Thermodynamic and transport properties of ionized solutes in molten state continuously miscible in organic solvents: A class of systems with interesting features

Sindhu S Seelan & Anil Kumar*

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

Received 11 June 1996; revised 17 October 1996

There exists a class of systems, in which a salt in its molten state exhibits continuous miscibility in a solvent. This situation is different from preparing a solution of salt in its solid state in a solvent, which restricts the solubility of the salt and forms a biphasic system. In the case of continuously miscible systems, a single phase is observed, as the salt is in its molten phase, dissolved in a liquid. Organic salts, in general, have low melting points and thus, can offer easier experimental conditions compared to the inorganic salts. The properties of such systems display some interesting features, such as anomalous viscosity behaviour, ion-pairing and predominant role of short-range interaction forces in determining the behaviour of these systems. Thermodynamic, surface, volumetric and transport behaviour of such systems are described with a view to exposing their peculiar characteristics. An application of Scaled Particle Theory for estimating the surface tension and compressibility of these systems is explored with a reasonable degree of success. It is hoped that the analysis of such systems as described herein, will throw light on the connectivity likely to be present between molten and ordinary liquid phases.

Anil Kumar (b. 31 December 1955) pursues his research activities in the areas of bio-physical chemistry of nucleic acids, physical organic chemistry besides his commitment to the physical chemistry of Ionic solutions. His earlier positions after his Ph.D. from National Chemical Laboratory, Pune include a post doc. with G. Atkinson (USA), Alexander von Humboldt fellowship with E.U. Franck (Germany) and a teaching-cum-research position at Deccan Sugar Institute, Pune

Miss Sindhu S Seelan (b. 22 December 1970) was awarded a M.Phil. degree (1996) in Chemistry after her M.Sc. in Analytical Chemistry (1993) from University of Pune, Pune. Currently she is working on a DST sponsored project at NCL, Pune

Since the development of Debye—Hückel theory some 70 years ago[1], a large number of experimental data on thermo dynamic and transport properties of aqueous electrolytes have been collected[2]. This experimental work led to the modifications of the Debye-Hückel theory applicable to very dilute solutions[3]. Empirical, semi-empirical and theoretical treatments have been limited to the moderate concentrations of ionic solids in aqueous and nonaqueous media. However, in last two decades, a few operational approaches[4] have been found successful in describing the thermodynamic properties of nearly concentrated solutions. It is the role of solvent on the solute, which has gained the attention of several workers in describing the thermodynamic properties of such systems[5-9]. Besides these developments, there exists a class of systems comprised of salt and solvent present in the liquid phase, which has not attracted attention of workers. Since both the components are in liquid state, it is possible to have a system with a single liquid phase existing throughout the composition range[5]. Such systems are primarily comprised of salts of organic compounds and a few nitrates in nonaqueous solvent and water[6]. In a broader sense, salt may or may not be
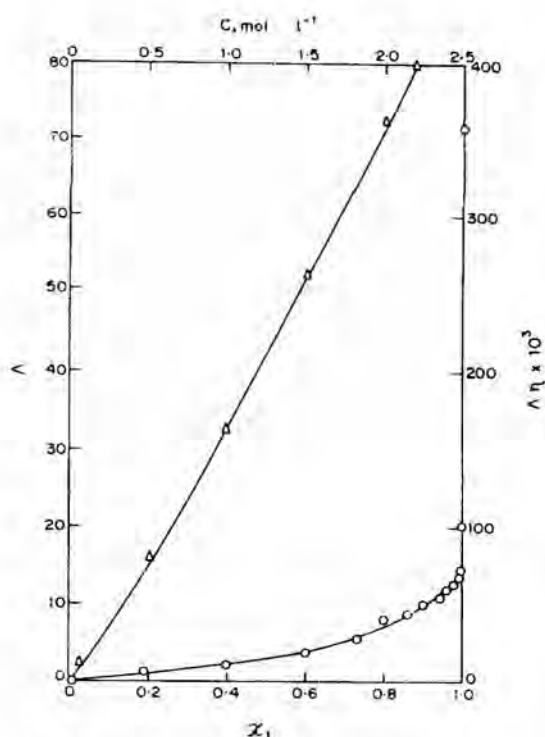
Fig. 1—Conductance, $\Lambda(\circ)$ and $\Lambda\eta(\Delta)$ against x_1 for n-butanol TP system at 364K; ref. 11.

Fig. 2—Plots of solvent activity a_1 for the (Ag, Tl)NO$_3$, NH$_4$NO$_3$, LiNO$_3$, (Li, K)NO$_3$ and LiCl systems; ref. 9, 10b

fully ionized in the solvent depending upon the dielectric constant of the solvent. Such territory of the systems is of considerable theoretical interest, particularly, if the dielectric constant of the solvent is too low, in which the process of ion-pairing occurs[7]. A full miscibility still exists in the range starting from an organic liquid to organic ionic melt. A systematic investigation of these systems is expected to be useful in obtaining deeper understanding of interactions present between a pure organic liquid and a molten salt. Such systems are continuously miscible from pure organic liquid to molten salts in a single liquid phase. Three regions, which warrant these studies are solvent rich, solvent poor and solute-solvent middle zones. On this account, an attempt has been made to discuss the thermodynamic, transport, surface and other related properties of such systems. It has also been shown that this class of systems is useful in organic reactions, electrochemical processes and crystallization.

Two properties, which are of immediate use in this connection are conductance and viscosity.

Conductance and viscosity

The solution properties conductance, Λ and visiocisity, η are important tools to identify the characteristics of such molten salt in solvent sys-
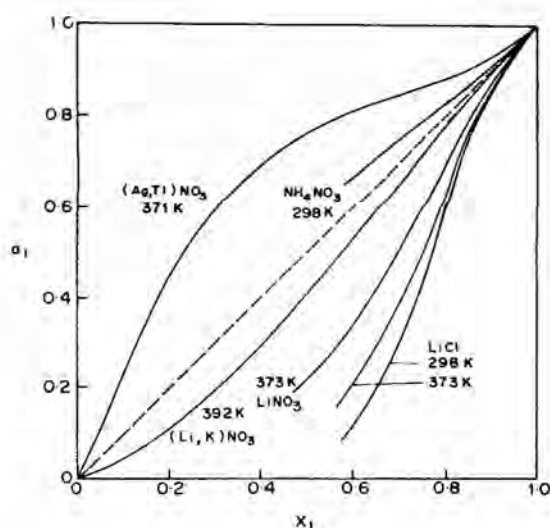
tems. In the case of an organic salt with organic solvent, ion-pairing is identified by the conductance, viscosity, and the Walden product $\Lambda\eta$. In general, an initial rapid decrease in $\Lambda\eta$ followed by a more gradual decrease as a function of concentration are noted. Experimental data on conductance[5,7,10] have shown that incomplete dissociation of such salts takes place at least in the dilute range. Ion-pairing in systems with monovalent salts and organic solvent with low dielectric constant is electrostatic in nature. The variation of Λ and **Ln** with the solvent mole fraction x_1 have been shown in Fig. 1. The solute fractions of ion pairs calculated by Davies theory[10] show a maximum and then decrease with respect to concentration. In aqueous electrolyte solutions, ion-pairing may occur only at higher temperature, as the dielectric constant of water decreases sharply with increase in temperature.

Vapour pressure and thermodynamic activity

In aqueous phase as a simplest case here, salts like lithium and potassium nitrates have been studied for their vapour pressure[8,9]. For the sake of illustration, these precise results on vapour pressure are shown in Fig. 2 as the plots of activity of water over water—salt solutions through out the composition range[8,9]. In the present work, mole fraction scale is preferred over other concentration scales. An examination of Fig. 2 shows a vapour pressure curve analogous to vapour pressure curves observed in the solution of non-electrolytes[6]. This is contrary to the observations made in aqueous electrolyte solutions under nor-
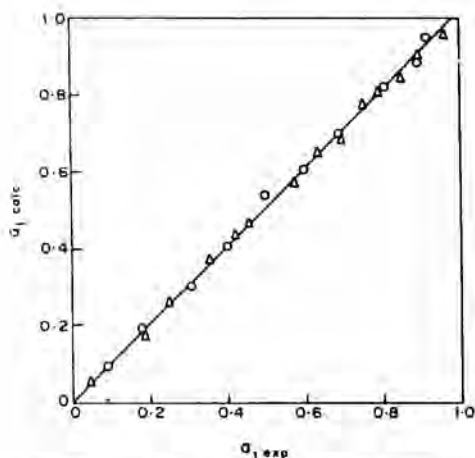
Fig. 3—Experimental a_1 against calculated a_1 by PSM for *n*-butanol-TP ($\triangle$); anisole-TP (O) systems; ref. 11, 13

Fig. 4—Plots of activity, a_1 and solvent mole fraction x_1 for the *n*-butanol-TP ($\triangle$) (ref. 11) and anisole-TP (O) (ref. 13) systems: solid lines are calculated by PSM

mal conditions[3]. Similar trends have been observed for other salts as well. In these systems, positive and negative deviations from the Raoult's law are observed. In view of the analogy in the shapes of the vapour pressure curves with those generally found in non-electrolytic mixtures, it may be possible to treat them by simple expressions like van laar or Margules etc. For lithium and potassium nitrates, no ion-pair formation is noted. As a matter of fact, a Debye Hückel term (DHT) for the long range interactions (lr) and van Laar or Margules terms for describing short range interactions (sr) have been noted to be useful in this regard[6,11,12]. The equations are:

$$\ln a_1 = \ln x_1 + w_1 z_2^2 \qquad \ldots (1a)$$

$$\ln a_2 = v(\ln x_2 + w_2 z_1^2) \qquad \ldots (1b)$$

$$z_1 = n_1 / [n_1 + v n_2 (b_2/b_1)] \qquad \ldots (2a)$$

$$z_2 = v n_2 / [n_1 (b_1/b_2) + v n_2]$$
$$= 1 - z_1 \qquad \ldots (2b)$$
$$w_2 = (b_2/b_1) w_1 \qquad \ldots (3)$$

In these equations x_1 and x_2 are mole fractions of solvent and salt, and a refers to the activity of component. Parameter w indicates the non-ideality of the system arising from the differences between the intermolecular attraction for pairs of like species and z is a van Laar parameter varying with compositions of the mixture. In the above equations, thed ratio indicated by b_2/b_1 is the volume ratio of components. v is the sum of number of cation and anion. If (b_1/b_2) is unity, z_1 and z_2 reduce to the mole fractions x_1 and x_2. The resultant expressions are given as:

$$\ln a_1 = \ln x_1 + w_1 x_2^2 \qquad \ldots (4a)$$
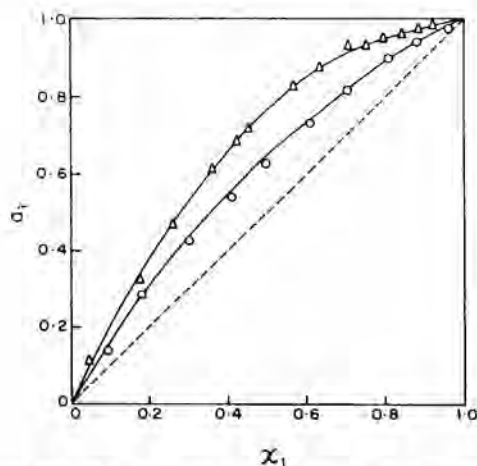
$$\ln a_2 = v(\ln x_2 + w_2 x_1^2) \qquad \ldots (4b)$$

Figure 3 depicts the experimental versus predicted activities of water in several systems at different temperatures. In addition to these equations, an interesting method called Brunauer-Emmett-Teller (BET) has been proposed by Stokes and Robinson[4e]. The central idea of this isotherm is that a fused or molten salt can attract water molecules presumably to the surface of cations, much as water is attracted to the surface of a crystal. As more water is added, the binding energy per molecule decreases slowly and gradually to that of pure water in a solution or with a multi-layer film. Unfortunately, this equation has failed to reproduce experimental activity data above $x_1 = 0.65$ in these systems. On the other hand, the conventional equations like van Laar or Margules offer greater convenience of a simple form expressing the activity as an explicit function of the mole fraction. This is equally true for the activity of fused salt component. With this guidance in mind, a search for a complete equation required for nonaqueous system is followed. The above sets of equations can describe the vapour pressures of such systems, but for more rigorous treatment as pointed above, the DHT should be included in the model. The DHT useful in the present case can be written as[12] given in Eq. (5)

$$\ln a_1 = (500/M_1)^{0.5} A_\phi \, x_1 x_2^{1.5} / (1 + \rho_2^{0.5} x_2^{0.5}) \qquad \ldots (5)$$

where M_1, A_ϕ and ρ represent molecular mass of solvent, Debye-Hückel slope and quantity calculated from hard-core diameter of salt, respectively[6].

Equation (5) has been noted[12] to be accurate in representing the solvent activities in systems, like (Ag, T1)NO_3-H_2O and (Li, K)NO_3— H_2O. Depar-

Table 1—Summary of results on the solvent activities analyzed by the PSM without and with ion-pairing

System	T/K	w_1	b_1/b_2	σ	Ref.
				$(\ln a_1)$	
$(Ag, Tl)NO_3 - H_2O$	371.6	1.02	0.5	0.003	10b
$(Li, K)NO_3 - H_2O$	373.0	−0.89	1.2	0.002	9
TP*-butanol	373.0	−0.419	1.46	0.0091	11
		(−0.453)	(1.25)	(0.0089)	
TP*-anisole	373.0	−1.437	0.27	0.009	13
		(−1.820)	(0.25)	(0.008)	

* tetra-n-butylammonium picrate; values in the parenthesis are obtained with ion-pairing.

ture from a random distribution of ions throughout the composition range except in the limit of infinite dilution is caused by electrostatic forces. Such a departure from the random distribution does not vary with the composition in general except in very low ionic concentrations.

It has been noted that many salts, like quaternary ammonium salts are generally fully ionized in several organic solvents, but some of them do exhibit strong ion-pairing in the solvent rich region[5,7,10,11,13]. In true sense, a model incorporating the effects accounting for long and short range forces should be built up. Confirmatory evidences for the strong ion-pairing, as pointed out above, are available from accurate η and Λ data. Some examples are already shown in Fig. 1. The $\eta\Lambda$ product, though a microscopic property, can be the best measure for degree of ionization over wide ranges of composition in the case of $LiClO_4$-H_2O at about 404.9K. Very moderate reduction in the Walden product was shown to follow from the dilute to concentrated solution. In the case of fused organic melts, like tetra-n-butylammonium picrate (TP) in n-butyl alcohol[11], anisole[13], etc. at 364.1K, a different trend is noted. In these systems, the viscosity changes less rapidly near TP and Λ is almost constant. Due to n-butanol (dielectric constant = 9.4) an incomplete ionization in salt poor solutions occurs. For the anisole based system, strong ion-pairing is observed in view of its very low dielectric constant[13].

Considering the importance of ionic interactions in such systems, we undertook a systematic collection of experimental data on transport, volumetric, thermodynamic and surface properties of a system comprised of TP and anisole. The vapour pressure data showed positive deviation from the Raoult's law as the case of TP-butanol system at the same temperature. It is important to know that dielectric constant of anisole is three times lower than that of butanol. The results on vapour pressure of TP with n-butanol and anisole

are shown in Fig. 4. A recent model proposed by Pitzer and Simonson[11] can be used for analyzing the vapour pressure data. The main equation is,

$$\Delta_m G/RT = \Delta_m G^{lr}/RT + \Delta_m G^{sr}/RT \qquad \ldots (6)$$

where the Gibbs energy of mixing term, $\Delta G^{lr}/RT$, of solute in solvent is given as a sum of long range (lr) and short range (sr) contributions. The long range or electrostatic contribution is calculated from van Laar or Margules equation as the case may be. The equations for the fully ionized system thus can be written as:

$$\Delta_m G/RT = n_1 \ln x_1 + 2n_2 \ln x_2 + w_1 n_1 z_2$$
$$+ 4n_2(A_x/\rho) \ln[(1 + \rho I_x^{0.5})/(1 + \rho/2^{0.5})] \qquad \ldots (7)$$

where n_1 and n_2 are the number of moles for components 1 and 2 respectively. A_x is Debye-Hückel slope on the basis of mole fraction. Application of the PSM has successfully demonstrated the fitting of vapour pressure data for n-butanol and anisole-TP systems shown as plots of a_1 versus x_1 in Fig. 4. Considering strong ion-pairing in very dilute solution and for a rigorous account, three factors i.e. Ion-pairing or association, Debye-Hückel and, short range forces should be considered in a thermodynamics model. Most accurate evidence for the ion-pairing is obtained by conductance data. Ion association constant, K_x for the ion-pairing is given by expression (8).

$$K_x = (x_p/x_i^2) \exp\{(2A_x[2/\rho) \ln(1 + \rho I_x^{0.5})$$
$$+ (I_x^{0.5}) - I_x^{1.5})/(1 + \rho I_x^{0.5})]\} \qquad \ldots (8)$$

The revised expression based on for estimating the solvent activity as obtained from the use of Eq. (7) and from the knowledge of K_x, is given by Eq. (9)

$$\ln a_1 = \ln x_1 + w_1 z_2^2 + (2A_x I_x^{1.5}/1 + \rho I_x^{0.5}) \qquad \ldots (9)$$

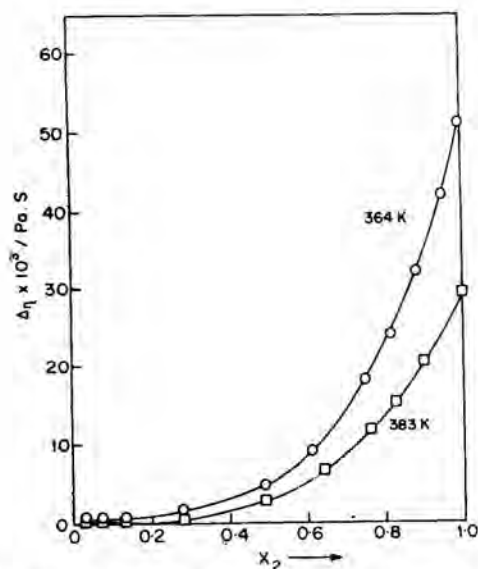Using the K_x value estimates of mole fractions are given by Eq. (10a)

Fig. 5—Change in viscosity $\Delta\eta$ as a function of x_2 for anisole-TP system at 364 and 383K; ref. 13

$$x_i = (1-\alpha)n_2/[n_1 + (2-\alpha)n_2] \qquad \ldots (10a)$$
$$= I_x$$

$$x_p = n_2/[n_1 + (2-\alpha)n_2] \qquad \ldots (10b)$$

$$x_{1p} = n_1/[n_1 + (2-\alpha)n_2] \qquad \ldots (10c)$$

where α as degree of ion pair formation

The mole fractions calculated from Eq. (10) are inserted in Eq. (9) to account for ion-pairing, the original mole fraction values appear in the calculations. The values of K_x are taken from the listed conductance data[7]. The calculated results for several systems obtained from the PSM are listed in Table 1, where the calculations are performed both with and without ion-pairing process. It is, however, recommended that a full version of the PSM be used for the calculations of thermodynamic parameters of such systems. Depending upon a system contribution of the long and short range terms may vary, but the most important fact is the net effect of short range forces, which is the primary determinant of the thermodynamic properties of these solutions[12].

An intriguing situation has been noted with respect to the viscosity behaviour of this system. The viscosity of the solution reduces dramatically about 100 times, when very few moles of solvent are added inionic melt. This observation shows anomalous behaviour as normal equations of viscosity cannot account for it. No theoretical analysis exists for such a drop in viscosity. Attempts are being made in this direction. Results on experimental data for several other systems in this laboratory have conformed this observation. In
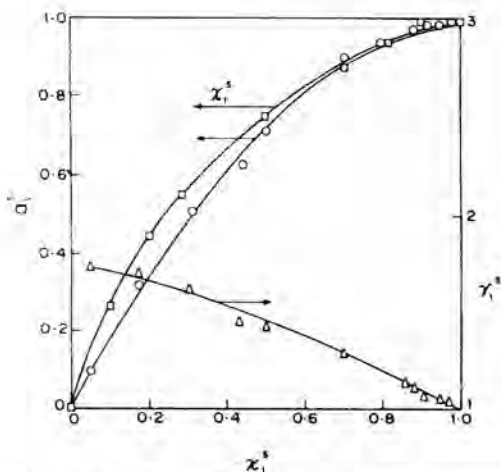

Fig.6 - Plots of activity and activity coefficients on surface, a^s_1 and γ^s_1 as a function of x_1 for anisole-TP system $a^s_1(0)$; $\gamma^s_1(\Delta)$ and $AgNO_3 - TlNO_3 - Ca(NO_3)_2 - H_2O$ ($\square$); ref. 10c.

Fig. 5 the viscosity behaviour of anisole-TP system, for example, is depicted in the form of plots between η and x_2. It has been noted that the activation energy decreases nonlinearly upon the addition of TP in different solvents. In literature, several theoretical equations have been used to account for the variation of η with concentration[4f]. In a recent work[13] reported from this laboratory, a modified equation based upon the expression of Mahiuddin and Ismail[14] has been applied successfully. The equation is of the form

$$\eta = \eta^- \exp(b_0 x_2 + b_1 x_2^2 + b_2 x_2^3) \qquad \ldots (11)$$

Where b_0, b_1 and b_2 are adjustable constants and η_1^- is viscosity of pure solvent. The viscosity data for such system can be fitted to within 1.6%. Another property of considerable importance to arrive at structural information on the interactions of the salt solvent system is surface tension of the system. The surface tension data of these systems do not exhibit any peculiar behaviour. These data at different temperatures can be used to yield entropy and enthalpy of surface. The activity of solvent in the surface phase are calculated using vapour pressure data[15,16]. The activity and activity coefficient of solvents in the surface phase for a few systems are shown in Fig. 6.

In terms of theory of hole formation in liquids[17], the free energy of hole formation calculated from surface tension data should be equal to the molar free energy of activation of viscous flow. An example is depicted in Fig. 7, where ΔG calculated from surface tension at constant composition is plotted against x_1, the mole fraction of liquid solvent. The agreement indicates that the formation of hole is an essential step for the viscous flow in systems.
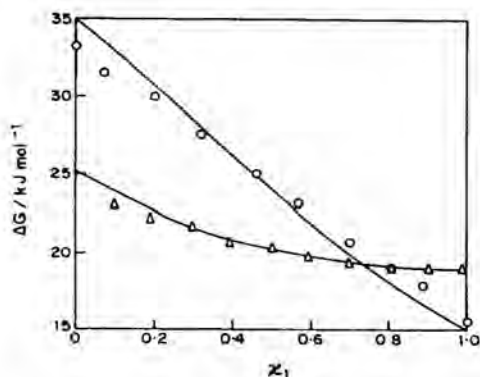
Fig. 7 - Plots of ΔG calculated from surface tension data against x_1. System anisole-TP(o) (ref. 13); AgNO$_3$-TlNO$_3$-H$_2$O(Δ) ref. (10c).
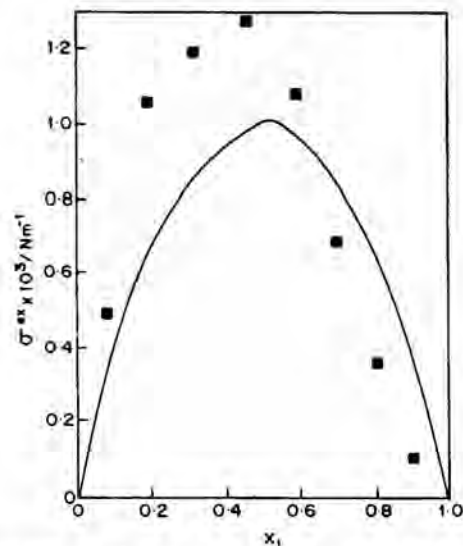

Fig. 8—Excess surface tension, σ^{ex} versus x_1 for TP-anisole system. Lines are predicted values; ref. 13

A possibility of applying Scaled Particle Theory (SPT) to the systems

With regard to the theoretical treatment of such systems, it is of interest to consider the Scaled Particle Theory (SPT), which has found many applications in quantifying energetics of mixture of hard spheres, real fluids, surface tension, solubilities, microemulsions, liquid crystals[18], etc. For the systems comprised of two components of very different sizes, the hard sphere model normally used for pure liquid molecules yields inaccurate estimations of the energetics. A mixing rule based on mole fractions of the components is necessary to calculate the mixture property. The linear mixing rule, however, is not a rigorous approach. Lebowitz et al.[19] and later Kumar[13] extended the pure component theory of hard sphere systems to calculate surface tensions of real systems. The theory is based on the consideration of an approximate expression for the work of adding an additional hard sphere to a mixture. Thus, the expression relating σ to the coupling parameters

$$\sigma = W''(0)/8\pi$$
$$= (3kT/2\pi)\{2[\delta_1/(1-\delta_3)] + 3[\delta_2/(1-\delta_3)]^2\} \qquad \ldots (12)$$

In Eq. (12) $W''(0)$ arises out of the cubic expression of $W(R)$, i.e. the change in the configuration part of Helmholtz free energy upon adding the solute hard sphere particles of radius r to the system. The term δ is

$$\delta_1 = 1/6^\pi \sum_{i=1}^{m} \rho^i (2r_i)^1 \qquad \ldots (13)$$

The radius r, signifies that a fluid particle of species i can come only as close as $(r + r_i)$ to the centre of a solute particle. The reduced density,

$$\rho_i' = N_i/\Omega^1 \qquad \ldots (14)$$

where N_i and Ω are the number of particles and volume, respectively.

The equations are tested against compressibility or surface tension data. The most difficult test for the validity of these equations is to predict excess surface tension, when hard sphere diameter for TP and anisole are used. The hard core diameters for TP and anisole are 7.2 Å and 5.61Å, respectively. The excess surface tension is defined by:

$$\sigma_{ex} = \sigma - \sum_i x_i \sigma_i \qquad \ldots (15)$$

In Fig. 8 are shown the numerical results on σ_{ex} as a function of x_1. During the calculation sufficient care is taken to ensure the use of correct radii. An examination of Fig. 8 shows that the sign of the excess surface tension is correct. Secondly, predictions in the solvent rich solutions is nearly accurate. Our recent calculations have shown that the proposed SPT is unable to describe the symmetry of curve. The reasons for the deviations in the symmetry region are currently being investigated.

Future work

Out of several aspects, one can investigate the treatment of short range interaction forces and how they influence the behaviour of the systems discussed above. As noted earlier, the quantitative explanations for the anomalous behaviour in transport properties like viscosity warrant attention.

Acknowledgement

References

1 Debye P & Huckel E, *Phys Z*, 24 (1923) 185; 24 (1923) 305.

2 For summary see: (a) Pytkowicz R M, *Activity coefficients in electrolyte solutions*, (CRC Press: Boca Raton, FL) 1979. and Horvath A L, *Handbook of aqueous electrolyte solutions*, (John Wiley, New York) (1985), (b) Robinson R A & Stokes R H, *Electrolyte solutions* (Butterworths, London) 1959.

3 Harned H S & Owen B B, *The physical Chemistry of electrolytic solutions* (Reinhold, New York), (1943).

4 (a) Pitzer K S, *J phys Chem*, 77 (1973) 268, (b) Fried man H L, *Ionic solution theory*, (Wiley Inter-science, New York), (1962), (c) Patwardhan V S & Kumar A, *AIChE J*, 32 (1986) 1419; 1429 (d) Kumar A, *Fluid Phase Equil*, 43 (1988) 21, (e) Kumar A, *Chem Eng Comm*, 66 (1988) 201, (f) Kumar A, *Can J Chem Eng*, 71 (1993) 948, (g) Stokes R H & Robinson R A, *J Am chem Soc*, 70 (1948) 1870.

5 (a) Seward R P, *J Am chem, Soc*, 73 (1951) 515, (b) Seward R P, *J phys Chem*, 462 (1958) 758.

6 (a) Pitzer K S, *J Am chem Soc* 102 (1980) 2902. (b) Pitzer K S, *J phys Chem* 88 (1984) 2689.

7 (a) Bien G S, Kraus C A & Fuoss R M, *J Am chem Soc*, 56 (1934) 1860 (b) Yao N P & Bennion D N, *J phys Chem*, 75 (1971) 3586.

8 (a) Braunstein H & Braunstein J, *J chem Thermodyn*, 3 (1971) 419, (b) Trudelle M C, Abraham M & Sangster J, *Can J Chem*, 55 (1977) 1713, (c) Abraham M, M−C Abraham & Ziogas I, *J Am chem Soc*, 113 (1991) 8583.

9 Tripp T B & Braunstein J, *J phys Chem*, 73 (1969) 1984.

10 Davies C W, *Ion association* (Butterworths, London), (1962) chapter 10.

11 Pitzer K S & Simonson J M, *J Am chem Soc*, 106 (1984) 1973.

12 Pitzer K S, *Ber Bunsen-Ges Phys Chem*, 85 (1981) 1952.

13 Kumar A, *J Am chem Soc*, 115 (1993) 9243.

14 Mahiuddin S & Ismail K, *J phys Chem* 87 (1983) 5241.

15 Guggenheim E A & Adam N K, *Proc R Soc London* A139 (1933) 218.

16 Butler J A V, *Proc R Soc London*, A135 (1932) 348.

17 Furth R, *Proc Cambridge Philos Soc* 27 (1941) 252.

18 Reiss H, *J phys Chem*, 96 (1992) 4736, Reiss H, Frisch H L & Lebowitz J L, *J Chem*, 32 (1960) 119.

19 Lebowitz J L, Helfand E & Praestgaard E, *J chem Phys*, 43 (1965) 774.