Electrolyte — Solvent Interaction

Conductance of Lithium Bromide in Acetone-Methanol Mixtures

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The variation of conductance with concentration for lithium bromide in solvent mixtures of acetone and methanol containing between 0.1 and 100 % methanol has been studied at 25°C and the data obtained have been analyzed by means of the 1957 Fuoss-Onsager equation. In the acetone rich region the ion-pair association constant, K_A, and the limiting molar conductance, $\Lambda\infty$, decrease rapidly with increasing methanol concentration. These changes are correlated with the tendency to solvation of the bromide ion through hydrogen-bond formation. The ion-size parameter, $\mathring{a}$, increases with decreasing permittivity of the solvent. Comparison with corresponding parameters for lithium bromide in acetone-water solvent mixtures is made.

The theory of electrolyte conductance ascribes the decrease of molar conductance with increasing electrolyte concentration to the effects of decreasing mobility of the free ions and to the relative concentration of free ions. The ions are represented by charged spheres and the solvent is regarded as a structureless continuum. This model gives a theory for the variation in conductance with the electrolyte concentration and makes it possible to calculate an association constant for the formation of ion pairs from experimental data.

A very large number of investigators have tested the conductance theory using different electrolytes and both aqueous and nonaqueous solvents. Especially electrolytes forming large ions, *e.g.* quaternary ammonium salts, have been extensively investigated, and the theory has been quite successful in accounting for the observed behaviour of this systems.[1-4]

Alkali halides, with their small ions, comparable in size with the solvent molecules, in polar solvents systems show complex behaviour due to strong ion-solvent interactions. This interaction may be studied by conductance measurements in mixed solvents.

Extensive conductometric studies of alkali halides in dioxane-water mixtures,[5-11] in aqueous alcohol,[12] and in mixtures of primary alcohols,[13] have been undertaken during the last decade.

The purpose of the present paper, which is the second part in a series [14] dealing with ion-solvent interactions in binary protic-aprotic solvent mixtures, is to report the result of a conductometric investigation of the behaviour of lithium bromide in acetone-methanol mixtures at 25°C and to make a comparison with the behaviour of the salt in acetone-water mixtures at this temperature.

EXPERIMENTAL

Materials. Lithium bromide (Merck, *suprapur*) was dried at 200°C for 2 h immediately before use.

Commercial acetone (*p.a.*) was allowed to pass through a column packed with Linde Molecular Sieve 4A and then fractionally distilled.[15] By repeated measurements acetone purified in this manner was found to have the following properties: $\varkappa < 2 \times 10^{-8}$ Ω^{-1} cm^{-1}; $d_4^{25} = 0.78429$ g cm^{-3}, $\eta = 0.00304$ P; $\varepsilon = 20.7$. Methanol (*p.a.*) was purified in the same manner as acetone and had the following properties: $\varkappa < 11 \times 10^{-8}$ Ω^{-1} cm^{-1}; $d_4^{25} = 0.78674$ g cm^{-3}; $\eta = 0.00543$ P; $\varepsilon = 32.7$. All the solvent properties were determined as described below.

Table 1. Properties of acetone-methanol mixtures at 25°C.

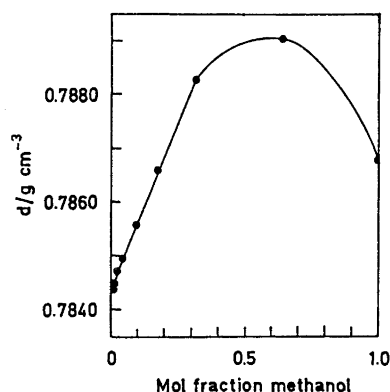| Wt. % methanol	d g cm^{-3}	η cP	ε
0.100	0.78435	0.300	20.6
0.300	0.78447	0.300	20.6
1.00	0.78468	0.301	20.7
2.00	0.78491	0.301	20.8
5.00	0.78563	0.301	21.1
10.0	0.78662	0.304	21.6
20.0	0.78828	0.314	22.7
50.0	0.79060	0.370	26.3
100.0	0.78674	0.543	32.7

Fig. 1. Density of acetone-methanol mixtures at 25°C as a function of the mol fraction methanol.

Acetone-methanol mixtures were prepared by weight. In all weighings bouyancy corrections were applied. The density of acetone-methanol was measured with a Lipkin pycnometer. Viscosities were determined by means of a calibrated Ubbelohde viscosimeter and permittivities by a Ferrisol M 803 A Q-meter. The properties of the various acetone-methanol mixtures thus established are listed in Table 1. The density of acetone-methanol mixtures shows a positive deviation from linearity (Fig. 1) with a maximum between 50 and 60 mol % methanol. The system acetone-ethanol [16] shows the same deviation while for the acetone-propanol [17] system density is a linear function of the mol fraction as in the case of acetone-water mixtures.[14]

In Figs. 2 and 3 permittivities and viscosities, respectively, are plotted as a function of the mol fraction of methanol together with the acetone-water system.
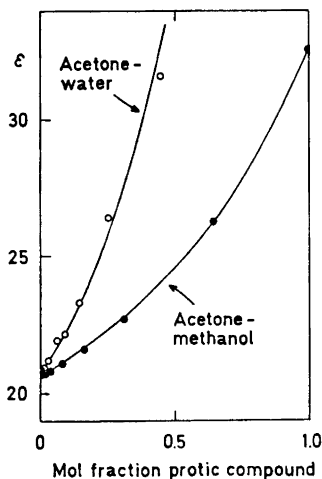

Fig. 2. Permittivity of the solvent mixtures at 25°C as a function of the composition (acetone-water mixtures according to Ref. 14).
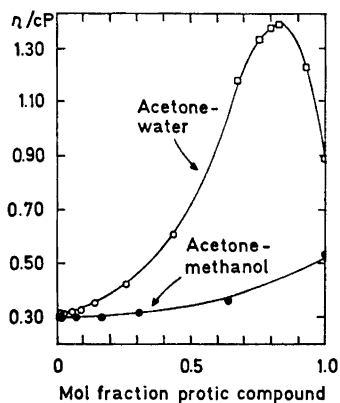
Fig. 3. Viscosity of the solvent mixtures at 25°C plotted against the mol fraction (open circles acetone-water (Ref. 14) and open squares acetone-water (Ref. 31)).

To enable exact calculations of lithium bromide concentrations, the density of solution was measured as a function of the salt concentration. For each solvent mixture investigated the density of the solution was found to vary lineary with the concentration of lithium bromide.

Conductivity measurements. The resistances of the solution were measured by means of a Leeds and Northrup 4666 conductivity bridge. A Dagget-Bair-Kraus conductivity cell fitted with two pairs of bright platinum electrodes [14] and a salt cup dispensing device was used.

The general technique for the conductance measurements was the same as previously described.[14] The temperature was determined by means of a Mueller temperature bridge 8069-B in connection with a high precision platinum resistance thermometer. The temperature was 25.000 ± 0.005°C.

RESULTS AND DISCUSSION

Conductance data for different molar concentrations, c, of lithium bromide are shown in Table 2, for the different acetone-methanol mixtures studied. The molar conductivities, Λ, have been corrected for the conductivity of the

Table 2. Molar conductivities of lithium bromide in acetone-methanol mixtures at 25°C.

	Run A		Run B
$c \times 10^4$ M	Λ cm^2 Ω^{-1} mol^{-1}	$c \times 10^4$ M	Λ cm^2 Ω^{-1} mol^{-1}
	0.100 wt. % methanol		
1.5441	139.51	2.0492	130.90
7.0899	93.225	6.4199	96.291
15.874	71.079	15.395	71.881
26.445	59.011	28.569	57.309
40.037	50.434	41.549	49.689
58.177	43.635		
	0.300 wt. % methanol		
0.8161	158.97	1.2973	149.06
2.7103	128.63	3.3883	122.19
6.7040	101.78	16.118	76.839
15.253	78.434	28.649	62.781
28.310	63.089	40.784	55.126
45.724	52.819		
62.656	46.856		
	1.00 wt. % methanol		
1.7786	148.48	1.1602	157.19
3.9249	128.90	3.3465	132.96
8.4896	107.07	7.5158	110.48
17.776	86.301	16.478	88.290
31.534	71.495	29.289	73.252
44.494	63.439	41.897	64.761
62.124	56.288	59.074	57.288
	2.00 wt. % methanol		
0.7696	164.11	1.0303	160.88
15.551	97.576	2.8180	142.39
28.700	81.448	6.6089	121.32
41.791	72.188	11.154	106.99
58.809	64.368	23.376	86.850
		35.473	76.184
		50.728	67.710
	5.00 wt. % methanol		
1.1958	157.55	1.1837	157.93
3.5135	141.57	3.6675	140.89
7.9386	124.33	8.3005	123.31
16.934	105.54	17.063	105.39
30.236	90.769	30.307	90.734
43.501	81.767	43.202	81.965
60.856	73.832	61.752	73.516

Table 2. Continued.

10.0 wt. % methanol

1.4282	153.07	2.1340	149.06
3.7624	141.94	6.1149	134.01
12.985	119.46	15.090	116.26
25.625	104.24	28.320	101.98
38.832	94.569	41.165	93.232
55.634	86.236	55.187	86.419

20.0 wt. % methanol

1.3539	145.41	0.9804	146.82
3.5373	138.79	2.9113	140.53
7.7014	130.59	15.884	120.08
16.790	119.33	28.544	110.01
30.003	109.19	41.804	102.70
41.294	103.10	58.582	96.196
59.165	96.011		

50.0 wt. % methanol

1.7538	122.96	1.4307	123.58
4.2070	119.52	21.470	108.37
8.2535	115.88	35.299	103.59
13.806	112.30	53.663	98.949
28.855	105.82		
40.784	102.18		
55.946	98.553		

100.0 wt. % methanol

1.6179	92.755	1.3243	93.024
3.8046	91.256	3.7439	91.298
8.3122	89.077	8.3533	89.022
17.604	86.255	17.787	86.174
31.455	83.437	31.433	83.408
45.083	81.377	45.520	81.290
63.398	79.238	64.263	79.090

solvent. The data in Table 2 were analyzed using a computer program previously described.[18] This program is based on the Fuoss-Onsager equation[19] of 1957:

$$\varLambda = \varLambda_\infty - S(c\alpha)^{1/2} + Ec\alpha^{10}\log c\alpha + Jc\alpha - K_A c\alpha\gamma^2\varLambda \qquad (1)$$

where $\varLambda_\infty$, α, and K_A have their usual meanings. The parameters S, E, and J are definied in Ref. 20. The mean molar activity coefficient, γ, is approximated by the mean rational activity coefficient. The latter was evaluated from the Debye-Hückel equation in its more complete form.[21]

Table 3. Conductance parameters for lithium bromide in acetone-methanol mixtures at 25°C.

Wt. % methanol	Λ_∞ cm^2 Ω^{-1} mol^{-1}	K_A M^{-1}	$\mathring{a} \times 10^8$ cm	$\sigma\Lambda$ %
0.0 [14]	195.01 ± 0.02	4202 ± 0.6	9.3	0.04
0.100	193.59 ± 0.06	3457 ± 3	7.8	0.14
0.300	190.61 ± 0.08	2613 ± 4	6.3	0.16
1.00	185.37 ± 0.05	1542 ± 1	5.0	0.11
2.00	181.41 ± 0.07	1069 ± 4	4.7	0.14
5.00	173.91 ± 0.06	598.8 ± 1.7	4.4	0.15
10.0	166.16 ± 0.07	317.5 ± 1.3	4.3	0.16
20.0	153.91 ± 0.04	105.6 ± 0.7	3.9	0.11
50.0	128.68 ± 0.04	6.20 ± 0.75	3.7	0.11
100.0	95.80 ± 0.01		3.1	0.05

Eqn. (1) was fitted to the conductance data by an iterative method [18] similar to one outlined by Kay.[22] The results of these calculations are shown in Table 3, in which values of Λ_∞ and K_A, together with their standard deviations, and the parameter $\mathring{a}$ are quoted. The standard deviation in single value of Λ, $\sigma\Lambda$, also is included.

According to Fuoss and Onsager,[19] eqn. (1) should not be used for 1:1 electrolytes for concentrations corresponding to $\varkappa\mathring{a} > 0.2$, where $\varkappa^2/c = \pi N e^2/\varepsilon kT$. Evans *et al.*[17] report for several electrolytes in acetone and acetone-propanol mixtures, if $\varkappa\mathring{a} > 0.1$ the conductance parameters depend upon the concentration range analyzed.

To investigate any dependence of Λ_∞, K_A, and $\mathring{a}$ on the concentration range of lithium bromide some of our conductance data where treated by means

Table 4. The dependence in the conductance parameters upon the concentration region analyzed.

Conc. interval $c \times 10^4$/M	Λ_∞ cm^2 Ω^{-1} mol^{-1}	KA M^{-1}	$\mathring{a} \times 10^8$ cm	$\sigma\Lambda$ %
	LiBr in acetone containing 0.100 wt % methanol			
1 – 15	194.30 ± 0.10	3544 ± 6	10.9	0.16
1 – 30	193.91 ± 0.08	3494 ± 5	8.9	0.14
1 – 41	193.70 ± 0.07	3469 ± 4	8.2	0.13
1 – 60	193.59 ± 0.06	3457 ± 3	7.8	0.14
	LiBr in acetone containing 50.0 wt. % methanol			
1 – 15	128.89 ± 0.01	34.7 ± 0.4	6.9	0.04
1 – 30	128.81 ± 0.03	19.4 ± 0.5	4.8	0.09
1 – 35	128.75 ± 0.04	13.6 ± 0.6	4.3	0.10
1 – 41	128.75 ± 0.03	13.5 ± 0.6	4.2	0.09
1 – 55	128.68 ± 0.04	6.2 ± 0.8	3.7	0.11

of eqn. (1) for successively broadening of the interval of concentration. This analysis was undertaken for two solvent compositions, *viz.* acetone containing 0.1 and 50 wt %, respectively of methanol. In the latter solvent the electrolyte is only slightly associated to ion pairs. The concentration intervals analyzed and the conductance parameters obtained are given in Table 4. In that table it can be seen that the parameters discussed are dependent upon the concentration interval analyzed even at low concentrations.

For acetone containing 0.1 wt % methanol the value of $\Lambda_\infty = 193.6$ cm^2 Ω^{-1} mol^{-1} calculated for the whole concentration interval $(1 \times 10^{-4} - 6 \times 10^{-3}$ M) may be compared with the corresponding $\Lambda_\infty = 194.3$ cm^2 Ω^{-1} mol^{-1} obtained on basis of the experimental points within the low concentration range $(1 \times 10^{-4} - 1.5 \times 10^{-3}$ M). The corresponding values for K_A are 3457 and 3544 M^{-1}, respectively, and for $å$ 7.8 and 10.9 Å.

A corresponding analysis for acetone containing 50 wt % methanol yields $\Lambda_\infty = 128.7$ cm^2 Ω^{-1} mol^{-1} $(1 \times 10^{-4} - 5.5 \times 10^{-3}$ M) and $\Lambda_\infty = 128.9$ cm^2 Ω^{-1} mol^{-1} $(1 \times 10^{-4} - 1.5 \times 10^{-3}$ M); $K_A = 6.2$ and 34.7 M^{-1}, respectively; $å = 3.7$ and 6.9 Å. Further systematic studies must be undertaken to determine if the observed effect is a consequence of the experimental precision or is a general inability in eqn. (1) to represent adequately the conductance data.

As can be seen in Table 3, K_A decreases rapidly with increasing methanol concentration. Fig. 4 shows that for a given mol fraction of protic compound
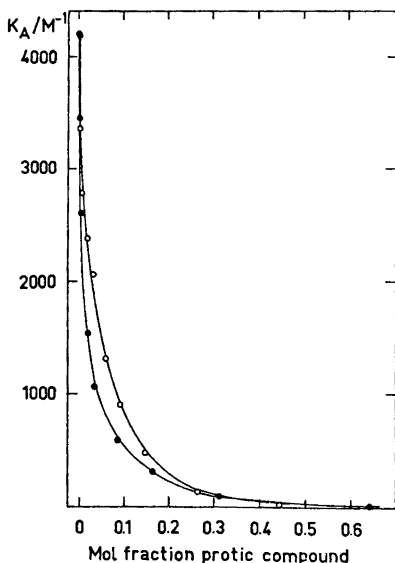

Fig. 4. Association constants at 25°C for lithium bromide in acetone-methanol and acetone-water mixtures plotted against the solvent composition (full circles acetone-methanol mixtures and open circles acetone-water mixtures (Ref. 14)).
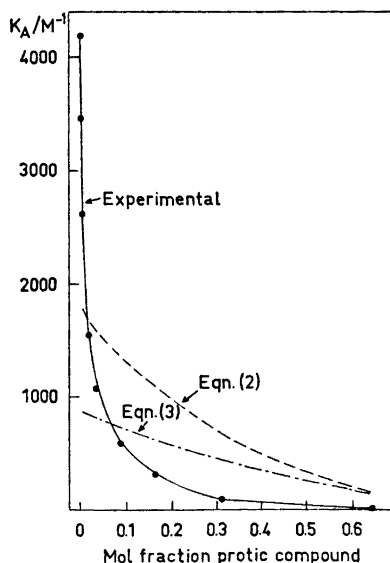
Fig. 5. Association constants for lithium bromide in acetone-methanol at 25°C.

in the acetone rich region, the association constant for the acetone methanol system is smaller than for the acetone-water mixture, although the permittivity of the former system is lower, see Fig. 2. The two isodielectric mixtures 5.00 wt. % methanol-acetone and 1.00 wt. % water-acetone [14] have association constants of 599 M^{-1} and 2073 M^{-1}, respectively. This may be an effect of different anion solvation from the protic compound in the solvent mixtures.

According to Fuoss [23] two ions may be regarded as an ion pair if they are in contact. Fuoss has derived the association constants of such ion pairs in a dielectric continuum to

$$K_A = \frac{4\pi N \mathring{a}^3}{3000} \exp\left(\frac{e^2}{\mathring{a}\varepsilon kT}\right) \qquad (2)$$

where N is the Avogadro number and $\mathring{a}$ means the distance of closest approach between the centres of the two ions.

Alternatively, two ions may be regarded as paired if the distance between their centres is less than the Bjerrum critical distance, q, where q, for a given charge type of electrolyte, is a parameter dependent only on the solvent.

Regarding the solvent as a continuum with permittivity, ε, Bjerrum [24] derived for an 1:1 electrolyte:

$$K_A = \frac{4\pi N}{1000} \int_{\mathring{a}}^{q} r^2 \exp\left(\frac{e^2}{\varepsilon kTr}\right) dr$$

or

$$K_A = \frac{4\pi N}{1000} \left(\frac{e^2}{\varepsilon kT}\right)^3 Q(b) \qquad (3)$$

where $Q(b)$ stands for $\int_{2}^{b} x^{-4}e^x dx$; $x = e^2/\varepsilon kTr$

r is the distance from the center of a reference ion. This integral has been tabulated in Ref. 25, as a function of $b = e^2/\mathring{a}k\varepsilon T$.

Values of K_A according to eqns. (2) and (3) has been calculated using $\mathring{a} = 2.55$ Å, the crystal radii sum of lithium bromide. Using the $\mathring{a}$-values in Table 3 obtained from eqn. (1) association constants of the magnitude 50 M^{-1} were obtained for both eqns. (2) and (3). The $\mathring{a}$-values obtained from eqn. (1) are not used in the following as a value for the distance of closest approach. The discrepancies between calculated and observed association constants are large as can be seen from Fig. 5. Both equations underestimate K_A in the acetone rich region, where the ion pair has greater stability than the theories above predict. Compare the opposite behaviour in the methanol rich region in which both equations overestimate K_A. This is not surprising as neither of eqns. (2) and (3) allow factors for solvent-solute interaction to appear in K_A. In addition there is the uncertainty about the values of the permittivity employed to account for the reduction of field strength in the immediate vicinity of an ion. The macroscopic permittivity is used.

Gilkerson [26,27] has elaborated eqn. (2) further in an attempt to include factors in K_A accounting for the solvent-solute interaction and for the free volume of the solute. He obtained the expression:

$$K_A = \frac{4\pi N \mathring{a}^3}{3000} \exp\left(\frac{\Delta G_s}{RT}\right) \exp\left(\frac{e^2}{\mathring{a}\varepsilon kT}\right) \qquad (4)$$

where ΔG_s is the difference in molar free energy of solvation of the free ions and the ion-pair, and $\mathring{a}$ is the distance of closest approach. Variations in the solvent composition not only change the dielectric constant but also ΔG_s and $\mathring{a}$.

The distance of closest approach of two ions should not vary with the solvent if the ions are not separated by solvent molecules in the ion pair or if the solvent molecules separating the ions do not change. The addition of a small amount of a protic compound to acetone decreases the association constants very rapidly and this indicates a change to selective solvation of the ions by the protic compound. One may assume ΔG_s and $\mathring{a}$ to be constant over a wide concentration interval of the protic compound. Assuming ΔG_s and $\mathring{a}$ are constant a plot of log K_A against $1/\varepsilon$ should yield a straight line. As the plots in Fig. 6 is linear in the protic region down to a concentration of about 6 mol % protic compound one may conclude that the solvation shells of the protic solvent around the ions is fully developed when the content of the protic component exceeds about 6 mol %.

From the slope and intercept according to eqn. (4) the estimated value of $\mathring{a}$ and ΔG_s are, for lithium bromide in acetone-water mixtures, 2.3 Å and -2.5 kJ mol^{-1}, respectively and, for lithium bromide in acetone-methanol mixtures, 1.2 Å and -26 kJ mol^{-1}, respectively.
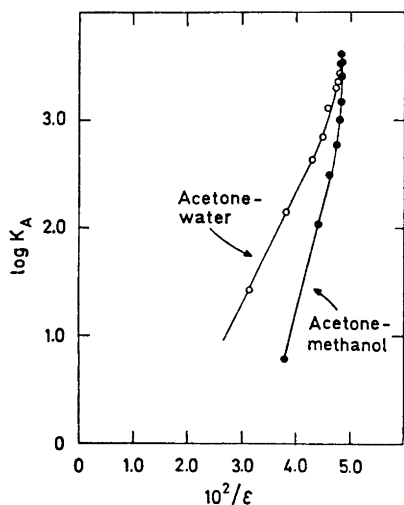

Fig. 6. The logarithms of the ion-pair association constants of lithium bromide vs. the reciprocal of the permittivity.
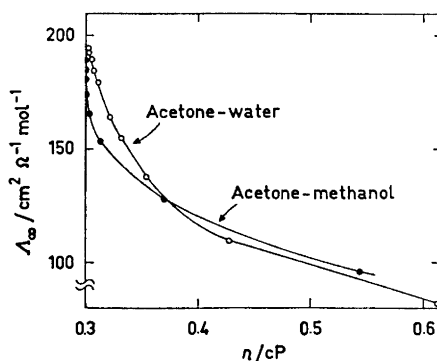
Fig. 7. Limiting molar conductivity at 25°C as a function of the viscosity of the solvent mixtures.

The distances of closest approach are unrealistically small, both less than the crystal radii sum for lithium bromide. The values of ΔG_s are negative indicating that the ions are more strongly solvated than the ion-pairs. The ΔG_s value for lithium bromide in acetone-methanol mixtures is ten times that in acetone-water, which may be correlated with a stronger hydrogen bonds formed by methanol.[28] The uncertainty in the quantitative results above is large because the linear part of the plots in Fig. 6 covers a rather small interval of the macroscopic permittivity of the solvent.

From values of Λ_∞ in Table 3 it can be seen that the limiting molar conductivity decreases with increasing methanol concentration. These values of Λ_∞ are reproduced in Fig. 7 as a function of the viscosity. From this figure it can be seen that for $\eta < 0.38$ cP the absolute value of Λ_∞ is significantly lower for the acetone-methanol system than for the acetone-water system. As transport numbers for the ions here concerned are not available in the literature no conclusions concerning differences in anion and cation solvation can be drawn.

As in most other solvents $\mathring{a}$ estimated from eqn. (1) seems more characteristic of the solvent than of the salt and can hardly be seen as the distance of closest approach between the centres of the ions in the ion pair. Recent spectroscopic studies [29] show that in anhydrous acetone the bromide ions compete with acetone molecules for a position in the solvent shell of the lithium ion, with the formation of a contact ion-pair. Eqn. (1) yields 9.3 Å as the distance of closest approach in anhydrous acetone while the crystal radii sum is 2.55 Å.

Justice [30] has recently suggested that Bjerrum's critical distance, q, should be used in the Fuoss-Onsager equation in place of the ion-size parameter $\mathring{a}$, and this has been experimentally verified by other authors.[13]

Bjerrum's critical distance, q, for the solvent mixtures investigated has been calculated from:

$$q = e^2/2\varepsilon kT \tag{5}$$

and is compared in Table 5 with the parameter, $\mathring{a}$, derived by means of eqn. (1) from experimental data. From this table it can be seen that though not un-

Table 5. Comparison between the parameters $\mathring{a}$ and Bjerrum critical distances, q, for the acetone-methanol mixtures at 25°C.

Wt. % methanol	$\mathring{a} \times 10^8$ cm	$q \times 10^8$ cm
0.100	7.8	13.6
0.300	6.3	13.6
1.00	5.0	13.5
2.00	4.7	13.5
5.00	4.4	13.3
10.0	4.3	13.0
20.0	3.9	12.3
50.0	3.7	10.7
100.0	3.1	8.6

expectedly different in magnitude, $\mathring{a}$, and q show the same tendency with changing solvent composition. A conclusion of this investigation is that none of the available theories for association gives an adequate representation of the association of lithium bromide in aprotic-protic solvent mixtures. The $\mathring{a}$-values obtained from eqn. (1) agree with Justice's interpretation and this suggests that a further development of the Bjerrum theory taking the ion-solvent interaction into account would be of interest.

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