J. Am. Chem. Soc. **1984**, *106*, 1973-1977 1973

Ion Pairing in a System Continuously Miscible from the Fused Salt to Dilute Solution

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Abstract: Electrostatic ion pairing is well-known for highly charged ionic systems in water or for 1–1 electrolytes in solvents of low dielectric constant. Davies first presented equations for the conductance of such systems in which the solute fraction of ion pairs reached a maximum and then decreased with further increase in concentration. This apparent "redissociation" phenomenon is investigated by experimental measurements, theory, and model calculations. The solvent activity is measured at 373 K for the system tetra-*n*-butylammonium picrate in 1-butanol for which the conductance and viscosity are known. Over the measured range from solute mole fraction 0.08 to 0.94 the activity data can be fitted without ion pairing by using a simple equation including a Debye–Hückel term and a van Laar term. But conductance data demonstrate ion pairing in more dilute solutions, and both sets of data can be fitted with a model including ion pairing. The ion distribution implied by this model is calculated. In the "redissociation" range the fraction of defined "ion pairs" does diminish, but the total probability of finding unlike ions near one another steadily increases with increasing concentration. Thus there is redissociation only in a formal sense in terms of a particular model.

In broadening the understanding of concentrated electrolytes, systems continuously miscible from a fused salt to dilute solution in polar solvent are of particular interest. Since the pure salt is clearly ionic, any ion pairing effects at lower concentration must arise primarily from electrostatic effects. Most systems for which data are available over the full composition range are aqueous, near 373 K, and show no significant ion pairing. But with lower dielectric constant one expects ion pairing and this is known to occur in many highly but not fully miscible systems. In water, ion pairing is important for higher valence salts at moderate temperature or for 1–1 salts at very high temperature. Thus a careful study of a fully miscible system showing ion pairing is of broad interest.

Seward[1] measured both conductance and viscosity for the system tetra-*n*-butylammonium picrate–1-butanol at 91 °C which is miscible over the full range. The conductance indicates substantial ion pairing in the range 0.0001–0.1 M, but the conductance–viscosity product for more concentrated solutions is similar to that for fully ionized systems. The pure fused picrate has properties typical of fully ionized fused salts. Thus it seems especially interesting to obtain activity data for this same picrate–butanol system over the full range of composition. Measurements of the vapor pressure of butanol are reported and the solvent activity calculated therefrom. These activity data are fitted to the equations corresponding to several models or theories, with and without simultaneous consideration of the conductance data, and the results are discussed with respect both to the structural implications and to the practical representation of thermodynamic properties.

Experimental Section

Chemicals. Tetra-*n*-butylammonium picrate was prepared by neutralizing tetra-*n*-butylammonium hydroxide with picric acid. The picrate salt was purified by recrystallization from ethanol and dried over P_2O_5 in a vacuum desiccator for at least 2 days before use. The observed melting point of the dry salt was 362.65–363.15 K. Spectrophotometric Grade 1-butanol (Mallinckrodt, Lot No. KHKX) was used as received.

Apparatus and Procedure. The apparatus and procedure employed in these experiments is described in detail elsewhere.[2] Briefly, Pyrex cells containing sample solutions were attached to a stainless steel valve manifold through an epoxy glass-to-metal seal. Solutions were degassed by repeated evacuation of the sample cell vapor space. The system was brought to the desired temperature in a cylindrical air-oven thermostat with the sample cell immersed in a mineral oil bath to smooth out temperature fluctuations. Both the oil bath and the sample were stirred magnetically. Sample cell temperatures were appproximately 373 K and were measured by using a calibrated 1000 ohm platinum resistance thermometer. Vapor pressures were measured by using an MKS 170 Series Baratron differential capacitance manometer; the reference side of the manometer was kept evacuated to ensure that all pressures measured were absolute solvent vapor pressures. The pressure transducer and inlet line were independently thermostated at approximately 383 K to prevent solvent condensation during the run. A separate Pyrex bulb containing pure degassed solvent allowed for prepressurization of the system dead volume to approximately the vapor pressure expected for the sample solution. This step was necessary in order to prevent bumping of the salt solution when opening the sample cell valve. Solution compositions were determined by weight after the vapor pressure measurements.

Results

If the solute AP is assumed to be completely dissociated

$$AP = A^+ + P^-$$

the mole fractions of solvent 1 and solvent 2 are

$$x_1 = n_1/(n_1 + 2n_2) \qquad x_2 = 2n_2/(n_1 + 2n_2) \tag{1}$$

where n_2 is the stoichiometric number of moles of the solute AP in the solution. Experimental compositions assuming complete solute dissociation, temperatures, observed vapor pressures, fugacities, and solvent activities are listed in Table I. Vapor pressures of pure 1-butanol at experimental temperatures were calculated by using the results of Butler, Ramchandani, and Thomson.[3] Fugacities were calculated from the vapor pressures by using the relation

$$f = p\,\exp(-Bp/RT) \tag{2}$$

where the second virial coefficient B is -1438 cm^3 mol^{-1} at 373 K.[4]

Calculations Assuming Complete Solute Dissociation

Thermodynamic properties of completely miscible aqueous electrolyte systems have been described[5,6] by using a representation for the Gibbs energy of mixing in which the electrostatic and nonelectrostatic (short-range) contributions are additive

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

The ionic strength on a mole fraction basis is

$$I_x = {}^1\!/_2 \sum x_i Z_i^2 \tag{4}$$

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0002-7863/84/1506-1973$01.50/0

Table I. Experimental Vapor Pressures and Derived Activities

T, K	x_2	p, kPa	f, kPa	f°, kPa	a_1 exptl	a_1 calcd[a]	a_1 calcd[b]
373.09	0.0800	52.56	51.29	52.12	0.984_2	0.986	0.983
373.57	0.1036	53.25	51.95	53.11	0.978_0	0.982	0.980
373.16	0.1496	51.38	50.17	52.27	0.959_7	0.973	0.972
372.89	0.2062	51.27	50.06	51.72	0.967_9	0.957	0.957
373.49	0.2500	50.72	49.54	52.95	0.935_6	0.941	0.942
372.63	0.2914	49.04	47.93	51.20	0.936_3	0.922	0.924
372.96	0.3732	46.04	45.06	51.86	0.868_9	0.875	0.876
372.91	0.4275	44.07	43.18	51.75	0.834_3	0.835	0.835
373.31	0.5469	37.89	37.23	52.57	0.708_2	0.722	0.721
372.70	0.5775	36.49	35.88	51.34	0.699_0	0.686	0.686
372.57	0.6376	31.66	31.20	51.09	0.610_7	0.611	0.610
372.87	0.7381	24.42	24.15	51.69	0.467_2	0.464	0.463
373.28	0.8197	16.95	16.82	52.31	0.321_5	0.328	0.329
373.39	0.9442	5.75	5.74	52.75	0.108_8	0.103	0.104

[a] Calculated as fully ionized. [b] Calculated with ion pairing.

where Z_i is the charge on the ith ion in protonic units, and in this case $x_i = x_2/2$ and $I_x = x_2/2$. The quantity z_2 is a van Laar composition measure

$$z_2 = x_2/(qx_1 + x_2) \qquad (5)$$

where q is the ratio b_1/b_2 sometimes taken as a volume ratio. We take q as a freely adjustable parameter. A_x is the Debye–Hückel slope on a mole fraction basis (which is larger than A_ϕ by the factor $(1000/M_1)^{1/2}$)

$$A_x = (1/3)(2\pi N_A d_1/M_1)^{1/2}(e^2/DkT)^{3/2} \qquad (6)$$

where M_1 is the solvent molecular mass, d_1 the solvent density, and D the relative permittivity on the dielectric constant. The parameter ρ is related to the hard-core diameter a by the relationship (for the mole fraction basis)

$$\rho = a(8\pi e^2 N_A d_1/M_1 DkT)^{1/2} \qquad (7)$$

In the last two equations D must be multiplied by $4\pi\epsilon_0$ for SI units (with ϵ_0 equal to the permittivity of free space).

At 373 K, we take[1] $d_1 = 0.758$ g.cm^{-3}, the dielectric constant[7,8] $D = 9.4$, and $M_1 = 74.12$ g.mol^{-1} and obtain $A_x = 21.5_8$. From eq 3 one may derive the activity of the solvent

$$\ln a_1 = \ln x_1 + w_1 z_2^2 + 2A_x I_x^{3/2}/(1 + \rho I_x^{1/2}) \qquad (8)$$

The optimum choice of the closest approach parameter ρ for this system is about 19.5; this corresponds to $a = 7.2$ Å which is very reasonable. One can take the quantity $(M_2/2N_A d_2)^{1/3} = 7.1$ Å as an estimate of this interionic distance at contact; the agreement is excellent. With this value of $\rho = 19.5$ selected by trial, the values of w_1 and q were optimized by least-squares fitting of the solvent activity data. The results are

$$w_1 = -0.419 \pm 0.062 \qquad q = 1.46 \pm 0.24$$

with a standard error of fit of 0.0091 in the solvent activity. The results of this fit are compared with the experimental values in Figure 1 and Table I. It is clear that the agreement is excellent and shows no systematic deviation between experimental and calculated values.

The Debye–Hückel term is much larger for this system than for the aqueous systems miscible to the fused salt which have been considered.[5] Indeed the marked positive departure from ideality shown on Figure 1 arises from a large positive contribution from the Debye–Hückel term diminished by a smaller negative contribution from the van Laar term. In contrast, the van Laar term was dominant for the aqueous systems with the larger dielectric constant.

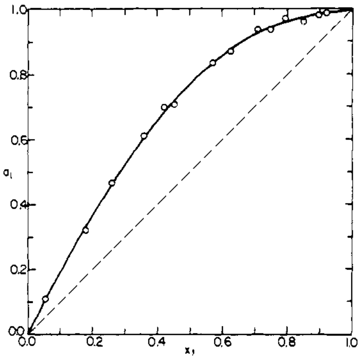

Figure 1. The activity of butanol in the system tetra-*n*-butylammonium picrate in 1-butanol with measured values and a calculated solid curve. The dashed line indicates ideal solution behavior.

The activity of the solute is

$$a_2 = x_2^2 \gamma_\pm^2 \qquad (9)$$

with the activity coefficient $\gamma_\pm$ given by

$$\ln \gamma_\pm = w_2 z_1^2 - A_x \left\{ \left(\frac{2}{\rho}\right) \ln \left(\frac{1 + \rho I_x^{1/2}}{1 + \rho/2^{1/2}} \right) + \frac{I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}} \right\} \qquad (10)$$

if the pure fused salt is the reference state. If one uses instead the infinitely dilute reference state, the solute activity coefficient becomes

$$\ln \gamma_\pm^\infty = w_2(z_1^2 - 1) - A_x \left\{ \left(\frac{2}{\rho}\right) \ln (1 + \rho I_x^{1/2}) + \frac{I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}} \right\} \qquad (11)$$

with $w_2 = w_1/q$ and $z_1 = 1 - z_2$. Values of $-\ln a_2^\infty$ referred to the infinitely dilute standard state and $-\ln a_2$ referred to the pure fused salt are given in Table II.

Conductance and Ion Pairing

Although the measurements of alcohol activity are consistent with full dissociation of the picrate salt, the conductance data are not. For the consideration of conductance in the alcohol-rich range, we assume an ion-pairing equilibrium with the ion-pair species making no contribution to the conductance. In these calculations the equations of the preceding section were generalized to include the ion-pair species. Thus, if the fraction of solute

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Table II. Calculated Activities with and without Ion Pairing

x_2	θ	$a_1{}^a$	$a_1{}^b$	$-\ln a_2{}^{\infty a}$	$-\ln a_2{}^{\infty b}$	$-\ln a_2{}^a$	$-\ln a_2{}^b$
0.05	0.201	0.990	0.987	13.766	13.997	2.418	2.364
0.10	0.107	0.983	0.981	13.578	13.831	2.230	2.199
0.20	0.055	0.959	0.959	13.303	13.582	1.954	1.950
0.30	0.038	0.918	0.919	13.044	13.329	1.695	1.697
0.40	0.031	0.857	0.857	12.786	13.070	1.437	1.438
0.50	0.026	0.771	0.771	12.529	12.811	1.180	1.179
0.60	0.023	0.659	0.658	12.275	12.555	0.927	0.923
0.70	0.022	0.522	0.521	12.027	12.306	0.678	0.674
0.80	0.020	0.362	0.362	11.787	12.067	0.438	0.435
0.90	0.020	0.185	0.186	11.559	11.841	0.211	0.209

[a] Calculated as fully ionized. [b] Calculated with ion pairing.

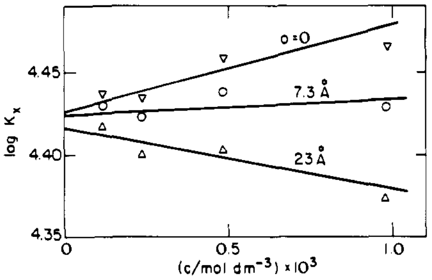

Figure 2. The ion-association constant calculated from conductance data for three values of a.

associated is θ, one can define mole fractions of free ions x_i (either + or −), of pairs x_p, and of a revised value for the solvent x_s

$$x_i = (1 - \theta)n_2/[n_1 + (2 - \theta)n_2] = I_x \tag{12a}$$

$$x_p = \theta n_2/[n_1 + (2 - \theta)n_2] \tag{12b}$$

$$x_s = n_1/[n_1 + (2 - \theta)n_2] \tag{12c}$$

Now the Gibbs energy of mixing can be appropriately revised and its derivative with respect to θ equated to zero to yield the ion-pairing equilibrium expression

$$K_x = \frac{x_p}{x_i^2} \exp\left\{2A_x\left[\frac{2}{\rho}\ln(1 + \rho I_x^{1/2}) + \frac{I_x^{1/2} - I_x^{3/2}}{1 + \rho I_x^{1/2}}\right]\right\} \tag{13}$$

The fraction ionized was calculated from the conductance data of Seward[1] by the standard method[9,10] for very dilute solutions by using the limiting Debye–Onsager slope; the resulting cubic equations were solved iteratively. For the conversion of concentration of picrate mole fraction the approximate equation $x_2 = 2M_1/1000d_1)c = 0.1953c$ was used, where M_1 and d_1 are the molecular weight and density of the alcohol solvent; thus no correlation was made for the contribution of picrate to the volume of the solution. Since the conductance measurements were made in very dilute solutions, this approximation introduces no significant error. Then values of K_x were calculated on three bases: (1) with $\rho = 0$, i.e., the limiting law, (2) with $\rho = 19.5$ ($a = 7.3$ Å) which is close to the best value for the thermodynamic data, and (3) with $a = 23$ Å, the Bjerrum value $e^2/2DkT$ as discussed below. Note that the conductance was measured at 364 K where $D = 10.0$.

Alternate values of the limiting conductance were tested, but Seward's value of 71.5 seemed best and was adopted. The resulting log K_x values for the range to 0.01 M are plotted vs. concentration in Figure 2. Extrapolation to zero concentration yields essentially the same K_x on all three bases; hence one concludes that the result $K_x = 2.65 \times 10^4$ in mole fraction or $K_a = 2.59 \times 10^3$ dm^3 mol^{-1} in concentration units is unambiguous. The uncertainty related to the scatter in the reported data is less than 2%, but Seward notes that there was a large and somewhat uncertain correction for the conductance of the pure solvent. Hence, the total uncertainty is probably larger than 2%.

If the assumptions about conductance and activity coefficients at finite concentration were correct, the apparent association constant K_x should not depend on concentration. Thus, from Figure 2 it is apparent that the alternate $a = 0$ is inadequate. The Bjerrum model $a = 23$ Å deviates in the opposite direction. As discussed below, this can be corrected by the assumption of additional conducting species such as ion triplets. While the intermediate case, using the a value consistent with the thermodynamic data, shows a small slope, it is not outside the uncertainty of the data. Thus, further refinement of the conductance treatment will not be considered here.

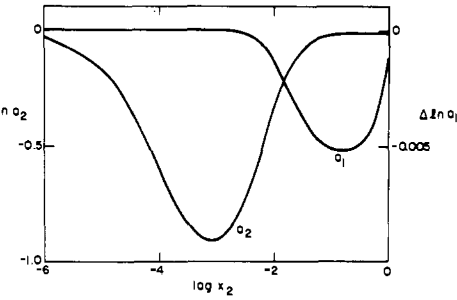

Figure 3. The change in ln a_1 and ln a_2 when ion pairing is introduced with other parameters fixed. Note the very different scales for ln a_1 and ln a_2.

With ion pairing included, the equation for the solvent activity becomes

$$\ln a_1 = \ln x_s + w_1 z_2^2 + 2A_x I_x^{3/2}/(1 + \rho I_x^{1/2}) \tag{14}$$

with I_x and x_s as defined in eq 12a and 12c, respectively.

The parameters w_1, q, and ρ were re-optimized by fitting the solvent activity values with ion pairing. First θ was determined, from eq 13 with $K_x = 2.65 \times 10^4$; then these parameters were optimized with respect to eq 14. The resulting parameters are

$$\rho = 18.5 \qquad w = -0.453 \pm 0.052 \qquad q = 1.25 \pm 0.17$$

and the values for the solvent activity are given in the last column of Table I. The standard deviation is now 0.0089 which is just slightly less than that for the equations without ion pairing.

The equation for the solute ion activity coefficient referred to the infinitely dilute state remains unchanged (eq 11), but the activity is now given by

$$a_2 = (2x_i)^2\gamma_\pm^2 \tag{15}$$

The equation for solute activity referred to the pure liquid is now complicated by the fact that θ is not necessarily zero in the pure fused salt. Thus it is best to obtain the activity related to the pure fused salt from eq 11 and 15 by difference.

Table II gives, for even mole fractions, calculated values of a_1 and of both ln a_2 and ln $a_2{}^\infty$ (referred to the fused salt and the infinitely dilute standard states, respectively). In each case values are given for the calculation with complete dissociation and for the model including ion pairing. Since both models fit the solvent activity over the full experimental range, the values of a_2 based on the real fused salt must and do agree for the more concentrated solutions. However, small differences in a_1 can cause large differences in a_2 for dilute solutions. In the limit at infinite dilution the difference between the two models becomes 0.283 in ln a_2.

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Figure 3 shows the difference in ln a_1 and in ln a_2 when ion pairing is introduced but with no change in other parameters. The correction to ln a_2 is large and negative in the range below 0.01 for x_2 as would be expected. At higher concentration, however, the fraction associated decreases rapidly, the Debye–Hückel term becomes substantial, and the correction to ln a_2 decreases to very small values. At low x_2, the correction to ln a_1 is positive but extremely small. In the range of our measurements, the Debye–Hückel term dominates and the correction to ln a_1 is negative but never large. The differences in a_1 in Tables I and II are smaller because w and q were optimized separately for each calculation. The structural picture and other implications of this model will be discussed below.

Theory and Discussion

In considering theory for the properties of this picrate–butanol system it is first important to note that the dielectric constant is relatively small, approximately 9.4 at 373 K, and consequently that the interionic electrostatic energy is larger than the thermal energy for distances less than 48 Å. Since the interionic distance at contact is only 7 Å, there is a substantial range in which the ions are separated by one or more solvent molecules yet still have an electrostatic energy of interaction several times kT. In this range the linearization approximation of Debye–Hückel theory is inadequate.

Two theoretical approaches are possible; one is an assumption of a separate ion-pair species at equilibrium with the free ions. Alternatively, one can now apply accurate statistical mechanics to the calculation of thermodynamic properties without the linearization approximation.[11-15] The corresponding calculation for conductance, however, is more difficult and, while possible in principle, is not a presently available procedure. Even for the thermodynamic properties, the direct, nonlinear methods require extensive numerical calculations. If an accurate potential model were independently available for the picrate–butanol system, such calculations would be very interesting. But with only very rough ideas concerning the short-range interparticle forces, it seems hardly worthwhile to make elaborate calculations when simpler methods are available.

The ion-pairing approach requires a division of the population of ions around a given ion into one subpopulation to be treated by linearized equations of the Debye-Hückel type and a second subpopulation or, strictly, a probability of a closely located counterion yielding an ion pair. Then an association equilibrium is assumed to determine the population of ion pairs while the remaining population is treated by Debye–Hückel methods.

Bjerrum[16] suggested this ion-pairing method almost immediately after the 1923 discovery of Debye and Hückel. He suggested that the division be made by distance from the central ion and at the radius $R_B = Z^2e^2/2DkT$. He showed that this was the minimum in the radial population density of counterions at very low concentration. While the electrostatic energy is still twice thermal energy at this radius, it is found that the equations of linearized theory give a good approximation for the more distant population as a whole. Presumably this is true because the approximation improves rapidly with increasing radius and with the screening which enters at finite concentration. Bjerrum also offered a theoretical value for the association constant K_A for the "restricted primitive model", i.e., continuation of the electrostatic potential with the macroscopic dielectric constant down to a hard-core diameter a. Since short-range forces in real systems certainly differ from this model, it is usually better to assume that the association constant itself is the parameter to be determined empirically. The dividing radius R_B (rather than the hard-core diameter a) enters the equation for the activity coefficient of the unassociated ions.

For conductance it is usually assumed[17,18] that ion pairs make no contribution and that equations for fully dissociated electrolytes apply for the separated ions again with the dividing radius R_B replacing the hard-core diameter a. In his most recent paper, however, Fuoss[19] further subdivides the ion-pair population and assumes some contribution to conductance from a less closely bound type of ion pairs.

This ion-pairing treatment is generally quite successful for very dilute solutions in solvents of dielectric constant down to about 10. At low dielectric constant, however, for even a moderate increase in concentration there is an increase above the expected conductance which Fuoss and Kraus[20] attributed to triple ions. For example, at 373 K with $D = 9.4$ the Bjerrum distance is 24 Å. Thus at 0.01 M with a central ion pair there is a random probability of 35% that either another ion or an ion pair is present with the radius R_B. If this is an ion, one has an ion triplet which contributes to conductance. For thermodynamic properties one must consider both ion triplets and quadruplets. This has been noted for 2–2 electrolytes in water.[21,22] Thus the Bjerrum division is self-consistent and generally satisfactory at very low concentration but becomes cumbersome as soon as larger ion clusters have to be included. Since we wish to consider the entire composition range to the fused salt, it is not useful.

We favor an ion-pairing approach but with a different division of populations.[23] Assume that around a test ion a Debye–Hückel distribution of other ions extends down to the repulsive force cut off at an effective radius a from a central ion, and then classify as ion pairs the excess of oppositely charged ions. The formal equations for conductance and thermodynamic properties remain the same, but the repulsive radius a enters the Debye–Hückel equation for the activity coefficient of the free ions instead of the Bjerrum radius R_B. We discuss below the ionic distribution of this basis.

In his extensive research on ion pairing, Davies[10] used a definition formally different but practically approximately equivalent to the one just described. He used a standard equation for the activity coefficient of the free ions which corresponds approximately to that for a hard-core repulsive diameter. He also showed that on this basis the fraction associated would reach a maximum for 2–2 electrolytes in water in the range 0.03–0.1 M and at even lower concentration for a case such as our picrate–butanol system. Davies showed that this was consistent with the conductance behavior.

This apparent redissociation of the ion pairs with an increase of concentration seems peculiar. Surely the probability that a positive ion has a near neighbor negative ion does not decrease with an increase in concentration. This topic is explored by calculations based on the ion-pairing model of the previous section; specifically these calculations assume $D = 9.4$, $R_B = 24$ Å, $a = 6.63$ Å, and $K_X = 2.65 \times 10^4$ at 373 K.

In considering ion populations in the Debye–Hückel theory it is convenient to define (for a symmetrical electrolyte)

$$q = [Z^2e^2/DkT(1 + \kappa a)]r^{-1} \exp[-\kappa(r - a)] \tag{16}$$

$$\kappa^2 = 8\pi Z^2e^2c/DkT \tag{17}$$

where c is the concentration of ions of one sign and the additional factor $4\pi\epsilon_0$ must be inserted in the denominator in each case for S.I. units. Then the radial distribution functions which were originally written in exponential form may be linearized to

$$g_{+-} = 1 + q \tag{18a}$$

$$g_{++} = g_{--} = 1 - q \tag{18b}$$

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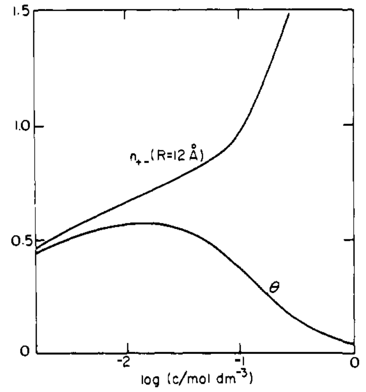

Figure 4. The total probability of finding oppositely charged ions within 12 Å as a function of concentration. Also shown is the ion-pair fraction θ.

On insertion of numerical values for the present case one finds that q is greater than unity for a considerable range of r. This leads to negative values of g_{++} which are impossible.

However, the actual linearization approximation was not made for individual distribution functions but rather for the net charge distribution which appears in the Poisson equation. Thus the only essential approximation is

$$g_{+-} - g_{++} = 2q \qquad (19)$$

While it is not without some approximation to assume the exponential form

$$g_{++} = \exp(-q) \qquad (20)$$

this cannot be significantly in error for our purpose since it yields values very near zero in the range of special interest. Hence, we assume

$$g_{+-} = 2q + \exp(-q) \qquad (21)$$

as an unlike ion distribution consistent with the activity and osmotic coefficients from a Debye-Hückel type of theory such as was used in this paper.

The total probability $n_{+-}(R)$ of finding an ion of the opposite charge between the hard-core distance 6.63 Å and radius R is the ion-pair fraction plus the product of the concentration of free ions times the volume integral of g_{+-} to R (together with a very small addition for the probability of a second ion pair within R).

This model does not distinguish contact and solvent-separated ion pairs nor does it introduce any realistic detail about short-range forces near hard-core contact. Hence it can only be expected to give a reasonable result on a somewhat coarse-grained basis. One layer of butanol solvent will occupy about 4 to 6 Å. The "ion-pair" population is that in excess of the Debye-Hückel distribution and this extends out to at least 24 Å, although it decreases rapidly with an increase in radius. Thus it seems that this calculation of n_{+-} is meaningful only for R including at least one solvent layer, i.e., about 12 Å or greater (with all of the "ion pairs" assumed to be within the 12 Å). The result is shown in Figure 4 which also shows the ion-pair fraction θ. While the ion-pair fraction decreases above 0.02 M, the actual probability of finding an ion of opposite charge increases steadily with concentration. Thus there is "redissociation" only in a formal sense. The model as a whole is reasonable and self-consistent in terms of ion distribution.

The more elaborate statistical calculations which avoid the linearization approximation yield ion distributions similar in most respects to those just described, but direct comparison is not possible because such calculations are unavailable for the parameters of this system. Features that imply triple ions have been discussed by Rossky, et al.[13] Also, it is known[12,14] that there will be oscillations in the true charge density at high concentration and that Debye-Hückel theory does not yield such oscillations. But this weakness does not seem to cause any serious problem in the calculation of thermodynamic properties. Also we note that where ion pairing has only a moderate effect on thermodynamic properties, those properties can be represented satisfactorily without the complexity of an ion-pairing equilibrium.[23]

There are very few investigations of systems at all comparable to this one. Most relevant is that of Yao and Bennion[24] on tetra-*n*-amylammonium thiocyanate in dimethyl sulfoxide where conductance and viscosity but not vapor pressure were measured. At mole fractions less than 0.5 salt the two systems show similar behavior. At higher mole fractions the conductance–viscosity product of the picrate system rises moderately but steadily to a value for the pure fused salt which is approximately equal to that at infinite dilution. This indicates essentially complete ionization of the fused salt. In contrast the conductance–viscosity product for the thiocyanate system shows a maximum near mole fraction 0.6 and then decreases with a value for the fused salt only about half of that at infinite dilution. The explanation may lie in the much smaller size of the SCN$^-$ ion as compared to the picrate. The SCN$^-$ may be able to form an ion pair with one large and flexible tetra-*n*-amylammonium ion whereas the larger picrate ion must retain several nearest neighbor cations in the pure fused salt.

Conclusions

Over most of the composition range the thermodynamic properties of the fully miscible system tetra-*n*-butylammonium picrate–1-butanol can be represented by a very simple equation including terms for ideal mixing, a van Laar term for differences in short range forces, and a Debye–Hückel term for electrostatic effects. Conductance data indicate ion pairing in very dilute solutions, and a more complex equation is developed which represents this aspect and fits even a little more accurately the thermodynamic data for higher concentration. This second equation is recommended as most accurate for all purposes. It is shown that the "redissociation" of the ion pairs with increase in concentration is a formal result of the equations but that the actual probability of finding ions of opposite charge near one another increases steadily.

Acknowledgment. We thank Dr. Albert G. Loomis for preparing the sample of tetra-*n*-butylammonium picrate. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering, Mathematics, and Geosciences of U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

Registry No. Butanol, 71-36-3; tetra-*n*-butylammonium picrate, 914-45-4.

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[24] Yao, N.-P.; Bennion, D. N. *J. Phys. Chem.* **1971**, *75*, 3586–3591.