Solvation and Ion-Pair Formation of Lithium Bromide in Acetone-Water Mixtures Studied by Reaction Kinetics

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The kinetics of the exchange of ^{82}Br between butyl bromide and lithium bromide in acetone — water mixtures containing between 5×10^{-3} to 1.5 wt. % water have been studied at 25°C for several different concentrations between 2×10^{-4} to 8×10^{-3} M of the ionic bromide. Application of the Acree equation to the kinetic data indicates that the ion-pairs of lithium bromide are kinetically inactive. A strong inhibitory effect on the exchange reaction of the water in the solvent mixture was observed. This effect is interpreted in terms of solvation. Ion-pair association constants calculated from the kinetic data are compared with the corresponding quantities evaluated from electrical conductance data.

The present investigation of the kinetics of the exchange of ^{82}Br between lithium bromide and butyl bromide in acetone — water mixtures at 25°C was undertaken to examine whether ion-pairs of lithium bromide in acetone containing small amounts of water are kinetically active species and also to establish how the tendency of the hydroxylic compound to solvate the bromide ions affects the rate of the exchange reaction.

Measurements were performed for lithium bromide concentrations between 2×10^{-4} M and 8×10^{-3} M in aqueous acetone containing between 5×10^{-3} and 1.505 % by weight of water.

EXPERIMENTAL

Acetone (Merck, *p.a.*) was passed slowly through a column filled with Fischer Sci. Co. type 4 A molecular sieve and subsequently distilled in a Widmer column. According to previous experience [1] this procedure reduces the water content of the acetone to 5×10^{-3} % by weight. The density of the solvent was $d_4{}^{25} = 0.7843$ g cm^{-3}. Solvent mixtures of acetone and water were prepared by weight using water distilled in a quartz apparatus.

Butyl bromide (Fluka, *puriss.*) was dried over phosphorus pentoxide and fractionally distilled. The middle fraction was used.

Lithium bromide (Fluka, *suprapur*) was dried at 200°C for 6 h and cooled in a vacuum desiccator.

Stock solutions of *ca.* 0.01 M lithium bromide in acetone — water mixtures were prepared by weight at 25°C. Less concentrated solutions were prepared by the weight dilution method. All weights were corrected to vacuum.

Radioactive lithium bromide, Li^{82}Br, was prepared from inactive lithium bromide of quality quoted above by the following procedure. About 0.87 mg of the salt was transferred to a quartz ampoule, which was closed and subjected to neutron irradiation in the R2 reactor of the Swedich Atomic Energy Company, Studsvik, Sweden. A thermal neutron flux of 1.6×10^{14} cm^{-2} s^{-1} was used. The time of irradiation was 24 h. After irradiation the ampoule was left for at least 3 days to allow short-lived radioactive nuclides to decay.
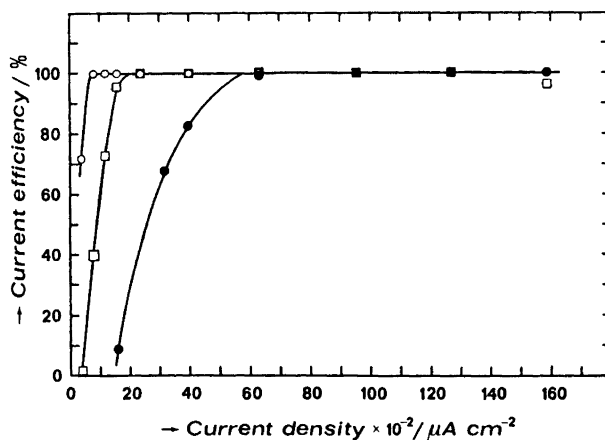

Fig. 1. Current efficiency as a function of current density and concentration for anodic deposition of bromide on silver electrodes from solutions of lithium bromide in aqueous acetone (0.106 wt. % water) agitated at 100 rpm. Volume of electrolytic cell:[3] 50 cm^3. Conc. of lithium bromide: 5.4×10^{-4} M (open circles); 2.13×10^{-3} M (squares); 6.27×10^{-3} M (filled circles). Temperature: 25.0°C. Anode area: 0.126 cm^2.
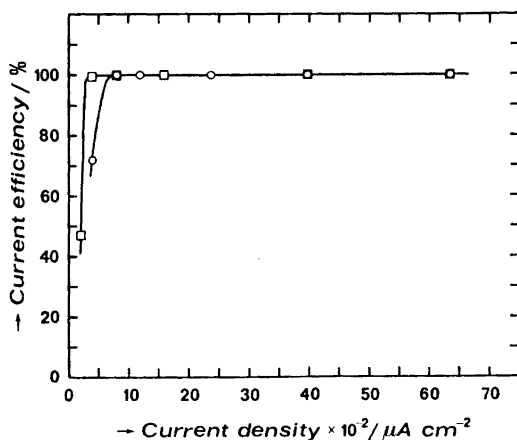

Fig. 2. Current efficiency as a function of current density and solvent composition for anodic deposition of bromide on silver electrodes from solutions of lithium bromide in aqueous acetone (squares, 1.505 wt. % water; open circles, 0.106 wt. % water) agitated at 100 rpm. Volume of electrolytic cell:[3] 50 cm^3. Conc. of lithium bromide: 5.4×10^{-4} M. Temperature: 25.0°C. Anode area: 0.126 cm^2.

The irradiated salt was then dissolved in distilled water and the solution transferred to a volumetric flask in which the solution was evaporated to dryness at 80°C under reduced pressure. The solid residue was further dried at 200°C and normal pressure for 2 h and subsequently cooled in a vacuum desiccator. It was finally dissolved in a known volume of the solvent mixture.

The course of the exchange reaction was studied by means of the electrodeposition method.[2] The equipment used and the kinetic procedure were the same as outlined previously.[3]

The anodic current density was chosen in the usual manner [4] to yield 100 % current efficiency with respect to the electrode reaction, $Ag + Br^- \rightarrow AgBr + e^-$, employed to establish the distribution of radioactivity between the reactants. Current efficiency − current density curves for this electrode reaction were determined for all acetone − water mixtures studied. A few examples are shown in Figs. 1 − 2. Fig. 1 illustrates how the shape of the curve depends on the concentration of lithium bromide at constant solvent composition (acetone containing 0.106 % by weight of water). The dependence of the current efficiency − current density curve on the composition of the solvent mixture at constant concentration of lithium bromide $(5.4 \times 10^{-4}$ M) can be seen in Fig. 2.

RESULTS AND DISCUSSION

The reaction studied may be represented by the overall formula

$$Li^{82}Br + BuBr \rightleftharpoons LiBr + Bu^{82}Br \tag{1}$$

where Bu stands for butyl.

According to McKay,[5] the total rate of exchange, R, may be evaluated by means of the equation

$$\ln (1 - F) = - Rt(b + c)/bc \tag{2}$$

where b is the concentration of butyl bromide, c the concentration of lithium bromide, t the reaction time, and F the fractional exchange, which may be evaluated by means of the expression

$$F = (1 + c/b) (1 - A/A_0) \tag{3}$$

where A_0 denotes the corrected radioactivity of the anode per unit amount of electricity at zero time of exchange and A the corresponding activity value at reaction time t.

Table 1. Kinetic data for exchange of ^{82}Br between lithium bromide and butyl bromide in acetone − water mixtures at 25.0°C.

$b \times 10^2$ M	$c \times 10^4$ M	$R \times 10^8$ M s^{-1}	$k \times 10^4$ M^{-1} s^{-1}	α
		0.005 wt. % water		
5.201	79.95	69.151	16.63	0.2041
5.166	40.13	44.759	21.59	0.2646
5.191	30.24	36.905	23.51	0.2936
5.165	20.05	28.302	27.33	0.3404
5.173	10.07	17.852	34.27	0.4307
5.122	5.041	10.852	42.03	0.5339
5.182	2.000	5.5758	53.80	0.6791

Table 1. Continued.

0.106 wt. % water

5.030	82.28	63.694	15.39	0.2290
5.067	62.43	52.606	16.63	0.2529
5.011	41.57	42.203	20.26	0.2924
5.019	31.69	35.819	22.52	0.3216
5.040	21.18	26.313	24.65	0.3692
5.053	10.59	16.048	29.99	0.4626
5.029	5.384	10.370	38.30	0.5643
4.984	2.122	5.1865	49.04	0.7077

0.305 wt. % water

5.098	82.79	43.641	10.34	0.2508
5.010	59.20	35.799	12.07	0.2820
5.093	40.21	26.868	13.12	0.3222
5.067	29.70	22.468	14.93	0.3570
5.020	20.07	17.007	16.88	0.4061
5.029	10.03	10.356	20.53	0.5033
5.003	5.066	6.2400	24.62	0.6073
5.040	2.066	3.1717	30.46	0.7416

0.605 wt. % water

4.975	78.52	38.400	9.83	0.2775
5.000	61.77	33.294	10.78	0.3008
5.060	41.47	24.635	11.74	0.3433
5.008	31.68	20.482	12.91	0.3748
5.001	21.01	15.403	14.66	0.4270
5.007	10.67	9.5577	17.89	0.5225
5.102	5.410	5.7301	20.76	0.6252
4.988	2.259	2.9680	26.34	0.7533

1.005 wt. % water

5.056	71.97	27.036	7.43	0.3027
4.994	58.10	23.067	7.95	0.3248
5.019	38.74	17.694	9.10	0.3706
5.039	29.20	14.905	10.13	0.4054
5.045	19.39	11.475	11.73	0.4598
5.027	9.732	6.7024	13.70	0.5597
5.007	4.905	4.0719	16.58	0.6633
5.021	2.004	2.0205	20.08	0.7887

1.505 wt. % water

4.953	83.44	20.664	5.00	0.3258
4.976	60.48	17.666	5.87	0.3596
5.006	40.49	13.053	6.44	0.4061
4.986	30.74	10.714	6.99	0.4408
5.022	20.48	8.2692	8.04	0.4953
4.990	10.32	4.9437	9.60	0.5943
5.012	5.168	2.9451	11.37	0.6961
4.970	2.121	1.4168	13.44	0.8136

The results of the kinetic measurements are summarized in Table 1, in which the rate constant, k, is defined by the expression

$$k = R/bc \qquad (4)$$

and α is the degree of dissociation of the inorganic bromide.

The latter quantity was calculated by successive approximations [6] from the ion-pair association constants, K_A, in Table 2 according to Refs. 7 − 8. Activity coefficients were calculated from the Debye-Hückel equation in the form quoted in Ref. 6 using the permittivities, ε, and ion-size parameters, $\mathring{a}$, in Table 2.

Table 2. Permittivities of acetone − water mixtures and conductance parameters for lithium bromide in acetone − water mixtures at 25.0°C according to Refs. 7 − 8.

Water conc. wt. %	ε	K_A M^{-1}	$\mathring{a} \times 10^8$ cm
0.005	20.7	4202	9.3
0.106	20.8	3360	6.6
0.305	20.8	2786	6.4
0.605	20.9	2383	5.2
1.005	21.2	2073	5.4
1.505	21.3	1640	3.9

Graphical representations of the dependence of the rate constant, k, according to eqn. (4) on the ionic strength, μ, are shown in Fig. 3. For all solvent mixtures investigated the rate constant, k, decreases with increasing
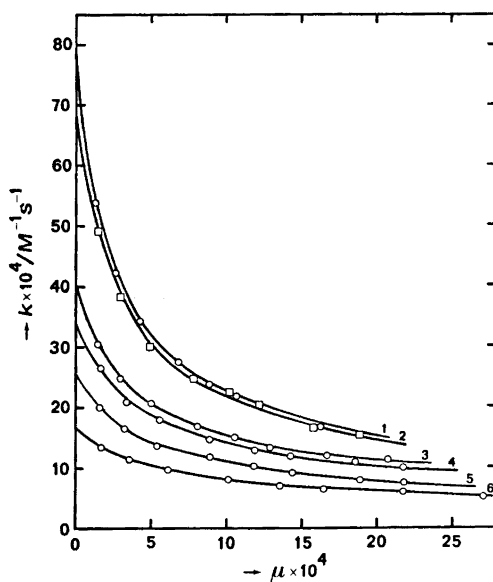

Fig. 3. Dependence of the rate constant, k, according to eqn. (4) on the ionic strength, μ, for the isotopic exchange between lithium bromide and butyl bromide in acetone − water mixtures at 25.0°C. The curves 1 − 6 represent data for solvent mixtures containing 0.005, 0.106, 0.305, 0.605, 1.005, and 1.505 wt. % water, respectively.

ionic strength. In part this effect may be due to a negative kinetic salt effect. This effect appears, however, to be of minor importance (*cf.* Refs. 9 – 10) and will be neglected in the following discussion.

To analyze the kinetic data with respect to any possible first-order contribution (rate constant k_1) and with respect to reactivities of free bromide ions and lithium bromide ion-pairs (second-order rate constants k_i and k_m, respectively) we shall employ the expression

$$R = k_1 b + k_i bc\alpha + k_m bc(1 - \alpha) \tag{5}$$

which reduces to

$$R = k_1 b + k_i bc\alpha \tag{6}$$

for low concentrations of lithium bromide when $\alpha \simeq 1$ and/or if the ion-pairs are kinetically inactive $(k_m = 0)$.
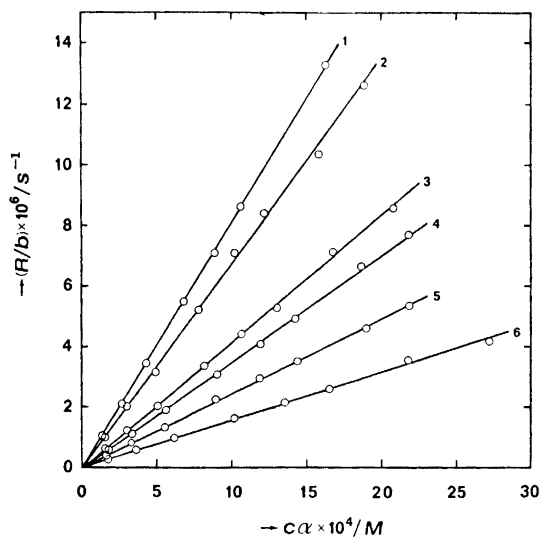

Fig. 4. Graphs of R/b *vs.* $c\alpha$ according to eqn. (6) for the same systems as in Fig. 3.

Graphs of R/b *vs.* $c\alpha$ according to eqn. (6) are shown in Fig. 4. For all solvent mixtures investigated the curve passes through the origin indicating absence of any first-order contribution to the reaction rate.

Hence, the term $k_1 b$ in eqn. (5) may be omitted. Combining the resulting expression with eqn. (4) yields the Acree equation [11]

$$k/\alpha = k_i + k_m(1 - \alpha)/\alpha \tag{7}$$

which may be employed to determine k_i and k_m.

The separated rate constants, k_i and k_m, were evaluated by fitting straight lines to values of k/α *vs.* $(1-\alpha)/\alpha$ according to eqn. (7) using the method of least squares. Graphical representations of eqn. (7) for the different solvent mixtures studied are shown in Fig. 5.

Table 3. Rate constants for reactions of ions and ion-pairs for the same systems as in Table 1.

Water conc. wt. %	$k_i \times 10^4$ M^{-1} s^{-1}	$k_m \times 10^4$ M^{-1} s^{-1}
0.005	78.50 ± 0.39	0.84 ± 0.17
	(78.13 ± 0.31)	(0.87 ± 0.14)
0.106	68.05 ± 1.50	-0.23 ± 0.71
0.305	40.67 ± 0.52	0.40 ± 0.28
0.605	33.70 ± 0.54	0.61 ± 0.33
1.005	25.33 ± 0.28	-0.35 ± 0.19
1.505	16.56 ± 0.20	-0.43 ± 0.16

Values of k_i and k_m for the different solvent·mixtures investigated are summarized in Table 3, where uncertainties quoted are standard deviations. The maximum value of k_m/k_i amounts to 0.018 (acetone containing 0.605 wt. % water) which may be regarded as zero within experimental errors. Hence, paired bromide ions appear to be unreactive species for all solvent mixtures investigated. Some reservation should, however, be attached to this conclusion because we have not corrected for any negative kinetic salt effect, which may
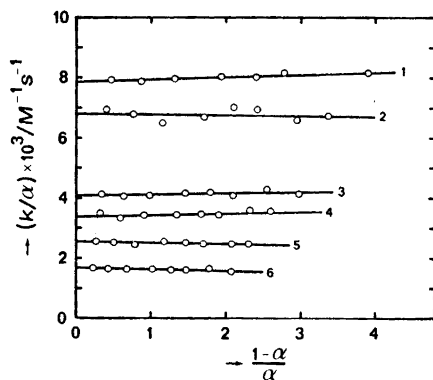

Fig. 5. Graphs of k/α vs. $(1 - \alpha)/\alpha$ according to eqn. (7) for the same systems as in Fig. 3.
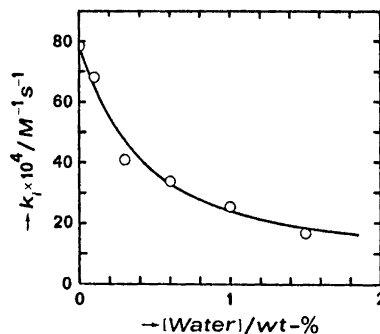
Fig. 6. Dependence of k_i according to eqn. (7) on solvent composition for the isotopic exchange between lithium bromide and butyl bromide in acetone − water mixtures at 25.0°C.

result in an underestimation of the value of k_m as discussed in a previous paper.[10] At present any unequivocal correction for this effect cannot be made (*cf.* Ref. 10).

The values of k_i and k_m within brackets in Table 3 for acetone containing 0.005 wt. % water were obtained by re-analyzing the kinetic data in Table 1 of a previous investigation [3] with the values, $\varepsilon = 20.7$, $K_A = 4202$ M^{-1}, and

$\mathring{a} = 9.3 \times 10^{-8}$ cm, according to Table 2 in this paper. The rate constants, $k_i = 78.13 \times 10^{-4}$ and $k_m = 0.87 \times 10^{-4}$ M^{-1} s^{-1}, obtained by this means and the figures, $k_i = 78.50 \times 10^{-4}$ and $k_m = 0.84 \times 10^{-4}$ M^{-1} s^{-1}, according to the present research are in excellent agreement.

From Fig. 6, in which the rate constant for exchange between unpaired bromide ions and butyl bromide has been plotted as a function of the water concentration of the solvent mixture, it is evident that water in acetone has a strong inhibitory effect on the exchange reaction. Addition of 1.5 wt. % of water to anhydrous acetone reduces k_i from 78.5×10^{-4} to 16.6×10^{-4} M^{-1} s^{-1}, *i.e.* by a factor of 4.7.

It may be noted that this addition of water only insignificantly alters the permittivity of the solvent, *viz.* from 20.7 to 21.3. The different solvent mixtures studied in this investigation are thus nearly isodielectric and the very strong retarding effect on the rate of the exchange reaction by the hydroxylic constituent of the solvent mixture might be attributed to solvation phenomena. Bromide ions would be more strongly solvated by water (hydrogen-bond formation) than by acetone. The presence of water in acetone should therefore increase the activation energy for the exchange reaction as compared with the activation energy in pure acetone as solvent medium. An interesting task would be to verify this experimentally.

A similar retarding effect was observed by Leary and Kahn,[12] who investigated the influence of small concentrations of protic compounds in acetone on the kinetics of the exchange of radio-iodine between potassium iodide and benzyl iodides. They developed a method for quantitative treatment of this effect, which we shall apply below to the bromine exchange reaction studied here.

Following the arguments of the aforementioned authors,[12] we shall assume that each bromide ion is solvated by either n molecules of acetone and no water or by $(n-1)$ molecules of acetone plus one molecule of water. We thus assume that the concentrations of bromide ions solvated by more than one molecule of water are sufficiently low to be neglected.

On these assumptions we have to consider the following equilibrium
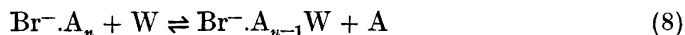
$$\text{Br}^-.\text{A}_n + \text{W} \rightleftharpoons \text{Br}^-.\text{A}_{n-1}\text{W} + \text{A} \tag{8}$$

where A stands for $(\text{CH}_3)_2\text{CO}$ and W stands for H_2O.

Denoting the equilibrium constant for the equilibrium (8) by K and molar concentrations by square brackets we have

$$\frac{[\text{Br}^-.\text{A}_{n-1}.\text{W}][\text{A}]}{[\text{Br}^-.\text{A}_n][\text{W}]} = K \tag{9}$$

assuming the activity coefficent ratio for all the species to be constant for the range of concentrations of water investigated.

Using $[\text{Br}^-]_{\text{tot}}$ to denote the total molar concentration of unpaired bromide ions we have the condition

$$[\text{Br}^-]_{\text{tot}} = [\text{Br}^-.\text{A}_n] + [\text{Br}^-.\text{A}_{n-1}.\text{W}] \tag{10}$$

which combined with eqn. (9) yields

$$\frac{[\text{Br}^-]_{\text{tot}}}{[\text{Br}^-.\text{A}_n]} = 1 + K\frac{[\text{W}]}{[\text{A}]} \tag{11}$$

The second-order rate constant for exchange of bromine between $\text{Br}^-.\text{A}_n$ and butyl bromide will be denoted k_A and the corresponding rate constant for exchange between $\text{Br}^-.\text{A}_{n-1}.\text{W}$ and the organic bromide denoted k_{AW}. We may then express the rate of exchange by means of the equation

$$R = k_A b[\text{Br}^-.\text{A}_n] + k_{\text{AW}}b[\text{Br}^-.\text{A}_{n-1}.\text{W}] \tag{12}$$

As shown above k_1 and k_m in eqn. (5) are both equal to zero, $i.e.$

$$R = k_i b[\text{Br}^-]_{\text{tot}} \tag{13}$$

which combined with eqn. (12) yields

$$k_i[\text{Br}^-]_{\text{tot}} = k_A[\text{Br}^-\text{A}_n] + k_{\text{AW}}[\text{Br}^-.\text{A}_{n-1}.\text{W}] \tag{14}$$

In view of eqn. (10) we may rewrite eqn. (14) in the form

$$\frac{[\text{Br}^-]_{\text{tot}}}{[\text{Br}^-.\text{A}_n]} = \frac{k_A - k_{\text{AW}}}{k_i - k_{\text{AW}}} \tag{15}$$

which together with eqn. (11) yields

$$\frac{k_A - k_{\text{AW}}}{k_i - k_{\text{AW}}} = 1 + K\frac{[\text{W}]}{[\text{A}]} \tag{16}$$

If bromide ions solvated by acetone plus one water molecule react with the organic bromide at a much lower rate than purely acetonated bromide ions, then $k_{\text{AW}} \ll k_A$. If, in addition, the concentration of water in the solvent mixture is sufficiently low to make $k_i \gg k_{\text{AW}}$, eqn. (16) may be approximated by the expression

$$\frac{k_A}{k_i} = 1 + K\frac{[\text{W}]}{[\text{A}]} \tag{17a}$$

which for evaluation of k_A and K may be conveniently rewritten in the form

$$\frac{1}{k_i} = \frac{1}{k_A} + \frac{K}{k_A}\frac{[\text{W}]}{[\text{A}]} \tag{17b}$$

According to eqn. (17b) a plot of $1/k_i$ $vs.$ $[\text{W}]/[\text{A}]$ should yield a straight line, the equation of which might be used to obtain k_A and K. Fig. 7 shows a graph of this kind. In calculating the molar concentrations of water and acetone involved in eqn. (17b) densities of acetone − water mixtures given in Ref. 7 were used.

From the equation of the straight line in Fig. 7, fitted by means of the relative deviation least squares method [13] since the relative error in $1/k_i$ appears to be independent of $[\text{W}]/[\text{A}]$, we obtain $k_A = 80.3 \times 10^{-4}$ M^{-1} s^{-1} and $K = 73$. For the corresponding equilibrium

$$\text{I}^-.\text{A}_n + \text{W} \rightleftharpoons \text{I}^-.\text{A}_{n-1}.\text{W} + \text{A} \tag{18}$$
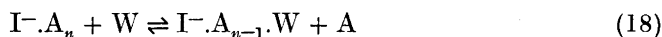
Leary and Kahn [12] obtained the value, $K = 15$, from kinetic data for the
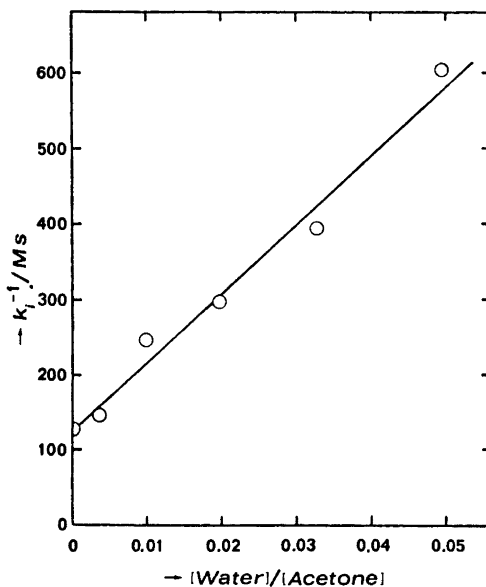
Fig. 7. Graph according to eqn. (17b) for the same systems as in Fig. 3.

potassium iodide — benzyl iodide exchange reaction in solvent mixtures of acetone and water at 0°C.

As found above there is no evidence of any ion-pair reactivity. Hence, we may put k_m in eqn. (7) equal to zero and calculate the ion-pair association constant, K_A, from the expression

$$\frac{1}{k} = \frac{1}{k_i} + \frac{c\gamma^2 k K_A}{k_i{}^2} \qquad (19)$$

derived in a previous paper.[6] In calculating mean molar activity coefficients, γ, involved in eqn. (19) we used the same form of the Debye-Hückel equation as in Ref. 6 and the permittivities and ion-size parameters listed in Table 2.

Table 4. Comparison of ion-pair association constants according to conductance data (K_A') and kinetic data (K_A'') for lithium bromide in acetone — water mixtures at 25.0°C.

Water conc. wt. %	K_A' M^{-1}	K_A'' M^{-1}	K_A''/K_A'
0.005	4202	3659	0.87
0.106	3360	3484	1.04
0.305	2786	2522	0.91
0.605	2383	2113	0.89
1.005	2073	2287	1.10
1.505	1640	1910	1.16

The results of these calculations are shown in the penultimate column of Table 4, in which comparison with the corresponding association constants derived from electrical conductance data according to Refs. 7 — 8 is also made. The agreement between the two different methods of determination appears from the quotients in the last column of this table.
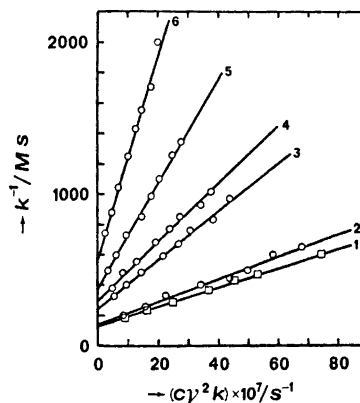

Fig. 8. Graphs according to eqn. (19) for the same systems as in Fig. 3.

Graphs of $1/k$ vs. $c\gamma^2 k$ according to eqn. (19) are shown in Fig. 8. As can be seen in this figure very satisfactory straight lines are obtained.

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