

**Studies on the Ion-Solvent Interactions of Some Electrolytes
in Propylene Carbonate and Its Binary Mixtures with Other
Organic Solvent Systems**

THESIS SUBMITTED FOR THE DEGREE OF
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**Dedicated
To
My Mother**

A C K N O W L E D G E M E N T

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PREFACE

SCOPE AND OBJECT OF THE WORK

The solution properties have always been of interest to physical chemists but in recent years there has been an unprecedented interest in solution chemistry by physical organic chemists, inorganic chemists, electrochemists and most notably by biochemists. The interest stems from the fact that the majority of reactions that are of chemical, electrochemical and biological importance occur in solution. It was previously believed that the solvent merely provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realised only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents. While proton transfer reactions are particularly sensitive to the nature of the solvent, it has become increasingly clear that the majority of the solutes are significantly modified by all solvents. Conversely, the nature of strongly structured solvents, such as water, is substantially modified by the presence of solutes. Complete understanding of the phenomena of solution chemistry will become a reality only when solute-solute, solute-solvent and solvent-solvent interactions are elucidated¹.

In spite of vast collections of data on the different electrolytic and non-electrolytic solutions in water, the structure of water and the different types of interactions that water undergoes

with electrolytes are yet to be properly understood. However, the studies on the properties of aqueous solutions have provided sufficient information on the thermodynamic properties of different electrolytes and non-electrolytes, the effects of variation in ionic-structure, ionic mobility and common ions on the properties of aqueous solutions and a host of other properties^{2,3}. Nevertheless, during recent years there has been an increasing interest in the behaviour of electrolytes in non-aqueous and mixed solvents with a view to investigating ion-ion and ion-solvent interactions under varied conditions. However, different sequence 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 the traditional boundaries of inorganic, physical, organic, analytical and electrochemistry⁴.

We have been mainly interested in the studies of ion-solvent interactions as these are the controlling forces in dilute solutions where ion-ion interactions are absent. Influence of these ion-solvent interactions on transfer of electrolytes between solvents is small, but sufficiently large to cause dramatic changes in chemical reactions involving ions. The changes in ionic solvation have important applications in such diverse areas as organic and inorganic syntheses, studies of reaction mechanisms, non-aqueous battery technology and extraction⁵. The importance of ionic hydration in biochemistry and

biophysics have also been stressed⁶.

The applications and implications of the studies of reactions in non-aqueous and mixed solvents have been summarized by Meck⁷, Franks^{8,9}, Popovych¹⁰, Bates^{11,12}, Parker^{13,14}, Criss and Salomon¹⁵, Marcus¹⁶ and others¹⁷⁻²³. The ion-ion and ion-solvent interactions have been the subject of wide interest as apparent from the discussions of Faraday Transactions of the Chemical Society²⁴.

The proper understanding of the ion-solvent interactions would form the basis of explaining quantitatively the influence of the solvent and the extent of interactions of ions in solvents and thus pave the way for the real understanding of the different phenomena associated with solution chemistry. Estimates of ion-solvent interactions can be obtained thermodynamically and also from the measurements of viscosity B-coefficients, limiting ionic conductivity etc.

However, single ion values can not be obtained thermodynamically. Therefore, various theoretical and semi-empirical extra thermodynamic assumptions have been made to estimate these values.

It is thus apparent that the real understanding of the ion-solvent interactions is a difficult task. The aspect embraces a wide range of topics but we concentrated only on the measurements of

transport properties like viscosity and conductivity along with such thermodynamic properties as solubilities, free energies of solution and free energies of transfer.

Attempts have been made to determine the single-ion values by the use of available methods and to elucidate the various aspects of ion-solvent interactions. Vibration spectroscopy has also been applied to study the ion-solvent interactions of some alkaline earth metal salts in non-aqueous solvent medium.

Solvent-solvent interactions also play a vital role in solution chemistry. An effort has been made here to focus some light on the solvent-solvent interactions by measuring excess thermodynamic properties with the help of densimetry and viscometry at different temperatures.

These are described in the subsequent Chapters.

Summary of the work done

Propylene carbonate (PC) and its binary mixtures with methanol have been chosen as the solvent system in the present study.

The present dissertation has been divided into nine chapters.

Chapter I forms the background of the present work. After presenting a brief review of notable works in the field of ion-

solvent interactions, such properties as solubility and free energy of solution, viscosity and conductance have been discussed in details. The importance and utility of the various methods in the determination of ion-solvent interactions are stressed. Critical evaluations of the different methods of obtaining the single-ion values and their implications have been made. The solvent properties are then discussed, stressing the importance of such work.

In Chapter II the different experimental techniques for obtaining the results presented in the dissertation have been described.

Chapter III entails the studies on the solubilities of some alkali metal salts, tetraphenylarsonium chloride and tetraphenylphosphonium bromide in PC at 25°C. Most of the alkali metal halides barring a few are scarcely soluble in PC and thus the more conventional methods like conductometry and viscometry can hardly be applied to understand the ion-solvent interactions of these electrolytes in this solvent medium. Solubilities for these salts have been measured by using ion selective electrode technique and the corresponding free energies of solution have been determined. Combination of these values with those in water has resulted the free energies of transfer of the electrolytes from water to PC. Transfer activity coefficients or medium effects have also been computed from their solubility products in water and in the non-

aqueous solvent. Single ion transfer functions have been evaluated by making use of extrathermodynamic assumptions involving "reference electrolyte" method.

Chapter IV comprises two parts. Part A describes the viscosities of some tetraalkylammonium bromides in propylene carbonate at different temperatures. Viscosity data have been analysed by the Jones-Dole equation for unassociated electrolytes²⁵. Single ion values have been estimated by using the "reference electrolyte" method. In Part B, the conductance measurements have been reported for the tetraalkylammonium bromides in PC at 25°C. Conductance data have been analysed by the 1978 Fuoss conductance equation²⁶. Single ion equivalent conductances at infinite dilution have been evaluated by using the "reference electrolyte" method.

Chapter V describes the determination of viscosities and electrical conductances of some tetraphenyl salts in PC. Viscosities have been measured at 25, 35 and 45°C and the B coefficients have been calculated. Conductance data have been analysed by the Fuoss conductance equation²⁶. Single ion values have also been evaluated. Results are discussed in terms of the interactions of the ions with the solvent medium.

Excess molar volumes (v^E), excess viscosities (η^E) and excess molar free energies of activation of flow (G^{*E}) have been

determined for four sets of binary mixtures of propylene carbonate with methanol, 2-methoxy ethanol, 1,2-dimethoxyethane and tetrahydrofuran at 25, 35 and 45°C and the results has been described in Chapter VI. The excess functions have been discussed from the view point of intermolecular interactions. The proper understanding of these interactions would enable us to extract useful information from the studies of ion-solvent interactions of electrolytes in these solvent mixtures.

Chapter VII describes the studies on the electrical conductances of some tetraalkylammonium bromides, R_4NBr ($R = Me$ to Hep), $NaBPh_4$ and Bu_4NBPh_4 in PC + methanol mixtures at 25°C. The data have been analysed and the characteristic parameters, Λ_o , K_A and Walden products have been evaluated. The single ion conductances have been determined using the "reference electrolyte" method. Results have been discussed in terms of the structural changes of the solvent mixtures.

In Chapter VIII infra-red and Laser-Raman spectroscopic measurements have been reported for some alkaline earth metal perchlorates in PC. The results have been interpreted in terms of ion-solvent interactions with the PC molecules.

The dissertation ends with some concluding remarks in Chapter IX.

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CHAPTER-I

INTRODUCTION

The majority of reactions that are of chemical or biological interest occur in solution. It was previously believed that solvent merely provides an inert medium for chemical reactions. The significance of solute-solvent interactions was realised only recently as a result of extensive studies in aqueous, non-aqueous and mixed solvents¹⁻¹⁰.

Water is the most abundant solvent in nature. In view of its extreme importance in chemistry, biology, agriculture, geology etc., water has been extensively used in kinetic and equilibrium studies. In spite of such extensive studies, our knowledge of molecular interactions in water is still limited. Moreover, the uniqueness of water as a solvent has been questioned^{11,12} in recent years and it has been realised that the studies in other solvent media (non-aqueous and mixed solvents) would be of great help in understanding different molecular interactions and a host of complicated phenomena¹⁻¹⁰.

Extensive studies on the physical properties of different solvent systems have been made but a lamentable gap still exists. Several classifications of organic solvents based on their dielectric constants, organic group types, acid-base properties or association through hydrogen-bonding¹⁰, donor-acceptor properties¹³, hard and soft acid-base principles¹⁴ etc. have been made; the properties of

different solvent systems show a wide divergence of properties which would naturally be reflected on the thermodynamic and transport properties of electrolytes and non-electrolytes in these solvents. The determination of thermodynamic and transport properties of different electrolytes in various solvents would thus provide an important step in this direction. Naturally, in the development of theories dealing with electrolyte solutions, much attention has been paid to ion-solvent interactions which are the "controlling forces" in infinitely dilute solutions where ion-ion interactions are absent. Ion-solvent (broadly speaking solute-solvent) interactions manifest themselves in all thermodynamic and transport properties of electrolytes generally obtained by extrapolation to infinite dilution. By separating these functions into ionic contributions, it is possible to determine the contributions due to cations and anions in the solute-solvent interactions. Thus ion-solvent (or solute-solvent) interactions play very important role in understanding the physico-chemical properties of solutions.

One of the reasons for the intricacies in solution chemistry is that the structure of the solvent molecule is not known with certainty. The introduction of an ion or solute modifies the solvent structure to an uncertain magnitude whereas the solute molecules are also modified and the interplay of forces like solute-solute, solute-solvent and solvent-solvent interactions becomes predominant though the isolated picture of any of them is still not known completely to the solution chemists.

The problem of ion-solvent interactions which is closely akin to ionic solvation can be studied from different angles using almost all the available physico-chemical techniques.

Ion-solvent interaction can be studied spectroscopically where spectral solvent shifts or the chemical shifts determine their qualitative and quantitative nature. But even qualitative and quantitative apportioning of the ion-solvent interactions into the various possible factors is still an uphill task.

The ion-solvent interactions can also be studied from the thermodynamic point of view where the changes in free energy, enthalpy and entropy associated with a particular reaction can be qualitatively and quantitatively evaluated (using various physico-chemical techniques) from which conclusions regarding the factors associated with the ion-solvent interactions can be worked out. Sometimes, higher derivatives of these properties (e.g. partial molal volume, compressibility etc.) have been interpreted more effectively in terms of molecular interactions.

Similarly, the ion-solvent interactions can be studied using solvational approaches involving the studies of different properties e.g. viscosity, conductance etc. of electrolytes and hence to derive the various factors associated with ionic solvation.

We shall particularly dwell upon the different aspects of transport and thermodynamic properties as the present dissertation

is intimately related to the studies of solubilities and free energies of transfer, viscosities, conductances and spectroscopic properties of tetraalkylammonium and tetraphenyl and some common salts in the dipolar aprotic solvent, propylene carbonate (PC) and in its binary mixtures with methanol.

Solubilities and free energies of solution

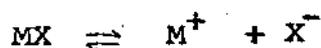
Precise and accurate solubility data have diverse applications in different branches of science and technology^{15,16}. And solubility measurement is one of the most direct and accurate technique for the determination of ion-solvent interactions of electrolytes in different solvent media. Knowledge of solubility data for the salts in different solvents reveal the suitability of the solvents as reaction media for the concerned electrolytes. Chemical equilibrium and reaction kinetics might change drastically with the change in solvent and this phenomenon is reflected among other factors on the comparative solubilities of the reactants in different media. Some very useful thermodynamic properties like free energies of solution, free energies of solvation etc. can be evaluated directly from the measured solubilities of the electrolytes in solvents. Again the free energies of solution of an electrolyte in different solvent systems helps one to understand whether the transfer process from one solvent to another is favourable or not. Further, the free energy of transfer of an electrolyte from one solvent to another provides a quantitative measurement of solute-solvent and ion-solvent interactions. This method is particularly of paramount importance and very

useful for the cases when the solubilities of the electrolytes under investigation in a solvent are low enough so that the other methods like conductometry and viscometry can not be applied to study the ion-solvent interactions. In the last few decades, many scientists all over the world have used solubility measurement as their experimental tool to understand the solution properties of the electrolytes in different solvent media¹⁷⁻²².

The relative solubilities of electrolytes in protic and dipolar aprotic solvents and their binary mixtures are influenced by the extent of solvation of the ions, solvent-solvent interactions and other specific properties such as volume energy. Solubility products and dissociation constants of salts in non-aqueous solvents can give insights into ionic solvation. It is normally found that solubilities of salts are not simple functions of dielectric constants of the solvents but depend more on specific interactions. According to basic principles of thermodynamics, when a solute is in equilibrium with its ions, ΔG becomes equal to zero and the standard free energy of solution is given by

$$\Delta G_{\text{Soln}}^{\circ} = -RT \ln K_{\text{sp}} \quad (1)$$

where K_{sp} is the equilibrium constant for the reaction



Thus, K_{sp} is the solubility product or the solubility in case of uncharged molecules.

Truely speaking, K_{sp} is the activity product and it is simply not possible to measure activity unless some approximations are made. Two approaches are most widely used to evaluate activity co-efficients of the ions. One is the application of Deby-Hückel expression²³ of mean ionic activity co-efficient and the second approach is the introduction of Davies equation²⁴.

Upon introduction of Deby-Hückel expression²³ for the mean activity coefficients into eqn. (1) one obtains

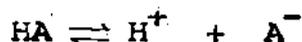
$$\Delta G_{\text{soln}}^{\circ} = 2.303RT \left[-\nu \log m - \log (\nu_+^{\nu_+} \nu_-^{\nu_-} + \nu \delta_{\nu} d_0^{1/2} m^{1/2}) \right] \quad (2)$$

where d_0 is the density of the solvent, δ_{ν} is the Deby-Hückel limiting slope, ν is the number of ions, ν_+ and ν_- are the number of positive and negative ions respectively and the other terms have their usual significance.

Equation (2) is applied to the data to obtain standard free energies of solution and these are combined with the reported free energies of formation²⁵ of the respective crystalline salts to obtain the corresponding standard free energies of formation for

the electrolytes²⁶.

In solubility method, the dissociation constant for the reaction (say, e.g. dissociation of an acid)



can be written as

$$K = \frac{c_{\text{H}^+} c_{\text{A}^-}}{c_{\text{HA}}} \times \frac{\gamma_{\pm}^2}{\gamma_{\text{HA}}} \quad (3)$$

$$K = \frac{c_{\text{H}^+}^2}{[C]_{\text{T}} - c_{\text{H}^+}} \times \gamma_{\pm}^2 \quad (4)$$

where $[C]_{\text{T}}$ is the total concentration of HA and C_{H^+} is the concentration of H^+ ions in the saturated experimental solutions determined experimentally (pH-metrically). The mean molar activity coefficient, γ_{\pm} , of the ions at different concentrations in aqueous and mixed solvents can also be determined using Davies equation²⁴ :

$$-\log \gamma_{\pm} = A z_+ z_- \sqrt{\mu} / (1 + \sqrt{\mu}) - 0.2 \mu \quad (5)$$

Values of γ_{\pm} thus obtained are generally used to calculate the dissociation constant by applying eqn. (4) and finally the free energy of solution by using eqn. (1), where the solubility product is simply replaced by the dissociation constant term.

Standard enthalpy of solution can also be obtained from the solubility data, if available, for an electrolyte in a solvent at different temperatures, by using the following relation

$$\left(\frac{\partial \ln K_{sp}}{\partial T}\right)_P = -\frac{1}{R} \times \left[\frac{\partial (\Delta G^\circ)/T}{\partial T}\right]_P = \frac{\Delta H^\circ_{soln}}{RT^2} \quad (6)$$

It is assumed that standard free energy of solution, ΔH°_{soln} , is constant over a moderate temperature range and thus the above equation upon integration becomes

$$\log K_{sp} = -\frac{\Delta H^\circ_{soln}}{R \ln 10} \left(\frac{1}{T}\right) + A \quad (7)$$

where A is the integration constant. ΔH°_{soln} is actually obtained from the slope of a plot of $\log K_{sp}$ vs T^{-1} .

Parker and his co-workers²⁷ have made extensive studies on solubility in some anhydrous solvents. They have reported the solubility products and dissociation constants of some alkali metal and silver salts in a variety of solvents like water, methanol, formamide, dimethylformamide, dimethylsulfoxide, acetonitrile and hexamethylphosphoramide. Solubilities were obtained in this study using a variety of techniques including potentiometric titrations, spectrophotometry, gravimetric analysis and atomic absorption measurements. Fairly extensive solubility measurements have been made

in different solvents by a number of workers during the last few years^{17-23,26}.

Standard free energy of solvation for an electrolyte as a whole in a solvent is obtained by subtracting the free energy of formation of the pair of gaseous ions i.e. the lattice energy from the standard free energy of solution:

$$\Delta G_{\text{Solv}}^{\circ} = \Delta G_{\text{Soln}}^{\circ} - \Delta G_{\text{latt}}^{\circ} \quad (8)$$

The sum total of all the solute-solvent interactions is reflected quantitatively on the solvation energy, $\Delta G_{\text{Solv}}^{\circ}$ of the dissolved substance. To have an idea about ionic solvation exclusively, ionic solvation energy is to be calculated and this can't be measured straight way from experimental approach. A modified Born equation was proposed by Latimer, Pitzer and Slansky²⁸ to calculate the standard free energies of solvation of single ions:

$$\Delta G_{\text{Solv}}^{\circ} = -\frac{Nz_1^2 e^2}{2} [1 - 1/\epsilon] / (r_1 + \delta) \quad (9)$$

where Z_1 and r_1 are the charge and radius of the ion respectively and the other terms have their usual significance. The same equation has been used by Criss and his co-worker²³ for the determination of solvation energies in dimethylformamide.

Free energies of transfer and medium effects

Differences between free energies, enthalpies and entropies of a solute in two solvents are known as thermodynamic transfer functions. From these thermodynamic transfer properties of electrolytes and ions, one can predict the values of rate constants and equilibria and also can express activities and electrode potentials in different media on a single, solvent-independent scale. Moreover, values of the free energies, enthalpies and entropies of transfer from one reference solvent to another provide a wealth of information on the energetics and mechanisms of solute-solvent and solvent-solvent interactions²⁶. These values also focus some light on the structure of the solvents and their solutions.

The standard free energy of transfer, $\Delta\bar{G}_t^\circ(i)$ or simply the transfer free energy for the solute i from one reference solvent to a given non-aqueous solvent is expressed in general, as the difference between partial molal free energies of that solute (i) in its reference and non-aqueous standard states:

$$\Delta\bar{G}_t^\circ(i) = {}_s\bar{G}_i^\circ - {}_w\bar{G}_i^\circ = RT \ln_m \gamma_i \quad (10)$$

And the corresponding activity coefficient, ${}_m\gamma_i$, is known as the transfer activity coefficient or medium effect of the solute i between the two solvents. Normally water is taken as the reference solvent (subscript w) from which a solute is transferred to a given

solvent (subscript s). It should also be noted that since m_i^j is a property of two ideal solutions (where ions are infinitely apart), it is determined solely by the nature of the solute and the two solvents and for a given temperature and pressure it is constant. m_i^j is also independent of concentration or of the other substances present in solution. In practice, m_i^j is a measure of the difference between the solute-solvent interactions only in the two (ideal) standard states with solute-solute interactions eliminated.

The partial molal free energy of a solute species in a saturated solution and in the solid in equilibrium with the solution are equal. So, naturally when the saturated solutions of a solute in different solvents are in equilibrium with the same solid phase their free energies are also equal. For a saturated aqueous solution of solute i

$$\bar{G}_i = {}_w\bar{G}_i^{\circ} + RT \ln {}_w a_i \text{ (satd.)} \quad (11)$$

and for the non-aqueous saturated solution of the same solute i at the same temperature and pressure

$$\bar{G}_i = {}_s\bar{G}_i^{\circ} + RT \ln {}_s a_i \text{ (satd.)} \quad (12)$$

Thus from eqns (11) and (12), since \bar{G}_i is the same in both equation,

$$\Delta \bar{G}_t^{\circ} (i) = {}_s\bar{G}_i^{\circ} - {}_w\bar{G}_i^{\circ} = RT \ln \frac{{}_w a_i \text{ (satd)}}{{}_s a_i \text{ (satd)}} = RT \ln_m \gamma_i \quad (13)$$

For an electrolyte, the activity in saturated solution is equivalent to the solubility or ion-activity product, K_{sp} . It is also a very common practice to calculate $m\gamma$ values in logarithmic form as

$$\log m\gamma \text{ (electrolyte)} = p(s^{K_{sp}}) - p(w^{K_{sp}}) \quad (14)$$

Thus, for any symmetrical electrolyte

$$\log m\gamma \text{ (electrolyte)} = \log m\gamma_{\pm}^2 = \log m\gamma_{+} + \log m\gamma_{-} \quad (15)$$

When standard transfer free energies rather than the activity coefficients are desired, the following equation is used

$$\Delta\bar{G}_t^{\circ} = s(\Delta\bar{G}_{\text{Soln}}^{\circ}) - w(\Delta\bar{G}_{\text{Soln}}^{\circ}) \quad (16)$$

For most purposes transfer free energies and transfer activity coefficients are sufficient enough but however additional information can be obtained from a consideration of the enthalpies, $\Delta\bar{H}_t^{\circ}$ and the entropies, $\Delta\bar{S}_t^{\circ}$ of transfer. The normal thermodynamic relationship between these functions holds for their transfer properties also:

$$\Delta\bar{G}_t^{\circ} = \Delta\bar{H}_t^{\circ} - T\Delta\bar{S}_t^{\circ} \quad (17)$$

In order to have a better insight into the ion-solvent interactions, the single ion values of thermodynamic transfer functions are needed. The transfer activity coefficient of an electrolyte can be written as the sum of the individual ionic transfer activity coefficients. So, for an electrolyte MX, in general,

$$\log_m \gamma (MX) = \log_m \gamma_{M^+} + \log_m \gamma_{X^-} \quad (18)$$

The additivity rule also makes it possible to measure the transfer activity coefficients for those electrolytes for which accurate K_{sp} values can not be determined directly in one or both of the two solvents owing to poor solubility or some other reasons. For example, the transfer activity coefficient for tetraphenylarsonium tetraphenylborate, which is sparingly soluble in water can be obtained from those of Ph_4AsPi , $KBPh_4$ and KPi ($Pi = Picrate$) for example by using the following equation

$$\log_m \gamma_{Ph_4As BPh_4} = \log_m \gamma_{Ph_4As Pi} + \log_m \gamma_{KBPh_4} - \log_m \gamma_{KPi} \quad (19)$$

Once the value of either $\Delta \bar{G}_t^\circ$ or $\log_m \gamma$ for an ion in solution is known the other can be calculated easily by using the relation, $\Delta \bar{G}_t^\circ = 1.364 \log_m \gamma$ in kcal mol⁻¹ at 25°C.

Thermodynamic transfer properties of single ions in aqueous and different non-aqueous solvents have been presented by a number of workers^{23,26,27,29-33}. And one of the biggest problems faced by the solution chemists is the derivation of single ion values of different thermodynamic and transport properties which can hardly be measured directly. The single ion values on the other hand are extremely important since it is the ion-solvent interaction involving anions and cations and the solvent molecules that bring about changes in rate processes, chemical equilibria and structural modifications with the change in solvents. To overcome this problem some models and assumptions are needed. Several extrathermodynamic assumptions have been proposed for the determination of the ionic transfer free energies and activity coefficients. Popovych^{34a)} and Kim^{34b)} have made excellent reviews in this field. Here, we are attempting to present a very concise and brief picture of the development of single-ion thermodynamics.

ΔG_t^0 of an electrolyte or an ion is the difference in its solvation energies between two solvents of which one is usually water (the reference solvent). Solvation energy of an ion in a solvent is actually composed of electrostatic, non-electrostatic and specific chemical interactions between the ion and the solvent. Non-electrostatic interaction comprises of ion-dipole, ion-quadrupole, ion-induced dipole and dispersion energy terms. Specific interactions are actually due to sharing of electrons (e.g. H-bonding) between ions and solvent molecules. Calculation of all these energy terms is not an easy one. Major problem lies with our

insufficient knowledge about the structures of non-aqueous solvents and their solvation shells around an ion including the magnitude of the various electrical and distance parameters required for the calculation.

Using Born model³⁵, the transfer free energy of an ion can be represented as

$$\Delta \bar{G}_t^{\circ} = \frac{Nz^2 e^2}{2r RT} \left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right] \quad \text{in k cal mol}^{-1} \quad (20)$$

$$= \frac{166}{r} \left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right] \quad \text{in k cal mol}^{-1} \quad (21)$$

where r is the radius in Angstroms and ϵ_s and ϵ_w are the dielectric constants of the non-aqueous solvent and water (or the reference solvent) respectively. Transfer activity coefficient, $\log m \gamma_1$ can thus easily be obtained from $\Delta \bar{G}_t^{\circ}$ value (using $\Delta \bar{G}_t^{\circ} = 1.364 \log m \gamma_1$ at 25°C). In this model, ion is taken as a rigid sphere of radius r and charge Ze and the solvent is assumed to be a structureless continuum of uniform dielectric constant, ϵ , corresponding to its bulk value. Although Born model is the first ever scientific attempt to derive an expression for ion-solvent interaction energy and Born energy of an ion constitutes the major portion of the solvation energy of an ion, true picture around an ionic species in a solvent is something different and many other interaction terms are to be evaluated. This factor generated further

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interest among the solution chemists.

Strehlow et al³⁶ and Coetzee and his co-workers³⁷ have also used Born equation to derive the values of $\Delta\bar{G}_t^{\circ}$ by adjusting the ionic radii of Born equation. At first Bjerrum and Larsson³⁸ and then Parker and his associates^{32,39} made some attempts to measure transfer activity coefficients of single ions from emf studies by using appropriate salt bridge technique so that the liquid junction potential could be neglected. In the sixties, extrapolation method for the estimation of $\Delta\bar{G}_t^{\circ}$ values for single ions were attempted by Izmaylov⁴⁰, Feakins and his co-workers⁴¹ and also by Deligny and Alfenaar⁴². Izmaylov assumed ionic solvation to be solely electrostatic in nature but the other groups of scientists have taken into account both electrostatic and non-electrostatic contributions. In this method, experimentally measured solvation energies were plotted as functions of inverse of ionic radius. Deligny et al^{43,44} further modified the extrapolation method by applying ion-quadrupole theory of solvation.

"Reference electrolyte" method seems to be far more advanced over all the previous assumptions and techniques, applied to evaluate single ion thermodynamic transfer properties. In this method, the transfer free energy of a 1:1 electrolyte composed of large ions that are very nearly equal in size and structure is divided equally between the anion and the cation. And the most widely used reference electrolyte for the determination of single ion thermodynamic transfer properties is tetraphenylarsonium tetraphenylborate

($\text{Ph}_4\text{AsBPh}_4$)^{32,39,45-48}. Here, it is assumed that for any given pair of solvents, transfer properties of electrolytes can be divided equally into its ionic components i.e. $m\gamma_{\text{Ph}_4\text{As}^+} = m\gamma_{\text{BPh}_4^-}$ or $\Delta\bar{G}_t^\circ(\text{Ph}_4\text{As}^+) = \Delta\bar{G}_t^\circ(\text{BPh}_4^-)$. Another reference electrolyte tetraphenylphosphonium tetraphenylborate (Ph_4PBPh_4)^{45,48,49} was also tested and found to be equivalent to $\text{Ph}_4\text{AsBPh}_4$ assumption⁴⁸. In fact, Marcus⁵⁰ believes that the use of Ph_4PBPh_4 as reference electrolyte would be more logical since Ph_4P^+ ion is nearly of the same size as that of the anion BPh_4^- though Kim^{34b)} has suggested that $\text{Ph}_4\text{AsBPh}_4$ is the best of all the reported reference electrolytes. Here, we have used both $\text{Ph}_4\text{AsBPh}_4$ and Ph_4PBPh_4 as the reference electrolytes and hence applied the following relationships in order to calculate the single ion values

$$\Delta\bar{G}_t^\circ(\text{Ph}_4\text{As}^+) = \Delta\bar{G}_t^\circ(\text{BPh}_4^-) \quad (22)$$

and

$$\Delta\bar{G}_t^\circ(\text{Ph}_4\text{P}^+) = \Delta\bar{G}_t^\circ(\text{BPh}_4^-) \quad (23)$$

Viscosity

Viscosity is one of the most important transport properties used for the determination of ion-solvent interactions and it has been studied extensively^{51,52}. Viscosity is not a thermodynamic quantity, but viscosity of an electrolyte solution together with the thermodynamic property, \bar{V}_2 , the partial molal volume gives much information and insight regarding ion-solvent interactions and the

structures of electrolytic solutions. The viscosity relationships of electrolytic solutions are highly complicated. There are strong electrical forces between the ions and the solvent, and the separation of these forces is not really possible. But from careful analysis, valid conclusion can be drawn regarding the structure and nature of solvation.

The first systematic measurement of viscosities of a number of electrolyte solutions over a wide concentration range was attempted by Grüneisen⁵³ in 1905. He noted non-linearity and negative curvature in the viscosity-concentration curves (irrespective of low or high concentrations). In 1929, Jones and Dole⁵⁴ suggested an empirical equation (24), quantitatively correlating the relative viscosities (η_r) of the electrolytes with molar concentration, C:

$$\eta_r = 1 + Ac^{\frac{1}{2}} + Bc \quad (24)$$

The equation reduces to

$$(\eta_r - 1) / c^{\frac{1}{2}} = A + Bc^{\frac{1}{2}} \quad (25)$$

where A and B are constants specific to ion-ion and ion-solvent interactions respectively. The equation is applicable equally to aqueous and non-aqueous solvent systems where there is no ion-association and has been used extensively. The term $Ac^{\frac{1}{2}}$, originally ascribed to Grüneisen effect, arose from the long range coulombic forces between the ions. The significance of the term had since then

been realized due to the development of Debye-Hückel theory⁵⁵ of interionic attractions (1923), Falkenhagen's⁵⁶⁻⁵⁸ theoretical calculation of the constant 'A', using the equilibrium theory and the theory of irreversible processes in electrolytes developed by Onsager and Fuoss⁵⁹. The A co-efficient depends on the ion-ion interactions and can be calculated from the physical properties of the solvent and solution using the Falkenhagen-Vernon equation⁵⁸

$$A_{\text{theo}} = \frac{0.2577 \Lambda^{\circ}}{\eta_0 (\epsilon T)^{1/2} \lambda_+^{\circ} \lambda_-^{\circ}} \left[1 - 0.6863 \left(\frac{\lambda_+^{\circ} - \lambda_-^{\circ}}{\Lambda^{\circ}} \right)^2 \right] \quad (26)$$

where Λ° , λ_+° and λ_-° are the limiting conductances of the electrolyte, cation and anion respectively at temperature T; ϵ and η_0 are the dielectric constant and viscosity of the solvent respectively. For most solutions, both aqueous and non-aqueous, the equation is valid upto 0.1 M^{51,60}. At higher concentrations, the extended Jones-Dole equation (24) involving an additional constant D, originally used by Kaminsky⁶¹, has been used by several workers^{62,63}.

$$\eta_r = 1 + Ac^{1/2} + Bc + Dc^2 \quad (27)$$

The constant D can not be evaluated properly and the significance of the constant is also not always meaningful and, therefore, the equation (24) is used by most of the workers.

The plots of $(\eta_r - 1)/c^{1/2}$ against $c^{1/2}$ for the electrolytes should give the value of A but in general the values come out to be

negative or considerable scatter or deviation from linearity occur^{60,64,65}. Thus, instead of determining the A-values from the plots or by least squares method, the A values are generally calculated using the Falkenhagen-Vernon equation (26).

The B co-efficient may be either positive or negative and it is actually the ion-solvent interaction parameter. It is conditioned by the ion-size and the solvent and can not be calculated a priori. The B co-efficients are obtained as slopes of the straight lines using the least squares method and the intercepts being equal to the A-values. The factors which influence B-values are^{66,67}.

- (1) The effect of ionic solvation and the action of the field of the ion in producing long range order, increases η or B-values.
- (2) The destruction of the three dimensional structure of solvent molecules (i.e. structure breaking effect or depolymerization effect) decreases η -values.
- (3) High molal volume and low dielectric constant, which yield high B-values for similar solvents.
- (4) Reduced B values are obtained when the primary solvation of ions is sterically hindered in high molal volume solvents or if either ion of a binary electrolyte cannot be specifically solvated.

Viscosities at higher concentrations:

It has been found that the viscosity values at high concentrations (1M to saturation) can be represented by the empirical formula suggested by Andrade⁶⁸

$$\eta = A \exp b/T \quad (28)$$

Several alternative formulations have been proposed for representing the results of viscosity measurements in the high concentration range⁶⁹⁻⁷⁴ and the equation suggested by Angel^{75,76} based on an extension of the free volume theory of transport phenomena in liquids and fused salts to ionic solutions is particularly noteworthy. The equation is

$$1/\eta = A \exp \left[-K'/(N_0 - N) \right] \quad (29)$$

where N represents the concentration of the salt in eqv. litre⁻¹, A and K' are constants supposed to be independent of the salt composition and N_0 is the hypothetical concentration at which the system becomes glass. The equation was recast by Majumdar *et al*⁷⁷⁻⁷⁹ introducing the limiting condition that $N \rightarrow 0$, $\eta \rightarrow \eta_0$, the viscosity of the pure solvent. Thus we have

$$\ln \frac{\eta}{\eta_0} = \ln \eta_{rel} = \frac{K'N}{N_0(N_0 - N)} \quad (30)$$

Equation (30) predicts a straight line through the origin for the plot of $\ln \eta_{rel}$ vs. $N/(N_0 - N)$, if a suitable choice for N_0 is made. This equation has been tested by Majumdar et al⁷⁷⁻⁷⁹ using the data from the literature and from their own experimental results. The best choice for N_0 and K' was selected by a trial and error method. The set of K' and N_0 which produces minimum deviation between η_{rel} (expt) and η_{rel} (theo) was accepted.

In dilute solutions, $N \ll N_0$ and we have

$$\eta_{rel} = \exp (K'N/N_0^2) \simeq 1 + K'N/N_0 \quad (31)$$

which is nothing but the Jones-Dole equation with the ion-solvent interaction term represented as $B = K'/N_0^2$. The agreement between B values determined in this way and those obtained using the Jones-Dole equation has been found to be good for several electrolytes.

Further, the equation (30) written in the form

$$\frac{N}{\ln \eta_{rel}} = \frac{N_0^2}{K'} - \frac{N_0 N}{K'} \quad (32)$$

closely resembles Vand's equation⁷² for fluidity (reciprocal of viscosity)

$$\frac{2.5C}{2.3 \log \eta_{rel}} = \frac{1}{V} - Qc \quad (33)$$

where c is the molar concentration of the solute and V is the effective rigid molar volume of the salt and Q is the interaction constant.

Division of B co-efficient into ionic values

The viscosity B co-efficients have been determined by a large number of workers in aqueous, mixed and non-aqueous solvents^{65,80-110}. However, the B co-efficients as determined experimentally using Jones-Dole equation, do not give any impression regarding ion-solvent interactions unless there is some way to identify the separate contributions of cations and anions in the total solute-solvent interactions. The division of B values into ionic components is quite arbitrary and based on some approximation or assumptions, the validity of which may be questioned.

The following methods have been used for the division of B-values into ionic components.

(1) Cox and Wolfenden¹¹¹ carried out the division on the assumption that B_{ion} values of Li^+ and IO_3^- in $LiIO_3$ are proportional to the third power of the ionic mobilities. The method of Gurney¹¹² and also of Kaminsky⁶¹ is based on

$$B_{K^+} = B_{Cl^-} \quad (\text{in water}) \quad (34)$$

The argument in favour of this assignment is based on the fact that the B co-efficient for KCl is very small and that the mobilities

of K^+ and Cl^- are very similar over the temperature range 15-45°C. The assignment is supported from other thermodynamic properties⁵¹. Nightingale¹¹³, however, preferred RbCl or CsCl rather than KCl from mobility considerations.

(2) The method suggested by Desnoyers and Ferron⁶² is based on the assumption that the ion Et_4N^+ in water is probably closest to being neither structure breaker nor a structure maker. Thus they suggest that it is possible to apply, with a high degree of accuracy, Einstein's equation¹¹⁴.

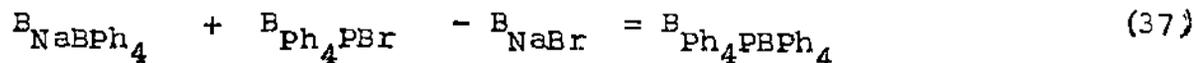
$$B = 0.0025 \bar{V}^{\circ} \quad (35)$$

and by having an accurate value of the partial molal volume of the ion \bar{V}° , it is possible to calculate the value of 0.359 for $B_{Et_4N^+}$ in water at 25°C.

Recently, Sacco et al¹⁰⁵ proposed the widely used "reference electrolyte" method. Thus for tetraphenylphosphonium tetraphenylborate in water, we have

$$B_{BPh_4^-} = B_{PPh_4^+} = B_{Ph_4PBPh_4} / 2 \quad (36)$$

$B_{\text{Ph}_4\text{PBPh}_4}$ (since Ph_4PBPh_4 is scarcely soluble in water) has been obtained from



The values obtained are in good agreement with those obtained by other methods.

The criteria adopted for the separation of B co-efficients in non-aqueous solvents differ from those generally used in water. However, the methods are based on the equality of equivalent conductances of counter ions at infinite dilution. Thus, (a) Criss and Mastraianni⁸³ assumed $B_{\text{K}^+} = B_{\text{Cl}^-}$ in methanol (based on equal mobilities of ions¹¹⁵). They also adopted $B_{\text{Me}_4\text{N}^+} = 0.25$ as the initial value for acetonitrile solutions.

(b) For acetonitrile solutions, Tuan and Fuoss¹¹⁶ proposed the equality



since they thought that these ions have similar mobilities. However, according to Kay et al¹¹⁷, $\lambda_{25}^\circ (\text{Bu}_4\text{N}^+) = 61.4$ and $\lambda_{25}^\circ (\text{Ph}_4\text{B}^-) = 58.3$ in acetonitrile.

(c) Gopal and Rastogi⁸¹ resolved the B co-efficients in N-methyl-propionamide solution assuming that

$$B_{\text{Et}_4\text{N}^+} = B_{\text{I}^-} \quad (39)$$

at all temperatures. In dimethylsulphoxide, the divisions of B-coefficients were carried out by Yao and Bennion⁶⁴ assuming

$$B[(i\text{-Pe})_3\text{BuN}^+] = B[\text{Ph}_4\text{B}^-] = \frac{1}{2} [(i\text{-Pe})_3\text{BuNBPh}_4] \quad (40)$$

at all temperatures. Wide use of this method has been made by other authors for dimethylsulphoxide⁶³, sulpholane⁹¹, hexamethylphosphotriamide⁹⁵ and ethylene carbonate¹¹⁸ solutions.

These methods, however, have been strongly criticized by Krungalz¹¹⁹. According to him, any method of resolution based on the equality of equivalent conductance for certain ion suffers from the drawback that it is impossible to select any two ions for which $\lambda_+^\circ = \lambda_-^\circ$ in all solvents at proper temperatures. Thus, though $\lambda^\circ(\text{K}^+) = \lambda^\circ(\text{Cl}^-)$ at 25°C in methanol, but not in ethanol and in other solvents. In addition, if the mobilities of some ions are even equal at infinite dilution, but it is not necessarily true at moderate concentrations for which the B-coefficient values are calculated. Further, according to him, equality of dimensions of $(i\text{-Pe})_3\text{BuN}^+$ or $(i\text{-Am})_3\text{BuN}^+$ and Ph_4B^- does not necessarily imply equality of B-coefficients of these ions and they are likely to be solvent and ion-structure dependent.

Krumgalz^{119,120} has recently proposed a method for the resolution of B-coefficients. The method is based on the fact that the large tetraalkylammonium ions are not solvated^{121,122} in organic solvents (in the normal sense involving significant electrostatic interaction). Thus, the ionic B values for large R_4N^+ ions (where $R \gg Bu$) in organic solvents are proportional to their ionic dimensions. Thus, we have

$$B_{R_4NX} = a + B \Gamma_{R_4N^+}^3 \quad (41)$$

where $a = B_{X^-}$ and b is a constant dependent on temperature and solvent nature.

The extrapolation of the plot of B_{R_4NX} ($R > Pr$ or Bu) against $\Gamma_{R_4N^+}^3$ to zero cation dimension gives directly B_{X^-} in the proper solvent from which other ionic B-values can be calculated.

The ionic B values can also be calculated from the equations

$$B_{R_4N^+} - B_{R_4N^+} = B_{R_4NX} - B_{R_4NX} \quad (42)$$

and

$$\frac{B_{R_4N^+}}{B_{R_4N^+}} = \frac{\Gamma_{R_4N^+}^3}{\Gamma_{R_4N^+}^3} \quad (43)$$

The radii of the tetraalkylammonium ions have been calculated from the accurate conductance data¹²³.

Gill and Sharma¹⁰⁶ used Bu_4NBPh_4 as a reference electrolyte. The method of resolution of B is based on the assumption, like Krungalz, that Bu_4N^+ and Ph_4B^- ions with large R-groups are not solvated in non-aqueous solvents and their dimensions in such solvents are constant. The ionic radii of Bu_4N^+ (5.00 Å) and of Ph_4B^- (5.35 Å) have been, in fact, found to remain constant in different non-aqueous and mixed non-aqueous solvents by Gill and co-workers. They proposed the equations

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \frac{r^3_{\text{Ph}_4\text{B}^-}}{r^3_{\text{Bu}_4\text{N}^+}} = \left[\frac{5.35}{5.00} \right]^3 \quad (44)$$

and

$$B_{\text{Bu}_4\text{NBPh}_4} = B_{\text{Bu}_4\text{N}^+} + B_{\text{Ph}_4\text{B}^-} \quad (45)$$

The method requires only the B values of Bu_4NBPh_4 and is equally applicable to mixed non-aqueous solvents. The ionic B values obtained by this method agree well with those reported by Sacco et al in different organic solvents using the assumption:

$$B_{i-\text{Am}_3\text{BuN}^+} = B_{\text{Ph}_4\text{B}^-} = B_{i-\text{Am}_3\text{BuNBPh}_4} / 2 \quad (46)$$

Recently Lawrence and Sacco^{107,108a} used Bu_4NBBu_4 (tetrabutylammonium tetrabutylborate) and Ph_4PBPh_4 (tetraphenylphosphonium tetraphenylborate) as reference electrolytes because the cation and anion in each case are symmetrically shaped and have

almost equal van der Waals volumes. Thus, we have,

$$\frac{B(\text{Bu}_4\text{N}^+)}{B(\text{Bu}_4\text{B}^-)} = \frac{V_w(\text{Bu}_4\text{N}^+)}{V_w(\text{Bu}_4\text{B}^-)} \quad (47)$$

or,

$$B(\text{Bu}_4\text{N}^+) = B(\text{Bu}_4\text{NBBu}_4) / \left[1 + \frac{V_w(\text{Bu}_4\text{B}^-)}{V_w(\text{Bu}_4\text{N}^+)} \right] \quad (48)$$

A similar division can be made for Ph_4PBPh_4 system.

Recently, Lawrence et al^{108b} reported the viscosity measurements of tetraalkylammonium bromides in DMSO and HMPI. The B-coefficients were plotted as functions of the van der Waals volumes, Stokes radii and formula weights of the cations, and the linear portions of the graphs were extrapolated to the zero value of each property. The intercepts thus obtained were compared with the ionic $B(\text{Br}^-)$ values obtained using $\text{Bu}_4\text{NBBPh}_4$ and Ph_4PBPh_4 as reference salts. They concluded that the 'reference salt' method is the best available method for the separation of viscosity B coefficients into ionic contributions. Their analysis is in agreement with the conclusions made by Thomson et al^{108c,d}.

Jenkins and Pritchett¹²⁴ suggested a least square analytical technique to examine additivity relationship for combined ion thermodynamic data, to effect apportioning into single ion components

for alkali halides by employing Fajan's competition principle¹²⁵ and 'volcano plots' of Moris¹²⁶. The principle was extended to derive absolute single ion B-values for alkali metals and halides in water. They also observed that $B(\text{Cs}^+) = B(\text{I}^-)$ suggested by Krungalz¹²¹ to be more reliable than $B(\text{K}^+) = B(\text{Cl}^-)$ in aqueous solutions. However, we require more data to test the validity of this method.

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

Temperature dependence of B_{ion} - values

A regularity in the behaviour of B_{\pm} and $\frac{dB_{\pm}}{dT}$ has been observed both in aqueous and non-aqueous solvents and useful generalisations have been made by Kaminsky⁶¹. He observed that

(i) Within a group of the periodic table, the B_{ion} - values decrease as the crystal ionic radii increase.

(ii) Within a group of periodic system, the temperature coefficient of B_{ion} values increases as the ionic radius increases. The results can be summarized as follows

$$(i) \quad A \text{ and } \frac{dA}{dT} > 0 \quad (49)$$

$$(ii) \quad B_{\text{ion}} < 0 \text{ and } \frac{dB_{\text{ion}}}{dT} > 0 \quad (50)$$

are characteristics of structure breaking ions, and

$$(iii) B_{ion} > 0 \quad \text{and} \quad dB_{ion}/dT < 0 \quad (51)$$

are characteristics of structure making ions.

When an ion is surrounded by a solvation sheath, the properties of the solvent molecules within this sheath may be different from those present in the bulk structure. This is well reflected in the 'cosphere' model of Gurney¹²⁷, A, B, C zone of Frank and Wen¹²⁸ and hydrated radius of Nightingale¹¹³.

Stokes and Mills⁵¹ gave an analysis of the viscosity data incorporating the basic ideas presented before. The viscosity of a dilute electrolyte solution has been equated to the viscosity of the solvent (η_0) plus the viscosity changes resulting from competition between various effects occurring in the ionic neighbourhood. Thus,

$$\eta = \eta_0 + \eta^* + \eta^E + \eta^A + \eta^D = \eta_0 + \eta_0 (A\sqrt{c} + Bc) \quad (52)$$

(Jones-Dole equation)

η^* is the positive increment in viscosity caused by coulombic interaction. Thus,

$$\eta^E + \eta^A + \eta^D = \eta_0 Bc \quad (53)$$

B-coefficient can thus be interpreted in terms of competitive viscosity effects.

Following Stokes and Mills⁵¹ and Krungalz¹¹⁹ we can write B_{ion} as

$$B_{ion} = B_{ion}^{Einst} + B_{ion}^{Orient} + B_{ion}^{Str} + B_{ion}^{Reinf} \quad (54)$$

whereas according to Lawrence and Sacco¹⁰⁷,

$$B_{ion} = B_w + B_{Solv} + B_{Shape} + B_{Ord} + B_{Disord} \quad (55)$$

B_{ion}^{Einst} is the positive increment arising from the obstruction to the viscous flow of the solvent caused by the shape and size of the ions (the term corresponds to η^E or B_{Shape}), B_{ion}^{Orient} is the positive increment arising from the alignment or structure-making action of the electric field of the ion on the dipoles of the solvent molecules (the term corresponds to η^A or B_{Ord}), B_{ion}^{Str} is the negative increment related to the destruction of the solvent structure in the region of ionic cosphere arising from the opposite tendencies of the ion to orient the solvent molecules around itself centrosymmetrically and solvent to keep its own structure (this corresponds to η^D or B_{Disord}), B_{ion}^{Reinf} is the positive increment conditioned by the effect of 'reinforcement of the water structure' by large tetraalkylammonium ions due to hydrophobic hydration. The phenomenon is inherent in the intrinsic water structure and absent

in organic solvents. B_w and B_{Solv} account for viscosity increases attributed to the van der Waals volume of the solvated ions.

Thus, small and highly charged cations like Li^+ and Mg^{+2} form a firmly attached primary solvation sheath around these ions (B_{ion}^{Einst} or η^E positive).

Ions of intermediate size (e.g. K^+ and Cl^-) have a close balance of viscous forces in their vicinity, i.e., $B_{ion}^{Einst} + B_{ion}^{Orient} = B_{ion}^{Str}$ so that B is close to zero.

Large molecular ions like tetraalkylammonium ions have large B_{ion}^{Einst} because of large size but B_{ion}^{Orient} and B_{ion}^{Str} would be small i.e. $B_{ion}^{Einst} + B_{ion}^{Orient} \gg B_{ion}^{Str}$ and B value would be positive and large. The values would be further reinforced in water arising from B_{ion}^{Reinf} due to hydrophobic hydrations.

The increase in temperature will have no effect on B_{ion}^{Einst} but the orientation of solvent molecules in the secondary layer will be decreased due to increasing thermal motion leading to decrease in B_{ion}^{Str} . B_{ion}^{Orient} will decrease slowly with the increase in temperature as there will be less competition between the ionic field and the reduced solvent structure. The positive or negative temperature coefficient will thus depend on the change of the relative magnitudes of B_{ion}^{Orient} and B_{ion}^{Str} .

It is clear that in case of structure-making ions, the ions are firmly surrounded by a solvation sheath and the secondary solvation zone will be considerably ordered leading to an increase in B_{ion} and concomitant decrease in entropy of solvation and the mobility of ions. Structure-breaking ions, on the other hand, are not solvated to a great extent and the secondary solvation zone will be disordered leading to a decrease in B_{ion} values and increase in entropy of solvation and the mobility of ions. Moreover, the temperature-induced change in viscosity of ions (or entropy of solvation or mobility of ions) would be more pronounced in case of smaller ions than in case of larger ions. So there is a clear correlation between the viscosity, entropy of solvation and the mobility of ions. Thus the ionic B coefficients and entropy of solvation of ions have rightly been used as probes of ion-solvent interactions and as a direct indication of structure-making and structure-breaking characters of ions.

The linear plot of ionic B-coefficients against the ratios of mobility-viscosity products at two temperatures (a more sensitive variable than ionic mobility) by Gurney^{112,127} clearly demonstrates a close relation between ionic B-coefficients and ionic mobilities.

Gurney also demonstrated a clear correlation between the molar entropy of solution values with B-coefficients of salts. The ionic B values show a linear relationship with the partial molar ionic entropies of hydration \bar{S}_h^o

$$\overline{s}_h^{\circ} = \overline{s}_{aq}^{\circ} - \overline{s}_g^{\circ} \quad (56)$$

where $\overline{s}_{aq}^{\circ} = \overline{s}_{ref}^{\circ} + \Delta S^{\circ}$ is the calculated sum of the rotational and translational entropies of the gaseous ions. Gurney obtained a single linear plot between ionic entropies and ionic B-coefficients for all monoatomic ions by equating the entropy of the hydrogen ion ($\overline{s}_{H^+}^{\circ}$) to $-5.5 \text{ cal mol}^{-1} \text{ deg}^{-1}$. Asmus¹²⁹ used the entropy of hydration to correlate ionic B-values and Nightingale¹¹³ showed that a single linear relationship can be obtained with it for both monoatomic and polyatomic ions.

The correlation was utilised by Abraham *et al*¹³⁰ to assign single ion B-coefficients so that a plot of ΔS_e° ^{131,132}, the electrostatic entropy of solvation or $\Delta S_{I,II}^{\circ}$ ^{131,132}, the entropic contributions of the first and second solvation layers of ions against B values (taken from the works of Nightingale) for both cations and anions lie on the same curve or line. There are excellent linear correlations between ΔS_e° and ΔS_I° , and the single ion B-coefficients. Both entropy criteria (ΔS_e° and $\Delta S_{I,II}^{\circ}$) and B_{ion} values indicate that in water the ions Li^+ , Na^+ , Ag^+ and F^- are net structure-makers, the ions Rb^+ , Cl^- , Br^- , I^- and ClO_4^- are structure breakers and K^+ is a border line case. [In non-aqueous solvents e.g., formamide, methanol, N-methyl formamide, dimethyl formamide, dimethylsulfoxide, acetonitrile, all the above ions are structure-makers with the exception of weakly structure-breaking ion ClO_4^- in formamide and the border line cases of ClO_4^- in methanol and I^- in formamide].

Thermodynamics of viscous flow

Assuming viscous flow as a rate process, the viscosity can be represented by using the Eyring approach¹³³

$$\eta = A e^{E_{vis}/RT} = \left(\frac{hN}{V}\right) e^{\Delta G^*/RT} = \left(\frac{hN}{V}\right) e^{\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}\right)} \quad (57)$$

where E_{vis} is the experimental energy of activation which is determined from the plot of $\log \eta$ against $1/T$. ΔG^* , ΔH^* and ΔS^* are the free energy, enthalpy and entropy of activation respectively.

The problem was dealt in a different way by Nightingale and Benck¹³⁴ who studied the thermodynamics of viscous flow of salts and ions in aqueous solution. E_{vis} value can be determined using the Jones-Dole equation neglecting the term $Ac^{\frac{1}{2}}$. Thus,

$$R \frac{d \ln \eta}{d(1/T)} = R \frac{d \ln \eta_0}{d(1/T)} + \frac{R}{1+B_c} \frac{d(1+B_c)}{d(1/T)} \quad (58)$$

$$\Delta E_{\eta}^{\neq}(\text{soln}) = \Delta E_{\eta_0}^{\neq}(\text{solv}) + \Delta E_v^{\neq} \quad (59)$$

ΔE_v^{\neq} can be interpreted as the increase or decrease in the activation energies for viscous flow for the pure solvents due to the presence of ions i.e., effective influence of the ions upon the

viscous flow of the solvent molecules.

Feakins et al¹³⁵ have suggested an alternative formulation based on the transition state treatment of the relative viscosity of the electrolytic solutions. They suggested the following expression

$$B = \frac{\bar{V}_1^{\circ} - \bar{V}_2^{\circ}}{1000} + \frac{\bar{V}_1^{\circ}}{1000} \left[\frac{\Delta /_2^{M^{\circ\ddagger}} - \Delta /_1^{M^{\circ\ddagger}}}{RT} \right] \quad (60)$$

where \bar{V}_1° and \bar{V}_2° are the partial molal volumes of the solvent and solute respectively; $\Delta /_1^{M^{\circ\ddagger}}$ is the free energy of activation for viscous flow per mole of the solvent which is given by¹³³

$$\Delta /_1^{M^{\circ\ddagger}} = \Delta G_1^{\circ\ddagger} = RT \ln \left(\frac{\eta_1 \bar{V}_1}{hV} \right) \quad (61)$$

and $\Delta /_2^{M^{\circ\ddagger}}$ is the contribution per mole of solute to the free energy of activation for viscous flow of solution.

The entropy (ΔS) and enthalpy (ΔH) of activation of viscous flow for the solvents and the solutions (subscripts 1 and 2 respectively) can be calculated using the following equations

$$\Delta S_2^{\circ\ddagger} = -d(\Delta /_2^{M^{\circ\ddagger}})/dT \quad \text{and} \quad \Delta S_1^{\circ\ddagger} = -d(\Delta /_1^{M^{\circ\ddagger}})/dT \quad (62)$$

$$\Delta H_2^{\circ\ddagger} = \Delta /_2^{M^{\circ\ddagger}} + T\Delta S_2^{\circ\ddagger} \quad \text{and} \quad \Delta H_1^{\circ\ddagger} = \Delta /_1^{M^{\circ\ddagger}} + T\Delta S_1^{\circ\ddagger} \quad (63)$$

Effects of shape and size

This aspect has been dealt extensively by Stokes and Mills⁵¹. The ions in solution can be regarded as rigid spheres suspended in continuum. The hydrodynamic treatment presented by Einstein¹¹⁴ leads to the equation

$$\eta/\eta_0 = 1 + 2.5 \phi \quad (64)$$

in case of small fractions of spherical particles where ϕ is the volume fraction occupied by the particles.

Modifications of the equation have been proposed by

(i) Sinha¹³⁶ on the basis of departures from spherical shape and
 (ii) Vand⁷² on the basis of the dependence of the flow patterns around the neighbouring particles at higher concentrations. However, considering the different aspects of the problem, spherical shapes have been assumed for electrolytes having hydrated ions of large effective size (particularly polyvalent monoatomic cations). Thus, we have from (24) and (64)

$$2.5 \phi = A\sqrt{c} + Bc \quad (65)$$

Since the term $A\sqrt{c}$ can be neglected in comparison with Bc and $\phi = c\bar{V}_1$ where \bar{V}_1 is the partial molal volume of the solute, we get

$$2.5 \bar{V}_1 = B \quad (66)$$

In the ideal case, the B coefficient is a linear function of the solute partial molal volume (\bar{V}_1) with slope equal to 2.5.

B_{\pm} can be equated to

$$B_{\pm} = 2.5 V_{\pm} = 2.5 \times \frac{4}{3} \pi \frac{R_{\pm}^3 N}{1000} \quad (67)$$

assuming that the ions behave like rigid spheres with an effective radii R_{\pm} moving in a continuum. R_{\pm} calculated using equation (67) 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 Einstein¹³⁷

$$B_{\pm} = \frac{2.5}{1000} (V_1 + nV_s) \quad (68)$$

where V_1 the bare ion molar volume, V_s is the molar volume of the solvent.

104,110,137

The above equation has been used by a number of workers to study the nature of solvation.

Conductance

Conductance measurement is one of the most accurate and widely used physical methods for investigation of electrolytic solutions^{138,139}. The measurements can be made in a variety of solvents over wide ranges of temperature and pressure and in dilute solutions where interionic interaction theories are not applicable. Fortunately for us, accurate theories of electrolytic conductance are available to explain the results even upto a concentration limit of Kd (K = Debye-Hückel length, d = distance of closest approach of free ions). Recent development of experimental techniques provides an accuracy to the extent of 0.1% or even more. Conductance measurements together with transference number determinations provide an unequivocal method of obtaining single-ion values. The chief limitation, however, is the colligative like nature of the information obtained.

Since the conductometric method primarily depends on the mobility of ions, it can be suitably utilised to determine the dissociation constants of weak acids and association constants of electrolytes in aqueous, mixed and non-aqueous solvents. This method in conjunction with the viscosity measurements gives us much information regarding the ion-ion and ion-solvent interactions.

However, the choice and application of theoretical equations as well as equipments and experimental techniques are of great importance for obtaining an accurate information from such studies.

These aspects have been described in details in a number of authoritative books and reviews¹³⁸⁻¹⁵¹.

The studies on electrical conductances were pursued vigorously both theoretically and experimentally during the last fifty years and a number of important theoretical equations have been derived. We shall dwell briefly on some of these aspects and our discussion will be limited to the studies in non-aqueous and mixed solvents.

The successful application of the Debye-Hückel theory of interionic associations was made by Onsager¹⁵² in deriving the Kohlrausch's equation

$$\Lambda = \Lambda^{\circ} - S\sqrt{c} \quad (69)$$

where

$$S = \alpha\Lambda^{\circ} + \beta \quad (70)$$

$$\alpha = \frac{(Ze)^2 \kappa}{3(2+\sqrt{2}) \epsilon_r k T c^{1/2}} = 82.406 \times 10^4 \frac{Z^3}{(\epsilon_r T)^{3/2}} \text{ in mol}^{-1/2} \text{ l}^{1/2} \quad (71)$$

$$\text{and } \beta = \frac{Z^2 e F \kappa}{3\pi \eta c^{1/2}} = 82.487 \frac{Z^3}{\eta (\epsilon_r T)^{1/2}} / \text{scm}^2 \text{ mol}^{-3/2} \text{ l}^{1/2} \quad (72)$$

η = viscosity in Poise.

The equation took no account for the short range interactions and shape or size of the ions in solution. The ions were regarded as

rigid charged spheres in an electrostatic and hydrodynamic continuum i.e., the solvent¹⁵³. In the subsequent years, Pitts (1953)¹⁵⁴ and Fuoss and Onsager (1957)^{143,155} independently worked out the solution of the problem of electrolytic conductance accounting for both long-range and short-range interactions.

However, the values obtained for the equivalent conductances at infinite dilution using Fuoss-Onsager theory differed considerably¹⁵³ from those obtained using Pitts theory and the derivation of the Fuoss-Onsager equation was questioned^{139,156,157}. The observation was confirmed by Fuoss-Hsia¹⁵⁸. The original F.O. equation was modified by Fuoss and Hsia¹⁵⁸ who recalculated the relaxation field, retaining the terms which had previously been neglected. The equation usually employed is of the form¹³⁹

$$\Lambda = \Lambda^{\circ} - \frac{\alpha \Lambda^{\circ} \sqrt{c}}{(1+\kappa a)(1+\kappa a/\sqrt{z})} - \frac{\beta \sqrt{c}}{1+\kappa a} + G(\kappa a) \quad (73)$$

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

$$\Lambda = \Lambda^{\circ} - s\sqrt{c} + Ec \ln c + J_1 c - J_2 c^{3/2} \quad (74)$$

is generally employed in the analysis of experimental results.

However, it has been found that these equations have certain limitations and in some cases fail to fit the experimental data. Some of these results have been discussed elaborately by Fernandez-Prini^{139,159,160}. Further correction of equation (74) was made by Fuoss and Accascina¹⁴³. They took into consideration the change in the viscosity of the solutions and assumed the validity of Walden's rule. The new equation is

$$\Lambda = \Lambda^{\circ} - S\sqrt{c} + Ec \ln c + J_1c - J_2c^{3/2} - B\Lambda^{\circ}c \quad (75)$$

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

It has been observed that Pitt's equation gives better fit to the experimental data in aqueous solutions¹⁶¹.

Ion-association

The equation (75) given above successfully represents the behaviour of completely dissociated electrolytes. The plot of Λ against \sqrt{c} (limiting Onsager equation) is used to assign the dissociation or association of electrolytes. Thus, if Λ° (experimental) is greater than Λ° (theoretical) i.e., if positive deviations occur (ascribed to short range hard-core repulsive interaction between ions), the electrolyte may be regarded as completely dissociated but if negative deviations ($\Lambda^{\circ}_{\text{expt}} < \Lambda^{\circ}_{\text{theo}}$) or positive deviations

from the Onsager limiting tangent ($\alpha \Lambda^\circ + \beta$) occur, the electrolytes may be regarded to be associated. Here the electrostatic interactions are large so as to cause association between cations and anions. The difference in $\Lambda^\circ_{\text{expt}}$ and $\Lambda^\circ_{\text{theo}}$ would be considerable with increasing association¹⁶².

Conductance measurements help us to determine the values of the ion-pair association constant K_A for the process



where
$$K_A = (1 - \alpha) / \alpha^2 c \gamma_{\pm}^2 \quad (77)$$

and
$$\alpha = 1 - \alpha^2 c K_A \gamma_{\pm}^2 \quad (78)$$

For strongly associated electrolytes, K_A and Λ° have been determined using Fuoss-Kraus equation¹⁶³ or Shedlovsky's equation¹⁶⁴

$$\frac{T(z)}{\Lambda} = \frac{1}{\Lambda^\circ} + \frac{K_A}{(\Lambda^\circ)^2} \times \frac{c \gamma_{\pm}^2 \Lambda}{T(z)} \quad (79)$$

where $T(z) = F(z)$ (Fuoss-Kraus) and

$$1/T(z) = S(z) \quad (\text{Shedlovsky})$$

$$F(z) = 1 - z (1 - z (1 - z (1 - \dots)^{-\frac{1}{2}})^{-\frac{1}{2}})^{-\frac{1}{2}} \quad (80)$$

and
$$S(z) = 1 + z + z^2/2 + z^3/8 + \dots \quad (81)$$

The plot of $T(Z)/\Lambda$ against $c^{1/2} \Lambda / T(Z)$ 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 determined values of Λ° and K_A from equation (79). The Fuoss-Hsia conductance equation for associated electrolytes is given by

$$\Lambda = \Lambda^\circ - S\sqrt{\alpha c} + E(\alpha c) \ln(\alpha c) + J_1(\alpha c) - J_2(\alpha c)^{3/2} - K_A \Lambda^\circ{}^2 (\alpha c) \quad (82)$$

This equation was modified by Justice¹⁶⁵. The conductance of symmetrical electrolytes in dilute solutions can be represented by the equations

$$\Lambda = \alpha \left[\Lambda^\circ - S\sqrt{\alpha c} + E(\alpha c) \ln(\alpha c) + J_1(R)\alpha c - J_2(R)(\alpha c)^{3/2} \right] \quad (83)$$

$$(1 - \alpha) / \alpha^2 c^{1/2} = K_A \quad (84)$$

$$\ln \gamma_{\pm} = - Kq^2 / (1 + K_R \sqrt{\alpha c}) \quad (85)$$

The conductance parameters are obtained from a least square treatment after setting

$$R = q = e^2 / 2 \epsilon k T \quad (86)$$

(Bjerrum's critical distance)

According to Justice, the method of fixing the J coefficient by setting $R = q$ clearly permits a better-defined value of K_A to be obtained. Since the equation (83) is a series expansion truncated at the $c^{3/2}$ term, it would be preferable that the resulting error be absorbed as much as possible by J_2 rather than by K_A , whose theoretical importance is greater as it contains the information concerning short-range cation-anion interaction.

From the experimental values of the association constant K_A , one can use two methods in order to determine the distance of closest approach a^0 of two free ions to form an ion-pair. The following equation has been proposed by Fuoss¹⁶⁶

$$K_A = (4\pi N a^3 / 3000) \exp(e^2 / a \epsilon kT) \quad (87)$$

In some cases, the magnitude of K_A was too small to permit a calculation of a^0 . The distance parameter was finally determined from the more general equation due to Bjerrum¹⁶⁷

$$K_A = (4\pi N / 1000) \int_{r=a}^{r=q} r^2 \exp(z^2 e^2 / r \epsilon kT) dr \quad (88)$$

The equation neglects specific short-range interactions except for solvation in which the solvated ion can be approximated by a hard sphere model. The method has been successfully utilised by Douh ret¹⁶⁸.

Ion-size parameter and ionic association

The equation (75) can be written as

$$\Lambda' = \Lambda^{\circ} + S\sqrt{c} - Ec \ln c = \Lambda^{\circ} + (J - B\Lambda^{\circ})c = \Lambda^{\circ} + J'c \quad (89)$$

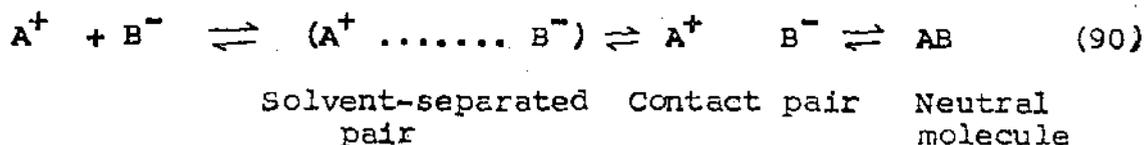
(with J_2 term omitted)

Thus, a plot of Λ' vs. C gives a straight line with Λ° as intercept and J' or $(J - B\Lambda^{\circ})$ as slope. Assuming $B\Lambda^{\circ}$ to be negligible, a° values can be calculated from J' . The a° values obtained by this method in DMSO were much smaller¹⁶² than would be expected from the sums of the crystallographic radii of the ions. One of the reasons attributed to it is ion-solvent interactions which are not included in the continuum theory on which the conductance equations are based. The inclusion of dielectric saturation results in an increase in a° values (much in conformity with the crystallographic radii) of alkali metal salts (having ions of high charge density) in sulpholane. The viscosity correction (which should be $B\Lambda c$ rather than $B\Lambda^{\circ}c$) leads to a larger value of a° ¹⁶⁹, still the agreement is poor. However, little or real physical significance may be attached to the distance of closest approach derived from J' ¹⁷⁰.

Fuoss¹⁷¹ in 1975 proposed a new conductance equation. He¹⁷¹ subsequently put forward another conductance equation in 1978 which replaced the old one. He classified the ions of electrolytic solutions in one of the three categories : (1) those which find an ion of opposite charge in the first shell of 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:



Contact pairs of ionogens may rearrange to neutral molecules

$A^+B^- \rightleftharpoons AB$ e.g. H_3O^+ and CH_3COO^- . Let γ be fraction of solute present as unpaired ($r > R$) ions. The concentration of unpaired ion is $c\gamma$. If α be the fraction of paired ions ($r \leq R$), the concentration of solvent-separated pair is $c(1 - \gamma)(1 - \alpha)$ and that of contact pair is $\alpha c(1 - \alpha)$.

The equilibrium constant for (90) are

$$K_R = (1 - \alpha)(1 - \gamma) / c\gamma^2 f^2 \quad (91)$$

$$K_S = \alpha / (1 - \alpha) = \exp(-E_S/kT) = e^{-\epsilon} \quad (92)$$

where K_R describes formation and separation of solvent-separated pairs by diffusion in and out of spheres of diameter R around cations and can be calculated by continuum theory; K_S is the constant

describing the specific short-range ion-solvent and ion-ion interactions by which contact pairs form and dissociate; E_s is the difference in energy between a pair in the states ($r = R$) and ($r = a$); ϵ is E_s measured in units of kT . From (92),

$$1 - \alpha = 1/(1 + K_s) \quad (93)$$

Substitution in (91) gives the conductometric pairing constant

$$K_A = (1 - \gamma) c \gamma^2 f^2 = K_R / (1 - \alpha) = K_R (1 + K_s) \quad (94)$$

which determines the concentration $c \gamma$ of active ions, 'active' in the sense that they produce the long-range interionic effects. The contact pairs behave like electrical dipoles to an external field X , contributing only to charging current. Both contact pairs and solvent-separated pairs are left as virtual dipoles by unpaired ions, their interaction with unpaired ions is therefore neglected in calculating long-range effects. The various patterns can be reproduced by theoretical functions of the form

$$\Lambda = p [\Lambda^\circ (1 + \Delta X/X) + \Delta \Lambda_e] \quad (95)$$

$$\Lambda = p [\Lambda^\circ (1 + R_X) + E_L] \quad (96)$$

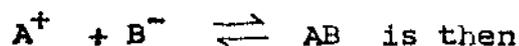
where R_X and E_L are relaxation and hydrodynamic terms respectively. The quantity p is the fraction of solute which contributes to conductance current and is given by

$$p = 1 - \alpha(1 - \gamma) \quad (97)$$

In case of ionogens or for ionophores in solvents of low dielectric constant, α is very near to unity ($-E_s/kT \gg 1$) and the equation becomes

$$\Lambda = \gamma \left[\Lambda^0 (1 + R_X) + E_L \right] \quad (98)$$

The equilibrium constant for the effective reaction



$$K_A = (1 - \gamma)/c \gamma^2 f^2 \approx K_R K_S \quad (99)$$

because $K_S \gg 1$

The parameters and the variables are related by the set of equations

$$\gamma = 1 - Kc \gamma^2 f^2 \quad (100)$$

$$-\ln f = \beta k/2 (1 + kR); \quad \beta = e^2 / (\epsilon kT) \quad (101)$$

$$-\epsilon = \ln[\alpha / (1 - \alpha)] \quad (102)$$

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

Limiting equivalent conductances

The limiting equivalent conductance of an electrolyte can be easily determined from the theoretical equations and experimental observations. At infinite dilution, the motion of an ion is limited solely by the interactions with surrounding solvent molecules as the ions are infinitely apart. Under these conditions, the validity of Kohlrausch's law of independent migration of ions is almost axiomatic. Thus

$$\Lambda^{\circ} = \lambda_{+}^{\circ} + \lambda_{-}^{\circ} \quad (103)$$

At present, the limiting equivalent conductance is the only function which can be divided into ionic components using experimentally determined transport number of ions, i.e.,

$$\lambda_{+}^{\circ} = t_{+} \Lambda^{\circ} \quad \text{and} \quad \lambda_{-}^{\circ} = t_{-} \Lambda^{\circ} \quad (104)$$

Thus from the accurate values of t_{\pm} of ions, it is possible to separate the contributions due to cations and anions in the solute-solvent interactions¹⁷². However, accurate transference number determinations are limited to few solvents only. Spiro¹⁷³ and more recently Krumgalz¹⁷⁴ have made extensive reviews on this subject.

In the absence of experimentally measured transference numbers, it would be useful to develop indirect methods to obtain the limiting ionic equivalent conductances in organic solvents for

which experimental transference numbers are not yet available.

The methods have been summarized by Krumgalz^{174a)} and some important points are mentioned below:

(i) Walden equation¹⁷⁵

$$(\lambda_{\pm}^{\circ})_{\text{acetone}}^{25} \eta_{\circ \text{acetone}} = (\lambda_{\pm}^{\circ})_{\text{water}}^{25} \eta_{\circ \text{water}} \quad (105)$$

$$\left. \begin{aligned} \text{(ii)} \quad \lambda_{\text{Pic}}^{\circ} \eta_{\circ} &= 0.267 \\ \lambda_{\text{Et}_4\text{N}^+}^{\circ} \eta_{\circ} &= 0.296 \end{aligned} \right\} \begin{array}{l} 175, 176 \\ \text{based on } \Lambda_{\text{Et}_4\text{N Pic}}^{\circ} = 0.563 \end{array} \quad (106)$$

Walden considered the products to be independent of temperature and solvent. However, the $\Lambda_{\text{Et}_4\text{N Pic}}^{\circ}$ values used by Walden were found to differ considerably from the data of subsequent more precise studies and the values of (ii) are considerably different for different solvents.

$$\text{(iii)} \quad \lambda_{25}^{\circ}(\text{Bu}_4\text{N}^+) = \lambda_{25}^{\circ}(\text{Ph}_4\text{B}^-) \quad (107)$$

(this equality holds good in nitrobenzene and its mixtures with CCl_4 but is not realized in methanol, acetonitrile and nitromethane).

$$\text{(iv)} \quad \lambda_{25}^{\circ}(\text{Bu}_4\text{N}^+) = \lambda_{25}^{\circ}(\text{Bu}_4\text{B}^-) \quad (108)$$

The method appears to be sound as the negative charge on boron in Bu_4B^- ion is completely shielded by four invert butyl groups as in the Bu_4N^+ ion while this phenomenon was not observed in case of Ph_4B^- . But the method could not be checked due to lack of accurate transference data

$$(v) \lambda_{25}^{\circ}(\text{R}_4\text{N}^+) = \frac{ZF^2}{6\pi(N\eta_0[r_1 - (0.0103\epsilon_0 + r_y)])}^{179} \quad (109)$$

where Z and r_1 are the charge and crystallographic radius of the proper ion; η_0 and ϵ_0 are the viscosity and dielectric constant of the medium; r_y is an adjustable parameter taken equal to 0.85 \AA for dipolar non-associated solvents and 1.13 \AA for hydrogen-bonded and other associated solvents.

However, large discrepancies were observed between the experimental and calculated values^{174a)}. In a recent paper^{174b)} Krumgalz examined Gill's approach more critically using conductance values in many solvents and found the method to be reliable in three solvents e.g., 1-butanol, acetonitrile and nitromethane.

$$(vi) \lambda_{25}^{\circ}(\text{i-Am}_3\text{BuN}^+) = \lambda_{25}^{\circ}(\text{Ph}_4\text{B}^-)^{180} \quad (110)$$

It has been found from transference measurements that the $\lambda_{25}^{\circ}(\text{i-Am}_3\text{BuN}^+)$ and $\lambda_{25}^{\circ}(\text{Ph}_4\text{B}^-)$ values differ from one another by 1%.

$$(vii) \lambda_{25}^{\circ}(\text{Ph}_4\text{B}^-) = 1.01 \lambda_{25}^{\circ}(\text{i-Am}_4\text{B}^-)^{181} \quad (111)$$

The equality is found to be true for various organic solvents.

Krumgalz^{174a)} suggested a method for determining the limiting ion conductances in organic solvents or organic mixtures. The method is based on the fact 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. The phenomenon of non-solvation is confirmed by N.M.R. measurements and is utilised as a suitable model for apportioning Λ° values into ionic components for non-aqueous electrolytic solutions.

Considering 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

$$r_s = \frac{|z|F^2}{A\eta N\eta_0\lambda_{\pm}^\circ} \quad (112)$$

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 dimension of the non-solvated tetraalkyl (aryl) onium ions, must be constant, we have

$$\lambda_{\pm}^\circ \eta_0 = \text{Constant} \quad (113)$$

This relation has been verified using λ_{\pm}° values determined with precise transference numbers. The product becomes constant and independent of the chemical nature of the organic solvents for the $i\text{-Am}_4\text{B}^{-}$, Ph_4As^{+} and Ph_4B^{-} ions and for tetraalkylammonium cations starting from Et_4N^{+} . The relationship can be well utilised to determine λ_{\pm}° values of ions in other organic solvents from the determined Λ° values.

We have used Bu_4NBPh_4 as the 'reference electrolyte', but instead of equal division, we divided the Λ° values using the method similar to that proposed by Krungalz¹¹⁹ for division of B-values

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^{+})}{\lambda^{\circ}(\text{Ph}_4\text{B}^{-})} = \frac{r(\text{Ph}_4\text{B}^{-})}{r(\text{Bu}_4\text{N}^{+})} = \frac{5.35}{5.00} = 1.07 \quad (114)$$

The r values have been taken from the works of Gill et al^{182,183}.

Though nothing can be said definitely regarding the accuracy of the method, some indirect evidences regarding the reliability of the values may be provided. The value of the ratio $\lambda^{\circ}(\text{BPh}_4^{-}) / \lambda^{\circ}(\text{Bu}_4\text{N}^{+})$ becomes 1.06 if we choose $r(\text{Bu}_4\text{N}^{+}) = 3.85 \text{ \AA}$ and $r(\text{BPh}_4^{-}) = 4.08 \text{ \AA}$ as suggested by Krungalz^{119,184}.

Fuoss et al¹⁸⁵⁻¹⁸⁸ assumed, from extensive measurements of R_4NBPh_4 salts in various mixed organic solvents, that the limiting

transference number of Bu_4N^+ in Bu_4NBPh_4 is 0.519 and independent of the solvent (this is claimed to be valid within $\pm 1\%$). This gives 1.079 for $\lambda^\circ(\text{Bu}_4\text{N}^+) / \lambda^\circ(\text{Ph}_4\text{B}^-)$ which is close to 1.07.

D'Aprano and Fuoss¹⁸⁸ used Bu_4NBPh_4 to calculate single-ion conductance in mixed organic solvents applying the relations

$$\lambda^\circ(\text{Bu}_4\text{N}^+) = 0.213/\eta_0 \text{ and } \lambda^\circ(\text{Ph}_4\text{B}^-) = 0.201/\eta_0 \text{ which means}$$

$$\lambda^\circ(\text{Bu}_4\text{N}^+) / \lambda^\circ(\text{Ph}_4\text{B}^-) = 1.06.$$

Moreover, since the charge is equal to the number of ions, the equivalent conductances of these ions depend on their mobilities, the divisions may be in terms of the reciprocal of their van der Waals' volume i.e.

$$\frac{\lambda^\circ(\text{Bu}_4\text{N}^+)}{\lambda^\circ(\text{Ph}_4\text{B}^-)} = \frac{186.8}{179.1} = 1.04 \quad (115)$$

The van der Waals volume have been taken from the works of Lawrence and Sacco¹⁰⁷. However, the ratio comes out to be slightly lower than the usual.

In absence of accurate transference data in binary mixtures of organic solvents, it is difficult to compare the single-ion values and to test the validity of equation (114), but the values calculated by this method appear to be correct in different organic or mixed organic solvents. However, in aqueous binary mixtures the

solvation pattern may be different and the validity of this method may be questioned. In absence of a suitable method, nothing can be said conclusively.

Recently, Gill et al¹⁸⁹ proposed the following equation

$$\frac{\lambda^{\circ}(\text{Bu}_4\text{N}^+)}{\lambda^{\circ}(\text{Ph}_4\text{B}^-)} = \frac{5.35 - (0.0103 (\epsilon_0 + r_y))}{5.00 - (0.0103 (\epsilon_0 + r_y))} \quad (116)$$

and the ratio is 1.07 as used by us.

Solvation number¹⁷²

If the limiting conductance of the ion i of charge Z_i is known, the effective radius of the solvated ion can easily be determined from the Stokes' law. The volume of the solvation shell, V_s can be written as

$$V_s^s = \frac{4}{3} \pi (r_s^3 - r_c^3) \quad (117)$$

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

$$n_s = V_s^s / \bar{v}_o \quad (118)$$

Assuming Stokes' relation to hold, the ionic solvated volume should be obtained, because of packing effects¹⁹⁰, from

$$V_s^{\circ} = 4.35 r_s^3 \quad (119)$$

when V_s° is expressed in mol/mole and r_s in angstroms. However, this method of determination of solvation numbers is not applicable to ions of medium size though a number of empirical^{58,63,144} and theoretical corrections¹⁹¹⁻¹⁹⁴ have been suggested in order to apply it to most of the ions.

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

$$\lambda_i^{\circ} = \frac{0.819 |z_i|}{\eta_0 R_i} \quad (120)$$

where, η_0 , the macroscopic viscosity of the solvent, is expressed in poise and R_i in angstroms. 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

$$\lambda_i^{\circ} \eta_0 = \frac{0.819 |z_i|}{R_i} = \text{constant} \quad (121)$$

This is known as Walden rule¹⁹⁵. The effective radii obtained using this equation can be used to estimate the solvation numbers. The failure of the Stokes' radii to give the effective size of the solvated ions for small ions is often attributed to the inapplicability of Stokes' law to molecular motion.

Robinson and Stokes¹⁴⁴, Nightingale¹¹³ and others¹⁹⁶⁻¹⁹⁸ have suggested a method of correcting the radii. The tetraalkylammonium ions were assumed to be not solvated and by plotting the Stokes' radii against the crystal radii of these large ions, a calibration curve was obtained for each solvent. This approach, however, suffers from one serious flaw. The basic assumption on which this approach rests is that the Walden product is invariant with temperature. Experimental results¹⁶² indicate that his assumption is incorrect and that the resulting solvation numbers obtained from this type of correction to Stokes' law are meaningless. The idea of microscopic viscosity¹⁹⁹ was invoked without much success^{200,201} but it has been found that

$$\lambda_i \eta^p = \text{constant} \quad (122)$$

where p is usually 0.7 for alkali metal or halide ions and $p = 1$ for the large ions^{202,203}.

Attempts to explain the change in Stokes' radius R_i have been made. The apparent increase in the real radius r has been attributed to ion-dipole polarisation and the effect of dielectric saturation on R . Fuoss²⁰⁴ noticed the dependence of the Walden product, $\Lambda^\circ \eta_0$, on the dielectric constant and considered the effect of electrostatic forces on the hydrodynamics of the system. He proposed that the dielectric relaxation in the solvent caused by ion motion leads to excess frictional resistance. He proposed the relation

$$\lambda_{i,0}^{\circ} = \frac{F e |z_i|}{6\pi R_{\infty} (1 + A/\epsilon R_{\infty}^2)} \quad (123)$$

from which the classical Stokes' radius, may be derived as

$$R_i = R_{\infty} + A/\epsilon \quad (124)$$

where R_{∞} is the hydrodynamic radius of the ion in a hypothetical medium of dielectric constant where all electrostatic forces vanish and A is an empirical constant.

In 1961, Boyd¹⁹² gave the expression

$$\lambda_i^{\circ} = \frac{F e |z_i|}{6\pi\eta_0 r_i} \left[1 + \frac{2}{27} \frac{1}{\pi\eta_0} \frac{z_i^2 e^2 \tau}{r_i^4 \epsilon_0} \right] \quad (125)$$

considering the effect of dielectric relaxation on ionic motion; τ is the Debye relaxation time for the solvent dipoles.

Zwanzig¹⁹³ treated the ion as a rigid sphere of radius r_i moving with a steady velocity V_i through a viscous incompressible dielectric continuum. The conductance equation suggested by Zwanzig is

$$\lambda_i^{\circ} = \frac{z_i e F}{A_v \pi \eta_0 r_i + A_0 [z_i^2 e^2 (\epsilon_r^{\circ} - \epsilon_r^{\infty}) \tau / \epsilon_r^{\circ} (2\epsilon_r^{\circ} + 1) r_i^3]} \quad (126)$$

where ϵ_r^o , ϵ_r^c are the static and limiting high frequency (optical) dielectric constants respectively, $A_v = 6$ and $A_D = 3/8$ for perfect sticking and $A_v = 4$ and $A_D = 3/4$ for perfect slipping. The above equation can be written as

$$\lambda_{11} = A v r_1^3 / (r_1^4 + B) \quad (127)$$

The theory predicts²⁰⁵ that λ_{11}^o passes through a maximum of $27^{1/4}/4B^{1/4}$ at $r_1 = (3B)^{1/4}$. The phenomenon of maximum conductance is well known. The relationship holds good to a reasonable extent for cations in aprotic solvents but fails in case of anions. The conductance, however, falls off rather more rapidly than predicted with increasing radius.

For comparison of the results in different solvents, equation (126) can be rearranged as²⁰⁶

$$\frac{Z_i^2 e F}{\lambda_i^o \eta_o} = A_v \pi r_i + \frac{A_D Z_i^2}{r_i^3} \frac{e^2 (\epsilon_r^o - \epsilon_r^c)}{\epsilon_r^o (2\epsilon_r^o + 1)} \frac{\tau}{\eta_o} \quad (128)$$

or

$$L^* = A_v \pi r_i + (A_D Z_i^2 / r_i^3) P^* \quad (129)$$

In order to test Zwanzig's theory, the equation (129) was applied to methanol, ethanol, acetonitrile, butanol and pentanol solutions where accurate conductance and transference data are available²⁰⁵⁻²¹⁰. All the plots were found to be linear. But the

radii calculated from the intercepts and slopes are far apart from equal except in some cases where moderate success is noted. It is noted that the relaxation effect is not the predominant factor in affecting ionic mobilities and that these mobility differences could be explained qualitatively if the microscopic properties of the solvent, dipole moment and free electron pairs were considered the predominant factors in the deviation from Stokes' law¹⁷².

It is noted that the Zwanzig theory is successful for large organic cations in aprotic media where solvation is likely to be minima and where viscous friction predominates over that caused by dielectric relaxation. The theory breaks down whenever the dielectric relaxation term becomes large i.e., for solvents of high P^* and for ions of small r_i . Like any continuum theory, Zwanzig theory has the inherent weakness of its ability to account for the structural features²¹¹ e.g.,

(1) It does not allow for any correlation in the reorientation of the solvent molecules as the ion passes by and this may be the reason why the equation does not apply to hydrogen-bonded solvents²¹².

(2) The theory does not distinguish between positively and negatively charged ions and therefore can not explain why certain anions in dipolar aprotic media possess considerably higher molar conductances than the faster cations²¹¹.

The Walden products in case of mixed solvents does not show any constancy but it passes through a maximum in case of DMF-H₂O and DMA - H₂O mixtures²¹³⁻²¹⁵ and other aqueous binary mixtures²¹⁶⁻²¹⁹. To derive expressions for the variation of the Walden products with the composition of mixed polar solvents, various attempts have been made^{192,193,220} with different models for ion-solvent interactions, but no satisfactory expression has been derived taking into account all types of ion-solvent interactions because:

(1) it is difficult to include all types of interactions between ions as well as solvents in a single mathematical expression;

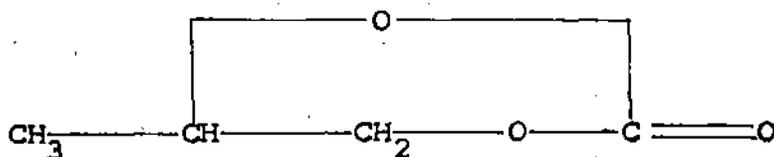
(2) it is not possible to account for some specific properties of different kinds of ions and solvent molecules²¹³. Ions moving in a dielectric medium experience a frictional force due to dielectric loss arising from ion-solvent interactions with the hydrodynamic force. Zwanzig's expression though accounts for a change in Walden product with solvent composition, does not account for the maxima. Hemmes²²¹ suggested that the major deviations in the Walden product are due to the variation of the electrochemical equilibrium between ions and solvent molecules with the composition of mixed polar solvents. In cases where more than one type of solvated complexes are formed, there should be a maximum and/or a minimum in the Walden product. This is supported by experimental observations. Hubbard and Onsager²²² have developed the kinetic theory of ion-solvent interaction within the framework of continuum mechanics where the

concept of kinetic polarisation deficiency has been introduced.

However, quantitative expression is still awaited. Further improvements^{223,224} naturally must be in terms of (1) sophisticated treatment of dielectric saturation, and (2) specific structural effects involving ion-solvent interactions.

Propylene Carbonate (PC)

Propylene carbonate (PC) or 4-methyl-1,3-dioxolan-2-one has drawn the first attention of physical chemists in early 1960s. PC is known to be a structureless dielectric ($\epsilon = 64.40$ at 25°C)²²⁵ with little if any, or no self-association present²²⁶. It is dipolar aprotic and inert (resistant to chemical attack) in nature. It has been extensively used in high energy batteries²²⁷ and various other electrochemical studies²²⁸ related to it. PC is actually a cyclic organic ester and has the following structure:



Propylene carbonate

Simple consideration of the molecular structure indicates that PC molecules in general, lack a well-developed centre of positive charge and thus, it is expected that the interactions with anions would be weak in nature. Moreover, the positive centres in PC molecule are much less accessible to ions. Yeager and his co-workers²²⁹

have reported the electron density distribution in PC molecule by using a semiempirical molecular orbital calculation assuming it to possess a planar structure having the double bond in the plane of the ring

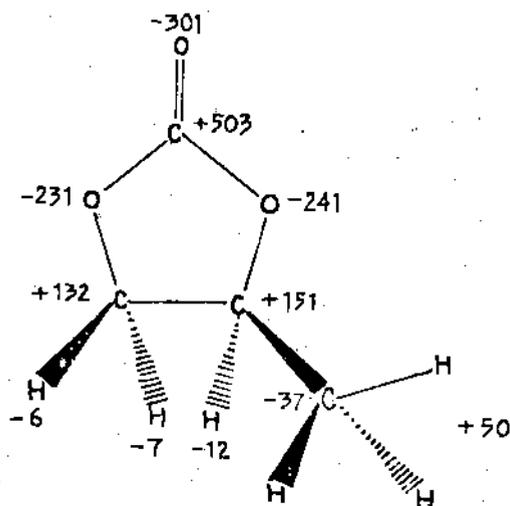


Fig. 1 Electron density distribution of the propylene carbonate molecule

From the above figure, it is observed that the interaction of cations with PC is not restricted to the carbonyl oxygen alone and may also have extensive ring interactions. It is further observed that the positive centre is not easily accessible to anions and hence it is expected to act as a poor anion solvator.

Commendable works in pure PC have already been reported in the literature. Of these, studies on the dielectric properties²²⁶ at various temperatures (220.15 - 293.15 K) of PC, solubilities^{225,230},

partial molar volumes of different electrolytes²³¹⁻²³³, solvation enthalpies^{31,234,235} and other thermodynamic properties including transfer functions²⁹ and emf studies²³⁶ of alkali metal salts are noteworthy. Kay et al²³⁷ have made an extensive study on the ionic volumes of a number of electrolytes from density, ultrasonic vibration potential and transference number measurements in PC at 25°C. Fuoss and Hirsch²³⁸ have reported the limiting equivalent conductance of tetrabutylammonium tetraphenylborate in PC at 25°C. Mukherjee et al^{239,240} and Yeager and his co-workers^{241,242} have made some studies on the viscosity and conductance behaviour of some common halides, perchlorates and trifluoroacetates etc. in PC at 25°C. Yeager²²⁹ further made some spectroscopic studies on ionic solvation by using IR and NMR techniques. Takeda et al²⁴³ have reported Stokes radii of some common ions in PC by using conductometry. Grigo and his co-workers²⁴⁴ have attempted ion-solvent interaction of some ions in PC from theoretical point of view.

Notably enough, relatively very few studies have been reported in binary mixed solvents of PC. Propylene carbonate and water are not miscible at all proportions, a separation of phase has been observed between 0.036 and 0.7 mole fractions of PC²⁴⁵. But however, PC is miscible with most of the organic solvents. Studies on the fundamental physico-chemical properties like density, viscosity and dielectric constant for PC-acetonitrile and PC-isopropanol binary mixtures over the entire composition range at different temperatures have been reported by Ritzoulis^{246,247} and

observed no specific interaction or association complex between the two unlike molecules. PC-1,2-dimethoxyethane mixture at a particular composition was tested for use in high energy batteries by Matsuda et al²⁴⁸. Few other non-aqueous binary solvent systems of PC were also investigated from the same view point²⁴⁹⁻²⁵¹. Pawlak and his co-workers²⁵² have studied the solvent effects of PC-methanol mixtures on the dissociation constants of some phenols and carboxylic acids. However, the transport properties in binary solvent mixtures of propylene carbonate have so far not been studied barring a few²⁴⁸⁻²⁵⁰. In PC-methanol mixtures, the dielectric constant and density are found to increase monotonically with increasing PC content in the mixture²⁵². Butler and his associates²⁵³ have investigated the selective solvation of some ions by water in propylene carbonate from proton magnetic resonance (chemical shift) measurements. Cox et al³⁰ have reported free energies, entropies and enthalpies of transfer for some alkali metal and silver halides from PC to PC-dimethylsulphoxide mixtures at 25°C.

Binary mixed organic solvent systems like PC-DME²⁴⁸, PC-THF²⁵⁴ at a particular composition have been tested and recommended for use in high energy battery technology. But their physico-chemical properties have so far not been studied over the entire composition range at different temperatures. For that reason, an attempt has been made here to investigate the solvent-solvent interactions from their physico-chemical properties at different temperatures. Again the knowledge of ion-solvent interactions of

different solutes in the solvent is capable of indicating the potential usefulness of PC in various technologies. Transport properties of electrolyte solutions such as ionic conductance and viscosity can provide information concerning the nature of kinetic entities from which the ion-solvent interaction can be inferred. Information on these interactions can also be had from the thermodynamic properties such as solubilities, free energies of solution and other thermodynamic transfer functions. Solubility technique finds unique application for understanding ion-solvent interactions in a solvent when the electrolytes under investigation are not soluble enough so that the more conventional methods like conductometry and viscometry can hardly be applied.

We have, therefore, devoted our attention to the studies on the thermodynamic, spectroscopic and transport properties of some electrolytes in PC and its binary mixtures with methanol.

The results have been described in subsequent chapters.

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CHAPTER-II

EXPERIMENTAL SECTION

(Materials and Methods)

Chemicals

Alkali metal chlorides and bromides (Fluka, purum or puriss) were dried in vacuo for a long time immediately prior to use and were used without further purification.

Lithium perchlorate (LiClO_4 ; Fluka, > 99% pure) was recrystallized three times from deionised distilled water and dried under vacuum for several days¹. Sodium perchlorate (NaClO_4 ; AR, E. Merck, Germany) was recrystallized several times from water + methanol mixtures and dried in vacuo at 423 K for 96 hours. Other alkali metal perchlorates were prepared by mixing equimolar solutions of corresponding alkali metal chloride and sodium perchlorate, washed with 1:1 methanol-water mixture and then recrystallized thrice from water and dried in vacuum at 473 K over calcium chloride and silica gel for several days².

Tetraalkylammonium bromides (Fluka, purum or puriss) were purified in the manner given in the literature^{3,4}. 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 .

Tetramethylammonium bromide (Me_4NBr) was recrystallized from a 1:1 mixture of methanol-water and dried at 363 K for 48 hours⁴.

Tetraethylammonium bromide (Et_4NBr) was recrystallized from methanol and dried at 363 K 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 333 K for 48 hours.

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

Lithium tetrafluoroborate (LiBF_4 ; Fluka) was dried under vacuum at high temperatures for 48 hours and was used without further purification.

Sodium tetraphenylborate (NaBPh_4 ; Fluka, puriss) was recrystallized three times from acetone and dried in vacuum at 353 K for 72 hours.

Tetrabutylammonium tetrabutylborate (Bu_4NBu_4 , Alfa products) was dissolved in methanol, reprecipitated from water and dried in vacuum at 343 K⁵.

Tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) was prepared by precipitation from Bu_4NBr and NaBPh_4 in water and the precipitate was washed 5 times by water. The bulky white precipitate was dried and recrystallized four times from 1:3 water-acetone and finally dried for several days at 313 K under vacuum⁶.

Tetraphenylarsonium chloride (Ph_4AsCl , Fluka) was recrystallized from absolute ethanol solution by dry ether twice and dried in vacuum⁷.

Tetraphenylphosphonium bromide (Ph_4PBr ; Fluka, purum) was dissolved in ethanol, reprecipitated by the addition of dry ether and vacuum dried at 373 K⁷.

Solvents

Propylene carbonate (PC) (E. Merck, Germany; > 99% pure) was dried over freshly ignited quicklime for several hours⁸ and then distilled three times under reduced pressure under nitrogen, the middle fraction being taken each time. The purified sample had a density $1.19883 \text{ g cm}^{-3}$, a coefficient of viscosity 2.471 cP and a specific conductance $0.73 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C; these values are in good agreement with the literature values⁹, which are $1.19965 \text{ g cm}^{-3}$, 2.48 cP and $10^{-7} \text{ S cm}^{-1}$ respectively.

Methanol (E. Merck, India, uvasol grade) was dried over 3A molecular sieves and distilled fractionally. Middle fraction was taken and further distilled¹⁰. Physical properties of the purified sample at 25°C ($\rho = 0.79663 \text{ g cm}^{-3}$) and $\eta = 0.5437 \text{ cP}$) agree well with the literature values¹¹ which are : $\rho = 0.78664 \text{ g cm}^{-3}$ and $\eta = 0.5445 \text{ cP}$.

2-methoxyethanol (ME) (G.R.E. Merck) was distilled in an all glass apparatus. The physical properties at 25°C of purified ME were : density $0.96002 \text{ g cm}^{-3}$ and viscosity 1.5414 cP. The viscosity and density values are in reasonable agreement with the literature values¹¹ which are 1.60 cP and $0.96204 \text{ g cm}^{-3}$ respectively.

1,2-dimethoxyethane (DME) (Fluka, purum) was shaken well with FeSO_4 (AR, BDH) for 1-2 hours, decanted and distilled. The distillate was refluxed for 12 hours and redistilled over metallic sodium¹². The boiling point (84.5°C) and density (0.86132 gcm^{-3} at 25°C) compared fairly well with the corresponding literature values¹³, which are 85°C and 0.86120 gcm^{-3} respectively.

Tetrahydrofuran (THF) (E. Merck, India) was kept over KOH, refluxed for 24 hours and distilled over LiAlH_4 ¹⁴. The density (0.88072 gcm^{-3}) and viscosity (0.4630 cP) at 25°C of the purified sample are in good conformity with the literature values¹⁵, 0.8811 gcm^{-3} and 0.46 cP respectively.

Mixed Solvents

The mixed solvents containing 0.10, 0.20, 0.40 and 0.60 mole fractions of PC were prepared by mixing the requisite amounts of methanol and PC by weight. Solvent properties of PC + Methanol mixtures at 25°C are given in Table 1.

Table 1. Solvent properties of (PC + methanol) mixtures at 25°C.

Mole fraction of PC	ϵ	ρ/gcm^{-3}	η/cP	Sp. conductance Scm^{-1}
0	32.64	0.78663	0.5437	$0.15 \times 10^{-6}^{\text{a}}$
0.10	39.20	0.86928	0.6264	1.52×10^{-6}
0.20	44.10	0.93460	0.7192	1.81×10^{-6}
0.40	51.30	1.03274	0.9747	2.25×10^{-6}
0.60	57.30	1.10363	1.2972	2.42×10^{-6}
1.00	64.40	1.19883	2.4712	0.73×10^{-6}

^afrom ref. 10

Preparation of experimental solutions

A stock solution for each salt in PC as well as in different mixed solvents was prepared by weight and the working solutions were obtained by weight dilution. The molar concentration of the solutions were calculated from molality and density values.

Methods:

(a) Density measurements

The densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 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. The precision of the density measurements was $\pm 3 \times 10^{-5} \text{ gcm}^{-3}$. The measurements were made in an oil bath maintained with an accuracy

of ± 0.005 °C of the desired temperature by means of a mercury in-glass thermoregulator and absolute temperature was determined by a platinum resistance thermometer and Muller bridge¹⁶.

(b) Viscosity measurement

The kinematic viscosities were measured by means of a suspended-level Ubbelohde¹⁷ viscometer with a flow time of about 539 s for distilled water at 25°C. The time of efflux was measured with a stop watch capable of recording 0.1 s. 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 $\pm 0.05\%$. In all cases, the experiments were performed at least in five replicates and the results were averaged.

Relative viscosities (η_r) were obtained using equation

(3):

$$\eta_r = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} \quad (3)$$

where $\eta, \eta_0; \rho, \rho_0$ and t, t_0 are the absolute viscosities, densities and flow times for the solution and solvent respectively.

The measurements were carried out in a thermostatic bath maintained with an accuracy of $\pm 0.01^\circ\text{C}$ of the desired temperature¹⁸. A 60W heating element and a toluene-mercury thermoregulator were used to maintain the temperature of the experimental thermostat which was placed in a hot-cum-cold thermostat. The temperature of the hot-cum-cold thermostat was preset at the desired temperature using a contact thermometer and relay system. The absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.

(c) Conductance measurements

Conductance measurements were carried out on a Philips Pye-Unicam PW 9509 conductivity meter with an accuracy of $\pm 0.1\%$. A 2000 Hz cycle was used. The cell constant (0.751 cm^{-1}) of the dip-type conductance cell was accurately determined using standard KCl solutions. Conductivity cell was sealed to the side of 500 cm^3 conical flask closed by a ground glass cap fitted with a side arm through which dry and pure nitrogen was passed to prevent the

admission of air into the cell when solvent or solution was added. The measurements were made in an oil bath maintained at $25 \pm 0.005^{\circ}\text{C}$ as described earlier under density measurements. All data were corrected with the specific conductance of the solvent.

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CHAPTER-III

Solubilities of Some Alkali Metal Salts, Tetraphenylarsonium Chloride and Tetraphenylphosphonium Bromide in Propylene Carbonate at 25°C Using the Ion Selective Electrode Technique

Solubility offers one of the most obvious ways of studying ionic solvation and ion-solvent interactions and it finds unique application particularly for those electrolytes which are poorly soluble in a solvent medium so that the other more conventional methods like viscometry and conductometry can hardly be applied, but in PC these values in general are not available, except of very few alkali metal halides^{1,2}. It is therefore desirable to obtain the useful solubility data particularly for the salts containing Ph_4As^+ or Ph_4P^+ ions and thus to have an idea of solute-solvent interactions in this non-aqueous medium.

Here, we have measured the solubilities of a number of 1:1 electrolytes in PC at 25°C using the ion selective electrode technique and from these, the solubility products and free energies of solution for the salts have been determined. The free energies of transfer of the electrolytes from water to PC or the corresponding transfer activity coefficients, $m\gamma_s$, have been evaluated and compared with the previous values obtained mainly from e.m.f. measurements³.

Experimental

Propylene carbonate (E. Merck, Germany; >99% pure) was purified as reported in Chapters II and VI.

All salts were of Fluka's either purum or puriss grade and were purified as described in Chapter II.

Saturated solutions were prepared by shaking the solid with the solvent in a glass-stoppered bottle at 27°C for 24 hours. The bottle was then placed in a thermostatic bath for further two days maintained at $25 \pm 0.01^\circ\text{C}$. Finally, the solution was transferred to a Campbell solubility apparatus⁴ fitted with a sintered disc and fine tube and allowed to equilibrate at 25°C. At regular intervals, the solutions were filtered by inverting the apparatus (while keeping it within the thermostat), appropriately diluted with the solvent (if necessary) and then the concentration was measured by using an Orion Ion Analyzer (Model EA 920) having an accuracy of $\pm 0.1\%$. A solution was considered saturated when two successive analysis at 2-3 days intervals indicated no change in concentration. Thus the concentrations of Cl^- , Br^- and ClO_4^- ions were determined by using specific Orion ion-selective electrodes. A double junction reference electrode was used with each of Cl^- and ClO_4^- ion electrode. However, for measuring ClO_4^- ion concentrations, the outer chamber of the reference electrode was filled with $(\text{NH}_4)_2\text{SO}_4$ solution as suggested in the brochure. A single junction

reference electrode was used in conjunction with the Br^- ion electrode. Each ion selective electrode was tested for Nernstian response. In order to check the correctness of the data, known concentration of the sample solution was measured by using the specific ion selective electrode and the results were compared. At least two trials were given for all the solutions which were under study.

Results and Discussion

Solubility data for the electrolytes in PC at 25°C (molar scale) are reported in Table 1.

The standard free energy of solution for a solute on the molar scale is usually given by the relation,

$$\Delta G_{\text{Solution}}^{\circ} = -RT \ln K \quad (1)$$

where, K is the equilibrium constant for the reaction, $\text{MX} \rightleftharpoons \text{M}^+ + \text{X}^-$. Upon introduction of the Debye-Hückel expression for the mean activity coefficient, one obtains⁵ :

$$\Delta G_{\text{Solution}}^{\circ} = 2.303 RT \left[-\nu \log m - \log \left(\gamma_+^{\nu_+} \gamma_-^{\nu_-} + \nu \delta_{\nu} d_0^{\frac{1}{2}} m^{\frac{1}{2}} \right) \right] \quad (2)$$

In equation (2), d_0 is the density of PC, δ_{ν} is the Debye-Hückel limiting slope, ν is the total number of ions and the other symbols

have their usual significance.

We have applied equation (2) to obtain the standard free energies of solution; further these were combined with the free energies of formation of the respective crystalline salts⁶ to obtain the corresponding standard free energies of formation for the alkali metal salts. Results of these calculations have been listed in Tables 1 and 2.

The transfer activity coefficients were calculated from the solubility products by using the relationship

$$\log m\gamma_{\pm} = \log m\gamma_{\pm}^2 = \log_w K_s - \log_s K_s \quad (3)$$

where, $m\gamma_{\pm}$ is the transfer activity coefficient (medium effect) and subscript w and s denote aqueous and non-aqueous solvent respectively. The values have been given in Table 2. The standard free energies of solution in water, $\Delta G_{\text{Soln}}^{\circ}(\text{H}_2\text{O})$, except for the tetraphenyl salts, have been taken from the literature^{3,7}. We have measured the solubilities of Ph_4AsCl and Ph_4PBr in water at 25°C (0.81M and 0.047M for Ph_4AsCl and Ph_4PBr respectively). Abraham *et al*⁸ have reported the free energies of solution for the tetraphenyl salts (3.48 and 4.38 for Ph_4AsCl and Ph_4PBr respectively) based on the osmotic pressure and activity coefficient data of Kalfoglou and Bowen⁹, which on comparison with the values reported in Table 2 would seem to be in error.

Single ion free energies of transfer from water to PC based on $\text{Ph}_4\text{AsBPh}_4$ convention have been reported in Table 3. The ΔG_t° values for Ph_4As^+ and Ph_4P^+ ions from water to PC have been taken from the literature³. Ionic transfer free energy values together with ionic transfer activity coefficients have been reported in Table 3. Following Latimer, Pitzer and Slansky¹⁰, we have also calculated the single ion free energies of solvation by the modified Born equation,

$$\Delta G_{\text{solv}}^\circ = -\frac{Nz^2e^2}{2} \left[1 - \frac{1}{\epsilon} \right] / (r_i + \delta) \quad (4)$$

taking $\delta_c = 0.85\text{\AA}$ and $\delta_a = 1.00\text{\AA}$ as taken by Criss et al in DMF medium⁵. The values thus obtained have been reported in Table 3.

An examination of the solubilities of the alkali metal salts (Table 1) show that most electrolytes are much less soluble in propylene carbonate than in water³ and also in some other dipolar aprotic solvents like DMSO² and DMF^{2,5}. Lithium salts are found to be more soluble in PC compared to other alkali metal salts, notable exception being NaClO_4 , which is more soluble in PC than LiClO_4 . Also with the exception of lithium, other alkali metal halides appear to be sparingly soluble and the solubilities are usually in the order: $\text{Cl}^- < \text{Br}^- < \text{ClO}_4^-$ as in water and other dipolar aprotic solvents. The poor solubility of these salts in such a high dielectric media may be due to the dipolar aprotic nature of this solvent medium. The perchlorates, we see, have a much higher

solubility than the halide ones. This indicates that ClO_4^- ion tends to increase the PC liquid structure more so than does Cl^- or Br^- ion. Further, salts having large or highly polarizable groups viz. Ph_4AsCl and Ph_4PBr are found to be reasonably soluble in this medium. However, Ph_4AsCl is found to be much more soluble than Ph_4PBr . This shows that Ph_4As^+ is more polarizable than Ph_4P^+ and is preferentially solvated, most probably through a combination of dispersion and ion-dipole interactions.

From Table 2 we see that in general, the standard free energies of transfer, ΔG_t^0 , of the electrolytes from water to PC are positive and so the transfer process is not favourable. Notable exception is Ph_4PBr . The negative sign reflects the fact that the distribution of its ions favours the non-aqueous phase, compared to the positive medium effects for most electrolytes. Cox and his coworkers³ have presented ΔG_t^0 values of some common salts from water to PC by taking the basic data from the literature. Our reported ΔG_t^0 values for the alkali metal halides are found to be in good agreement with theirs. This avoids the uncertainties in the solubility method due to ion pairing and activity coefficient measurements. Salomon¹¹ has also reported ΔG_t^0 values of LiCl and LiBr from water to PC as 14.74 and 12.98 K Cal mol⁻¹ from potentiometric study, whereas we have found it to be 14.47 and 12.89 K Cal mol⁻¹ respectively from direct solubility measurements.

Ionic transfer free energies and ionic transfer activity coefficients are very important parameters in non-aqueous solution

Chemistry. These two terms actually determine how the equilibrium constant and rate properties change with the nature of solvents. Ionic free energies of transfer from water to PC at 25°C have been reported in Table 3. ΔG_t° values of the ions have been calculated taking $\text{Ph}_4\text{AsBPh}_4$ as the 'reference electrolyte'³. An attempt was made to calculate ΔG_t° value of $\text{Ph}_4\text{AsBPh}_4$ from water to PC by measuring the solubilities of Ph_4AsCl , NaCl and NaBPh_4 in PC. But NaBPh_4 was found to be highly soluble in PC and to avoid the experimental error we discarded the idea. From the table we see that among the cations, Li^+ , Na^+ and K^+ ions have a positive value of transfer free energy, whereas Rb^+ , Cs^+ , Ph_4As^+ and Ph_4P^+ have got negative ΔG_t° values. The positive values of ΔG_t° and $\log m \gamma_1$ indicate that these ions are more favourably solvated by the reference medium (water) than by the non-aqueous medium (PC) to which it is transferred. For negative values of ΔG_t° , it is just the reverse. The ΔG_t° values of alkali metal ions decrease in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. As the size of the anion increases, its free energies of transfer from water to PC decreases ($\text{ClO}_4^- < \text{Br}^- < \text{Cl}^-$). On transferring Cl^- or Br^- ion from water to PC, there is a large increase in free energy and this increase in free energy is the cause behind the increased reactivity of these ions in this solvent medium. For example, the transfer activity coefficient of Cl^- ion in PC is 6.7 (Table 3), which means that a solution of Cl^- ion in PC has an activity of $10^{6.7}$ times greater than a solution of the same Cl^- ion concentration in water. And this causes major changes in the rate and equilibrium constants

of chemical reactions (involving Cl^- ion) in PC, compared to that in aqueous medium. Solvation of small cations is generally determined by the relative basicity of the solvents i.e. by their donor ability. Dipolar aprotic solvents containing oxygen atoms with localized negative charge e.g. DMSO, solvate cations better than water as evidenced from the negative values of free energies of transfer from water to DMSO³. DMSO is regarded to be more basic than PC^{12,13}. PC has got weakly basic oxygen and so cations are poorly solvated in this medium than DMSO resulting in positive ΔG_t° values (Table 3). However, for Rb^+ and Cs^+ ions, the ΔG_t° values are negative in PC. From this evidence we may come to the conclusion that the transfer of Rb^+ and Cs^+ ions from water to PC is more favourable compared to other alkali metal cations.

Table 1. Solubilities (S , mol lit $^{-1}$), Standard Free Energies of Solution ($\Delta G_{\text{soln}}^{\circ}$, kJ mol $^{-1}$) and Standard Free Energies of Formation ($\Delta G_{\text{F}}^{\circ}$, kJ mol $^{-1}$) and Solvation ($\Delta G_{\text{solv.}}^{\circ}$, kJ mol $^{-1}$) of the Electrolytes in PC at 25 $^{\circ}$ C

Salt	S	$\Delta G_{\text{soln.}}^{\circ}$	$-\Delta G_{\text{F}}^{\circ}$	$-\Delta G_{\text{solv.}}^{\circ}$
LiCl	0.019 + 0.002	19.12	364.55	824.79
NaCl	0.00017 + 0.00002	42.97	341.08	726.47
KCl	0.00058 + 0.00004	36.82	371.50	667.35
RbCl	0.0033 + 0.0006	28.07	376.94	653.08
CsCl	0.0076 + 0.0007	23.85	380.33	633.88
Ph $_4$ AsCl	0.50 + 0.02	1.51	-----	-----
LiBr	1.10 + 0.008	-2.97	342.71	802.11
NaBr	0.0036 + 0.0010	27.66	320.03	706.64
KBr	0.0030 + 0.0006	28.58	350.62	643.79
RbBr	0.0099 + 0.0005	22.51	355.64	634.80
CsBr	0.0098 + 0.0007	22.55	360.70	610.07
Ph $_4$ PBr	0.120 + 0.003	9.97	-----	-----
LiClO $_4$	1.40 + 0.03	-4.35	-----	-----
NaClO $_4$	2.50 + 0.08	-7.70	264.60	-----
KClO $_4$	1.40 + 0.03	-4.35	-----	-----
NaClO $_4$	2.50 + 0.08	-7.70	264.60	-----
KClO $_4$	0.017 + 0.001	19.71	284.47	-----
RbClO $_4$	0.025 + 0.002	17.70	288.53	-----
CsClO $_4$	0.052 + 0.003	13.85	292.75	-----

Table 2. Free Energies of Transfer (ΔG_t°) and Transfer Activity Coefficients ($\log m\gamma$) of the Electrolytes from Water to PC at 25°C

salt	$\Delta G_{\text{soln.}}^\circ$ (H ₂ O) kJ mol ⁻¹	ΔG_t° kJ mol ⁻¹	$\log m\gamma$
LiCl	-41.42	60.54	10.61
NaCl	-8.79	51.76	9.07
KCl	-5.02	41.84	7.33
RbCl	-8.37	36.44	6.39
CsCl	-9.20	33.05	5.79
Ph ₄ AsCl	-0.59	2.09	0.37
LiBr	-56.90	53.93	9.45
NaBr	-17.15	44.81	7.85
KBr	-5.86	34.43	6.04
RbBr	-6.69	29.20	5.12
CsBr	-1.67	24.23	4.25
Ph ₄ PBr	14.64	-5.27	-0.92
LiClO ₄	very soluble	-----	-----
NaClO ₄	very soluble	-----	-----
KClO ₄	11.30	8.41	0.52
RbClO ₄	14.23	3.47	0.61
CsClO ₄	13.81	0.04	0.007

Table 3. Crystallographic Radius (r_c , Å^o), Free Energies of Transfer (ΔG_t^o , kJ mol⁻¹); Transfer Activity Coefficients ($\log m \gamma_i$) and Free Energies of Solvation ($\Delta G_{\text{solv.}}^o$, kJ mol⁻¹) of Single Ions in PC at 25°C

Ion	r_c	ΔG_t^o	$\log m \gamma_i$	$-\Delta G_{\text{solv.}}^o$
Li ⁺	0.60 ^b	22.47	3.94	471.58
Na ⁺	0.95 ^b	13.68	2.40	379.87
K ⁺	1.33 ^b	3.77	0.66	313.63
Rb ⁺	1.48 ^b	-1.63	-0.29	293.47
Cs ⁺	1.69 ^b	-5.02	-0.88	269.20
Ph ₄ As ⁺	6.40 ^c	-35.98	-6.31	94.31
Ph ₄ P ⁺	6.30 ^c	-35.98	-6.31	95.65
Cl ⁻	1.81 ^b	38.07	6.67	243.34
Br ⁻	1.95 ^b	30.71	5.38	231.79
ClO ₄ ^{-a}	2.16 ^b	5.06	0.89	216.40

^aCalculated by using the relation, $\Delta G_t^o(\text{ClO}_4^-) = \Delta G_t^o(\text{CsClO}_4) - \Delta G_t^o(\text{Cs}^+)$

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CHAPTER-IV

PART - A

Electrical Conductances for Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate, Tetrabutylammonium Tetrabutylborate and Tetrabutylammonium Tetraphenylborate in Propylene Carbonate at 25°C

Propylene carbonate (PC, 4-methyl 1,3-dioxolan-2-one) has drawn much attention in recent years as a solvent medium for various electrochemical studies^{1,2} relating to high energy batteries^{3,4} and free radical species⁵. It is a stable solvent of moderately high dielectric constant⁶ (64.40 at 25°C) and has good solvent properties^{7,8} for a variety of organic and inorganic salts. Hence, it is of much interest to study the behaviour of electrolytes in such solvent medium. The conductometric method is also well known⁹ to give valuable information regarding the ion-solvent interactions of electrolytes in non-aqueous and mixed solvents.

In this part an attempt has been made by us to understand the nature of ion-solvent interactions of some tetraalkylammonium bromides, R_4NBr ($R =$ methyl to heptyl), $LiBF_4$ and two reference electrolytes, viz. Bu_4NBBu_4 and Bu_4NBPh_4 in PC by using conductometric method. Single ion conductivities have been evaluated by using two reference electrolytes in an effort to provide reliable values of ionic mobilities. Conductance measurements on Bu_4NBr ¹⁰, Bu_4NBBu_4 ¹¹ and Bu_4NBPh_4 ¹² though earlier have been reported by

different authors but these have further been investigated by us in order to maintain the internal consistency amongst the derived values with these electrolytes.

Experimental

Propylene Carbonate (E. Merck Germany, > 99% pure) was dried over freshly ignited quicklime for several hours¹³ and then distilled thrice under reduced pressure in nitrogen gas atmosphere, the middle fraction being taken each time. The purified sample had a density of 1.1988 g cm⁻³, viscosity of 2.471 cP and a specific conductance of ca. 0.73×10^{-6} S cm⁻¹ at 25°C; these values are in good agreement with the literature values^{10,14}.

Tetraalkylammonium bromides were of Fluka's puram or puriss grade and were purified as described in the literature^{15,16} and also described earlier in Chapter-II. The salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure maximum purity. The recrystallized salts were dried in vacuo at elevated temperatures for 12 h.

Lithium tetrafluoroborate (Fluka, puriss) was dried under vacuum at high temperature for around 48 hrs immediately prior to use and was used without further purification.

Tetrabutylammonium tetrabutylborate (Alfa Products) was purified as suggested by Lawrence et al.¹⁷. Tetrabutylammonium tetraphenylborate was prepared by mixing equimolar quantities of NaBPh_4 and Bu_4NBr . It was purified by recrystallization from 1:3 water-acetone mixture and dried under vacuum at 40°C .¹⁸

Conductance measurements were made by a Pye-Unicam PW 9509 conductivity meter at a frequency of 2,000 Hz using a dip-type immersion cell of cell constant 0.751 cm^{-1} and having an accuracy of $\pm 0.1\%$. The cell constant was determined frequently using the standard KCl solutions. Measurements were made in an oil bath maintained at $25 \pm 0.005^\circ\text{C}$. The details of experimental procedure have been described in Chapter - II. Several independent solutions were prepared and measurements were made with each of these to ensure the reproducibility of the results. All data were corrected with the specific conductance of the solvent. The corrected values were analysed by means of Fuoss conductance equation^{19,20}.

Results

The measured equivalent conductances and the corresponding concentrations, C , in molarities are given in Table 1. The data were analyzed with the Fuoss conductance equation^{19,20} which can be expressed as,

$$\Lambda = P \left[\Lambda_0 (1 + R_x) + E_L \right] \quad (1)$$

$$P = [1 - \alpha (1 - \gamma)] \quad (2)$$

$$\gamma = 1 - K_{Ac} \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta c / 2 (1 + cR) \quad (4)$$

$$\beta = \frac{e^2}{\epsilon k_B T} \quad (5)$$

where R_X and E_L are relaxation and hydrodynamic terms, respectively, as derived by Fuoss, and the other terms have their usual significance. The parameters Λ_0 , K_A and R were obtained by solving the above equations. Initial Λ_0 values for the iteration procedure were obtained from Shedlovsky extrapolation of the data.

In practice, calculations were made by finding the values of Λ_0 and α which minimize for a sequence of R -values, and then plotting $\sigma\% = 1000\sigma/\Lambda_0$ against R ; the best fit R corresponds to

$$\sigma^2 = \sum_j [\Lambda_j(\text{calc}) - \Lambda_j(\text{obs})]^2 / (n-2) \quad (6)$$

a minimum of the $\sigma\%$ vs R curve. First approximate runs over a fairly wide range of R values were made to locate the minimum and

then a fine scan around the minimum was made. Finally, with this minimized value of R , the corresponding Λ_0 and αC were calculated.

The values of Λ_0 , K_A and R obtained by this procedure are recorded in Table 2. The limiting ionic conductances based on the values of Bu_4NBBu_4 and Bu_4NBPh_4 are given in Table 3. The limiting ion conductance value for Li^+ ion was taken from the literature¹⁰ to calculate the single ion mobility for BF_4^- ion, assuming that the rule of additivity holds too in this case.

Discussion

Table 2 shows that the limiting equivalent conductances (Λ_0) of the tetraalkylammonium bromides decrease as the alkyl chain-length increases. This is found to be in absolute agreement with earlier findings for tetraalkylammonium bromides in other aprotic solvents²¹. The size and structure forming effect decrease as the alkyl chain-length increases and consequently the mobility is in the reverse order. The Λ_0 value of Bu_4NBr was earlier reported by Jansen and Yeager¹⁰. A comparison of the limiting equivalent conductance value for Bu_4NBr as obtained by us with that of Jansen and Yeager¹⁰ shows a difference of ca. 0.4%, indicating the closeness of our values with theirs. Also, a comparison of the reported Λ_0 value of Bu_4NBBu_4 by Takeda et al¹¹ with ours shows a difference of ca. 1%. While Takeda et al¹¹ took the Λ_0 value directly from the extrapolation of Λ vs. \sqrt{C} plots, on the other hand we have calculated it by

Fuoss method²⁰ and hence the observed difference. It is most likely that for similar reasons, our reported Λ_0 value for Bu_4NBPh_4 is 6.8% larger than the reported value $(17.14)^{12}$.

The association constant values in Table 2 show that the salts studied by us are essentially unassociated with the minor exception of LiBF_4 . Presumably this salt indicates slight ion-pairing though the association constant is much less than that of LiCl^7 and LiBr^7 . It may be due to the very large size of tetra-fluoroborate ion which has a lower affinity for the lithium ion than the smaller Cl^- and Br^- ions. This decrease in the association constant as the anion size increases also agrees with the general contention of the theories of Denison and Ramsey²², and Gilkerson²³. The greater Λ_0 value of LiBF_4 than that of LiCl and LiBr also corroborates the above view point. However, for R_4N^+ ions, the general decrease in the association constant as the cation size increases is in agreement with the charge density values of these ions.

The single ion conductances have been evaluated from the division of Λ_0 value of Bu_4NBu_4 using the following relationship^{17,24}

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Bu}_4\text{B}^-) \quad (7)$$

The reason behind the choice of Bu_4NBu_4 as the reference electrolyte is in the fact that the cation and anion in this case are symmetrical

in shape and have almost equal van der Waals volume.

Bu_4NBPh_4 has also been utilized by various authors^{12,25} to calculate limiting ion conductances assuming that λ_0 values of its constituent ions viz. Bu_4N^+ and BPh_4^- are equal. But the validity of this assumption has been questioned in several solvents owing to the unequal size of the cation and anion and also to the unequal electronic environment of the positive charge on the nitrogen atom and the negative charge on the boron atom. Instead of equal division, we have divided the λ_0 values using the method similar to that proposed by Krumgalz²⁶ for division of viscosity B-values

$$\frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{BPh}_4^-)} = \frac{r(\text{BPh}_4^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (8)$$

The r -values have been taken from the works of Gill et al^{24,27}.

The λ_0 values obtained by using the above two methods have been presented in Table 3. It can be readily seen that the limiting ionic conductances obtained from the above two methods are in very close agreement with each other. This suggests that either of the two methods can be used to calculate the limiting ionic conductances in organic solvents. Kay and coworkers⁸ previously analysed the conductance data of several workers and calculated the best estimate of limiting ion conductances in PC at 25°C. Comparison of our

results with theirs reveals that in the case of Me_4N^+ , Et_4N^+ and Pr_4N^+ ions, the λ_0 values obtained by us are 1-11% lower and for Bu_4N^+ , the value is 5% higher than the values proposed by Kay ^{10,11,13,28} et al⁸. This discrepancy is due to the different procedures adopted for the calculation of λ_0 values and also on the choice of the 'reference electrolyte'^{8,10}, which was also different for calculating the limiting ion conductances in non-aqueous solvents.

The Walden products ($\lambda_0^{\pm} \eta_0$) and Stokes radii (r_s) of the ions are reported in Table 3. The Walden product values are usually employed to discuss the ion-solvent interactions of the ions with the solvent medium. From the table, we see that for large R_4N^+ ions, $\lambda_0^{\pm} \eta_0$ is larger, the smaller is the size of the cation and for the electrolyte taken as a whole, it follows the same sequence (Table 2). It therefore leads to the fact that electrostatic ion-solvent interaction, is very weak in these cases. On the other hand, the alkali metal ions are small enough to possess the high electrostatic charge density on them resulting in strong ion-solvent interactions¹⁰. From Table 3, we also see that Stokes radii increase with the increasing size of the tetraalkylammonium ions and this is most likely due to less ionic mobilities of these cations. For Li^+ ion, however, the Stokes radius is much greater than its crystallographic radius (0.93 \AA)²⁹ indicating it to be substantially solvated in this solvent medium. On the other hand, the higher mobility of Br^- ion than the cations relative to its crystallographic size (1.80 \AA)²⁹ indicates that it is poorly solvated in this medium. The

slight difference in limiting ionic conductance values of Br^- and BF_4^- ions seem to indicate that the effective sizes of these anions in PC are almost the same and thus very little solvation, if any, is involved in these cases. On the other hand, very low mobility of the tetrabutylboride ion has been attributed to its much larger size. Thus, from the result it appears that the large size of R_4N^+ ions, its low charge density and high dielectric constant of PC render these ions to be free, unassociated and almost unsolvated in this medium.

Table 1. Equivalent conductances and corresponding molarities of the tetraalkylammonium bromides, tetrabutylammonium tetrabutylborate, lithium tetrafluoroborate and tetrabutylammonium tetraphenylborate in propylene carbonate at 25°C

$c/10^{-4} \text{ mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$	$c/10^4 \text{ mol dm}^{-3}$	$\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$
	Me ₄ NBr		Et ₄ NBr
131.702	27.18	90.445	26.67
100.094	27.67	73.080	27.03
84.861	27.97	62.226	27.26
60.056	28.44	44.137	27.71
50.047	28.73	36.540	27.89
40.037	28.95	29.304	28.12
24.760	29.40	18.089	28.53
10.536	29.99		
	Pr ₄ NBr		Bu ₄ NBr
444.474	22.85	622.737	20.51
375.533	23.31	498.190	21.34
300.067	23.84	400.628	21.99
226.398	24.54	298.914	22.75
159.916	25.04	201.352	23.54
100.621	25.79	100.261	24.74
75.466	26.10	79.974	25.04
50.059	26.49	60.156	25.35
25.155	27.07	40.164	25.76
		20.052	26.28
	Pen ₄ NBr		Hex ₄ NBr
519.858	19.30	506.841	18.63
348.875	20.19	349.720	19.54
199.279	21.29	199.357	20.63
100.506	22.11	99.679	21.69
90.109	22.33	89.542	21.85
74.513	22.61	74.337	22.16

Contd..

Table 1 (Contd..)

60.304	22.82	60.097	22.16
45.027	23.10	45.073	22.50
30.152	23.45	30.048	22.80
		10.016	23.36
	Hep ₄ NBr		LiBF ₄
523.988	18.12	529.635	19.64
399.977	18.68	398.992	20.73
300.450	19.05	300.127	21.70
200.862	19.73	199.496	23.06
99.558	20.51	100.631	24.66
75.105	20.93	90.038	24.90
60.084	21.00	74.149	25.21
45.063	21.55	60.025	25.59
30.042	21.80	45.019	26.01
		30.013	26.39
		10.004	27.39
	Bu ₄ NBBu ₄		Bu ₄ NBPh ₄
206.727	15.38	217.489	14.52
149.532	15.85	187.250	14.79
120.591	16.17	158.174	15.10
89.582	16.48	138.402	15.31
74.422	16.64	118.630	15.50
60.364	16.85	98.859	15.73
39.692	17.18	79.087	16.00
24.807	17.54	59.315	16.28
9.923	18.00	39.543	16.65

Table 2. Conductance parameters of tetraalkylammonium bromides, lithium tetrafluoroborate tetrabutylammonium tetrabutylborate and tetrabutylammonium tetraphenylborate in PC at 25°C

Salts	$\Lambda_w/S \text{ cm}^2 \text{ mol}^{-1}$	$K_A/\text{dm}^3 \text{ mol}^{-1}$	walden product	$R/\overset{\circ}{\text{A}}$	σ
Me_4NBr	31.09 (± 0.02)	6.82 (± 0.11)	0.768	14.00	0.06
Et_4NBr	29.94 (± 0.01)	8.15 (± 0.10)	0.740	17.00	0.03
Pr_4NBr	28.57 (± 0.02)	4.20 (± 0.07)	0.706	13.30	0.12
Bu_4NBr	27.68 (± 0.01)	5.00 (± 0.04)	0.684	12.30	0.07
Pen_4NBr	25.10 (± 0.03)	3.92 (± 0.12)	0.620	8.30	0.20
Hex_4NBr	24.38 (± 0.03)	4.71 (± 0.16)	0.602	13.00	0.27
Hep_4NBr	23.41 (± 0.03)	3.65 (± 0.10)	0.578	10.50	0.19
Bu_4NBu_4	18.88 (± 0.01)	5.79 (± 0.12)	0.467	13.10	0.10
Bu_4NPh_4	18.30 (± 0.02)	8.16 (± 0.12)	0.452	18.20	0.08
LiBF_4	28.48 (± 0.02)	10.09 (± 0.11)	0.794	13.20	0.15

Table 3. Limiting ionic conductances, Walden products and Stokes radii of the ions in PC at 25°C

Ion	λ_0^\pm	$\lambda_0^{\pm c}$	$\lambda_0^\pm \eta^a$	$\lambda_0^\pm \eta^c$	r_s^a	r_s^c
Me_4N^+	12.85 ^a	12.87	0.319	0.319	2.56	2.56
Et_4N^+	11.70 ^a	11.72	0.290	0.291	2.82	2.81
Pr_4N^+	10.33 ^a	10.35	0.255	0.257	3.21	3.18
Bu_4N^+	9.44 ^a	9.46	0.234	0.235	3.49	3.48
Pen_4N^+	6.86 ^a	6.88	0.170	0.171	4.81	4.78
Hex_4N^+	6.14 ^a	6.16	0.152	0.153	5.38	5.35
Hep_4N^+	5.17 ^a	5.19	0.128	0.129	6.39	6.34
Li^+	8.89 ^b	-----	0.220	-----	3.72	-----
Br^-	18.24 ^a	18.22	0.452	0.450	1.81	1.82
BBu_4^-	9.44 ^a	9.42	0.234	0.234	3.49	3.50
BPh_4^-	8.86 ^a	8.84	0.219	0.218	3.74	3.75
BF_4^-	19.59	-----	0.486	-----	1.68	-----

^a Calculations based on Bu_4NBBu_4

^b λ_0^\pm of Li^+ ion taken from ref. 10

^c Calculations based on Bu_4NBPh_4

PART - B

Viscosity B Coefficients of Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate and Tetrabutylammonium Tetraphenyl borate in Propylene Carbonate at 25, 35 and 45°C

Studies on the transport properties of electrolytes in different solvents are of great importance to obtain information on the behaviour of ions in solutions. Recent years have therefore witnessed increased interest in this topic as are evidenced from numerous publications^{9,21,30-33} in this field. One method employed for these investigations is to study solution viscosity. Viscometry is one of the important tools for the determination of ion-solvent interactions which are the controlling forces in dilute solutions where ion-ion interactions are absent²⁶. The variations of solvational properties are reflected in the viscosity B-coefficients of ions.

In Part-A of the present chapter, we have studied ion-solvent interactions of some tetraalkylammonium bromides, R_4NBr and a few other salts in PC at 25°C from conductance measurements. We have now extended this work to study the viscometric behaviour of these electrolytes at different temperatures to obtain more information about specific ion-solvent interactions in this solvent. Ionic B values have been derived on the basis of the reference electrolyte ' Bu_4NBPh_4 ' and the transition-state treatment have been applied to analyse the results.

Experimental

Propylene Carbonate (E. Merck Germany, > 99% pure) was purified according to the procedure described earlier in Chapter-II and also in Part-A of the present chapter. The solvent properties have been recorded in Table 1.

The purification of tetraalkylammonium bromides, LiBF_4 and Bu_4NBr have been reported earlier in Chapter - II.

The concentrations of the salts generally varied in the range of $0.01\text{--}0.08 \text{ mol dm}^{-3}$ which were prepared by weight dilution of the stock solution (ca. 0.1 mol kg^{-1}). The conversion of the molality into molarity was done by using the density values. The kinematic viscosities were measured at the desired temperature (accuracy $\pm 0.01 \text{ }^\circ\text{C}$) using a suspended Ubbelohde-type viscometer. The densities were measured using an Ostwald-Sprengel type pycnometer (25 ml) calibrated with distilled water. The details of the experimental procedure have been described previously in Chapter-II. The accuracies of viscosity and density measurements were 0.05% and $\pm 3 \times 10^{-5} \text{ gcm}^{-3}$ respectively. Viscosity measurement for Me_4NBr in PC could not be performed owing to its poor solubility in this solvent medium.

Results

The density (ρ) and viscosity (η) data for the electrolytes in the molarity range 0.01-0.08 mol dm⁻³ at temperatures 25, 35 and 45°C have been reported in Table 2.

The experimental data have been analysed by the Jones-Dole equation³⁴

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B \sqrt{c} \quad (1)$$

where η and η_0 are the viscosities of the solution and solvent, respectively, c is the molar concentration and the other terms have their usual significance.

The plots of $(\eta/\eta_0 - 1) / \sqrt{c}$ against \sqrt{c} (Figure 1) for the electrolytes are linear and the experimental A values at 25, 35 and 45°C have been calculated using the least squares method. The A coefficients were also calculated theoretically at 25°C from the physical properties of the solvent and the limiting ionic equivalent conductance by using the Falkenhagen and Vernon equation³⁵ :

$$A_{\text{theo}} = \frac{0.2577 \Lambda_0}{\eta_0 (\epsilon T)^{1/2} \lambda_+^+ \lambda_-^-} \left[1 - 0.6863 \left(\frac{\lambda_+^+ - \lambda_-^-}{\Lambda_0} \right)^2 \right] \quad (2)$$

The conductance data required in the above calculations were taken from Part-A of the present chapter. These A values have been used for analysis of the viscosity data. In view of the weak temperature dependence of the A coefficients, the A values at 25°C have been utilized at the other two temperatures. Theoretical A coefficients obtained from eqn. 2 along with the experimental A values are reported in Table 3.

Viscosity B coefficients obtained at various temperatures using the least squares method have been presented in Table 4.

Viscosity data have also been analysed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions as suggested by Feakins et al.³⁶

$$B = \frac{\bar{V}_1^{\circ} - \bar{V}_2^{\circ}}{1000} + \frac{\bar{V}_1^{\circ}}{1000} \left(\frac{\Delta M_2^{\ddagger} - \Delta M_1^{\ddagger}}{RT} \right) \quad (3)$$

In the above equation \bar{V}_1° and \bar{V}_2° are the partial molar volumes of solvent and solute respectively. ΔM_2^{\ddagger} , 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 reported in Table 4. ΔM_1^{\ddagger} , the free energy of activation per mole of the pure solvent is given by the equation³⁷ :

$$\Delta \mu_1^{\circ \ddagger} = \Delta G_1^{\circ \ddagger} = RT \ln \left(\frac{\eta_0 \bar{V}_1^{\circ}}{hN} \right) \quad (4)$$

Discussion

The A coefficients shown in Table 3 are found to be small and positive for all the electrolytes and the experimental results at 25°C agree well with the theoretical ones within 20% for the quarternary ammonium salts. This error in the small A values corresponds to the experimental uncertainty of 0.05% in the viscosity data. Similar results have been found earlier also in other systems³⁸.

The viscosity B coefficients (Table 4) are large and positive and the values increase in PC as we go from tetraethylammonium to tetraheptylammonium bromide. Our reported viscosity B coefficient (1.043) at 25°C for Bu₄NBr is slightly greater than the B value (0.960) reported previously by Boden et al⁷ by simply plotting relative viscosity against concentration of Jones-Dole equation. The B value of lithium tetrafluoroborate is found to be approximately equal to that of Pen₄NBr. The B coefficients show a moderate or weak temperature dependence and the values decrease with increase of temperature as observed earlier in some dipolar aprotic solvents like acetonitrile^{38,39}, sulfolane⁴⁰ and DMSO^{16,41}.

Further, from Table 4 we see that although $\partial B/\partial T$ is small but it is negative in sign for all the electrolytes, indicating that they behave as structure makers in this solvent medium.

The ionic B values were calculated by eqn. 6 using Bu_4NBPh_4 as the 'reference electrolyte'^{42,43}.

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{N}^+) + B(\text{BPh}_4^-) \quad (5)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \left(\frac{5.35}{5.00} \right)^3 \quad (6)$$

The ionic B values along with the ionic $\Delta \mu_{\pm}^{\text{oz}}$ data obtained from the above relationships have been recorded in Table 5. Table 5 shows that the viscosity B coefficients for cations and anions are all positive and also very high. Ionic B value for Li^+ at 25°C was calculated from the reported viscosity B value of LiBr^7 in PC / with the help of additivity rule. The observed order of B_{\pm} coefficients, $\text{HeP}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$, shows that the obstruction to solvent viscous flow increases with decrease of ion charge density and with the decrease of the size of hydrodynamic entity by solvation. For anions, the B-value is seen to be in the order $\text{BPh}_4^- > \text{Br}^- > \text{BF}_4^-$. The $\partial B_{\pm}/\partial T$ values of cations and anions are generally found to be negative (structure-making). This

behaviour of tetraalkylammonium ions in PC, arising mainly from the interactions of alkyl groups and solvent molecules is similar to that as observed earlier in sulfolane by Sacco and coworkers^{40,44}.

The values of $\Delta \mu_{\ddagger}^{\ddagger}$ for tetraalkylammonium ions decrease in the order : $\text{Hep}_4\text{N}^+ > \text{Hex}_4\text{N}^+ > \text{Pen}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Et}_4\text{N}^+$ and for anions $\text{BPh}_4^- > \text{Br}^-$. However, these values are found to be positive and thus the formation of transition-state is less favourable in the presence of these ions.

Ionic B_{\ddagger} coefficients have also been analysed on the basis of Einstein's equation⁴⁵.

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

where R_{\ddagger} is the radius at the ion assumed as the rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number of solvent molecules (n_s) bound to the ion in the primary sphere of solvation can be calculated by combination of the Jones-Dole equation with that of Einstein's⁴⁶.

$$B_{\ddagger} = \frac{2.5}{1000} (V_1 + n_s V_s) \quad (8)$$

where V_1 represents the bare ion molar volume and is related to the crystallographic radius, r_c , of the ions. V_s is the solvent molar volume. The values of R_{\ddagger} and n_s are shown in Table 6.

The R_{\pm} values for tetraalkylammonium ions are found to be in reasonable agreement with the Stokes and crystallographic radii. The results indicate that these ions are scarcely solvated in PC and behave as spherical entities. However, R_{\pm} value of Li^+ ion is much higher than its crystallographic radius, indicating that it is highly solvated in PC by ion-dipole interactions. Similar results have been obtained by conductometric measurements³³ which shows that Li^+ is highly solvated in this medium. Thus, it appears that the large size of R_4N^+ ions, their low charge density and the high dielectric constant of PC render these ions to be free, unassociated and almost unsolvated in this medium.

Table 1. Solvent properties of propylene carbonate

Temperature (°C)	Density (gcm ⁻³)	Viscosity (cP)	Dielectric Constant
25	1.19883	2.4712	64.40 ^a
35	1.18970	2.0476	63.41 ^b
45	1.17796	1.7234	60.92 ^c

^a from ref. 6

^b from G. Ritzoulis, *Can. J. Chem.*, 67, 1105, 1989

^c from G. Moumouzias, D.K. Panopoulos and G. Ritzoulis, *J. Chem. Eng. Data*, 36, 20, 1991.

Table 2. Concentration, c /(mol dm⁻³), density, ρ /(gcm⁻³) and relative viscosity, η_r of tetraalkylammonium bromides, LiBF₄ and Bu₄NBPh₄ in PC at 25, 35 and 45°C

c	ρ	η_r	c	ρ	η_r
	Et ₄ NBr	25°C		Pr ₄ NBr	25°C
0.01002	1.19000	1.0081	0.00995	1.19870	1.0096
0.01644	1.19910	1.0130	0.02020	1.19856	1.0188
0.02506	1.19925	1.0193	0.03015	1.19843	1.0351
0.03509	1.19941	1.0266	0.05005	1.19816	1.0452
0.04511	1.19957	1.0343	0.06001	1.19803	1.0540
0.05514	1.19973	1.0418	0.08020	1.19776	1.0716
	Bu ₄ NBr	25°C		Pen ₄ NBr	25°C
0.01015	1.19837	1.0116	0.00990	1.19817	1.0130
0.01999	1.19792	1.0224	0.02011	1.19749	1.0253
0.03076	1.19743	1.0337	0.03001	1.19682	1.0382
0.05014	1.19654	1.0538	0.05011	1.19547	1.0619
0.05998	1.19609	1.0642	0.06002	1.19480	1.0750
0.07997	1.19517	1.0871	0.08012	1.19343	1.0991

Contd...

Table 2. (Contd..)

Hex ₄ NBr 25°C			HeP ₄ NBr 25°C		
0.00999	1.19779	1.0149	0.01007	1.19750	1.0159
0.02498	1.19621	1.0368	0.03002	1.19485	1.0458
0.03997	1.19464	1.0583	0.04009	1.19351	1.0606
0.04996	1.19359	1.0715	0.04996	1.19219	1.0761
0.06994	1.19149	1.1017	0.06003	1.19084	1.0904
LiBF ₄ 25°C			Bu ₄ NBPh ₄ 25°C		
0.01031	1.19937	1.0134	0.00998	1.19796	1.0149
0.02508	1.20013	1.0311	0.01997	1.19708	1.0293
0.04020	1.20091	1.0503	0.02995	1.19620	1.0418
0.05017	1.20142	1.0623	0.04502	1.19487	1.0513
0.06013	1.20193	1.0784	0.05990	1.19356	1.0844
0.08007	1.20294	1.0975			

Contd..

Table 2. (Contd..)

Et ₄ NBr 35°C			Pr ₄ NBr 35°C		
0.00995	1.18992	1.0077	0.00988	1.18955	1.0089
0.01632	1.19006	1.0119	0.02004	1.18938	1.0175
0.02487	1.19025	1.0186	0.02992	1.18923	1.0255
0.03483	1.19047	1.0248	0.04967	1.18891	1.0425
0.04478	1.19069	1.0326	0.05954	1.18875	1.0499
0.05473	1.19091	1.0391	0.07958	1.18843	1.0676
Bu ₄ NBr 35°C			Pen ₄ NBr 35°C		
0.01007	1.18898	1.0113	0.00982	1.18799	1.0125
0.01983	1.18828	1.0215	0.01992	1.18622	1.0244
0.03050	1.18751	1.0325	0.02918	1.18460	1.0361
0.04970	1.18612	1.0523	0.04956	1.18101	1.0587
0.05945	1.18542	1.0625	0.05931	1.17929	1.0716
0.07923	1.18398	1.0828	0.07963	1.17570	1.0949

Contd..

Table 2. (Contd..)

Hex ₄ NBr 35°C			Hep ₄ NBr 35°C		
0.00991	1.18808	1.0145	0.00999	1.18803	1.0155
0.02475	1.18563	1.0352	0.02976	1.18472	1.0446
0.03958	1.18318	1.0558	0.03974	1.18303	1.0584
0.04945	1.18155	1.0693	0.04951	1.18138	1.0730
0.06917	1.17827	1.0961	0.05947	1.17969	1.0879
LiBF ₄ 35°C			Bu ₄ NBPh ₄ 35°C		
0.01022	1.19025	1.0125	0.00906	1.18873	1.0141
0.02487	1.19104	1.0295	0.01944	1.18762	1.0277
0.03987	1.19184	1.0424	0.02971	1.18651	1.0411
0.04976	1.19237	1.0572	0.04464	1.18490	1.0621
0.05966	1.19290	1.0683	0.05939	1.18331	1.0808
0.07947	1.19396	1.0909			

Contd..

Table 2. (Contd..)

Et ₄ NBr 45°C			Pr ₄ NBr 45°C		
0.00985	1.17827	1.0071	0.00977	1.17785	1.0077
0.01616	1.17847	1.0117	0.01985	1.17773	1.0161
0.02463	1.17873	1.0174	0.02963	1.17761	1.0241
0.03449	1.17904	1.0243	0.04919	1.17737	1.0401
0.04435	1.17935	1.0310	0.05897	1.17725	1.0401
0.05421	1.17965	1.0374	0.07881	1.17701	1.0480
					1.0640
Bu ₄ NBr 45°C			Pen ₄ NBr 45°C		
0.00998	1.17707	1.0108	0.00972	1.17541	1.0120
0.01966	1.17621	1.0200	0.01969	1.17279	1.0235
0.03025	1.17526	1.0315	0.02935	1.17026	1.0354
0.04933	1.17355	1.0500	0.04885	1.16514	1.0574
0.05903	1.17267	1.0601	0.05840	1.16263	1.0679
0.07875	1.17089	1.0798	0.07911	1.15719	1.0912

Contd..

Table 2. (Contd..)

Hex ₄ NBr 45°C			Hep ₄ NBr 45°C		
0.00981	1.17568	1.0147	0.00990	1.17598	1.0151
0.02452	1.17226	1.0347	0.02951	1.17206	1.0435
0.03921	1.16884	1.0546	0.03942	1.17007	1.0585
0.04899	1.16657	1.0678	0.04913	1.16813	1.0711
0.06853	1.16202	1.0940	0.05762	1.16643	1.0836
LiBF ₄ 45°C			Bu ₄ NBPh ₄ 45°C		
0.01012	1.17877	1.0117	0.00980	1.17681	1.0144
0.02463	1.17992	1.0272	0.01926	1.17570	1.0272
0.03951	1.18110	1.0435	0.02943	1.17451	1.0406
0.04932	1.18187	1.0538	0.04423	1.17277	1.0597
0.05915	1.18265	1.0636	0.05886	1.17105	1.0787
0.07882	1.18420	1.0839			

Table 3. Theoretical A values and experimental A Coefficients,
 $A_{\text{obs}} / (\text{dm}^{3/2} \text{mol}^{-1/2})$ at 25, 35 and 45°C

Salts	A_{theo}	A_{obs}		
		25°C	35°C	45°C
Et ₄ NBr	0.0102	0.0082	0.0089	0.0066
Pr ₄ NBr	0.0108	0.0104	0.0080	0.0080
Bu ₄ NBr	0.0113	0.0093	0.0109	0.0083
Pen ₄ NBr	0.0130	0.0106	0.0117	0.0138
Hex ₄ NBr	0.0136	0.0079	0.0125	0.0189
Hep ₄ NBr	0.0147	0.0115	0.0128	0.0139
LiBF ₄	0.0114	0.0072	0.0095	0.0152
Bu ₄ NBPh ₄	0.0176	0.0135	0.0198	0.0237

Table 4. Viscosity B coefficients, $B/(\text{cm}^3 \text{mol}^{-1})$ and Δ/μ_2^{oz} (kJ mol^{-1}) values in propylene carbonate at different temperatures

Salts	25°C		35°C		45°C	
	B	Δ/μ_2^{oz}	B	Δ/μ_2^{oz}	B	Δ/μ_2^{oz}
Et ₄ NBr	0.716±0.004	38.56	0.674±0.009	37.86	0.653±0.003	37.57
Pr ₄ NBr	0.855±0.001	44.70	0.810±0.007	44.26	0.788±0.001	44.24
Bu ₄ NBr	1.043±0.012	52.31	1.005±0.001	52.89	0.975±0.007	53.41
Pen ₄ NBr	1.194±0.007	58.59	1.145±0.010	61.04	1.106±0.006	63.36
Hex ₄ NBr	1.385±0.019	66.43	1.339±0.002	67.98	1.315±0.008	70.41
Hep ₄ NBr	1.454±0.009	70.45	1.416±0.010	71.73	1.391±0.015	73.34
LiBF ₄	1.203±0.036	49.95	1.105±0.032	47.00	1.021±0.006	44.52
Bu ₄ NBPh ₄	1.302±0.061	66.68	1.283±0.013	68.08	1.256±0.002	68.92

Table 5. Ionic B coefficients, $B_{\pm}/(\text{dm}^3 \text{mol}^{-1})$ and ionic $\Delta/M_2^{\ddagger}/(\text{kJ mol}^{-1})$ values in PC at different temperatures

Ion	25°C		35°C		45°C	
	B_{\pm}	Δ/M_2^{\ddagger}	B_{\pm}	Δ/M_2^{\ddagger}	B_{\pm}	Δ/M_2^{\ddagger}
Et ₄ N ⁺	0.258	16.22	0.246	15.57	0.242	15.13
Pr ₄ N ⁺	0.397	22.36	0.382	21.97	0.377	21.80
Bu ₄ N ⁺	0.585	29.97	0.577	30.60	0.564	30.97
Pen ₄ N ⁺	0.736	36.25	0.717	38.75	0.695	40.92
Hex ₄ N ⁺	0.927	44.09	0.911	45.69	0.904	47.97
Hep ₄ N ⁺	0.996	48.11	0.988	49.44	0.980	50.90
Li ⁺	0.792	-----	-----	-----	-----	-----
Br ⁻	0.458	22.34	0.428	22.29	0.411	22.44
BF ₄ ⁻	0.411	-----	-----	-----	-----	-----
BPh ₄ ⁻	0.717	36.71	0.706	37.48	0.692	37.95

Table 6. Ionic radii, R_{\pm}° (Å) and solvation number, n_s , of ions in PC at 25°C

Ion	r_c (Å)	r_s (Å)	R_{\pm}° (Å)	n_s
Et ₄ N ⁺	4.00	2.82	3.45	-1.94
Pr ₄ N ⁺	4.52	3.21	3.98	-2.68
Bu ₄ N ⁺	4.94	3.49	4.53	-3.18
Pen ₄ N ⁺	5.29	4.81	4.89	-3.82
Hex ₄ N ⁺	5.59	5.38	5.28	-4.24
Hep ₄ N ⁺	5.88	6.39	5.41	-5.32
Li ⁺	0.60	3.72	5.01	3.71
Br ⁻	1.95	1.81	4.17	1.78
BF ₄ ⁻	2.01	1.68	4.02	1.53
BPh ₄ ⁻	4.20	3.76	4.84	-0.28

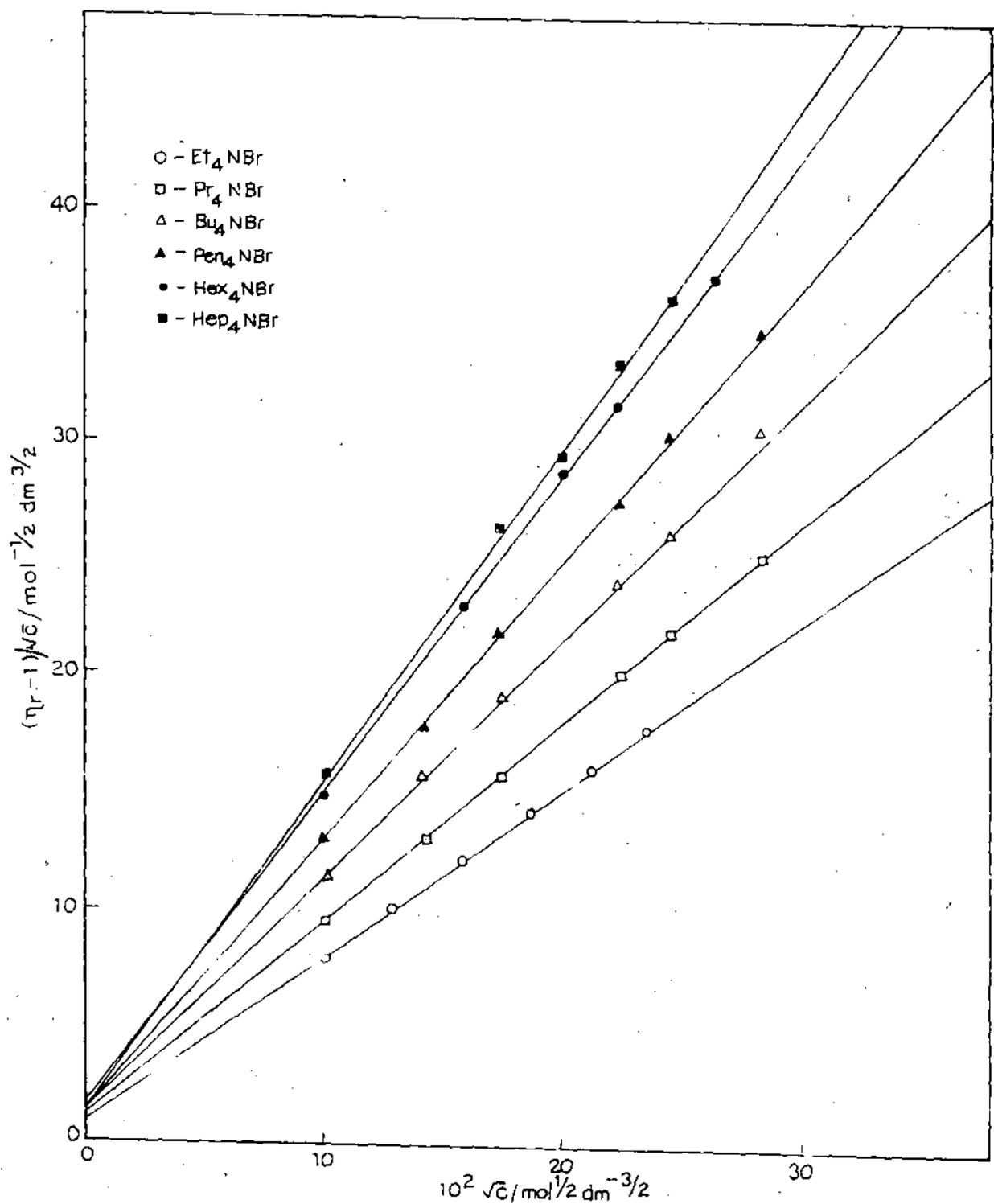


Fig. 1. Representative plot of $(\eta_r - 1)/\sqrt{C}$ against \sqrt{C} for some electrolytes in PC at 25°C

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CHAPTER-V

A Study on the Ion-Solvent Interactions of Tetraphenyl-
arsonium, Tetraphenylphosphonium and Some Common Ions
from Viscosity and Conductance Data

The viscosity measurements have been widely used¹⁻⁴ as an important experimental tool to provide information on the nature of ion-solvent interactions and the structural modifications of solvents by ions in solution. Although for a long time much attention has been paid to the viscosity B co-efficients of ions in aqueous solutions, measurements of B co-efficients in non-aqueous solutions are still scarce⁵. Similarly, conductance data also provides us valuable information regarding the ion-solvent interactions of electrolytes⁶ in aqueous, non-aqueous and mixed solvents. The potentiality of propylene carbonate (PC) as a solvent for a variety of applications of technological importance has already been mentioned in Chapters I and III. Moreover, the salts such as Ph_4AsCl , Ph_4PBr containing tetraphenyl ions play a very important role in Solution Chemistry and are often recommended as reference electrolytes^{2,7-10}. Thus, in the present chapter an attempt has been made to reveal the nature of ion-solvent interactions of Ph_4AsCl , Ph_4PBr and NaBPh_4 in propylene carbonate (PC) from their viscosity and conductance data. The viscosities have been measured at three different temperatures while conductance measurements were done at 25°C only. As the electrolytes are found to be unassociated in this medium, the viscosity data have been analysed using the Jones-

Dole equation in the form of unassociated electrolytes and the viscosity B co-efficients have been evaluated. Ionic B values have been derived on the basis of the reference electrolyte ' Bu_4NBPh_4 '. The conductance data are analysed by the Fuoss (1978) conductance equation and the limiting equivalent conductances have been evaluated. The single ion conductances have been derived by using two reference electrolytes ' Bu_4NBBu_4 ' and ' Bu_4NBPh_4 ' and the results have been compared.

Experimental

The purifications of the electrolytes have been described in Chapters II and IV. Freshly distilled solvent was always used for each experiment solvent properties of propylene carbonate (PC) at 25, 35 and 45°C have been mentioned earlier (Chapter - IV, Part - B).

For viscometric study, the concentrations of the salt solutions generally varied in the range 0.01-0.08 mol dm⁻³ and the solutions were prepared by weight dilution of the stock solution (ca 0.1 mol dm⁻³). The kinematic viscosities were measured at the desired temperature (accuracy $\pm 0.01^\circ\text{C}$) using a suspended Ubbelohde-type viscometer. Densities were measured using an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm³. The precisions of density and viscosity measurements were $\pm 3 \times 10^{-5}$ gcm⁻³ and 0.05% respectively.

For conductance measurements, ten to thirteen solutions of different concentrations ranging from 0.05-0.005 mol dm⁻³ were prepared for each salt. The electrical conductances were measured at 25°C with a Pye Unicam PW 9509 conductivity meter at a frequency of 2000 Hz. The details of experimental procedure have been given in Chapters II and IV.

Results

The density and viscosity data for the electrolytes at 25, 35 and 45°C have been recorded in Table 1.

The experimental viscosity data have been analysed by the Jones-Dole equation¹¹

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (1)$$

where, η and η_0 are the viscosities of the solution and the solvent respectively, c is the molar concentration and the other terms have their usual significance.

The plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ against \sqrt{c} for the electrolytes are linear (Fig. 1) and the experimental A values at 25, 35 and 45°C have been calculated using the least squares method. The A co-efficients were also calculated theoretically at 25°C from the

physical properties of the solvent and the limiting ionic equivalent conductances by using the Falkenhagen and Vernon equation¹²:

$$A_{\text{theo}} = \frac{0.2577 \Lambda_0}{\eta_0 (\epsilon T)^{1/2} \lambda_+^+ \lambda_-^-} \left[1 - 0.6863 \left(\frac{\lambda_+^+ - \lambda_-^-}{\Lambda_0} \right)^2 \right] \quad (2)$$

These A_{theo} values have been used for analysis of the viscosity data. In view of the weak temperature dependence of the A coefficients and non-availability of limiting ion-conductance values at different temperatures, A_{theo} values at 25°C have been utilized at the other two temperatures also. Theoretical A coefficients obtained from eqn. 2 along with the experimental A values are reported in Table 2.

Viscosity B coefficients obtained at 25, 35 and 45°C by using the least squares method have been recorded in Table 2.

Viscosity data have also been analysed on the basis of the transition state treatment of the relative viscosity of electrolyte solutions as suggested by Feakins et al¹³

$$B = \frac{\overline{V}_1^0 - \overline{V}_2^0}{1000} + \frac{\overline{V}_1^0}{1000} \left(\frac{\Delta \nu_2^{M^\ddagger} - \Delta \nu_1^{M^\ddagger}}{RT} \right) \quad (3)$$

In the above equation, \overline{V}_1^0 and \overline{V}_2^0 are the partial molar volumes of propylene carbonate and solute respectively. $\Delta \mu_2^{\ddagger}$, 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 the values have been reported in Table 3. $\Delta \mu_1^{\ddagger}$ is the free energy of activation per mole of pure solvent¹⁴.

Ionic B co-efficients along with the ionic $\Delta \mu_2^{\ddagger}$ values at three different temperatures are presented in Table 4.

Table 5 deals with the ionic radii and solvation numbers of ions at 25°C.

The measured equivalent conductances and the corresponding molarities for Ph_4AsCl , Ph_4PBr and NaBPh_4 in PC are given in Table 6. The conductance data were analysed with the help of the Fuoss conductance equation^{15,16} as described earlier (Chapter - IV).

The values of Λ_0 , K_A and R are recorded in Table 7.

The limiting ionic conductances (λ_0^{\pm}) based on the reference electrolytes viz. Bu_4NBBu_4 and Bu_4NBPh_4 (Λ_0 values taken from Chapter - IV) are given in Table 8, the λ_0^{\pm} value of Cl^- ion was taken from the literature¹⁷. The Walden products and Stokes radii of ions are also recorded in Table 8.

Discussion

The A coefficients reported in Table 2 are found to be small and positive for all the electrolytes and the observed A coefficients for Ph_4AsCl and NBPh_4 at 25°C agree very well with the theoretical ones. For Ph_4PBr , the experimental A coefficient at 25°C differs from the theoretical A value. Similar differences between theoretical and experimental A coefficients, however, have been observed in other systems⁷ also.

Viscosity B coefficients (Table 3) are large and positive and the values decrease in the order $B(\text{Ph}_4\text{AsCl}) > B(\text{NBPh}_4) > B(\text{Ph}_4\text{PBr})$. Viscosity B coefficients for Ph_4AsCl and Ph_4PBr in PC are greater than those in water (1.08 and 0.98 for Ph_4AsCl and 1.05 and 0.95 for Ph_4PBr at 25 and 35°C respectively)⁴. Viscosity B value for Ph_4PBr in PC at 25 and 35°C are smaller than the corresponding values in DMSO⁷ (viz. 1.356 and 1.270 at 25 and 35°C respectively). With the rise of temperature, the B values decrease in general (though it has a very weak temperature dependence), indicating that the tetraphenyl salts behave as structure makers in the solvent. This behaviour is similar to those observed in aqueous system⁴ and in other dipolar aprotic solvents like acetonitrile^{5,18}, dimethylsulphoxide^{7,19} and sulfolane²⁰.

The ionic B values were calculated by eqn. (4) using Bu_4NBPh_4 as the reference electrolyte^{8,9}

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{N}^+) + B(\text{Ph}_4\text{B}^-) \quad (4)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \left(\frac{5.35}{5.00} \right)^3 \quad (5)$$

Ionic B coefficients obtained from the above relationships have been recorded in Table 4. Viscosity B coefficient for the reference electrolyte, Bu_4NBPh_4 , has been taken from Chapter - IV. An attempt was made to measure the B coefficient of $\text{Ph}_4\text{AsBPh}_4$ in PC so that the internal consistency could be maintained for ionic B values. But owing to the poor solubility of $\text{Ph}_4\text{AsBPh}_4$ in PC, the experiment could not be performed. For this reason, ionic B value of Cl^- ion at 25°C was calculated by taking the B value of Et_4N^+ ion ($B_+ = 0.258$) from Chapter - IV and that of Et_4NCl ($B = 0.51$) from the literature²¹ assuming that the rule of additivity also holds too in this case. Table 4 shows that the ionic B values decrease in the order : $\text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+ > \text{Na}^+$ and $\text{Ph}_4\text{B}^- > \text{Br}^- > \text{Cl}^-$. With the increase of temperature the B_{\pm} values decrease in general indicating that these ions behave as structure makers in this solvent. Ionic free energies of activation of viscous flow based on the division of Bu_4NBPh_4 have also been presented in Table 4. $\Delta \int_2^{\mu^{\ddagger}}$ for Ph_4As^+ and Cl^- ions could not be calculated owing to the non-availability of ionic contributions of any one of these two ions. Values of $\Delta \int_2^{\mu^{\ddagger}}$ for the other ions are in the order : for cations, $\text{Ph}_4\text{P}^+ > \text{Na}^+$ and for anions $\text{Ph}_4\text{B}^- > \text{Br}^-$. It may be noted that $\Delta \int_2^{\mu^{\ddagger}}$

values for all the ions are positive and thus the formation of transition state is less favourable in the presence of these ions.

Ionic B_{\pm} co-efficients have also been analysed on the basis of Einstein's equation²²

$$B_{\pm} = 2.5 \frac{4}{3} \pi \frac{R_{\pm}^3 N}{1000} \quad (6)$$

where the terms have their usual significance. The number of solvent molecules (n_s) bound to the ion in the primary region can be calculated by the combination of the Jones-Dole equation with that of Einstein²³

$$B_{\pm} = \frac{2.5}{1000} (V_1 + n_s V_s) \quad (7)$$

where, V_1 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. The values of R_{\pm} and n_s are shown in Table 5. It can be seen that for cations, R_{\pm} values are in the order : $\text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+ > \text{Na}^+$. Comparison with their ionic radii indicates that the tetraphenyl ions are scarcely solvated in propylene carbonate. However, R_{\pm} value for Na^+ ions is about four times of its crystallographic radius indicating that this ion is highly solvated in this medium. Amongst the anions, although the ionic radius of BPh_4^- ion is larger than its crystallographic radius by a small amount but the ionic radii for Cl^- and Br^- ions are much greater than their crystallographic radii indicating that these two ions are solvated

in this medium. Similar observation for solvation of Br^- ion in PC has been reported by Yeager et al²⁴ from spectroscopic studies. It should be noted that from conductance studies of Br^- ion in PC (Chapter - IV) poor solvation was predicted. However, similar observation was also made by others¹⁷.

Table 7 shows that the limiting equivalent conductance (Λ_0) of the tetraphenyl salts decrease in the order $\text{Ph}_4\text{PBr} > \text{Ph}_4\text{AsCl} > \text{NaBPh}_4$. Since, ionic radii of Ph_4P^+ and Ph_4As^+ are close to each other and both of them are large enough, it appears that the higher mobility of Br^- ion compared to Cl^- ion is primarily responsible for the larger Λ_0 value of Ph_4PBr .

The association constants (K_A) in Table 7 show that these salts are almost unassociated ($K_A < 10$) in this solvent medium. This is quite expected owing to the high dielectric constant of PC, very large size of the tetraphenyl salts and their low charge density values.

The single ion conductances were calculated on the basis of reference electrolytes viz. Bu_4NBBu_4 ^{7,25} and Bu_4NBPh_4 ²⁶ by using the following relationships:

$$\lambda(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Bu}_4\text{B}^-) \quad (8)$$

$$\frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{Ph}_4\text{B}^-)} = \frac{r_{\text{Ph}_4\text{B}^-}}{r_{\text{Bu}_4\text{N}^+}} = \frac{5.35}{5.00} = 1.07 \quad (9)$$

The reason behind the choice of Bu_4NBBu_4 as the reference electrolyte lies in the fact that the cation and anion in this electrolyte are symmetrical in shape and have almost equal van der Waals volume.

The Λ_0 value for Bu_4NBBu_4 was taken from our earlier work (Chapter - IV) and the λ_0^\pm values thus calculated are presented in Table 8. The limiting ion conductances based on eqn. (9) have also been recorded in Table 8. It can readily be seen that the limiting ionic conductances obtained from the above relationships are in very close agreement with each other, suggesting that either of the above two reference electrolytes may be used for the division of Λ_0 values into ionic components in this medium. We also made an attempt to measure the limiting equivalent conductance of $\text{Ph}_4\text{AsBPh}_4$ so that the ionic λ_0 values for all the ions could be exclusively evaluated from the experimental results. However, due to the poor solubility of $\text{Ph}_4\text{AsBPh}_4$, the idea was discarded. The limiting ionic equivalent conductance for Ph_4As^+ ion was calculated by taking λ_0 value of Cl^- ion (15.90) from the literature¹⁷. Table 8 shows that the λ_0 values for the ions decrease in the order : $\text{Ph}_4\text{As}^+ > \text{Ph}_4\text{P}^+ > \text{Na}^+$ and $\text{Br}^- > \text{Cl}^- > \text{Ph}_4\text{B}^-$. The λ_0^\pm values for Na^+ and Br^- ions obtained by us are in good agreement with the values reported by Takeda et al [$\lambda_0(\text{Na}^+) = 10.45$ and $\lambda_0(\text{Br}^-) = 18.70$]¹⁷. Results indicate that the mobility of Br^- ion is greater than that of Cl^- ion.

The Walden product ($\lambda^{\pm} \eta$) and Stokes radii (r_s) of the ions have also been given in Table 8. From the table we can see that the Stokes radii of tetraphenyl ions are much less than the corresponding crystallographic radii (Table 5) and this shows that these ions are scarcely solvated in this solvent system. However, for Na^+ ion, the Stokes radius is much greater than its crystallographic radius (0.95 Å) indicating that this ion is substantially solvated in this solvent medium. This is also in consistent with the result obtained from the present viscometric study. Moreover, the Stokes radius of Na^+ ion in PC obtained by us (3.09 Å) is in excellent agreement with the literature value (3.10 Å)¹⁷. Table 8 further shows that the Br^- ion has the highest ionic mobility amongst the anions. The lower mobility of Cl^- ion than Br^- ion may be due to its enhanced ion-solvent interactions in this medium which effectively increases the size of this ion in solution. Larger Stokes radius of Cl^- ion compared to Br^- ion also supports the above view point. On the other hand it appears that large sizes of tetraphenyl ions, their low charge density values and the high relative permittivity of PC render these ions to be free, unassociated and almost unsolvated in this solvent medium.

Table 1. Concentration, c /(mol dm⁻³), density, ρ /(gcm⁻³) and relative viscosity, η_r of Ph₄AsCl, Ph₄PBr and NaBPh₄ in PC at 25, 35 and 45°C

c	ρ	η_r	c	ρ	η_r
Ph ₄ AsCl 25°C			Ph ₄ PBr 25°C		
0.01374	1.19953	1.0174	0.01512	1.19967	1.0195
0.02762	1.20023	1.0348	0.03001	1.20049	1.0373
0.03255	1.20046	1.0404	0.03993	1.20104	1.0492
0.03753	1.20074	1.0465	0.05506	1.20188	1.0668
0.04249	1.20099	1.0523	0.06994	1.20270	1.0841
0.05260	1.20150	1.0644			
NaBPh ₄ 25°C			Ph ₄ AsCl 35°C		
0.01003	1.19896	1.0134	0.01353	1.19019	1.0168
0.02506	1.19915	1.0342	0.02740	1.19069	1.0334
0.04010	1.19936	1.0505	0.03229	1.19087	1.0394
0.05013	1.19946	1.0625	0.03723	1.19105	1.0452
0.05982	1.19958	1.0744	0.04214	1.19123	1.0510
0.08020	1.19982	1.0988	0.05217	1.19159	1.0631

Table 1 (Contd..)

Ph ₄ PBr 35°C			NaBPh ₄ 35°C		
0.01501	1.19041	1.0180	0.01044	1.18998	1.0104
0.02977	1.19111	1.0346	0.02832	1.19040	1.0308
0.03962	1.19158	1.0455	0.04541	1.19081	1.0485
0.05462	1.19228	1.0621	0.05702	1.19109	1.0605
0.06938	1.19298	1.0786	0.06790	1.19135	1.0717
			0.09133	1.19191	1.0957
Ph ₄ AsCl 45°C			Ph ₄ PBr 45°C		
0.01350	1.17825	1.0164	0.01486	1.17857	1.0170
0.02712	1.17854	1.0325	0.02948	1.17917	1.0329
0.03196	1.17865	1.0382	0.03922	1.17957	1.0433
0.03684	1.17875	1.0438	0.05406	1.18018	1.0593
0.04171	1.17886	1.0496	0.06867	1.18078	1.0750
0.05162	1.17907	1.0614			

Contd..

Table 1 (Contd..)

	NaBPh ₄ 45°C	
0.00985	1.17832	1.0121
0.02464	1.17886	1.0297
0.03943	1.17939	1.0469
0.04930	1.17975	1.0584
0.05885	1.18010	1.0696
0.07893	1.18083	1.0930

Table 2. Theoretical A values and experimental A co-efficients, $A_{\text{obs}}/\text{dm}^{3/2}\text{mol}^{-1/2}$ at 25, 35 and 45°C

Salts	A_{theo} (25°C)	A_{obs}		
		25°C	35°C	45°C
Ph_4AsCl	0.0112	0.0111	0.0066	0.0066
Ph_4PBr	0.0106	0.0207	0.0149	0.0126
NaBPh_4	0.0154	0.0166	0.0134	0.0081

Table 3. Viscosity B co-efficients, $B/\text{dm}^3\text{mol}^{-1}$ and $\Delta/\mu^{\circ\pm}/\text{kJ mol}^{-1}$ values in propylene carbonate at different temperatures

Salts	25°C		35°C		45°C	
	B	$\Delta/\mu^{\circ\pm}$	B	$\Delta/\mu^{\circ\pm}$	B	$\Delta/\mu^{\circ\pm}$
Ph_4AsCl	1.176±0.007	56.22	1.166±0.003	57.42	1.146±0.003	58.27
Ph_4PBr	1.150±0.003	55.78	1.087±0.001	55.25	1.049±0.001	55.28
NaBPh_4	1.175±0.001	55.31	1.158±0.004	55.46	1.130±0.002	55.41

Table 4. Ionic B co-efficients^a, $B_{\pm}/\text{dm}^3\text{mol}^{-1}$ and ionic $\Delta\mu_{\pm}^{\ddagger}/\text{kJ mol}^{-1}$ values in PC at different temperatures

Ion	25°C		35°C		45°C	
	B_{\pm}	$\Delta\mu_{\pm}^{\ddagger}$	B_{\pm}	$\Delta\mu_{\pm}^{\ddagger}$	B_{\pm}	$\Delta\mu_{\pm}^{\ddagger}$
Ph_4As^+	0.924	-	-	-	-	-
Ph_4P^+	0.692	33.44	0.659	32.96	0.638	32.84
Na^+	0.458	18.60	0.452	17.98	0.438	17.46
Cl^-	0.252	-	-	-	-	-
Br^-	0.458	22.34	0.428	22.29	0.411	22.44
BPh_4^-	0.717	36.71	0.706	37.48	0.692	37.95

^a Division on the basis of Bu_4NBPh_4

Table 5. R_{\pm}° and solvation number (n_s) of ions in PC at 25°C

Ion	$r_c^* / \text{\AA}$	R_{\pm}°	n_s
Ph_4As^+	6.40 ^a	5.27	-8.55
Ph_4P^+	6.30 ^a	4.79	-9.05
Na^+	1.17 ^b	4.18	2.12
Cl^-	1.64 ^b	3.42	0.89
Br^-	1.80 ^b	4.17	1.78
BPh_4^-	4.20 ^c	4.84	-0.28

r_c^* = Crystallographic radii

^a C.V. Krishnan and H.L. Friedman, *J. Phys. Chem.*, **73**, 3934, 1969.

^b B.S. Gourary and F.J. Adrian, *Solid State Phys.*, **10**, 127, 1960.

^c R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1959.

Table 6. Equivalent conductances and corresponding molarities of the salts in PC at 25°C

$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{mol}^{-1}$	$10^4 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{mol}^{-1}$
Ph_4AsCl		Ph_4PBr	
526.010	20.95	503.161	22.01
424.854	21.54	425.378	22.56
375.326	21.85	390.417	22.81
325.538	22.21	352.436	23.11
276.169	22.63	300.803	23.49
226.221	22.98	271.034	23.74
175.895	23.42	240.035	24.06
125.065	23.98	210.937	24.30
90.716	24.46	191.420	24.53
51.498	25.03	152.793	24.97
		127.613	25.27
		80.867	26.03
		51.653	26.63
NaBPh_4			
495.579	13.66		
426.918	14.08		
380.736	14.36		
351.022	14.58		
298.843	14.92		
271.135	15.16		
239.549	15.41		
210.876	15.65		
189.741	15.83		
155.893	16.21		
125.704	16.51		
90.385	16.94		
52.179	17.53		

Table 7. Conductance parameters of the electrolytes in PC at 25°C

Salts	$\Lambda_{\infty}/\text{Scm}^2\text{mol}^{-1}$	$K_A/\text{dm}^3\text{mol}^{-1}$	walden product	$R/\text{\AA}$	σ
Ph_4AsCl	27.21 ± 0.02	4.57 ± 0.07	0.672	11.20	0.10
Ph_4PBr	29.01 ± 0.02	5.52 ± 0.05	0.717	9.30	0.07
NaBPh_4	19.58 ± 0.02	7.75 ± 0.08	0.484	14.00	0.09

Table 8. Limiting ionic conductances, Walden products and Stokes radii of the ions in PC at 25°C

Ion	$\lambda_{\infty}^{+a} / \text{Scm}^2 \text{mol}^{-1}$	$\lambda_{\infty}^{+b} / \text{Scm}^2 \text{mol}^{-1}$	$\lambda_{\infty}^{+\eta a} / \text{Scm}^2 \text{mol}^{-1} \text{P}$	$\lambda_{\infty}^{+\eta b} / \text{Scm}^2 \text{mol}^{-1} \text{P}$	$r_s^a / \text{\AA}$	$r_s^b / \text{\AA}$
Ph_4As^+	11.31	-	0.279	-	2.93	-
Ph_4P^+	10.77	10.79	0.266	0.267	3.03	3.06
Na^+	10.72	10.74	0.255	0.265	3.09	3.09
Cl^-	15.90 ^c	-	0.393	-	2.08	-
Br^-	18.24	18.22	0.451	0.450	1.81	1.82
Ph_4S^-	8.86	8.34	0.219	0.218	3.74	3.75

^a Calculations based on Bu_4NBBu_4 .

^b Calculations based on Bu_4NBPh_4 .

^c from ref. 17

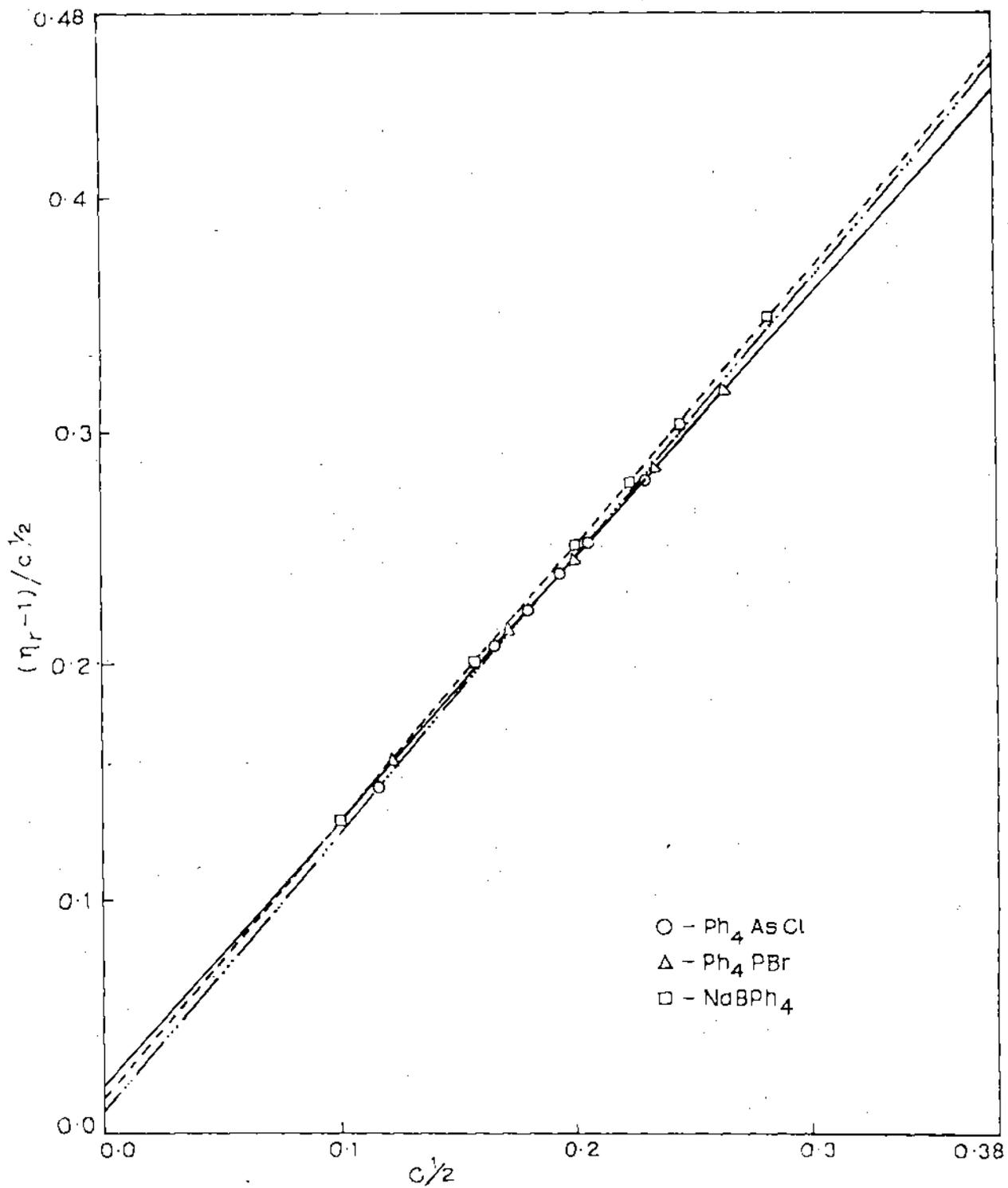


Fig. 1. Representative plot of $(\eta_r - 1)/c^{1/2}$ against $c^{1/2}$ for some electrolytes in PC at 25°C

R E F E R E N C E S

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CHAPTER-VI

Excess Properties for Binary Mixtures of Propylene Carbonate with 2-Methoxyethanol, 1,2-Dimethoxyethane, Tetrahydrofuran and Methanol at 25, 35 and 45°C

Recent years have witnessed considerable interest¹⁻⁵ in the thermodynamic excess properties of binary liquid mixtures. These properties have been very helpful to obtain information on the intermolecular interactions and geometrical effects in these systems⁴. The potentiality of propylene carbonate (PC) as solvent for a variety of applications particularly in high energy batteries has been mentioned earlier (Chapters I and III). Solvents like 2-methoxyethanol (ME; methyl cellosolve), 1,2-dimethoxyethane (DME), tetrahydrofuran (THF) and methanol too find a wide range of applications of technological importance namely, as solvents and solubilizing agents in organic syntheses⁶, reaction kinetics and electrochemical studies^{6,7}. However, barring a few^{8,9}, the binary liquid systems of propylene carbonate with other non-aqueous solvents have not been studied.

In the present study, densities and viscosities have been measured for four binary liquid mixtures of PC + ME, PC + DME, PC + THF and PC + Methanol at different temperatures. The excess molar volumes (V^E), excess viscosities (η^E) and excess molar free energies of activation of flow (G^{*E}) have been determined for these binary systems over the entire range of their compositions at 25, 35 and 45°C. Attempts have been made to explain the behaviour of

the liquid mixtures on the basis of sign and magnitude of these properties. McAllister equation¹⁰ has also been used to calculate the interaction parameters (ν_{ij}) from the kinematic viscosity data.

Experimental

Propylene carbonate (E. Merck, Germany; > 99% pure) was purified as described earlier (Chapter - II).

2-methoxyethanol [ME] (G.R. E. Merck) was distilled in an all-glass distillation apparatus before use. The physical properties at 25°C of purified ME were : density 0.96002 gcm⁻³ and viscosity 1.5414 cp. The viscosity and density values are in reasonable agreement with the reported literature values¹¹ which are 1.60 cp and 0.96024 gcm⁻³ respectively.

1,2-dimethoxyethane [DME] (Fluka, purum) was shaken well with FeSO₄ (AR, BDH) for 1-2 h, decanted and distilled. The distillate was refluxed for 12 h and redistilled over metallic sodium¹². The boiling point (84.5°C) and density (0.86132 gcm⁻³ at 25°C) compared fairly well with the corresponding literature values¹³ which are 85°C and 0.86120 gcm⁻³ respectively.

Tetrahydrofuran [THF] (E. Merck, India) was kept over KOH, refluxed for 24 h and distilled over LiAlH_4 ¹⁴. The density (0.88072 gcm^{-3}) and viscosity (0.4630 cP) at 25°C of the purified sample are in good conformity with the literature values¹⁵ ($\rho = 0.8811 \text{ gcm}^{-3}, \eta = 0.46 \text{ cP}$).

Methanol (E. Merck, India, Uvasol grade) was dried over 3A molecular sieves and distilled fractionally. Middle fraction was taken and further distilled¹⁶. Physical properties of purified methanol at 25°C ($\rho = 0.78663 \text{ gcm}^{-3}$ and $\eta = 0.5437 \text{ cP}$) agreed well with the literature values¹¹ which are : $\rho = 0.78664 \text{ gcm}^{-3}$ and $\eta = 0.5445 \text{ cP}$.

Freshly distilled solvents were always used for the preparation of solvent mixtures. All solutions were prepared by weight and special air-tight bottles were used for mixture preparation. When once the mixtures were made, all measurements were done on the same day to avoid vapour loss, moisture absorption, contamination and oxidation of the mixtures.

Densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of capillary of about 1 mm. The pycnometer was calibrated at $25, 35$ and 45°C with doubly distilled deionized water. The temperature control had an accuracy of $\pm 0.01^\circ\text{C}$. The precision of density measurement was $\pm 3 \times 10^{-5} \text{ gcm}^{-3}$.

Kinematic viscosities were measured at the desired temperature (accuracy $\pm 0.01^\circ\text{C}$) by using a suspended Ubbelohde-type viscometer. The precision of viscosity measurements was $\pm 0.05\%$. The kinematic viscosities were converted into the absolute viscosities by multiplying the former with density.

In all the cases, the experiments were performed in three replicates for each composition and at each temperature and the results were averaged.

Results and Calculations

The experimental results of density and viscosity measurements at various mole fractions are reported in Table 1.

The kinematic viscosity data have been analyzed by means of McAllister equation¹⁰:

$$\ln \nu = x_1^3 \ln \nu_1 M_1 + x_2^3 \ln \nu_2 M_2 - \ln(x_1 M_1 + x_2 M_2) + 3x_1^2 x_2 \ln \nu_{12} \left(\frac{2M_1 + M_2}{3} \right) + 3x_2^2 x_1 \ln \nu_{21} \left(\frac{2M_2 + M_1}{3} \right) \quad (1)$$

The interaction parameters ν_{ij} along with the kinematic viscosity data at different temperatures are also reported in Table 1.

The excess functions have been calculated by the following equations,

$$V^E = (x_1 M_1 + x_2 M_2) / \rho - x_1 M_1 / \rho_1 - x_2 M_2 / \rho_2 \quad (2)$$

$$\eta^E = \eta - x_1 \eta_1 - x_2 \eta_2 \quad (3)$$

$$G^{*E} = RT [\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (4)$$

where, x_1 and x_2 are the mole fractions of components 1 and 2 respectively; V , V_1 and V_2 are the molar volumes and η , η_1 and η_2 are the measured co-efficients of viscosity of the mixture, component 1 and PC respectively. The subscript 1 refers either to ME or DME or THF or CH_3OH in the concerned binary mixture. The molar volume V is defined by the relationship

$$V = (x_1 M_1 + x_2 M_2) / \rho \quad (5)$$

where, M_1 and M_2 are the molecular weights of component 1 and 2 respectively and ρ is the density of the mixture. The excess properties of the binary mixtures at different temperatures have been recorded in Table 2.

Graphical representations of V^E and η^E as functions of the mole fraction of pure component in the binary mixtures are given in

the figures 1A to 1D and 2A to 2D respectively.

The excess functions have been fitted to Redlich-Kister equation¹⁷,

$$X^E = x_1 x_2 \sum_{j=0}^n A_j (x_1 - x_2)^j \quad (6)$$

where X^E is V^E or η^E and A_0, A_1, A_2, \dots etc. are the adjustable parameters. These parameters were evaluated by the method of least squares. The values of these parameters along with the standard deviations, $\sigma(X^E)$ of X^E as defined by

$$\sigma(X^E) = \left[\frac{\sum (X_{\text{exptl}}^E - X_{\text{calcd}}^E)^2}{N - M} \right]^{0.5} \quad (7)$$

are recorded in Table 3. In equation (7), N is the total number of experimental points and M is the number of adjustable parameters. The results obtained from the correlation equation (eq. 6) are quite satisfactory for majority of the systems investigated with the possible exception of V^E values for PG + ME binary mixture. Owing to the unsymmetrical nature of the variation of V^E with respect to mole fraction in this mixture, higher $\sigma(V^E)$ s are obtained.

Discussion

Kinematic viscosity data for the binary solvent mixtures were correlated with McAllister equation¹⁰ of three body interactions. In all the studied binary mixtures viz. PC + ME, PC + DME, PC + THF and PC + CH₃OH, the values of ν_{ij} are found to change with temperature. From Table 1, it is observed that in PC + ME mixtures, values of ν_{12} are slightly greater than the corresponding ν_{21} values at each temperature. In PC + ME binary system, ν_{12} and ν_{21} refer to the interactions of types ME-ME-PC and PC-PC-ME respectively. However, for the other three binary solvent systems, the values of ν_{12} are less than the corresponding ν_{21} values. It indicates that the interaction parameters resulting from the interactions of PC-PC-DME, PC-PC-THF and PC-PC-CH₃OH types are greater than the parameters originating from the corresponding DME-DME-PC, THF-THF-PC and CH₃OH - CH₃OH - PC interactions in PC + DME, PC + THF and PC + CH₃OH solvent mixtures respectively. Further, the values of ν_{ij} and ν_{ji} decrease with increase of temperature in general, for all the systems. Similar results have also been observed in other non-aqueous-non-aqueous solvent mixtures.¹⁸

It is well known¹⁹ that the sign and magnitude of V^E give a good estimate of the strength of unlike interactions in the binary mixtures. Large positive V^E values are taken as indicative of weak intermolecular interactions, whereas, large negative values of V^E are attributed to different sizes of molecules or to the dipole-

dipole interactions between them¹⁹.

From Fig. 1A, it is observed that in PC + ME solvent mixtures, the excess molar volume varies with the mole fraction of pure component in an unsymmetrical fashion. IR studies^{20,21} on 2-methoxyethanol indicate that the predominant configuration of ME molecule is the gauche form and it favours the intramolecular hydrogen bonding in ME. The unsymmetrical nature of V^E vs mole fraction curves of PC + ME mixtures, appears to be due to the steric factors arising from a change in the proportion of the different geometric forms of ME molecules with change in its mole fraction. Similar unsymmetrical variation of V^E has been reported for THF + p-dioxane binary system in the literature²².

From Fig. 1B, we see that the V^E values of PC + DME binary mixtures are negative over the entire composition range and become more negative as the temperature rises. This can be explained in terms of like and unlike intermolecular interactions. Studies on the dielectric and spectroscopic properties of liquid propylene carbonate²³ indicate that it behaves as a normal polar liquid with strong dipole-dipole interactions with little or no specific interaction present. It appears that the intermolecular interactions between PC and DME molecules in the mixture predominate over the intermolecular interactions between like molecules. Another effect which may result for negative values of V^E in binary solven

mixtures having components of different sizes is the accommodation of one component into the structure of the other. By considering the molar volumes of PC and DME (85.16 and 104.63 $\text{cm}^3\text{mol}^{-1}$ respectively), the interstitial accommodation of one component into the other seems not to be easy in this mixture. Thus, it appears that the dipolar forces between the different kinds of molecules cause the decrease in volume of this mixture. This model is also in accordance with Prigogine theory¹⁹, which attributes the negative V^E values to different sizes of molecules or to the dipole-dipole interactions between them.

In PC + THF solvent mixtures, the excess molar volumes at different temperatures are negative over the whole range of compositions (Fig.1C). The magnitude of V^E increases with increase in temperature. The minima of V^E appear at a mole fraction of 0.5. Several effects may contribute to the V^E values and out of these, three may be considered as being important : (a) break-up of intermolecular dipolar interactions in PC, (b) dipole-dipole interactions between unlike molecules and (c) interstitial accommodation of one component into the other. It appears that on mixing THF with PC, the dipole-dipole interactions between PC molecules become weaker and the dipolar interactions between unlike molecules predominate, as a result of which a sharp decrease in volume occurs. Again, since the molar volumes of PC and THF (85.16 and 81.88 $\text{cm}^3\text{mol}^{-1}$ respectively) are not far apart from each other, the third

effect i.e. the possibility of accommodation of one molecule into the structure of the other may be neglected for this system.

In PC + CH₃OH binary system, the excess molar volumes are negative at each temperature. With rise in temperature, the values of V^E decrease further and the minima of V^E appear in the vicinity of 0.7 mole fraction of CH₃OH, as shown in Fig. 1D. In the present system, considerable amount of positive contributions to V^E values are expected from the break-up of interactions between like molecules viz. the disruption of intermolecular hydrogen bonds in methanol and loosening of the dipolar interactions between PC molecules. Results indicate that the negative contributions predominate in this mixture. The important source for negative contributions is the interactions between unlike molecules. However since methanol (with a donor number 19.1) is a stronger base and thus probably a stronger hydrogen bond acceptor than PC (donor number 15.1) and PC has no such desired hydrogen atom, it appears that the hydrogen bond formation between these two unlike molecules is not favoured in this system. Another possibility of specific interaction lies with the bonding through hydroxyl group of CH₃OH. But there is a lack of well-developed centre of positive charge²⁴ in PC and thus the hydrogen bonding between CH₃OH and PC even if occurs, appears to be weak. Considering these factors, we think that the contributions due to PC-CH₃OH heteroassociation alone are not sufficient enough to override the positive contributions. Simple dipole-dipole interactions between PC and CH₃OH molecules may also

contribute to the negative values of V^E . However, the most important source for negative contributions appears to be the differences in size and shape of the pure components in the mixture. The molar volumes of PC and CH_3OH at 25°C are 85.16 and $40.73 \text{ cm}^3 \text{ mol}^{-1}$ respectively and it might allow the components to fit into each other's structure causing the reduction in volume of the mixture.

Values of the quantity, η^E , which refer to the deviations from a rectilinear dependence²⁵ of the viscosity of the mixture on mole fraction, can be discussed from the view point of intermolecular interactions^{9,25}. For systems, where dispersion and dipolar forces are operating, the values of η^E are found to be negative, whereas, the existence of charge-transfer and hydrogen bond interactions leading to the formation of complex species between the two components of the binary system make the values of η^E positive. For systems where, all types of intermolecular forces are operating, the values of η^E will be due to the net effect of individual contributions from all types of interactions.

The system, PC + ME shows negative deviations of η^E from ideality over the entire mole fraction range and over the whole range of temperatures (Fig. 2A). The minima of η^E values correspond to 0.4 mole fraction of ME. As the temperature increases, the magnitude of excess viscosity decreases, showing a tendency towards ideal behaviour. The negative deviation of η^E indicates that mixing of ME with PC tends to loosen the strong dipolar forces

between PC molecules and intermolecular dipolar or dispersion interactions between unlike molecules (PC and ME) predominate in the mixture.

In PC + DME binary system, the negative contributions to η^E , arising from the intermolecular interactions are predominant. Fig. 2B further shows that the minima of η^E lie at 0.4 mole fraction of DME at each temperature. Results indicate that the system lacks heteroassociation or specific interaction between the two different kinds of molecules and the dispersion and dipolar interactions between PC and DME molecules are primarily responsible for negative values of excess viscosity.

The third system i.e. PC + THF, also shows negative excess viscosity values. Like PC + ME and PC + DME binary systems, PC + THF mixtures also have the same trend of η^E , as is evident from Figs. 2A-2C. Negative values of η^E appear to be due to the predominant dispersion and dipolar interactions between the unlike molecules.

Binary mixtures of PC and CH_3OH also show negative values of η^E over the entire composition range and over the whole range of temperatures. The minima of η^E correspond to 0.4 mole fraction of CH_3OH at each temperature (Fig. 2D). As the temperature increases, the magnitude of η^E decreases and approaches towards the ideal behaviour. According to Fort and Moore²⁵, negative values of η^E

occur for systems of different molecular sizes and the dispersion forces are primarily responsible for the interactions. The molar volume of PC ($85.16 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C) is much greater than that of CH_3OH ($40.73 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C) and it might allow one component to fit into the structure of the other, resulting in a decrease in viscosity of the binary system. However, intermolecular association between PC and CH_3OH molecules, if present, might have some positive contributions to the η^E values. The other possible effect i.e. the intermolecular dipolar interactions between unlike molecules (PC and CH_3OH) may also have some negative contribution to η^E . However in the present system, the interstitial accommodation of one component into the structure of the other appears to be predominant over the other effects.

Another thermodynamic function, which has also been investigated, is the excess molar free energy of activation of flow (G^{*E}). Values of G^{*E} have been calculated from eqn. (4), which results from the Eyring equation⁹ of viscosity flow modified for a binary mixture. According to Reed and Taylor²⁶ and Meyers et al²⁷, the G^{*E} parameter may be considered as a reliable measure to detect the presence of interactions between molecules. Positive values of G^{*E} can be seen in binary systems where specific interactions between unlike molecules take place. The binary systems PC + ME, PC + DME and PC + THF have distinct negative values of G^{*E} at all compositions over the entire range of temperatures (Table 2).

The negative signs of G^{*E} indicate that the specific interactions between unlike molecules even if present, are not predominant in these systems. In fact, mixtures where a strong specific interaction between unlike molecules is predominant, are characterized by distinct maxima in the viscosity vs composition curves, by positive excess viscosities and positive values of G^{*E} ^{25,28-31}.

The negative values of η^E and the absence of any maxima in viscosity as a function of mole fraction indicate further that the intermolecular association between unlike molecules is likely to be absent in the binary mixtures of PC + ME, PC + DME and PC + THF. It further supports the view point that the dispersion and dipolar forces between unlike molecules are the controlling forces and play the major role in the stabilization of these systems. However, for PC + CH₃OH mixtures, signs of G^{*E} are positive and its magnitudes are small at each temperature. Small positive values of G^{*E} along with negative v^E and η^E have also been found for other binary mixtures⁹ where a strong dipole-dipole and dispersion interactions are predominant. Analysis of viscosity, excess molar volume and excess viscosity data for PC-CH₃OH mixtures reveals that the system lacks a strong specific interaction between unlike molecules. Considering all findings, it appears that the interstitial accommodation of one component into the structure of the other play the major role for the stabilization of PC-CH₃OH binary system.

Table 1. Experimental Density (ρ)/gcm⁻³, Kinematic Viscosity (ν)/St, Absolute Viscosity (η)/cP and Interaction Parameters (ν_{1j}) Data for the Binary Mixtures of Propylene Carbonate 25, 35 and 45°C

x_1	ρ	ν	η	ν_{12}	ν_{21}
PC + ME at 25°C					
0.0000	1.19883	2.0613	2.4711		
0.0632	1.18541	1.9384	2.2977		
0.1045	1.17620	1.8648	2.1934		
0.1523	1.16489	1.8060	2.1038		
0.2117	1.14959	1.7430	2.0037		
0.2527	1.14046	1.7097	1.9499		
0.3050	1.13021	1.6725	1.8902	1.5363	1.4861
0.3489	1.12038	1.6446	1.8425		
0.3970	1.10935	1.6170	1.7938		
0.4547	1.09591	1.5923	1.7450		
0.4979	1.08566	1.5814	1.7169		
0.5531	1.07227	1.5668	1.6801		

Contd..

Table 1 (Contd..)

0.5954	1.06174	1.5672	1.6640
0.6954	1.03576	1.5636	1.6195
0.7346	1.02571	1.5535	1.5934
0.7959	1.01037	1.5580	1.5742
0.8414	0.99902	1.5701	1.5686
0.9025	0.98376	1.5706	1.5451
0.9593	0.96985	1.5941	1.5460
1.0000	0.96002	1.6056	1.5414

PC + ME at 35°C

0.0000	1.18970	1.7211	2.0476	
0.0632	1.17626	1.6267	1.9134	
0.1045	1.16722	1.5628	1.8241	
0.1523	1.15630	1.5189	1.7563	
0.2117	1.14207	1.4699	1.6786	
0.2527	1.13256	1.4429	1.6341	
0.3050	1.12061	1.4110	1.5811	
0.3489	1.11068	1.3838	1.5370	
0.3970	1.09980	1.3596	1.4925	1.3027
				1.2591

Contd..

Table 1 (Contd..)

0.4547	1.08661	1.3399	1.4559
0.4979	1.07218	1.3334	1.4296
0.5954	1.05260	1.3159	1.3851
0.6388	1.04182	1.3064	1.3610
0.6954	1.02764	1.3053	1.3413
0.7346	1.01770	1.3017	1.3247
0.7959	1.00234	1.3068	1.3099
0.8414	0.99098	1.3084	1.2966
0.9025	0.97570	1.3078	1.2760
0.9593	0.96228	1.3156	1.2659
1.0000	0.95356	1.3192	1.2579

PC + ME at 45°C

0.0000	1.17796	1.4630	1.7234
0.0632	1.16485	1.3841	1.6123
0.1045	1.15626	1.3326	1.5409
0.1523	1.14614	1.2947	1.4840
0.2117	1.13323	1.2557	1.4230

Contd..

Table 1 (Contd..)

0.2527	1.12441	1.2278	1.3813		
0.3050	1.11252	1.2035	1.3389		
0.3489	1.10261	1.1850	1.3065		
0.3970	1.09156	1.1662	1.2729	1.1087	1.0808
0.4547	1.07799	1.1352	1.2237		
0.4979	1.06769	1.1372	1.2142		
0.5531	1.05423	1.1225	1.1834		
0.5954	1.04369	1.1226	1.1716		
0.6388	1.03295	1.1100	1.1466		
0.6954	1.01878	1.1065	1.1273		
0.7346	1.00883	1.1013	1.1110		
0.7959	0.99359	1.1046	1.0976		
0.8414	0.98236	1.1019	1.0825		
0.9025	0.96743	1.1123	1.0760		
0.9593	0.95418	1.1061	1.0554		
1.000	0.94715	1.1080	1.0494		

Contd..

Table 1 (Contd..)

PC + DME at 25°C					
0.0000	1.19883	2.0613	2.4711		
0.0493	1.18024	1.8869	2.2270		
0.0999	1.16206	1.6863	1.9600		
0.1524	1.14235	1.5335	1.7518		
0.1867	1.13033	1.4479	1.6366		
0.2298	1.11468	1.3524	1.5075		
0.3128	1.08643	1.1864	1.2889		
0.3708	1.06594	1.0898	1.1617		
0.4036	1.05526	1.0400	1.0974	0.7566	0.96687
0.4686	1.04097	0.9318	0.9699		
0.5193	1.01609	0.8742	0.8882		
0.6382	0.97683	0.7444	0.7272		
0.6767	0.96394	0.7142	0.6885		
0.7589	0.93705	0.6453	0.6047		
0.8103	0.92058	0.6071	0.5589		
0.8432	0.91034	0.5963	0.5429		
0.9035	0.89135	0.5466	0.4872		
0.9483	0.87695	0.5204	0.4564		
1.0000	0.86132	0.4918	0.4236		

Contd..

Table 1 (Contd..)

PC + DME at 35°C			
0.0000	1.18970	1.7211	2.0476
0.0493	1.17117	1.5653	1.8332
0.0999	1.15234	1.4396	1.6589
0.1524	1.13349	1.3194	1.4955
0.1867	1.12093	1.2507	1.4019
0.2298	1.10559	1.1727	1.2966
0.2769	1.08843	1.0867	1.1828
0.3708	1.05560	0.9448	0.9973
0.4036	1.04482	0.9412	0.9447
0.5193	1.00622	0.7731	0.7779
0.5704	0.98953	0.7254	0.7178
0.6767	0.95613	0.6385	0.6105
0.8103	0.91468	0.5523	0.5052
0.8432	0.90450	0.5228	0.4728
0.9035	0.88518	0.4949	0.4381
0.9483	0.87025	0.4680	0.4073
1.0000	0.85129	0.4519	0.3847

0.6214

0.9547

Contd..

Table 1 (Contd..)

PC + DME at 45°C			
0.0000	1.17796	1.4631	1.7234
0.0493	1.15999	1.3460	1.5614
0.0999	1.14185	1.2406	1.4166
0.1524	1.12302	1.1368	1.2766
0.2298	1.09638	1.0152	1.1130
0.3128	1.06819	0.9058	0.9676
0.3708	1.04842	0.8403	0.8810
0.4036	1.03767	0.7972	0.8272
0.5193	0.99856	0.6837	0.6827
0.5704	0.98137	0.6510	0.6389
0.6382	0.95858	0.5976	0.5728
0.6767	0.94547	0.5763	0.5449
0.7589	0.91810	0.5209	0.4782
0.8103	0.90116	0.5073	0.4571
0.8432	0.89078	0.4913	0.4376
0.9035	0.87144	0.4555	0.3970
0.9483	0.85667	0.4378	0.3750
1.0000	0.84076	0.4158	0.3496

0.5700

0.8230

Contd..

Table 1 (Contd..)

PC + THF at 25°C			
0.0000	1.19883	2.0613	2.4711
0.0524	1.18373	1.8813	2.2270
0.1036	1.16899	1.7301	2.0225
0.1429	1.15743	1.6153	1.8695
0.2064	1.13888	1.4695	1.6736
0.2431	1.12777	1.3891	1.5666
0.3083	1.10786	1.2576	1.3932
0.3478	1.09581	1.1894	1.3034
0.4095	1.07679	1.0877	1.1712
0.6094	1.01221	0.8315	0.8417
0.6479	0.99923	0.7842	0.7836
0.7082	0.97900	0.7324	0.7171
0.7635	0.96036	0.6820	0.6549
0.8062	0.94620	0.6547	0.6195
0.8388	0.93489	0.6237	0.5831
0.9035	0.91352	0.5864	0.5357
0.9631	0.89326	0.5430	0.4850
1.0000	0.88072	0.5257	0.4630

0.7517

1.1677

Contd..

PC + THF at 35°C

0.0000	1.18970	1.7211	2.0476		
0.0524	1.17480	1.5817	1.8581		
0.1036	1.15960	1.4738	1.7090		
0.1429	1.14834	1.3888	1.5948		
0.2054	1.12941	1.2680	1.4321		
0.2431	1.11855	1.2079	1.3511		
0.3083	1.09884	1.0993	1.2080		
0.3478	1.08681	1.0425	1.1330		
0.4095	1.06788	0.9595	1.0247		
0.5098	1.03638	0.8446	0.8753	0.6745	1.0408
0.5621	1.01955	0.7889	0.8044		
0.6094	1.00412	0.7473	0.7503		
0.6479	0.99130	0.7077	0.7016		
0.7082	0.97123	0.6636	0.6445		
0.7635	0.95253	0.6257	0.5960		
0.8388	0.92667	0.5786	0.5361		
0.9035	0.90441	0.5387	0.4872		
0.9631	0.88035	0.5053	0.4449		
1.0000	0.87033	0.4914	0.4277		

Contd..

Table 1 (Contd..)

PC + THF at 45°C

0.0000	1.17796	1.4630	1.7234		
0.0524	1.16457	1.3648	1.5894		
0.1036	1.14998	1.2689	1.4592		
0.1429	1.13889	1.2074	1.3751		
0.2064	1.12024	1.1057	1.2386		
0.2431	1.10988	1.0516	1.1672		
0.3083	1.09041	0.9689	1.0565		
0.3478	1.07857	0.9197	0.9920		
0.5098	1.02837	0.7567	0.7782	0.5981	0.9404
0.5621	1.01179	0.7138	0.7222		
0.6094	0.99665	0.6742	0.6719		
0.6479	0.98406	0.6446	0.6343		
0.7082	0.96425	0.6043	0.5827		
0.8062	0.93169	0.5472	0.5098		
0.8388	0.92053	0.5220	0.4805		
0.9035	0.89934	0.4921	0.4425		
0.9631	0.87570	0.4613	0.4040		
1.0000	0.86140	0.4530	0.3902		

Contd..

Table 1 (Contd..)

PC + CH₃OH at 25°C

0.0000	1.19883	2.0613	2.4711		
0.0512	1.18900	1.9060	2.2662		
0.0983	1.17959	1.1778	2.0971		
0.1406	1.17072	1.6724	1.9579		
0.1883	1.16007	1.5607	1.8106		
0.2587	1.14283	1.4138	1.6157		
0.3430	1.12018	1.2627	1.4144		
0.3986	1.10408	1.1758	1.2982	0.9084	1.2641
0.4723	1.08032	1.0802	1.1670		
0.5124	1.06648	1.0379	1.1069		
0.5819	1.04009	0.9624	1.0009		
0.6762	0.99933	0.8684	0.8678		
0.7580	0.95820	0.8042	0.7707		
0.8297	0.91668	0.7513	0.6887		
0.9256	0.84986	0.7038	0.5981		
0.9495	0.83021	0.6992	0.5805		
1.0000	0.78663	0.6912	0.5437		

Contd..

Table 1 (Contd..)

PC + CH ₃ OH at 35°C			
0.0000	1.18970	1.7211	2.0476
0.0512	1.17991	1.6062	1.8952
0.0983	1.17095	1.5007	1.7572
0.1406	1.16178	1.4184	1.6479
0.1883	1.15091	1.3323	1.5334
0.2587	1.13389	1.2147	1.3773
0.3430	1.11119	1.0915	1.2129
0.4723	1.07151	0.9351	1.0020
0.5124	1.05738	0.8966	0.9480
0.5819	1.03107	0.8390	0.8651
0.6762	0.99425	0.7625	0.7581
0.8297	0.90779	0.6647	0.6034
0.8931	0.86530	0.6376	0.5517
0.9256	0.84155	0.6277	0.5282
0.9495	0.82210	0.6225	0.5118
1.0000	0.77718	0.6175	0.4799

0.7847

1.1093

Contd.. .

Table 1 (Contd..)

PC + CH ₃ CH at 45°C						
0.0000	1.17796	1.4630	1.7234			
0.0512	1.16875	1.3638	1.5939			
0.0983	1.15927	1.2770	1.4804			
0.1406	1.15085	1.2105	1.3931			
0.1883	1.14050	1.1361	1.2958			
0.2587	1.12410	1.0398	1.1688			
0.3430	1.10199	0.9383	1.0340			
0.3986	1.08592	0.8847	0.9607	0.6933		0.9509
0.4723	1.06278	0.8170	0.8663			
0.5124	1.04879	0.7849	0.8232			
0.5819	1.02251	0.7383	0.7549			
0.8297	0.89905	0.5874	0.5281			
0.8931	0.85658	0.5637	0.4829			
0.9256	0.83204	0.5554	0.4621			
0.9495	0.81301	0.5518	0.4486			
1.000	0.76720	0.5495	0.4216			

Table 2--Excess Molar Volumes (V^E)/ $\text{cm}^3 \text{mol}^{-1}$, Excess Viscosities (η^E)/ cP and Excess Molar Free Energies of Activation of Flow (G^{*E})/ J mol^{-1} for the Binary Mixtures of Propylene Carbonate at 25, 35 and 45°C

x_1	V^E	η^E	G^{*E}
PC + ME at 25°C			
0.0000	0.0000	0.0000	0.000
0.0632	-0.0493	-0.1146	-107.381
0.1045	-0.0553	-0.1806	-174.249
0.1523	-0.0198	-0.2257	-220.357
0.2117	-0.1079	-0.2706	-267.709
0.2527	-0.0882	-0.2863	-287.659
0.3050	-0.0467	-0.2973	-307.290
0.3489	-0.0756	-0.3042	-320.060
0.3970	-0.0942	-0.3082	-330.692
0.4547	-0.1083	-0.3034	-331.990
0.4979	-0.1103	-0.2913	-321.707
0.5531	-0.0978	-0.2768	-310.519
0.5954	-0.0729	-0.2536	-284.172
0.6954	0.0529	-0.2051	-230.762
0.7346	0.0856	-0.1947	-224.200
0.7959	0.0978	-0.1570	-182.515
0.8414	0.0975	-0.1203	-138.324
0.9025	0.0889	-0.0870	-104.823
0.9593	0.0476	-0.0332	-39.408
1.0000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + ME at 35°C			
0.0000	0.0000	0.0000	0.000
0.0632	-0.0365	-0.0843	-95.447
0.1045	-0.0463	-0.1410	-166.393
0.1523	-0.0297	-0.1708	-203.002
0.2117	0.0325	-0.2018	-242.583
0.2527	0.0478	-0.2139	-259.583
0.3050	0.0487	-0.2256	-278.559
0.3489	0.0366	-0.2351	-293.377
0.3970	0.0170	-0.2416	-312.294
0.4547	-0.0037	-0.2326	-304.422
0.4979	-0.0085	-0.2248	-287.010
0.5954	0.0517	-0.1923	-254.865
0.6388	0.0806	-0.1821	-244.766
0.6954	0.1213	-0.1571	-210.324
0.7346	0.1541	-0.1428	-192.472
0.7959	0.1796	-0.1092	-144.069
0.8414	0.1936	-0.0866	-113.333
0.9025	0.2007	-0.0589	-78.091
0.9593	0.1318	-0.0241	-29.982
1.0000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + ME at 45°C

0.0000	0.0000	0.0000	0.000
0.0632	-0.0362	-0.0685	-93.938
0.1045	-0.0627	-0.1121	-160.138
0.1523	-0.0857	-0.1368	-197.410
0.2117	-0.0970	-0.1577	-230.428
0.2527	-0.1161	-0.1718	-255.781
0.3050	-0.0998	-0.1789	-268.863
0.3489	-0.0964	-0.1817	-275.816
0.3970	-0.0836	-0.1829	-281.165
0.4547	-0.0518	-0.1796	-308.707
0.4976	-0.0222	-0.1736	-271.637
0.5531	0.0317	-0.1672	-265.497
0.5954	0.0862	-0.1505	-234.840
0.6388	0.1314	-0.1463	-233.680
0.6954	0.1964	-0.1274	-202.250
0.7246	0.2476	-0.1173	-187.854
0.7959	0.2936	-0.0894	-138.310
0.8414	0.3142	-0.0738	-114.634
0.9025	0.3188	-0.0391	-50.573
0.9593	0.2593	-0.0214	-29.436
1.000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd.)

PC + DME at 25°C

0.0000	0.0000	0.0000	0.000
0.0493	-0.1186	-0.1432	-43.064
0.0999	-0.2794	-0.3070	-141.124
0.1524	-0.3543	-0.4073	-189.342
0.1867	-0.4517	-0.4522	-209.345
0.2298	-0.5135	-0.4931	-224.956
0.3128	-0.7268	-0.5417	-253.969
0.3708	-0.7678	-0.5502	-258.047
0.4036	-0.8514	-0.5473	-257.480
0.4686	-0.9143	-0.5417	-280.171
0.5193	-0.9137	-0.5196	-276.752
0.6382	-0.8936	-0.4372	-252.925
0.6767	-0.8284	-0.3971	-219.147
0.7589	-0.6817	-0.3126	-179.513
0.8103	-0.5743	-0.2531	-148.521
0.8432	-0.5186	-0.2018	-76.653
0.9035	-0.3501	-0.1340	-79.307
0.9483	-0.1528	-0.0731	-42.577
1.000	0.0000	0.0000	0.000

Contd.

Table 2 (Contd..)

PC + DME at 35°C

0.0000	0.0000	0.0000	0.000
0.0493	-0.1346	-0.1324	-73.281
0.0999	-0.2584	-0.2226	-113.560
0.1524	-0.4098	-0.2987	-156.343
0.1867	-0.4723	-0.3352	-175.278
0.2298	-0.5672	-0.3689	-191.986
0.2769	-0.6136	-0.4043	-225.277
0.3708	-0.7386	-0.4337	-261.532
0.4036	-0.8173	-0.4318	-261.649
0.5193	-0.9361	-0.4062	-266.296
0.5704	-0.9783	-0.3813	-254.394
0.6767	-1.0780	-0.3118	-217.417
0.8103	-1.0500	-0.1950	-132.844
0.8432	-1.0086	-0.1726	-161.223
0.9035	-0.8137	-0.1071	-95.956
0.9483	-0.5582	-0.0634	-86.427
1.0000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + DME at 45°C

0.0000	0.0000	0.0000	0.000
0.0493	-0.1785	-0.0943	-55.515
0.0999	-0.3572	-0.1696	-102.016
0.1524	-0.5126	-0.2374	-157.624
0.2298	-0.7765	-0.2947	-198.377
0.3128	-1.0187	-0.3261	-222.836
0.3708	-1.1352	-0.3330	-228.011
0.4036	-1.2213	-0.3417	-257.957
0.5193	-1.3120	-0.3273	-279.069
0.5704	-1.3018	-0.3009	-238.944
0.6382	-1.2319	-0.2738	-239.719
0.6767	-1.1432	-0.2489	-207.942
0.7589	-0.9387	+0.2026	-202.471
0.8103	-0.8172	-0.1531	-102.229
0.8432	-0.6343	-0.1274	-77.878
0.9035	-0.4673	-0.0852	-77.898
0.9483	-0.2076	-0.0456	-34.839
1.000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + THF at 25°C

0.0000	0.0000	0.0000	0.000
0.0524	-0.0687	-0.1389	-42.203
0.1036	-0.1435	-0.2406	-70.544
0.1429	-0.1863	-0.3146	-103.478
0.2064	-0.2731	-0.3830	-116.754
0.2431	-0.2987	-0.4163	-128.896
0.3083	-0.3386	-0.4588	-150.364
0.3478	-0.3682	-0.4693	-152.288
0.4095	-0.4057	-0.4776	-162.359
0.6094	-0.3486	-0.4057	-149.898
0.6479	-0.3023	-0.3865	-166.051
0.7082	-0.2410	-0.3319	-133.778
0.7635	-0.1827	-0.2830	-127.284
0.8062	-0.1613	-0.2327	-87.342
0.8388	-0.1042	-0.2036	-100.271
0.9035	-0.0897	-0.1211	-41.677
0.9631	-0.0325	-0.0521	-39.004
1.000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + THF at 35°C

0.0000	0.0000	0.0000	0.000
0.0524	-0.0935	-0.1046	-41.244
0.1036	-0.1446	-0.1708	-51.649
0.1429	-0.2174	-0.2213	-73.237
0.2064	-0.2878	-0.2812	-96.340
0.2431	-0.3382	-0.3027	-99.674
0.3083	-0.4040	-0.3402	-126.908
0.3478	-0.4416	-0.3512	-133.739
0.4095	-0.4962	-0.3596	-145.381
0.5098	-0.5447	-0.3465	-148.193
0.5621	-0.5453	-0.3327	-154.896
0.6094	-0.5326	-0.3101	-142.894
0.6479	-0.5039	-0.2965	-159.722
0.7082	-0.4631	-0.2559	-134.031
0.7635	-0.4063	-0.2148	-110.845
0.8388	-0.2987	-0.1527	-76.801
0.9035	-0.2083	-0.0969	-59.613
0.9631	-0.0931	-0.0426	-50.001
1.0000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + THF at 45°C

0.0000	0.0000	0.0000	0.000
0.0524	-0.1983	-0.0641	-14.108
0.1036	-0.2869	-0.1261	-41.758
0.1429	-0.3672	-0.1578	-46.796
0.2064	-0.4489	-0.2096	-76.210
0.2431	-0.5326	-0.2321	-91.692
0.3083	-0.6077	-0.2559	-101.453
0.3478	-0.6541	-0.2677	-114.241
0.5098	-0.7495	-0.2655	-122.773
0.5621	-0.7613	-0.2518	-115.342
0.6094	-0.7649	-0.2390	-120.456
0.6479	-0.7478	-0.2253	-121.133
0.7082	-0.7188	-0.1965	-107.767
0.8062	-0.6524	-0.1387	-74.093
0.8388	-0.6038	-0.1246	-101.388
0.9035	-0.4537	-0.0763	-64.853
0.9631	-0.2132	-0.0354	-59.700
1.0000	0.0000	0.0000	0.000

Cohtd..

Table 2 (Contd.)

PC + CH₃OH at 25°C

0.0000	0.0000	0.0000	0.000
0.0512	-0.0376	-0.1062	2.953
0.0983	-0.0813	-0.1845	8.838
0.1406	-0.1213	-0.2422	15.007
0.1883	-0.1594	-0.2976	18.532
0.2587	-0.1907	-0.3568	24.782
0.3430	-0.2316	-0.3956	34.290
0.3986	-0.2728	-0.4046	41.120
0.4723	-0.3002	-0.3938	63.392
0.5124	-0.3241	-0.3766	85.104
0.5819	-0.3415	-0.3486	96.339
0.6762	-0.3574	-0.3000	85.373
0.7580	-0.3528	-0.2394	77.899
0.8297	-0.3307	-0.1832	40.973
0.9256	-0.2035	+0.0890	27.436
0.9495	-0.1204	-0.0605	6.449
1.0000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + CH₃OH at 35°C

0.0000	0.0000	0.0000	0.000
0.0512	-0.0449	-0.0721	17.897
0.0983	+0.1236	-0.1363	19.948
0.1406	-0.1468	-0.1793	31.212
0.1883	-0.1735	-0.2190	43.169
0.2587	-0.2243	-0.2647	53.945
0.3430	-0.2670	-0.2970	64.995
0.4723	-0.3539	-0.3052	76.156
0.5124	-0.3618	-0.2963	86.206
0.5819	-0.3874	-0.2703	109.311
0.6762	-0.4123	-0.2294	100.068
0.8297	-0.3832	-0.1435	46.812
0.8931	-0.3122	-0.0958	21.909
0.9256	-0.2774	-0.0683	11.649
0.9495	-0.2013	-0.0473	6.666
1.0000	0.0000	0.0000	0.000

Contd..

Table 2 (Contd..)

PC + CH₃OH at 45°C

0.0000	0.0000	0.0000	0.000
0.0512	-0.0876	-0.0628	9.166
0.0983	-0.1294	-0.1150	11.546
0.1406	-0.2035	-0.1473	25.533
0.1883	-0.2637	-0.1825	30.083
0.2587	-0.3527	-0.2178	42.819
0.3430	-0.4268	-0.2429	55.002
0.3986	-0.4683	-0.2438	78.478
0.4723	-0.5299	-0.2403	93.780
0.5124	-0.5412	-0.2332	104.599
0.5819	-0.5592	-0.2110	133.664
0.8297	-0.5032	-0.1152	50.313
0.8931	-0.4159	-0.0779	18.355
0.9256	-0.3318	-0.0563	6.177
0.9495	-0.2699	-0.0387	2.438
1.0000	0.0000	0.0000	0.000

Table 3. Coefficients of Least-square Fit by Equation (6) for Excess Molar Volumes and Excess Viscosities at 25, 35 and 45°C

Property	Temperature	A_0	A_1	A_2	A_3	A_4	$\sigma(X^E)$
				PC + ME			
V^E	25°C	-0.4593	0.2245	-4.0510	-1.8413	-4.3483	0.039
	35°C	0.0944	0.0327	1.5310	-2.7296	-0.2745	0.020
	45°C	0.0465	-1.1076	-0.2040	-2.9147	4.5610	0.031
η^E	25°C	-1.1487	-0.5278	-0.4743	-0.1158	0.1315	0.005
	35°C	-0.8865	-0.4349	-0.2059	-0.0730	-0.0269	0.004
	45°C	-0.6958	-0.3135	-0.1750	-0.1116	-0.0516	0.003

Contd..

Table 3 (Contd..)

		PC + DME					
v^E	25°C	-3.6259	-0.9344	0.3058	-0.6439	0.5591	0.026
	35°C	-3.6537	1.6564	-2.6306	3.7041	-2.0226	0.022
	45°C	-5.1634	1.0595	0.7986	-0.7305	0.5523	0.026
η^E	25°C	-2.0639	-1.1171	-0.9847	0.1500	0.8107	0.013
	35°C	-1.6672	-0.6583	0.0695	-0.2123	-0.6540	0.004
	45°C	-1.3088	-0.5272	-0.1560	-0.0979	-0.0543	0.005

Contd..

Table 3 (Contd..)

PC + THF

v^E	25°C	-1.5753	-0.6710	1.0392	0.4804	-0.6790	0.012
	35°C	-2.1799	0.4211	1.0100	-0.0240	-1.2610	0.007
	45°C	-3.0046	0.9241	-0.4780	0.2448	-2.2059	0.017
η^E	25°C	-1.8582	-0.6661	-0.1397	-0.1191	-0.2310	0.004
	35°C	-1.4198	-0.4252	0.1714	-0.0984	-0.5239	0.004
	45°C	-1.0778	-0.3930	-0.0057	0.2345	-0.0852	0.003

Contd..

Table 3 (Contd..)

PC + CH₃OH

ν^E	25°C	-1.2160	0.8540	-1.4431	0.2948	0.9537	0.012
	35°C	-1.4192	0.6055	-0.9593	1.3855	-0.7141	0.016
	45°C	-2.1560	0.6085	0.0096	1.8400	-2.2453	0.011
η^E	25°C	-1.5631	-0.6403	-0.1394	0.1970	-0.0677	0.011
	35°C	-1.1825	-0.4085	-0.1675	0.1499	0.1057	0.003
	45°C	-0.9375	-0.3505	-0.2078	0.1006	0.0737	0.002

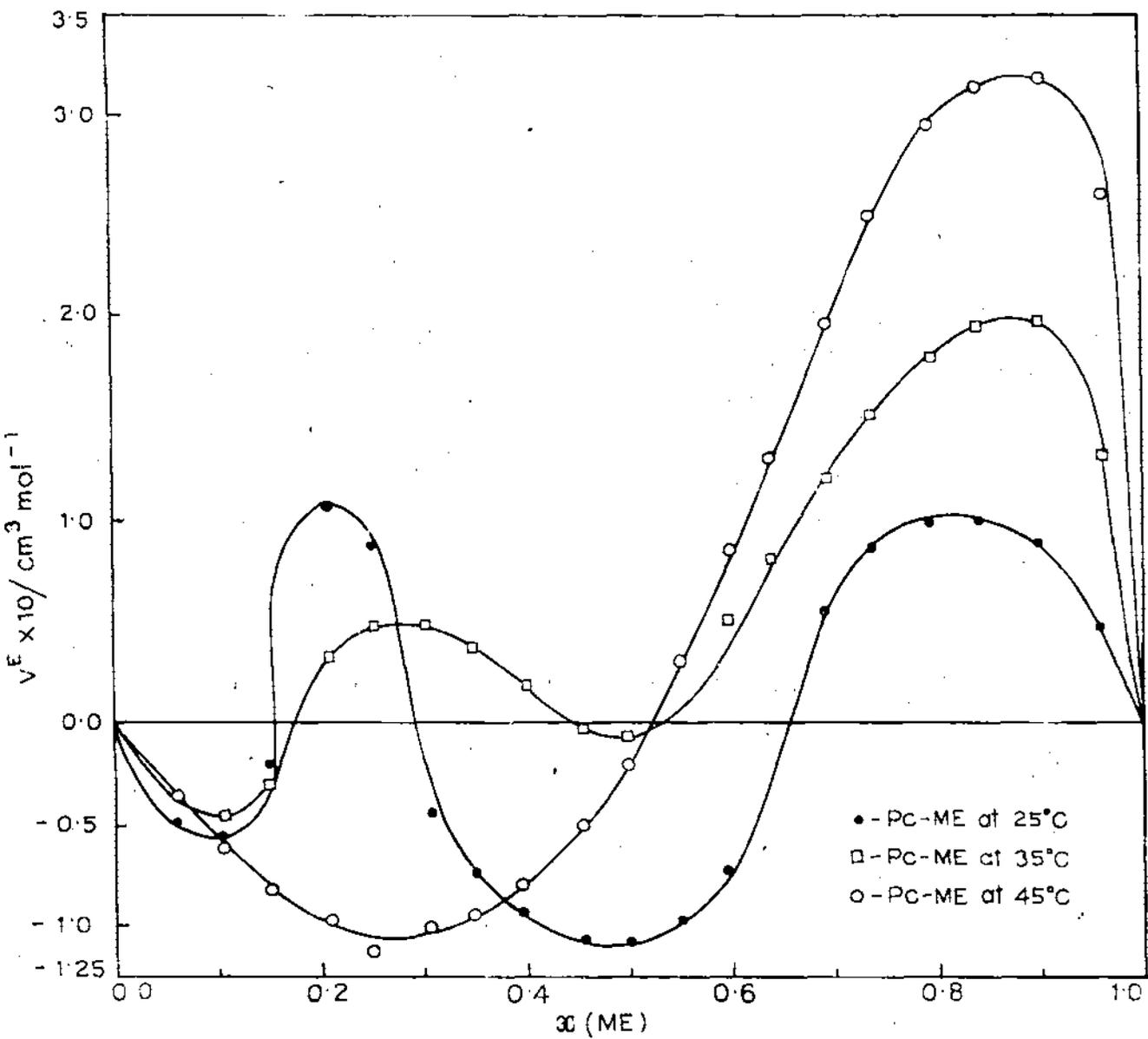


Fig. 1A. Variation of excess molar volume with the mole fraction of ME for PC + ME mixtures.

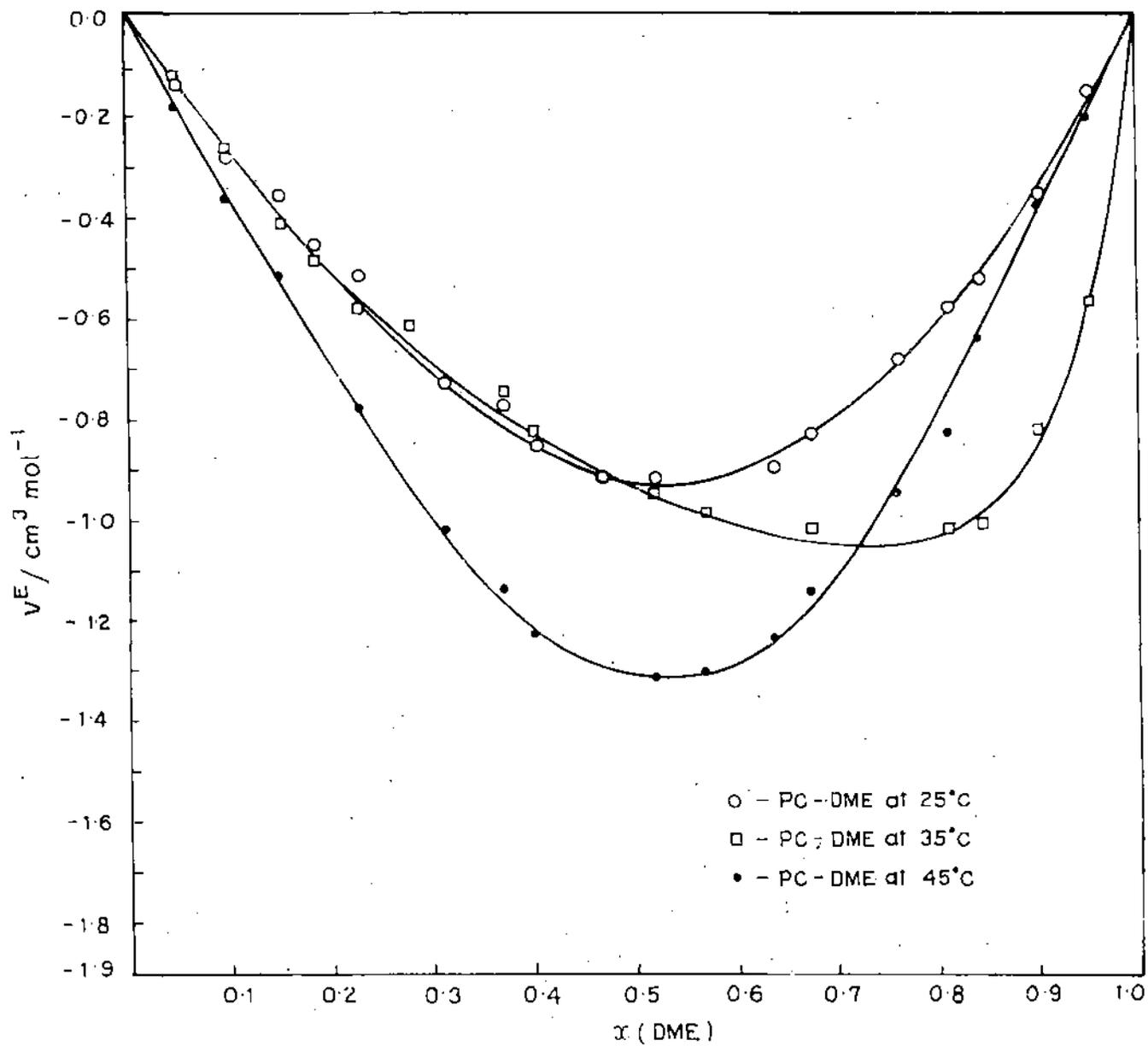


Fig. 1B. Variation of the excess molar volume with the mole fraction of DME for PC + DME mixtures.

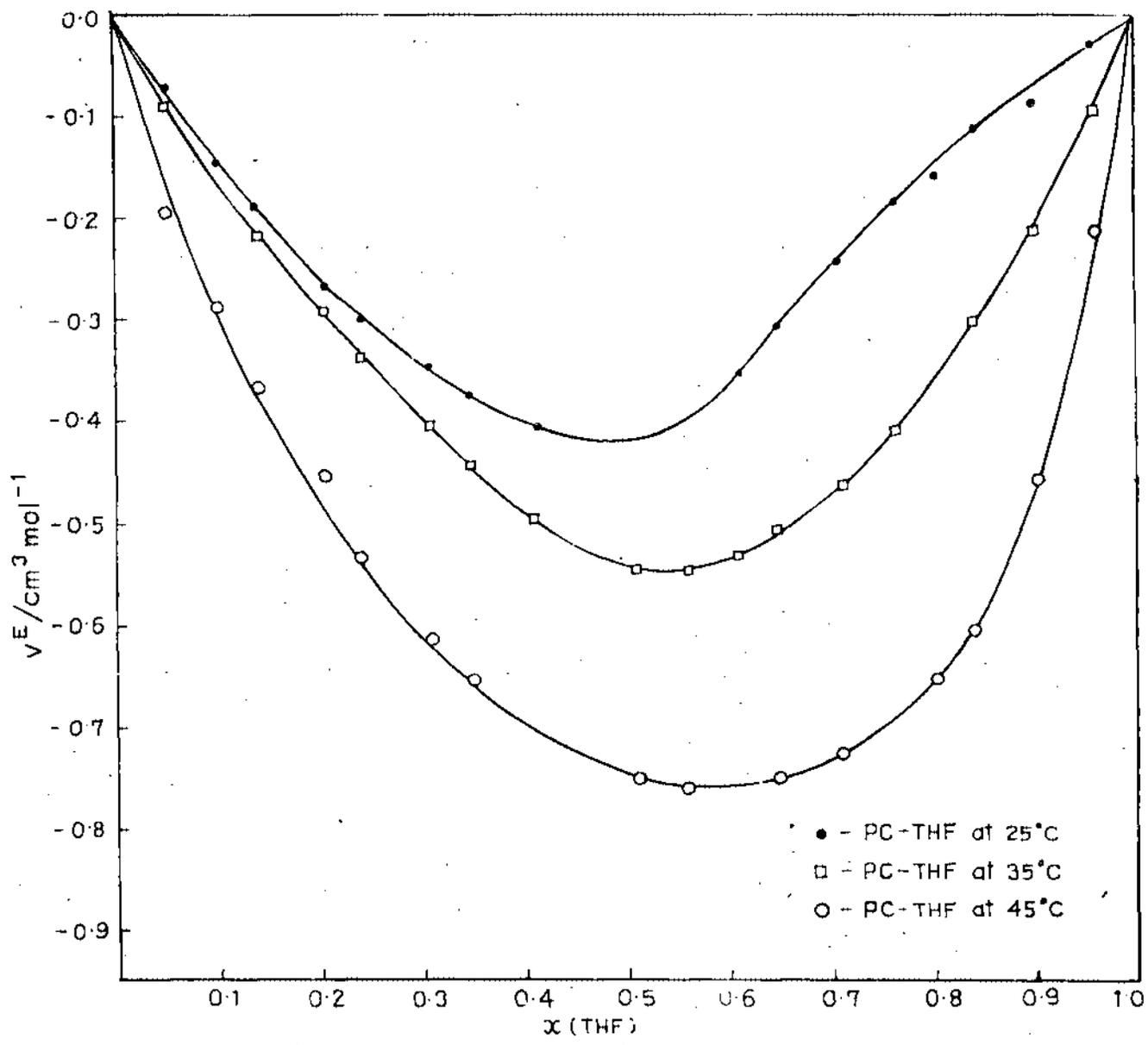


Fig. 1C. Variation of excess molar volume with the mole fraction of THF for PC+THF mixtures.

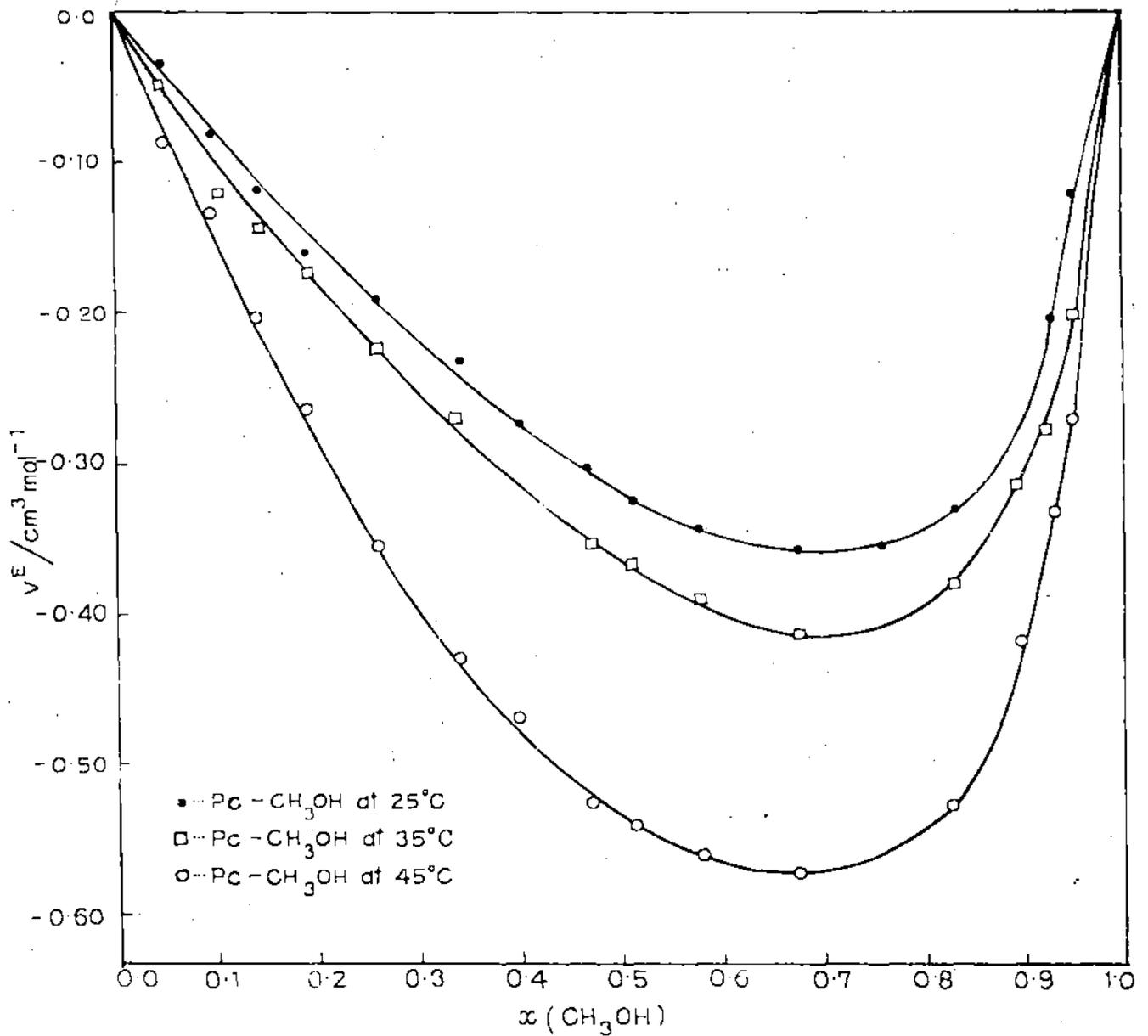


Fig. 1D. Variation of excess molar volume with the mole fraction of CH_3OH for PC + CH_3OH mixtures.

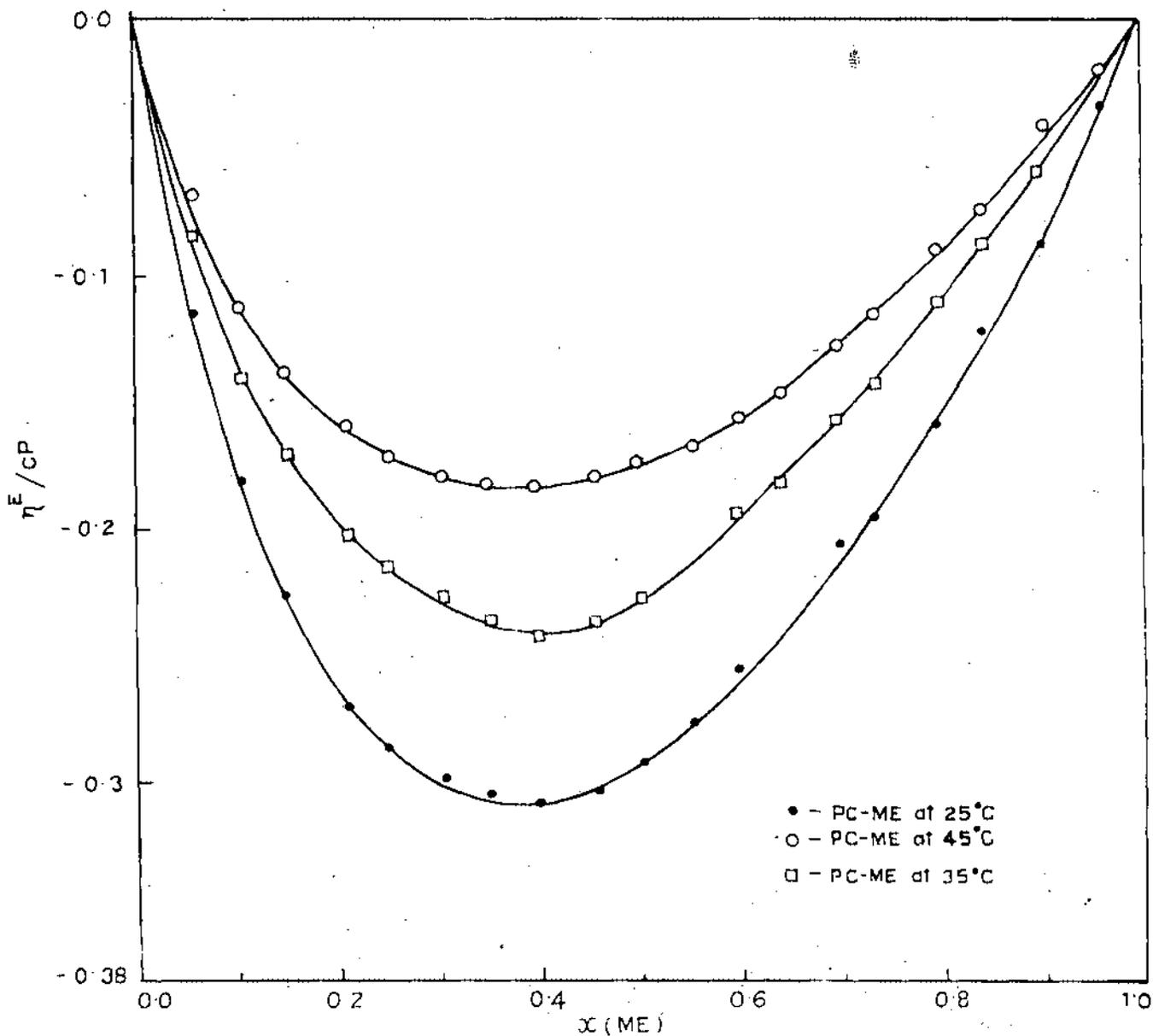


Fig. 2A. Variation of excess viscosity with the mole fraction of ME for PC+ME mixtures.

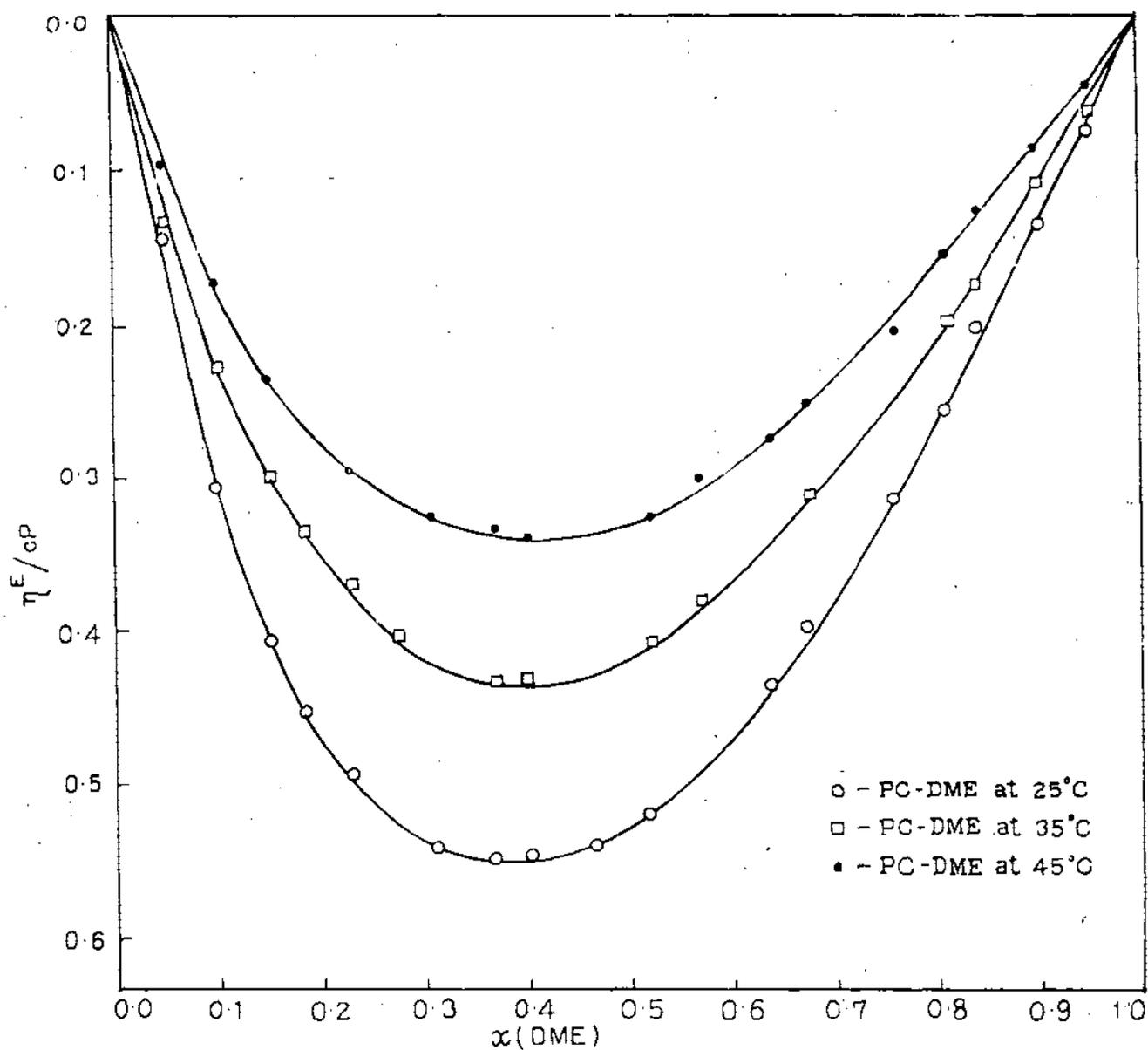


Fig. 2B. Variation of excess viscosity with the mole fraction of DME for PC + DME mixtures.

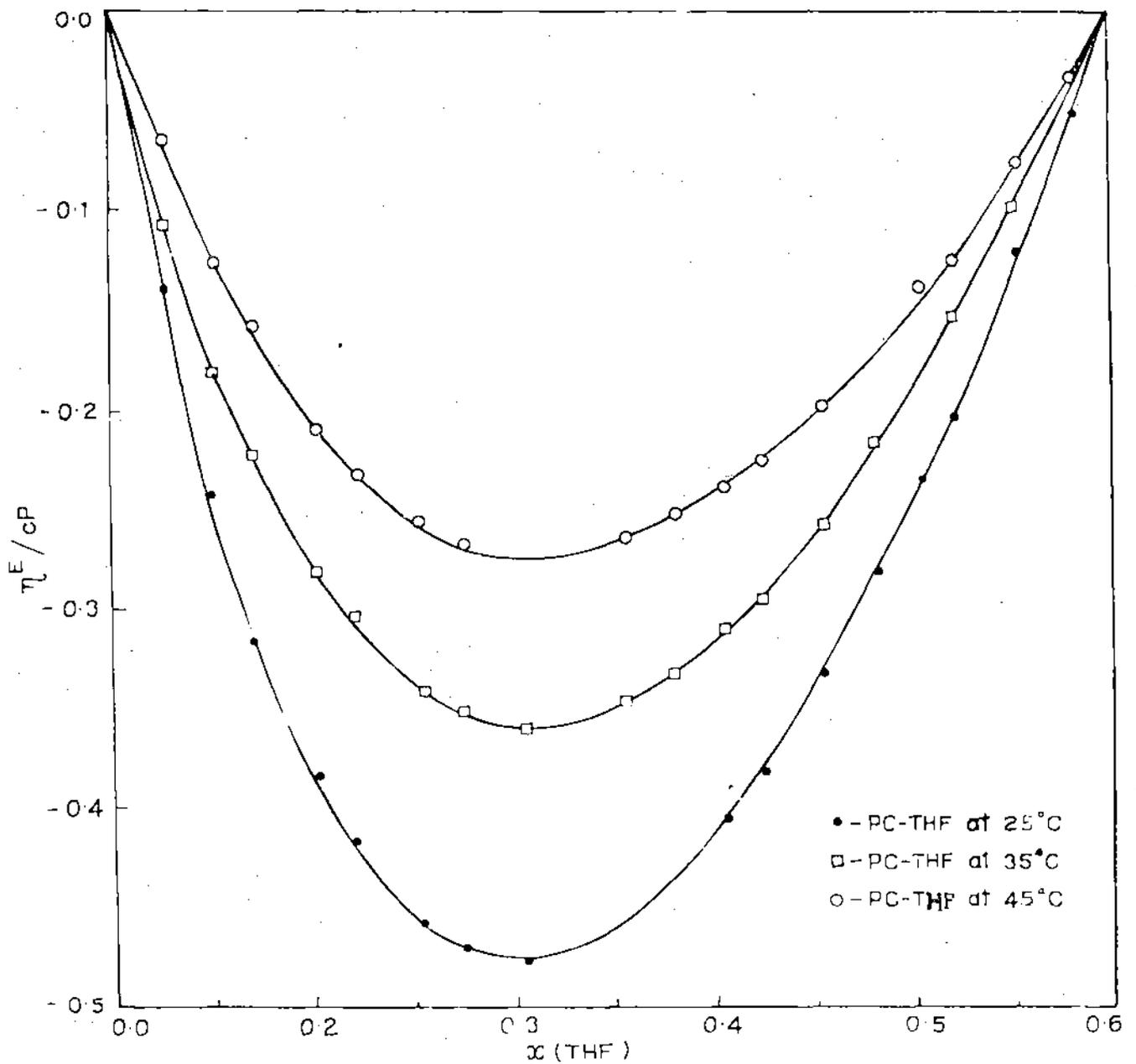


Fig. 2C. Variation of excess viscosity with the mole fraction of THF for PC+THF mixtures.

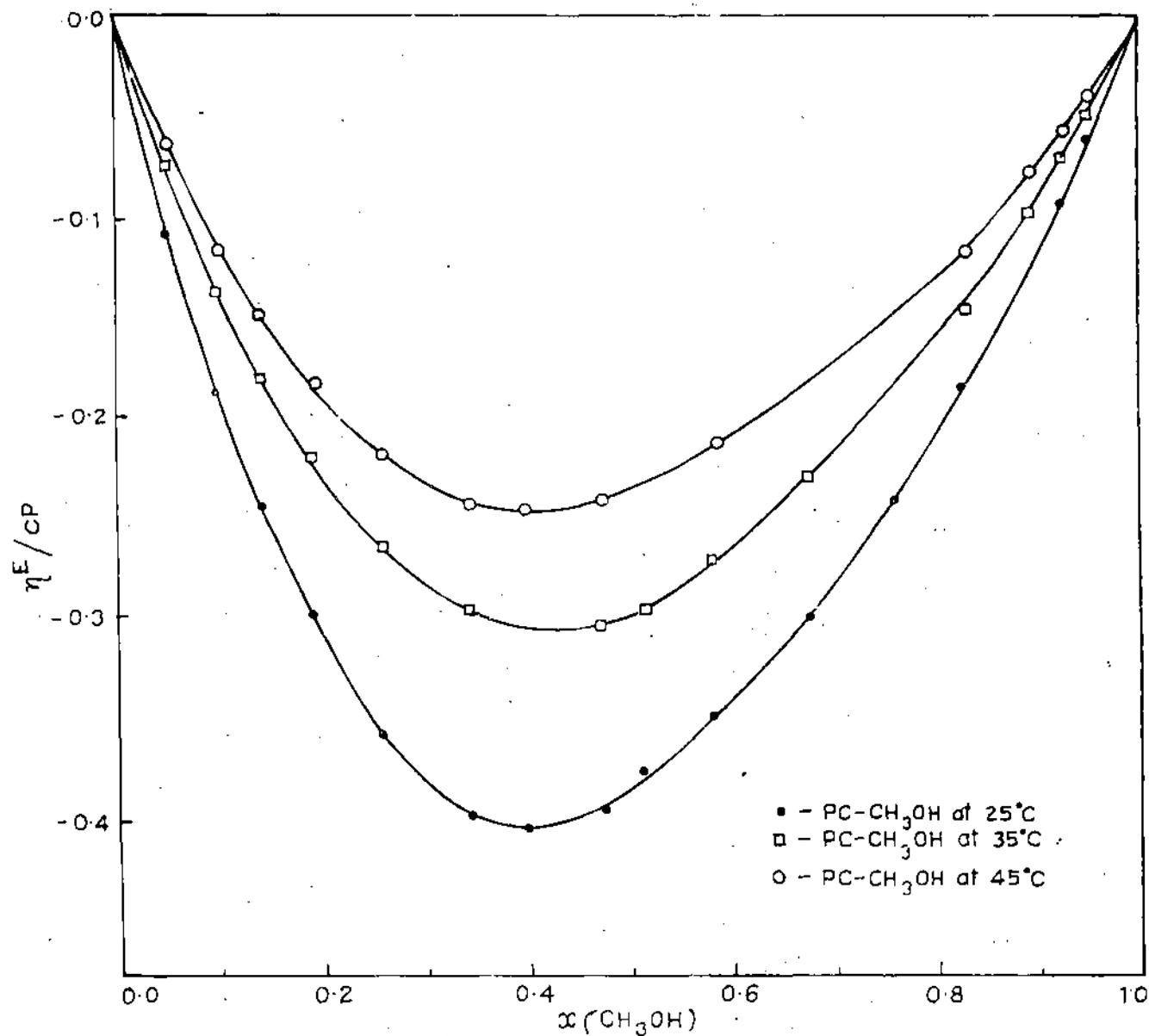


Fig. 2D. Variation of excess viscosity with the mole fraction of CH_3OH for PC+ CH_3OH mixtures.

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CHAPTER-VII

**Ion-Solvent Interactions in Mixed Non-Aqueous Solvents:
Conductance Measurements of Tetraalkylammonium Bromides,
NaBPh₄ and Bu₄NBPh₄ in Propylene Carbonate + Methanol
Mixtures at 25°C**

Studies on the transport properties of electrolytes in different solvents are of great importance to obtain information on the behaviour of ions in solution. Recently, attempts have been made to study ion-solvent interactions in different dipolar aprotic media¹⁻³ having extensive use as solvents and solubilizing agents in different electrochemical investigations⁴⁻⁷. These factors have also stimulated some interest for the study of their binary aqueous mixtures^{3,8-9}. The transport properties in non-aqueous binary mixtures having propylene carbonate (PC) as one of the components have not been extensively studied barring a few^{3,10-11} (PC and water are not miscible at all proportions¹²). In the previous sections [Chapters IV and V], we have reported the transport properties of some tetraalkylammonium bromides and tetraphenyl salts in PC from their viscosity and conductance data. In the present chapter, we report the behaviour of tetraalkylammonium bromides, NaBPh₄ and Bu₄NBPh₄ in the binary mixed solvents of PC with methanol from their conductance measurements.

Experimental

The purifications of propylene carbonate and methanol have been described in Chapters II and VI. Salts were purified in accordance with the procedure given earlier (Chapters II and IV).

Solvent mixtures were prepared by weight and in practice, four sets of solvent mixtures of different mole fractions of PC viz. 0.10, 0.20, 0.40 and 0.60 were prepared. Physical properties of the solvent mixtures have been given in Table 1. Freshly distilled solvents were always used and solvent mixtures were prepared immediately prior to use.

A stock solution for each salt in the appropriate solvent mixture was prepared by weight and the working solutions were obtained by weight dilution. The molar concentrations of the solutions were calculated from molality and density values. Viscosity and density of the solvent mixtures were determined in the same way as described earlier [Chapters II & IV]. Dielectric constants of mixtures were taken from the literature¹³.

A Pye-Unicam conductivity meter (PW 9509) was used for measuring the conductances of the solutions at a frequency of 2 kHz with a dip-type cell of cell constant 0.751 cm^{-1} and having an accuracy of $\pm 0.1\%$. The measurements were carried out in a thermostatic oil bath maintained at $25 \pm 0.005^\circ\text{C}$. Conductance values of all salt solutions were corrected to avoid the contribution of the solvent.

Results

The measured equivalent conductances (Λ) of electrolyte solutions as a function of molar concentrations (c) have been reported in Table 2.

The experimental results have been analysed by the Fuoss 1978 conductance equation¹⁴ in the same way as described previously (Chapter-IV). The values of Λ^0 , K_A , R and σ have been recorded in Table 3.

Discussion

Table 1 shows that viscosity of PC + CH₃OH mixtures increases with increase in PC content of the mixture. Densities of the solvent mixtures also gradually increase with increase in the amount of PC in the mixture. The present observations indicate the possible absence of any heteroassociation or structure formation or any other type of specific interaction between unlike molecules.

The variation of limiting equivalent conductance, Λ^0 , with the solvent composition is represented in Fig. 1. The limiting equivalent conductance decreases with the corresponding increase in the viscosity of the mixture. Although, it is evident that the variations in Λ^0 do not exactly compensate each other to give the

Walden product a constant value (Fig. 2) but the changes in Walden products for an electrolyte in different solvent compositions are sufficiently small compared to other binary mixed solvent systems. It thus reflects that the differences in solvation of ions are not primarily responsible for the observed changes in ionic mobility or Λ° of the electrolytes.

The assumption that the dielectric constant is not involved in affecting the values of Λ° is untenable as the change in Λ° values is not due to any change in the number of ions. The difference in the mobilities of ions is actually responsible for the change in λ_+° and λ_-° of the ions. The cations and anions are moving in the opposite directions, the attractive forces of the opposite ions decrease with increasing dielectric constant of the solvent medium and the mobilities of the ions are inversely proportional to the dielectric constant of the medium.

PC is a structureless dielectric having moderately high dielectric constant and large dipole moment (values are 64.40 and 4.98 D respectively)¹⁵. It is thus expected that the solvodynamic entity around the tetraalkylammonium salts are likely to be greater in PC than in methanol (dielectric constant¹³ 32.64 and dipole moment 1.70 D¹⁵). On the other hand, methanol molecules are associated through the intermolecular hydrogen bonding. From conductance¹⁶, viscosity¹⁷ and volumetric¹⁸ studies, it has been established that the tetraalkylammonium ions are not solvated in

methanol. However, unlike the cations, Br^- ion has been found to be solvated in this medium. It appears that very large size of tetraalkylammonium ions and hence their low charge densities and the low dipole moment of methanol molecules are primarily responsible for the weak ion-solvent interactions in this medium. The interaction energy (ion-solvent) appears to be too weak to break up the intermolecular H-bonding in methanol and thus can't orient solvent dipoles properly in its solvation sheath. Increased values of Λ^0 in methanol might be due to greater freedom of ions to move through this polar, hydrogen bonded solvent system and also due to the low viscosity of the medium.

It is well established that if the viscosities of the media differ widely, the conductance in the less viscous medium will be greater. In comparison to pure methanol, the transport process of ions is obviously difficult in PC + CH_3OH mixtures as the solvent viscosity is increased and the hydrogen bonded structure in methanol loosens or breaks up and most probably, the interstitial spaces are withdrawn. Another factor that also plays a vital role for the decrease in Λ^0 values of the electrolytes in PC + CH_3OH mixtures is the dielectric constant of the media. Since, the dielectric constant decreases in PC + CH_3OH mixtures from PC, the ionic mobilities increase and hence greater Λ^0 values are obtained in the mixture than in pure PC. The tetraalkylammonium ions generally remain unsolvated in PC medium (Chapter - IV). As the PC + CH_3OH mixture is enriched by PC, the viscosity and dielectric

constant increase further (compared to CH_3OH and methanol-rich regions) causing a general decrease in Λ^0 values, as observed.

The variation of Walden products of the tetraalkylammonium salts with solvent compositions is shown in Fig. 2. It is observed that the changes in Walden products of an electrolyte with compositions of the mixture are very small. Since the electrolytes are not solvated either in PC or in methanol so it is expected that these salts would also remain unsolvated in their binary mixtures. This is reflected by the very small variation in Walden product values. Results thus support the earlier view point that for large cations, the Walden product values are solvent independent and remain almost unchanged¹⁹.

From Table 3 we see that K_A values of the salts generally increase with increase in CH_3OH content in the mixture i.e. with the decrease in dielectric constant of the mixture. Among all the electrolytes studied here, tetrabutylammonium tetraphenylborate is seen to be associated to the greatest extent followed by sodium tetraphenylborate. Kay *et al*¹⁶ studied some tetraalkylammonium salts in methanol with the help of Fuoss-Onsager conductance equation and observed that among the bromides, only tetramethylammonium and tetraethylammonium salts are associated (K_A values are 14.0 and 10 respectively). However, Papadopoulos²⁰ reanalysed the conductance data of Kay *et al* for Pr_4NBr in CH_3OH at 25°C using Lee-wheaton conductance equation²¹. They obtained the K_A value of

24 whereas, Kay et al¹⁶ found it to be only 6.3. Thus, it appears that the association constants of the R_4NBr salts in CH_3OH as reported by Kay and coworkers may be much larger. Kay et al¹⁶ further observed that Bu_4NBPh_4 is much more associated than the R_4NBr salts in methanol. Since, the association constants of R_4NBr salts vary by small amounts from Me_4NBr to Hep_4NBr , so a regular trend in association constant values was difficult to obtain. K_A , is generally, a function of the parameters such as the size of the ions and the dielectric constant of the medium. Besides electrostatic forces, solvation forces also exist which are completely system specific and their contribution can not be predicted. Thus, specific solvent effects also play a vital role in the association process. Generally, useful results in binary mixed solvents can be obtained when the ions are solvated only by the polar component of the mixture. And when the polar compound is a hydrogen bonded solvent, the solvation energy is complicated by the solvent structural effects and the interpretation becomes difficult. As the sizes of the cation and anion increase, it is reasonable to anticipate that the specific interaction with the solvent molecules will become less important and then the association should be a function of dielectric constant of the medium only. However, association process in polar hydrogen bonded solvents like alcohol and so also in their binary mixtures is not so simple as anticipated. A comparison of the association constant values of Bu_4NClO_4 in two isodielectric solvents viz. acetone and propanol was made by Evans and Gardam.²²

Taking into consideration the dielectric constants of the two media, the ions of the salt, Bu_4NClO_4 is expected to be equally associated in accordance with the electrostatic theory. But K_A value for the large Bu_4NClO_4 salt in propanol is much greater than that in acetone. It is thus apparent that the simple solvation is not the major factor controlling the association process in propanol. Evans and Gardam further concluded that the alcohols appear to constitute a separate class of solvents, distinct in behaviour from many other non-aqueous solvents but similar in some respects to water. However difference with water exists in the presence of three-dimensional structures in water. In PC - CH_3OH solvent mixtures, the solvation energy is complicated by the solvent structural effects arising from the presence of alcohol in the mixture. It thus demands much more investigations on the solvent structures and the behaviour of different electrolytes in such types of binary non-aqueous solvent mixtures. Evans and coworkers²² have further shown that the ionic association in the hydrogen bonded solvents like ethanol and propanol does not exhibit the simple dependence upon ionic size as predicted by electrostatic theory. Among the tetraalkylammonium halides, although the bromides and chlorides exhibit K_A values in the manner predicted by the relative sizes of the cations in these two solvent systems but anomalous and large K_A values were obtained for the iodide salts. They have treated these K_A values as almost unchanged and concluded that the tetraalkylammonium iodides irrespective of their sizes

are equally associated in ethanol and propanol. One point that should be noted here is the fact that the decrease in K_A values from Me_4NBr to Bu_4NBr in either of these two solvent systems is not consistent enough. In fact Pr_4NBr and Bu_4NBr have got almost equal K_A values in ethanol (78 and 75 respectively) and propanol (270 and 266 respectively). Again in our case, K_A values of the tetraalkylammonium salts in PC - CH_3OH mixtures are small enough (Table 3) and the solvent mixture is quite complicated from structural point of view. It thus can be said that for any given composition of PC - CH_3OH mixtures, the R_4NBr salts are equally associated which is most likely due to peculiar nature of the alcohol (methanol here) present in the mixture and the complicated structural features of the mixture arising from it.

From Table 4, we see that for any particular composition of PC - CH_3OH solvent mixtures, the Walden products of the R_4NBr salts decrease in the order : $\text{Me}_4\text{NBr} > \text{Et}_4\text{NBr} > \text{Pr}_4\text{NBr} > \text{Bu}_4\text{NBr} > \text{Pen}_4\text{NBr} > \text{Hex}_4\text{NBr} > \text{Hep}_4\text{NBr}$. So, the lowest value is obtained for the largest molecule and it indicates the lack of solvation of these salts in these mixtures. The quantitative explanation for the variation of the Walden products with solvent composition is yet unknown though some attempts have been made to derive a satisfactory expression taking into account all types of ion-solvent interactions. In spite of some qualitative agreements, the complicated expression derived by Zwanzig²³ involving the (solvent) dielectric relaxation

time, the solvent viscosity, static and infinite frequency dielectric constant fails to predict quantitatively the variation of Walden product with composition. This is quite natural as no single mathematical expression can cover all the ions and their interactions with various solvents as the ion-solvent interaction is quite specific for an ion and a particular solvent. However, it is reasonable to believe like Hemes²⁴ that the variation of the Walden product with solvent composition is due to the variation of the electrochemical equilibrium between the ions and the solvent molecules at one hand and selective solvation of ions and complex formation between unlike solvent molecules on the other. It has already been mentioned that majority of the ions studied here lack selective solvation in PC - CH₃OH mixtures and also in either of these two components. Studies on thermodynamic properties in PC - CH₃OH mixtures (Chapter- VI) also indicate the lack of specific interaction or complex formation between unlike molecules. This has also been supported by the fact that the Λ^0 values of the salts do not exhibit any maxima or minima at any intermediate composition of the mixture. The change in Walden product from one composition to another in PC - CH₃OH mixtures is so small that no fruitful and definite conclusion should be drawn from it rather we think, the Walden product values should be treated as almost unchanged over the composition range.

In absence of transport number data in these mixed solvents, we have used "reference electrolyte" method for the division of into single ion values. Bu_4NBPh_4 ²⁵ has been used as the reference electrolyte. Bu_4NBPh_4 was utilized by Fuoss and Kirsch²⁶ to calculate the limiting ion conductances in several organic solvents assuming the equality:

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Ph}_4\text{B}^-) \quad (1)$$

But instead of equal division, we divided Λ^0 values using the method similar to that proposed by Krumgalz²⁷ for division of B values:

$$\frac{\lambda_0(\text{Bu}_4\text{N}^+)}{\lambda_0(\text{Ph}_4\text{B}^-)} = \frac{r(\text{Ph}_4\text{B}^-)}{r(\text{Bu}_4\text{N}^+)} = \frac{5.35}{5.00} = 1.07 \quad (2)$$

The r values have been taken from the works of Gill et al^{28,29}. The virtual organic solvent independence of the solvation radii of large Bu_4N^+ and Ph_4B^- ions found by Krumgalz²⁷ (and Gill^{28,29}) suggests that these ions are unsolvated in organic solvents and therefore, their ionic radii calculated as

$$r_{\pm} = \frac{|z| F^2}{6\pi\eta_0 N \lambda_{\pm}^{\mp}} \quad (3)$$

correspond to their true dimensions in the solvent.

The limiting ionic conductances calculated from equation (2) are given in Table 5. Stokes radii of the ions from equation (3) are given in Table 6.

From Table 5, we see that the λ_i^0 values decrease as we go from Me_4N^+ to Hep_4N^+ in PC + CH_3OH mixtures and PC similar to those observed in methanol¹⁶ and water³⁰. If the R_4N^+ ions were solvated in PC or in its binary mixtures with methanol, then the λ_i^0 values for R_4N^+ ions should have been in the reverse order. Most studies for electrolyte solutions in the non-aqueous media involving different techniques indicate that the cationic solvation is strong while the anionic solvation is weak. But owing to the very large size of tetraalkylammonium ions, these are most likely not solvated either in PC or in PC + CH_3OH mixtures. However, Na^+ ion is substantially solvated both in PC and CH_3OH and also in their binary mixtures because of its small crystallographic radius and large charge density. Results thus indicate (Table 6) that the R_4N^+ ions in PC + CH_3OH mixtures remain almost as bare ions. For anions, Br^- ion is found to be solvated in methanol and also in PC + CH_3OH binary mixtures though the probability decreases as PC content in the mixture increases. However, BPh_4^- ion is found to be almost unsolvated in pure as well as in mixed solvents. Since, PC lacks a well-developed centre of positive charge, the anions appear to have

weak interactions with its molecules. Obviously, the decrease in size of the anion favours the solvation process.

More extensive studies, however, are required to arrive at reasonable conclusions about the conductance behaviour and about the nature of ion-solvent interactions in different non-aqueous organic mixtures, particularly in the mixtures in which a component is a hydrogen bonded organic solvent like alcohol.

Table 1. Solvent properties of PC + methanol mixtures at 25°C

Property	Mole fraction of PC					
	0.00	0.10	0.20	0.40	0.60	1.00
Density/g cm ⁻³	0.7866	0.8693	0.9346	1.0327	1.1036	1.1988
Viscosity/cP	0.544	0.626	0.719	0.975	1.297	2.471
Dielectric constant	32.64	39.20	44.10	51.30	57.30	64.40
Specific conductance /Scm ⁻¹	0.15x10 ⁻⁶	1.52x10 ⁻⁶	1.81x10 ⁻⁶	2.25x10 ⁻⁶	2.42x10 ⁻⁶	0.73x10 ⁻⁶

Table 2. Equivalent conductances of tetraalkylammonium bromides, NaBPh_4 and Bu_4NRPh_4 in PC + methanol mixtures at 25°C

$10^4 \text{C/mol dm}^{-3}$	$\wedge/\text{Scm}^2 \text{mol}^{-1}$	$10^4 \text{C/mol dm}^{-3}$	$\wedge/\text{Scm}^2 \text{mol}^{-1}$	$10^4 \text{C/mol dm}^{-3}$	$\wedge/\text{Scm}^2 \text{mol}^{-1}$
Me_4NBr		0.10 mole fraction of PC			
		Et_4NBr		Pr_4NBr	
120.214	89.47	120.047	85.34	120.519	75.11
105.491	90.96	105.304	86.67	105.215	76.46
90.312	92.405	90.261	88.03	90.336	77.81
75.134	94.17	75.217	89.54	74.926	79.35
59.955	96.06	60.174	91.23	60.047	81.03
45.536	98.12	45.130	93.27	45.168	82.92
30.357	100.68	30.087	95.42	29.758	85.22
10.625	105.34	15.043	98.39	14.879	88.23

Contd..

Table 2 (Contd..)

0.10 mole fraction of PC

	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr	
120.632	69.61	120.637	66.77	120.078	64.75	
105.230	70.94	105.496	67.99	105.007	65.95	
89.945	72.27	89.981	69.29	90.182	67.14	
75.248	73.78	75.088	70.78	75.358	68.67	
59.963	75.47	60.195	72.31	59.916	70.24	
45.267	77.32	45.301	74.07	45.091	72.08	
29.982	79.61	30.408	76.22	30.267	74.12	
15.285	82.47	12.411	79.73	12.354	77.58	

Contd..

Table 2 (Contd..)

	Hep ₄ NBr		NaBPh ₄		Bu ₄ NBPh ₄	
120.280	62.64	120.223	58.01	111.842	54.41	
105.183	63.81	105.607	59.13	95.649	55.83	
90.334	65.05	90.032	60.35	80.153	57.33	
75.484	66.37	75.139	61.71	60.022	59.56	
60.016	67.93	60.247	63.15	49.956	60.87	
45.164	69.68	45.354	64.82	39.890	62.24	
30.317	71.62	30.462	66.83	30.197	63.75	
12.374	74.94	12.184	70.06	20.131	65.52	
				10.065	68.03	

Contd..

Table 2 (Contd..)

0.20 mole fraction of PC					
	Me ₄ NBr		Et ₄ NBr		Pr ₄ NBr
170.471	77.64	170.052	74.63	169.965	65.26
149.864	79.01	155.751	75.41	154.719	66.02
130.121	80.39	140.117	76.23	139.990	66.87
115.165	81.46	120.214	77.46	120.227	68.05
100.208	82.63	100.311	78.77	100.464	69.29
90.017	84.38	79.612	80.28	80.700	70.77
70.503	85.22	59.709	81.90	60.113	72.51
59.826	86.38	39.806	83.79	40.350	74.42
40.382	88.74	19.903	86.41	20.586	76.97
20.191	91.66				
	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr
170.225	59.69	172.079	58.47	174.410	56.78
144.944	61.08	159.984	59.03	150.077	57.93
131.972	61.75	140.086	60.04	129.834	58.96
120.506	62.38	120.187	61.03	110.289	60.11
100.281	63.74	100.288	62.27	90.046	61.36
80.056	65.03	80.390	63.52	70.501	62.68
59.831	66.71	60.491	64.95	50.258	64.26
40.449	68.54	39.797	66.77	30.015	66.31
20.224	71.02	19.898	69.06	15.356	68.21

Contd..

Table 2 (Contd..)

		0.20 mole fraction of PC			
Hep ₄ NBr		NBPh ₄		Bu ₄ NBPh ₄	
170.144	55.51	170.283	49.72	131.370	48.48
155.738	56.18	154.827	50.46	110.790	49.77
140.410	56.94	140.233	51.23	91.547	51.19
120.588	58.01	120.199	52.31	70.964	52.76
90.939	59.21	100.166	53.49	60.177	53.72
80.116	60.50	80.133	54.76	49.958	54.75
60.294	61.89	60.099	56.24	40.023	55.84
40.471	63.61	40.066	58.03	30.088	57.02
20.813	65.82	20.033	60.31	20.152	58.48
				15.044	59.33
		0.40 mole fraction of PC			
Me ₄ NBr		Et ₄ NBr		Pr ₄ NBr	
250.935	61.23	269.917	57.58	270.393	51.10
230.304	61.90	246.389	58.38	245.943	51.81
210.567	62.68	220.335	59.21	229.770	52.28
190.736	63.31	201.260	59.91	209.176	52.92
170.199	64.26	180.384	60.63	190.417	53.50
130.923	66.01	140.433	62.23	149.795	54.89
100.374	67.50	110.167	63.60	120.597	56.00
69.825	69.28	79.901	65.17	90.131	57.39
44.732	71.08	50.846	66.95	59.664	59.01
25.093	72.84	30.265	68.59	30.466	60.97

Contd..

Table 2 (Contd..)

0.40 mole fraction of PC

	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr	
	270.317	46.21	268.821	43.78	271.259	42.75
	249.449	46.85	240.083	44.64	249.861	43.33
	230.734	47.48	210.216	45.58	230.341	43.96
	210.184	48.17	180.349	46.61	200.151	44.85
	180.158	49.26	160.537	47.33	169.960	45.70
	139.737	50.82	140.144	48.12	140.888	46.82
	110.866	52.10	110.277	49.37	110.698	48.03
	79.685	53.69	80.410	50.82	80.507	49.28
	49.658	55.52	50.543	52.62	55.908	50.75
	30.026	57.09	29.866	54.30	30.190	52.35
	Hep ₄ NBr		NaBPh ₄		Bu ₄ NBPh ₄	
	221.389	43.20	269.297	36.68	147.394	37.50
	180.263	44.31	249.834	37.17	131.376	38.19
	149.806	45.28	230.364	37.66	109.710	39.13
	129.881	45.98	201.036	38.46	90.062	40.07
	109.956	46.70	169.742	39.40	75.052	40.84
	90.031	47.52	139.982	40.31	60.123	41.70
	70.106	48.44	110.222	41.37	49.899	42.35
	55.347	49.21	80.462	42.59	40.163	43.03
	39.850	50.16	49.600	44.09	30.061	43.79
	19.925	51.64	25.351	45.69	19.878	44.81

Contd..

Table 2 (Contd...)

0.60 mole fraction of PC

	-Me ₄ NBr		Et ₄ NBr		Pr ₄ NBr	
190.613	48.82	353.944	43.69	346.817	38.74	
162.131	49.81	311.372	44.72	300.574	39.78	
124.840	51.07	278.333	45.50	260.834	40.74	
109.708	51.64	225.344	46.84	225.431	41.68	
90.252	52.47	175.792	48.27	174.564	43.12	
70.256	53.46	125.060	50.02	124.854	44.67	
50.260	54.63	89.665	51.36	90.172	46.10	
30.264	56.03	68.919	52.31	69.363	47.10	
15.132	57.42	47.342	53.56	49.710	48.02	
7.566	58.40	33.602	54.39	30.057	49.31	
	Bu ₄ NBr		Pen ₄ NBr		Hex ₄ NBr	
373.447	37.12	371.387	34.78	355.918	33.70	
300.002	38.55	302.884	35.97	279.988	35.13	
261.317	39.42	261.784	36.77	250.683	35.81	
225.313	40.32	225.617	37.57	220.669	36.51	
175.520	41.57	175.622	38.70	169.654	37.76	
124.482	43.10	125.627	40.09	125.757	39.02	
90.872	44.31	91.016	41.17	90.165	40.23	
69.710	45.15	70.505	41.94	69.997	40.96	
49.792	46.12	49.999	42.75	51.014	41.89	
31.120	47.21	30.766	43.79	31.926	42.89	

Contd.

Table 2 (Contd..)

0.60 mole fraction of PC

	Hep ₄ NBr		NaBPh ₄		Bu ₄ NBPh ₄	
373.723	32.69	325.739	27.52	231.946	27.60	
300.192	34.00	251.165	28.94	175.863	28.93	
261.935	34.69	175.986	30.57	149.793	29.62	
225.796	35.55	145.700	31.28	130.442	30.23	
174.894	36.57	120.325	32.06	110.374	30.84	
125.297	37.89	94.951	32.83	90.306	31.51	
90.057	38.94	75.306	33.50	71.671	32.26	
70.479	39.69	55.660	34.28	50.170	33.17	
50.902	40.42	35.197	35.19	30.102	34.28	
30.019	41.49	20.463	36.09	20.068	34.97	

Table 3. Conductance parameters of tetraalkylammonium bromides, sodium tetraphenylborate and tetrabutylammonium tetraphenylborate in propylene carbonate (PC) + methanol mixtures at 25°C

Mole fraction of PC	Salt	$\Lambda_{\infty} / S \text{ cm}^2 \text{ mol}^{-1}$	$K_A / \text{dm}^3 \text{ mol}^{-1}$	$\Lambda_{\infty} \eta_{\infty}$	R / \bar{A}	σ
0.10	Me ₄ NBr	112.05 ± 0.04	20.80 ± 0.09	0.702	15.8	0.03
	Et ₄ NBr	105.79 ± 0.05	18.52 ± 0.14	0.663	16.8	0.05
	Pr ₄ NBr	95.50 ± 0.02	21.71 ± 0.06	0.598	16.6	0.02
	Bu ₄ NBr	89.75 ± 0.02	23.55 ± 0.08	0.562	17.1	0.03
	Pen ₄ NBr	86.10 ± 0.03	22.98 ± 0.09	0.539	17.0	0.03
	Hex ₄ NBr	83.87 ± 0.05	23.74 ± 0.19	0.525	17.8	0.06
	Hep ₄ NBr	81.04 ± 0.03	22.86 ± 0.11	0.508	18.0	0.03
	NaBPh ₄	76.01 ± 0.03	24.28 ± 0.13	0.476	18.5	0.04
	Bu ₄ NBPh ₄	73.68 ± 0.04	33.23 ± 0.19	0.462	20.9	0.05

Contd..

Table 3 (Contd..)

	Me ₄ NBr	98.99 ± 0.05	16.30 ± 0.10	0.712	15.3	0.05
	Et ₄ NBr	92.97 ± 0.03	12.75 ± 0.06	0.669	14.8	0.03
	Pr ₄ NBr	83.64 ± 0.03	15.40 ± 0.08	0.602	14.7	0.04
	Bu ₄ NBr	77.38 ± 0.04	16.01 ± 0.11	0.557	15.4	0.05
C.20	Pen ₄ NBr	75.11 ± 0.03	14.30 ± 0.08	0.540	15.3	0.04
	Hex ₄ NBr	73.52 ± 0.03	14.97 ± 0.08	0.529	16.1	0.04
	Hep ₄ NBr	72.21 ± 0.19	15.10 ± 0.54	0.519	12.9	0.03
	NaBPh ₄	66.22 ± 0.02	17.88 ± 0.05	0.476	17.1	0.02
	Bu ₄ NBPh ₄	64.85 ± 0.02	25.25 ± 0.11	0.466	18.9	0.04

Contd..

Table 3 (Contd..)

	Me ₄ NBr	78.15 ± 0.04	10.92 ± 0.07	0.762	14.4	0.05
	Et ₄ NBr	74.17 ± 0.02	10.37 ± 0.03	0.723	14.2	0.03
	Pr ₄ NBr	66.27 ± 0.02	10.13 ± 0.04	0.646	13.8	0.04
	Bu ₄ NBr	62.43 ± 0.01	13.32 ± 0.03	0.609	15.9	0.02
0.40	Pen ₄ NBr	59.59 ± 0.03	13.69 ± 0.07	0.581	14.7	0.05
	Hex ₄ NBr	57.41 ± 0.06	11.99 ± 0.15	0.560	15.3	0.11
	Hep ₄ NBr	55.68 ± 0.03	10.86 ± 0.08	0.543	14.4	0.05
	NaBPh ₄	50.02 ± 0.02	12.14 ± 0.04	0.488	15.7	0.03
	Bu ₄ NBPh ₄	48.84 ± 0.02	18.32 ± 0.10	0.476	19.9	0.05

Contd..

Table 3 (Contd..)

	Me ₄ NBr	60.57 ± 0.02	10.58 ± 0.07	0.786	9.3	0.05
	Et ₄ NBr	58.83 ± 0.03	10.70 ± 0.06	0.763	14.2	0.06
	Pr ₄ NBr	53.39 ± 0.03	12.11 ± 0.08	0.693	15.3	0.08
	Bu ₄ NBr	51.16 ± 0.02	10.88 ± 0.04	0.664	14.6	0.04
0.60	Pen ₄ NBr	47.50 ± 0.02	9.88 ± 0.06	0.616	14.2	0.06
	Hex ₄ NBr	46.76 ± 0.02	11.40 ± 0.07	0.607	15.1	0.06
	Hep ₄ NBr	45.01 ± 0.03	9.88 ± 0.08	0.584	15.0	0.09
	NaBPh ₄	38.96 ± 0.02	12.68 ± 0.09	0.505	17.0	0.06
	Bu ₄ NBPh ₄	37.89 ± 0.02	15.79 ± 0.08	0.492	18.3	0.05

Table 4. Walden products ($\Lambda \cdot \eta_0$) of tetraalkylammonium bromides, NaBPh_4 and Bu_4NBPh_4 in PC + methanol mixtures at 25°C

Salt	Mole fraction of PC					
	0.00	0.10	0.20	0.40	0.60	1.00
Me_4NBr	0.680	0.702	0.712	0.762	0.786	0.768
Et_4NBr	0.636	0.663	0.669	0.723	0.763	0.740
Pr_4NBr	0.558	0.598	0.602	0.646	0.693	0.706
Bu_4NBr	0.519	0.562	0.557	0.609	0.664	0.684
Pen_4NBr	0.497	0.539	0.540	0.581	0.616	0.620
Hex_4NBr	-----	0.525	0.529	0.560	0.607	0.602
Hep_4NBr	0.466	0.508	0.519	0.543	0.584	0.578
NaBPh_4	0.444	0.476	0.476	0.488	0.505	0.484
Bu_4NBPh_4	0.413	0.462	0.466	0.476	0.492	0.452

Table 5. Limiting ionic conductances (λ_0^+ , λ_0^-) in PC + methanol mixtures at 25°C
(λ_0 values are taken from Table 3).

Ion	Mole fraction of PC					
	0.00 ^a	0.10	0.20	0.40	0.60	1.00
Me ₄ N ⁺	68.7	60.39	55.13	43.97	29.00	12.87 ^b
Et ₄ N ⁺	60.5	54.13	49.11	39.99	27.26	11.72 ^b
Pr ₄ N ⁺	46.1	43.84	39.78	32.09	21.82	10.35 ^b
Bu ₄ N ⁺	39.0	38.09	33.52	28.25	19.59	9.46 ^b
Pen ₄ N ⁺	34.8	34.44	31.25	25.41	15.93	6.88 ^b
Hex ₄ N ⁺	---	32.21	29.66	23.23	15.19	6.16 ^b
Hep ₄ N ⁺	29.3	29.38	28.35	21.50	13.44	5.19 ^b
Na ⁺	45.2	40.42	34.89	26.43	20.66	10.74 ^c
Br ⁻	56.4	51.66	43.86	34.18	31.57	18.22 ^b
Ph ₄ B ⁻	36.6	35.59	31.33	23.59	18.30	8.84 ^b

^aData taken from ref. 3, p. 673

^bData taken from Chapter - IV

^cData taken from Chapter - V

Table 6. Stokes radii (r_s) in \AA of the ions in PC + methanol mixtures at 25°C

Ion	$r_c / \text{\AA}$	Mole fraction of PC					
		0.00	0.10	0.20	0.40	0.60	1.00
Me_4N^+	3.47 ^a	2.19	2.16	2.06	1.91	2.18	2.57
Et_4N^+	4.00 ^a	2.49	2.41	2.32	2.10	2.31	2.82
Pr_4N^+	4.52 ^a	3.26	2.98	2.86	2.62	2.89	3.20
Bu_4N^+	4.94 ^a	3.86	3.43	3.39	2.97	3.22	3.50
Pen_4N^+	5.29 ^a	4.32	3.79	3.64	3.30	3.95	4.81
Hex_4N^+	5.59 ^a	---	4.05	3.83	3.61	4.15	5.37
Hep_4N^+	5.88 ^a	5.13	4.44	4.01	3.90	4.70	6.38
Na^+	1.17 ^a	3.33	3.23	3.26	3.18	3.05	3.08
Br^-	1.80 ^b	2.67	2.53	2.59	2.46	2.00	1.82
Ph_4B^-	4.20 ^a	4.11	3.67	3.63	3.56	3.45	3.74

^aR.A. Robinson and H. Stokes, in *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1959.

^bB.S. Gourary and F.J. Adrian, *Solid State Phys.*, 10, 127, 1960.

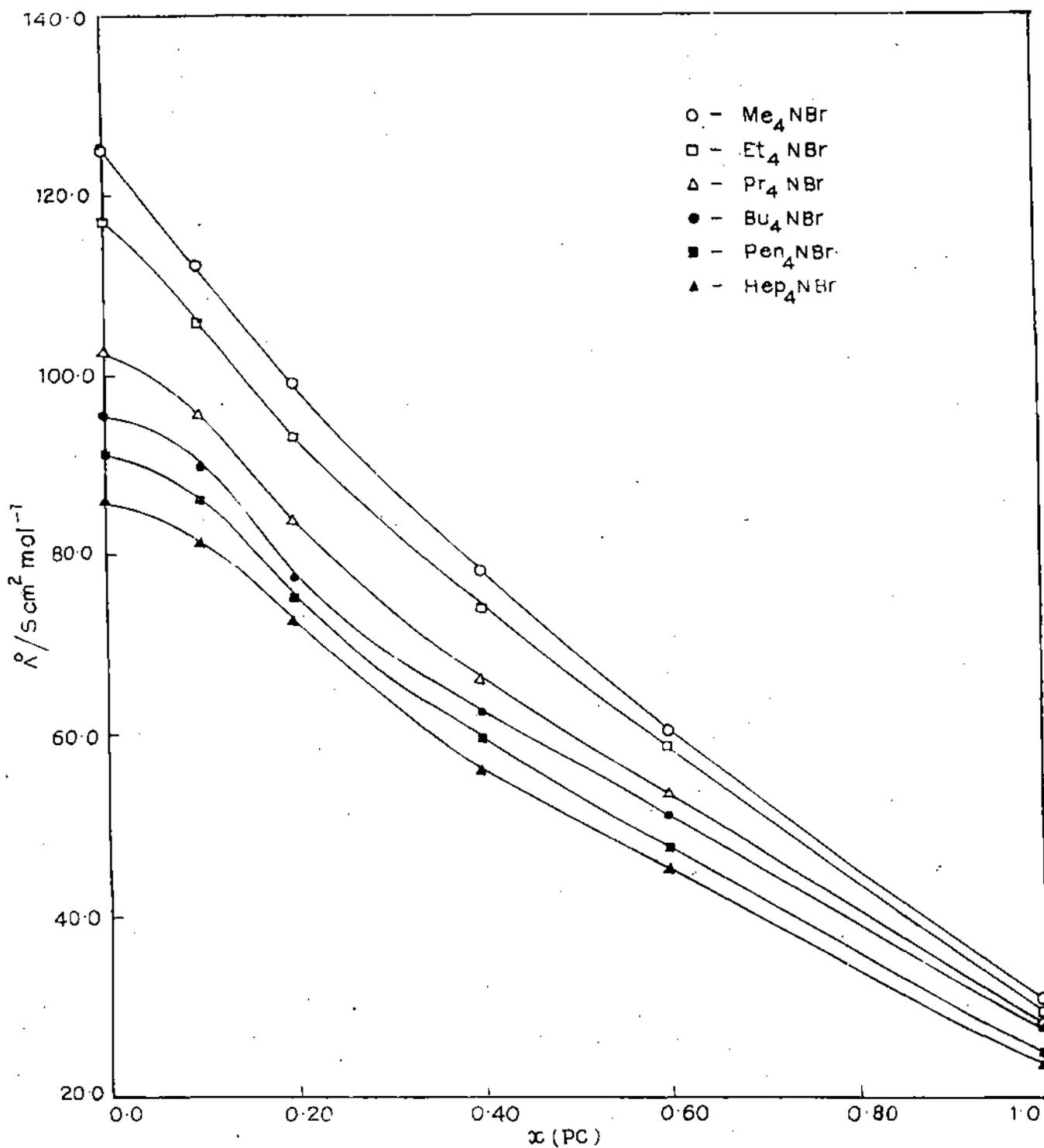


Fig. 1. Variation of limiting equivalent conductance (Λ°) with composition of the solvent mixture.

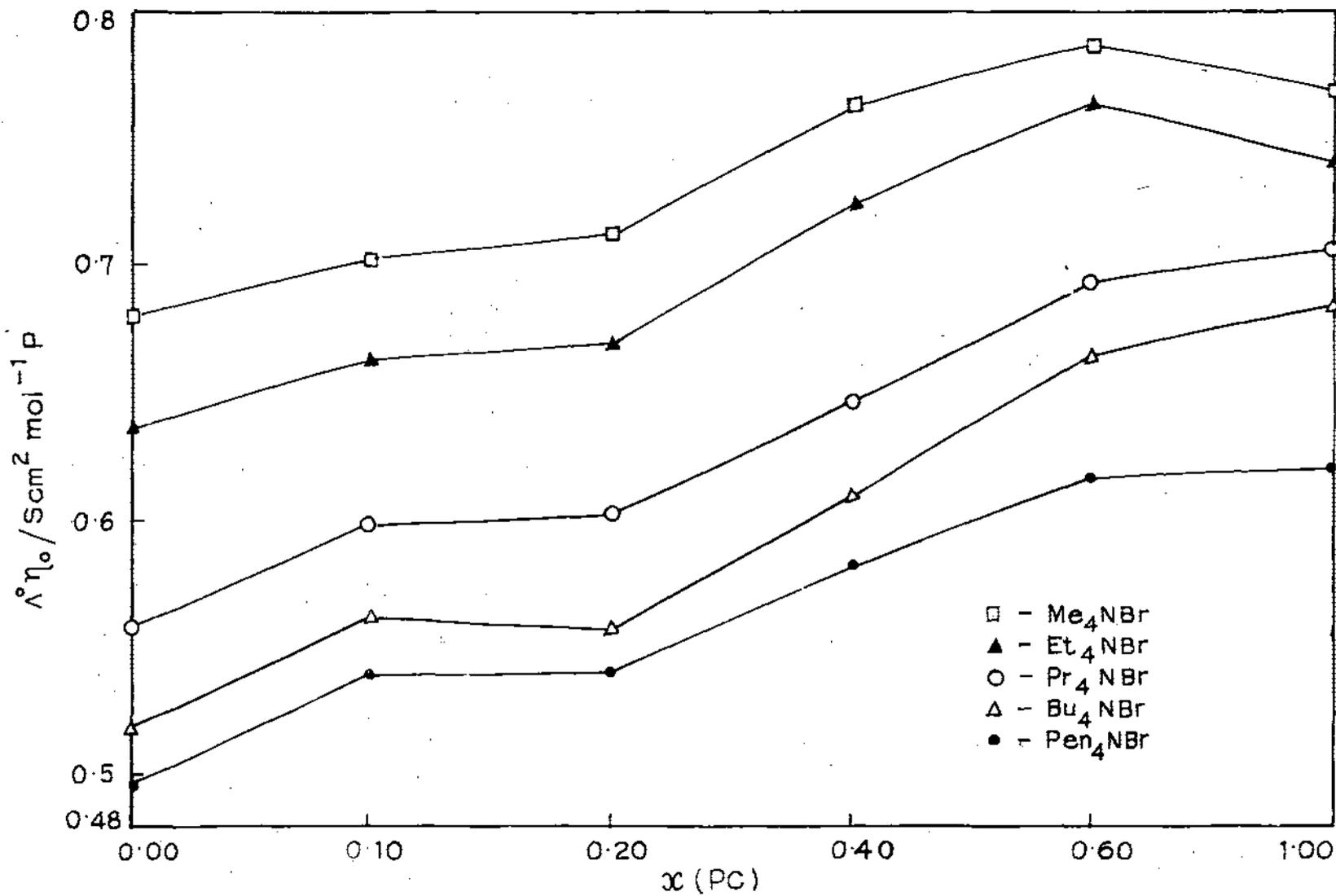


Fig. 2. Variation of Walden product with composition of the solvent mixture.

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CHAPTER-VIII

Infrared and Raman Spectra of Solutions of Some Alkali and Alkaline Earth Metal Perchlorates in Propylene Carbonate

Investigations on Raman and infrared spectra in aqueous and non-aqueous solutions have been extensively used to explore the types of interactions arising in electrolyte systems¹⁻⁶. The present chapter reports the results of infrared and Raman spectral investigations of $\text{Ba}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, $\text{Mg}(\text{ClO}_4)_2$, LiClO_4 and NaClO_4 in propylene carbonate (PC). The perchlorate salts have been chosen because of the small charge densities of perchlorate anions and their relatively weak tendency to form complex ions, particularly with cations of the alkali and alkaline earth metals. PC has generated much interest as a solvent medium for electrochemical studies⁷ relating to high energy batteries^{8,9} and free radical species¹⁰. Hence, it is of much interest to study the behaviour of electrolytes in such a solvent medium. The present chapter is believed to shed new light on the nature of intermolecular and interionic interactions in PC.

Experimental

Propylene carbonate (E. Merck, Germany; > 99% pure) was purified as described in Chapter - II.

Calcium (II) perchlorate and Strontium (II) perchlorate were prepared by neutralising the corresponding carbonates with perchloric acid. Anhydrous barium (II) perchlorate and magnesium (II) perchlorate were commercially available (Fluka). All these perchlorate salts were purified by at least triple recrystallisation from distilled water and dried at 373 K in vacuum over silica gel for few days¹¹.

Lithium perchlorate (Fluka, >99% pure) and sodium perchlorate (AR, E. Merck, Germany) were purified according to the procedure given in Chapter - II.

All solutions were prepared at 25°C and the perchlorate concentrations were determined with an Orion ion-selective electrode meter (model EA 920) after standardisation with known solution of the perchlorate electrode system.

Laser Raman spectroscopic measurements were made at 25°C with a DILOR Z24 RAMAN spectrometer using 4880 Å^o excitation. The spectral slit width was kept at $\sim 4 \text{ cm}^{-1}$. The laser power used was 300 mW. The spectra were recorded by the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras.

The infrared spectral measurements were made at 25°C on a Perkin-Elmer 983 spectrophotometer. Polythene windows were used for all measurements.

All spectra were scanned at least twice to ensure repeatability.

Results

Infrared spectra of pure propylene carbonate and of $\text{Ca}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$, $\text{Ba}(\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$ in PC at 298K are shown in Figs. 1-5. The principal bands observed for the pure solvent (PC) and its solutions have been listed in Tables 1 and 2 respectively.

Partial band assignments have been made for the infrared spectrum of PC (Table 1). The carbonyl stretching band appears at 1790 cm^{-1} . Four bands are observed in the C-O stretching region at 1182, 1118, 1050 and 1076 cm^{-1} . The 1468 cm^{-1} line has been assigned to the CH_3 deformation mode and CH_3 symmetric stretching frequency appears at 2985 and 2915 cm^{-1} . The IR spectrum of pure PC agreed well with those found in the literature^{2,12,13}.

We found that the spectra of calcium, strontium, barium and magnesium salt solutions showed several changes from that of pure PC. The 1790 cm^{-1} C = O stretching line of pure PC is used as the reference for intensity changes.

In all the salt solutions, a slight downward shift of the 1790 cm^{-1} and 1182 cm^{-1} bands was noticed. The intensities of the

peaks corresponding to the 1790 cm^{-1} and 1182 cm^{-1} bands of pure PC are found to be in the order:



In the infrared spectra of all the salt solutions, two new bands appear at $\sim 940\text{ cm}^{-1}$ and $\sim 624\text{ cm}^{-1}$, the later of which arises due to the triply degenerate bending vibration of perchlorate ion. The origin of the band at 940 cm^{-1} is not properly understood since the totally symmetric vibration of perchlorate ion is infrared inactive (it appears in the Raman spectrum).

The Raman spectra of pure PC and of LiClO_4 , NaClO_4 , $\text{Ba}(\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$ in PC at 298K are shown in Figs. 6-10. Some important bands observed for PC are recorded in Table 1. The Raman frequencies observed are given in Table 3. Comparison of the Raman bands of pure PC with literature values was not possible, because this solvent was not studied by Raman spectral techniques so far. The lines at 3001 and 2769 cm^{-1} have been assigned to the components of a Fermi resonance doublet arising out of the interaction between the symmetric CH_3 stretching mode (2892 cm^{-1}) and the first overtone of the CH_3 deformation mode (2949 cm^{-1}), the fundamental of which is found at 1473 cm^{-1} in pure PC.

Like the infrared spectrum of pure PC, the carbonyl stretching in the Raman spectrum occurs at 1799 cm^{-1} . But only two bands

are observed in the C-O region namely at 1188 and 1138 cm^{-1} ; the other two bands observed in the infrared spectrum of PC remain absent from the Raman spectrum because of the fact that they might be only infrared active. Both 1799 cm^{-1} and 1188 cm^{-1} bands of pure PC exhibited similar changes in frequency and intensity in the salt solutions as that of the infrared spectra.

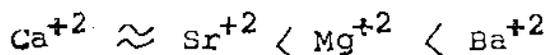
A new band appears at $\sim 940 \text{ cm}^{-1}$ in the solution spectra. This band is attributed¹⁴ to the infrared forbidden totally symmetric vibration of perchlorate ion.

Discussion

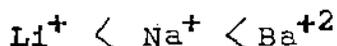
Because of the large dipole moment (4.94 D)¹⁵ propylene carbonate molecules should orient themselves with the negative poles in the direction of the cations and the positive poles in the direction of the anions. Thus it would seem that cations should disturb primarily the C = O band and only indirectly affect the C-O band. The disturbances caused by the cations will tend to weaken the C = O band because of the decrease in the electron density in this bond, in part, as a result of the flow of part of the s electrons in the direction of the free electron pairs of the oxygen atom of the C = O group. As a result of the induction effect the electron density in the C-O bonds within the ring should also decrease but the extent of weakening of the bond will be less than in the case of the C = O bond. It would seem that this type of change should lead to a

considerable decrease in the 1790 cm^{-1} band frequency and a smaller decrease in the 1182 cm^{-1} band frequency. In the present study, the intensities of both 1790 and 1182 cm^{-1} bands were found to decrease for all the salt solutions compared to the solvent spectrum; the extent of decrease in intensity was greater in the case of 1790 cm^{-1} band than in the case of 1182 cm^{-1} bands in all cases. This obviously indicates that the linkages of the metal ions with the PC molecule are actually taking place through the $\text{>C}=\text{O}$ group. But the frequencies corresponding to CH_2 stretching and CH_2 deformation modes of pure PC are not affected to a considerable extent in presence of these salts. This observation is in excellent agreement with the electron density distribution of the propylene carbonate molecule. The semi empirical molecular orbital calculation² shows a considerable electron density on the ring oxygen as well as on the carbonyl oxygen (Fig. 1 of Chapter 1). It is reasonable to assume that the interaction of cations with PC is not restricted to the carbonyl oxygen atom and may also involve extensive ring interactions. The positive centres, on the other hand, are much less accessible to anions. This agrees with observations that PC is a poor anion solvator². Exactly the same conclusion has been derived from the conductometric and viscometric investigations of alkali metal salts in this medium^{16,17}.

From the trends in the frequencies of the bands corresponding to 1790 and 1182 cm^{-1} bands in pure PC, it appears that the interactions of the cations with carbonyl oxygen increase in the order:



On the basis of the frequency shifts of the C = O band for the investigated perchlorates, the strength of the disturbance for the cation would seem to follow the order:



This indicates that the greatest changes occur in the propylene carbonate for $\text{Ba}(\text{ClO}_4)_2$ system, though Li^{+} ion has the maximum charge density amongst the three ions compared (Na^{+} and Ba^{+2} ions have almost the same charge density). On the basis of the charge density, Li^{+} ion should interact most strongly with the C = O group of propylene carbonate molecules. But the reverse is observed in the present investigation. This obviously, is an indication of the fact that the extent of the changes of the Raman spectral parameters is dependent not only on the charge density of the disturbing ions but also on their surface area. This is particularly important in the comparison of the action of cations belonging to different groups of the periodic system of elements. Thus, in the present study, the maximum interaction of Ba^{+2} with propylene carbonate molecules can be ascribed to the maximum surface area of the Ba^{+2} ion (as a matter of fact Ba^{+2} ion has about five times the surface of Li^{+} ion and twice that of Na^{+} ion). The observed differences in the change of frequency can not be explained on the basis of the fact that there are two perchlorate ions for every barium cation, since in accordance with the assumptions made, the anions should

lead to an increase in the frequency of the 1799 cm^{-1} band and a decrease in the frequency of the 1188 cm^{-1} band.

However, the observed differences in the behaviour of the cations may not depend only on such quantities as charge density or surface area of ions. Other factors leading to specific interactions may also play a role here, such as acceptor hybridisation of ions etc. The model given here, however, needs theoretical support and some calculations will be attempted in future in this direction.

Table 1. Infrared and Raman Spectra of liquid PC (cm^{-1})

Infrared	Raman	Assignment
2985 (s)	3001 (s)	CH_3 antisym. str.
2915 (s)	2949 (vs)	CH_3 sym. str.
1790 (vs)	1799 (s)	$\text{>C} = \text{O}$ str.
1468 (m)	1473 (m)	CH_3 def.
1182 (s)	1188 (s)	O-C-O skeletal str.
918 (w)	931 (w)	C-O-C sym. mode

vs = very strong; s = strong; m = medium; w = weak

Table 2. Infrared Spectra of PC and various Salt Solutions (cm^{-1})

PC	$\text{Ca}(\text{ClO}_4)_2$	$\text{Sr}(\text{ClO}_4)_2$	$\text{Ba}(\text{ClO}_4)_2$	$\text{Mg}(\text{ClO}_4)_2$
2985 (m)	2982 (m)	2980 (m)	2980 (m)	2980 (m)
2915 (s)	2915 (s)	2915 (s)	2920 (s)	2915 (s)
2345 (w)	2345 (w)	2340 (w)	2340 (w)	2345 (w)
1790 (vs)	1778 (vs)	1780 (vs)	1784 (vs)	1790 (vs)
-----	1620 (s)	1620 (s)	1610 (s)	1618 (s)
1548 (m)	1550 (m)	1546 (s)	1548 (s)	1548 (m)
1468 (m)	1470 (s)	1474 (s)	1474 (s)	1470 (m)
1445 (m)	1443 (m)	1443 (s)	1444 (s)	1444 (s)
1383 (s)	1383 (s)	1380 (s)	1382 (s)	1382 (s)
1344 (s)	1344 (s)	1345 (s)	1344 (s)	1344 (s)
1182 (s)	1177 (sh)	1177 (sh)	1180 (m)	1176 (m)
1118 (s)	1140 (sh)	1143 (sh)	1144 (w) 1115 (w)	1135 (sh) 1112 (w)
1050 (m)	-	1054 (sh)	1050 (w)	1054 (w)
1076 (sh)	1085 (s)	1080 (s, broad)	1080 (w)	1079 (vw)
959 (w)	956 (w)	960 (w)	955 (w)	956 (w)
-	940 (w)	940 (w)	944 (sh)	940 (w)
918 (w)	920 (w)	920 (w)	917 (w)	920 (w)
846 (m)	844 (m)	850 (m)	846 (s)	846 (m)
772 (s)	775 (s)	775 (vs)	774 (vs)	776 (vs)
708 (s)	708 (s)	708 (s)	708 (s)	708 (s)
626 (w)	624 (vs)	625 (vs)	624 (vs)	622 (vs)
532 (w)	536 (w)	533 (m)	536 (m)	532 (vw)
440 (vw)	448 (vw)	444 (vw)	440 (m)	448 (m)

vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

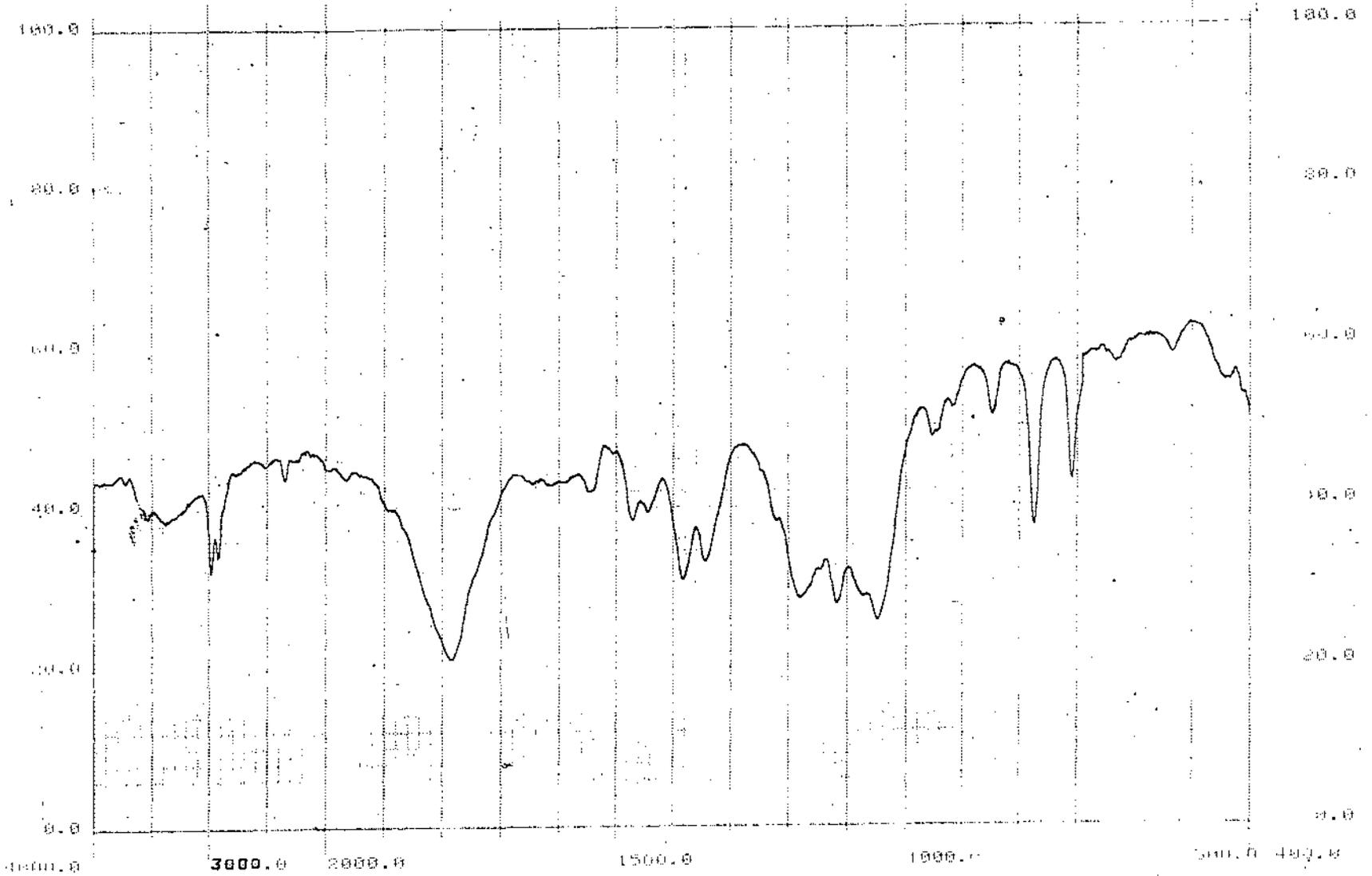
sh =

Table 3. Laser Raman Spectra of PC and various Salt Solutions(cm^{-1})

PC	LiClO_4	NaClO_4	$\text{Ba}(\text{ClO}_4)_2$	$\text{Mg}(\text{ClO}_4)_2$
3001 (s)	2986 (s)	2984 (s)	2974 (s)	
2949 (vs)	2944 (vs)	2927 (vs)	2919 (vs)	
2892 (s)	2877 (s)	2870 (s)	2857 (s)	
2769 (m)	2756 (m)	2745 (m)	2740 (m)	
1799 (s)	1790 (vs)	1767 (m)	1758 (m)	1784 (m)
1508 (m)	1489 (s)	1465 (m)	1453 (m)	1486 (m)
1473 (m)	1460 (m)	1437 (m)	1424 (m)	1460 (m)
1245 (m)	1228 (s)	1209 (m)	1201 (m)	1227 (m)
1188 (m)	1158 (m)	1131 (m)	1127 (m)	1151 (m)
1138 (m)	1122 (m)	1108 (m)	1101 (m)	1124 (m)
-	1068 (m)	1041 (m)	1038 (m)	1058 (m)
974 (s)	960 (s)	-	-	959 (s)
-	935 (s)	941 (s)	937 (s)	934 (s)
931 (m)	913 (s)	920 (s) 899 (sh)	913 (s) 900 (sh)	
861 (s)	853 (vs)	836 (vs)	838 (s)	851 (s)
728 (s)	716 (s)	702 (s)	705 (s)	716 (s)
653 (m)	658 (m)	625 (m)	626 (m)	631 (m)
-	546 (s)	537 (s)	-	541 (s)
464 (m)	457 (s)	451 (s)	449 (m)	455 (m)
326 (w)	315 (w)	320 (w)	-	317 (w)

vs = very strong, s = strong, m = medium, w = weak, vw = very weak;

sh =

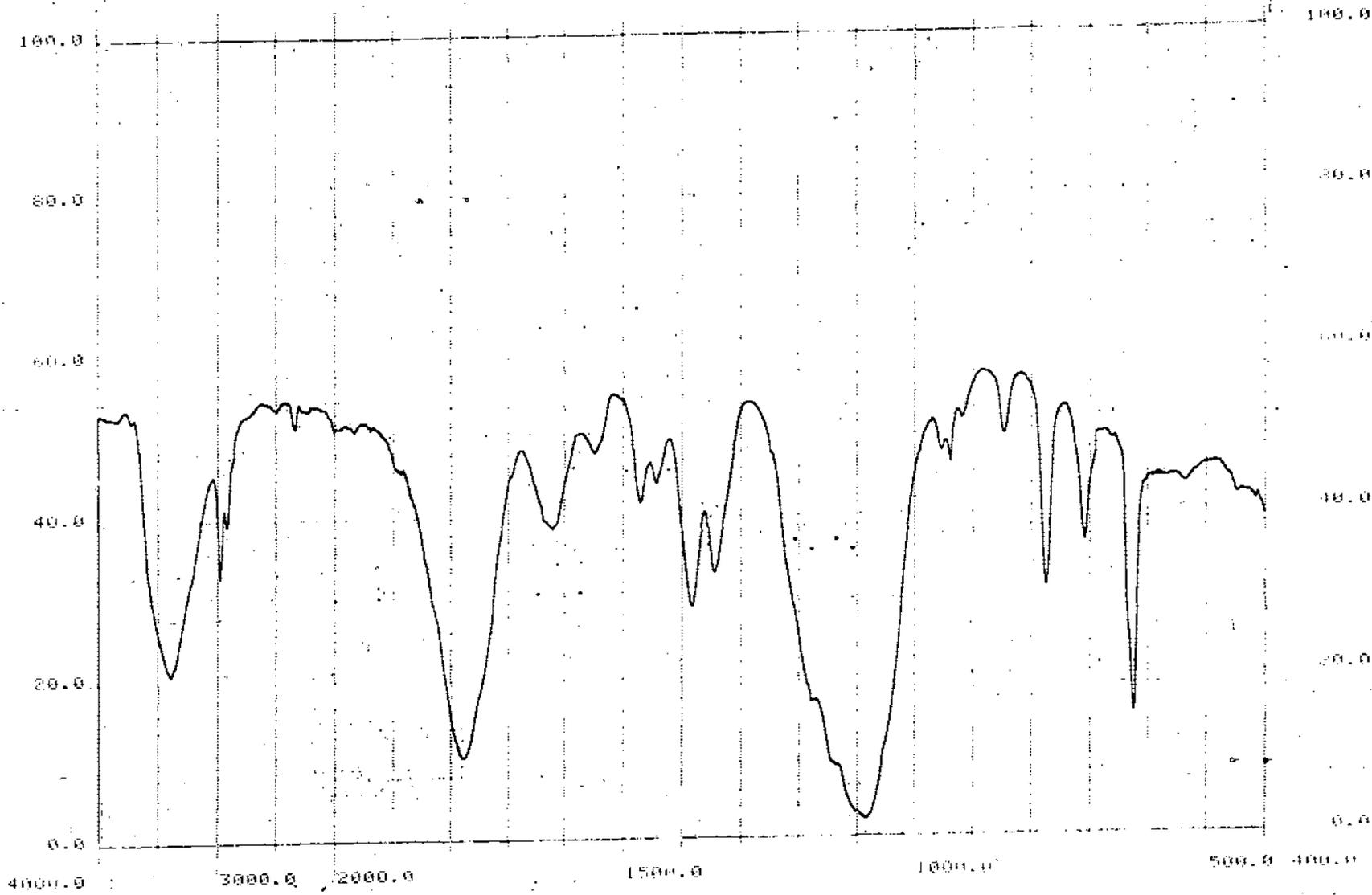


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PC

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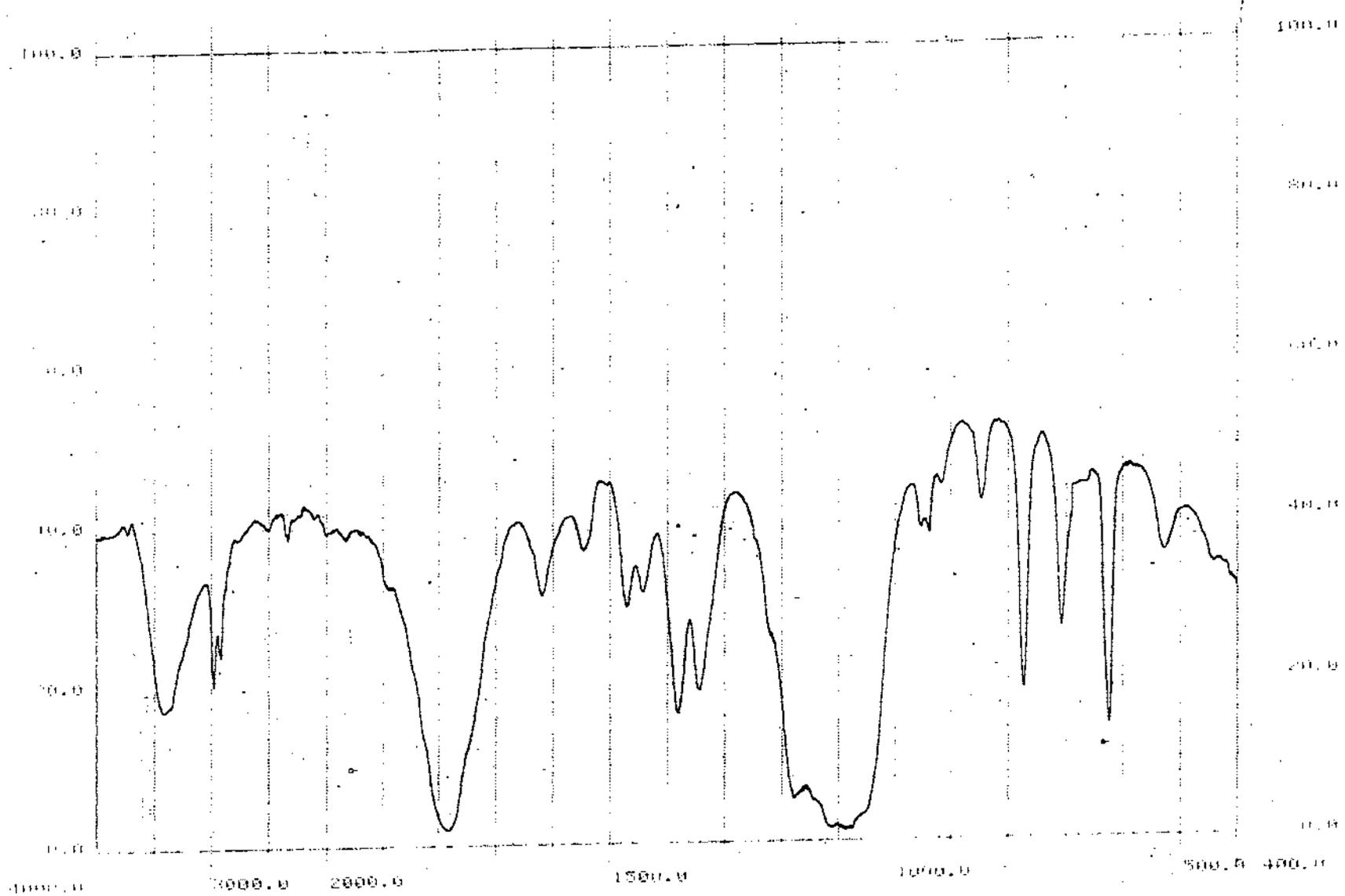
Fig.1 I.R. spectrum of propylene carbonate (PC)



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Fig.2 I.R. spectrum of $\text{Ca}(\text{ClO}_4)_2$ in Propylene Carbonate



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Fig. 3 I.R. spectrum of $\text{Sr}(\text{ClO}_4)_2$ in Propylene Carbonate

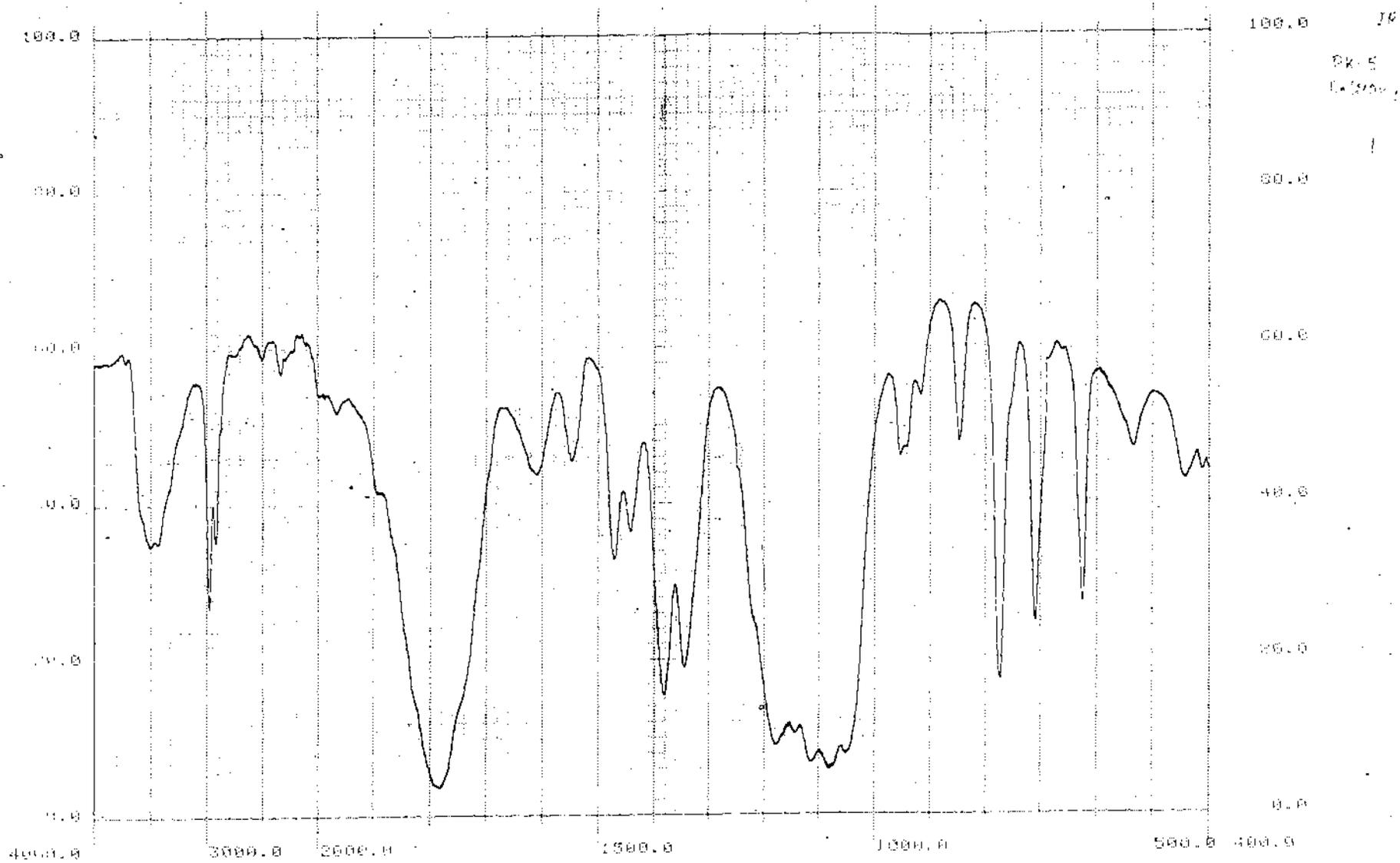
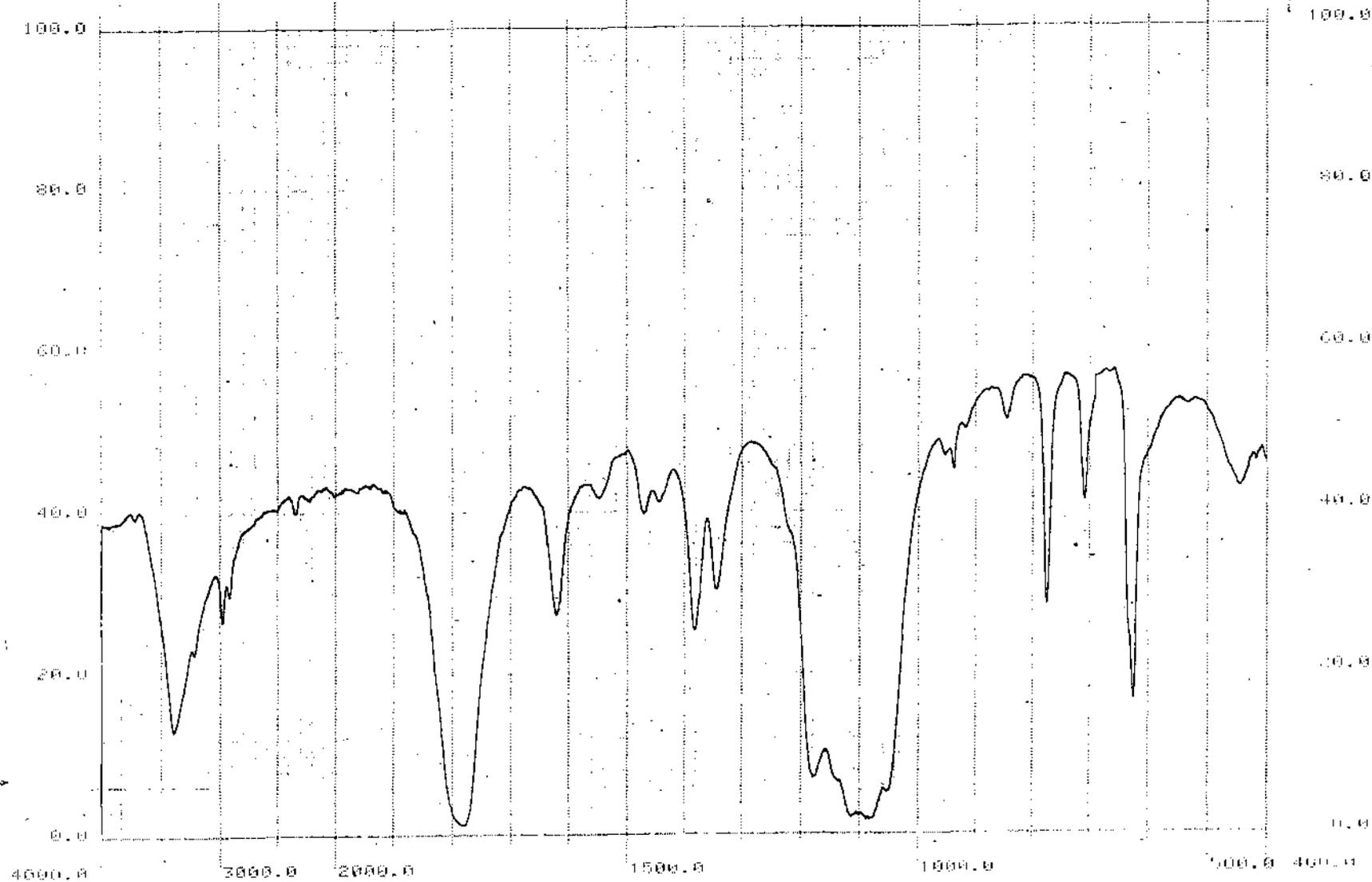


Fig.4 I.R. spectrum of $Ba(ClO_4)_2$ in Propylene Carbonate



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Fig.5 I.R. spectrum of $Mg(ClO_4)_2$ in Propylene Carbonate

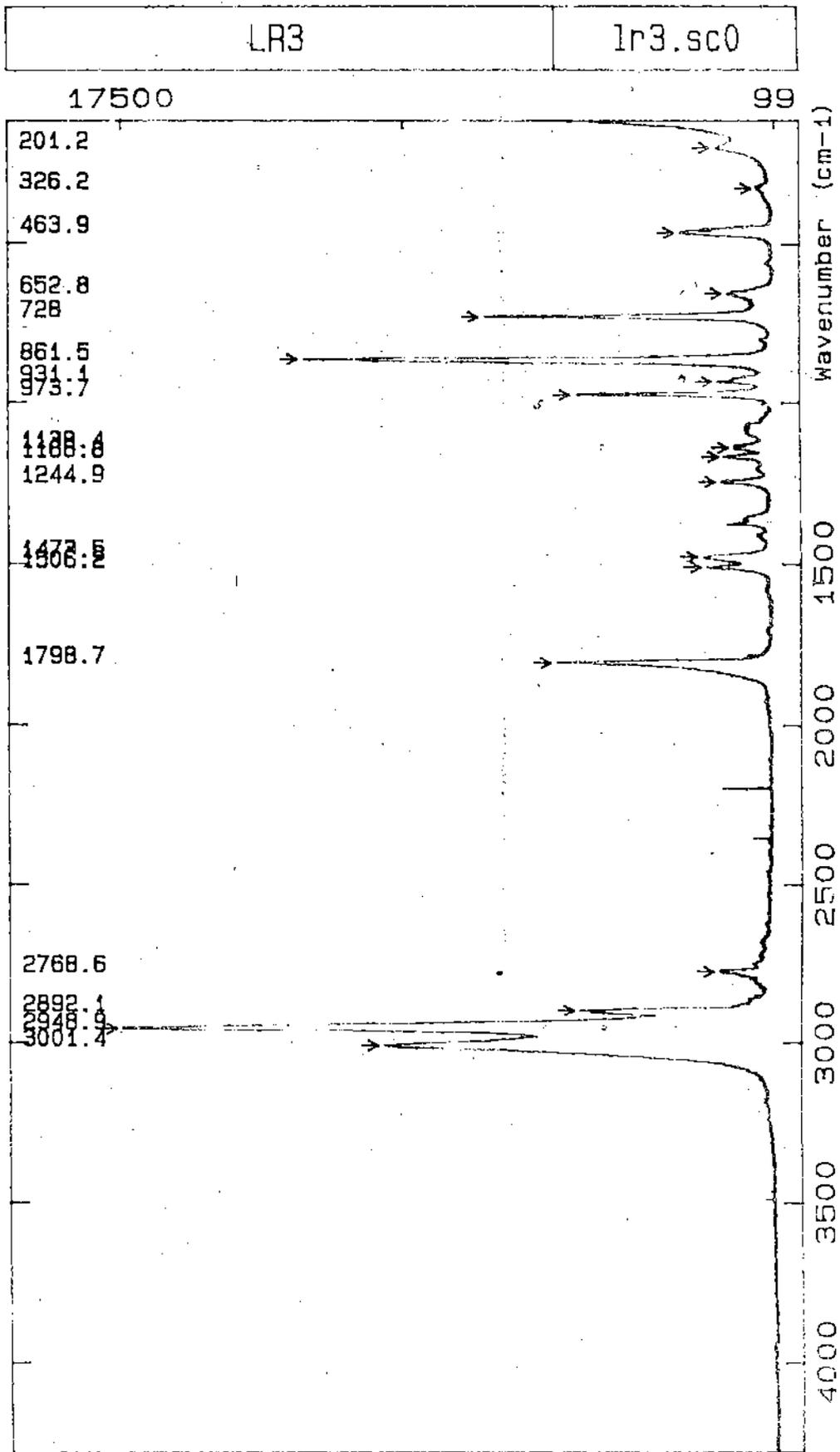


Fig. 6 Raman spectrum of Propylene Carbonate (PC)

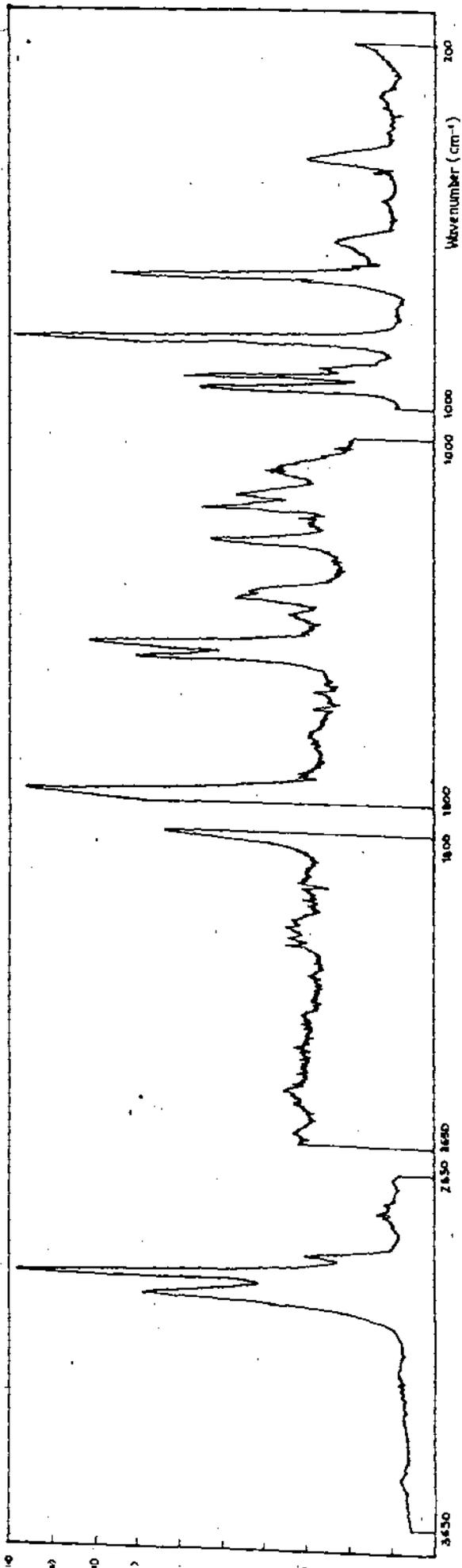


Fig-7 Raman Spectrum of LiClO_4 in PC

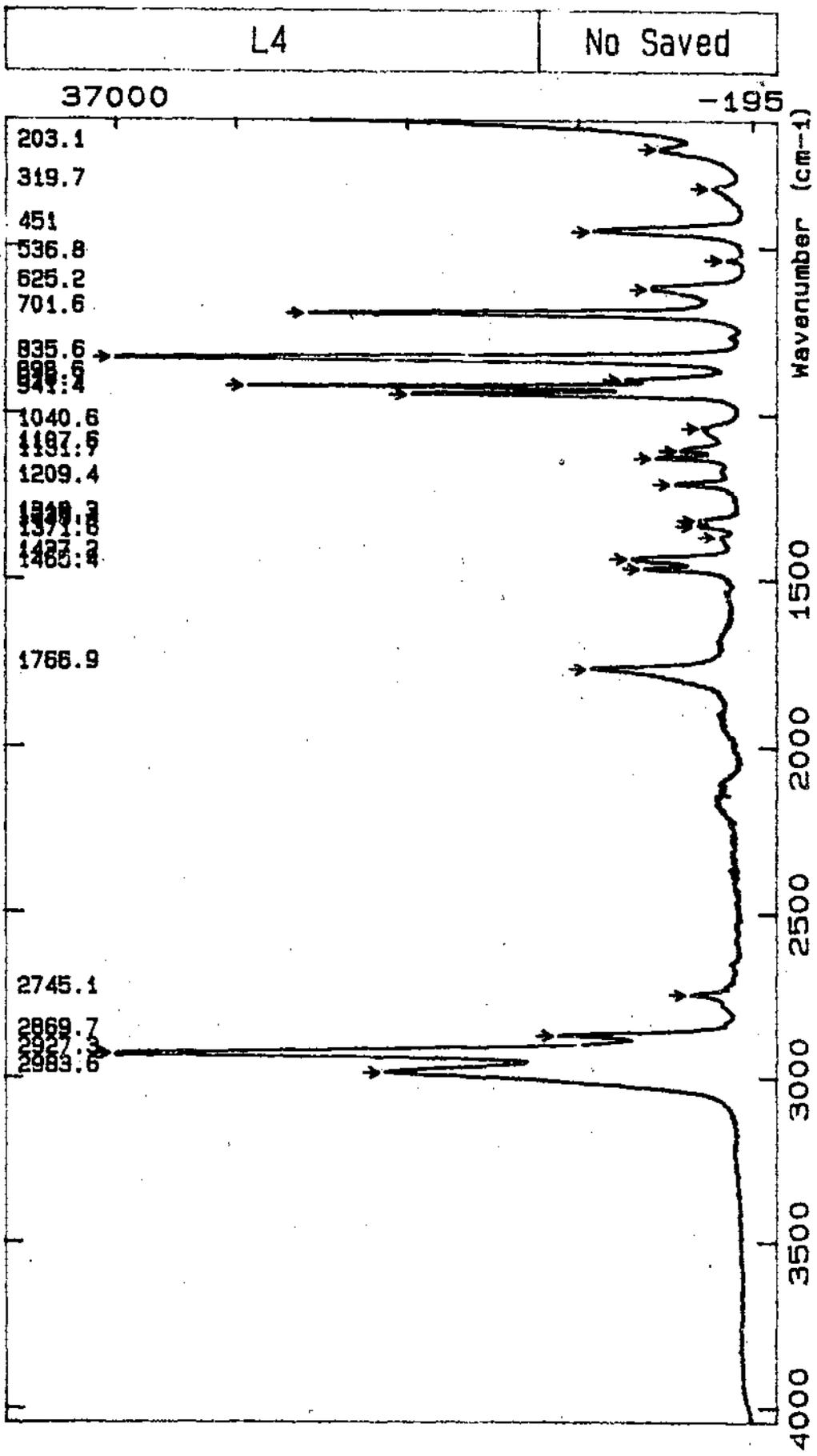


Fig. 8 Raman spectrum of NaClO₄ in propylene carbonate

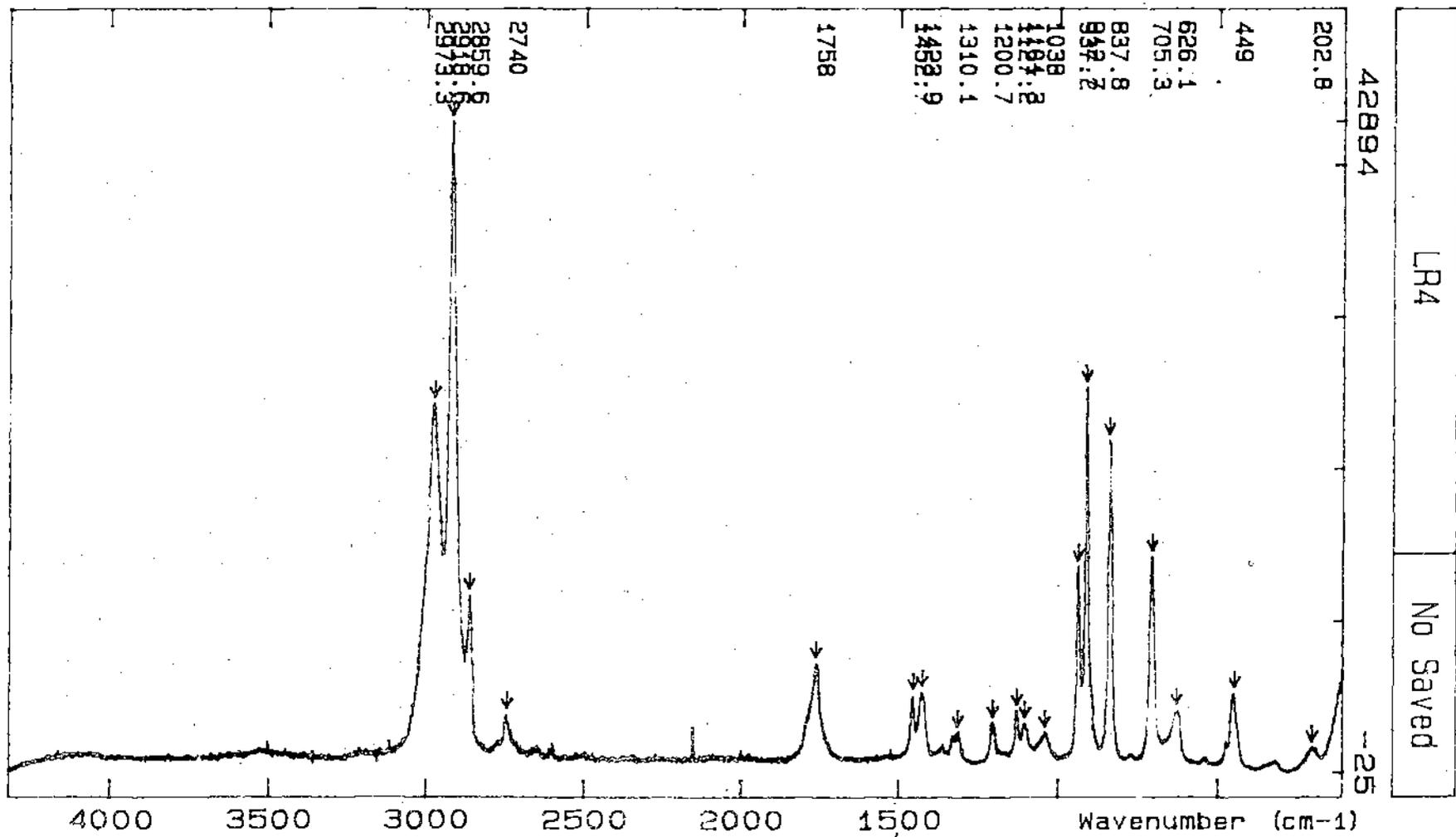


Fig.9 Raman spectrum of $Ba(ClO_4)_2$ in propylene carbonate

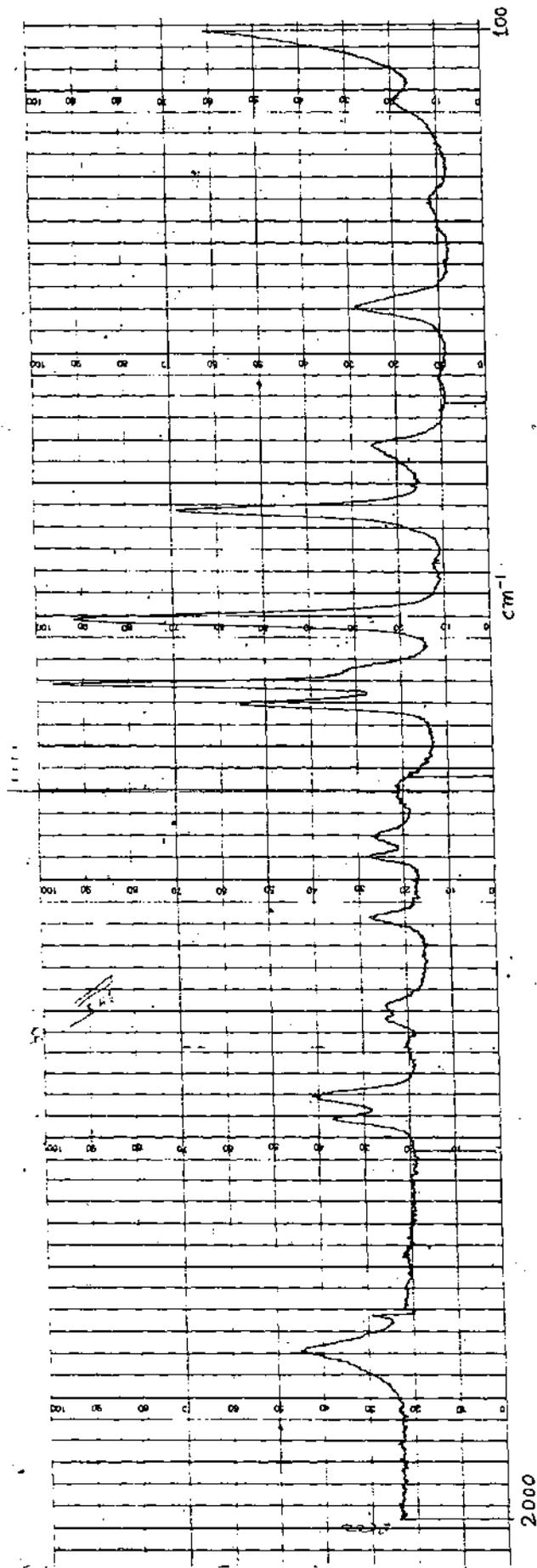


Fig. 10 Raman spectrum of $\text{Mg}(\text{ClO}_4)_2$ in propylene carbonate

R E F E R E N C E S

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CHAPTER-IX

Concluding Remarks

Symmetrical tetraalkylammonium and alkali metal salts show numerous interesting properties that are now being investigated in many laboratories. Most of the present day knowledge on non-aqueous solutions has come from studies on various thermodynamic properties e.g. solubilities, free energies of solution, transfer free energies, 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, alkali metal and tetraphenyl salts in propylene carbonate and in its non-aqueous binary mixtures from their viscosity, conductance and solubility measurements. Solvent-solvent interactions in four binary non-aqueous mixtures of propylene carbonate have also been attempted from volumetric and viscometric studies. Infrared and Raman spectral investigations of some alkaline-earth metal and alkali metal perchlorates have also been attempted since these are potentially capable of yielding more precise information on the nature of interactions taking place in solution.

The viscosity B co-efficients give us quantitative values of the ion-solvent interactions, but still we have no unambiguous method of division of B-coefficients into ionic B values in all solvents. The use of Bu_4NBBu_4 and Bu_4NPh_4 appears to be sound, but we lack sufficient data measured in different solvents to arrive at a definite conclusion. It is desirable to use different methods of division of B values to have reasonably consistent ionic B values.

Accurate B_{ion} values would give the solvation number of ions.

It is known that

$$B_{ion} = B_{ion}^{Einst.} + B_{ion}^{Str} + B_{ion}^{Disord}$$

but it is not possible to calculate the individual constituents like B_{ion}^{Einst} etc. so that the effect of charges on the nature of solvation can be properly explored. Efforts should be made to know at least B_{ion}^{Einst} values experimentally.

Similarly, different methods are to be used to find out limiting conductances of the ions from the limiting equivalent conductances of electrolytes. Proper evaluation of the limiting equivalent conductance, Λ° , the single-ion conductance, λ_{\pm}° , the ionic association constant, K_A and the ion size parameter a° and their dependence on the dielectric constant would be of great help in determining ion-ion and ion-solvent interactions. However, the variation of λ_{\pm}° values for ions depends not only on their solvodynamic entity but also on their movement through different solvents. This aspect needs consideration and further study.

However, it is necessary to remember that ion-solvent interactions are very complex in nature. There are strong electrical forces between ions and between the ions and solvents and it is not really possible to separate them all. Nevertheless, if careful

judgement is used, valid conclusions can be drawn in many cases from solubility, viscosity, conductivity and spectroscopic measurements relating to degree of structure and order of the system.

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

Electrical Conductances for some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate and Tetrabutylammonium Tetrabutylborate in Propylene Carbonate at 25 °C

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Conductance measurements are reported for several symmetrical tetraalkylammonium bromides, lithium tetrafluoroborate (LiBF_4) and tetrabutylammonium tetrabutylborate (Bu_4NBBu_4) in propylene carbonate (PC) at 25 °C. The data have been analysed by the 1978 Fuoss conductance equation in terms of the limiting molar conductivity, Λ° , the association constant, K_A , and the association distance R . The single-ion conductances have been determined from the Λ° value of Bu_4NBBu_4 using it as a 'reference electrolyte'. The results indicate that with the exception of LiBF_4 to some extent, other salts are almost unassociated in this solvent medium. The evaluation of Stokes radii of the ions indicate that Li^+ is extensively solvated while the other ions remain almost unsolvated. The results have been discussed in terms of the ion-solvating ability of PC and also compared with the previous values in this system.

Propylene carbonate (PC) has drawn much attention in recent years as a solvent medium for electrochemical studies¹ relating to high-energy batteries^{2,3} and free-radical species.⁴ It is a stable solvent of moderately high relative permittivity⁵ (64.40 at 25 °C) and has good solvent properties^{6,7} for a variety of organic and inorganic salts. Hence, it is of much interest to study the behaviour of electrolytes in such a solvent medium. The conductometric method is well known⁸ to give valuable information regarding ion-solvent interactions of electrolytes in non-aqueous and mixed solvents. Although conductance measurements on alkali-metal iodides⁹⁻¹¹ and quaternary ammonium perchlorates^{6,11} have been reported in PC, no such experimental data for tetraalkylammonium bromides (except tetrabutylammonium bromide) and lithium tetrafluoroborate are available in the literature. Conductance measurements on tetrabutylammonium tetrabutylborate have been reported by Takeda and co-workers,¹² but this compound has been further investigated by us in order to maintain an internal consistency amongst the derived values with these electrolytes.

We have therefore repeated a few of the earlier measurements and have also measured the electrical conductances of several additional tetraalkylammonium bromides, R_4NBr ($\text{R} = \text{methyl to heptyl}$), LiBF_4 and Bu_4NBBu_4 in PC at 25 °C. Single-ion conductances have been derived using Bu_4NBBu_4 as the 'reference electrolyte' in an effort to provide reliable values of the ionic mobilities for these ions in this medium.

Experimental

PC (Merck >99% pure) was dried over freshly ignited quicklime for several hours¹³ and then distilled three times under reduced pressure under nitrogen, the middle fraction being taken each time. The purified sample had a density of 1.1988 g cm^{-3} , viscosity of 2.471 cP and a specific conductance of ca. $0.73 \times 10^{-6} \text{ S cm}^{-1}$ at 25 °C; these values are in good agreement with the literature values.^{13,14}

Tetraalkylammonium bromides were of purum or puriss grade (Fluka) and were purified as described in the literature.^{15,16} The salts were purified by recrystallization and the higher homologues were recrystallized twice to ensure maximum purity. The recrystallized salts were dried *in vacuo* at elevated temperatures for 12 h.

Lithium tetrafluoroborate (Fluka, puriss) was dried under vacuum at high temperature for ca. 48 h immediately prior to use and was used without further purification.

Tetrabutylammonium tetrabutylborate (Alfa Products) was purified as suggested in ref. 17.

Conductance measurements were made using a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type immersion cell of cell constant 0.751 cm^{-1} and having an accuracy of $\pm 0.1\%$. The cell constant was checked frequently using standard KCl solutions. Measurements were made in an oil bath maintained at 25 ± 0.005 °C. Details of the experimental procedure have been described previously.¹⁸ Several independent solutions were prepared and measurements were made with each of these to ensure the reproducibility of the results. All data were corrected with the specific conductance of the solvent. The corrected values were analysed by means of the Fuoss conductance equation.^{19,20}

Results

The measured equivalent conductances and the corresponding concentrations, C , in molarities are given in Table 1. The data were analysed with the Fuoss conductance equation^{19,20} which can be expressed as

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

$$P = [1 - \alpha(1 - \gamma)] \quad (2)$$

$$\bar{\gamma} = 1 - K_A c \gamma^2 f^2 \quad (3)$$

$$-\ln f = \beta k/2(1 + kR) \quad (4)$$

$$\beta = \frac{e^2}{\epsilon k_B T} \quad (5)$$

where R_x and E_L are relaxation and hydrodynamic terms, respectively, and the other terms have their usual meanings. The parameters Λ° , K_A and R were obtained by solving the above equations. Initial Λ° values for the iteration procedure were obtained from Shedlovsky extrapolation of the data.

In practice, calculations were made by finding the minimum values of Λ° and α for a sequence of R values and then plotting

$$\sigma^2 = \sum_j [\Lambda_j(\text{calc.}) - \Lambda_j(\text{obs.})]^2 / (n - 2) \quad (6)$$

Table 1 Equivalent conductances and corresponding molarities of the tetraalkylammonium bromides, tetrabutylammonium tetrabutylborate and lithium tetrafluoroborate in propylene carbonate at 25 °C

$C/10^{-4}$ mol dm ⁻³	Λ/S cm ² mol ⁻¹	$C/10^3$ mol dm ⁻³	Λ/S cm ² mol ⁻¹
Me₄NBr		Et₄NBr	
131.702	27.18	90.445	26.67
100.094	27.67	73.080	27.03
84.861	27.97	62.226	27.26
60.056	28.44	44.137	27.71
50.047	28.73	36.540	27.89
40.037	28.95	29.304	28.12
24.760	29.40	18.089	28.53
10.536	29.99		
Pr₄NBr		Bu₄NBr	
444.474	22.85	622.737	20.51
375.533	23.31	498.190	21.34
300.067	23.84	400.628	21.99
226.398	24.54	298.914	22.75
159.916	25.04	201.352	23.54
100.621	25.79	100.261	24.74
75.466	26.10	79.874	25.04
50.059	26.49	60.156	25.35
25.155	27.07	40.104	25.76
		20.052	26.28
Pen₄NBr		Hex₄NBr	
519.858	19.30	506.841	18.63
348.875	20.19	349.720	19.54
199.279	21.29	199.357	20.63
100.506	22.11	99.679	21.69
90.109	22.33	89.542	21.85
74.513	22.61	74.337	22.16
60.304	22.82	60.097	22.16
45.027	23.10	45.073	22.50
30.152	23.45	30.048	22.80
		10.016	23.36
Hep₄NBr		LiBF₄	
523.988	18.12	529.635	19.64
399.977	18.68	398.992	20.73
300.450	19.05	300.127	21.70
200.862	19.73	199.496	23.06
99.558	20.51	100.631	24.66
75.105	20.93	90.038	24.90
60.084	21.00	74.149	25.21
45.063	21.55	60.025	25.59
30.042	21.80	45.019	26.01
		30.013	26.39
		10.004	27.39
Bu₄NBBu₄			
206.727	15.38		
149.532	15.85		
120.591	16.17		
89.582	16.48		
74.422	16.64		
60.364	16.85		
39.692	17.18		
24.807	17.54		
9.923	18.00		

Table 3 Limiting ionic conductances, Walden products and Stokes radii of the ions in PC at 25 °C

ion	λ_0^\pm/S cm ² mol ⁻¹	$\lambda_0^\pm \eta_0/S$ cm ² mol ⁻¹ P ¹	r_s/nm
Me ₄ N ⁺	12.85	0.319	0.26
Et ₄ N ⁺	11.70	0.290	0.28
Pr ₄ N ⁺	10.33	0.255	0.32
Bu ₄ N ⁺	9.44	0.234	0.35
Pen ₄ N ⁺	6.86	0.170	0.48
Hex ₄ N ⁺	6.14	0.152	0.54
Hep ₄ N ⁺	5.17	0.128	0.64
Li ⁺	8.89	0.220	0.37
Br ⁻	18.24	0.452	0.18
BBu ₄ ⁻	9.44	0.234	0.35
BF ₄ ⁻	19.59	0.486	0.17

$\sigma(\%) = 100\sigma/\Lambda^0$ against R ; the best-fit R corresponds to a minimum of the $\sigma(\%)$ vs. R curve. First, approximate runs over a fairly wide range of R values were made to locate the minimum and then a fine scan around the minimum was made. Finally, with this minimized value of R , the corresponding Λ^0 and α were calculated.

The values of Λ^0 , K_A and R obtained by this procedure are recorded in Table 2. The limiting ionic conductances (λ_0^\pm) based on the value of Bu₄NBBu₄ are given in Table 3. The λ_0^\pm value for the Li⁺ ion was taken from ref. 11 to calculate the single-ion mobility for BF₄⁻ ion, assuming that the rule of additivity holds in this case.

Discussion

Table 2 shows that the limiting equivalent conductances (Λ^0) of the tetraalkylammonium bromides decrease as the alkyl chain-length increases. This is in agreement with earlier findings for tetraalkylammonium bromides in other aprotic solvents.²¹ The size and structure-forming effect decrease as the alkyl chain-length increases and consequently the mobility is in the reverse order. Λ^0 for Bu₄NBr was reported by Jansen and Yeager.¹¹ A comparison of the limiting equivalent conductance for Bu₄NBr as obtained by us with that of ref. 11 shows a difference of ca. 0.4%, indicating the closeness of our values with theirs. Also, a comparison of the reported Λ^0 value of Bu₄NBBu₄ by Takeda and co-workers¹² with ours shows a difference of ca. 1%. Takeda and co-workers¹² reported the Λ^0 value directly from the extrapolation of Λ vs. \sqrt{C} plots, while our value was determined by the Fuoss method,²⁰ hence the observed difference.

The association constants in Table 2 show that these salts are essentially unassociated with the minor exception of LiBF₄. Presumably this salt shows slight ion-pairing though the association constant is much less than that of LiCl⁶ and LiBr.⁶ This may be due to the very large size of the tetrafluoroborate ion which has a lower affinity for the lithium ion

Table 2 Conductance parameters of tetraalkylammonium bromides, lithium tetrafluoroborate and tetrabutylammonium tetrabutylborate in PC at 25 °C

salts	Λ^0/S cm ² mol ⁻¹	K_A/dm^3 mol ⁻¹	Walden product	R/nm	σ
Me ₄ NBr	31.09 ± 0.02	6.82 ± 0.11	0.768	1.40	0.06
Et ₄ NBr	29.94 ± 0.01	8.15 ± 0.10	0.740	1.70	0.03
Pr ₄ NBr	28.57 ± 0.02	4.20 ± 0.07	0.706	1.33	0.12
Bu ₄ NBr	27.68 ± 0.01	5.00 ± 0.04	0.684	1.23	0.07
Pen ₄ NBr	25.10 ± 0.03	3.92 ± 0.12	0.620	0.83	0.20
Hex ₄ NBr	24.38 ± 0.03	4.71 ± 0.16	0.602	1.30	0.27
Hep ₄ NBr	23.41 ± 0.03	3.65 ± 0.10	0.578	1.05	0.19
Bu ₄ NBBu ₄	18.88 ± 0.01	5.79 ± 0.12	0.467	1.31	0.10
LiBF ₄	28.48 ± 0.02	10.09 ± 0.11	0.704	1.32	0.15

than the smaller Cl^- and Br^- ions. The decrease in the association constant with increasing anion size agrees with the theories of Denison and Ramsey,²² and Gilkerson.²³ The higher Λ^0 value of LiBF_4 than that of LiCl and LiBr also corroborates the above viewpoint. However, for R_4N^+ ions, the general decrease in the association constant with increasing cation size is in agreement with the charge density values of these ions.

The single-ion conductances were evaluated from the division of Λ^0 value of Bu_4NBBu_4 using the relationship:^{17,24}

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{Bu}_4\text{B}^-) \quad (7)$$

The reason behind the choice of Bu_4NBBu_4 as the reference electrolyte is in the fact that the cation and anion in this case are symmetrical in shape and have almost equal van der Waals volumes.

The λ_0 values of the ions thus obtained are presented in Table 3. Kay and co-workers⁷ previously analysed the conductance data of several workers and calculated the best estimate of limiting ion conductances in PC at 25°C. Comparison of our results with theirs reveals that in the case of Me_4N^+ , Et_4N^+ and Pr_4N^+ ions, the λ_0 values obtained by us are 1–11% lower, and for Bu_4N^+ the value is 5% higher than the values proposed by Kay and co-workers. This discrepancy is due to the different procedures adopted^{10–13} for the calculation of Λ^0 values and also on the choice of the 'reference electrolyte',^{7,11} which was also different for calculating the limiting ion conductances in non-aqueous solvents.

The Walden products ($\lambda_0^\pm \eta_0$) and Stokes radii (r_s) of the ions are reported in Table 3. Walden products are usually employed to discuss the interactions of the ions with the solvent medium. From Table 3, we see that for large R_4N^+ ions, $\lambda_0^\pm \eta_0$ increases from the tetraheptylammonium ion to the tetramethylammonium ion and for the electrolyte taken as a whole it follows the same sequence (Table 2). This leads to the fact that 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.¹¹ From Table 3, it can be seen that the Stokes radii increase with increasing size of the tetraalkylammonium ions and this is most likely due to the lower ionic mobilities of these cations. For Li^+ , however, the Stokes radius was much greater than its crystallographic radius (0.93 Å),²⁵ indicating that it was substantially solvated in this solvent medium. On the other hand the higher mobility of the Br^- ion than the cations relative to its crystallographic size (1.80 Å)²⁵ indicates that it is poorly solvated in this medium. The slight difference in limiting ionic conductance values of Br^- and BF_4^- ions seems to indicate that the effective sizes of these anions in PC are almost the same and

thus very little solvation, if any, is involved. On the other hand, the very low mobility of the tetrabutylborate ion has been attributed to its very much larger size. Thus, it appears that the large sizes of R_4N^+ ions, their low charge densities and the high relative permittivity of PC render these ions to be free, unassociated and almost unsolvated in this medium.

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Viscosity *B* Coefficients of Some Tetraalkylammonium Bromides, Lithium Tetrafluoroborate and Tetrabutylammonium Tetraphenyl borate in Propylene Carbonate

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The viscosities of solutions of tetraalkylammonium bromides, R_4NBr ($R = -C_2H_5$ to $-C_7H_{15}$), lithium tetrafluoroborate ($LiBF_4$) and tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) in propylene carbonate (PC) have been measured at 25, 35 and 45 °C. The relative viscosities have been analyzed using the Jones-Dole equation in the form of unassociated electrolytes, and the viscosity *B*-coefficients have been evaluated. The thermodynamic parameters have been calculated using the transition-state treatment and the measured temperature dependencies. Ionic *B* values have also been derived and discussed in terms of Einstein's equation. The analysis shows that Li^+ is highly solvated compared to other cations and anions in this medium.

Introduction

Recently we have reported [1] the results of conductance measurements on $LiBF_4$ and tetraalkylammonium bromides in propylene carbonate (PC) at 25 °C. These salts have been found to be almost unassociated in this solvent of a moderately high dielectric constant (64.40 at 25 °C). Single ion mobilities were also derived and discussed in terms of the ion solvating ability of PC.

We have now extended this work to study the viscometric behaviour of these electrolytes at different temperatures to obtain more information about specific ion-solvent interactions in this solvent. Ionic *B* values have been derived on the basis of the reference electrolyte " Bu_4NBPh_4 ", and the transition-state treatment has been applied to analyse the results.

Experimental

Propylene carbonate (E. Merck, Germany, >99% pure) was purified according to the procedure described previously [1]. The solvent properties have been recorded in Table I.

The purification of tetraalkylammonium bromides, $LiBF_4$ and Bu_4NBPh_4 have been reported earlier [1].

The concentrations of the salts, generally varying in the range of 0.01–0.08 mol dm⁻³, were prepared by

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weight dilution of the stock solution (ca. 0.1 mol kg⁻¹). The conversion of the molality into molarity was done by using the density values. The kinematic viscosities were measured at the desired temperature (accuracy ±0.01 °C) using a suspended Ubbelohde-type viscometer. The densities were measured using a Ostwald-Sprengel type pycnometer (25 ml) calibrated with distilled water. The details of the experimental procedure have been described in [2, 3]. The accuracies of the viscosity and density measurements were 0.05% and ±3 × 10⁻³ g cm⁻³, respectively.

Density and Viscosity Data

The density (ρ) and viscosity (η) data for the electrolytes in the molarity range 0.01–0.08 mol dm⁻³ at temperatures 25, 35, and 45 °C are reported in Table 2.

Viscosity *A* and *B* Coefficients

The experimental data have been analysed with the Jones-Dole equation [4]

$$(\eta_r - 1)\sqrt{C} = A + B\sqrt{C}, \quad \eta_r = \eta/\eta_0 \quad (1)$$

Table 1. Solvent properties of propylene carbonate.

Temp. (°C)	Density (g cm ⁻³)	Viscosity (cP)	Dielectric constant
25	1.19883	2.4712	64.40
35	1.18970	2.0476	63.41
45	1.17796	1.7234	60.92

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Table 2. Concentration, C (mol dm⁻³), density, ρ (g cm⁻³) and relative viscosity, η_r , of tetraalkylammonium bromides, LiBF₄ and Bu₄NBPh₄ in propylene carbonate at 25, 35 and 45 °C.

C	ρ	η_r	C	ρ	η_r	C	ρ	η_r	C	ρ	η_r
Et₄NBr 25 °C			Pr₄NBr 25 °C			Hex₄NBr 35 °C			Hep₄NBr 35 °C		
0.01002	1.19000	1.0081	0.00995	1.19870	1.0096	0.00991	1.18808	1.0145	0.00999	1.18803	1.0155
0.01644	1.19910	1.0130	0.02020	1.19856	1.0188	0.02475	1.18563	1.0352	0.02976	1.18472	1.0446
0.02506	1.19925	1.0193	0.03015	1.19843	1.0351	0.03958	1.18318	1.0558	0.03974	1.18303	1.0584
0.03509	1.19941	1.0266	0.05005	1.19816	1.0452	0.04945	1.18155	1.0693	0.04951	1.18138	1.0730
0.04511	1.19957	1.0343	0.06001	1.19803	1.0540	0.06917	1.17827	1.0961	0.05947	1.17969	1.0879
0.05514	1.19973	1.0418	0.08020	1.19776	1.0716						
Bu₄NBr 25 °C			Pen₄NBr 25 °C			LiBF₄ 35 °C			Bu₄NBPh₄ 35 °C		
0.01015	1.19837	1.0116	0.00990	1.19817	1.0130	0.01022	1.19025	1.0125	0.00906	1.18873	1.0141
0.01999	1.19792	1.0224	0.02011	1.19749	1.0253	0.02487	1.19104	1.0295	0.01944	1.18762	1.0277
0.03076	1.19743	1.0337	0.03001	1.19682	1.0382	0.03987	1.19184	1.0424	0.02971	1.18651	1.0411
0.05014	1.19654	1.0538	0.05011	1.19547	1.0619	0.04976	1.19237	1.0572	0.04464	1.18490	1.0621
0.05998	1.19609	1.0642	0.06002	1.19480	1.0750	0.05966	1.19290	1.0683	0.05939	1.18331	1.0808
0.07997	1.19517	1.0871	0.08012	1.19343	1.0991	0.07947	1.19396	1.0909			
Hex₄NBr 25 °C			Hep₄NBr 25 °C			Et₄NBr 45 °C			Pr₄NBr 45 °C		
0.00999	1.19779	1.0149	0.01007	1.19750	1.0159	0.00985	1.17827	1.0071	0.00977	1.17785	1.0077
0.02498	1.19621	1.0368	0.03002	1.19485	1.0458	0.01616	1.17847	1.0117	0.01985	1.17773	1.0161
0.03997	1.19464	1.0583	0.04009	1.19351	1.0606	0.02463	1.17873	1.0174	0.02963	1.17761	1.0241
0.04996	1.19359	1.0715	0.04996	1.19219	1.0761	0.03449	1.17904	1.0243	0.04919	1.17737	1.0401
0.06994	1.19149	1.1017	0.06003	1.19084	1.0904	0.04435	1.17935	1.0310	0.05897	1.17725	1.0480
						0.05421	1.17965	1.0374	0.07881	1.17701	1.0640
LiBF₄ 25 °C			Bu₄NBPh₄ 25 °C			Bu₄NBr 45 °C			Pen₄NBr 45 °C		
0.01031	1.19937	1.0134	0.00998	1.19796	1.0149	0.00998	1.17707	1.0108	0.00972	1.17541	1.0120
0.02508	1.20013	1.0311	0.01997	1.19708	1.0293	0.01966	1.17621	1.0200	0.01969	1.17279	1.0235
0.04020	1.20091	1.0503	0.02995	1.19620	1.0418	0.03025	1.17526	1.0315	0.02935	1.17026	1.0354
0.05017	1.20142	1.0623	0.04502	1.19487	1.0513	0.04933	1.17355	1.0500	0.04885	1.16514	1.0574
0.06013	1.20193	1.0784	0.05990	1.19356	1.0844	0.05903	1.17267	1.0601	0.05840	1.16263	1.0679
0.08007	1.20294	1.0975				0.07875	1.17089	1.0798	0.0911	1.15719	1.0912
Et₄NBr 35 °C			Pr₄NBr 35 °C			Hex₄NBr 45 °C			Hep₄NBr 45 °C		
0.00995	1.18992	1.0077	0.00988	1.18955	1.0089	0.00981	1.17568	1.0147	0.00990	1.17598	1.0151
0.01632	1.19006	1.0119	0.02004	1.18938	1.0175	0.02452	1.17226	1.0347	0.02951	1.17206	1.0435
0.02487	1.19025	1.0186	0.02992	1.18923	1.0255	0.03921	1.16884	1.0546	0.03942	1.17007	1.0585
0.03483	1.19047	1.0248	0.04967	1.18891	1.0425	0.04899	1.16657	1.0678	0.04913	1.16813	1.0711
0.04478	1.19069	1.0326	0.05954	1.18875	1.0499	0.06853	1.16202	1.0940	0.05762	1.16643	1.0836
0.05473	1.19091	1.0391	0.07958	1.18843	1.0676						
Bu₄NBr 35 °C			Pen₄NBr 35 °C			LiBF₄ 45 °C			Bu₄NBPh₄ 45 °C		
0.01007	1.18898	1.0113	0.00982	1.18799	1.0125	0.01012	1.17877	1.0117	0.00980	1.17681	1.0144
0.01983	1.18828	1.0215	0.01992	1.18622	1.0244	0.02463	1.17992	1.0272	0.01926	1.17570	1.0272
0.03050	1.18751	1.0325	0.02918	1.18460	1.0361	0.03951	1.18110	1.0435	0.02943	1.17451	1.0406
0.04970	1.18612	1.0523	0.04956	1.18101	1.0587	0.04932	1.18187	1.0538	0.04423	1.17277	1.0597
0.05945	1.18542	1.0625	0.05931	1.17929	1.0716	0.05915	1.18265	1.0636	0.05886	1.17105	1.0787
0.07923	1.18398	1.0828	0.07968	1.17570	1.0949	0.07882	1.18420	1.0839			

1.0784

1.172

where η and η_0 are the viscosities of the solution and solvent, respectively, η_r is the relative viscosity and C is the molar concentration.

The plots of $(\eta_r - 1)/\sqrt{C}$ against \sqrt{C} (Fig. 1) for the electrolytes are linear, and the experimental A values at 25, 35, and 45 °C have been calculated using the least squares method. The A coefficients were also calculated at 25 °C from the physical properties of the

solvent and the limiting ionic equivalent conductance by using the Falkenhagen and Vernon equation [5]

$$A_{theo} = \frac{0.2577 A_0}{\eta_0 (\epsilon T)^{1/2} \lambda_0^+ \lambda_0^-} \left[1 - 0.6863 \left(\frac{\lambda_0^+ - \lambda_0^-}{A_0} \right)^2 \right] \quad (2)$$

The conductance data required in these calculations were taken from our earlier work [1]. The A_{theo} coeffi-

coefficients obtained from (2) along with the experimental *A* values are reported in Table 3.

Viscosity *B* coefficients obtained at various temperatures using the least squares method are presented in Table 4.

Activation Parameters for the Viscous Flow

The viscosity data have also been analysed on the basis of the transition-state treatment of the relative viscosity of electrolyte solutions as suggested by Feakins et al. [6]:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000} \left(\frac{\Delta\mu_2^{0*} - \Delta\mu_1^{0*}}{RT} \right) \quad (3)$$

In the above equation \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of solvent and solute, respectively. $\Delta\mu_2^{0*}$, 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 as reported in Table 4. $\Delta\mu_1^{0*}$, the free energy of activation per mole of the pure solvent is given by the equation [7]

$$\Delta\mu_1^{0*} = \Delta G_1^{0*} = RT \ln \left(\frac{\eta_0 \bar{V}_1^0}{hN} \right) \quad (4)$$

N = Avogadro's number.

Table 3. Theoretical *A* values and experimental *A* coefficients, *A*_{obs}/(dm³ mol⁻¹) at 25, 35 and 45 °C.

Salts	<i>A</i> _{theo}	<i>A</i> _{obs}		
		25 °C	35 °C	45 °C
Et ₄ NBr	0.0102	0.0082	0.0089	0.0066
Pr ₄ NBr	0.0108	0.0104	0.0080	0.0080
Bu ₄ NBr	0.0113	0.0093	0.0109	0.0083
Pen ₄ NBr	0.0130	0.0106	0.0117	0.0138
Hex ₄ NBr	0.0136	0.0079	0.0125	0.0189
Hep ₄ NBr	0.0147	0.0115	0.0128	0.0139
LiBF ₄	0.0114	0.0072	0.0095	0.0152
Bu ₄ NBPh ₄	0.0176	0.0135	0.0198	0.0237

Discussion

The *A* coefficients shown in Table 3 are found to be small and positive for all the electrolytes, and the experimental results at 25 °C agree well with the theoretical one within 20% for the quarternary ammonium salts. This error in the small *A* values corresponds to the experimental uncertainty of 0.05% of the viscosity data. Similar results have been found in other systems [8].

The viscosity *B* coefficients (Table 4) are large, positive and increase in PC as we go from tetraethylammonium to tetraheptylammonium bromide. Our reported viscosity *B* coefficient (1.043) at 25 °C for Bu₄NBr is slightly greater than the *B* value (0.960) reported previously by Boden et al. [9] by simply plotting the relative viscosity against the concentration in the Jones-Dole equation. The *B* value of lithium tetrafluoroborate is found to be approximately equal to that of Pen₄NBr. The *B* coefficients show moderate temperature dependence and the values decrease with increase of temperature as observed earlier in some dipolar aprotic solvents like acetonitrile [8, 10], sulfolane [1] and DMSO [2, 12]. Further, from Table 4 we see that, although *dB/dT* is small, it is negative in sign for all the electrolytes, indicating that they behave as structure makers in this solvent medium.

The ionic *B* values were calculated using Bu₄NBPh₄ as the "reference electrolyte" [13, 14]:

$$B(\text{Bu}_4\text{NBPh}_4) = B(\text{Bu}_4\text{N}^+) + B(\text{BPh}_4^-) \quad (5)$$

$$\frac{B_{\text{Ph}_4\text{B}^-}}{B_{\text{Bu}_4\text{N}^+}} = \left(\frac{5.35}{5.00} \right)^3 \quad (6)$$

The ionic *B* values along with the ionic $\Delta\mu_2^{0*}$ data obtained from the above relationships are given in Table 5. Table 5 shows that the viscosity *B* coefficients for cations and anions are all positive and also very high. The ionic *B* value for Li⁺ at 25 °C was calculated

Table 4. Viscosity *B* coefficients, *B* (dm³ mol⁻¹) and $\Delta\mu_2^{0*}$ /(kJ mol⁻¹) values in propylene carbonate at different temperatures.

Salts	25 °C		35 °C		45 °C	
	<i>B</i>	$\Delta\mu_2^{0*}$	<i>B</i>	$\Delta\mu_2^{0*}$	<i>B</i>	$\Delta\mu_2^{0*}$
Et ₄ NBr	0.716 ± 0.004	38.56	0.674 ± 0.009	37.86	0.653 ± 0.003	37.57
Pr ₄ NBr	0.855 ± 0.001	44.70	0.810 ± 0.007	44.26	0.788 ± 0.001	44.24
Bu ₄ NBr	1.043 ± 0.012	52.31	1.005 ± 0.001	52.89	0.975 ± 0.007	53.41
Pen ₄ NBr	1.194 ± 0.007	58.59	1.145 ± 0.010	61.04	1.106 ± 0.006	63.36
Hex ₄ NBr	1.385 ± 0.019	66.43	1.339 ± 0.002	67.98	1.315 ± 0.008	70.41
Hep ₄ NBr	1.454 ± 0.009	70.45	1.416 ± 0.010	71.73	1.391 ± 0.015	73.34
LiBF ₄	1.203 ± 0.036	49.05	1.105 ± 0.032	47.00	1.021 ± 0.006	44.52
Bu ₄ NBPh ₄	1.302 ± 0.061	66.68	1.283 ± 0.013	68.08	1.256 ± 0.002	68.92

[11]

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Table 5. Ionic B coefficients, $B_{\pm}/(\text{dm}^3 \text{mol}^{-1})$ and ionic $\Delta\mu_{\pm}^{\circ}/(\text{kJ mol}^{-1})$ values in PC at different temperatures.

Ion	25 °C		35 °C		45 °C	
	B_{\pm}	$\Delta\mu_{\pm}^{\circ}$	B_{\pm}	$\Delta\mu_{\pm}^{\circ}$	B_{\pm}	$\Delta\mu_{\pm}^{\circ}$
Et ₄ N ⁺	0.258	16.22	0.246	15.57	0.242	15.13
Pr ₄ N ⁺	0.397	22.36	0.382	21.97	0.377	21.80
Bu ₄ N ⁺	0.585	29.97	0.577	30.60	0.564	30.97
Pen ₄ N ⁺	0.736	36.25	0.717	38.75	0.695	40.92
Hex ₄ N ⁺	0.927	44.09	0.911	45.69	0.904	47.97
Hep ₄ N ⁺	0.996	48.11	0.988	49.44	0.980	50.90
Li ⁺	0.792	—	—	—	—	—
Br ⁻	0.458	22.34	0.428	22.29	0.411	22.44
BF ₄ ⁻	0.411	—	—	—	—	—
BPh ₄ ⁻	0.717	36.71	0.706	37.48	0.692	37.95

Table 6. Ionic radii, $R_{\pm}/(\text{Å})$ and solvation number, n_{\pm} , of ions in PC at 25 °C.

Ion	r_c (Å)	r_s (Å)	R_{\pm} (Å)	n_{\pm}
Et ₄ N ⁺	4.00	2.82	3.45	-1.94
Pr ₄ N ⁺	4.52	3.21	3.98	-2.68
Bu ₄ N ⁺	4.94	3.49	4.53	-3.18
Pen ₄ N ⁺	5.29	4.81	4.89	-3.82
Hex ₄ N ⁺	5.59	5.38	5.28	-4.24
Hep ₄ N ⁺	5.88	6.39	5.41	-5.32
Li ⁺	0.60	3.72	5.01	3.71
Br ⁻	1.95	1.81	4.17	1.78
BF ₄ ⁻	2.01	1.68	4.02	1.53
BPh ₄ ⁻	4.20	3.76	4.84	-0.28

from the reported viscosity B value of LiBr [9] in PC assuming additivity. The observed order of the B_{\pm} coefficients, Hep₄N⁺ > Hex₄N⁺ > Pen₄N⁺ > Bu₄N⁺ > Pr₄N⁺ > Et₄N⁺, shows that the obstruction of the solvent viscous flow increases with decrease of the ion charge density and with decrease of the size of the hydrodynamic entity by solvation. For anions, the B -values are seen to be in the order BPh₄⁻ > Br⁻ > BF₄⁻. The dB_{\pm}/dT values of the cations and anions are generally found to be negative (structure-making). This behaviour of tetraalkylammonium ions in PC, arising mainly from the interactions of alkyl groups and solvent molecules, is similar to that observed in sulfolane by Sacco and coworkers [11, 15].

The values of $\Delta\mu_{\pm}^{\circ}$ for tetraalkylammonium ions decrease in the order Hep₄N⁺ > Hex₄N⁺ > Pen₄N⁺ > Bu₄N⁺ > Pr₄N⁺ > Et₄N⁺, and for anions BPh₄⁻ > Br⁻. However, these values are found to be positive, and thus the formation of the transition-state is less favourable in the presence of these ions.

Ionic B_{\pm} coefficients have also been analysed on the basis of Einstein's equation [16]

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

where R_{\pm} (in Å) is the radius at the ion assumed to be a rigid sphere moving in a continuum and 2.5 is the shape factor for a sphere. The number of solvent molecules (n_{\pm}) bound to the ion in the primary sphere of solvation can be calculated by combination of the Jones-Dole equation with that of Einstein [17]

$$B_{\pm} = \frac{2.5}{1000} (V_i + n_{\pm} V_s), \quad (8)$$

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. The values of R_{\pm} and n_{\pm} are shown in Table 6.

The R_{\pm} values for tetraalkylammonium ions are found to be in reasonable agreement with the Stokes and crystallographic radii. The results indicate that these ions are scarcely solvated in PC and behave as spherical entities. However, the R_{\pm} value of Li⁺ is much higher than its crystallographic radius, indicating that it is highly solvated in PC by ion-dipole interactions. Similar results have been obtained by conductometric measurements [1], which shows that Li⁺ is highly solvated in this medium. Thus, it appears that the large size of the R₄N⁺ ions, their low charge density and the high dielectric constant of PC render these ions to be free, unassociated and almost unsolvated in this medium.

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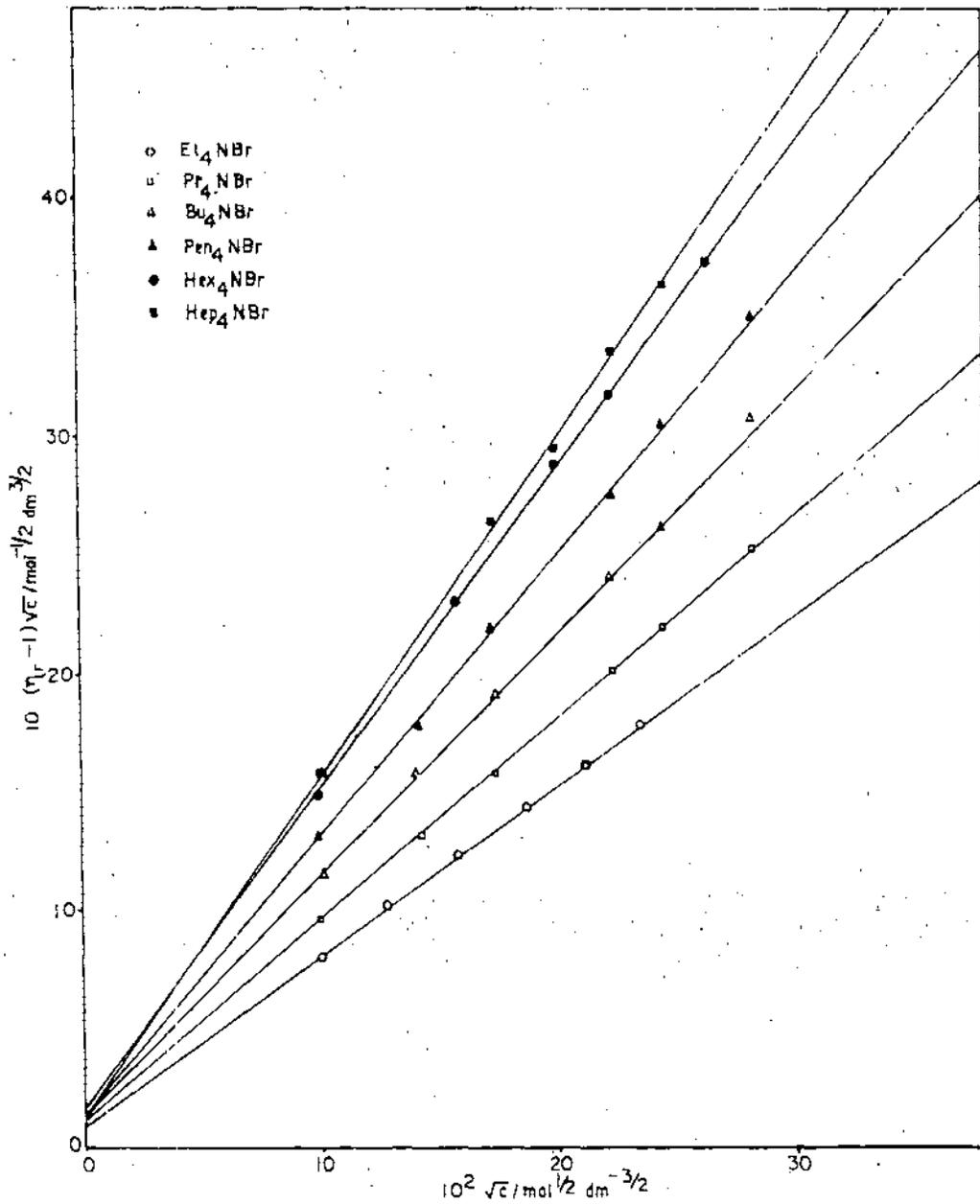


Fig. 1 Representative plot of $(\eta_r - 1) / \sqrt{c}$ against \sqrt{c} for some electrolytes in PC at 25°C

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Solubilities of Some Alkali-Metal Salts, Tetraphenylarsonium Chloride, and Tetraphenylphosphonium Bromide in Propylene Carbonate at 25 °C Using the Ion-Selective Electrode Technique

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The solubilities of 15 alkali-metal salts, MX ($M^+ = \text{Li, Na, K, Rb, and Cs}$; $X^- = \text{Cl, Br, and ClO}_4$), tetraphenylarsonium chloride, and tetraphenylphosphonium bromide are reported in propylene carbonate (PC) at 25 °C, and the free energies of solution for these electrolytes in this solvent have been determined. Combination of these values with solubility results in water yields the free energies of transfer of the electrolytes from water to propylene carbonate. Transfer activity coefficients for the electrolytes have also been computed from their solubility products in water and in the nonaqueous solvent. The results indicate that the perchlorates are more soluble in propylene carbonate compared to the corresponding chloride or bromide salts.

Introduction

Propylene carbonate (4-methyl-1,3-dioxolan-2-one, PC), a dipolar aprotic solvent with high dielectric constant (64.40 at 25 °C) and dipole moment (4.94 D) has been assumed to be an "ideal structureless dielectric" solvent for studies of electrolytes (1, 2). The chemical properties of this solvent have given it an important place in the development of high-energy batteries (3), and thus there has been a growing interest to study various electrochemical reactions in this medium (4, 5). Solubility offers one of the most obvious ways of studying ionic solvation, but in PC these values in general are not available, except of a very few alkali-metal halides (2, 6). It is therefore desirable to obtain the useful solubility data particularly for the salts containing Ph_4As^+ or Ph_4P^+ ions and thus to have an idea of solute-solvent interactions in this nonaqueous medium.

Hence, we have measured the solubilities of a number of 1:1 electrolytes in PC at 25 °C using the ion-selective electrode technique, and from these the solubility products and free energies of solution for the salts have been determined. The free energies of transfer of the electrolytes from water to PC or the corresponding transfer activity coefficients, $m\gamma$'s, have been evaluated and compared with the previous values obtained mainly from emf measurements (7).

Experimental Section

Materials. Propylene carbonate (E. Merck, Germany; >99% pure) was purified as reported earlier (8); the viscosity and density were 2.4711 mPa s and 1.1988 g cm⁻³ at 25 °C, respectively. Solutions were always prepared with the freshly distilled solvent.

All salts were of Fluka's either purum or puriss grade.

The alkali-metal chlorides and bromides were dried in vacuo for a long time immediately prior to use and were used without further purification.

Lithium perchlorate was recrystallized three times from distilled water and then heated under vacuum for several days (2). Sodium perchlorate was heated under vacuum over silica gel and calcium chloride for 5-7 days. These were tested with silver nitrate solution to detect any chloride before use. Other alkali-metal perchlorates were prepared by mixing equimolar solutions of the corresponding alkali-metal chloride and sodium perchlorate (9), washed with a 1:1 methanol-water mixture, recrystallized three times from water, and dried in vacuum over calcium chloride and silica gel for several days.

Tetraphenylarsonium chloride (Fluka) was recrystallized from absolute ethanol solution by dry ether and dried in vacuum (10). Tetraphenylphosphonium bromide (Fluka, puriss grade) was dissolved in absolute ethanol, reprecipitated by the addition of dry ether, and vacuum dried at 100 °C (10).

Solubility Measurements. Saturated solutions were prepared by shaking the solid with the solvent in a glass-stoppered bottle at 27 °C for 24 h. The bottle was then placed in a thermostatic bath maintained at 25 ± 0.01 °C for 2 days. Finally, the solution was transferred to a Campbell solubility apparatus (11) fitted with a sintered disk and fine tube and allowed to equilibrate at 25 °C. At regular intervals, the solution was filtered by inverting the apparatus (while keeping it within the thermostat) and appropriately diluted with the solvent (if necessary), and then the concentration was measured by using an Orion ion analyzer (model EA 920) having an accuracy of $\pm 0.01\%$. A solution was considered saturated when two successive analyses at 2-3-day intervals indicated no change in concentration. Thus, the concentrations of Cl^- , Br^- , and ClO_4^- ions were determined by using specific Orion ion-selective electrodes. A double junction reference electrode was used with each of the Cl^- and ClO_4^- ion electrodes. However, for measuring ClO_4^- ion concentrations, the outer chamber of the reference electrode was filled with $(\text{NH}_4)_2\text{SO}_4$ solution as suggested in the brochure. A single junction reference electrode was used in conjunction with the Br^- ion electrode. Each ion-selective electrode was tested for a Nernstian response. In order to check the correctness of the data, a known concentration of the sample solution was measured by using the specific ion-selective electrode and the results were compared. At least two trials were given for all the solutions which were under study.

Results and Discussion

Solubility data for the electrolytes in PC at 25 °C (molar scale) are reported in Table I along with their standard deviations.

The standard free energy of solution for a solute on the molar scale is usually given by the relation

$$\Delta G^\circ_{\text{soln}} = -RT \ln K \quad (1)$$

where K is the equilibrium constant for the reaction $\text{MX} = \text{M}^+ + \text{X}^-$. Upon introduction of the Debye-Hückel expression

Table I. Solubilities S , Standard Free Energies of Solution $\Delta G^\circ_{\text{soln}}$, and Standard Free Energies of Formation ΔG°_f , and Solvation $\Delta G^\circ_{\text{solv}}$ of the Electrolytes in Propylene Carbonate at 25 °C

salt	S (mol L ⁻¹)	$\Delta G^\circ_{\text{soln}}$ (kJ mol ⁻¹)	$-\Delta G^\circ_f$ (kJ mol ⁻¹)	$-\Delta G^\circ_{\text{solv}}$ (kJ mol ⁻¹)
LiCl	0.019 ± 0.002	19.12	364.55	824.79
NaCl	0.00017 ± 0.00002	42.97	341.08	726.47
KCl	0.00058 ± 0.00004	36.82	371.50	667.35
RbCl	0.0033 ± 0.0006	28.07	376.94	653.08
CsCl	0.0076 ± 0.0007	23.85	380.33	633.88
Ph ₄ AsCl	0.50 ± 0.02	1.51		
LiBr	1.10 ± 0.008	-2.97	342.71	802.11
NaBr	0.0036 ± 0.0010	27.66	320.03	706.64
KBr	0.0030 ± 0.0006	28.58	350.62	643.79
RbBr	0.0099 ± 0.0005	22.51	355.84	634.80
CsBr	0.0098 ± 0.0007	22.55	360.70	610.07
Ph ₄ PBr	0.120 ± 0.003	9.37		
LiClO ₄	1.40 ± 0.03	-4.35		
NaClO ₄	2.50 ± 0.08	-7.70	264.60	
KClO ₄	0.017 ± 0.001	19.71	284.47	
RbClO ₄	0.025 ± 0.002	17.70	288.53	
CsClO ₄	0.052 ± 0.003	13.85	292.75	

Table II. Free Energies of Transfer, ΔG°_t , and Transfer Activity Coefficients, $\log m\gamma_t$, of the Electrolytes from Water to Propylene Carbonate at 25 °C

salt	$\Delta G^\circ_{\text{soln}}(\text{H}_2\text{O})$ (kJ mol ⁻¹)	ΔG°_t (kJ mol ⁻¹)	$\log m\gamma_t$
LiCl	-41.42	60.54	10.61
NaCl	-8.79	51.76	9.07
KCl	-5.02	41.84	7.33
RbCl	-8.37	36.44	6.39
CsCl	-9.20	33.05	5.79
Ph ₄ AsCl	-0.59	2.09	0.37
LiBr	-56.90	53.93	9.45
NaBr	-17.15	44.81	7.85
KBr	-5.86	34.43	6.04
RbBr	-6.69	29.20	5.12
CsBr	-1.67	24.23	4.25
Ph ₄ PBr	14.64	-5.27	-0.92
LiClO ₄	very soluble		
NaClO ₄	very soluble		
KClO ₄	11.30	8.41	0.52
RbClO ₄	14.23	3.47	0.61
CsClO ₄	13.81	0.04	0.007

for the mean activity coefficient, one obtains (12)

$$\Delta G^\circ_{\text{soln}} = 2.303RT[-\nu \log m - \log(\nu_+ \nu_- \nu_\pm + \nu \delta_0 d_0^{1/2} m^{1/2})] \quad (2)$$

In eq 2, d_0 is the density of PC, δ is the Debye-Hückel limiting slope, ν is the total number of ions, and the other symbols have their usual significance.

We have applied eq 2 to obtain the standard free energies of solution; further, these were combined with the free energies of formation of the respective crystalline salts (13) to obtain the corresponding standard free energies of formation for the alkali-metal salts. Results of these calculations have been listed in Tables I and II.

The transfer activity coefficients were calculated from the solubility products by using the relationship

$$\log m\gamma_t = \log m\gamma_\pm^2 = \log_w K_s - \log_a K_s \quad (3)$$

where, $m\gamma_t$ is the transfer activity coefficient (medium effect) and subscripts w and a denote aqueous and nonaqueous solvents, respectively. The values have been given in Table II. The standard free energies of solution in water, $\Delta G^\circ_{\text{soln}}(\text{H}_2\text{O})$, except for the tetraphenyl salts, have been taken from the literature (7, 14). We have measured the solubilities of Ph₄AsCl and Ph₄PBr in water at 25 °C (0.81 and 0.047 M for Ph₄AsCl and Ph₄PBr, respectively). Abraham et al. (15) have reported the free energies of solution for the tetraphenyl salts

Table III. Crystallographic Radii, r_c , Free Energies of Transfer, ΔG°_t , Transfer Activity Coefficients, $\log m\gamma_t$, and Free Energies of Solvation, $\Delta G^\circ_{\text{solv}}$, of Single Ions in Propylene Carbonate at 25 °C

ion	$r_c/\text{Å}$	ΔG°_t (kJ mol ⁻¹)	$\log m\gamma_t$	$-\Delta G^\circ_{\text{solv}}$ (kJ mol ⁻¹)
Li ⁺	0.60	22.47	3.94	471.58
Na ⁺	0.95	13.68	2.40	379.87
K ⁺	1.33	3.77	0.66	313.63
Rb ⁺	1.48	-1.63	-0.29	293.47
Cs ⁺	1.69	-5.02	-0.88	269.20
Ph ₄ As ⁺	6.40	-35.98	-6.31	94.31
Ph ₄ P ⁺	6.30	-35.98	-6.31	95.65
Cl ⁻	1.81	38.07	6.67	243.34
Br ⁻	1.95	30.71	5.38	231.79
ClO ₄ ⁻	2.16	5.06	0.89	216.40

^a Calculated by using the relation $\Delta G^\circ_t(\text{ClO}_4^-) = \Delta G^\circ_t(\text{CsClO}_4) - \Delta G^\circ_t(\text{Cs}^+)$.

(3.48 and 4.38 for Ph₄AsCl and Ph₄PBr, respectively) on the basis of the osmotic pressure and activity coefficient data of Kalfoglou and Bowen (10), which on comparison with the values reported in Table II would seem to be in error.

Single ion free energies of transfer from water to PC based on Ph₄AsBPh₄ convention have been reported in Table III. The ΔG°_t values for Ph₄As⁺ and Ph₄P⁺ ions from water to PC have been taken from the literature (7). Ionic transfer free energy values together with ionic transfer activity coefficients have been reported in Table III. Following Latimer, Pitzer, and Slansky (16), we have also calculated the single ion free energies of solvation by the modified Born equation:

$$\Delta G^\circ_{\text{solv}} = -\frac{Nz^2e^2}{2} [1 - 1/\epsilon] / (r_i + \delta) \quad (4)$$

taking $\delta_c = 0.85 \text{ Å}$ and $\delta_a = 1.00 \text{ Å}$ as taken by Criss et al. in DMF medium (12). The values thus obtained have been reported in Table III.

An examination of the solubilities of the alkali-metal salts (Table I) shows that most electrolytes are much less soluble in propylene carbonate than in water (7) and also in some other dipolar aprotic solvents like DMSO (6) and DMF (6, 12). Lithium salts are found to be more soluble in PC compared to other alkali-metal salts, a notable exception being NaClO₄, which is more soluble in PC than LiClO₄. Also with the exception of lithium, other alkali-metal halides appear to be sparingly soluble and the solubilities are usually in the order Cl⁻ < Br⁻ < ClO₄⁻ as in water and other dipolar aprotic solvents. The poor solubility of these salts in such a high dielectric medium may be due to the dipolar aprotic nature of this solvent medium. The perchlorates, we see, have a much higher solubility than the halides. This indicates that ClO₄⁻ ion tends to increase the PC liquid structure more so than does Cl⁻ or Br⁻ ion. Further, salts having large polarizable groups, viz., Ph₄AsCl and Ph₄PBr, are found to be reasonably soluble in this medium. However, Ph₄AsCl is found to be much more soluble than Ph₄PBr. This shows that Ph₄As⁺ is more polarizable than Ph₄P⁺ and is preferentially solvated, most probably through a combination of dispersion and ion-dipole interactions.

From Table II we see that, in general, the standard free energies of transfer, ΔG°_t , of the electrolytes from water to PC are positive and so the transfer process is not favorable. A notable exception is Ph₄PBr. The negative sign reflects the fact that the distribution of its ions favors the nonaqueous phase, compared to the positive medium effects for most electrolytes. Cox and his co-workers (7) have presented ΔG°_t values of some common salts from water to PC by taking the basic data from the literature. Our reported ΔG°_t values for the alkali-metal halides are found to be in good agreement

with theirs. This avoids the uncertainties in the solubility method due to ion pairing and activity coefficient measurements. Solomon (17) has also reported ΔG° values of LiCl and LiBr from water to PC as 14.74 and 12.98 kcal/mol⁻¹ from a potentiometric study, whereas we have found them to be 14.47 and 12.89 kcal mol⁻¹, respectively, from direct solubility measurements.

Ionic ΔG° values have been calculated taking Ph₄AsBPh₄ as the "reference electrolyte" (7). An attempt was made to calculate the ΔG° value of Ph₄AsBPh₄ from water to PC by measuring the solubilities of Ph₄AsCl, NaCl, and NaBPh₄ in PC. But NaBPh₄ was found to be highly soluble in PC, and to avoid the experimental error we discarded the idea. From the table we see that among the cations, Li⁺, Na⁺, and K⁺ have a positive value of transfer free energy, whereas Rb⁺, Cs⁺, Ph₄As⁺, and Ph₄P⁺ have negative ΔG° values. The positive values of ΔG° , and log $m\gamma$, indicate that these ions are more favorably solvated by the reference medium (water) than by the nonaqueous medium (PC) to which it is transferred. For negative values of ΔG° , it is just the reverse.

Solvation of small cations is generally determined by the relative basicity of the solvents, i.e., by their donor ability. PC has weakly basic oxygen, and so cations are poorly solvated in this medium, resulting in positive ΔG° values (Table III). However, for Rb⁺ and Cs⁺ ions, the ΔG° values are negative in PC. From this evidence we may come to the conclusion that the transfer of Rb⁺ and Cs⁺ ions from water to PC is more favorable compared to other alkali-metal cations.

Conclusion

The solubilities of alkali-metal salts are comparable, although smaller than the corresponding solubilities in water as well as in other dipolar aprotic solvents. The perchlorates,

however, are more soluble than the halides. The higher solubility of NaClO₄ compared to LiClO₄, somehow, tends to indicate its more compactness with the solvent dipoles than the latter. The single ion free energies of transfer from water to PC correlate well with the free energies of transfer of the ions derived by other methods.

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