Table III. Comparison of Arrhenius Parameters and Room Temperature Rate Constants for the Hydrogen-Abstraction Reaction by OH, NH_2, and CH_3 from Ethane, Propane, and Isobutane[a]

	log A, $M^{-1}\ s^{-1}$	E, kcal mol^{-1}	log k(300 K), $M^{-1}\ s^{-1}$
		Ethane	
OH	10.05	2.5	8.23
NH_2	8.6	7.15	3.42
CH_3	9.3	12.1	0.53
		Propane	
OH	9.85	1.3	8.90
NH_2	8.65	6.15	4.20
CH_3	8.85	11.6	0.45
		Isobutane	
OH	9.7	0.77	9.13
NH_2	8.4	4.9	4.85
CH_3	8.5	8.2	2.56

[a] Data for OH and CH_3 are from ref 1.

accuracy of the experimental determination yielding the ratio of 10 in the case of isobutane[6] and the approximations made in the above calculation, the agreement is acceptable. Note that the value calculated for n-butane is about twice that of propane, which is the same ratio as the number of secondary hydrogen atoms.

As expected, hydrogen abstraction takes place essentially on tertiary or secondary positions of the molecule. This is consistent with the good agreement between the overall activation energies determined experimentally and those calculated for a specific C-H bond. It also explains the good linearity of the Arrhenius plots since essentially a single activation energy is involved in the reaction. Even in the case of propane, where the abstraction on the primary position is significant, it is not large enough to cause a curvature of the Arrhenius plot (the activation energies measured for primary and secondary hydrogen atoms are moreover not much different).

Finally, it is interesting to compare NH_2 radicals with other radicals, particularly the isoelectronic OH and CH_3 species, in hydrogen-abstraction reactions.

Large differences in reactivity are observed between these three radicals, the reactivity of NH_2 being intermediate between those of OH and CH_3. This is shown in Table III, in which are compared the Arrhenius parameters and the rate constants at room temperature in the cases of ethane, propane, and isobutane. The difference of reactivity from one radical to other is essentially due to the large difference in the activation energies as also shown in Figure 6. The preexponential factors are similar for NH_2 and CH_3 (though slightly higher for CH_3 but perhaps not significantly). However, they are generally an order of magnitude higher for OH, which results in a very high reactivity for this radical.

The behavior found for NH_2, in the compared reactivity with OH and CH_3, is similar in both hydrogen abstraction and addition to a double bond.[5]

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Electrolytes. From Dilute Solutions to Fused Salts

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Abstract: Solutions with composition extending continuously from molecular liquids such as water to fused salts are relatively unusual but of considerable interest. Conductance and thermodynamic properties are considered for several examples. New equations for the activities of the respective components represent the data more accurately than previous treatments and delineate the similarities and differences between such systems and nonelectrolyte solutions.

Electrolyte systems extending in the liquid phase from a dilute solution in a polar molecular solvent (such as water or an alcohol) to a pure fused salt constitute an interesting but infrequently studied type. In a 1954 article with the same title as this paper, Kraus[1] summarized the information then available concerning such systems. Kraus emphasized measurements of conductance but also considered the few thermodynamic data then available for such systems. In the following 25 years, the vapor pressure and thereby the activity of water have been measured for the systems $(Li,K)NO_3-H_2O$ and $(Ag,Tl)NO_3-H_2O$ over the entire range from pure water to fused salt. In each case there is a fixed, nearly equal ion

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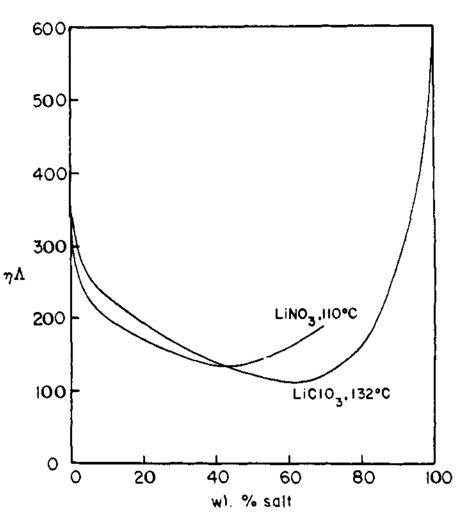

Figure 1. The conductance-viscosity product for water-salt solutions over the full range of composition.

fraction of cations so that either can be regarded as a two-component MNO_3-H_2O system. The mixing of the salts reduces the melting point and allows the experiments to be carried out at low pressure near 100 °C.

With the availability of these thermodynamic data it seemed worthwhile to examine again the nature of these novel systems. A new interpretation will be given to the thermodynamic data which has many advantages over that previously presented, although it uses a form of equation which has been commonly used for nonelectrolytes.

Conductance

Before dealing in detail with the thermodynamic data, it is desirable to review the situation with respect to conductance, both as Kraus described it and as it has changed since. The appropriate function giving a simple picture of the character of the solution is the product of the equivalent conductance and the viscosity, $\eta\Lambda$. Figure 1 shows the results for two systems from the measurements of Campbell and Paterson[2] and Campbell, Debus, and Kartzmark.[3] In the dilute aqueous solution the well-known electrostatic effects cause a reduction in conductance from its limiting value as explained by Debye and Hückel[4] and Onsager.[5] These data follow the theoretical equations for a fully ionized solute as far as they are valid, and it now appears to me, as it did to Kraus, that there is no reason to assume other than complete ionization at higher concentration. In the middle range the $\eta\Lambda$ product passes through a shallow minimum but, in the absence of an exact theory, it is not possible to draw any precise conclusions. The near constancy of the $\eta\Lambda$ product, however, suggests continued full ionization. The increase in $\eta\Lambda$ in approaching the pure fused $LiClO_3$ is striking. For the addition of a little water to the fused salt, the viscosity decreases faster than the conductance increases. The writer is not aware of any theoretical analysis of this region; such a study would be interesting.

There are also organic systems which have been investigated over the full range from dilute electrolyte solution to fused salt. An example is tetra-*n*-butylammonium picrate in *n*-butyl alcohol, measured by Seward[6] and discussed by Kraus.[1] In this case there is ion pairing in the dilute soluion range with a sharper drop in the $\eta\Lambda$ product. The minimum in $\eta\Lambda$ occurs at about 5% salt after which that product rises to about the same value as it had at infinite dilution in the alcohol solvent. Thus there appears to be a redissociation in the intermediate composition range. This redissociation puzzled Kraus but it is explained by Davies.[7]

With this brief review of the situation with respect to conductance, we turn to the thermodynamic data.

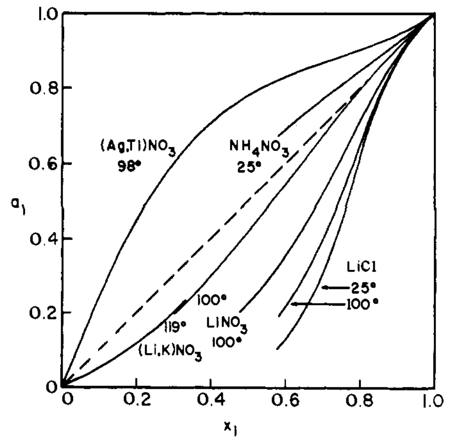

Figure 2. The activity of water for water-salt solutions over the full range of composition.

Activity. Preliminary Survey

The activity of water is given by its vapor pressure above the solution; this has been measured for $(Li,K)NO_3$-H_2O by Tripp and Braunstein,[8] for that system, for $LiNO_3$-H_2O, and for several others by Braunstein and Braunstein,[9] for LiCl-H_2O by Gibbard and Scatchard,[10] and for $(Ag,Tl)NO_3$-H_2O by Trudelle, Abraham, and Sangster.[11] Robinson and Stokes[12] summarize earlier results for other systems including NH_4NO_3-H_2O. The activity of water for many of these systems is shown in Figure 2. The composition variable is the mole fraction on an ionized basis, i.e, $x_1 = n_1/(n_1 + \nu n_2)$ where n_1 and n_2 are moles of water and salt, respectively, and ν is the number of ions in the salt. On this basis Raoult's law applies in the very dilute range, with the Debye-Hückel correction applicable as the concentration increases.

The similarity of the curves on Figure 2 to those for nonelectrolyte solutions is striking. The dashed line representing $a_1 = x_1$ can be called "ideal-solution behavior" for these systems, as it is for nonelectrolytes, but it is realized that a statistical model yielding that result would be more complex for the ionic case. Also the Debye-Hückel effect is a departure from this ideal behavior. Nevertheless, it seems worthwhile to explore the use for these systems of the simple equations for nonelectrolytes. One of the simplest and most successful had its origin in the work of van Laar[13] and has been widely used since. Prausnitz[14] discusses this and related equations as well as the contributions of Margules, Hildebrand, Scatchard, Guggenheim, and others to this topic. For the activity of either component, referenced to the pure liquid, one has

$$\ln a_1 = \ln x_1 + w_1 z_2^2 \tag{1a}$$

$$\ln a_2 = \ln x_2 + w_2 z_1^2 \tag{1b}$$

$$z_1 = n_1/[n_1 + \nu n_2(b_2/b_1)] \tag{1c}$$

$$z_2 = \nu n_2/[n_1(b_1/b_2) + \nu n_2] = 1 - z_1 \tag{1d}$$

$$w_2 = (b_2/b_1)w_1 \tag{1e}$$

Note first that, if (b_1/b_2) is unity, z_1 and z_2 reduce to the mole fractions x_1 and x_2. Then one has the even simpler equations

$$\ln a_1 = \ln x_1 + w x_2^2 \tag{2a}$$

$$\ln a_2 = \ln x_2 + w x_1^2 \tag{2b}$$

In either (1) or (2) the nonideality parameter w (sometimes written w/RT) arises from the difference between the intermolecular attraction of unlike species as compared to the mean of the intermolecular attraction for pairs of like species. The second parameter in eq 1, (b_1/b_2), is sometimes ascribed to the

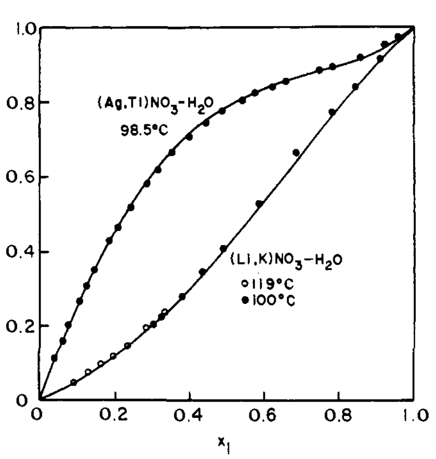

Figure 3. Comparison of the experimental activity of water with that calculated from eq 1.

ratio of the volumes of the molecules or to the ratio of molal volumes in the liquid. (Originally van Laar related b_1 and b_2 to the b quantity in the van der Waals equation, which is in turn related to the volume of the molecules, but this relationship to an approximate equation for the imperfect gas is less useful.) In some systems, especially metallic solutions, eq 1 is still quite satisfactory but (b_1/b_2) departs greatly from the ratio of molal or atomic volumes. For fused salt-water mixtures it seems best to regard (b_1/b_2) as a freely adjustable parameter and subsequently to compare the values with ratios of molal volumes.

Equation 1 was fitted to the two systems remaining liquid over the full range of composition with the results $w_1 = 1.02$, $(b_1/b_2) = 0.50$ for $(Ag,Tl)NO_3-H_2O$ and $w_1 = -0.89$, $(b_1/b_2) = 1.2$ for $(Li,K)NO_3-H_2O$. Water is component 1 and the salt component 2. For the latter system the simpler equation (2) serves almost as well with $w = -0.80$ (this implies $b_1/b_2 = 1.0$). The calculated curves based on eq 1 are compared with the experimental data in Figure 3, where it is apparent that the agreement is excellent.

This treatment of very concentrated electrolytes in a manner analogous to that of nonelectrolytes seems to me to be the simplest and most useful initial approach, but it has not been used to the writer's knowledge. A favorite method has been the use of the Brunauer-Emmett-Teller adsorption isotherm as proposed by Stokes and Robinson.[15] Here the rationale is that the fused salt can attract water molecules, presumably to the surfaces of the 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. Braunstein and Braunstein[9] and Trudelle, Abraham, and Sangster[11] summarize the results of fitting several sets of recent data to the BET equation which is

$$a_w(1 - x_w)/x_w(1 - a_w) = 1/cr + (c - 1)a_w/cr \qquad (3)$$

Here $a_w = a_1$ is the activity of water, x_w is its mole fraction on an un-ionized basis, and both c and r are empirical parameters. While this equation fits reasonably well up to $x_w = 0.65$, the fit is not so good as that for eq 1. Above $x_w = 0.65$ the BET equation is much less satisfactory. Also eq 1 and 2 have the great convenience of a simple form expressing the activity as an explicit function of the mole fraction and an equally simple expression for the activity of the fused salt component. With this preliminary survey, we now consider a more complete equation including a Debye-Hückel term.

Activity. Further Consideration

Although eq 1 gives a remarkably accurate representation over most of the composition range of the activity of water in a water-fused salt system, it becomes somewhat inaccurate for dilute solutions in water and it does not include the Debye-Hückel limiting law. Clearly electrostatic forces cause a departure from a random distribution of ions throughout the composition range except in the limit of infinite dilution. Possibly this departure from randomness is nearly constant at most compositions; this would be consistent with, but probably is not required for, the observed agreement with eq 1. In any case, the ionic distribution does become random in the limit of zero solute concentration, and it is desirable to include this aspect in a more complete equation. This can be accomplished by adding a Debye-Hückel term to eq 1. We wish to use mole fraction (on an ionized basis) as the measure of composition. Also it seems best to adopt an extended form of Debye-Hückel equation which gives some recognition to the repulsive forces between ions. The form obtained by the writer[16,17] from the pressure equation of statistical mechanics is especially simple for the solvent activity; with conversion to a mole fraction basis, the electrical contribution to the activity coefficient of the solvent becomes

$$\ln \gamma_1^{el} = 2(1000/M_1)^{1/2}A_\phi I_x^{3/2}/(1 + \rho I_x^{1/2}) \qquad (4)$$

where A_ϕ is the usual Debye-Hückel parameter (for molality and the osmotic coefficient)

$$A_\phi = (1/3)(2\pi N_0 d_w/1000)^{1/2}(e^2/DkT)^{3/2} \qquad (5)$$

I_x is the ionic strength on a mole fraction basis

$$I_x = \frac{1}{2}\sum z_i^2 x_i \qquad (6)$$

where x_i is the mole fraction of ion i. Also ρ is a parameter related to the closest approach of ions but increased by the factor $(1000/M_1)^{1/2}$ from the parameter b used on the molality basis.

For our case of a 1:1 electrolyte these equations reduce to $I_x = {}^1/_2 x_2$ and

$$\ln \gamma_1^{el} = (500/M_1)^{1/2}A_\phi x_2^{3/2}/[1 + (\rho/2^{1/2})x_2^{1/2}] \qquad (7)$$

In our earlier work[16] we found that a value of 1.2 was optimum for the "closest approach" parameter for a variety of simple electrolytes and with the use of particular forms for the terms expressing the effects of short-range forces. Conversion of the 1.2 by the factor $(1000/M_1)^{1/2}$ yields $\rho = 8.94$ on the new basis. But the expression for the effects of short-range forces is now different, eq 1; hence it seems reasonable to allow ρ to be adjusted provided that the result is of the same general magnitude. Also to maintain simplicity in equations for more complex mixed electrolytes, it is desirable that ρ should have the same value for a wide variety of salts. For the two examples considered here a somewhat larger value, 14.9 (corresponding to 2.0 on the old basis), seems quite satisfactory. A somewhat different choice may be desirable eventually, when a larger body of data can be considered.

If this expression for the electrostatic contribution is combined with eq 1, we have (for a 1:1 electrolyte)

$$\ln \gamma_1 = w_1 z_2^2 + (500/M_1)^{1/2}A_\phi x_2^{3/2}/(1 + \rho 2^{-1/2}x_2^{1/2}) \qquad (8a)$$

$$a_1 = x_1\gamma_1 \qquad (8b)$$

This expression fits the experimental data for the two systems $(Ag,Tl)NO_3-H_2O$ and $(Li,K)NO_3-H_2O$ very well with standard deviations in a_1 of 0.003 and 0.002, respectively. The parameters are $w_1 = 0.835$, $(b_1/b_2) = 0.56$ for $(Ag,Tl)NO_3-H_2O$ at 98.5 °C. For $(Li,K)NO_3-H_2O$ the data are at 119 °C near the fused salt and at 100 °C for the less concentrated solutions. Since w represents an energy divided by kT, the w values were adjusted correspondingly, with the result $w_1 = -1.124$ at 100 °C, -1.070 at 119 °C, $(b_1/b_2) = 1.0$. The

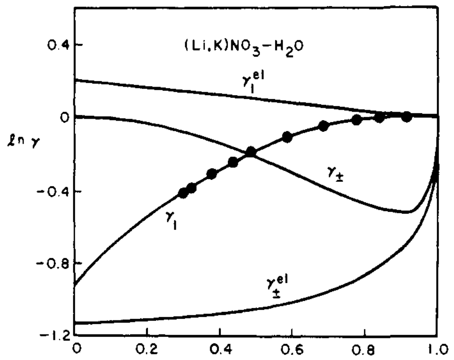

Figure 4. Activity coefficients for both water and salt for the system (Li,K)NO$_3$-H$_2$O at 100 °C. It is a numerical accident that the curves for $\gamma_\pm$ based on the pure liquid or the infinitely dilute standard states are indistinguishable on the scale of the graph.

Debye-Hückel parameter, $A_\phi = 0.461$ at 100 °C, was taken from Bradley and Pitzer.[18]

A few words are needed at this point concerning the measure of composition of salt components and the definition of their activities and activity coefficients. One cannot use the familiar molality basis because the molality becomes infinite for the pure salt. Also we wish the sum of mole fractions to be unity; hence we include the number of ions in the salt in the definition of its mole fraction in contrast to the practice for the molality of a salt. We use the mole fraction for each ion as well as that for the complete salt and for the molecular component. Then, if n_i is the number of moles of the ith ion with n_1 the number of moles of molecular component

$$x_1 = n_1/(n_1 + \sum n_j),\ x_i = n_i/(n_1 + \sum n_j) \qquad (9)$$

with the sums including all ionic species. Also the mole fraction of the salt is the sum over its constituent ions

$$x_2 = \sum x_i \qquad (10)$$

One then defines activities and activity coefficients as

$$a_1 = x_1\gamma_1 \qquad (11a)$$

$$a_i = x_i\gamma_i \qquad (11b)$$

However, one does not ordinarily measure the activity of an ion but rather that of a neutral salt; hence one must define for a simple neutral salt MX

$$a_{MX} = a_M a_X = x_M x_X \gamma_{MX}{}^2 \qquad (12)$$

If there is but a single solute, $\gamma_\pm = \gamma_{MX}$ and $x_M = x_X = \frac{1}{2}x_2$; consequently

$$a_2 = a_{MX} = x_2{}^2\gamma_\pm{}^2/4 \qquad (13)$$

Note that the factor of 4 arises because x_2 is the sum of mole fractions of both ions, whereas in the usual definition m is the molality of either ion.

For more complex types of salts such as CaCl$_2$, AlCl$_3$, etc., the formulas become more complex but in a manner analogous to those[19] for the conventional molality basis. In general for three-component systems MX-NX-1, the activities and activity coefficients can be measured separately for MX and NX if the proportion of these components is varied. But the data we are considering is for fixed (and unit) ratio of x_M to x_N; hence only the average chemical potential or the geometric mean of activity can be determined. Thus for the apparent single salt

$$a_2 = (a_M a_N a_X{}^2)^{1/2} = (x_M x_N x_X{}^2)^{1/2}(\gamma_{MX}\gamma_{NX}) = x_2{}^2\gamma_\pm{}^2/8 \qquad (14)$$

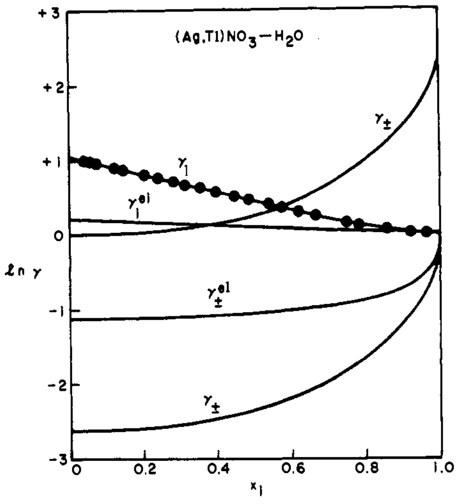

Figure 5. Activity coefficients for both water and salt for the system (Ag,Tl)NO$_3$-H$_2$O at 98 °C. Separate curves give $\gamma_\pm$ on the pure liquid standard state (above) and the infinitely dilute standard state (below).

with $x_2 = 2x_X = 4x_M = 4x_N$ and $\gamma_\pm$ the geometric mean of the activity coefficients of MX and NX.

The expression for the electrostatic contribution to the activity coefficient of the water, eq 4, is consistent with the following equation for the electrostatic excess Gibbs energy:

$$G^{ex,el}/RT = -(\Sigma n_k)(1000/M_1)^{1/2}(4A_\phi I_x/\rho)\ln(1 + \rho I_x{}^{1/2}) \qquad (15)$$

where the sum includes all species, neutral as well as ions.

The derivative yields for the activity coefficient of any species

$$\ln\gamma_i = -(1000/M_1)^{1/2}A_\phi\{(2z_i{}^2/\rho)\ln(1 + \rho I_x{}^{1/2}) + (z_i{}^2 I_x{}^{1/2} - 2I_x{}^{3/2})/(1 + \rho I_x{}^{1/2})\} \qquad (16)$$

which reduces to eq 4 for a neutral component with $z_i = 0$. For various valence types of solutes, the result given in eq 16 can be combined for the appropriate charges of the ions to obtain the mean activity coefficient. In the case of 1:1 salts, this is trivial and yields

$$\ln\gamma_\pm = -(500/M_1)^{1/2}A_\phi\{(2^{3/2}/\rho)\ln(1 + \rho 2^{-1/2}x_2{}^{1/2}) + (x_2{}^{1/2} - x_2{}^{3/2})/(1 + \rho 2^{-1/2}x_2{}^{1/2})\} \qquad (17)$$

For the complete expression for the activity coefficient of the solute, alternate standard states must be considered. If the pure fused salt exists at the temperature of interest, it is usually preferable to take it as the standard state, $\gamma_\pm = 1$, at $x_2 = 1$. Then for a 1:1 electrolyte

$$\ln\gamma_\pm = w_2 z_2{}^2 - (500/M_1)^{1/2}A_\phi\{(2^{3/2}/\rho)\ln[(1 + \rho 2^{-1/2}x_2{}^{1/2})/(1 + \rho 2^{-1/2})] + (x_2{}^{1/2} - x_2{}^{3/2})/(1 + \rho 2^{-1/2}x_2{}^{1/2})\}$$
$$\text{(pure salt standard state)} \qquad (18)$$

The standard state based on the infinitely dilute solute must be used if the pure solute is not liquid or may be desired for comparative purposes. This basis, $\gamma_\pm = 1$ at $x_2 = 0$, requires just a change in eq 18 by a constant and yields

$$\ln\gamma_\pm = w_2(z_1{}^2 - 1) - (500/M_1)^{1/2}A_\phi[(2^{3/2}/\rho)\ln(1 + \rho 2^{-1/2}x_2{}^{1/2}) + (x_2{}^{1/2} - x_2{}^{3/2})/(1 + \rho 2^{-1/2}x_2{}^{1/2})]$$
$$\text{(infinitely dilute standard state)} \qquad (19)$$

The activity-coefficient curves, including those for the electrostatic terms separately, are shown in Figures 4 and 5 for the two systems (Li,K)NO$_3$-H$_2$O and (Ag,Tl)NO$_3$-H$_2$O, respectively. Experimental points for γ_1 are shown (except those at 119 °C, for which a separate curve would be needed). It is a numerical accident that the two standard states for $\gamma_\pm$ yield results so nearly the same as to be indistinguishable on Figure 4. The meaning of these results is discussed in the next section.

Discussion

Most apparent in Figures 4 and 5 is the large electrostatic effect for $\gamma_\pm$ as compared to the small effect for γ_1 in the region of dilute aqueous solution. Thus, without the guidance from Debye-Hückel theory, one would not obtain even approximately correct curves for the activity of the salt on the infinitely dilute standard state. However, on the fused salt standard state, where $\gamma_\pm = 1$ at $x_2 = 1$, the major portion of the curve for $\gamma_\pm$ is reasonably well defined by the experiments on water activity with the simple equations of the nonelectrolyte type.

The postulate mentioned above, that the departure from random distribution of ions is roughly constant from concentrated solutions through to the pure fused salt, is supported by the relative constancy of $\gamma_\pm^{\mathrm{el}}$ over that range of composition. There is, of course, some ambiguity in the separation of the electrostatic effect; hence, this postulate cannot be proven exactly from data such as these.

It is interesting to compare volumetric data[20] with the ratio (b_1/b_2) from the activity equations. For $(Li,K)NO_3$–H_2O the ratio of molar volume of water to the average volume per ion is 0.87. The more exact equation with the Debye-Hückel term was fitted with $(b_1/b_2) = 1.0$, whereas the more approximate equation fitted rather well with either 1.2 or 1.0 for this ratio. For the system $(Ag,Tl)NO_3$–H_2O, the experimental volume ratio is 0.82 while the (b_1/b_2) values are 0.56 from eq 18 or 0.50 from eq 1. While the (b_1/b_2) ratios are in the general vicinity of the volume ratios in each case, they depart in opposite directions in the two examples. Thus other factors in addition to molecular volumes affect the (b_1/b_2) value for these systems as is the case for intermetallic solutions and to some extent even for organic molecular solutions.

Further study, both theoretical and experimental, of these fused salt–molecular liquid systems will be interesting.

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Rates of Proton Transfer between Pyridine Bases in the Gas Phase. Steric and Isotope Effects

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Abstract: The rates of proton and deuteron transfer between various pyridine bases have been studied in the gas phase by pulsed ion cyclotron resonance spectroscopy. The results show that as the reactants become increasingly substituted in the 2 and 6 positions the reaction efficiencies decrease. Some of the least efficient reactions show a small normal kinetic deuterium isotope effect. These results are interpreted in terms of a general mechanism which includes an intrinsic barrier to proton transfer. The reaction efficiencies and isotope effects are modeled using RRKM theory, and an estimate for the intrinsic barrier height is obtained.

Introduction

Proton transfer is one of the most fundamental and ubiquitous of chemical reactions. It is, therefore, not surprising that it has long been an important area of study, and a great deal of progress has been made in understanding both the thermodynamic and kinetic aspects of the reaction.[2] An increasingly important goal has been to understand the intrinsic (solvent-free) properties of the reaction as well as those properties which are primarily due to the nature of the solvent. A major thermodynamic breakthrough in this regard came with the advent of a variety of methods for studying gas-phase ion–molecule reactions. The quantitative study of acid–base equilibria in the gas phase[3] has resulted in the compilation of extensive tables[4] of intrinsic acidities and basicities. Comparison of these results with solution data has led to a much clearer understanding of substituent effects on the acidity and basicity of many major classes of compounds, as well as providing a means for quantifying solvation effects.[5] In principle, gas-phase ion–molecule kinetic studies should be of comparable value in helping to probe the nature of the potential surface for proton transfer in the absence of complications

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