

# Ionic Association and Ion-Solvent Interactions. The Conductance of Lithium Bromide in Acetone-Water Mixtures at 15—35 °C

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The electrical conductance of lithium bromide in several aqueous acetone mixtures containing from  $5 \times 10^{-3}$  to 20 wt-% water at 15, 25, and 35 °C has been studied. The data were treated by means of the conductance equation of Fuoss and Hsia in the form of Fernández-Prini to obtain the ion pair association constant,  $K_A$ , and the limiting molar conductivity,  $\Lambda_0$ . The minimum center-to-center distance of the ions in the ion pair, derived according to the Gilkerson-Fuoss and Bjerrum theories, and the solvation energies of the free ions relative to the ion pair varies with the composition of the solvent mixture. The heat of activation,  $\Delta H_0^\ddagger$ , for migration of free ions, obtained from the temperature dependence of  $\Lambda_0$ , increases with increasing proportion of water in the solvent.

The dependence of reaction rate on solvent composition for nucleophilic substitution reactions in mixed solvents may give information concerning preferential solvation of ionic species. In recent investigations <sup>1,2</sup> of this kind the kinetics of the halogen exchange between lithium bromide and butyl bromide in acetone-water mixtures were investigated over the temperature range 15–35 °C.

Under the prevailing conditions lithium bromide is subject to significant ion pair formation which affects the overall reaction rate because of different reactivities of anionic nucleophile ( $\text{Br}^-$ ) and ion paired nucleophile ( $\text{Li}^+\text{Br}^-$ ). To separate the observed rate constant of the overall exchange reaction into the different rate constants of the two exchange reactions involving free and paired bromide ions, respectively, precise knowledge of the extent of ion pair formation was required. To obtain the information sought the electrical conductance measurements previously performed <sup>3</sup> at 25 °C were extended to 15 and 35 °C. The objective of the present paper is to discuss the results of these measurements.

## EXPERIMENTAL

Lithium bromide (Merck, *suprapur*), acetone (Merck, *pro analysi*), and water were treated as before.<sup>3</sup> Solutions were prepared by weight. The determinations of densities,  $\rho_0$ , viscosities,  $\eta$ , and permittivities,  $\epsilon$ , of mixtures of acetone and water have been described.<sup>3</sup> The results of these determinations are given in Table 1.

Table 1. Properties of acetone-water mixtures at 15 and 35 °C.

Water conc. wt-%	$\rho_0$ g cm <sup>-3</sup>	$\eta$ cP	$\epsilon$	$\rho_0$ g cm <sup>-3</sup>	$\eta$ cP	$\epsilon$
	15 °C			35 °C		
0.005	0.79565	0.331	21.62	0.77275	0.273	19.65
0.10	0.79600	0.332	21.69	0.77311	0.274	19.68
0.30	0.79663	0.334	21.79	0.77366	0.275	19.80
1.00	0.79867	0.341	22.19	0.77590	0.280	20.17
2.00	0.80166	0.352	22.75	0.77890	0.287	20.67
5.00	0.81076	0.393	24.51	0.78820	0.315	22.23
10.0	0.82561	0.483	27.33	0.80345	0.371	24.82
20.0	0.85352	0.722	33.05	0.83218	0.514	30.12

For each solvent mixture the density,  $\rho$ , of the most concentrated solution of lithium bromide was determined. Densities of less concentrated solutions were calculated assuming a linear relationship,<sup>3</sup>

$$\rho = \rho_0 + Am \quad (1)$$

where  $m$  is the molality of lithium bromide. The value of the constant,  $A$ , was found to be of the order  $0.06 - 0.08 \text{ kg}^2 \text{ mol}^{-1} \text{ dm}^{-3}$ .

Electrolytic conductivities of acetone-water mixtures and of lithium bromide solutions were measured by means of a Leeds and Northrup 4866 conductivity bridge. A modified version<sup>3</sup> of a Daggett-Bair-Kraus conductivity cell,<sup>4</sup> provided with a Hawes-Kay salt cup dispensing device<sup>5,6</sup> was used. A detailed account of the equipment and of the performance of the measurements has been reported.<sup>3</sup>

## RESULTS AND CALCULATIONS

Molar conductivities,  $\Lambda$ , corrected for the conductivity of the solvent, and the corresponding concentrations,  $c$ , of lithium bromide in eight different acetone-water mixtures at 15 and 35 °C are quoted in Tables 2 and 3.

The conductance data were analyzed by means of the equation of Fuoss and Hsia<sup>7,8</sup> in the form of Fernández-Prini.<sup>9</sup> For pair-wise associated electrolytes the molar conductivity may be expressed,

$$\Lambda = \alpha[\Lambda_0 - S(\alpha)^{1/2} + E\alpha^{10}\log(\alpha) + J_1\alpha - J_2(\alpha)^{3/2}] \quad (2)$$

where  $\alpha$  is the degree of dissociation of the salt,  $S$  and  $E$  are coefficients<sup>10</sup> which depend upon

Table 2. Electrical conductance data for lithium bromide in acetone-water mixtures at 15 °C.

Run A		Run B		Run A		Run B	
$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$	$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$	$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$	$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$
0.005 wt-% water				2.00 wt-% water			
1.1920	134.53	1.0412	137.58	2.7461	113.09	1.0093	128.65
3.1873	108.07	4.0179	101.58	5.6086	98.086	2.4356	115.23
6.5803	87.706	10.555	75.216	11.095	82.505	4.9259	100.99
12.758	70.504	17.843	62.599	16.952	72.917	10.169	84.63
20.443	59.588	26.954	53.787	24.057	65.265	15.648	74.715
28.940	52.364	38.710	46.883	37.924	55.899	24.641	64.754
41.452	45.662	40.571	46.052			38.016	55.849
0.10 wt-% water				5.00 wt-% water			
1.2269	136.28	1.3841	133.41	1.0834	111.48	1.1236	111.26
3.4179	110.15	3.5519	108.98	2.2247	105.88	2.4261	105.10
7.0930	90.048	7.2003	89.576	4.5525	97.970	4.6602	97.675
14.938	70.732	15.008	70.629	9.6218	87.035	9.7262	86.881
23.150	60.639	22.720	61.003	15.113	79.404	15.040	79.398
35.782	51.669	34.160	52.542	24.306	70.926	23.626	71.385
52.117	44.797	42.096	48.573	37.456	63.093	36.731	63.413
0.30 wt-% water				10.0 wt-% water			
1.0765	138.84	1.0031	140.36	0.98596	89.346	0.82645	89.655
2.5750	118.60	2.5991	118.46	4.7092	82.754	3.7321	84.059
4.8420	101.92	4.8536	101.87	9.6429	77.451	8.7821	78.234
8.9427	85.496	9.4336	84.102	14.678	73.532	14.224	73.736
16.944	69.445	17.235	69.050	23.053	68.700	23.143	68.592
25.971	59.767	25.801	59.915	35.967	63.388	36.544	63.135
31.177	55.925	37.733	52.112				
1.00 wt-% water				20.0 wt-% water			
3.3508	109.99	1.1905	131.68	0.99431	65.658	1.1065	65.539
6.6958	92.805	3.0811	111.80	2.1059	64.702	2.3999	64.515
13.538	75.389	6.3078	94.188	4.2132	63.318	4.3273	63.264
21.090	65.075	12.691	76.860	8.7446	61.364	8.4286	61.453
29.591	57.785	19.908	66.317	13.210	59.821	13.448	59.738
43.681	50.094	28.330	58.647	21.939	57.527	26.252	56.601
		40.927	51.275	33.865	55.170	35.467	54.845

Table 3. Electrical conductance data for lithium bromide in acetone-water mixtures at 35 °C.

Run A		Run B		Run A		Run B	
$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$	$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$	$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$	$c \times 10^4$ M	$\Lambda$ $\text{cm}^2 \Omega^{-1}$ $\text{mol}^{-1}$
0.005 wt-% water				2.00 wt-% water			
2.5812	126.69	2.0369	134.79	1.0167	158.76	2.2820	142.89
4.8959	105.03	3.8790	112.79	2.3477	142.06	4.2343	127.26
9.0956	85.558	6.9233	93.899	4.6173	124.88	8.4508	107.93
15.846	70.062	13.200	74.962	9.1748	105.54	14.706	92.169
24.761	59.181	23.129	60.776	15.574	90.548	23.259	79.688
37.415	50.393	36.317	51.013	24.187	78.642	35.632	68.870
0.10 wt-% water				5.00 wt-% water			
0.98592	161.89	1.1803	156.77	0.92678	145.74	0.83810	146.26
1.9739	140.31	2.6627	130.41	2.1883	136.71	2.0229	137.71
3.7329	118.95	4.7856	110.64	4.1592	126.99	3.9390	127.90
8.6198	91.747	9.3381	89.282	8.1880	113.96	8.0380	114.29
15.977	73.906	16.675	72.786	14.588	101.13	14.296	101.58
25.181	62.437	27.454	60.423	23.828	89.624	23.431	90.022
39.236	52.655	40.959	51.773	36.209	79.784	35.569	80.201
0.30 wt-% water				10.0 wt-% water			
0.84161	168.28	0.81647	168.68	1.0584	121.79	0.94340	122.20
2.3324	139.32	2.3303	139.32	2.3754	117.61	2.4169	117.44
4.7272	116.20	4.6339	116.79	4.4901	112.74	4.3395	113.08
9.7394	93.080	8.8837	95.876	8.6754	105.83	8.1853	106.44
15.469	79.526	16.165	78.293	15.708	97.845	14.598	98.882
25.176	66.707	26.023	65.877	24.793	90.719	23.486	91.575
39.216	56.446	40.258	55.871	37.012	83.919	36.684	84.053
1.00 wt-% water				20.0 wt-% water			
1.0460	162.09	1.1945	159.17	0.90058	96.052	0.86462	96.134
2.4568	140.61	2.5975	139.12	2.1879	94.269	2.0497	94.481
4.1008	125.49	4.7345	121.18	4.2901	92.239	3.9714	92.535
7.9431	105.29	8.8696	101.94	8.3246	89.335	7.7610	89.746
14.124	88.147	15.531	85.455	14.899	85.952	13.650	86.556
22.130	75.743	24.411	73.190	24.209	82.390	23.137	82.767
34.388	64.666	36.578	63.208	37.159	78.671	35.845	79.021

$\Lambda_0$ ,  $\eta$ ,  $\epsilon$ , and the absolute temperature,  $T$ , while the coefficients  $J_1$  and  $J_2$  depend, in addition, upon the maximum center-to-center distance,  $R$ , between the ions in the ion pair.<sup>11,12</sup>

The association constant for the equilibrium between free and paired ions is defined by the expression,

$$K_A = (1 - \alpha)/(c\gamma^2\alpha^2) \quad (3)$$

where  $\gamma$  is the mean molar activity coefficient of free ions, which was calculated using the Debye-Hückel equation,

$$^{10}\log \gamma = -A(c\alpha)^{1/2}/[1 + BR(c\alpha)^{1/2}] \quad (4)$$

where  $A$  and  $B$  are functions of  $\epsilon$  and  $T$ .

Using eqns. (2-4) the values of  $\Lambda_0$  and  $K_A$  which minimize  $\sigma(\Lambda)$ , the standard deviation between measured and calculated  $\Lambda$ -values, were determined as a function of the distance parameter,  $R$ , using a computer program described.<sup>13</sup> Typical examples of the dependence of  $\Lambda_0$  and  $K_A$  on  $R$  are shown in Fig. 1.

In most instances the curve obtained upon plotting  $\sigma(\Lambda)$  vs.  $R$  was found to exhibit two minima for two quite different values of  $R$ , cf. Fig. 2.

This behaviour, which is not uncommon as has been recently demonstrated,<sup>14</sup> indicates that the condition,  $\sigma(\Lambda) = \text{minimum}$ , is not useful as criterion of "best set" conductance parameters.

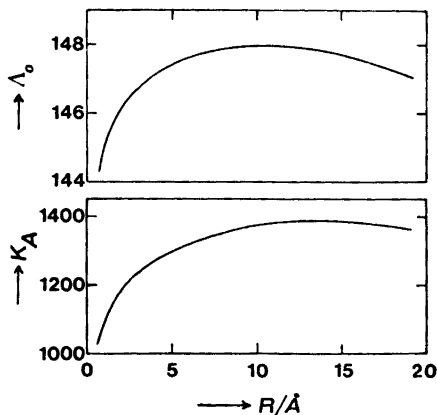


Fig. 1. Dependence of  $\Lambda_0$  and  $K_A$  on the distance parameter,  $R$ , for LiBr in aqueous acetone (2 wt-%  $\text{H}_2\text{O}$ ) at 15°C.

Since there exists at present no method of determining the value of  $R$  uniquely, this distance parameter will in the following be set equal to the Bjerrum radius,  $q$ , which for univalent electrolytes is given by the expression,

$$q = e^2/2ekT \quad (5)$$

where  $e$  is the electronic charge and  $k$  is Boltzmann's constant.<sup>15</sup>

A compilation of the values derived for  $\Lambda_0$ ,  $K_A$ , and  $\sigma(\lambda)$  for this choice of  $R$  is given in Table 4. The relative standard deviations in  $\Lambda_0$  and  $K_A$  were usually less than 0.2 and 0.5 %, respectively. The values of  $K_A$  obtained indicate that association to pairs increases with temperature.

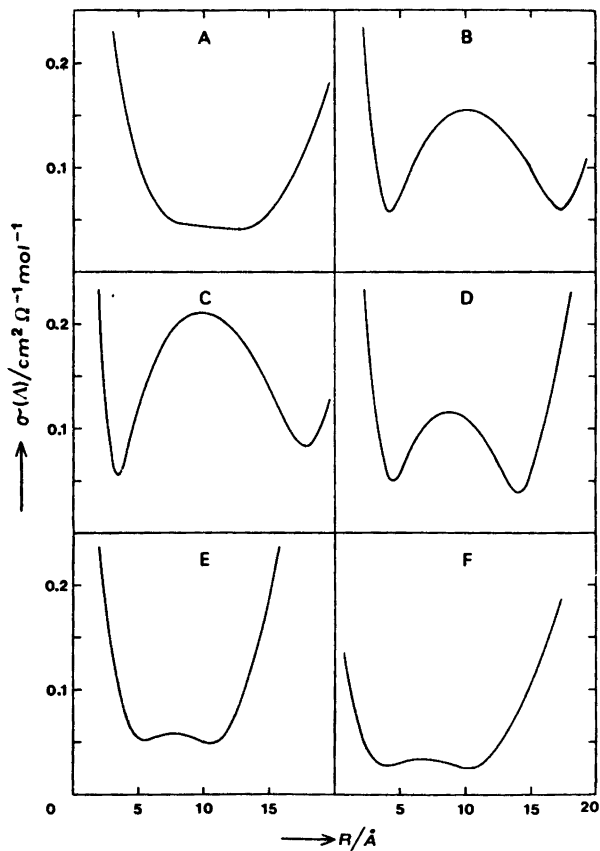


Fig. 2. Dependence of  $\sigma(\lambda)$  on the distance parameter,  $R$ , for LiBr in aqueous acetone at 15°C. The curves A – F refer to solvent mixtures containing 0.3, 1, 2, 5, 10, and 20 wt-%  $\text{H}_2\text{O}$ , respectively.

Table 4. Conductance parameters for lithium bromide in acetone-water mixtures.

Water conc. wt.-%	$q$ Å	$A_0$ $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$	$K_A$ $\text{M}^{-1}$	$\sigma(A)$ $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$
15 °C				
0.005	13.41	177.0	3 424	0.10
0.10	13.37	174.4	2 813	0.07
0.30	13.31	171.3	2 503	0.04
1.00	13.07	160.4	2 018	0.13
2.00	12.74	147.9	1 385	0.19
5.00	11.83	120.8	516	0.08
10.0	10.61	93.5	171	0.05
20.0	8.77	67.6	42	0.03
25 °C				
0.005	13.54	194.3	4 160	0.11
0.10	13.47	192.7	3 413	0.08
0.30	13.47	189.9	2 839	0.06
1.00	13.22	179.8	2 163	0.17
2.00	12.79	165.7	1 449	0.29
5.00	12.03	138.4	552	0.19
10.0	10.74	110.1	186	0.07
20.0	8.87	82.5	47	0.05
35 °C				
0.005	13.80	211.0	4 513	0.10
0.10	13.78	211.0	3 918	0.10
0.30	13.69	206.9	3 163	0.10
1.00	13.44	196.4	2 230	0.09
2.00	13.12	184.2	1 534	0.19
5.00	12.20	157.4	603	0.10
10.0	10.92	128.1	205	0.04
20.0	9.00	98.8	52	0.02

## DISCUSSION

Taking into account solvent-ion and solvent-ion pair interaction energies, Gilkerson<sup>16</sup> arrived at the following equation for the ion pair association constant,

$$K_A = (2\pi\mu kT/h^2)^{-3/2} (g\nu\bar{\sigma})^{-1} \exp(E_s/RT) \exp(Ne^2/\epsilon a RT) \quad (6)$$

where  $R$  = gas constant and  $N$  = Avogadro's number. The other symbols are explained in the original paper.<sup>16</sup>

Eqn. (6) contains three adjustable parameters: the minimum distance,  $a$ , between the charges in the ion pair; the difference,  $E_s$ , between solvent-ion and solvent-ion pair interaction energies ( $E_s = E_+ + E_- - E_{\pm}$ ); and  $(g\nu\bar{\sigma})$  which is a function of the free volumes available to the ions and the ion pair.

Later a transformation was made from Gilkerson's free-volume approach<sup>16</sup> by grafting

a specific solvation term<sup>17</sup> to Fuoss' hard sphere in a continuum model<sup>18</sup> resulting in the expression:

$$K_A = (4\pi N a^3 / 3000) \exp(E_s/RT) \exp(Ne^2/\epsilon a RT) \quad (7)$$

The logarithmic form of this equation indicates that a straight line should be obtained upon plotting  $\ln K_A$  vs.  $1/\epsilon$  at constant temperature provided that  $a$  and  $E_s$  are independent of the composition of the solvent mixture. However, the graphs shown in Fig. 3 for the systems concerned exhibit significant curvature which increases with decreasing proportion of the protic component.

For a given composition of the solvent mixture ( $a$  and  $E_s$  constant) the minimum center-to-center distance between the ions in the ion pair may be calculated from the derivative,

$$\frac{d \ln K_A}{d(1/\epsilon)} = \frac{Ne^2}{a RT} \quad (8)$$

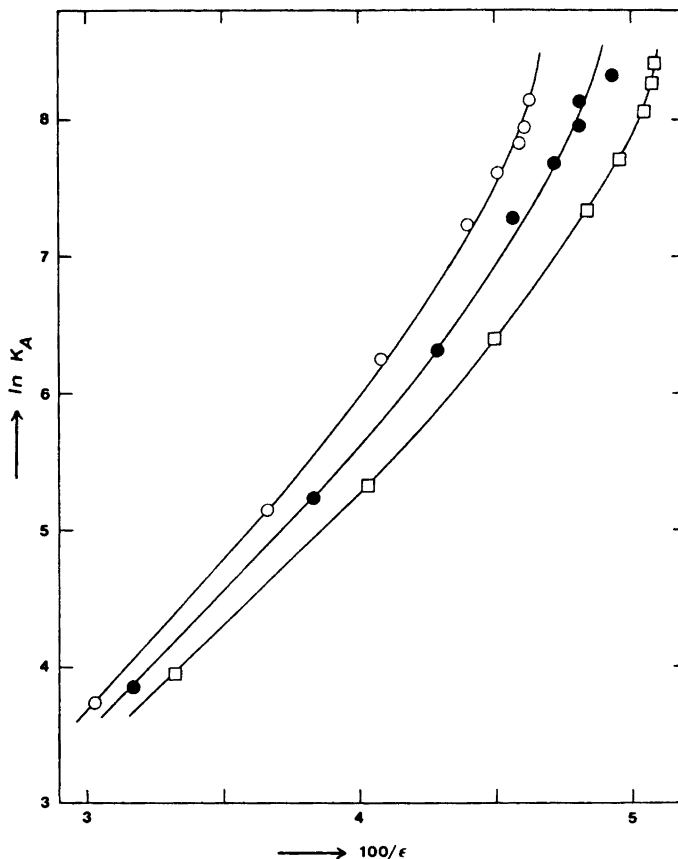


Fig. 3. Graphs of  $\ln K_A$  vs.  $100/\epsilon$  for LiBr in aqueous acetone at 15 °C (open circles), 25 °C (full circles), and 35 °C (squares).

obtained from eqn. (7). Values of  $a$  according to eqn. (7) were calculated from the slopes of the curves in Fig. 3 at four different concentrations of water in the solvent mixture, viz. 0.3, 2, 5, and 20 wt-%.

The values of  $a$  obtained for the three different temperatures investigated are given in the next to last column of Table 5 in which the corresponding values derived from the Bjerrum equation,<sup>15</sup>

$$K_A = \frac{4\pi N}{1000} \int_a^q r^2 \exp\left(\frac{e^2}{\epsilon k T r}\right) dr \quad (9)$$

are included in the second column. The following conclusions may be drawn.

For a given composition of the solvent mixture the minimum center-to-center distance

between the ions in the ion pair appears to be independent of temperature. According to the Gilkerson-Fuoss equation, eqn. (7), the average values of  $a$  at the three different temperatures investigated amount to 1.1, 1.8, 2.1, and 2.7 Å for the solvent mixtures containing 0.3, 2, 5, and 20 wt-% water, respectively. The corresponding average values of  $a$  according to Bjerrum's equation, eqn. (9), are 2.1, 2.2, 2.3, and 2.9 Å. These values of  $a$ , being in most instances less than the crystal radii sum of  $\text{Li}^+$  and  $\text{Br}^-$  (2.6 Å), obviously underestimate the minimum center-to-center distance between the ions in the ion pair.

The trend of the  $a$  values to decrease with decreasing proportions of water in the solvent mixture may possibly be taken as evidence that the character of  $\text{Li}^+\text{Br}^-$  as solvent separated

Table 5. Parameters according to eqns. (7) and (9) for LiBr in aqueous acetone.

Water conc. wt.-%	$a$ , eqn. (9) Å	$a$ , eqn. (7) Å	$E_s$ kJ mol <sup>-1</sup>
15 °C			
0.3	2.11	1.12	-24.4
2.0	2.22	1.79	-6.9
5.0	2.34	2.13	-2.9
20.0	2.94	2.63	+0.4
25 °C			
0.3	2.12	1.20	-22.3
2.0	2.24	1.81	-7.0
5.0	2.34	2.06	-3.8
20.0	2.85	2.71	+0.7
35 °C			
0.3	2.15	1.03	-32.3
2.0	2.24	1.82	-7.4
5.0	2.36	2.11	-3.6
20.0	2.81	2.80	+1.1

ion pair decreases with decreasing concentration of the protic constituent.

The values of  $E_s$  in Table 5 suggest that the difference in solvation energies of the ions and the ion pair decreases with increasing proportions of water in the solvent mixture. For acetone containing 0.3 wt.-% water  $E_s$  is of the order -20 to -30 kJ mol<sup>-1</sup>. The negative value of  $E_s$  indicates that the solvent-ion pair interaction term,  $E_{\pm}$ , is greater than the solvation interaction terms, ( $E_+ + E_-$ ). For the solvent mixture containing 20 wt.-% water  $E_s$  is close to zero for all three temperatures studied indicating approximately equal solvation energies for the ion pair and the free ions.

On the assumption that the ions migrate through the liquid by successive jumps from one equilibrium position to another and that a characteristic free energy of activation,  $\Delta G_{oi}^{\ddagger}$ , is required for each jump the limiting molar conductivity of i-ions may be expressed,<sup>19</sup>

$$\lambda_{oi} = \frac{1}{6} \frac{zeF}{h} L_i^2 \exp\left(-\frac{\Delta G_{oi}^{\ddagger}}{RT}\right) \quad (10)$$

where  $L_i$  is the jump distance. The other notations in eqn. (10) have their usual significance.

Differentiation of the logarithmic form of eqn. (10) with respect to temperature at constant pressure and use of the relations,<sup>19</sup>

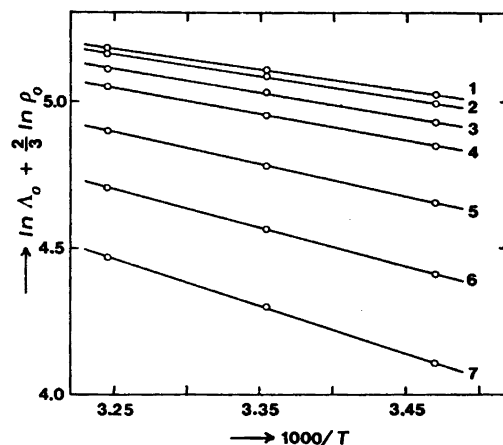


Fig. 4. Graphs according to eqn. (13) for LiBr in aqueous acetone. The straight lines 1-7 refer to solvent mixtures containing 0.005, 0.3, 1, 2, 5, 10, and 20 wt.-% H<sub>2</sub>O.

$$\left(\frac{\partial \ln L_i}{\partial T}\right)_P = \frac{1}{3} \left(\frac{\partial \ln V}{\partial T}\right)_P = -\frac{1}{3} \left(\frac{\partial \ln \rho_0}{\partial T}\right)_P \quad (11)$$

results in the following expression,

$$\Delta H_{oi}^{\ddagger} = RT^2 \left(\frac{\partial \ln \lambda_{oi}}{\partial T}\right)_P + \frac{2}{3} RT^2 \left(\frac{\partial \ln \rho_0}{\partial T}\right)_P \quad (12)$$

where  $\Delta H_{oi}^{\ddagger}$  is the enthalpy change referring to the unit displacement (one jump) of one mol of ions.

Provided that the transport numbers,  $t_i$  and  $t_j$ , do not change significantly with temperature the integrated form of eqn. (12) may be written,

$$\ln A_0 + \frac{2}{3} \ln \rho_0 = -\frac{\Delta H_0^{\ddagger}}{RT} + B \quad (13)$$

where  $\Delta H_0^{\ddagger} = t_i \Delta H_{oi}^{\ddagger} + t_j \Delta H_{oj}^{\ddagger}$  and  $B$  is an integration constant, cf. Ref. 20.

Graphs according to eqn. (13) for lithium bromide in several aqueous acetone mixtures are shown in Fig. 4. For the temperature interval studied no temperature dependence of the heat of activation can be detected. Application of eqn. (13) to the experimental data using the method of least squares yields the values of  $\Delta H_0^{\ddagger}$  quoted in Table 6.

It is found that  $\Delta H_0^{\ddagger}$  increases with increasing proportions of water in the solvent mixture, viz. from 6 kJ mol<sup>-1</sup> for anhydrous acetone to 13 kJ mol<sup>-1</sup> for acetone containing 20 wt.-%

Table 6. Dependence of  $\Delta H_0^\ddagger$  according to eqn. (13) on solvent composition of LiBr in aqueous acetone.

Water conc. wt.-%	$\Delta H_0^\ddagger$ kJ mol <sup>-1</sup>
0.005	5.8
0.10	6.3
0.30	6.2
1.00	6.8
2.00	7.4
5.00	9.1
10.0	11.0
20.0	13.4

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water. Compare  $\Delta H_0^\ddagger = 15$  kJ mol<sup>-1</sup> for lithium bromide in water at 25 °C. This value was calculated from the temperature dependence of  $\Lambda_0$  obtained from limiting molar conductivities and transport numbers for LiCl and KBr.<sup>21</sup>

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