A STUDY ON THE TRANSPORT PROPERTIES OF ELECTROLYTES

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I certify that the thesis entitled "A Study on the Transport Properties of Electrolytes", submitted by Mr. Shekh Mahiuddin for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

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GENERAL INTRODUCTION

One of the major aims of physical chemistry since its earliest days has been to study the thermodynamic and transport properties of electrolyte solutions. Most of this effort for understanding the behaviour of electrolytes has been devoted to solutions containing water, solvent in general, in large excess. This is mainly because there are successful empirical, semi-empirical, and theoretical expressions for describing the properties of electrolytes in the dilute region. On the other hand, the attempt to interpret properties of electrolyte solutions at concentrations far from the very dilute region has not been very successful. The major handicap in interpreting the properties of electrolyte solutions at higher concentrations is due to the lack of a feasible analytical expression in this region to account quantitatively for the electrolyte property. Continuous efforts have been going on to overcome the above difficulty in extending the studies on electrolyte properties to concentrated solutions and the importance of this kind of study has been highlighted very recently by Pitzer.[1]

Among the equilibrium and non-equilibrium properties of electrolytes, their transport properties are relatively more difficult to deal with and have provided a most challenging field for experimental as well as theoretical research.

In the present work our main interest is to obtain an expression for describing quantitatively the behaviour of transport properties, viscosity and conductance in particular, of electrolyte solutions in the concentration region from dilute to saturation point. Before presenting the actual study made it would be worthwhile to review the existing models available for describing the viscosities and conductances of electrolyte solutions and molten salt systems.

Expressions for Viscosity of Electrolytes

The earliest equation used for describing the concentration dependence of viscosity, η is the Einstein's equation[2] originally developed for dilute suspensions based on the classical principles of hydrodynamics and is of the form

$$\eta = \eta_o (1+2.5\theta) \qquad (0-1)$$

where η is the viscosity of the pure solvent and θ is the volume fraction of one litre solution occupied by the solute. θ can be written as $\theta=c\theta_s$, where θ_s and c are the molar volume and molar concentration of the solute, respectively. Therefore, Eq(0-1) becomes

$$\eta = \eta_o (1+Bc) \qquad (0-2)$$

where $B = 2.5\,\theta_s$.

Falkenhagen and Dole[3] considered the viscosity of electrolyte solutions in terms of the interionic forces between the adjacent layers of an electrolyte solution. They proposed that the electrical forces between ions in the solution tend to establish and maintain a preferred rearrangement and thus to 'stiffen' the solution thereby causing its viscosity to increase. This resulted in a mathematical expression of the form

$$\eta = \eta_o (1 + Ac^{1/2}) \qquad (0\text{-}3)$$

where A is a positive constant and depends on the solvent properties, ionic charges, ionic mobilities, and temperature. Eq (0-3) was found to be applicable only upto a very low concentration of electrolytes ($< 0.01M$) and practically this equation was of little use in calculating the viscosity.

The most widely used equation for describing the concentration dependence of viscosity in the dilute region is the empirical equation of Jones and Dole[4] which is essentially a hybrid equation of Eqs (0-2) and (0-3) and it is of the form

$$\eta = \eta_o \left[1 + Ac^{1/2} + Bc \right] \qquad (0\text{-}4)$$

A and B are the same constants occurring in Eqs(0-3) and (0-2), respectively. A represents the ion-ion interaction and B supposedly represents the ion-solvent interaction. The B coefficient is found to be greater or less than zero depending on the salt and to have a characteristic value for a given electrolyte at a particular temperature. The B coefficients are also found to be fairly accurately additive properties of the constituent ions. Negative values for B are observed for ions which exert a 'structure-breaking' effect on the solution and the B values are found to be fairly large and positive for strongly hydrated ions (structure makers). The Jones-Dole equation is generally valid upto a few tenths of molar concentrations. Modified Jones-Dole equations by including higher terms of c have been tried.[5,6] However, no new interpretive information has been revealed by this approach.

Another theoretical expression employed to interpret the viscosity data in the dilute region is of Vand.[7] Vand's equation was developed by considering that the solvated solute particles distort the stream lines of flow of the solvent and it is generally written as

$$\ln(\eta/\eta_0) = k'c/(1-qc) \qquad (0-5)$$

where k' and q are constant parameters. q is proposed to be the hydrodynamic interaction parameter. Several alternative expressions[8-10] which are essentially based on Vand's equation have also been used for describing the viscous behaviour of electrolyte solutions. Vand's type equations have been found to be successful in describing the concentration dependence of viscosity at higher concentrations also. However, the theoretical concept based on which Vand's equation was derived cannot be expected to be valid at those higher concentrations due to the fact that in concentrated solutions solvated particle does not behave like a suspended particle in the solvent medium (amount of solvent is comparatively less). Consequently, the reason for the applicability of Vand's equation in the concentrated solutions must be of a different theoretical origin.

There are a few more other empirical equations[11,12] which have been employed to describe the viscous behaviour of concentrated solutions. Suryanarayana and Venkatesan[13,14] reported that an empirical equation of the type

$$\eta_p = A' \exp(B' X_p) \qquad (0\text{-}6)$$

adequately describes the variation of electrolyte viscosity throughout the high concentration range. In Eq (0-6),

A′ and B′ are empirical constants, η_p represents the ratio of the viscosity of the solution at a given concentration to that at saturation at the same temperature, and X_p is the ratio of the mole fraction of the solute at a given concentration to that at saturation at the same temperature.

Temperature dependence of viscosity has also been widely studied. Normally, at higher temperatures the temperature dependence of viscosity is explainable by the Andrade[15] or Arrhenius type equation

$$\eta = A'' \exp (B''/T) \qquad (0-7)$$

where A″ and B″ are constant parameters. T is the absolute temperature. Eq (0-7) was derived theoretically using the absolute rate theory approach[16] and the equation so obtained is of the form

$$\eta = (Nh/V) \exp (\Delta G^*/RT) \qquad (0-8)$$

where h is the Planck's constant, N Avogadro's number, V the molar volume of the hole in the liquid, ΔG^* the molar free energy of activation for creating this hole in the liquid, and R the gas constant.

Goldsack and Franchetto[17] by splitting V and ΔG^* terms into ionic and solvent contributions suggested another exponential relation between η and concentration which was found to explain the concentration dependence of η of alkali and ammonium halides in the range 1-10 molal. However, for electrolytes whose viscosity-temperature dependence is non-Arrhenius, which is true for all electrolytic systems at lower temperatures, the isothermal equation of Goldsack and Franchetto cannot be employed.

Expressions for Conductance of Electrolytes

The widely used expression for describing the electrical conductivity of electrolytes in the dilute region is the famous square-root law of Kohlrausch. The theoretical account of this square-root law was first given by Debye and Huckel[18] by employing basically the concept of primitive model in which aqueous solutions of simple salts were considered as a mixture of charged hard spheres in a continuous dielectric medium, the solvent water. The square-root law is written as

$$\Lambda = \Lambda_o - Sc^{1/2} \qquad (0\text{-}9)$$

where Λ_o is the molar conductance at concentration c moles

per litre, Λ_o the molar conductance at infinite dilution, and S is a constant which depends upon the viscosity (electrophoretic effect) and dielectric constant (relaxation effect) of the solvent. S is generally known as the limiting-law slope.

The range of validity of Eq (O-9) was extended by a considerable margin by introducing the ion-size parameter, a°, into both the electrophoretic and relaxation parts of the conductance. This extension was done by several workers[19-26] and the modified conductance equation for non-associating electrolytes is of the form

$$\Lambda = \Lambda_o - Sc^{1/2} + Ec\ln c + B_o c \qquad (O-10)$$

Similar to S, the E and B_o parameters are also dependent on viscosity and dielectric constant of the solvent. The modified conductance equation for associating electrolytes is of the form

$$\Lambda = \Lambda_o - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + B_o(\alpha c) - K_c(\alpha c)^2 f \qquad (O-11)$$

where α is the degree of dissociation, f the activity coefficient, and K_c the equilibrium constant for the association.

However, in spite of the improvement over the original square-root law of the conductance, the range of validity of Eq (0-10) or (0-11) has been found to be still confined to the dilute region.

In the concentrated region no theoretical expression is yet available to interpret the conductance data. The only semi-empirical expression which has made some success in describing the conductance data of concentrated electrolytic solutions is of Wishaw and Stokes[27]. This equation is of the form

$$\Lambda = (\eta_0/\eta)\left[(\Lambda_0 - \alpha' c^{1/2})(1-\beta' c^{1/2})\right] \qquad (0\text{-}12)$$

where the parameters α' and β' depend upon the viscosity and dielectric constant of the solvent as well as on the temperature and concentration of the solution. Although, theoretical explanation to the success of Wishaw-Stokes equation is not available, a qualitative explanation has been proposed according to which the multiplication of the theoretical term inside the square-bracket of Eq (0-12) by the reciprocal of the relative solution viscosity might be accounting for the ion-solvent interaction which contributes significantly to the conductance of the electrolytic solution at higher concentrations.

Models for Transport Properties of Molten Salts

Normally, the temperature dependence of viscosity and conductance of fused salts at higher temperatures is found to be Arrhenius and is explainable by Eq (0-8) based on the transition state theory. When the temperature of viscosity or conductance measurement is lowered, it has been observed in the case of melts or liquids (this is true for electrolytes also) that there is always a change-over from Arrhenius type temperature dependence of transport property to a non-Arrhenius type dependence. Several theoretical models[28-32] have been advanced to account for the non-Arrhenius temperature dependence of transport property. Among the various expressions the Vogel-Tammann-Fulcher (VTF) equation[33] has been extensively employed for describing the non-Arrhenius behaviour of transport properties. The VTF equation is of the form

$$Y(\Lambda, \phi) = A_1 \exp\left[-B_1/(T-T_0)\right] \qquad (0\text{-}13)$$

where Y refers to either conductance, Λ or fludity ($\phi = 1/\eta$). A_1, B_1, and T_0 are the three constant parameters. T_0 is a significant parameter known as ideal glass transition

temperature. The VTF equation has been theoretically derived from the Cohen-Turnbull free volume model[28] as well as from the Adam-Gibbs configurational entropy model.[29]

As we have based our study on the Adam-Gibbs model (AGM), it would be worthwhile to review this theory here. Adam and Gibbs viewed that at low temperatures the transport property of a liquid is determined by the probabilities of cooperative rearrangements. In order to evaluate these transition probabilities, Adam and Gibbs defined a cooperatively rearranging region as a sub-system of the sample which, upon a sufficient fluctuation in energy, can rearrange into another configuration independently of its environment. Considering the probability of a cooperative rearrangement in a fixed subsystem as a function of its size, the expression for the average transition probability, $\bar{\omega}(T)$, was obtained as

$$\bar{\omega}(T) = \bar{A} \exp\left[-\Delta\mu\, s_c^*/kT\, S_c\right] \qquad (0\text{-}14)$$

where $\bar{A}$ is a frequency factor, $\Delta\mu$ the free energy barrier per mole of particles hindering the cooperative rearrangement, s_c^* the critical configurational entropy which a

region of the liquid must possess in order to undergo cooperative rearrangement, k the Boltzmann constant, and S_c the configurational entropy per mole of the liquid.

For obtaining the VTF equation from Eq(0-14), one equates T_o to the temperature at which the configurational entropy, S_c vanishes. S_c may then be evaluated as

$$S_c = \int_{T_o}^{T} \Delta C_p \, d\ln T \qquad (0-15)$$

where ΔC_p is the difference between the liquid and glass heat capacities. On assuming ΔC_p as constant, Eq(0-15) takes the form

$$S_c = \Delta C_p \ln(T/T_o) \qquad (0-16)$$

In the light of this result and realizing that the transport property, $Y(\Lambda,\phi)$, is proportional to $\bar{\omega}(T)$, Eq(0-14) becomes

$$Y(\Lambda,\phi) = A^* \exp\left[-B^*/T \ln(T/T_o)\right] \qquad (0-17)$$

where A^* and B^* $(=s_c^* \Delta\mu/k\Delta C_p)$ are constant parameters. For temperatures T not too far above T_o, it may be shown that

$$T \ln(T/T_o) \approx T - T_o \qquad (0-18)$$

which on substitution into Eq (O-17) gives the VTF equation.

Temperature Dependence of Heat Capacity

As mentioned above Eq (O-17) has been derived from the Adam-Gibbs model[29] with the assumption that the configurational heat capacity, ΔC_p is independent of temperature. Strictly speaking, the heat capacity of a crystal, glass or liquid is always found to show an intricate dependence on temperature. Accounting for the temperature dependence of ΔC_p in Eq (O-14) is essential for obtaining an improved Adam-Gibbs equation for the transport property of liquids or glasses. Therefore, it would be relevant to review here the nature of the dependence shown by heat capacity on temperature.

The thermodynamic relation between the two heat capacity terms, C_p(at constant pressure) and C_v (at constant volume), is given as

$$C_p = C_v + (\alpha_o^2 / \kappa)\, TV \qquad (O-19)$$

where α_o is the coefficient of volume expansion and κ the compressibility. Einstein[34] calculated C_v for crystals by considering a crystal as an ensemble of independent and

distinguishable harmonic oscillators. A more successful theory of heat capacities of solids was formulated by Debye.[34] In this model also a crystal is pictured as a collection of harmonic oscillators, but the oscillations are considered to be due to the vibrations of the entire crystal and not due to the single atoms; a crystal is considered to be a 'huge molecule'. According to Debye's model C_v of crystals at low temperatures is proportional to the third power of temperature. At very high temperatures the value of C_v approaches 3 R. At intermediate temperatures it is, however, difficult to precisely represent the temperature dependence of C_v by a simpler mathematical form. The contribution to crystal heat capacity due to electronic degree of freedom has also been calculated ($\approx 3RT/E_F$, where E_F is the Fermi energy) and it shows a linear dependence on temperature. This contribution becomes significant only at temperatures very near to 0°K.

In the case of amorphous materials theoretical description of the temperature dependence of heat capacity is more complicated. Even at low temperatures a departure from the Debye T-cube law was observed in these materials. A distinct feature of many amorphous substances is the 'super-Debye' excess heat capacity at low temperatures.

Recently, DiMarzio and Dowell[35] by taking into account the configurational (Gibbs-DiMarzio[36] configurational entropy model) as well as the vibrational (Einstein[34] model) degrees of freedom could predict the specific heat discontinuity at the glass transition to within 20%.

In liquids also since the exact evaluation of partition functions is hardly possible, a precise theoretical calculation of their heat capacities as a function of temperature is an extremely difficult task.

The Glass Transition Phenomenon

In describing the transport behaviours of melts, liquids, and electrolytic solutions since glass transition temperature has been considered as a more significant and important parameter, it would be worthwhile to give here a brief account of the glass transition phenomenon.

In the conventional sense the temperature range of the liquid state is usually considered to be from the normal boiling point (upper limit) to the equilibrium freezing point (lower limit). It is, however, possible to extend this normal temperature range of the liquid state by bypassing both the upper and lower limits. The upper limit may be extended by performing measurements at pressures higher

than the atmospheric pressure. In such cases the upper boundary for the liquid state is more appropriately taken as the critical temperature, T_c. The lower limit may like wise be bypassed by supercooling a liquid as liquids have a tendency to remain in a state of internal equilibrium even below their normal freezing points. In nature some of the liquids have inherent tendency to supercool whereas in rest of the liquids supercooling may be induced. The inherent tendency of some of the liquids to supercool is, in fact, due to their failure to crystallize at or below the equilibrium freezing point which may be understood in terms of the model developed by Turnbull and Cohen[37] based on the kinetic considerations of crystallization. According to this model noticeable crystallization will not occur in the absence of foreign nucleating agents if $\gamma\beta^{1/3} \geq 0.9$ and $\Delta G' \geq 0$, or if $\Delta G'$ or $\Delta G''$ $\geq 30(\Delta H_f/\beta) = 30\,RT_m$, where γ is the ratio of the molar liquid-solid interfacial tension to the heat of fusion (ΔH_f), β the ratio of the entropy of fusion to the gas constant, $\Delta G'$ the kinetic free energy barrier to nucleation, $\Delta G''$ the kinetic free energy barrier to the growth of the finite crystal, and T_m the equilibrium freezing point. In those liquids which do not have an inherent tendency to supercool, crystallization may be averted by the sudden quenching of the system during which process there may not be sufficient time for the crystal nuclei to form.

The extent to which a liquid may be supercooled and kept in the supercooled state for a long enough time to perform measurements on it varies considerably from system to system. If the properties of a supercooled liquid are measured at increasingly low temperatures without the onset of crystallization, a point is eventually reached at which equilibrium properties can no longer be determined for the liquid due to the intervention of a nonequilibrium process, the glass transition. The transition of supercooled liquid into glass is characterized by a more or less sudden decrease in the intensive thermodynamic properties like heat capacity, expansion coefficient, and compressibility from liquid-like values to values very close to, but generally greater than, those of the crystalline phase of the substance. In this sense the glass transition, although it is a non-equilibrium phenomenon, possesses many of the characteristics of a second order thermodynamic transition in that the transition occurs at constant volume and entropy and is marked by discontinuities in the second derivatives of the Gibbs free energy. In the temperature region where these changes occur, the viscosity increases rapidly, but not discontinuously, to values in the vicinity of 10^{13} P. It must be emphasized that changes in termodynamic properties do not occur merely because the viscosity becomes high, rather the changes must

occur in order to avert the occurrence of a thermodynamic catastrophe as pointed out by Kauzmann,[38] viz., the production of an amorphous phase of lower entropy than the crystalline phase of the same substance at the same temperature. It may be pointed out that the experimental glass transition temperature, T_g is generally $\sim$ 10-20°K higher than the ideal (reversible) glass transition temperature, T_o.

In the present work we have measured the viscosities and conductances of six aqueous electrolytic solutions as functions of temperature and concentration with a view to developing, as mentioned above, an expression for describing quantitatively the transport behaviour of electrolytic solutions and to examining the applicability of such an expression. This work has been presented in Part I of the thesis in the form of three chapters, viz., Chapters I, II, and III. In Part II of the thesis which contains two more chapters, viz., Chapters IV and V, we have extended our study to molten salt systems also.

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