Vapor Pressures of Nitrobenzene + Tetrabutylammonium Picrate at 373 K

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Vapor pressures of the system nitrobenzene + tetrabutylammonium picrate, which is continuously miscible from dilute solution to molten salt, are presented at 373 K over the full concentration range. The solvent activities in these systems are analyzed with the Pitzer−Simonson model and a local composition model proposed by Chen. Ion pairing has been considered for both models. The Pitzer−Simonson equations based on a combination of Debye−Huckel and van Laar terms accounting for the long- and short-range interactions, respectively, can accurately reproduce the experimental activity data using ion pairing. The activity data can also be fitted by the local composition model using two parameters.

In a recent publication from this laboratory, we presented experimental data on thermodynamic, transport, surface, and volumetric properties of anisole−tetrabutylammonium picrate at several temperatures (Kumar, 1993). These types of systems consist primarily of an organic salt and organic liquid preferably with low dielectric constant. The solutions prepared from these components are miscible throughout as the temperature of the system is kept above melting point of the salt. Organic salts are selected for our study in view of their low melting points.

As a part of our research program to study these infrequently available systems for theoretical purposes, we now present activities obtained from the vapor pressure measurements on nitrobenzene with tetrabutylammonium picrate at a temperature above the melting point of tetrabutylammonium picrate. Experimental activity data on nitrobenzene with tetrabutylammonium picrate are analyzed in terms of empirical and semiempirical thermodynamic models.

Experimental Section

The picrate salt with molar mass 470.60 g mol^{-1} was prepared by neutralizing tetra-*n*-butylammonium hydroxide with picric acid. The resulting precipitate was filtered, washed with water, and redissolved in hot 95% (v/v) ethanol + water. Water was added to the alcohol solutions, precipitating the picrate. The residual alcohol was removed from the filtered precipitate by washing it with water. Water was removed from the salt by storing over P_2O_5 in a vacuum desiccator. Nitrobenzene (Aldrich Chem. Co.) was refluxed over calcium hydride for several hours at reduced pressures and then distilled in a dry nitrogen atmosphere under reduced pressure. The purification methods of both the components were also employed by Seward (1958) for the conductance measurements.

Our experimental procedure for measuring vapor pressures has been reported elsewhere (Pitzer and Simonson, 1984; Kumar, 1993). Vapor pressures of solutions were measured using a differential capacitance manometer.

Table 1. Vapor Pressures, *p*/kPa, and Activities, a_1, of Nitrobenzene in Nitrobenzene + Tetrabutylammonium Picrate Solution at 373 K

x_1	p/kPa	a_1
0.0920	0.412	0.145
0.1883	0.795	0.280
0.3058	1.201	0.423
0.4122	1.515	0.534
0.5059	1.765	0.623
0.6114	2.038	0.715
0.7093	2.269	0.800
0.8125	2.522	0.889
0.8826	2.642	0.931
0.9655	2.789	0.982
1	2.837	1

Pyrex cells containing solutions were kept in an oil bath at 373 (±0.1) K. Accuracy of vapor pressure measurements based on the calibration against the 1-butanol−tetrabutylammonium picrate system at 373 K (Pitzer and Simonson, 1984) was estimated to be 1%. Our vapor pressures were precise to ±0.3%. Uncertainty in compositions was estimated to be 5×10^{-4}.

Results and Discussion

In Table 1 are listed the values of vapor pressures, p, of nitrobenzene (1) + tetrabutylammonium picrate (2) solutions at different mole fractions, x_1, of NB at 373 K. The $p - x_1$ values can be represented using a polynomial equation

$$p/\mathrm{kPa} = 0.0645 + 4.06x_1 - 1.29x_1^2 \qquad (1)$$

with

$$\sigma = 0.017\ \mathrm{kPa}$$

These vapor pressures were converted into activities of nitrobenzene, a_1, using a value of second virial coefficient, B, as -2.8742×10^{-3} $\mathrm{m}^3\ \mathrm{mol}^{-1}$ at 373 K. The plot of a_1 vs x_1 (Figure 1) shows positive deviation from Raoult's law. The value of B was calculated from the corresponding states correlations described in detail by Prausnitz (1969) employing the reduced temperature T_r and reduced pressure P_r data given elsewhere (Simmrock et al., 1986).

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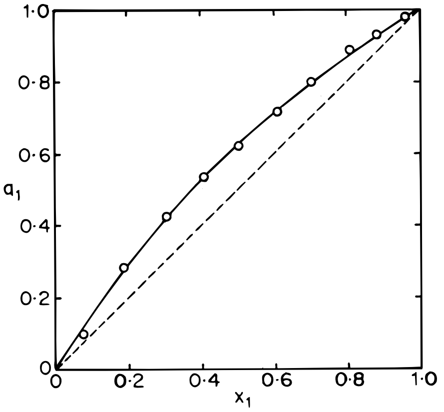

Figure 1. Activity, a_1, of nitrobenzene in nitrobenzene + tetrabutylammonium picrate at 373 K.

Another accurate method for calculating the *B* value was proposed by Hayden and O'Connell (1975).

To analyze the $p-x_1$ data for the system, we have attempted to undertake three different models as: Stokes−Robinson hydration model (Stokes and Robinson, 1948); Pitzer−Simonson model (Pitzer and Simonson, 1984), and a local composition model of Chen et al. (1982) and Chen and Evans (1986). The Stokes−Robinson hydration model was chosen for examining its validity in describing the vapor pressures of nonaqueous solvent−molten organic salt systems. This model has been used earlier in the case of aqueous systems. The semiempirical models proposed by Pitzer and Simonson (1984), and Chen et al. (1982) and Chen and Evans (1986) describe the short-range forces by the use of simple nonelectrolytic and local composition terms, respectively. It was, therefore, thought worthwhile to analyze the data by using these models. The nonelectrolytic term in the Chen model has more rigorous theoretical basis as compared to that in the Pitzer−Simonson model.

The Stokes−Robinson model is based on the concept of hydration of ionic species in water and has been applied for analyzing the vapor pressure data of several concentrated salt solutions. The model uses two adjustable parameters. The Brunauer−Emmett−Teller (BET) adsorption isotherm is used in this model. The central idea is that the molten salt can attract solvent molecules, presumably to the surfaces of cations, much as water is attracted to the surface of a crystal. As more water is added, the binding energy per molecule decreases gradually to that of pure water in a dilute solution or with a multilayer film. According to Braunstein and Braunstein (1971) and Trudelle et al. (1977) the operational equation is

$$a_1(1 - x_1)/x_1(1 - a_1) = 1/cr + (c - 1)a_1/cr \qquad (2)$$

Accordingly, a plot between the values calculated from the left-hand side of the above equation and a_1 is expected to yield a straight line with $1/cr$ and $(c - r)/cr$ as intercept and slope, respectively. The resultant adjustable parameters *c* and *r* for our molten system, as obtained by the use of eq 2, are $c = 1.044$ and $r = 0.595$. For the purpose of comparison, the left-hand side of eq 2 has been plotted against a_1 in Figure 2 for two other systems, i.e., anisole (Kumar 1993) and 1-butanol (Pitzer and Simonson, 1984), involving tetrabutylammonium picrate as a common salt. Examination of Figure 2 reveals that the experimental a_1 values begin to deviate from linearity at $x_1 > 0.84$, 0.9, and 0.7 for tetrabutylammonium picrate + nitrobenzene, + anisole, and + 1-butanol, respectively. The SRM represents the activity data for these systems with standard deviations $\sigma = 0.007$, 0.009, and 0.001 up to the point of deviation from linearity while compared to experimental data of tetrabutylammonium picrate + nitrobenzene, + anisole, and + 1-butanol, respectively (Kumar, 1993; Pitzer and Simonson, 1984). This limitation of the Stokes−Robinson model in describing the activity data of aqueous systems in entire concentration range is documented elsewhere (Braunstein, 1971).

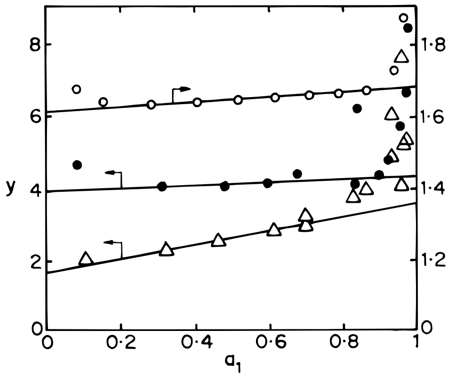

Figure 2. Plots of the Stokes and Robinson Model; *y* (defined in text) against a_1; ○, tetrabutylammonium picrate + nitrobenzene; ●, tetrabutylammonium picrate + anisole; △, tetrabutylammonium picrate + 1-butanol.

Considering the success of the Pitzer−Simonson model in the cases of systems consisting of tetrabutylammonium picrate + anisole and + 1-butanol, the experimental a_1 data on nitrobenzene + tetrabutylammonium picrate were analyzed by this model. The Pitzer−Simonson model employs a combination of "electrostatic long-range term" expressed by the Debye−Huckel component (DHC) with "nonelectrostatic short-range component" (NEC), like van Laar or Margules having two adjustable parameters. This model is based both on the full dissociation of salt throughout the composition and incomplete dissociation due to ion-pair formation in the low-salt region. Ion pairing, as calculated from conductance data, allows the revised calculations of mole fractions of cation, anion, and ion pair and solvent. Although the details of PSM are documented elsewhere (Pitzer and Simonson, 1984) useful equations for the present purpose are described below.

The Gibbs free energy of mixing (dimensionless), $\Delta_m G/RT$, is given by

$$\Delta_m G/RT = n_1 \ln x_1 + 2n_2 \ln x_2 + w_1 n_1 z_2 + 4n_2(A_x/\rho) \ln[(1 + \rho I_x^{0.5})/(1 + \rho/2^{0.5})] \qquad (3)$$

where *n* indicate the number of moles with subscripts 1 and 2 for nitrobenzene and tetrabutylammonium picrate, respectively. Quantities w_1 and z_2 are nonideality and composition parameters, respectively, contributing to NEC. Parameter z_2 is defined in terms of volume ratio and composition as $z_2 = x_2/(qx_1 + x_2)$ with *q* being the ratio of molar volumes given by b_1/b_2. The last term in the above expression is a DHC written on the mole fraction basis. A_x, Debye−Huckel slope, and ρ, a parameter related to hard-core diameter used in this study at 373 K, are 12.25 and 9.66, respectively. Ionic strength, I_x, is calculated on the mole fractions basis as $I_x = 0.5\sum x_i z_i^2$.

The a_1 values were obtained from

$$\ln a_1 = \ln x_1 + w_1 z_2^2 + 2A_x I_x^{1.5}/(1 + \rho I_x^{0.5}) \qquad (4)$$

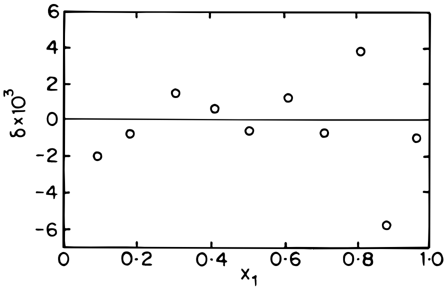

Figure 3. δ (difference between experimental and calculated a_1) by PSM with $\alpha \neq 0$ as a function of x_1 for nitrobenzene + tetrabutylammonium picrate at 373 K.

Because of ion pairing, the mole fractions of cation, anion, and solvent species are recalculated using the ion association constant, K_x, being obtained from conductance data (Seward, 1958). The revised mole fractions of cation, anion, ion pair (ip) as described below are inserted in eq 4 for calculating the solvent activities. Thus, the revised mole fractions for the species are

$$x_i = (1 - \alpha)n_2/F = I_x \tag{5a}$$

$$x_p = n_2/F \tag{5b}$$

$$x_{ip} = n_1/F \tag{5c}$$

with $F = [n_1 + (2 - \alpha)n_2]$ and subscripts i, p, and ip indicate free ions (cation T^+ or anion P^-), ion pairs, and nitrobenzene with ion pairing, respectively. The degree of ion-pair formation is given by α.

Equation 4 was applied to the vapor pressure data of nitrobenzene + tetrabutylammonium picrate listed in Table 1. Input quantities for the treatment were relative permittivity = 24.80, $A_x = 12.25$, and $\rho = 9.66$. In the case of complete ionization of tetrabutylammonium picrate in nitrobenzene ($\alpha = 0$), the values of parameters, i.e., $w_1 = -0.565$ and $q = 0.341$ along with $\sigma = 0.004_6$ were obtained using eq 4. However, when the same equation with the revised mole fractions (eq 5) accounting for ion pairing was employed to fit the $p-x$ data, resultant parameters were noted to be as $w_1 = -0.589$ and $q = 0.338$ with $\sigma = 0.0035$. Though the improvement in the fitting of the activity data with ion pairing is not highly remarkable, it is important to note that the equations involving ion pairing should be preferred over those derived for full dissociation of salt. This is stated in view of conductance data on the system (Seward, 1958).

The value of q obtained in the above calculation is close to the ratio of molar volumes of nitrobenzene and tetrabutylammonium picrate, 0.297. A similar observation was noted in the case of tetrabutylammonium picrate + anisole. Once the experimental data on a large number of systems are available, it may then be possible to determine if PSM can successfully fit the vapor pressure data with a single parameter w_1 with q being calculated a priori. In Figure 3 are shown the deviation δ obtained from the difference of experimental data and the PSM with $\alpha \neq 0$.

We also examine our $p-x$ data using the local composition model of Chen et al. (1982) and Chen and Evans (1986), who described the contribution due to short-range interactions with the concept of local composition. The local composition concept and the Debye–Huckel equations are consistent in the sense that they both account for nonrandomness by introducing local compositions through Boltzmann-like factors. Our present treatment differs from that of Chen et al. (1982), as we have explicitly considered the ion-pair formation in our treatment of short-range interactions. We retain the expression for long-range interactions of Pitzer as such and modify the calculations for short-range interactions with ion-pair formation. The equations are based on a simple system of nitrobenzene, T^+, P^-, and $[TP]^0$. Different cells are assumed in this model: (i) the first consists of a central nitrobenzene molecule with other nitrobenzene molecules, T^+, P^-, and neutral ion pair $[TP]^0$ in its neighborhood. This type of cell follows the assumption of local neutrality; the surrounding T^+, P^- are such that the neighborhood of nitrobenzene is electrically neutral. (ii) The other kind of cell consists of either a central T^+ or P^- with nitrobenzene molecules and ions of opposite charge in its immediate neighborhood. These two cells follow the assumption of like ion repulsion: no ions of like charge exists near each other.

In short, the local mole fractions x_{ij} and x_{ii} of the species j and i, respectively, are related in the immediate neighborhood of a central species i via interaction energies as:

$$x_{ji}/x_{ii} = (x_j/x_i)G_{ji} \tag{6}$$

where the quantity G_{ji} is defined as

$$G_{ji} = \exp(\alpha\tau_{ji}) \tag{7}$$

In eq 7, τ_{ji} is the difference of energies of interaction between ji (g_{ji}) and ii (g_{ii}) pairs of species shown below:

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \tag{8}$$

The terms g_{ji} and g_{ii} are inherently symmetric, i.e., $g_{ji} = g_{ii}$. In the Chen model, the parameter $\tau_{1,TP}$ is the difference of dimensionless interaction energies between the solvent–ion and the cation–anion pair, whereas the parameter $\tau_{TP,1}$ is the difference of the dimensionless interaction energies between the ion–solvent pair and solvent–solvent pair.

We used a commercial software (Chen et al., 1984) for fitting these data. We obtain Chen parameters as $\tau_{1,TP} = 12.211 \pm 0.010$ and $\tau_{TP,1} = -8.231 \pm 0.009$ with $\sigma = 0.006$ in a_1. It is noted that both the PSM and Chen models represent the activity data with reasonable accuracy.

In extremely dilute solutions, the interaction between the cation and anion in a solvent with a low relative permittivity is stronger than the interaction between the two solvent molecules. Our reported values for binary parameters have much larger difference than those for the (Ag,Tl,Na)–NO_3–H_2O) system (Chen et al., 1982; Chen and Evans, 1986), thus suggesting strong interactions between cation and anion and greater tendency for the ions to make ion pairs in a very low concentration range.

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