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The Thermodynamic Properties of Tetraalkylammonium Halides in Acetone*

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The vapor-pressure depressions of solutions of four tetraalkylammonium halides in acetone were determined by means of a vapor-pressure osmometer. The experimental results were discussed by analyzing the relationship between the $h(=1000 \ln a_1/M_1 m+1)$ function and the concentration. The following conclusions are obtained: tetraalkylammonium salts are dissociated in acetone, and the thermodynamic behavior of the dissociated species is described by the Debye-Hückel-Onsager limiting formula with sufficient accuracy, where the undissociated species are assumed to behave ideally.

Except for $(n\text{-Bu})_4\text{NCl}$, the dissociation constants determined by the present work are in good agreement with those found in the literature, which were determined conductometrically.

In our previous papers,[1,2] we presented the results of our thermodynamic study of solutions of various strong electrolytes in such solvents as acetone, methanol, ethanol, ethyl methyl ketone, and *N,N*-dimethylformamide. The activities of solvents in these solutions were determined by vapor-pressure osmometry, and the unusual behavior of the activity coefficients of solutes in the vicinity of infinite dilution derived from those of solvents was ascribed to existence of an association or a dissociation equilibrium.

In the present paper, the results of a similar study of solutions of a series of tetraalkylammonium salts in acetone will be presented.

Theoretical

In vapor-pressure osmometry, the activity of a solvent in the solutions, a_1, is related to the change in electrical resistance, Δr, of the thermistor by the following equation:

$$\Delta r = \frac{BrR}{\Delta H} \ln a_1 = K_e \ln a_1 \tag{1}$$

where B is the thermistor-constant; r, the electrical resistance of the thermistor; R, the gas constant, and ΔH, the enthalpy change in the evaporation of the pure solvent. The proportional constant, K_e, is determined by measurement with a standard substance, the activity of which is known.

If the dissolved salt, MX, is dissociated into the ions, M^+ and X^-, as:

$$\text{MX} \rightleftharpoons \text{M}^+ + \text{X}^- \tag{2}$$

the activities of undissociated salt and ions are related to the activity of the solvent by the Gibbs-Duhem equation as:

$$N_1 \mathrm{d} \ln a_1 + m_2 \mathrm{d} \ln a_2 + m_3 \mathrm{d} \ln a_3 + m_4 \mathrm{d} \ln a_4 = 0 \tag{3}$$

where a_2, a_3, and a_4 are the activities of MX, M^+, and X^- respectively, N_1 is the mole-number of the solvent $(=1000/M_1)$, and m_2, m_3, and m_4 are the molalities of MX, M^+, and X^- respectively.

In order to calculate the activity of the solute from that of the solvent by using the Gibbs-Duhem equation, a function, h, defined as:

$$h = \frac{1000 \ln a_1}{M_1 m} + 1 \tag{4}$$

is usually used. Here, m is the molal concentration of the added solute. The apparent activity of the added solute a_2', is given by the integration of h as:

$$\ln \frac{a_2'}{m} = -h - \int_0^m \frac{h}{m} \mathrm{d}m \tag{5}$$

The unusual behavior of the h/m function of strong electrolytes in organic solvents at an infinite dilution has been fully discussed in our previous papers.[1,2]

Experimental

The lowering of the vapor pressure of a solution was measured by means of a vapor-pressure osmometer, Hitachi-Perkin-meter, Type 115. When the concentrations of the solutions were in the range from *ca.* 1×10^{-3} to 30×10^{-3} mol/kg. solvent, the reading of the meter became stable within 5 min after the solution was dropped. As the standard substance for the determination of the K_e constant, a standard sample of benzyl supplied by Nissei Sangyo Co., Ltd., was used. The tetraalkylammonium salts used were $(n\text{-Pr})_4\text{NI}$, $(n\text{-Bu})_4\text{NCl}$, $(n\text{-Bu})_4\text{NI}$, and $(n\text{-Bu})_4\text{NBr}$. The former three were supplied by Nakarai Chemicals Co., Ltd., and the last one, by Tokyo Kasei Co., Ltd. The guaranteed pure-grade reagents were used without further purification. The acetone, solvent, used was obtained by drying and distilling the guaranteed pure-grade commercial product by the usual method. The measuring temperatures were 40.3 °C for all samples and furthermore, 43.8 and 33.3 °C for benzyl and $(n\text{-Bu})_4\text{NI}$.

Results and Discussion

As an illustration, the plots of Δr against m for $(n\text{-Bu})_4\text{NI}$ and benzyl, the standard sample, at the temperatures of 33.0, 40.3, and 43.8 °C are shown in Fig. 1. As may clearly be seen in Fig. 1, the plots of $(n\text{-Bu})_4\text{NI}$ do not fall on the straight lines of benzyl, the activity coefficient of which is believed to be unity. As has been reported in the previous paper,[1] Eq. (1) holds true under the conditions of thermodynamic equilibrium. The value of K_e empirically obtainable is, however, that of the steady state, which we will designate as K_s hereafter. The K_s/K_e ratio was examined for benzyl, the standard sample. K_e was obtained from the data of the heat of vaporization of the solvent, ΔH, and the noted value of the thermistor-constant, B. The results are shown in Table 1. As may be seen in Table 1, the values of the K_s/K_e ratio are nearly constant at these temperatures. On the basis of these

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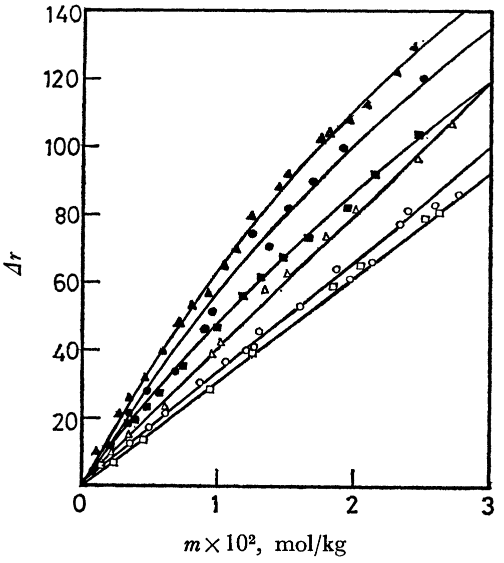

Fig. 1. Relationships between h and the concentration for benzil and $(n\text{-Bu})_4\text{NI}$ at three different temperatures.
□ benzil at 43.8 °C, ○ benzil at 40.3 °C,
△ benzil at 33.3 °C, ■ $(n\text{-Bu})_4\text{NI}$ at 43.8 °C,
● $(n\text{-Bu})_4\text{NI}$ at 40.3 °C, ▲ $(n\text{-Bu})_4\text{NI}$ at 33.3 °C

TABLE 1. K_s, K_e AND K_s/K_e at THREE DIFFERENT TEMPERATURES

	33.3 °C	40.3 °C	43.8 °C
$K_s \times 10^4$	7.11	5.79	5.38
$K_e \times 10^4$	7.38	5.84	5.22
K_s/K_e	0.96	0.99	1.03

results, we assume that present results can be used as the thermodynamic standard values at all temperatures.

As has been reported in the previous papers,[1,2] the plots of h/m against m show the existence of dissociation when $\lim_{m\to 0} h/m = -\infty$ and of association when $\lim_{m\to 0} h/m = +\infty$. The plots of h/m vs. m are, however, not adequate for the curve-fitting to determine the activity coefficients, since the errors become larger when m approaches zero. In the present paper, therefore, the plots of h vs. m are used for this purpose.

In Fig. 2, the plots of h against m at 40.3 °C are shown. The value of h is, as may be seen in Figs. 2 and 3 in the $-1 \leq h \leq 0$ range, which shows the existence of a dissociation equilibrium.

According to the Gibbs-Duhem equation, the behavior of h at low concentrations may be formulated on the basis of the following assumptions:

(I) There exists neither dissociation nor association, and the activity coefficient of the solute is unity over all the concentration range. Then:

$$\ln a_1 = -\frac{m}{N_1} \tag{6}$$

and

$$\lim_{m\to 0} h = 0 \tag{7}$$

(II) There exists a dissociation equilibrium. The activity coefficients of MX, M^+, and X^-, γ_2, γ_3, and γ_4, are all unity. Then (see Appendix)

$$h = \frac{K - \sqrt{K^2 + 2mK}}{2m} \tag{8}$$

and:

$$\lim_{m\to 0} h = -1 \tag{9}$$

where K represents a dissociation constant.

(III) The activity coefficient of MX, γ_2, is unity, while those of the dissociated ions, γ_3 and γ_4, obey the Debye-Hückel-Onsager limiting formula. Then (see Appendix):

$$h = \frac{1}{m}\left\{m_4 - \frac{2A(\sqrt{m_4})^3}{3}\sigma(x)\right\} \tag{10}$$

$$\sigma(x) = \frac{1}{x^3}\left\{(1+x) - 2\ln(1+x) - \frac{1}{(1+x)}\right\} \tag{11}$$

$$x = Ba_0\sqrt{m} \tag{12}$$

$$m_4 = \frac{-K + \sqrt{K^2 + 4mK\gamma_\pm^2}}{2\gamma_\pm^2} \tag{13}$$

$$\ln \gamma_\pm = -\frac{A|Z_1Z_2|\sqrt{m_4}}{1 + Ba_0\sqrt{m_4}} \tag{14}$$

(IV) The activity coefficient of the undissociated

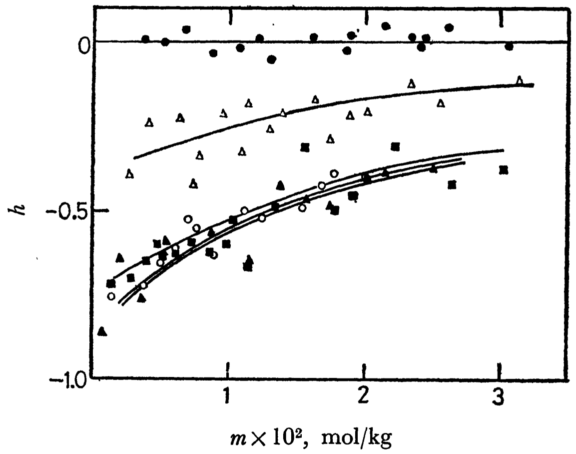

Fig. 2. Relationships between h and the concentration at 40.3 °C.
● benzil, ■ $(n\text{-Bu})_4\text{NBr}$, △ $(n\text{-Bu})_4\text{NCl}$
▲ $(n\text{-Bu})_4\text{NI}$ ○ $(n\text{-Pr})_4\text{NI}$

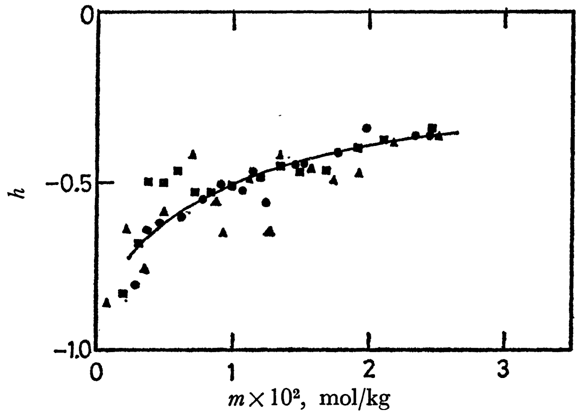

Fig. 3. Relationships between h and the concentration for $(n\text{-Bu})_4\text{NI}$ at three different tempertures.
■ at 43.8 °C, ▲ at 40.3 °C, ● at 33.3 °C

molecule, γ_2, is also not unity. Then (see Appendix):

$$h = \frac{1}{m}\left\{\frac{1}{2}\beta_2 m_2^2 - \frac{2}{3}\beta_3 m_2^3 - m_4 + \frac{2A(\sqrt{m_4})^3}{3}\sigma(x)\right\} \tag{15}$$

$$\ln \gamma_2 = -\beta_2 m_2 + \beta_3 m_2^2 + \cdots \tag{16}$$

$$m_2 = m - m_4 \tag{17}$$

As may clearly be seen in Fig. 2, the (I) assumption is not satisfied in the present results. Most strictly speaking, the behavior of the solutes in solution must be analyzed on the basis of the (IV) assumption. In the present work, however, in order to determine the dissociation equilibrium constant, the curve-fitting was attempted by using Eq. (8) or (9) because of the difficulties in calculation and the obscurities of the parameters in Eq. (15) in their physical meanings. The calculations were carried out by means of a computer, HITAC 10. The calculated values of the dissociation constants obtained from either Eq. (8) or (10) are shown in Tables 2 and 3. The numerical values of a_0 appearing in Eqs. (12) and (14) are those of Evans *et al.*[3] ,obtained from the electric conductivity measurements. Table 4 shows the means errors for the h function, $|h_{\text{exp}} - h_{\text{theor}}|$.

TABLE 2. DISSOCIATION CONSTANTS K IN ACETONE AT 40.3 °C

	Eq. (8)	Eq. (10)
$(n\text{-Bu})_4\text{NCl}$	6.4×10^{-4}	5.5×10^{-4}
$(n\text{-Bu})_4\text{NBr}$	6.2×10^{-3}	4.5×10^{-3}
$(n\text{-Bu})_4\text{NI}$	5.6×10^{-3}	4.0×10^{-3}
$(n\text{-Pr})_4\text{NI}$	6.8×10^{-3}	4.4×10^{-3}

TABLE 3. DISSOCIATION CONSTANTS K OF $(n\text{-Bu})_4\text{NI}$ IN ACETONE

	Eq. (8)	Eq. (10)
33.3 °C	5.4×10^{-3}	3.9×10^{-3}
40.3 °C	5.6×10^{-3}	4.0×10^{-3}
43.8 °C	4.6×10^{-3}	3.3×10^{-3}

TABLE 4. MEAN ERRORS FOR THE h FUNCTION ($=|h_{\text{exp}} - h_{\text{theor}}|$) IN ACETONE AT 40.3 °C

	Eq. (8)	Eq. (10)
$(n\text{-Bu})_4\text{NCl}$	0.042	0.041
$(n\text{-Bu})_4\text{NBr}$	0.053	0.048
$(n\text{-Bu})_4\text{NI}$	0.064	0.060
$(n\text{-Pr})_4\text{NI}$	0.032	0.030

As may be seen in Tables 2, 3, and 4, Eqs. (8) and (10) showed almost no significant difference in the values of the equilibrium constant and of h. Therefore, it can not be decided from the present results whether the activity coefficient of the undissociated molecule is unity or not.

Table 5 compares our values of the dissociation constant obtained from Eq. (10) and those found in the literature[4,5] obtained from the electric conductivity measurements. The agreement among them is satisfactory except for $(n\text{-Bu})_4\text{NCl}$.

TABLE 5. COMPARISON OF THE DISSOCIATION CONSTANTS K BY THE PRESENT WORK WITH THOSE BY THE CONDUCTOMETRY

	Present work	Kraus *et al.*[4,5]	Evans *et al.*[3]
$(n\text{-Bu})_4\text{NCl}$	0.55×10^{-3}	2.28×10^{-3}	2.33×10^{-3}
$(n\text{-Bu})_4\text{NBr}$	$4.5\ \times10^{-3}$	3.29×10^{-3}	3.51×10^{-3}
$(n\text{-Bu})_4\text{NI}$	$4.0\ \times10^{-3}$	6.48×10^{-3}	6.45×10^{-3}
$(n\text{-Pr})_4\text{NI}$	$4.4\ \times10^{-3}$	4.98×10^{-3}	5.75×10^{-3}

In the above comparison, the following two points were taken in consideration. First: in the electric conductivity measurements reported in the literature,[4,5] the concentration was given in terms of molarity, whereas that in our present result in terms of molality. The effect of this difference in the concentration on the final result is, however, considered not to be significant. Second: in Table 5, the measuring temperature of our present data is 40.3 °C, while that of the conductivity measurements is 25 °C. The effect of these temperature differences is also not taken into account since the temperature dependence of the equilibrium constant of the tetraalkylammonium salts in methanol reported by Kay *et al.*[6] is not very large.

Conclusion

Tetraalkylammonium salts dissolved in acetone are dissociated. The equilibrium constant of dissociation was determined on the assumption that the behavior of dissociated ions is represented by the Debye-Hückel-Onsager limiting formula. The extraordinarily small value in the equilibrium constant of $(n\text{-Bu})_4\text{NCl}$ can not be explained at present.

References

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Appendix

Derivation of Eq. (8): In the case of the (II) assumption, $a_2 = m_2$, $a_3 = m_3$, and $a_4 = m_4$ as well as $m = m_2 + m_4$ and $m_3 = m_4$. The substitution of these relations into Eq. (3) gives, after integration:

$$\ln a_1 = -\frac{1}{N_1}(m + m_4) \tag{1a}$$

On the other hand, from the equation of the dissociation constant:

$$K = \frac{m\alpha^2}{1-\alpha} = \frac{m_4^2}{m - m_4} \tag{2a}$$

we obtain this relation:

$$m_4 = \frac{-K+\sqrt{K^2+4mK}}{2} \tag{3a}$$

On combining Eqs. (1a) and (3a) with Eq. (4), we obtain Eq. (8).

Derivation of Eq. (10): In the case of the (III) assumption, Eq. (3) reduces to:

$$N_1 \mathrm{d} \ln a_1 + \mathrm{d}m_2 + 2\mathrm{d}m_4 + 2m_4 \mathrm{d} \ln \gamma_\pm = 0 \tag{4a}$$

where $\gamma_\pm = (\gamma_3 \gamma_4)^{1/2}$.

By substituting Eq. (13) in Eq. (4a) and intergrating the equation, we obtain:

$$\ln a_1 = -\frac{1}{N_1}\left\{m_2 + 2m_4 - \frac{2A(\sqrt{m_4})^3}{3}\sigma(x)\right\} \tag{5a}$$

On combining Eq. (5a) with Eq. (4), we obtain Eq. (10).

Derivation of Eq. (15): we assume, for the activity coefficient, Eq. (16). Calculations similar to those for the derivation of Eq. (9) leads us to Eq. (15).