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Surface Tension, Viscosity, Vapor Pressure, Density, and Sound Velocity for a System Miscible Continuously from a Pure Fused Electrolyte to a Nonaqueous Liquid with a Low Dielectric Constant: Anisole with Tetra-*n*-butylammonium Picrate[†]

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Abstract: In view of very little progress reported in the study of the physical chemistry of systems which are miscible continuously from a pure fused electrolyte to a pure nonaqueous liquid with a low dielectric constant, a detailed study on several properties like surface tension, viscosity, vapor pressure, density, and compressibility is presented at different temperatures for anisole–tetra-*n*-butylammonium picrate (TP) over the full composition range. An attempt has been made to correlate the investigated properties. Good agreement between the molar free energy of viscous flow calculated from the Eyring equation and from the hole formation indicates that holes are essential entities from pure anisole to TP. Ultimately, the Scaled Particle Theory (SPT) has been employed to estimate the surface tension of the system with good agreement barring the asymmetry of the excess surface tension–composition curve.

1. Introduction

The physical chemistry of systems which are miscible continuously from the pure fused electrolyte to another liquid component is of considerable theoretical interest.[1–3] In such systems, the liquid component acts like a solute rather than a solvent. This liquid component can be aqueous or nonaqueous in nature. Notable experimental and theoretical contributions on water-containing systems have been made by the independent research groups led by Braunstein,[1] Abraham,[4] and Pitzer.[3,5,6] With regard to the systems consisting of a liquid nonaqueous component with a very low dielectric constant, very little progress has been reported with the exception of the excellent thermodynamic work by Pitzer and Simonson.[7] These authors have measured and modeled the vapor pressures of *n*-butanol with tetra-*n*-butylammonium picrate (henceforth abbreviated as TP) at 373 K. Some other measurements like conductance and viscosity have been reported at one temperature by Seward[8,9] and Bien, Kraus, and Fuoss.[10]

In this paper, we report systematic measurements on surface tension (σ), viscosity (η), vapor pressure (p), density (d), and sound velocity (u) of the system consisting of anisole with TP at several temperatures over the full composition range. We also attempt to correlate these experimental quantities with a view to understanding the physical chemistry of such a system. Ultimately, we extend the Scaled Particle Theory (SPT) as put forward by Reiss, Frisch, and Lebowitz,[11] and later applied to the mixtures of hard spheres by Lebowitz, Helfand, and Praestgaard,[12] to estimate the surface tension of the present system over the range beginning from pure TP to anisole.

2. Experimental Section

TP was prepared by neutralizing tetra-*n*-butylammonium hydroxide with picric acid. The picrate salt was purified by recrystallizing the reaction product from methanol and drying at about 323 K before use. The observed melting point of dry TP was 363.85 K. Anisole (Aldrich Chemical Co.) used in this investigation was dried over calcium hydride and redistilled under reduced pressure. The purity of the anisole as determined by the procedure of Herrington and Handley[13] was 99.993 ± 0.002 mol %. The conductance of the anisole was 10^{-13} mho or less. It should be noted that similar purification techniques for both the components were adapted by Seward[9] and Bien, Kraus, and Fuoss[10] while measuring the conductance of this system.

The surface tension measurements were made using a classical capillary rise method. The details of the experimental method were the same as those given by Campbell and Williams.[14] The inner tube was a precision bore capillary tube with an internal diameter of 0.05×10^{-2} m. The rise in the capillary tube was measured using a microcathetometer capable of reading $\pm 0.01 \times 10^{-4}$ m. The measurement cell was kept in an oil thermostat bath. The assembly was calibrated on carbon tetrachloride and water in between 343 and 370 K with an accuracy within $\pm 0.4 \times 10^{-3}$ N m^{-1} of the literature values.[15] The precision of surface tension measurements was better than 1%.

Viscosities were measured using an Ostwald–Ubbelhode viscometer. Abraham, Abraham, Combey, and Sangster[16] have given the experimental method in detail. The cell filling procedure was adapted from Campbell and Nagrajan.[17] The viscometer was calibrated against the literature data[15,18] on water, aniline, and sodium chloride–water systems up to 423 K. The viscosities were precise to ±1% in the investigated temperature range.

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Table I. Surface Tension, σ (NM^{-1}), of the Anisole–TP System in Contact with Air as a Function of the Mole Fraction of Anisole (x_1)

364 K		373 K		383 K		393 K	
x_1	$\sigma \times 10^3$	x_1	$\sigma \times 10^3$	x_1	$\sigma \times 10^3$	x_1	$\sigma \times 10^3$
0.0000	40.43	0.0000	38.61	0.0000	36.89	0.0000	35.19
0.1001	39.74	0.0758	38.09	0.1247	35.91	0.0756	34.53
0.2092	38.69	0.1997	37.00	0.2495	34.58	0.1728	33.42
0.3105	37.64	0.3230	35.41	0.3652	33.19	0.3153	31.89
0.4229	36.19	0.4611	33.69	0.4998	31.50	0.4652	31.03
0.5404	34.48	0.5760	31.99	0.6238	29.58	0.6058	28.31
0.6505	32.78	0.7021	29.91	0.7505	27.69	0.7241	26.61
0.7487	30.82	0.8124	28.12	0.8998	25.38	0.8301	25.20
0.9295	27.42	0.8910	26.81	1.0000	24.17	0.9312	23.79
1.0000	26.42	1.0000	25.25			1.0000	23.02

Densities were measured with a pycnometer having a volume of 50 × 10^{-3} m^3 with a precision of ±0.05%. The pycnometer was calibrated against densities of aniline,[15] water,[15] and aqueous sodium chloride[18] with an accuracy of 0.1%.

The sound velocities were measured with a single-crystal interferometer (Mittal Enterprises). The calibration of the interferometer was done against the literature data[19] on aqueous magnesium chloride with an accuracy of 0.05%. The sound velocities were precise to within 0.01%.

Our experimental procedure for measuring vapor pressure was essentially the same as that of Pitzer and Simonson.[7] Vapor pressures of solutions were measured by a differential capacitance manometer. The reference side of the manometer was kept evacuated, so that all the pressures measured were absolute anisole vapor pressures. Pyrex cells containing solutions were maintained approximately at 373 K using an oil bath. Repeated evacuation of the sample cell vapor space was done in order to degas the solutions. The compositions of solutions were determined by weight after each experiment. Each experiment was repeated twice and an average was treated as a final value. The accuracy of vapor pressure measurements based on the calibration against the *n*-butanol–TP system[7] at 373 K was estimated to be 1%. Our vapor pressures were precise to ±0.3%.

The temperature for all the above measurements was kept constant to within 0.1 K. This variation in temperature resulted in the uncertainity in the calculation of the activity of anisole by 0.0004. Throughout this study, subscripts 1 and 2 refer to anisole and TP, respectively.

3. Results and Discussion

3.1 Surface Tension. Our measurements of surface tension, σ, were made at 364, 373, 383, and 393 K over the full composition range. The results on σ as a function of x_1 at various temperatures are summarized in Table I. Figure 1 plots results on σ as a function of x_1 at various temperatures. There are no reported results in the literature with which the present results could be compared. Our results do not exhibit linear dependence of σ on x_1 up to 0.8 and above. However, the positive deviations from linearity decrease with an increase in temperature. We analyzed the present data sets on σ with the equation of Goldsack and Sarvas:[20]

$$\sigma = \sigma_1 x_1 + \sigma_2 x_2 + (x_1 RT/A_1)(\ln(1 + x_2\Delta)) + (x_2 RT/A_2)(\ln(1 - x_1\Delta)) \quad (1)$$

where

$$\Delta = (\sigma_2 - \sigma_1)A_1A_2/(A_1x_1 + A_2x_2)RT \quad (2)$$

Δ is a dimensionless quantity that accounts for deviations from linearity, R and T have the usual significance, and A_1 and A_2 are the particle areas of anisole and TP given by

$$A = \pi r^2 \quad (3)$$

where r is the radius. We calculated the value of r, i.e. 2.9 Å, for anisole by the method of Kim,[21] while for TP, a value of 3.6 Å for r was taken from the work of Bien, Kraus, and Fuoss.[10] The equation of Goldsack and Sarvas fitted the surface tension data with excellent accuracy (average root mean squares deviation (rmsd) = 0.06 × 10^{-3} N m^{-1}).

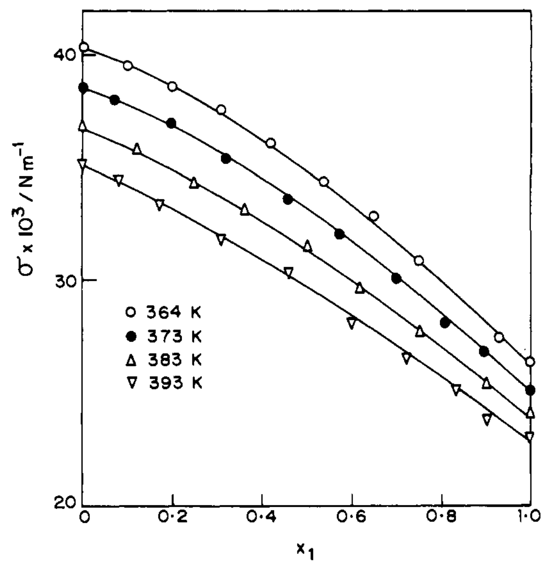

Figure 1. Plot of the surface tension, σ, as a function of the mole fraction of anisole, x_1, for the anisole–TP system.

Table II. Coefficients K and K' for Equation 4 as a Function of x_1

x_1	$K \times 10^3$ (N m^{-1})	$-K' \times 10^6$ (N m^{-1} K^{-1})	x_1	$K \times 10^3$ (N m^{-1})	$-K' \times 10^6$ (N m^{-1} K^{-1})
0.0	105.2	178.2	0.6	100.8	186.5
0.1	107.9	187.6	0.7	91.1	163.5
0.2	107.4	188.7	0.8	83.7	148.2
0.3	108.1	193.6	0.9	72.3	122.4
0.4	106.6	192.5	1.0	68.9	117.2
0.5	103.2	187.5			

Information on surface enthalpy, H_σ, and surface entropy, S_σ, can be extracted from the temperature dependence of σ at a fixed composition. At a given x_1, the values of σ can be fitted linearly with T using an expression of the form

$$\sigma = K + K'T \quad (4)$$

The values of K and K' are listed in Table II. The average rmsd with the use of eq 4 was noted to be 0.08 × 10^{-3} N m^{-1}. Now constants K and K' in eq 4 give the measure of H_σ and S_σ, respectively, as $H_\sigma = \sigma - T(\mathrm{d}\sigma/\mathrm{d}T)$ and $S_\sigma = -\mathrm{d}\sigma/\mathrm{d}T$.

The temperature coefficient of σ varies considerably when one moves from $x_1 = 0$ to 1. The temperature coefficient of anisole (as can be seen from density results given later in the article) is about two times higher than that of TP, which accounts for the increase in the temperature coefficient of σ when anisole is added to TP. Bloom, Davies, and James[22] suggested that bonding characteristics of a substance can be correlated with the magnitude of H_σ, which appears to be a temperature-independent quantity. Our H_σ value for pure anisole (68.9 × 10^{-3} N m^{-1}) is within the range of covalent bonding character as observed by Bloom, Davies, and James.[22] However, in the case of TP, which is a fully ionized electrolyte in the molten state,[23] we obtain a value of 105.2 × 10^{-3}N m^{-1} for H_σ showing semi-ionic characteristics. For a fully ionized electrolyte in the molten state, a value of 216.7 × 10^{-3} N m^{-1} has been noted.[23] A similar kind of disagreement in the correlation of Bloom, Davies, and James[23] was noted by Campbell and Williams,[14] Abraham, Abraham, and Ziogas,[4] and Janz, Reeves, and Ward.[23]

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Table III. Viscosity, η (Pa s), as a Function of the Mole Fraction of TP (x_2) for the Anisole–TP System at 364, 373, and 383 K

364 K		373 K		383 K	
x_2	$\eta \times 10^3$ (Pa s)	x_2	$\eta \times 10^3$ (Pa s)	x_2	$\eta \times 10^3$ (Pa s)
0.0000	0.457	0.0000	0.417	0.0000	0.375
0.0241	0.51	0.0253	0.45	0.0247	0.42
0.0690	0.63	0.0618	0.50	0.0622	0.48
0.1279	0.84	0.1291	0.62	0.1304	0.64
0.2857	1.85	0.2884	1.38	0.2909	1.43
0.4867	5.17	0.4909	3.94	0.4955	3.57
0.6142	9.71	0.5929	6.87	0.6514	7.02
0.7541	18.6	0.7602	15.6	0.7683	11.9
0.8184	24.7	0.8251	19.7	0.8339	15.4
0.8871	32.8	0.8994	26.0	0.9041	20.4
0.9592	42.5	0.9622	30.1	1.0000	29.9
1.0000	51.4	1.0000	32.9		

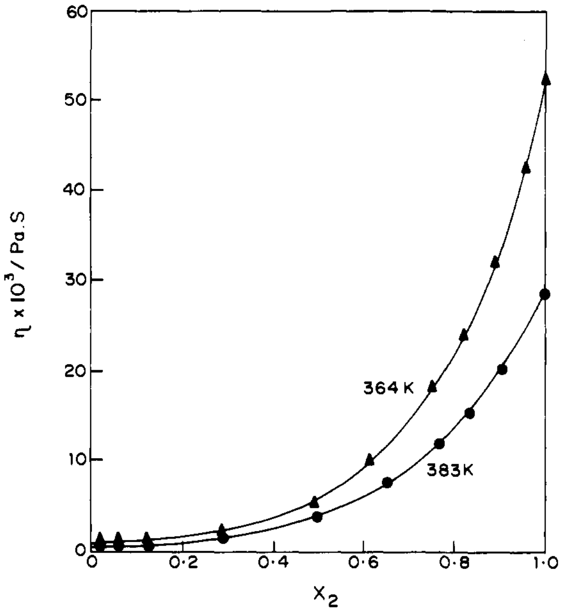

Figure 2. Plot of the viscosity, η, as a function of the mole fraction of TP, x_2, for the anisole–TP system at 364 and 383 K.

3.2 Viscosity. The only experimental data available for this system are from Seward,[9] who measured the viscosity at a single temperature of 364 K. In Table III are listed the viscosity data as functions of x_2 at 364, 373, and 383 K. Our measurements at 364 K were in agreement with those of Seward[9] to within 0.05 × 10^{-3} Pa s. Figure 2 depicts plots of η as a function of x_2 at 364 and 383 K. It is evident from this figure that there is a considerable decrease in the viscosity of TP upon addition of anisole. Pitzer[3,5] also commented on such behavior. One also notes that this sharp drop in η is greater at 364 K, just above the melting point of TP, i.e. 362 K. This drop decreases with an increase in temperature. At present, we are unable to provide an explanation for this behavior. It may be noted that Campbell and Williams[14] also observed this trend in the water–lithium chlorate system. The $\eta - T$ relationship can be represented by the Arrhenius equation.[24] Over the temperature range studied in the present investigation, η isotherms show negative deviation from linear dependence on mole fractions. This behavior is consistent with earlier studies.[14] The calculation of the activation energy shows that it decreases nonlinearly upon addition of anisole in TP. It also demonstrates that the average size of the mass unit of viscous flow decreases upon addition of anisole. This decrease in Arrhenius activation energy is probably the result of the sharp decrease in η upon addition of anisole in TP.

Table IV. Coefficients of Equation 5 Correlating η with x_2 at Different Temperatures

coeffs	364 K	373 K	383 K[a]
b_0	4.633	2.608	4.012
b_1	1.288	6.219	2.619
b_2	1.208	4.468	3.826

[a] Contains an additional term $b_3 = 1.5776$.

Table V. Vapor Pressure, p, of the Anisole–Tetra-n-butylammonium Picrate System at 373 K and the Fraction of Ions Associated (α) Calculated from the Conductance Data

T (K)	x_2	p (kPa)	α
373.1	0	18.60	
372.8	0.0799	18.38	0.252
373.2	0.1356	18.30	0.165
373.1	0.1748	18.12	0.126
373.2	0.2500	17.41	0.090
372.7	0.3022	16.89	0.078
373.1	0.4247	15.72	0.056
372.9	0.5389	15.66	0.048
372.8	0.6652	12.72	0.042
373.0	0.7266	11.23	0.041
373.2	0.8053	9.13	0.040
373.1	0.8949	5.81	0.039
373.0	0.9760	1.61	0.038

In the literature, several empirical and theoretical equations[25–27] have been used to account for the concentration dependence of η, but they deviate sharply when applied to highly concentrated solutions. However, the Vand equation[28] and its modifications[29] have been able to account for the concentration dependence of η at an extreme concentration of electrolyte, although the theoretical concept on which the Vand equation and its modifications are based cannot be validated for highly concentrated solutions. Very recently, Mahiuddin and Ismail[30] proposed an empirical equation which was successfully applied to up to saturated concentrations of calcium nitrate, magnesium chloride, and nickel chloride in water. More interestingly, their equation was shown to be deducible to the famous Jones–Dole equation[26] in the dilute range and was found to be consistent with the Adam–Gibbs theoretical model.[31]

Our experimental data on η can be represented with the similar form of the empirical equation as given by Mahiuddin and Ismail,[30] but we prefer to fit the data against x_2 as

$$\eta = \eta_1 \exp(b_0 x_2 + b_1 x_2^{\,2} + b_2 x_2^{\,3}) \qquad (5)$$

where b_0, b_1, and b_2 are empirical constants. A least-squares analysis of data using the above equation is given in Table IV. The average rmsd of fit for η in the temperature range of the present study is 1.6%.

3.3 Vapor Pressure. The experimental values of the vapor pressure, p, of the anisole–TP system at 373 K are given in Table V. The vapor pressure of pure anisole at 373 K (18.62 kPa) measured in our laboratory was in excellent agreement with the reported value.[32] To calculate the activities of anisole, a_1, from the experimental vapor pressures, the fugacities, f_1, of anisole were calculated by means of the equation

$$f_1 = p \exp(Bp/RT) \qquad (6)$$

where B is the second virial coefficient of anisole (−1937 × 10^{-6} m^3 mol^{-1} at 373 K) taken from Dymond and Smith.[33] Activities

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were then calculated as the ratios f_1/f_1^*, f_1^* being the fugacity of pure anisole.

We analyzed vapor pressure data using the recent model of Pitzer and Simonson[7] (PSM), who combined the Debye–Hückel term with the van Laar term to fit the activity of the solvent in the *n*-butanol–TP system. The PSM has been discussed in detail elsewhere.[3,5–7,34]

The useful expression[7] for the activity of anisole, a_1, in solution is

$$\ln a_1 = \ln x_1 + w_1 z_2^{\,2} + (2A_x I_x^{\,1.5}/1 + \rho I_x^{\,0.5}) \tag{7}$$

where w_1 is the nonideality parameter commonly used for nonelectrolytes. z_2 is a van Laar composition measure given by

$$z_2 = x_2/(qx_1 + x_2) \tag{8}$$

with $q = b_1/b_2$, i.e. the volume ratio of components. A_x is the Debye–Hückel slope defined as

$$A_x = {}^1/_3(2N_A d_1/M_1)^{0.5}(e^2/DkT)^{1.5} \tag{9}$$

where M_1, d_1, and D are the molecular mass, density, and dielectric constant of anisole. The parameter ρ is the closest approach parameter given by

$$\rho = a(8e^2 N_A d_1/M_1)^{0.5}(e^2/DkT)^{1.5} \tag{10}$$

where a is the hard core diameter.

The PSM maks use of both the fully ionized and ion-pair formation concept. Following recommendations made in the PSM and in view of the low dielectric constant of anisole, we preferred to account for ion-pair equilibria[9,10] in the present calculations. Thus mole fractions for various species are given by the following set of equations:

$$x_{\mathrm{i}} = (1-\alpha)n_2/[n_1 + (2-\alpha)n_2] = I_x \tag{11a}$$

$$x_{\mathrm{p}} = n_2/[n_1 + (2-\alpha)n_2] \tag{11b}$$

$$x_{\mathrm{1p}} = n_1/[n_1 + (2-\alpha)n_2] \tag{11c}$$

where subscripts *i*, *p*, and 1p indicate free ions (T^+ or P^-), ion pairs, and anisole with ion pairing, respectively. I_x refers to the ionic strength defined on the basis of the mole fraction and n_1 and n_2 to the number of moles of anisole and TP, respectively. α is the degree of ion-pair formation. The ion association constant, K_x, is related to I_x by

$$K_x = (x_{\mathrm{p}}/x_{\mathrm{i}}^{\,2}) \exp\{2A_x[(2/\rho)\ln(1 + I_x^{\,0.5}) + (I_x^{\,0.5} - I_x^{\,1.5})/(1 + \rho I_x^{\,0.5})]\} \tag{12}$$

Values of α involved in eq 11 were calculated using the standard procedures[35,36] and the conductance data of Bien, Kraus, and Fuoss.[10] The value of ρ was fixed with primary guidance of the interionic distance of TP, i.e. 7.2 Å, correspondeing to $\rho = 28.50$. We obtained $\log K_x = 13.20$ from eq 12 using $\rho = 28.50$, comparing exceedingly well with the literature value[10] of $\log K_x = 13.58$. Now eq 7 was employed to fit activity data using $A_x = 82.56$. The resultant parameters are recorded in Table VI along with the rmsd of fit. It was observed that a_1 values could be fitted by eq 7 using the listed parameters over the full composition range. No systematic deviations between the experimental and calculated a_1 values were observed in both anisole-rich and -poor composition regions. Figure 3 demonstrates experimental (points) and calculated values (solid line) of a_1 as a function of x_1, where the agreement is excellent. It should be noted that the newly arrived value of $\rho = 24.01$ corresponding to $a = 5.98$ Å agrees well with the literature value[10] of $a = 5.61$ Å. The w_1 parameter indicates contribute due to the nonelectrostatic interactions. The q value, in principle, is the ratio of molar volumes of components but is treated as an adjustable parameter for this type of system. The experimental q value (≈ 0.29) for this system, however, is in excellent agreement with the tabulated q value in Table VI.

Table VI. Parameters of Equation 7 for Calculating the Activity of Anisole in Tetra-*n*-butylammonium Picrate at 373 K with the PSM with Ion-Pair Equilibria ($\alpha \neq 0$) and Full Ionization Concept ($\alpha = 0$)

	$\alpha \neq 0$	$\alpha = 0$
ρ	24.01	28.50
w_1	−1.820 ± 0.091	−1.437 ± 0.057
q	0.25 ± 0.07	0.27 ± 0.05
rmsd in a_1	0.008	0.009

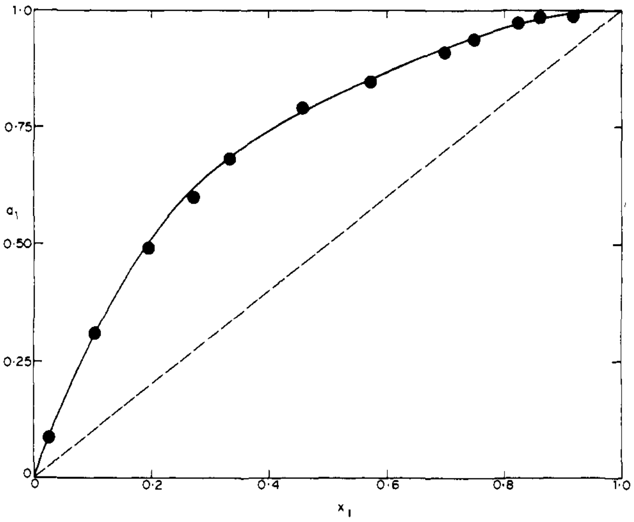

Figure 3. Plot of the activity of anisole, a_1, as a function of the mole fraction of anisole, x_1, for the anisole–TP system at 373 K: points, experimental values; solid line, fitting by the PSM.

The anisole activity data were also fitted by the PSM assuming the full ionization of TP, i.e. $\alpha = 0$. We list the resultant parameters of the fitting in Table VI. We did not notice any systematic deviation throughout. Although, in the PSM, both the alternates with and without α give reliable calculations of a_1, a more complete treatment is obtained by including ion-pair equilibria.

It is noted that the Brunauer–Emmett–Teller (BET) adsorption isotherm as proposed by Stokes and Robinson[37] has been employed in a modified form by Braunstein and Braunstein[38] and Trudelle, Abraham, and Sangster.[39] These authors[38,39] and also Pitzer[3] have noted that the BET equation does not fit the activity data above the mole fraction of 0.65 of water. In view of this, we opted to use the PSM, as it has been found to fit the activity data over the full composition range. Besides this, both the Debye–Hückel term and ion-pair equilibria are incorporated in the PSM.

3.4 Volume Properties. The density, d, of the system at various temperatures can be represented by the relationship

$$d\ (\mathrm{kg\ m^{-3}}) = d_1 + Ax_2 + Bx_2^{\,2} \tag{13}$$

The values of d_1, A, and B are given in Table VII along with the standard deviations of fits. The densities can be converted to the apparent molar volume, ϕ_V, by the equation given by Millero.[40]

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Table VII. Correlation of Density, d (kg m^{-3}), with the Mole Fraction of TP (x_2)

T(K)	$d_1 \times 10^{-3}$	$A \times 10^{-3}$	$-B \times 10^{-3}$	rmsd × 10^{-3} (kg m^{-3})
364	0.936	0.291	0.128	0.002
373	0.926	0.299	0.131	0.003
383	0.918	0.306	0.138	0.002

The ϕ_V values thus obtained, when extrapolated to zero concentration of TP, yielded the partial molar volume at infinite dilution, i.e. $\phi_V^\circ = \bar{V}^\circ$. The ϕ_V° values at 364, 373, and 383 K were found to be 405.6 × 10^{-6}, 414.3 × 10^{-6}, and 424.3 × 10^{-6} m^3 mol^{-1}, respectively.

The measured sound velocities, u, of the system at 373 K are represented by

$$u(\mathrm{m\ s^{-1}}) = 1106.2 + 29.14x_2 + 66.30x_2^2 + (23.92 \times 10^2)x_2^3 - (45.58 \times 10^2)x_2^4 + (24.55 \times 10^2)x_2^5 \quad (14)$$

with a rmsd of 0.15%.

Allam and Lee[41] discussed the concentration dependence of u for several ionic systems and concluded that the aqueous systems with heavy ions exhibited decreases in u with increasing concentration. As a matter of fact, though TP is comprised of larger ions, this situation of decreasing u with increase in concentration is not observed in the present system.

The adiabatic compressibility, β, can be calculated with the help of u and d at a given composition as

$$\beta = 1/u^2 d \quad (15)$$

which was later converted[40] to give the apparent molar compressibility, ϕ_K. Our experimental value of β_1 for anisole (88.76 × 10^{-7} Pa^{-1}) is in excellent agreement with the literature value[42] of 88.40 × 10^{-7} Pa^{-1}). The value of ϕ_K° determined at 373 K is 4.16 × 10^{-11} m^3 mol^{-1} Pa^{-1}. Unfortunately, there are no literature data with which to compare this value. However, Conway and Verrall[43] and Laliberte and Conway[44] noted very small negative or slight positive values for tetraalkylammonium salts in water, which indicates that ϕ_V° and ϕ_K° from the present work are in an acceptable range. The higher ϕ_K° value for TP is not limited to the T$^+$ ion, but even NH_4^+ itself has a very less negative compressibility value when compared to that of simple ionic systems. One now can think in terms of the local compressibility of the anisole molecules near the ions. In view of the bulkiness of large T$^+$ ions, their intrinsic molecular compressibilities might account for some of the apparent increase of compressibilities in relation to those of normal electrolytes. The reason for somewhat greater compressibility may be due to some free space between the methylene (CH_2) groups in the n-butyl group of TP.

It should be noted that our measurements on d and u do not extend to the very dilute range, thus our ϕ_V° and ϕ_K° values are not accurate. This is the reason we have not attempted to account for volume and compressibility changes for ion-pair formation in this system.

3.5 Derived Surface Properties. One can now exploit the surface tension and vapor pressure data at 373 K to obtain knowledge about the surface phase. With regard to the surface mole fraction, we employed the Guggenheim and Adam method,[45] while for the surface activity, the Butler equation[46] was used. Since Abraham, Abraham, and Ziogas[4] have described these equations for the mixed nitrate–water systems, we do not discuss them in detail here. In short, the Gibbs adsorption parameter is calculated from the derivative ($d\sigma/d(\ln a_1)$) at fixed compositions. The number of anisole molecules is related to the Gibbs adsorption parameter through the areas of anisole and TP molecules and their mole fraction ratios. The surface mole fraction of anisole, x_1^s, is calculated by the ratio of anisole molecules over the total molecules of anisole and TP.

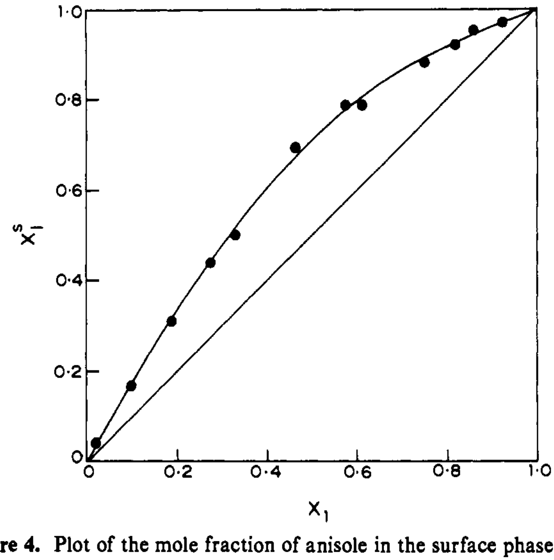

Figure 4. Plot of the mole fraction of anisole in the surface phase, x_1^s, against that in the bulk phase, x_1, for anisole–TP at 373 K.

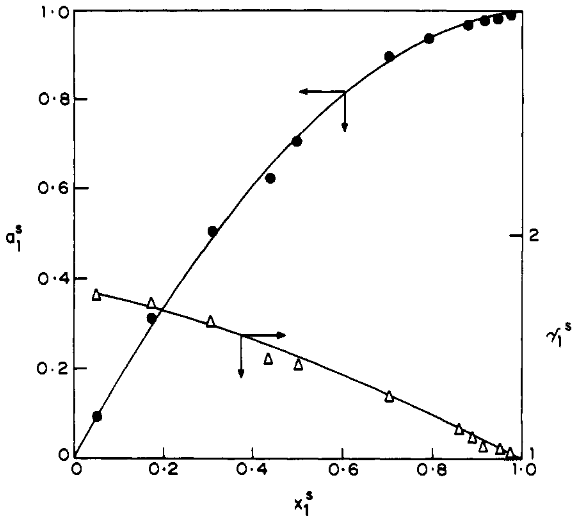

Figure 5. Plot of the activity, a_1^s, and the activity coefficient, γ_1^s, of anisole in the surface phase as a function of x_1^s for the anisole–TP system at 373 K.

Finally the activity of anisole in the surface phase, a_1^s, is computed as[46]

$$a_1^s = a_1 \exp[A_1(\sigma - \sigma_1)/kT] \quad (16)$$

and the anisole activity coefficient, γ_1^s, in the surface phase was obtained as $\gamma_1^s = a_1^s/x_1^s$. In Figure 4 is plotted the variation of x_1^s with x_1 at 373 K, showing the enrichment of anisole in the surface phase. In Figure 5, a_1^s and γ_1^s are shown as functions of x_1^s.

3.6 Hole Formation. We now examine the importance of hole formation from pure fused TP to pure anisole. Several years ago, Furth[47] presented the theory of hole formation in liquids and calculated the molar free energy of hole formation, ΔG(hole), using the surface tension data. On the other hand, in the theory of rate process, viscous flow is seen as a transport process in

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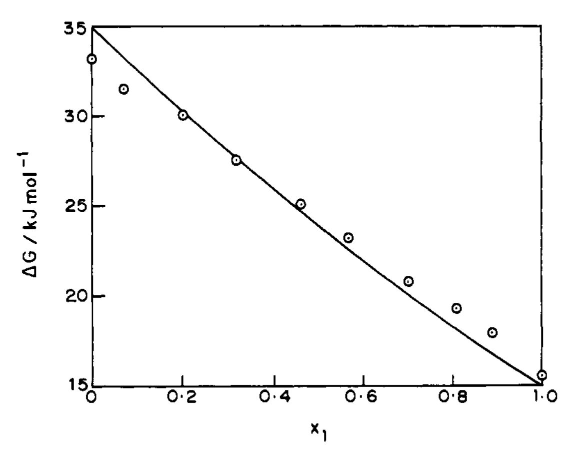

Figure 6. Plot of the molar free energy (ΔG) versus x_1 for the anisole–TP system at 373 K: points, ΔG(hole); solid line, $\Delta G\#$(vis).

which a basic act is the passing of a molecule from one equilibrium position to another over a potential energy barrier. This requires an availability of holes or empty sites in the quasi-crystalline lattice and may be pictured as a jump of a single flow species. Accordingly, the molar free energy of activation of viscous flow,[48] i.e. $\Delta G\#$(vis), calculated from the viscosity data should be equal to the ΔG(hole) obtained from the surface tension data. Abraham, Abraham, and Ziogas[4] have recently noted such an agreement for mixed nitrate–water systems. The quantities ΔG(hole) and $\Delta G\#$(vis) obtained from the relevant equations[4,47,48] are plotted in Figure 6 at a single temperature of 373 K for the purpose of illustration. The close agreement between the ΔG(hole) and $\Delta G\#$(vis) shown in this figure indicates that, when one moves from the fused organic electrolyte (TP) to the pure nonaqueous organic liquid (anisole) with a low dielectric constant, the hole formation is an essential step of the viscous flow mechanism throughout the concentration range. Also Janz and Saegusa[49] have applied this method to molten carbonates.

3.7 Scaled Particle Theory (SPT). The SPT has been used to study a variety of problems. In a recent article, Reiss[50] has presented an excellent summary of the SPT. One of the problems studied by the SPT is its application to the mixtures of hard spheres. Lebowitz, Helfand, and Praestgaard[12] extended the pure component theory of hard sphere systems to calculate surface tensions of real systems. Their theory is based on consideration of an approximate expression for the work of adding an additional hard sphere to a mixture.

The expression relating σ to the coupling parameters δ_l is

$$\sigma = W''(\mathrm{O})/8\pi$$

$$= (3kT/2\pi)\{2[\delta_1/(1-\delta_3)] + 3[\delta_2/(1-\delta_3)]^2\} \quad (17)$$

In eq 17, $W''(\mathrm{O})$ arises out of the cubic expression of $W(\mathrm{R})$, i.e. the change in the configuration part of the Helmholtz free energy upon adding the solute hard sphere particles of radius r to the system. The term δ is

$$\delta_l = {}^1/_6\pi\sum_{i=1}^{m}\rho_i'(2r_i)^l \quad (18)$$

The radius r signifies that a fluid particle of species i can come only as close as $(r + r_i)$ to the center of a solute particle. The reduced density, ρ_i', is defined as $\rho_i' = N_i/\Omega^1$, where N_i and Ω are the number of particles and volume, respectively. The numerical results in terms of excess surface tension defined by $\sigma^{ex} = \sigma - \sum x_i\sigma_i$ and based on the hard sphere diameters for TP and anisole given in the text are shown in Figure 7, where σ^{ex} is plotted as a function of x_1. Due care was taken to ensure that pure component hard sphere diameters generated the required σ_i. In Figure 7, we find that the sign of σ^{ex} is correctly represented by the SPT and the estimates are in good agreement with the experimental quantities throughout the composition. We, however, note that the experimental σ^{ex} values indicate an asymmetric parabola with the maximum value at $x_1 = 0.4$, which is not correctly predicted by the SPT. Lebowitz, Helfand, and Praestgaard[12] also noted this observation. We do not intend to stress the theoretical development and reasoning of this cause but wish to demonstrate that the SPT can yield reasonable estimates of the surface tension of a system continuously miscible from a pure fused organic electrolyte to a pure nonaqueous liquid over the full composition range.

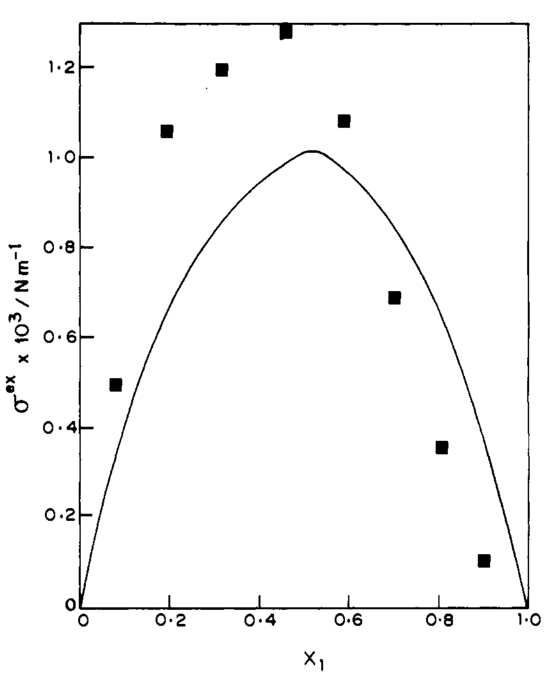

Figure 7. Plot of the excess surface tension, σ^{ex}, as a function of x_1 for the anisole–TP system at 373 K: points, experimental values; solid line, estimation by the SPT.

4. Conclusions

In summary, we have presented several experimental measurements on quantities like surface tension, viscosity, vapor pressure, density, and compressibility of a system where an organic ionic electrolyte is fully miscible over the whole composition range in a nonaqueous liquid component. Useful information has been extracted on surface properties and hole formation. The Scale Particle Theory for the mixtures of hard spheres has been employed to describe the surface tension with reasonable accord, except that the maximum in excess surface tension with respect to composition is not fully accounted for. It is expected that these results will be useful in reducing the gap in our understanding of the physical chemistry of systems where one moves from a pure fused electrolyte to a pure organic liquid with a low dielectric constant.

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Supplementary Material Available: Tables of density data at 364, 373, and 383 K and sound velocity data at 373 K (2 pages). Ordering information is given on any current masthead page.

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