283.68	36.00	285.98	20.50
253.82	36.20	255.88	20.62
223.96	36.43	225.78	20.75
Bu ₄ NBr			
435.90	21.14		
405.84	21.33		
375.78	21.55		
345.72	21.77		
315.65	21.98		
285.59	22.13		
255.53	22.42		
225.47	22.68		

Table 2. Conductivity Parameters of Electrolytes in N,N-Dimethylacetamide + Water (50% v/v) at 298.15K

Salt	$\Lambda^0 / \text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$K_A / \text{dm}^3\cdot\text{mol}^{-1}$	$R / \overset{\circ}{A}$	$\sigma / \%$
LiCl	26.61 ± 0.03	5.19 ± 0.06	14.0 ± 0.5	0.04
LiBr	24.40 ± 0.03	4.58 ± 0.06	9.5 ± 0.5	0.04
LiI	20.25 ± 0.03	2.47 ± 0.08	12.5 ± 0.5	0.05
LiClO ₄	22.30 ± 0.03	4.77 ± 0.10	6.5 ± 0.5	0.06
LiBF ₄	25.19 ± 0.03	4.47 ± 0.10	6.5 ± 0.5	0.04
NaBr	35.76 ± 0.02	3.88 ± 0.04	8.0 ± 0.5	0.02
NaBPh ₄	25.52 ± 0.01	3.12 ± 0.03	6.0 ± 0.5	0.03
KBr	38.50 ± 0.03	1.99 ± 0.04	8.5 ± 0.5	0.04
RbBr	38.81 ± 0.02	1.68 ± 0.02	12.0 ± 0.5	0.02
CsBr	39.50 ± 0.01	3.45 ± 0.02	8.0 ± 0.5	0.01
Bu ₄ NBr	25.54 ± 0.08	6.86 ± 0.19	16.0 ± 0.5	0.01

**Table 3. Limiting Ionic Conductances, Walden products and Stokes radii in
N,N- Dimethylacetamide + Water (50% v/v) at 298.15K**

ion	$\lambda_{\pm}^0 / \text{S cm}^2 \text{ mol}^{-1}$	$\lambda_{\pm}^0 \eta_0 / \text{S cm}^2 \text{ mol}^{-1} \cdot \text{Pa.s}$	$r_s^0 / \text{\AA}$
Li^+	6.76	0.022	3.66
Na^+	18.13	0.060	1.36
K^+	20.87	0.069	1.18
Rb^+	21.18	0.070	1.17
Cs^+	21.87	0.072	1.13
Bu_4N^+	7.81	0.026	3.12
Cl^-	19.85	0.066	1.24
Br^-	17.63	0.058	1.40
I^-	13.49	0.044	1.83
ClO_4^-	15.53	0.051	1.59
BF_4^-	18.42	0.061	1.34
BPh_4^-	7.39	0.024	3.35

CHAPTER VII

SECTION A

VISCOSITIES AND ELECTRICAL CONDUCTANCES OF SOME TETRAALKYLMONIUM AND COMMON IONS IN AQUEOUS BINARY MIXTURES OF N,N-DIMETHYLACETAMIDE AT 298.15K.

The use of amide + water mixtures has attracted much attention as solvents in the study of various physico-chemical properties of electrolytic solution.¹⁻³ The present chapter is to study such a system through conductance and viscosity measurements which are very much useful to provide information regarding ion-ion and ion-solvent interactions.⁴⁻⁶ In chapter IV and V, we have reported the transport properties of some lithium and tetraalkylammonium salts in pure DMA from the measurements of their viscosities and conductances. The study has now been extended to binary mixtures with water as cosolvent, in order to understand the nature of ion-solvent interactions and other structural changes that may occur due to the addition of water to DMA.

Experimental

N,N-dimethylacetamide (G.R.E. Merck, India, >99.5%) was distilled twice in an all-glass distillation set as described earlier (chapter III). The purified solvent had a density of $0.93652 \text{ g.cm}^{-3}$, a coefficient of viscosity 0.9370 mPa-s and a specific conductance of about $1.01 \times 10^{-6} \text{ S.cm}^{-1}$ at 298.15K. Triply distilled water with a specific conductance of less than $10^{-6} \text{ S.cm}^{-1}$ was used for the preparation of

the mixtures. Freshly distilled solvents were always used, and the solvent mixtures were prepared immediately prior to use. Solvent mixtures, prepared by weight had a density of 0.99853 g.cm⁻³, a coefficient of viscosity 3.318 mPa-s, a specific conductance of about 3×10^{-6} S.cm⁻¹ and a dielectric constant 59.92 at 298.15K.

The tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described earlier (chapter III).

Conductance measurements were carried out on a Pye-Unicam PW9509 conductivity meter at a frequency of 2000Hz as described in chapter III. The kinematic viscosities were measured using a suspended-level Ubbelohde type viscometer and results were then converted into absolute viscosities by multiplying the former with the density values. Measurements were made in a thermostatic water bath maintained within specified temperature. Solutions were prepared by mass for viscosity and conductance runs, the molalities being converted to molarities using the densities measured with an Ostwald-Sprengel type Pycnometer of about 25cm³ capacity. Several independent solutions were prepared and the runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent.

Results and Discussion

The measured molar conductance (Λ) of electrolyte solutions as a function of molar concentration (c) at 298.15K are given in Table 1.

The conductance data have been analysed by the 1978 Fuoss conductance-concentration equation⁷ as given in chapter IV.

For computation, the initial Λ° values were obtained from Shedlovsky extrapolation of the data. In practice, calculations are made by finding the values of Λ° and σ which minimize the standard deviation, σ ,

$$\sigma^2 = \sum_{j=1}^n [\Lambda_j (\text{calc.}) - \Lambda_j^{\circ} (\text{obs.})]^2 / (n-2) \quad (1)$$

for a sequence of R values and then plotting σ against R, the best-fit R corresponds to the minimum in σ vs R curve. However, since a rough scan using unit increment of R values from 4 to 20 gave no significant minima in the $\sigma(\%)$ vs R curves, the R value was assumed to be $R = a + d$, where a is the sum of the crystallographic radii and d is given by⁷

$$d = 1.183 (M / \rho_0)^{1/3} \quad (2)$$

where M is the molecular weight of the solvent and ρ_0 its density.

The values of Λ° , K_A and R obtained by this procedure have been recorded in Table 2.

In absence of accurate transference data in the mixed solvent, we have to use the 'reference electrolyte' method for the division of Λ° into single-ion values. The Bu_4NBPh_4 has been used as the 'reference electrolyte', and the Λ° -value has been derived from the relation :

$$\Lambda^{\circ}_{\text{Bu}_4\text{NBPh}_4} = \Lambda^{\circ}_{\text{Bu}_4\text{NBr}} + \Lambda^{\circ}_{\text{NaBPh}_4} - \Lambda^{\circ}_{\text{NaBr}} \quad (3)$$

To obtain single ion values we have divided Λ° values of Bu_4NBPh_4 using the method similar to that proposed by Krumgalz⁸

$$\frac{\lambda^\circ_{\text{Bu}_4\text{N}^+}}{\lambda^\circ_{\text{Ph}_4\text{B}^-}} = \frac{\Gamma_{\text{Ph}_4\text{B}^-}}{\Gamma_{\text{Bu}_4\text{N}^+}} = \frac{5.35}{5.00} = 1.07 \quad (4)$$

The r-values have been taken from the works of Gill and Sekhri⁹. The limiting ionic conductances based on the above relationship are presented in Table 3.

The density (ρ) and viscosity (η) data for the electrolytes in the molarity range $0.008 - 0.20 \text{ mol dm}^{-3}$ at 298.15K are given in Table 4.

The relative viscosity (η_r) data of the electrolytes in solution have been analysed with the Jones-Dole equation.¹⁰:

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (5)$$

where A and B are the characteristic parameters for salt and solvent, depend on ion-ion and ion-solvent interactions respectively.

Plots of $(\eta_r - 1)/\sqrt{c}$ against \sqrt{c} for the electrolytes have been found to be linear and the experimental A values have been calculated using the least squares method. The A coefficients have also been calculated at 298.15K from the physical properties of the solvent by using Falkenhagen-Vernon equation:

$$A_{\text{theo}} = \frac{0.2577\Lambda^\circ}{\eta_o(\epsilon T)^{1/2}\lambda_o^+\lambda_o^-} \left[1 - 0.6863 \left(\frac{\lambda_o^+ - \lambda_o^-}{\Lambda_o} \right)^2 \right] \quad (6)$$

The conductance data required in these calculations have been taken from the present work. A coefficients (A_{theo}) thus calculated from Eq. (6) are recorded in Table 5. These A_{theo} values have been used for the analysis of viscosity data.

Viscosity β -coefficients calculated by using the least squares method are also presented in Table 5. Viscosity β -coefficient values of the electrolytes have been divided into ionic components using similar method described above in equations (3) and (4) for division of the limiting molar conductances. The ionic β -coefficients obtained from these relationships are given in Table 6.

Ionic β -values have also been analysed⁴ on the basis of Einstein's equation and the corresponding ionic radii evaluated :

$$B_{\pm} = \frac{2.5(4/3)\pi}{1000} \frac{R_{\pm}^3 N}{(7)}$$

The number n_s of solvent molecules bound to the ion in the primary shell of solvation can be calculated by combining the Jones-Dole equation with that of Einstein:

$$B_{\pm} = (2.5/1000)(V_i + n_s V_s) \quad (8)$$

Where V_i represents the bare ion molar volume and is related to the crystallographic radius (R_c) of the ion. V_s is the solvent molar volume. Table 7 deals with the crystallographic radius (R_c), experimental ionic radii (R_{\pm}) and solvation number (n_s) of ions at 298.15K.

Table 2 shows that the limiting equivalent conductivities (Λ°) of tetraalkylammonium bromides decrease with increasing length of the alkyl chain and the difference becomes very small in cases of higher homologues. This is in agreement with our earlier findings in pure DMA as described in chapter V. In

order to investigate the specific behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting molar electrolyte conductances into their ionic components. It is seen from Table 3 that for the tetraalkylammonium ions, the λ° values decrease in the following order : $\text{Et}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Hex}_4\text{N}^+$ i.e. the limiting ionic conductivity values decrease with increasing size of these cations. The trends become similar with the earlier observation made by Ramanamurti et al¹¹ in this aqueous binary system at higher temperature and can be attributed to the size and structure forming effect of cations (anion Br^- , being the same). Size and structure forming effects (hydrophobic solvation) of cations increase in the order : $\text{Et}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Bu}_4\text{N}^+ < \text{Pen}_4\text{N}^+ < \text{Hex}_4\text{N}^+$, so the mobility should be in the reverse order and this explains the order observed for limiting equivalent conductance. In cases of anions the λ° values decrease with increasing size of the ions i.e. $\text{Br}^- > [\text{B}(\text{Ph})_4]^-$. Table 2 clearly indicates that in almost all cases except tetraethylammonium bromide, association constants are less than 10, so little emphasis should be given to numerical values of K_A . This implies that a preponderant portion of each salt remains dissociated in this solvent medium. However, in solvent mixtures having dielectric constants less than 60, the value of K_A seems to decrease with increasing chain length of tetraalkylammonium bromide salts.¹¹ This is expected because the charge density of tetraalkylammonium ions decrease in the same order.

The Walden products ($\lambda^\circ \pm \eta_o$) of the ions are also included in Table 3. Walden products are usually employed to discuss the interactions of the ions with

the solvent medium. From this table, we see that for the tetraalkylammonium ions, the value of the Walden product decreases from tetraethylammonium ion to tetrahexylammonium ion. This points out that the electrostatic ion-solvent interaction is very weak in these cases. Such type of behaviour is also found in pure DMA as reported earlier. In comparison to the Walden product values of these electrolytes in pure DMA it is observed that except tetraethylammonium ion the other tetraalkylammonium ion maintains nearly same value in this present aqueous binary mixture. The phenomena can be explained by the hydrophobic dehydration of cations by the cosolvent (DMA) which is responsible for the similarity of the Walden product. Further, the hydrophobic dehydration effect will be more in the case of an ion which is more hydrophobic in nature. This hydrophobic character of cations varies in the order: $\text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$. Due to the greater hydrophobic dehydration effect of higher homologues of tetraalkylammonium cation the ability to promote the structure of water becomes reduced and as a result of it the Walden product remains the same value. The Stokes radii (Table 3) of the tetraalkylammonium cations are, however, found to be either close to or smaller than their corresponding crystallographic radii. This observation indicates that these ions are scarcely solvated in this medium.

In addition to conductance measurements the result of the viscosity measurements of different tetraalkylammonium salts from Et_4NBr to Pen_4NBr and some common salts except Hex_4NBr (solubility too low to perform viscosity experiments) are also reported.

The viscosity β -coefficients which represents solute - solvent interactions shown in Table 5 are positive for all the electrolytes studied. The β -values for the tetraalkylammonium bromides increase regularly as we go from tetraethylammonium bromide to tetrapentylammonium bromide. The same kind of behaviour has also been found for these electrolytes in Ethyl - methyl ketone and Ethyl - methyl ketone + Dimethylformamide mixtures.¹²

In order to make further investigation for the specific behaviour of the individual ions the viscosity β -coefficients values of electrolyte resolved into ionic β_{\pm} coefficients by using "reference electrolyte" method and are given in Table 6. The table shows that the viscosity β - coefficients for all cations and anions are positive and are also large with the exception of bromide ion. The observed order may be attributed to greater electrostatic ion-solvent interaction and resistance to the movement of ion due to large size of cation. In case of Br^- ion the very low viscosity β -coefficient value indicates that the viscosity of the solvent mixture is very little modified by its presence due to the poor solvation of the ion and this is also supported by the conductance data. The other anion, Ph_4B^- , however, is found to be very efficient in modifying the solvent viscosity as manifested by its large and positive viscosity β value. The A - coefficients reported in Table 5 are small and positive for all the electrolytes indicating the presence of weak ionic interactions. The A values, calculated theoretically from the physical parameters of the solvent and the limiting ionic equivalent conductances using Falkenhagen and Vernon

equation given in Table 5 are almost similar with the experimental A-value. The values of crystallographic radius (R_c), Ionic radii (R_{\pm}) and solvation number (n_s) shown in Table 7 can provide us important information regarding the solvation of some tetraalkylammonium, Na^+ , Br^- and Ph_4B^- ions in this present aqueous binary mixture. With the exception of Na^+ , Br^- and Ph_4B^- ions, the R_{\pm} values for the other ions are always found to be less than R_c values of the ions indicating that they are not so solvated in this mixture. Although the negative values of solvation number have no physical significance, it seems to an indication of the poor solvation of these ions. For Na^+ and Br^- ions, the greater value of ionic radii (R_{\pm}) than crystallographic radii (R_c) and positive solvation number clearly demonstrate that these ions are significantly solvated in this solvent medium. The results obtained from viscosity measurements are found to be in good agreement with the conductometric investigation.

SECTION B

ULTRASONIC VELOCITIES AND ISENTROPIC COMPRESSIBILITIES OF SOME SYMMETRICAL TETRAALKYLAMMONIUM AND ALKALI-METAL SALTS IN N,N-DIMETHYLACETAMIDE-WATER MIXTURE AT 298.15 K

The thermodynamic properties are generally convenient parameters for interpreting solute-solute, and solute-solvent interactions occurring in solution phase. Fundamental properties such as enthalpy, entropy, and Gibbs energy represent the macroscopic state of a system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomena is generally difficult. Higher derivatives of these properties, however, can be interpreted in terms of molecular interactions. The compressibility behaviour of solutes, which is the second derivative of the Gibbs energy, is a very sensitive indicator of molecular interactions and can provide useful information about these phenomena.¹³⁻¹⁸ In Chapter V, Section C we have reported the results of our compressibility measurements on some selected symmetrical tetraalkylammonium bromides in *N,N*-dimethylacetamide at 298.15 K. The present work reports the study of the apparent molar isentropic compressibility behaviour of some tetraalkylammonium and alkali salts in *N,N*-dimethylacetamide + water (50% v/v) mixture at 298.15 K to elucidate the nature of interactions prevailing in these salt solutions.

Experimental

For the preparation of the solution of each salt, a different batch of solvent was used and the properties of the mixed solvent used in each case are recorded in Table 8.

In order to minimize the moisture contaminations, all solutions were prepared in a dehumidified room with utmost care. A stock solution for each salt was prepared by mass and the working solutions were prepared by mass dilution from the stock. The conversion of molality to molarity was performed using the density values.

The velocities of sound were measured with an accuracy of 0.3%, using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 4 MHz. The interferometer was calibrated with water, methanol and benzene. The temperature stability was maintained within ± 0.01 K by circulating thermostated water around the measuring cell.

Results and Discussion

Adiabatic compressibility coefficients were derived from the following equation

$$\kappa_s = \frac{1}{u^2 \rho} \quad (9)$$

where ρ is the density and u is the velocity of sound in the solution. The apparent

molar isentropic compressibility (κ_ϕ) of the electrolyte solutions was then calculated from the relationship

$$\kappa_\phi = \frac{M\kappa_s^0}{\rho_0} + \frac{1000(\kappa_s\rho_0 - \kappa_s^0\rho)}{m\rho\rho_0} \quad (10)$$

where m is the molal concentration of the salt solution and the other symbols have their usual significance.

The molality (m), the density (ρ), the sound velocity (u), and the apparent molar isentropic compressibility (κ_ϕ) of the electrolyte solutions at 298.15 K are reported in Table 8.

The limiting apparent molar isentropic compressibility (κ_ϕ^0) have been obtained by extrapolating the linear plots of κ_ϕ versus the square root of the molal concentration of the solutes to zero concentration by the method of least-squares

$$\kappa_s = \kappa_s^0 + S_K \sqrt{m} \quad (11)$$

where S_K is the experimental slope. The values of the limiting apparent molar isentropic compressibilities (κ_ϕ^0), and the experimental slopes (S_K) are listed in Table 9.

The limiting apparent molar isentropic compressibilities (κ_ϕ^0) of the tetraalkylammonium salts investigated here are found to increase in the order:



It is also interesting to note that the κ_ϕ^0 values of Et₄NBr and NaBr are negative while those of the other three tetraalkylammonium bromides and NaBPh₄ are found to be positive.

The negative κ_ϕ^0 values of the electrolytes can be interpreted in terms of loss of compressibility of the solvent due to the presence of these solutes in solution. The positive κ_ϕ^0 values, on the other hand, indicate an increase in the compressibility of the solution compared to the pure solvent.

Several factors may contribute to the compressibility of the electrolyte solutions and we will now examine the important factors in order to elucidate the effects of the solutes on the solvent structure and their role on compressibility.

The bromide ion is found to remain unsolvated in the mixed *N,N*-dimethylacetamide + water system under investigation from our conductivity study. Moreover, it is not a molecular ion, thus ruling out the possibility of having intrinsic compressibility. This ion, therefore, does not influence the compressibility of the medium. The sodium ion, however, is found to be solvated from conductivity study. This ion will, therefore, cause a loss of solvent compressibility resulting from the electrostriction of the solvent molecules around the ion.

Most of the interpretations of the limiting apparent molar isentropic compressibilities in terms of solvation effects¹⁹⁻²³ assume κ_ϕ^0 of unsolvated ions is negligibly small, although Conway and Verral²⁴ recognized that large organic ions could have some intrinsic compressibility due to the intermolecular free space which

makes the medium more compressible. This could also be expected for the unsolvated large tetraalkylammonium and tetraphenylborate ions investigated in this study.

Another effect which is possible for large organic ions is the penetration of the solvent molecules within the intraionic free space. This is the result of the interaction of the positively charged nitrogen central atom of the tetraalkylammonium ions (or of the negatively charged boron central atom in the case of the tetraphenylborate ion) with the neighboring solvent molecules. This is essentially an electrostriction effect and causes constriction of the solution volumes, thus resulting in a more compact and, hence, a less compressible medium.

In view of the factors delineated above which control the compressibility of the electrolyte solutions, it can be concluded that since the bromide ion has no influence on the compressibility of the solution, the interplay of the other factors would actually determine the overall compressibility of the solution.

The negative limiting apparent molar isentropic compressibility value for Et₄NBr solution can be attributed to the predominance of the penetration effect over the effect of the intrinsic compressibility of the tetraethylammonium ions. For Pr₄NBr, Bu₄NBr, and Pen₄NBr solutions exhibiting positive κ_ϕ^0 values, on the other hand, the effect of intrinsic compressibility of the large tetraalkylammonium ions overrides the penetration effect. This observation is quite expected since the extent of penetration of the solvent molecules should be maximum for tetraethylammonium ion with the lowest crystal radius and hence the highest surface charge density

among the tetraalkylammonium ions studied here. For higher homologues, the surface charge density decreases with the radius, thus lowering the possibility of penetration.

For NaBr solution, however, the negative κ_ϕ^0 value arises from the loss of solvent compressibility caused by the sodium ions.

The positive κ_ϕ^0 value for NaBPh₄ solution indicates that the intrinsic compressibility of the tetraphenylborate ion is playing the major role as compared to the penetration effect of this ion and the electrostriction effect of the sodium ion.

In order to investigate the behaviour of the individual ions comprising these electrolytes, it is necessary to split the limiting apparent molar isentropic compressibilities into their ionic components. However, there exist no reliable method for the division of κ_ϕ^0 values into ionic contributions. Millero²³ has suggested a method for the division of the limiting partial molar volumes of the "reference electrolyte" tetraphenylarsonium tetraphenylborate ($\text{Ph}_4\text{As}^+\text{Ph}_4\text{B}^-$) into ionic parts, but such a method cannot be used here since we do not know the ratio of the compressibilities of the pure (solid or gaseous) ions. A similar model based on another "reference electrolyte" tetrabutylammonium tetraphenylborate ($\text{Bu}_4\text{N}^+\text{Ph}_4\text{B}^-$) originally used for the splitting of the viscosity B -coefficients of electrolytes into the contributions from individual ions was attempted²⁵ to split the κ_ϕ^0 values. But, this approach is inappropriate since it assumes that the ratio of the volumes of these ions is equal to the ratio of their compressibilities which is not possible since the

compressibilities of these large ions are not a simple function of their volumes. The extrapolation method as suggested by Conway et. al.²⁶ for volumes can also not be used for the division of the κ_ϕ^0 values in view of the large contribution of the compressibilities of the tetraalkylammonium ions which does not seem to be a simple function of the size of the ion. Interestingly, we tried both the extrapolation method and the "reference electrolyte" method using tetrabutylammonium tetraphenylborate ($Bu_4N^+Ph_4B^-$) to perform the division of the κ_ϕ^0 values into ionic components. But, unfortunately, the results obtained by these two methods differ appreciably. The method used by Davidson et. al.¹³ for acetonitrile, which assumes the limiting ionic compressibility of the tetraphenylborate ion to be zero is also not appropriate as the tetraphenylborate ion is large (its crystal radius is 0.535 nm), and therefore, its intrinsic compressibility contribution cannot be taken as zero.

Under these circumstances, and also in view of the compressibility behaviour of bromide ion in the mixed solvent system under study as discussed above, the choice of $\kappa_\phi^0(Br^-) = 0$ seems to be the best at this moment. Ionic κ_ϕ^0 values based on this assumption are given in Table 3, which fit quite well with the discussion made above on the basis of the κ_ϕ^0 values of the electrolytes as whole thus substantiating the present protocol for the division of limiting apparent molar isentropic compressibilities of these electrolytes in *N,N*-dimethylacetamide + water mixed solvent system.

Thus the above study shows the effect of penetration of the solvent molecules into the intraionic free space of the tetraethylammonium ions to predominate over the effect of their intrinsic compressibility for tetraethylammonium bromide solution. For sodium bromide solution, however, the negative κ_{ϕ}^0 value arises from the loss of solvent compressibility caused by the sodium ions. For tetrapropylammonium bromide, tetrabutylammonium bromide, and tetrapentylammonium bromide solutions exhibiting positive κ_{ϕ}^0 values, on the other hand, the effect of intrinsic compressibility of the large tetraalkylammonium ions overrides the penetration effect. The positive κ_{ϕ}^0 value for sodium tetraphenylborate solution indicates that the intrinsic compressibility of the tetraphenylborate ion is playing the major role as compared to the penetration effect of this ion and the electrostriction effect of the sodium ion.

References

1. C.de.Visser and G.Somsen, *J.Phys.Chem.*, **78**, 1719, 1974.
2. D.Singh, N.P.Singh and L.Bahadur, *Ind.J.Chem.*, **13A**, 1177, 1975.
3. J.M.McDowall, N.Martinus and C.A.Vincent, *J.Chem.Soc., Faraday Trans.*, **1**, **72**, 654, 1976.
4. D.Nandi, S.Das and D.K.Hazra, *J.Chem.Soc., Faraday Trans.*, **1**, **85**, 1531, 1989.
5. B.Das and D.K.Hazra, *Bull. Chem.Soc.Jpn.*, **65**, 3470, 1992.
6. D.Das, B. Das and D.K.Hazra, *J.Soln.Chem.*, **31**, 425, 2002.
7. R.M.Fuoss, *J.Phys.Chem.*, **82**, 2427, 1978.
8. B.S.Krumgalz, *J.Chem.Soc., Faraday Trans.*, **1**, **76**, 1275, 1980.
9. D.S.Gill and M.B.Sekhri, *J.Chem.Soc., Faraday Trans.*, **1**, **78**, 119, 1982.
10. G.Jones and M.Dole, *J.Am.Chem.Soc.*, **51**, 2950, 1929.
11. L.Bahadur and M.V.Ramanamurti, *J.Chem.Soc., Faraday Trans.*, **1**, **76**, 1409, 1980.
12. B.S.Patial, S.Chauhan, V.S.Chauhan and V.K.Syal, *Ind. J.Chem.*, **41A**, 2039, 2002.
13. I.Davidson, G.Perron and J.E.Desnoyers, *Can. J.Chem.*, **59**, 2212, 1981.
14. F.Kawaizumi, S.Koda, M.Kimura and H.Nomura, *J.Soln. Chem.*, **20**, 1129, 1991.
15. B.Das, P.K.Muhuri and D.K.Hazra, *Acoustics. Lett.*, **18**, 69, 1994.
16. P.K.Muhuri, B.Das and D.K.Hazra, *Ind. J.Chem.*, **35A**, 288, 1996.

17. P.J.Victor, P.K.Muhuri, B.Das and D.K.Hazra, *J.Phys.Chem.*, **B**, **103**, 11227, 1999.
18. P.J.Victor, B.Das and D.K.Hazra, *J.Soln. Chem.*, **30**, 435, 2001.
19. J.G.Matheisan and B.E.Conway, *J.Soln.Chem.*, **3**, 455, 1973 ; *J.Chem.Soc., Faraday Trans.*, **1**, **70**, 752, 1974.
20. F.J.Millero, G.K.Ward and P.V.Chetrikin, *J.Acoust. Soc. Amer.*, **61**, 1492, 1977.
21. J.Padova, *Bull. Res. Council Israel A.*, **10**, 63, 1961.
22. K.O.Tamura and T.Sasaki, *Bull.Chem.Soc.Jpn.*, **36**, 975, 1963.
23. F.J.Millero, *J.Phys.Chem.*, **75**, 280, 1971.
24. B.E.Conway and R.E.Verral, *J.Phys.Chem.*, **70**, 3952, 1966.
25. J.Singh, T.Kaur, V.Ali and D.S.Gill, *J.Chem.Soc., Faraday Trans.*, **90**, 579, 1994.
26. B.E.Conway, R.E.Verral and J.E.Desnoyers, *Trans. Faraday Soc.*, **62**, 2738, 1966.

Table 1 - Equivalent conductances and corresponding molarities of electrolytes in aqueous binary mixture of N,N-dimethyl acetamide at 298.15K.

$10^4 c$ (mol dm ⁻³)	$\hat{\Lambda}$ (S cm ² mol ⁻¹)	$10^4 c$ (mol dm ⁻³)	$\hat{\Lambda}$ (S cm ² mol ⁻¹)
Et_4NBr		Pr_4NBr	
442.48	24.25	435.51	21.57
411.96	24.60	405.47	21.83
381.44	24.98	375.44	22.09
350.93	25.39	345.40	22.33
320.41	25.78	315.37	22.62
290.00	26.21	285.34	22.92
259.40	26.67	255.30	23.23
228.87	27.14	225.26	23.54
Bu_4NBr		Pen_4NBr	
435.90	21.14	434.23	20.47
405.84	21.33	404.29	20.64
375.78	21.55	374.34	20.85
345.72	21.77	344.39	21.05
315.65	21.98	314.44	21.28
285.59	22.13	284.50	21.50
255.53	22.42	254.55	21.77
225.47	22.68	224.60	22.01

contd....

$10^4 c$ (mol dm ⁻³)	\wedge (S cm ² mol ⁻¹)	$10^4 c$ (mol dm ⁻³)	\wedge (S cm ² mol ⁻¹)
Hex ₄ NBr			NaBr
436.55	19.57	436.72	31.41
406.44	19.72	406.60	31.59
376.33	19.89	376.48	31.78
346.22	20.08	346.36	31.95
316.12	20.24	316.24	32.14
286.01	20.43	286.12	32.33
255.90	20.62	256.01	32.55
225.80	20.72	225.89	32.78
Na[B(Ph) ₄]			
436.50	20.00		
406.40	20.10		
376.29	20.20		
346.19	20.29		
316.09	20.40		
285.98	20.50		
255.88	20.62		
225.78	20.75		

Table 2 - Conductivity parameters of electrolytes in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Salt	κ_o ($S\ cm^2\ mol^{-1}$)	K_A ($dm^3\ mol^{-1}$)	R (°A)	$\sigma\%$
Et ₄ NBr	34.74± 0.15	18.12± 0.41	5.80	0.09
Pr ₄ NBr	27.34±0.03	9.31±0.08	18.40	0.04
Bu ₄ NBr	25.54±0.08	6.86±0.20	16.00	0.10
Pen ₄ NBr	25.43±0.03	8.50±0.10	8.00	0.04
Hex ₄ NBr	23.40±0.11	6.19±0.30	7.40	0.16
NaBr	35.76±0.02	3.88±0.04	8.00	0.02
Na[B(Ph) ₄]	25.52±0.01	3.12±0.03	6.00	0.02

Table 3 - Limiting ionic conductances (λ°_{\pm}), Walden products ($\lambda^{\circ}_{\pm} \eta_0$) and Ionic Stokes' Radii (r_s) in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Ion	λ°_{\pm} (S cm ² mol ⁻¹)	$\lambda^{\circ}_{\pm} \eta_0$ (S cm ² mol ⁻¹ P _{a.s})	r_s (\AA)
Et ₄ N ⁺	17.11	0.056	1.44
Pr ₄ N ⁺	9.71	0.032	2.55
Bu ₄ N ⁺	7.91	0.026	3.13
Pen ₄ N ⁺	7.80	0.025	3.17
Hex ₄ N ⁺	5.76	0.019	4.30
Na ⁺	18.13	0.060	1.36
Br ⁻	17.63	0.058	1.40
[B(Ph) ₄] ⁻	7.39	0.024	3.35

Table 4 - Concentration (c), density (ρ) and relative viscosity (η_r) of electrolytes in aqueous binary mixture at 298.15K.

C (mol dm ⁻³)	ρ (g cm ⁻³)	η_r	C (mol dm ⁻³)	ρ (g cm ⁻³)	η_r
Et ₄ NBr					
0.10186	1.0032	1.0395	0.10233	1.0027	1.0615
0.07276	1.0021	1.0280	0.07309	1.0017	1.0444
0.05238	1.0012	1.0206	0.05262	1.0010	1.0322
0.03201	1.0003	1.0129	0.03216	1.0002	1.0204
0.02037	0.9998	1.0084	0.02046	0.9997	1.0130
0.00873	0.992	1.0037	0.00877	0.9992	1.0063
Bu ₄ NBr					
0.10470	1.0016	1.0743	0.10235	0.99942	1.0832
0.07479	1.0009	1.0535	0.07310	0.99929	1.0601
0.05385	1.0003	1.0390	0.05264	0.99914	1.0436
0.03290	0.9997	1.0240	0.03217	0.99893	1.0268
0.02094	0.9993	1.0156	0.02047	0.99877	1.0174
0.00897	0.9989	1.0070	0.00877	0.99858	1.0076
NaBr					
0.10954	1.0065	1.0322	0.10386	1.0022	1.1049
0.07824	1.0044	1.0233	0.07418	1.0013	1.0729
0.05633	1.0028	1.0169	0.05341	1.0006	1.0544
0.03442	1.0012	1.0105	0.03264	0.9998	1.0337
0.02191	1.0002	1.0069	0.02077	0.9994	1.0217
0.00939	0.9991	1.0031	0.00890	0.9989	1.0096
Na[B(Ph) ₄]					

Table 5 - Theoretical and experimental A-coefficients and viscosity B-coefficients for the electrolytes in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Salt	A_{theo} (dm $^{3/2}$ mol $^{-1/2}$)	A_{expt} (dm $^{3/2}$ mol $^{-1/2}$)	B (dm 3 mol $^{-1}$)	σ
Et $_4$ NBr	0.0068	0.0062	0.366	0.03
Pr $_4$ NBr	0.0086	0.0132	0.558	0.04
Bu $_4$ NBr	0.0096	0.0088	0.683	0.05
Pen $_4$ NBr	0.0099	0.0082	0.790	0.06
NaBr	0.0064	0.0052	0.279	0.01
Na[B(Ph) $_4$]	0.0110	0.0113	0.964	0.08

Table 6 - Ionic B-values in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Ions	B ₂ (dm ³ mol ⁻¹)
Et ₄ N ⁺	0.298
Pr ₄ N ⁺	0.490
Bu ₄ N ⁺	0.615
Pen ₄ N ⁺	0.722
Na ⁺	0.211
Br ⁻	0.068
Ph ₄ B ⁻	0.753

Table 7 - Theoretical and experimental Ionic radii (R_t) and solvation numbers (n_s) of ions in aqueous binary mixture of N,N-dimethylacetamide at 298.15K.

Ions	R_c (\AA)	R_t (\AA)	n_s
Et_4N^+	4.00	3.60	-0.358
Pr_4N^+	4.52	4.20	-0.345
Bu_4N^+	4.94	4.60	-0.236
Pen_4N^+	5.29	4.80	-0.303
Na^+	1.17	3.20	0.968
Br^-	1.80	2.20	0.465
Ph_4B^-	4.80	4.90	-0.075

Table 8. Concentration (*c*), density (ρ), ultrasonic velocity (*u*), and apparent molar isentropic compressibility ($10^{10} \kappa_f$) of the electrolyte solutions in *N,N*-dimethylacetamide + water mixture (50% v/v) at 298.15 K

<i>c</i> / mol.dm ⁻³	ρ / g.cm ⁻³	<i>u</i> / cm.s ⁻¹	$10^{10} \kappa_f$ / cm ³ .mol ⁻¹ .bar ⁻¹	<i>c</i> / mol.dm ⁻³	ρ / g.cm ⁻³	<i>u</i> / cm.s ⁻¹	$10^{10} \kappa_f$ / cm ³ .mol ⁻¹ .bar ⁻¹
Et₄NBr							
0.00000	0.99877	173938	-	0.00000	0.99877	173938	-
0.00873	0.99922	174058	-12.74	0.00877	0.99919	174032	19.90
0.02037	0.99979	174177	-6.36	0.02046	0.99970	174130	24.28
0.03201	1.00030	174284	-1.50	0.03216	1.00020	174208	28.09
0.05238	1.00120	174423	4.62	0.05262	1.00100	174326	32.94
0.07276	1.00210	174517	9.80	0.07309	1.00170	174424	37.04
0.10186	1.00320	174624	15.85	0.10233	1.00270	174513	41.97
Bu₄NBr							
0.00000	0.99854	173818	-	0.00000	0.99841	173770	-
0.00897	0.99888	173880	52.07	0.00877	0.99858	173840	81.68
0.02094	0.99930	173954	56.77	0.02047	0.99877	173929	84.24
0.03290	0.99969	174020	59.55	0.03217	0.99893	174010	86.49
0.05385	1.00030	174117	63.68	0.05264	0.99914	174139	89.79
0.07479	1.00090	174189	66.87	0.07310	0.99929	174253	92.61
0.10470	1.00160	174274	70.87	0.10235	0.99942	174400	95.79

Table 8. contd..

c/ mol.dm ⁻³	ρ / g.cm ⁻³	u/ cm.s ⁻¹	$10^{10}\kappa_\phi$ / cm ³ .mol ⁻¹ .bar ⁻¹	c/ mol.dm ⁻³	ρ / g.cm ⁻³	u/ cm.s ⁻¹	$10^{10}\kappa_\phi$ / cm ³ .mol ⁻¹ .bar ⁻¹
NaBPh ₄							
0.00000	0.99853	173696	-	0.00000	0.99831	173842	-
0.00890	0.99891	173575	137.77	0.00939	0.99915	173815	-13.64
0.02077	0.99939	173381	144.30	0.02191	1.00020	173781	-12.28
0.03264	0.99984	173168	149.14	0.03442	1.00120	173752	-11.43
0.05341	1.00060	172753	155.93	0.05633	1.00280	173720	-10.41
0.07418	1.00130	172300	161.48	0.07824	1.00440	173683	-9.57
0.10386	1.00220	171611	168.17	0.10954	1.00650	173648	-8.55

Table 9. Limiting apparent molar isentropic compressibilities (κ_ϕ^0), and the experimental slopes (S_K) of the electrolyte solutions in N,N -dimethylacetamide + water mixture (50% v/v) at 298.15 K

Electrolyte	$10^{10} \kappa_\phi^0 / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$	$10^{10} S_K / \text{cm}^3 \cdot \text{mol}^{3/2} \cdot \text{kg}^{1/2} \cdot \text{bar}^{-1}$
Et_4NBr	-24.41 ± 0.20	125.63 ± 0.92
Pr_4NBr	10.49 ± 0.20	98.16 ± 0.93
Bu_4NBr	44.72 ± 0.29	81.21 ± 1.31
Pen_4NBr	75.40 ± 0.31	63.30 ± 1.41
NaBPh_4	124.83 ± 0.83	134.44 ± 0.38
NaBr	-15.09 ± 0.01	19.73 ± 0.05

Table 10. Ionic standard apparent molar isentropic compressibilities ($\kappa_{\phi\pm}^0$) in *N,N*-dimethyl-acetamide + water mixture (50% v/v) at 298.15 K

ion	$10^{10}\kappa_{\phi\pm}^0 / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$	ion	$10^{10}\kappa_{\phi\pm}^0 / \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{bar}^{-1}$
Et_4N^+	-24.41	Na^+	-15.09
Pr_4N^+	10.49	Ph_4B^-	139.92
Bu_4N^+	44.72	Br^-	0.00
Pen_4N^+	75.40		

CHAPTER VIII

SECTION A

EXCESS MOLAR VOLUMES AND VISCOSITY DEVIATIONS IN BINARY MIXTURES OF N,N-DIMETHYLACETAMIDE WITH FORMAMIDE AND N,N-DIMETHYL FORMAMIDE AT (298.15, 308.15 AND 318.15)K.

Amides are very interesting compounds and they possess the very common in nature donor-acceptor – CO-NH-peptide bond and display the property of self association by the H-bond¹. Further , tertiary amides offer great interest because they are related to structural problems in molecular biology. This lead us to investigate the excess properties of the mixtures of N,N-dimethylacetamide (DMA) with familiar solvents formamide (FA) and N,N-dimethylformamide (DMF). DMA is a dipolar aprotic solvent and due to the moderate dielectric constant ($\epsilon = 37.8$ at 298.15K) it is likely to be moderately structured.² On the other hand, formamide mainly consists of the chain like hydrogen bonded structure by combining through – NH₂....O = CH – interactions³ and its dielectric constant and dipole moment ($\epsilon = 109.5$ and $\mu = 3.86\text{D}$ at 298.15K)⁴ are very high. DMF manifests no significant intermolecular H-bonding ability⁵ and has moderate dielectric constant and high dipole moment ($\epsilon = 36.71$ and $\mu = 3.86 \text{ D}$ at 298.15K)⁶. Thus a systematic study of the structural and energetic consequence of the interactions between DMA and FA and between DMA and DMF will enable us to understand how primary and tertiary

amide exercises thermodynamic and kinetic control over the chemical activities of peptide bonds in another tertiary amide i.e. N,N-dimethylacetamide. In the present study, we have tried to explore the sensitivity of the composition dependence of the excess molar volume (V^E) plus viscosity deviations ($\Delta\eta$) of liquid mixtures containing the amide functional group which constitute an important tool in the interpretation of complex molecules of biological interest.

Experimental

The purification of solvents and the experimental technique has been described earlier in chapter III. In all cases, the experiments were performed at least in five replicates for each composition and at each temperature and the results averaged.

Results and Discussion

The densities, viscosities, excess molar volumes and viscosity deviations of N,N-dimethylacetamide + formamide mixture and N,N-dimethylacetamide + N,N-dimethyl formamide mixture as a function of mole fraction of N,N-dimethylacetamide at (298.15, 308.15 and 318.15)K are presented in Tables 1 and 2 respectively. The excess functions have been calculated using the following equations

$$V^E = V - (v_1x_1 + v_2x_2) \quad (1)$$

$$\Delta\eta = \eta - (\eta_1x_1 + \eta_2x_2) \quad (2)$$

where V and η are the respective solution properties and v_1 and v_2 and η_1 and η_2 are the molar volumes and the viscosities of the pure components. The molar volume V is defined by the relation

$$V = \frac{M_1x_1 + M_2x_2}{\rho} \quad (3)$$

where M_1 and M_2 are the molecular masses of pure substances and ρ is the density of the mixture.

Graphical representations of Y^E and $\Delta\eta$ as functions of mole fraction of DMA are given in Figs. 1 and 2 respectively.

The excess properties Y^E were fitted to the Redlich-Kister equations.⁷

$$Y^E = x_1(1 - x_1) \sum A_i(1 - 2x_1)^i \quad (4)$$

where A_0, A_1, A_2 are adjustable parameters. These parameters were evaluated by fitting $Y^E/x_1(1 - x_1)$ to equation 4 by the method of least squares. The values of these parameters along with the standard deviation $\sigma(Y^E)$ of Y^E as defined by the equation.

$$\sigma(Y^E) = [\sum (Y_{\text{obs}}^E - Y_{\text{cal}}^E)^2 / (N - M)]^{0.5} \quad (5)$$

are recorded in Table 3. In equation 5, N is the total no. of points and M is the number of parameters.

Excess Molar Volume

The systems DMA + FA and DMA + DMF show negative V^E values over the entire range of mole fraction and over the range of temperatures studied (Fig. 1). Such trends in V^E values have been observed in other systems also. Though both the systems show minima at a mole fraction of about 0.55 of DMA but the substitution of H by CH_3 at the N site in N,N-dimethylformamide caused a noticeable effect on the V^E values which may be explained qualitatively by postulating the two opposing set of contributions : (i) expansion due to dipole-dipole interactions of the unlike components of amide mixtures and size differences; (ii) contraction due to multiple hydrogen bonding between unlike molecules of the mixture or self association of the components. The actual value would be the balance between the two opposing effects. However, the experimental results suggest that the latter effect is more prominent than the former. The value of V^E in case of formamide mixture is much more -ve than in DMF mixture. This indicates that primary amide has a greater H-bonding ability than tertiary amide in amide-amide mixtures. The steric hindrance of the two methyl groups of DMF⁸ makes DMF weaker in hydrogen bonding ability than formamide which has a capability of three hydrogen bond donors and three acceptors.¹ From Fig. 1 we see that as the temperature increases, the V^E values become more -ve in formamide system but in DMF system the result becomes reversed. The decrease of V^E with the increase in temperature is explained by considering the difference in the molar volumes of the two liquids at different temperatures. The difference in the

molar volumes of DMA and FA is $52.94 \text{ cm}^3 \text{ mol}^{-1}$ at 298.15K while its value at 318.15K is $54.08 \text{ cm}^3 \text{ mol}^{-1}$. This shows that as the temperature of the mixture increases, the difference in the molar volumes of the two liquids also increases, but the smaller size molecules of FA easily fit⁹ into the voids created by larger molecules of DMA resulting in less increase in the volume of the mixture with increase of temperature. In case of DMF mixtures, the difference in the molar volumes of DMA and DMF is very low i.e. $15.56 \text{ cm}^3 \text{ mol}^{-1}$ at 298.15K, so the interstitial accommodation of one component into the other is ruled out. A rise in temperature leads to the breaking of hydrogen bonded structures between unlike molecules and thus the dipole-dipole interactions of the unlike components make the V^E values less -ve compared to lower temperature.

Viscosity

The experimental viscosities as a function of mole fraction of DMA for both the systems are given in the Tables 1 and 2. The broad maxima observed in case of FA + DMA mixture at about 0.25 mole fraction of DMA suggest high association or complex formation between formamide and DMA. On the other hand, the viscosities of DMF + DMA system increase almost linearly without any maxima or minima with an increase in the DMA content in the mixture. The absence of any maxima in the intermediate composition gives an indication of the possible absence of specific interaction between DMF and DMA.

Viscosity Deviations

The DMA + FA system exhibits a sharp positive deviation of $\Delta\eta$ over the entire mole fraction range and over the three temperatures investigated (Fig. 2) with maxima corresponding to a mole fraction of about 0.3 in DMA. Such trends are also observed in DMA + ME and DMA + H₂O system. These $\Delta\eta$ values indicate specific hydrogen bonding interactions between DMA and formamide molecules. This is also supported by the excess molar volume studies as reported above. As the temperature increases, the magnitude of the viscosity deviation sharply decreases due to the rapid breaking up of the hydrogen bonds in the system and ultimately tend to approach ideality.

The DMA + DMF system displays very slight negative deviation of $\Delta\eta$ from ideality over the entire mole fraction range at the studied temperatures. The minima correspond to the mole fraction of about 0.5 of DMA (Fig.2). Further, with the increase of temperature $\Delta\eta$ values become more and more negative. The moderately structured DMA seems to undergo a structure-breaking effect when mixed with DMF, similar to N-methylacetamide's behaviour with DMF.¹⁰ Apart from this, dispersion and dipolar forces between these two aprotic and unlike solvents may also give rise to negative $\Delta\eta$ values. Such negative deviations from ideality are also observed in propylene carbonate (PC) + methanol and PC + tetrahydrofuran mixtures.¹¹

So far the results discussed reveal that in the DMA + FA system strong heteroassociation is present through multiple hydrogen bonding between the polar groups of the unlike molecules. Also large negative V^E and large positive $\Delta\eta$ values of this system are indicators for this phenomenon. On the other hand, there is a weak dipole-dipole interaction and a slight structure breaking effect in the DMA + DMF mixture as observed from the experimental data.

SECTION B

MOLECULAR INTERACTION STUDY IN BINARY MIXTURES OF N,N-DIMETHYLACETAMIDE WITH 2-ETHOXYETHANOL AT THREE DIFFERENT TEMPERATURES.

Thermodynamic excess properties of the binary liquid mixtures have been very useful to obtain information on the intermolecular interactions and geometrical effects in the systems.^{1,12} Solvents like 2-ethoxyethanol (EE) commercially known as 'cellosolves', are widely used as components of solvents, co-emulsifiers and stabilisers of emulsions, dyes and lacquers.¹³ They can be considered to be ethylene glycol derivatives obtained by the replacement of one of the hydroxy groups by an alkoxy group. Their molecules contain both hydroxylic and ether groups (as well as an alkyl group). The cellosolves in their pure state are self-associated and form cyclic dimers in which the hydroxy proton of one cellosolve molecule is bound to the ether oxygen atom of the other.¹⁴⁻¹⁷ They can also form intramolecularly hydrogen bonded five membered ring monomers.^{14,15,18-20} In view of their properties and structure the 2-ethoxyethanol is often regarded as 'quasi-aprotic' solvent²¹ On the other hand N,N-dimethylacetamide (DMA) is a dipolar aprotic solvent and due to the moderate dielectric constant ($\epsilon = 37.8$ at 298.15K), it is likely to be moderately structured. In this work, we made an attempt to study the behaviour of a dipolar aprotic solvent in a binary mixture with a 'quasi-aprotic' solvent over the entire range of their compositions at 298.15, 308.15 and 318.15K by measurement of their densities, viscosities and ultrasonic velocities. From these

experimental data excess volume (v^E), excess viscosity ($\Delta\eta$), excess intermolecular free length (L_f^E) and isentropic compressibility changes (β^E) were calculated.

Experimental

The purification of solvents and the experimental technique has already been discussed in chapter III

Results and Discussion

The experimental values of density ρ , viscosity η , and ultrasonic velocity u , of pure liquids and their binary mixtures at three different temperatures have been used to calculate the values of isentropic compressibility β , intermolecular free length L_f , relative association R_A , acoustic impedance Z and molar sound speed R_m using the following standard relations :

$$\beta = 1/u^2 \rho, \quad (6)$$

$$L_f = K / u \rho^{1/2}, \quad (7)$$

$$R_A = (\rho / \rho_0) (u_0 / u)^{1/3}, \quad (8)$$

$$Z = u \rho, \quad (9)$$

$$R_m = V u^{1/3}, \quad (10)$$

where K is a temperature dependent constant [$= (93.875 + 0.375 T) \times 10^{-8}$]²², T is the absolute temperature; ρ_0 , ρ and u_0 , u are the densities and ultrasonic speeds

of the solvent (2-ethoxyethanol) and solution, respectively. The molar volume (V) of the binary mixtures was calculated using the equation

$$V = \frac{M_1 X_1 + M_2 X_2}{\rho} \quad (11)$$

where M_1 and M_2 are the molecular masses of pure substances and ρ is the density of the mixture. The values of ρ , η , u , β , L_f , R_A , Z and R_m as a function of mole fraction X_1 of DMA at 298.15, 308.15 and 318.15K are listed in Table 4. The non-linear increase/decrease in ρ , η , u , β , L_f , R_A , Z and R_m values (Table 4) with composition indicates significant interactions between the component molecules.

The excess functions are found to be more sensitive towards intermolecular interactions in liquid mixtures. The excess volume V^E , excess intermolecular free length L_f^E , viscosity deviations $\Delta\eta$ and excess isentropic compressibility β^E have been calculated using the following relation :

$$Y^E = Y - [x_1 Y_1 + x_2 Y_2] \quad (12)$$

Where Y^E is V^E or L_f^E or $\Delta\eta$ or β^E ; x is mole fraction of pure solvent in the mixture and subscripts 1 and 2 stand for DMA and 2-ethoxyethanol respectively.

Graphical representations of V^E , L_f^E , $\Delta\eta$ and $\Delta\beta$ as function of mole fraction of N,N-dimethylacetamide are given in Figures 3-6, respectively.

The excess properties Y^E were fitted to the Redlich - Kister equation.⁷

$$Y^E = x_1(1-x_1) \sum A_j (1-2x_1)^j \quad (13)$$

where A_0, A_1, A_2 are adjustable parameters. These parameters were evaluated by fitting $Y^E/x_1(1-x_1)$ to eq. (13) by the method of least squares. The values of these parameters along with standard deviation $\sigma(Y^E)$ of Y^E as defined by the equation

$$\sigma(Y^E) = [\sum (Y_{\text{obs}}^E - Y_{\text{calc}}^E)^2 / (N - M)]^{0.5} \quad (14)$$

are recorded in Table 5. In eq. (14), N is the total number of experimental points and M is the number of parameters.

It is observed from Table 4. that u and Z increases while β , L_f , R_A and R_m decreases as mole fraction (x_1) of DMA increases in the mixture. The decrease in β and L_f with x_1 in the present investigation indicates significant interaction between DMA and EE molecules. The addition of DMA to alkoxy alkanol tends to cause breaking of self associated alkanol molecules with a consequent increase in u and L_f . However, because of simultaneous formation of strong hydrogen bonds between the unlike molecules, there is a compensating effect resulting in an overall decrease in β and L_f or increase in u with x_1 . The rise in temperature makes the intermolecular free length to increase, as expected due to the thermal expansion of the liquid medium. In the present investigation, relative association R_A is found to decrease with mole fraction of DMA at all the three temperatures. The result signifies that unlike interactions are relatively weak compared to like interactions

in the studied mixture. A slight increase in Z with x_1 also supports weak interaction between DMA and EE molecules.

The system N,N-dimethylacetamide + 2-ethoxyethanol shows negative V^E and L_f^E values over the entire range of mole fraction and over the range of temperatures studied as given in Figures 3-4. The system shows broad minima of V^E and L_f^E at a mole fraction of about 0.5 and 0.4 of DMA respectively. The observed V^E and L_f^E values may be explained from several effects which can be divided into physical, chemical and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution to V^E and L_f^E . The chemical or specific interactions result due to forming and/or breaking of hydrogen bonds and other complex-forming interactions. It is well known that alkoxy ethanols exist as associated structures like the alcohols^{7,23} in the liquid state; the association may be due to the intramolecular hydrogen bond formation between the ether oxygen atom and the - OH group. The interaction between a moderately structured DMA and 2-ethoxyethanol may disrupt the hydrogen bonds in 2-ethoxyethanol molecules, accompanied by weak hydrogen bond formation between the unlike molecules and thus offer a negative contribution to V^E ²⁴ and L_f^E .

The N,N-dimethylacetamide + 2-ethoxyethanol system displays a sharp positive deviation of $\Delta\eta$ over the entire mole fraction range and over the three temperatures investigated (Fig.5). The positive deviation from a rectilinear dependence on mole fraction of DMA indicates the predominance of hydrogen

bonding interactions between the unlike molecules (DMA and EE) over the dissociation effects in the system. With the rise in temperature, the $\Delta\eta$ values become less and less positive indicating a tendency of the decrease of these interactions thereby the system approaches ideal behaviour. The results of deviations in isentropic compressibility versus mole fraction of DMA has been represented in Figure 6. The figure shows that the values of $\Delta\beta$ are negative over the entire composition range and at all the three studied temperatures, suggesting a predominant hydrogen bond interaction between DMA and 2-ethoxyethanol and thereby causing an increase in the ultrasonic velocity and a decrease in the compressibility of this solution. The process continues until the minima is reached and then these parameters follow the reverse trend.

Thus from the present investigation it may be concluded that due to the presence of highly polar ether group in 2-ethoxyethanol molecule, the hydrogen bonding interaction playing a predominate role over dispersion and other forces that are likely to be operative in non-aqueous solvent mixtures. This interaction accompanied by a minor disruption of 2-ethoxyethanol structure is responsible for the negative contribution of excess values in the experimental data.

References

1. B. Garcia, R. Alcalde, J. M. Leal and J. S. Matos, *J. Phys. Chem. B*, **101**, 7991, 1997.
2. A.J.Parker, *Quart Rev.*, **16**, 162, 1962.
3. H. Ohtaki, A. Funaki and B.M.Rode, *Bull. Chem. Soc. Jpn.*, **56**, 2116, 1983.
4. "Lange's Hand Book of Chemistry", ed. J.A.Dean, 12th ed., McGraw-Hill, New York, 1956.
5. H.Ohtaki, S. Itoh, T. Yamaguchi and S. Ishiguro, *Bull. Chem. Soc. Jpn.*, **56**, 3406, 1983.
6. "Physical Chemistry of Organic Solvent Systems", eds. A.K.Covington and T. Dickinson, Plenum Press, New York, p. 5, 1973.
7. O. Redlich and A.T.Kister, *Ind. Eng. Chem.*, **40**, 345, 1948.
8. U. Sen, *Ind. J.Chem. A*,**18**, 104, 1978.
9. A. Ali and A.K.Nain, *Ind J. Chem. A*, **35**, 751, 1996.
10. P.J.Victor and D.K.Hazra, *J.Chem.Eng.Data*, **47**, 79, 2002.
11. P.K.Muhuri, B.Das and D.K.Hazra, *J. Chem. Eng. Data*, **41**, 1473, 1996.
12. A. Ali and H. Soghra, *Ind. J. Phys.*, **B76**, 23, 2002.
13. M. Piekarski and M.Tkaczyk, *J. Chem. Soc. Faraday Trans.*, **91**, 2299, 1995.

14. S. Prabhumirashi, *J. Chem. Soc., Faraday trans.*, **74**, 1567, 1978.
15. L.S. Prabhumirashi and C. I. Jose, *J.Chem. Soc. Faraday Trans.*, **71**, 1545, 1975.
16. A. V. Deo, S. B. Kulkarni, M.K. Gharpurey and A. S. Biswas, *Ind. J. Chem.*, **2**,43,1964.
17. V.P.Lodygina, A.I. Ivanov, S. M. Baturinand .G. Entelis., *Zh. Fiz . Khim.*, **44**, 1887, 1970
18. L.P.Kuhn, *J. Am. Chem. Soc.*,**74**, 2482,1952.
19. H.Takeuchi and M.Tasumi, *Chem. Phys.*, **77**, 21, 1983.
20. P.Buckley and M. Brochu, *Can. J. Chem.*,**50**, 1149,1972.
21. F. Franks and D.J.G.Ives, *Quart. Rev. Chem. Soc.*,**20**, 1, 1966.
22. B.Jacobson,*J. Chem. Phys.*, **20**,297,1952.
23. J. C. Cobos and C. Casanova, *J. Chem. Thermodyn.*, **25**, 51,1993.
24. M. I. Aralaguppi, C.V.Jadar and T. M. Aminabhavi, *J. Chem. Eng. Data*, **42**, 301,1997.

Table 1 Experimental density (ρ), absolute viscosity (η), excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) for the binary mixtures of N, N-dimethylacetamide with formamide at 298.15, 308.15 and 318.15K.

X_1	ρ gm cm ⁻³	η mPas	V^E cm ³ mol ⁻¹	$\Delta\eta$ mPas
N,N-dimethylacetamide (1) + formamide (2)				
$T = 298.15K$				
0.0000	1.1254	2.953	0.000	0.000
0.0350	1.1120	3.217	-0.044	0.335
0.0700	1.0997	3.457	-0.091	0.646
0.1110	1.0866	3.656	-0.149	0.928
0.1500	1.0752	3.822	-0.204	1.172
0.2053	1.0606	3.966	-0.272	1.428
0.2414	1.0518	3.971	-0.323	1.506
0.3009	1.0387	3.932	-0.402	1.587
0.3563	1.0275	3.789	-0.463	1.556
0.4177	1.0162	3.537	-0.517	1.428
0.4580	1.0092	3.338	-0.544	1.310
0.5011	1.0021	3.094	-0.564	1.153
0.5474	0.9948	2.826	-0.575	0.979
0.5972	0.9873	2.530	-0.569	0.783
0.6500	0.9797	2.251	-0.548	0.611
0.7092	0.9717	1.916	-0.505	0.395
0.7500	0.9663	1.720	-0.462	0.282
0.7948	0.9607	1.540	-0.404	0.192
0.8910	0.9492	1.210	-0.242	0.057
1.0000	0.9371	0.933	0.000	0.000

Contd.....

X_1	ρ gm cm^{-3}	η mPas	V^E $\text{cm}^3 \text{mol}^{-1}$	$\Delta\eta$ mPas
N,N-dimethyl acetamide (1) + formamide (2)				
$T = 308.15 \text{ K}$				
0.0000	1.1118	2.384	0.000	0.000
0.0350	1.1045	2.532	-0.051	0.203
0.0700	1.0923	2.677	-0.104	0.403
0.1110	1.0791	2.847	-0.164	0.637
0.1500	1.0677	2.950	-0.224	0.800
0.2053	1.0522	3.037	-0.304	0.974
0.2414	1.0442	3.057	-0.354	1.050
0.3009	1.0307	3.027	-0.424	1.113
0.3563	1.0195	2.920	-0.484	1.093
0.4177	1.0080	2.741	-0.544	1.010
0.4580	1.0011	2.594	-0.575	0.926
0.5011	0.9940	2.430	-0.600	0.830
0.5474	0.9867	2.235	-0.615	0.707
0.5972	0.9791	2.028	-0.609	0.578
0.6500	0.9715	1.812	-0.584	0.445
0.7092	0.9632	1.579	-0.532	0.305
0.7500	0.9578	1.441	-0.482	0.231
0.7948	0.9522	1.289	-0.429	0.148
0.8910	0.9406	1.035	-0.268	0.046
1.0000	0.9283	0.819	0.000	0.000
$T = 318.15 \text{ K}$				
0.0000	1.1072	1.951	0.000	0.000
0.0350	1.0944	2.077	-0.070	0.169
0.0700	1.0826	2.180	-0.140	0.315
0.1110	1.0700	2.286	-0.221	0.471
0.1500	1.0590	2.357	-0.299	0.590
0.2053	1.0446	2.416	-0.397	0.716
0.2414	1.0361	2.420	-0.459	0.764
0.3009	1.0228	2.389	-0.541	0.806
0.3563	1.0117	2.310	-0.609	0.795
0.4177	1.0001	2.160	-0.660	0.720
0.4580	0.9930	2.076	-0.686	0.686
0.5011	0.9859	1.953	-0.707	0.616
0.5474	0.9785	1.810	-0.715	0.529
0.5972	0.9709	1.650	-0.706	0.430
0.6500	0.9632	1.505	-0.678	0.350
0.7092	0.9550	1.316	-0.623	0.233
0.7500	0.9795	1.205	-0.564	0.172
0.7948	0.9437	1.096	-0.492	0.118
0.8910	0.9318	0.901	-0.291	0.041
1.0000	0.9193	0.726	0.000	0.000

Table 2 Experimental density (ρ), absolute viscosity (η), excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) for the binary mixtures of N, N-dimethylacetamide with N,N-dimethylformamide at 298.15, 308.15 and 318.15K.

X_1	ρ gm cm ⁻³	η mPas	V^E cm ³ mol ⁻¹	$\Delta\eta$ mPas
N,N-dimethylacetamide (1) + N,N-dimethylformamide (2)				
$T = 298.15K$				
0.0000	0.9436	0.802	0.000	0.000
0.0500	0.9433	0.809	-0.009	-0.012
0.1062	0.9429	0.816	-0.016	-0.025
0.1500	0.9426	0.822	-0.021	-0.034
0.2171	0.9421	0.831	-0.025	-0.046
0.2600	0.9418	0.837	-0.027	-0.051
0.3094	0.9414	0.843	-0.029	-0.057
0.3500	0.9411	0.849	-0.031	-0.060
0.4050	0.9407	0.856	-0.032	-0.063
0.4550	0.9404	0.863	-0.033	-0.064
0.5042	0.9400	0.870	-0.034	-0.065
0.5500	0.9397	0.876	-0.034	-0.063
0.6071	0.9393	0.883	-0.033	-0.060
0.6550	0.9389	0.890	-0.032	-0.056
0.7140	0.9385	0.898	-0.030	-0.051
0.7500	0.9383	0.903	-0.028	-0.047
0.7968	0.9379	0.909	-0.025	-0.041
0.8500	0.9375	0.916	-0.020	-0.032
0.9112	0.9370	0.925	-0.013	-0.020
0.9500	0.9368	0.930	-0.007	-0.012
1.0000	0.9364	0.937	0.000	0.000

Contd.....

X_1	ρ gm cm ⁻³	η mPas	V^E cm ³ mol ⁻¹	$\Delta\eta$ mPas
N,N-dimethyl acetamide (1) + N,N-dimethylformamide (2)				
$T = 308.15K$				
0.0000	0.9348	0.713	0.000	0.000
0.0500	0.9345	0.718	-0.008	-0.017
0.1062	0.9341	0.724	-0.014	-0.034
0.1500	0.9338	0.729	-0.018	-0.045
0.2171	0.9332	0.737	-0.023	-0.059
0.2600	0.9330	0.742	-0.025	-0.065
0.3094	0.9326	0.747	-0.027	-0.072
0.3500	0.9323	0.752	-0.029	-0.077
0.4050	0.9319	0.758	-0.030	-0.081
0.4550	0.9316	0.763	-0.031	-0.083
0.5042	0.9313	0.769	-0.032	-0.084
0.5500	0.9309	0.774	-0.032	-0.081
0.6071	0.9305	0.781	-0.031	-0.079
0.6550	0.9302	0.786	-0.030	-0.074
0.7140	0.9298	0.793	-0.028	-0.069
0.7500	0.9295	0.797	-0.026	-0.064
0.7968	0.9292	0.803	-0.023	-0.056
0.8500	0.9288	0.809	-0.018	-0.043
0.9112	0.9284	0.816	-0.012	-0.028
0.9500	0.9281	0.820	-0.006	-0.017
1.0000	0.9277	0.826	0.000	0.000
$T = 318.15K$				
0.0000	0.9256	0.638	0.000	0.000
0.0500	0.9253	0.642	-0.006	-0.022
0.1062	0.9249	0.647	-0.012	-0.043
0.1500	0.9246	0.652	-0.016	-0.056
0.2171	0.9242	0.658	-0.021	-0.072
0.2600	0.9239	0.662	-0.023	-0.080
0.3094	0.9235	0.666	-0.026	-0.088
0.3500	0.9233	0.670	-0.027	-0.094
0.4050	0.9229	0.675	-0.028	-0.099
0.4550	0.9226	0.679	-0.029	-0.101
0.5042	0.9223	0.684	-0.030	-0.102
0.5500	0.9219	0.688	-0.030	-0.100
0.6071	0.9216	0.694	-0.029	-0.097
0.6550	0.9213	0.698	-0.028	-0.093
0.7140	0.9209	0.704	-0.026	-0.086
0.7500	0.9206	0.707	-0.024	-0.080
0.7968	0.9203	0.712	-0.021	-0.071
0.8500	0.9199	0.717	-0.017	-0.055
0.9112	0.9196	0.723	-0.011	-0.036
0.9500	0.9193	0.727	-0.006	-0.022
1.0000	0.9189	0.732	0.000	0.000

Table 3 Coefficients of equation 3 and the standard deviations

Function	T / K	A₀	A₁	A₂	A₃	A₄	σ (F)
N,N-dimethylacetamide + formamide							
$\mathbf{V}^E/\text{cm}^3 \text{ mol}^{-1}$	298.15K	-0.0025	-1.1334	-1.9690	4.8761	-1.7709	0.0005
	308.15K	-0.0041	-1.2927	-1.6146	4.4368	-1.5255	0.0011
	318.15K	0.0001	-2.0253	-0.1598	3.3254	-1.1380	0.0006
$\Delta\eta/\text{m Pas}$	298.15K	-0.0470	12.0894	-27.7521	18.0097	-2.2704	0.0066
	308.15K	-0.0488	8.2506	-18.0947	10.6810	-0.7675	0.0056
	318.15K	-0.0210	5.9409	-13.1388	8.0087	-0.7775	0.0029
N,N-dimethylacetamide + N,N-dimethylformamide							
$\mathbf{V}^E/\text{cm}^3 \text{ mol}^{-1}$	298.15K	-0.0010	-0.1771	0.3763	-0.4151	0.2179	0.0001
	308.15K	-0.0005	-0.1582	0.3019	-0.3017	0.1592	0.0001
	318.15K	-0.0001	-0.1383	0.2260	-0.1884	0.1010	0.0001
$\Delta\eta/\text{m Pas}$	298.15K	0.0000	-0.0028	0.0034	-0.0007	0.0002	0.0001
	308.15K	0.0000	-0.0037	0.0051	-0.0027	0.0013	0.0001
	318.15K	0.0000	-0.0047	0.0072	-0.0052	0.0026	0.0001

Table 4 : Values of experimental density (ρ) ; absolute viscosity(η), ultrasonic velocity (u), isentropic compressibility (β), intermolecular free length (L_f), relative association (R_A), acoustic impedance (Z) and molar sound speed (R_m) of binary mixtures of DMA and EE at 298.15, 308.15 and 318.15K.

x_1 (DMA)	ρ (kg m ⁻³)	η (10 ⁻³ kg m ⁻¹ s ⁻¹)	u (ms ⁻¹)	β (10 ⁻¹⁰ m ² N ⁻¹)	L_f (10 ⁻¹¹ m)	R_A	Z (10 ⁶ kg m ⁻² s ⁻¹)	R_m [10 ⁴ m ³ mol ⁻¹ (ms ⁻¹) ^{1/3}]
T = 298.15K								
0.000	925.0	1.8243	1306.9	6.3290	5.1746	1.0000	1.2089	10.6518
0.0500	926.0	1.8031	1316.6	6.2300	5.1337	0.9986	1.2192	10.6489
0.1042	926.9	1.7780	1327.3	6.1235	5.0899	0.9969	1.2303	10.6480
0.1500	927.6	1.7517	1335.7	6.0420	5.0560	0.9955	1.2390	10.6461
0.2075	928.6	1.7147	1345.5	5.9485	5.0164	0.9942	1.2494	10.6400
0.2500	929.2	1.6834	1352.7	5.8808	4.9881	0.9931	1.2569	10.6369
0.3097	930.0	1.6350	1362.6	5.7910	4.9497	0.9915	1.2672	10.6323
0.3650	930.8	1.5868	1371.5	5.7113	4.9155	0.9902	1.2766	10.6264
0.4111	931.4	1.5449	1378.8	5.6480	4.8879	0.9891	1.2842	10.6219
0.4600	931.9	1.4986	1386.4	5.5824	4.8598	0.9878	1.2919	10.6181
0.5115	932.6	1.4473	1394.4	5.5151	4.8301	0.9866	1.3004	10.6119
0.5650	933.1	1.3916	1402.6	5.4474	4.8006	0.9853	1.3087	10.6078
0.6110	933.6	1.3433	1409.5	5.3910	4.7758	0.9842	1.3159	10.6029
0.6550	934.0	1.2968	1416.1	5.3385	4.7525	0.9831	1.3226	10.5990
0.7096	934.5	1.2391	1424.0	5.2770	4.7249	0.9818	1.3307	10.5933
0.7550	934.9	1.1912	1430.4	5.2282	4.7027	0.9807	1.3373	10.5881
0.8073	935.2	1.1359	1437.3	5.1756	4.6794	0.9795	1.3441	10.5828
0.8500	935.5	1.0907	1443.1	5.1326	4.6599	0.9785	1.3500	10.5782
0.9041	935.9	1.0339	1450.3	5.0795	4.6357	0.9773	1.3573	10.5716
1.000	936.4	0.9329	1463.5	4.9860	4.5927	0.9748	1.3704	10.5630

Contd....

x_I (DMA)	ρ (kg m ⁻³)	η (10 ⁻³ kg m ⁻¹ s ⁻¹)	u (ms ⁻¹)	β (10 ⁻¹⁰ m ² N ⁻¹)	L_f (10 ⁻¹¹ m)	R_A	Z (10 ⁶ kg m ⁻² s ⁻¹)	R_m (10 ⁻⁴ m ³ mol ⁻¹ (ms ⁻¹) ^{1/3})
$T = 308.15K$								
0.0000	916.4	1.4800	1274.4	6.7180	5.4304	1.0000	1.1678	10.6619
0.0500	917.4	1.4668	1284.5	6.6067	5.3830	0.9985	1.1784	10.6606
0.1042	918.4	1.4522	1295.3	6.4895	5.3352	0.9967	1.1896	10.6594
0.1500	919.1	1.4369	1303.8	6.4006	5.2984	0.9953	1.1983	10.6583
0.2075	920.1	1.4129	1313.5	6.2994	5.2565	0.9939	1.2085	10.6525
0.2500	920.7	1.3916	1320.5	6.2291	5.2269	0.9929	1.2158	10.6493
0.3097	921.5	1.3573	1329.9	6.1357	5.1877	0.9914	1.2255	10.6438
0.3650	922.3	1.3224	1338.3	6.0536	5.1529	0.9901	1.2343	10.6371
0.4111	922.9	1.2913	1345.2	5.9880	5.1248	0.9891	1.2415	10.6319
0.4600	923.5	1.2566	1352.4	5.9206	5.0958	0.9880	1.2489	10.6263
0.5115	924.1	1.2174	1359.8	5.8520	5.0665	0.9868	1.2566	10.6203
0.5650	924.7	1.1747	1367.4	5.7834	5.0367	0.9856	1.2644	10.6138
0.6110	925.2	1.1375	1373.9	5.7260	5.0115	0.9846	1.2711	10.6083
0.6550	925.6	1.1017	1380.1	5.6721	4.9879	0.9835	1.2774	10.6038
0.7096	926.1	1.0570	1387.6	5.6081	4.9596	0.9823	1.2850	10.5975
0.7550	926.5	1.0197	1393.7	5.5567	4.9368	0.9813	1.2913	10.5919
0.8073	926.9	0.9773	1400.6	5.4998	4.9115	0.9801	1.2982	10.5859
0.8500	927.2	0.9422	1406.3	5.4539	4.8908	0.9791	1.3039	10.5813
0.9041	927.5	0.8981	1413.5	5.3961	4.8650	0.9778	1.3110	10.5763
1.0000	927.9	0.8204	1426.3	5.2970	4.8204	0.9752	1.3234	10.5686

Contd.....

x_1 (DMA)	ρ (kg m ⁻³)	η (10 ⁻³ kg m ⁻¹ s ⁻¹)	u (ms ⁻¹)	β (10 ⁻¹⁰ m ² N ⁻¹)	L_f (10 ⁻¹¹ m)	R_A	Z (10 ⁶ kg m ⁻² s ⁻¹)	R_m [10 ⁻⁴ m ³ mol ⁻¹ (ms ⁻¹) ^{1/3}]
T = 318.15K								
0.000	907.9	1.2220	1242.2	7.1380	5.6956	1.000	1.1278	10.6714
0.0500	908.8	1.2135	1252.5	7.0134	5.6459	0.9982	1.1383	10.6708
0.1042	909.8	1.2060	1263.5	6.8850	5.5937	0.9964	1.1495	10.6706
0.1500	910.6	1.1986	1271.9	6.7878	5.5543	0.9951	1.1582	10.6693
0.2075	911.5	1.1840	1281.2	6.6780	5.5113	0.9937	1.1678	10.6641
0.2500	912.1	1.1697	1288.4	6.6043	5.4787	0.9925	1.1751	10.6618
0.3097	912.9	1.1456	1297.5	6.5067	5.4379	0.9910	1.1845	10.6561
0.3650	913.7	1.1204	1305.6	6.4210	5.4018	0.9898	1.1929	10.6490
0.4111	914.2	1.0974	1312.2	6.3524	5.3731	0.9887	1.1996	10.6456
0.4600	914.8	1.0708	1319.0	6.2823	5.3437	0.9876	1.2066	10.6383
0.5115	915.4	1.0402	1326.1	6.2120	5.3133	0.9865	1.2139	10.6319
0.5650	916.0	1.0070	1333.2	6.1413	5.2833	0.9854	1.2212	10.6246
0.6110	916.5	0.9779	1339.3	6.0823	5.2578	0.9844	1.2274	10.6183
0.6550	916.9	0.9499	1345.2	6.0263	5.2336	0.9834	1.2334	10.6134
0.7096	917.4	0.9146	1352.5	5.9589	5.2039	0.9822	1.2408	10.6070
0.7550	917.8	0.8850	1358.5	5.9041	5.1798	0.9812	1.2468	10.6016
0.8073	918.2	0.8519	1365.4	5.8420	5.1525	0.9799	1.2537	10.5959
0.8500	918.4	0.8242	1371.0	5.7927	5.1309	0.9788	1.2591	10.5926
0.9041	918.7	0.7893	1378.4	5.7292	5.1025	0.9774	1.2663	10.5885
1.0000	919.1	0.7285	1390.9	5.6230	5.0556	0.9749	1.2783	10.5808

Table 5 : Coefficients A_i of eq. (13) and standard deviations $\sigma(Y^E)$ for binary mixtures N,N-dimethylacetamide +2-ethoxy ethanol at 298.15, 308.15 and 318.15K.

Function	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
T = 298.15K						
$V^E (10^{-6} \text{m}^3 \text{mol}^{-1})$	-0.0014	-0.8416	1.0933	-0.4183	0.1686	0.0005
$\Delta\eta (10^{-3} \text{N m}^{-2} \text{S}^{-1})$	-0.0013	0.5766	-1.1516	0.7099	-0.1330	0.0001
$\Delta\beta (10^{-10} \text{m}^2 \text{N}^{-1})$	-0.0045	-0.8271	2.8121	-4.0417	2.0783	0.0126
$L_f^E (10^{-11} \text{m})$	-0.0004	-0.2618	0.4654	-0.3143	0.1121	0.0001
T = 308.15K						
$V^E (10^{-6} \text{m}^3 \text{mol}^{-1})$	-0.0010	-0.9418	1.4826	-1.0197	0.4817	0.0004
$\Delta\eta (10^{-3} \text{N m}^{-2} \text{S}^{-1})$	-0.0021	0.5257	-0.9811	0.5069	-0.0484	0.0002
$\Delta\beta (10^{-10} \text{m}^2 \text{N}^{-1})$	-0.0003	-0.9347	1.9575	-1.5724	0.5515	0.0003
$L_f^E (10^{-11} \text{m})$	-0.0007	-0.3639	0.8033	-0.6913	0.2534	0.0001
T = 318.15K						
$V^E (10^{-6} \text{m}^3 \text{mol}^{-1})$	-0.0008	-1.0313	1.8262	-1.5570	0.7655	0.0004
$\Delta\eta (10^{-3} \text{N m}^{-2} \text{S}^{-1})$	-0.0029	0.4746	-0.8098	0.3019	0.0374	0.0003
$\Delta\beta (10^{-10} \text{m}^2 \text{N}^{-1})$	-0.0014	-1.2952	3.3347	-3.3269	1.2921	0.0019
$L_f^E (10^{-11} \text{m})$	0.0001	-0.4213	0.9674	-0.8389	0.2929	0.0001

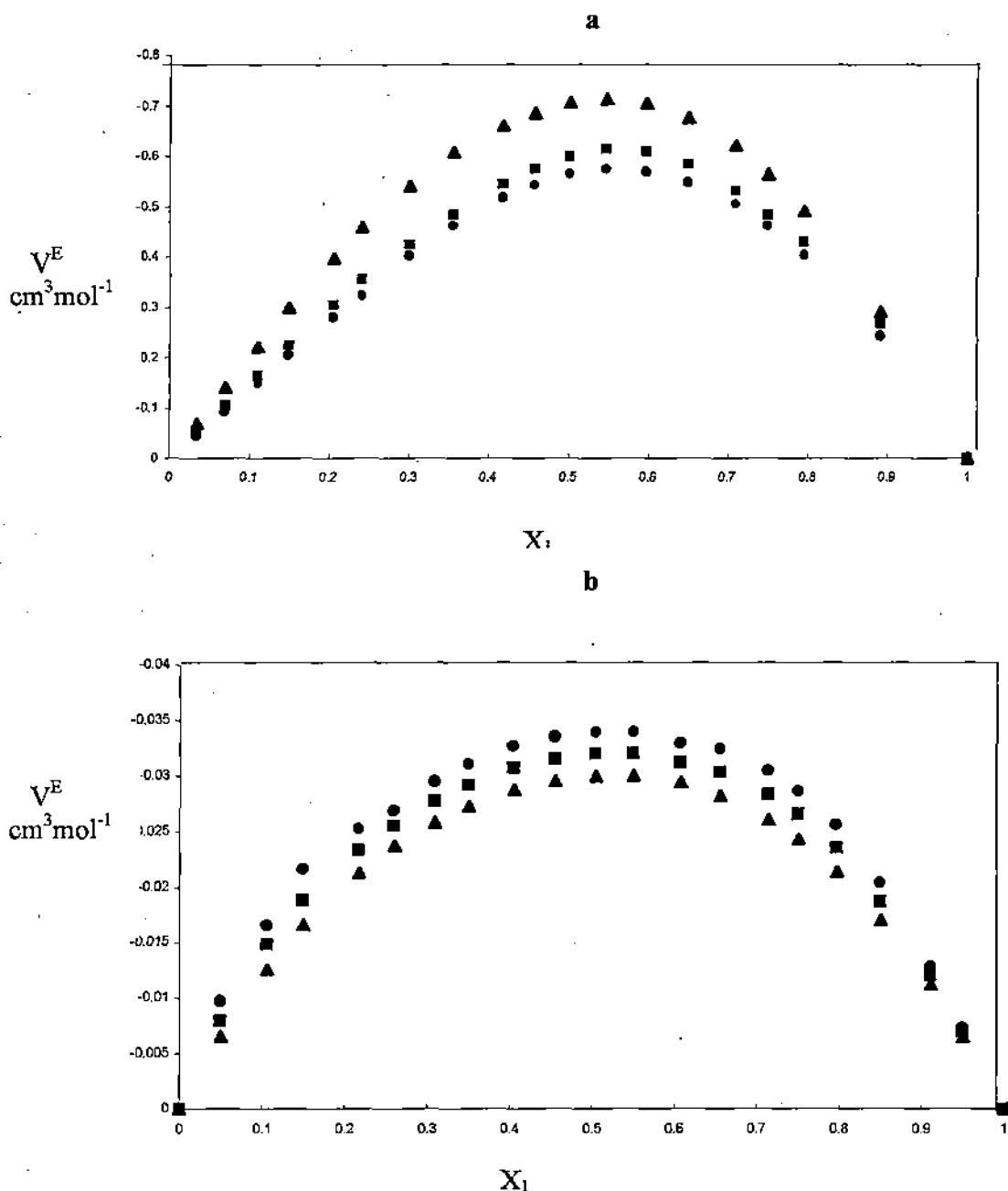
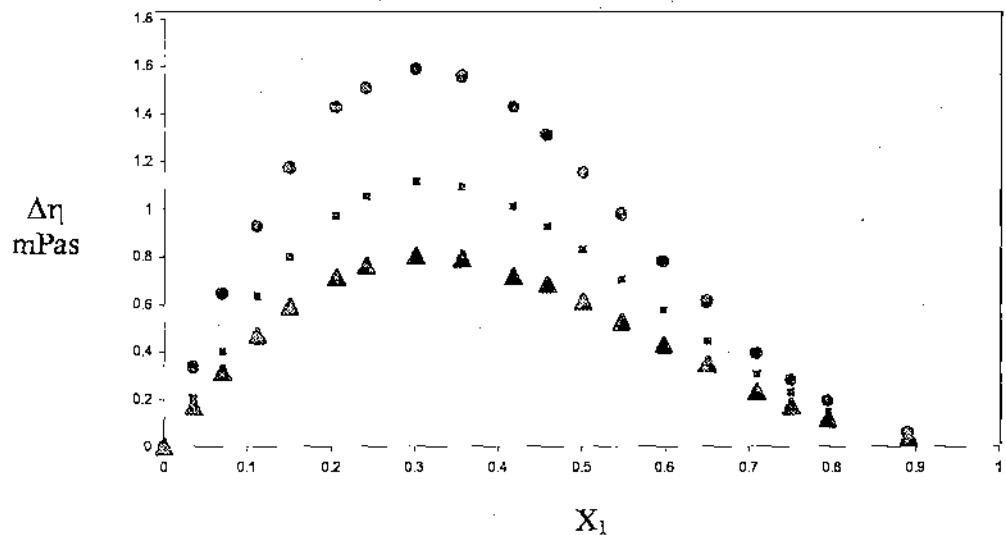


Figure 1. Variation of excess molar volume of the binary mixtures N,N-dimethylacetamide (a) with formamide and (b) with N,N-dimethylformamide at 298.15K (●), 308.15K (■) and 318.15K(▲).

a



b

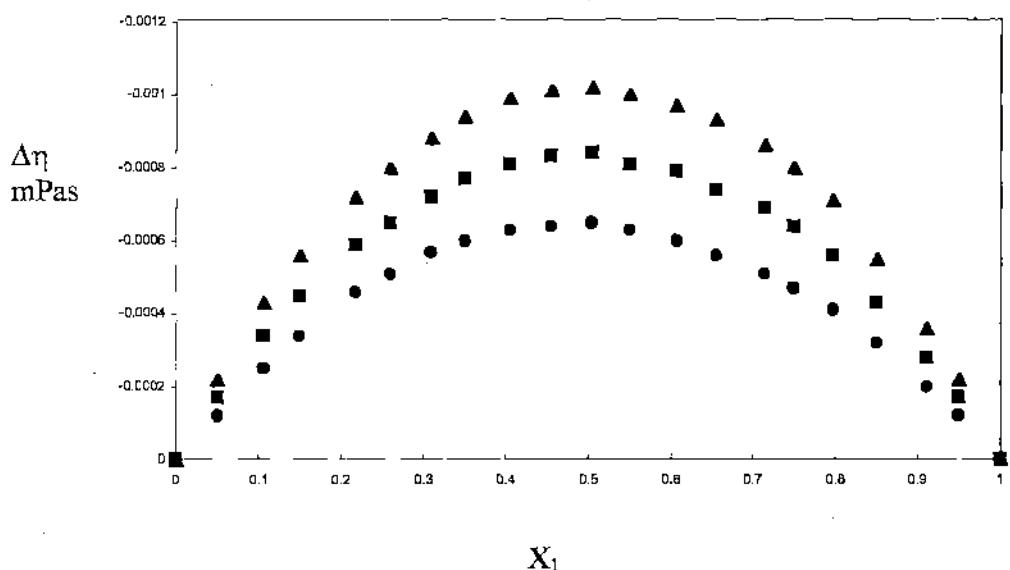


Figure 2. Variation of viscosity deviations of the binary mixtures of N,N -dimethylacetamide (a) with formamide and (b) with N,N -dimethylformamide at 298.15K(\bullet), 308.15K(\blacksquare) and 318.15K(\blacktriangle).

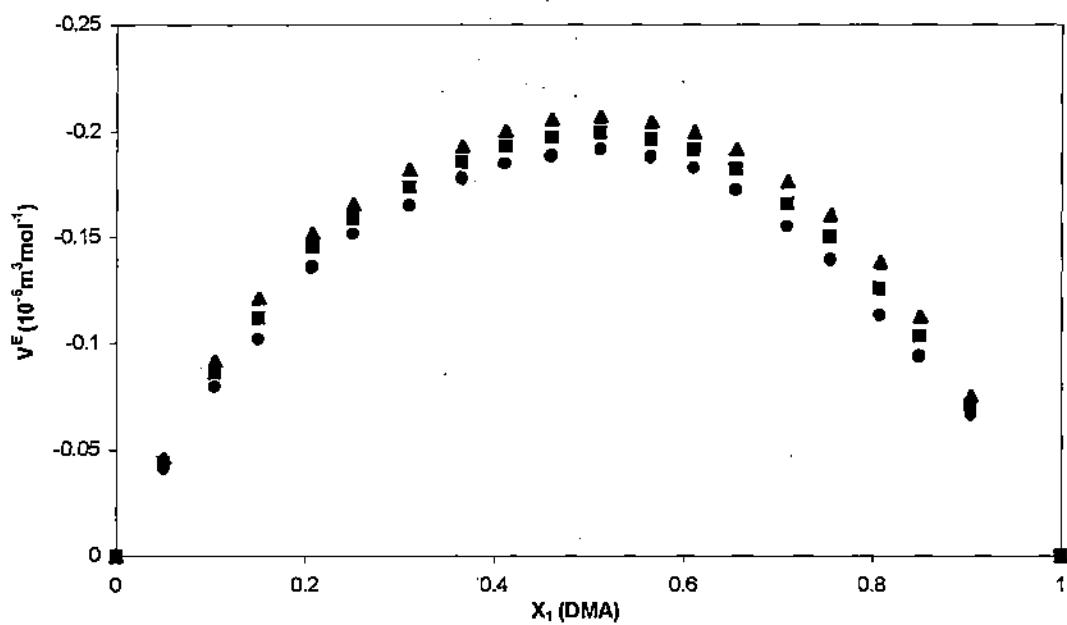


Figure 3. Variation of excess volume (V^E) versus mole fraction (x_1) of DMA
at 298.15K (•) ; 308.15K (■) ; 318.15 K(▲)

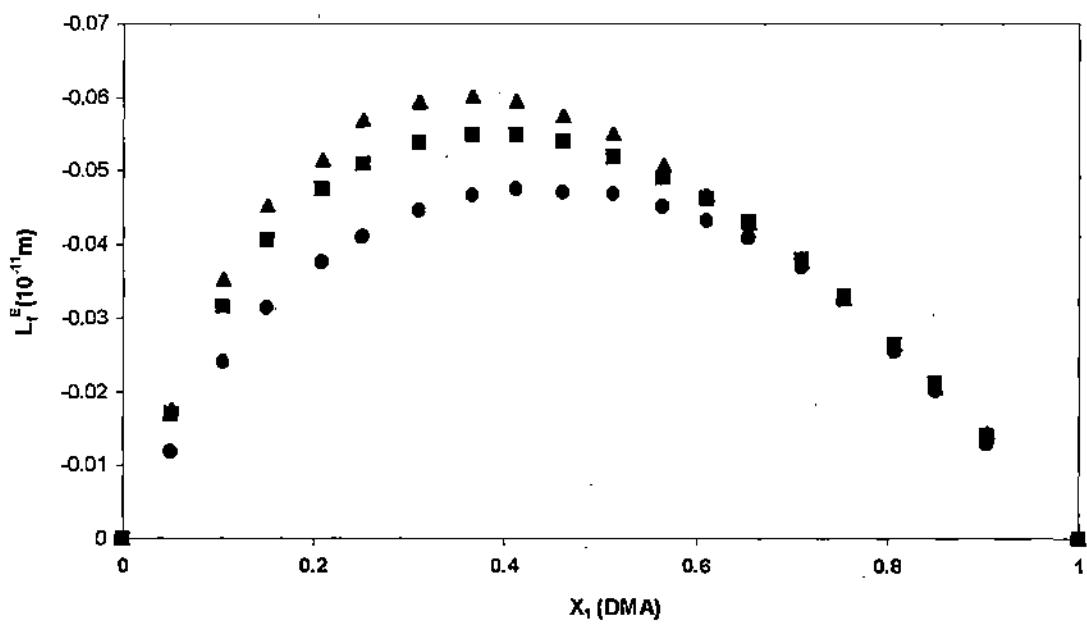


Figure 4 : Variation of intermolecular free length (L_f^E) versus mole fraction (x_1) of DMA at 298.15K (•) ; 308.15K (■) ; 318.15 K(▲)

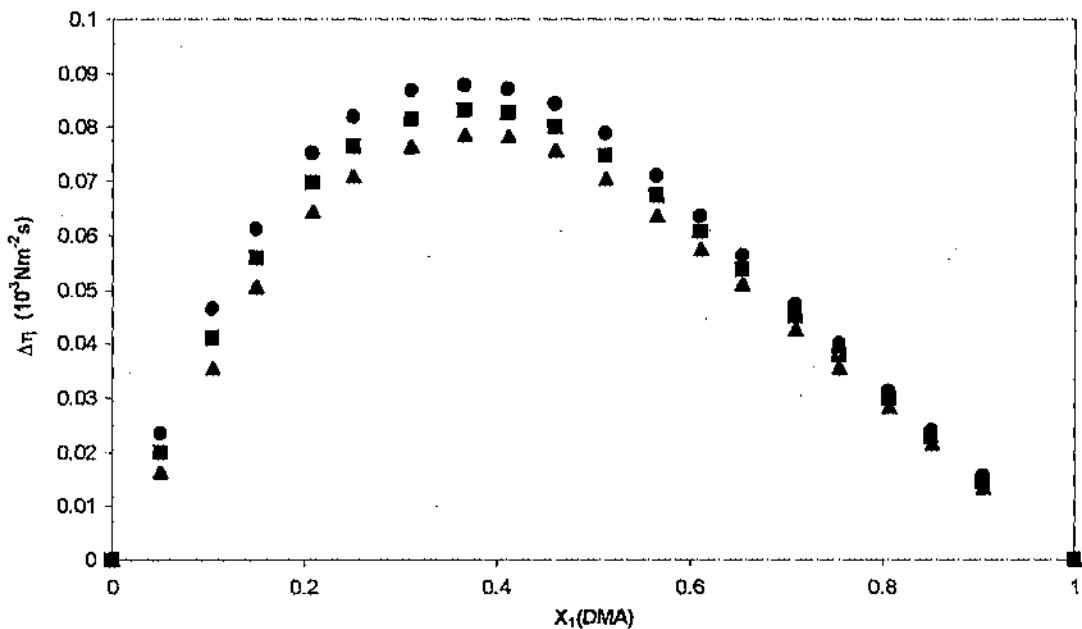


Figure 5. Variation of excess viscosity ($\Delta\eta$) versus mole fraction (x_1) of DMA at 298.15K (●); 308.15K (■); 318.15K (▲).

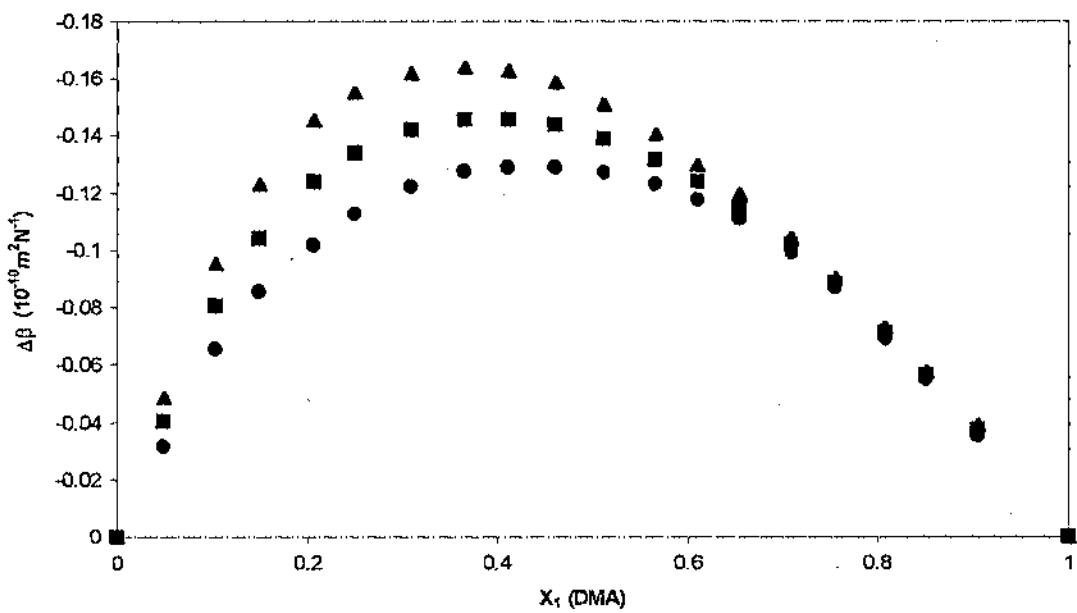


Figure 6. Variation of excess isentropic compressibility ($\Delta\beta$) versus mole fraction (x_1) of DMA at 298.15K (●); 308.15K (■); 318.15K (▲).

CHAPTER IX

CONCLUDING REMARKS

Symmetrical tetraalkylammonium and alkali metal salts show numerous interesting properties that are now being actively investigated in many laboratories. Most of the present day knowledge on non-aqueous solutions has come from studies on various thermodynamic properties e.g., apparent molal volumes, adiabatic compressibilities, heat capacities etc. as well as on transport properties e.g., conductance, viscosity and transference numbers. We therefore determined the thermodynamic and transport properties of some tetraalkylammonium and alkali metal salts in N,N-dimethylacetamide and its aqueous binary mixtures from the measurements of their viscosities, conductances, apparent molal volumes and adiabatic compressibilities. Raman spectral investigations of some alkali metal salts have also been attempted since these are potentially capable of yielding more precise information on the nature of interactions taking place in solutions. Excess properties of DMA + FA, DMA + DMF and DMA + EE systems were also studied, at three different temperatures. The measurements were analyzed with the appropriate equations and interpreted. The findings are summarized as follows.

In DMA, conductance and viscosity studies indicate that tetraalkylammonium bromide salts and the investigated alkali metal salts remain slightly associated in solutions. Lithium, sodium and potassium ions found to be significantly solvated while the tetraalkylammonium ions remain scarcely solvated in this medium. The viscosity of the solvent is greatly modified with the presence of all these ions

investigated here with the exception of the bromide ion. From the compressibility data we find that the lithium salts studied here exhibit appreciable ion-ion interaction in N,N-dimethylacetamide and the lithium ion is solvated through electrostriction of solvent molecules around the ions. The comparatively larger size anions show greater electrostatic solvation in this medium in contrast to electrostriction effect where smaller size anions predominate over others. The large tetraalkylammonium ion accomodate the solvent molecule inside the space between the alkyl chain attached to the nitrogen atom. In other words solvent molecules penetrate into these alkyl chains. For BPh_4^- ion neither electrostriction nor penetration of solvent molecules seems to be important. BF_4^- ions remains largely unsolvated.

Analaysis of excess properties of the three systems indicate that in the DMA + FA system, strong heteroassociation is present through multiple hydrogen bonding between the polar groups of unlike molecules. On the other hand, there is weak dipole-dipole interaction and a slight structure-breaking effect in the DMA + DMF mixture as observed from the experimental data. In DMA + EE mixture, due to the presence of the highly polar ether group in 2-ethoxyethanol molecule, the hydrogen bonding interaction is playing a predominate role over the dispersion and other forces that are likely to be operative in non-aqueous solvent mixtures.

The viscosity B-coefficients give us quantitative values of ion-solvent interactions. But, we do not yet have an unambiguous method to divide the B-coefficients into their ionic values in all solvents. We have successfully used Bu_4NBPh_4 as the "reference electrolyte" for the division of the viscosity B-

coefficients in all our calculations. However, we lack sufficient data from different solvents to arrive at a definite conclusion about its validity and applicability. It is desirable to use various methods for this purpose and determine reasonably consistent ionic B-values.

Similarly, different methods may be used to find out the limiting ionic conductances from the limiting equivalent conductances of the electrolytes. Again, we have calculated the limiting apparent molar isentropic compressibilities of some electrolytes on the assumption that the limiting apparent molar isentropic compressibility of $\text{BF}_4^- = 0$. Although our assumption seems to be reasonable, proper evaluation of such properties would be of great help in determining ion-solvent interactions.

Solvation phenomena are very complex in nature. There are strong electrical forces between the ions and solvents and it is not really possible to separate them all. Nevertheless, by using careful judgement, valid conclusions can be drawn in many cases from conductivity, viscosity, apparent molar volume and apparent molar isentropic compressibility measurements, relating to the structure and order of a system.

More extensive studies of the various thermodynamic and transport properties of the electrolytes will be of immense help in understanding the nature of ion-solvent interactions and the role of solvents in different chemical processes.

Thermodynamic studies do not directly address questions related to molecular scale features. They may only furnish some striking features of concentration or composition dependence that might reasonably be associated with important changes in the patterns of molecular interaction or aggregation. Perhaps we need to gather a lot of experimental data of a particular solvent and construct an appropriate model, incorporating the solvent's different modes of behaviour with a variety of electrolytes and non-electrolytes. The recent attempts at building such universal solvation models are moving in the right direction towards achieving this.

We may also need to carry out large scale computer simulations on a wide variety of solvents using such models and test their validity with the available experimental data. Such molecular modeling techniques may go a long way in updating our theoretical knowledge. They will also offer the chemists an inexpensive tool to conduct a host of experiments that may normally involve very expensive equipment.

LIST OF PUBLICATIONS

1. Conductance of Some 1:1 Electrolytes in N,N-Dimethylacetamide at 25°C, Debashis Das, Bijan Das and Dilip K. Hazra, *J. Solution Chem.*, **31**, 425, 2002.
2. A Study on volumetric and Compressibility Properties of Some Lithium Salts in N,N-dimethylacetamide at 25°C, Debashis Das, Subrata K Ray and Dilip K Hazra, *Indian J. Chem.*, **41A**, 1812, 2002.
3. Electrical Conductance of Some Tetraalkylammonium and Alkali Salts in N,N-Dimethylacetamide at 25°C, Debashis Das, Bijan Das and Dilip K. Hazra, *J. Solution Chem.*, **32**, 77, 2003.
4. Viscosities of Some Tetraalkylammonium and Alkali Salts in N,N-Dimethylacetamide at 25°C, Debashis Das, Bijan Das and Dilip K. Hazra, *J. Solution Chem.*, **32**, 85, 2003.
5. Excess molar volumes and viscosity deviations in binary mixtures of N,N-dimethylacetamide with formamide and N,N-dimethylformamide at 298.15K, 308.15 and 318.15K, Debashis Das, Subrata K. Ray and Dilip K. Hazra, *J. Indian Chem. Soc.*, **80**, 385, 2003.
6. Molecular interaction study in binary mixtures of N,N-dimethylacetamide with 2-ethoxyethanol at three different temperatures, Debashis Das and Dilip K. Hazra, *Indian J. Phys.*, **77B**, 519, 2003.

