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The Study of Solutions of Alkali Halides in Acetone by Means of Vapor-pressure Osmometry and Conductometry

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Vapor-pressure depressions and electric conductivities at 40.3 °C have been measured for LiCl, LiBr, NaI, KI, and RbI in acetone. The greatest care has been taken to minimize the contact of salts and their solutions with air. In order to account for the data of vapor-pressure osmometry (VPO) for lithium salts in acetone, the dissociation-association equilibria of the salts, MX, expressed as

$$M^+ + X^- \rightleftharpoons MX \rightleftharpoons 1/2(MX)_2$$

are proposed. The analysis of the conductance data of LiCl and LiBr, without considering the dimerization of the salts, leads to irrationally large values of the ionic association constants. For LiCl, NaI, and KI, VPO and conductometry give similar values of the dissociation constants, while for LiBr and RbI the agreement is not so satisfactory, though still within a factor of ten.

In a series of papers,[1–4] the vapor-pressure depression of various electrolytes in non-aqueous solutions has been measured by means of a vapor-pressure osmometer (VPO), and the concentration dependence of the activities of the salts has been analyzed, assuming the existence of a dissociation equilibrium.

In the first paper[1] (I) of this series, however, it has been reported that some lithium salts show an anomalous behavior in their acetone solutions. In order to account for it, it was assumed that an association equilibrium is present between the neutral salt molecules and their dimers.

In the present paper, the vapor-pressure depression of LiCl and LiBr in acetone is measured. Great care is taken to prevent moisture from coming in contact with the samples and their solutions, and measurements of the electric conductivity are also carried out in order to examine the existence of the dissociated ions. In order to account for the present data of VPO for lithium salts in acetone, an assumption of the existence of dissociation-association equilibria is proposed. Measurements of the VPO and conductometry for such salts as NaI, KI, and RbI are also made for the sake of reference.

Theoretical

When a salts, MX, dissolved in a non-aqueous solvent exhibits two-step equilibrium of dissociation and association as

$$M^+ + X^- \overset{K_d}{\rightleftharpoons} MX \overset{K_a}{\rightleftharpoons} 1/2(MX)_2 \tag{1}$$

the Gibbs-Duhem equation becomes

$$\ln a_1 = -(1/N_1)(m_2+2m_4+m_d+2\int_0^{m_4} m_4\,\mathrm{d}\ln\gamma_4), \tag{2}$$

$$\begin{aligned} m_3 &= m_4 = m\alpha, \\ m_2 &= m(1-\alpha-2\beta), \\ m_d &= m\beta, \end{aligned} \tag{3}$$

where

a_1: the activity of the solvent,

N_1: the mole number of 1 kg of the solvent,

m: the molality of the salt as-a-whole,

m_2: the molality of undissociated or unassociated salt, MX,

m_3, m_4: the molalities of the M^+ and X^- ions, respectively,

m_d: the molality of the dimer, $(MX)_2$,

α, β: the degrees of dissociation and association respectively,

γ_4: the mean activity coefficient of the ions,

K_d: the equilibrium constant of dissociation,

K_a: the equilibrium constant of association.

In Eq. 2, the activity coefficients of MX and $(MX)_2$ are assumed to be unity. If we assume that the activity coefficients of the ions are represented by the Debye-Hückel limiting law, we obtain

$$2\int_0^{m_4} m_4\,\mathrm{d}\ln\gamma_4 = -\frac{4.604A}{3d_0}(\sqrt{m_4 d_0})\,\sigma(x), \tag{4}$$

$$x = Ba_0\sqrt{m_4 d_0}, \tag{5}$$

$$\sigma(x) = \frac{3}{x^3}\left\{(x+1) - \frac{1}{x+1} - 2\ln(x+1)\right\}. \tag{6}$$

The notations in these equations are shown in the preceding paper[4] in detail. As in the previous papers, a function, h, defined as

$$h = \frac{N_1 \ln a_1}{m} + 1, \tag{7}$$

was used for the analysis of the experimental results.

Experimental

Materials. LiCl, LiBr, KI, and RbI used were guaranteed pure-grade reagents supplied by the Merck Co., Ltd. (Germany). Before use, the salts were dried over a period of five days in a vacuum oven at 50 °C with molecular sieves 3 A (1/8 in. pellects). The molecular sieves were renewed each day. The dryness reached by this method was much the same as that obtained by heating in an oven at temperatures as high as 400 °C. The method used in preparing acetone, KCl, and conductivity water was the same as reported in the preceding paper.[4] To avoid the contact of salts and their solutions with moisture in the air, a dry box filled with nitrogen gas was used, as before.

Conductometry and Vapor-pressure Osmometry. The experimental methods were reported in the preceding paper[4] in detail. The measurements were made at 40.3 °C for

Table 1. *h* values of alkali halides in acetone at 40.3 °C

$m\times10^2$	*h*	$m\times10^2$	*h*	$m\times10^2$	*h*	$m\times10^2$	*h*
LiCl		LiCl		LiBr		KI	
0.0719	−0.1928	1.2558	0.0868	1.6477	−0.1251	0.1418	−0.8135
0.0986	0.0707	1.2891	0.1127	1.6552	−0.1279	0.2230	−0.7897
0.1021	−0.0137	1.5049	0.1299	1.6615	−0.1069	0.3729	−0.6725
0.1026	−0.1806	1.5152	0.1105	1.8049	−0.1145	0.3813	−0.6466
0.1033	−0.0015	1.5259	0.1206	1.8110	−0.0951	0.5525	−0.6156
0.1143	−0.1121	1.5774	0.1212	2.0080	−0.0872	0.5901	−0.5777
0.1268	−0.0957	1.6652	0.1178	2.0277	−0.1131	0.7691	−0.5549
0.1271	0.0002	1.7732	0.1182	2.0434	−0.1022	0.7786	−0.5185
0.1362	−0.1933	2.0600	0.1520	2.0842	−0.0849	1.0047	−0.5092
0.1439	−0.0888	2.0862	0.1471	2.2317	−0.0744	1.0581	−0.4888
0.1491	−0.1103	2.1291	0.1546	2.2862	−0.0950	1.2344	−0.4764
0.1844	−0.0823	2.3802	0.1829	2.4141	−0.0686	1.2702	−0.4501
0.1898	−0.0121	2.3888	0.1710	2.4835	−0.0921	1.3015	−0.4716
0.1993	−0.1122	2.4773	0.1851	2.5070	−0.0623	1.3102	−0.4574
0.2010	−0.0590	2.5625	0.1799	2.5194	−0.0817	1.5817	−0.4351
0.2244	−0.0801	2.6041	0.1885			1.6475	−0.4413
0.2477	−0.0622			NaI		1.7746	−0.4074
0.2683	−0.0905	LiBr		0.2017	−0.7761	1.7848	−0.4242
0.2719	−0.0870	0.1802	−0.4139	0.3666	−0.6852	2.0395	−0.3898
0.2748	−0.0973	0.2177	−0.3846	0.3828	−0.7000	2.0419	−0.3983
0.2903	−0.0754	0.2432	−0.2954	0.5826	−0.6134	2.2624	−0.3890
0.3401	−0.0169	0.3472	−0.3026	0.5852	−0.6262	2.2713	−0.3846
0.3896	−0.0243	0.3618	−0.2988	0.8112	−0.5740	2.4953	−0.3646
0.3989	−0.0224	0.4961	−0.2189	0.8176	−0.5437	2.5285	−0.3572
0.4151	0.0105	0.5582	−0.2538	1.0322	−0.5405		
0.4195	0.0347	0.5666	−0.2343	1.0708	−0.5044	RbI	
0.5002	−0.0104	0.6768	−0.2228	1.2558	−0.5016	0.1692	−0.8058
0.5190	0.0091	0.7415	−0.2102	1.2706	−0.4772	0.1782	−0.7880
0.5872	0.0085	0.7828	−0.2007	1.2775	−0.4742	0.3220	−0.6744
0.6129	−0.0031	0.9860	−0.1619	1.3679	−0.4844	0.3602	−0.6494
0.6271	−0.0040	0.9910	−0.1781	1.5909	−0.4602	0.3957	−0.6509
0.7915	0.0664	1.0036	−0.1680	1.6859	−0.4305	0.5794	−0.5844
0.8169	0.0592	1.0224	−0.1783	1.7895	−0.4403	0.6053	−0.5869
0.8181	0.0499	1.1772	−0.1439	1.9047	−0.4199	0.6277	−0.5624
0.8188	0.0651	1.1829	−0.1569	1.9961	−0.4230	0.8081	−0.5303
0.8274	0.0533	1.2504	−0.1550	2.0510	−0.4036	0.8247	−0.5160
0.9281	0.0414	1.2850	−0.1501	2.2351	−0.4150	1.0292	−0.4905
1.1032	0.0811	1.3624	−0.1411	2.2814	−0.3927	1.0474	−0.4703
1.1819	0.0922	1.3716	−0.1162	2.4623	−0.3972	1.2484	−0.4395
1.1913	0.0696	1.4618	−0.1234	2.5464	−0.3731	1.2622	−0.4378
1.2262	0.0985	1.4815	−0.1392	0.1978	−0.7780	1.2716	−0.4504
1.2549	0.0979	1.5820	−0.1064			1.3027	−0.4453

both methods.

Results and Discussion

The numerical values of *h* obtained by the VPO at 40.3 °C for the salts, NaI, KI, RbI, LiCl, and LiBr, are listed in Table 1, while the plots of *h vs.* the molality, *m*, are shown in Figs. 1 and 2. The profiles of the plots are similar to those reported in the preceding paper.4) It should be noted, however, that the values of *h* for LiCl are positive at the concentrations higher than 3×10^{-3} mol kg^{-1}.

In the earlier paper (I), the values of h/m (not *h*) were plotted against *m*, and the curves obtained for LiCl and LiBr showed a tendency for h/m to increase with decrease in *m* at low concentrations. To account for this result, we assumed that an equilibrium

$$2\mathrm{MX} \rightleftharpoons (\mathrm{MX})_2$$

prevails at these concentrations. According to this assumption,

$$\lim_{m\to0}\frac{h}{m} = K_\mathrm{a}.^{8)}$$

In this paper, on the contrary, *h* tends to $-\infty$ at $m\to0$. This discrepancy is probably due to the in-

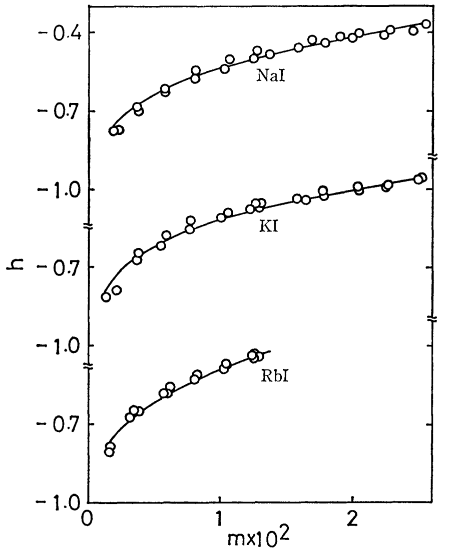

Fig. 1. Relationships between h and concentration for NaI, KI, and RbI at 40.3 °C.

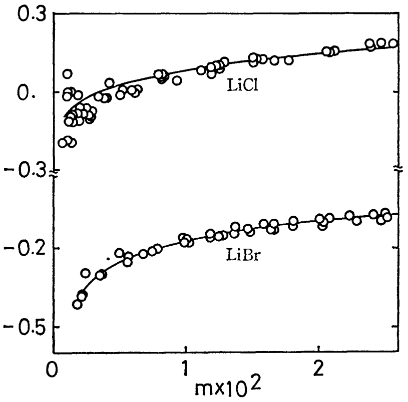

Fig. 2. Relationships between h and concentration for LiCl and LiBr at 40.3 °C.

TABLE 2. K_a AND K_d FOR LiCl AND LiBr (40.3 °C IN MOLALITY SCALE)

	$K_d \times 10^3$	$K_a \times 10^3$	Standard deviation for the h function
LiCl	0.00952	18.8	0.047
LiBr	0.432	4.19	0.015

TABLE 3. DISSOCIATION CONSTANT OF NaI, KI, AND RbI (40.3 °C IN THE MOLALITY SCALE)

	$K_d \times 10^3$	β_2	Standard deviation for the h function
NaI	10.99	29.6	0.017
KI	8.64	22.2	0.022
RbI	10.00	80.9	0.019

TABLE 4. CONDUCTANCE PARAMETERS FOR ACETONE-ALKALI HALIDE SYSTEMS (Λ IN Ω^{-1} cm^2 mol^{-1})

	This research (40.3 °C)		Literature (25 °C)	
	K_A	Λ_0	K_A	Λ_0
LiCl	2114×10^2	227.1	3030×10^2	214 (6)
LiBr	5146	219.6	4570	194 (6)
NaI	157	218.7	160	184.4(7)
KI	153.5	218.0	110	197.3(7)
			179.5	197.5(6)
RbI	254.8	224.3		

TABLE 5. COMPARISON OF DISSOCIATION CONSTANTS BY VPO AND CONDUCTOMETRY AT 40.3 °C (IN TERMS OF MOLALITY)

	VPO	Conductometry
LiCl	0.00952×10^{-3}	0.00617×10^{-3}
LiBr	0.432×10^{-3}	0.253×10^{-3}
NaI	10.99×10^{-3}	8.31×10^{-3}
KI	8.64×10^{-3}	8.49×10^{-3}
RbI	10.00×10^{-3}	5.11×10^{-3}

complete drying of the lithium salts in the previous experiments.

In order to represent the experimental curves for LiCl and LiBr, we assume the two-step equilibria of Eq. 1. The dissociation equilibrium of the left-hand side is necessary in order to represent the shapes of curves at low concentrations, and the association equilibrium is inevitable to account for the fact that h is positive at moderate concentrations.

We have tried to estimate the most probable values of K_a and K_d by means of curve-fitting Eqs. 2, 3···, and 7. The curve-fitting was made by the method of non-linear least-squares. The results are shown in Table 2.

The measurements for NaI, KI, and RbI were also made for comparison. In the preceding paper,[4] the data were analyzed on the basis of the assumption that only the dissociation equilibrium exists, and the deviation from the ideality of undissociated molecules was taken in account. Similar analyses were carried out in the present investigation; the results are shown in Table 3, where β_2 is a parameter, given in the preceding paper, for compensating for the non-ideal behavior of the MX species in solution (not β in Eq. 3). The curves in Figs. 1 and 2 are theoretical ones calculated by the use of the parameters shown in the tables. The agreements with the experimental values are satisfactory.

The electric conductances of the acetone solutions of LiCl, LiBr, NaI, KI, and RbI were measured at 40.3 °C. The results were analyzed by the use of Shedlovsky's equation.[5] The parameters, K_A and Λ_0, in Shedlovsky's equation, as obtained from our experimental results, are shown in Table 4, where those at 25 °C found in the literature[6] are also given for comparison. Shedlovsky's equation is

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{C\Lambda f_{\pm}{}^2 S(z) K_A}{\Lambda_0{}^2}, \qquad (8)$$

$$S(z) = \left\{\frac{S\sqrt{C\Lambda}}{2\Lambda_0{}^{3/2}} + \left[1 + \left(\frac{S\sqrt{C\Lambda}}{2\Lambda_0{}^{3/2}}\right)^2\right]\right\}^2, \qquad (9)$$

$$\ln f_{\pm} = -\frac{4.606A\sqrt{C\alpha}}{1+Ba_0\sqrt{C\alpha}}, \qquad (10)$$

where Λ_0 is the equivalent conductance at an infinite dilution, K_A; the association constant $(=1/d_0K_d$, d_0 being the density of the solvent) has its usual meaning, and α is the degree of dissociation.

The values of K_A thus obtained are converted to K_d and are shown in Table 5, together with the values from VPO. In the table, the agreement between the values from VPO and conductometry is really satisfactory for LiCl, NaI, and KI. For LiBr and RbI, the agreement is not satisfactory, but it is still within a factor of ten.

In order to account for the profiles of the *h-m* plots for LiCl and LiBr, it is assumed that an equilibrium of the monomer-dimer exists at the higher concentration. The conductometry data can tell nothing about the presence of the dimer because of its electrically neutral nature. It should be emphasized here that the study with VPO is essentaılly necessary for the study of the solution properties of non-aqueous solutions.

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8) Equation 13 in (I) should read $h/m=K_a+\cdots$.