

Solvent Effects and Activation Parameters for the Isotopic Exchange Reaction between Lithium Bromide and Butyl Bromide in Acetone—Water Mixtures

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The effect of minute amounts of water (≤ 1.5 wt.-%) in acetone on the kinetics of the isotopic exchange between lithium bromide and butyl bromide has been investigated over a range of temperatures (15–35 °C) using ^{82}Br as a radioactive indicator. The observed rapid decrease in the specific rate of exchange with increasing concentration of water in the solvent mixture is interpreted in terms of preferential solvation of the bromide ion. Activation parameters, ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger have been calculated. The inhibitory effect of the protic constituent on the exchange reaction is reflected in a decreasing entropy of activation with increasing water concentration rather than in an increasing enthalpy of activation. Transfer activity coefficients for the transfer of bromide ions from pure to aqueous acetone have been estimated from the kinetic data and are used together with ion-pair association for lithium bromide to obtain information about solvation of the ion-pairs.

Preferential solvation of bromide ions in aqueous acetone at 25 °C was studied kinetically in a previous investigation¹ by following the exchange of radiobromide between lithium bromide and butyl bromide in acetone containing from 0.005 to 1.5 wt.-% of water. For these low concentrations of water, the macroscopic permittivity of the solvent mixtures used to carry out the exchange reaction remains almost constant; in addition self-association of the water molecules is minimized. The protic constituent of the solvent mixture was found to inhibit the exchange reaction very strongly. Addition of 1.5 wt.-% of water to anhydrous acetone decreased the specific reaction rate by a factor of 5.

The aim of the present research was to obtain more detailed insight into the various factors influencing the kinetics of the exchange reaction discussed above. To that end the kinetic measurements have now been extended to cover a range of temperatures, *viz.* from 15 to 35 °C.

EXPERIMENTAL

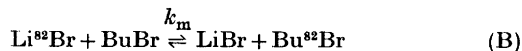
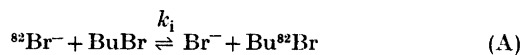
Acetone (Merck, *p.a.*) and water were purified according to Ref. 1. The density of the purified acetone was $0.7843 \text{ kg dm}^{-3}$ at 25 °C. Acetone–water solvent mixtures were prepared by weight at 25 °C. The reactants, *i.e.* butyl bromide (Fluka, *puriss.*) and lithium bromide (Fluka, *suprapur*), were purified according to Ref. 1. Radioactive lithium bromide, Li^{82}Br , was prepared by neutron irradiation of known amounts of inactive lithium bromide in the R 2 reactor of the Swedish Atomic Energy Company, Studsvik, Sweden. The irradiated salt was dissolved in a known volume of the solvent mixture.

The time dependence of the exchange reaction was followed by anodic deposition of bromide on silver electrodes.^{2,3} The anodic current density was chosen⁴ to yield 100 % current efficiency with respect to the electrode reaction, $\text{Ag} + \text{Br}^- \rightarrow \text{AgBr} + \text{e}^-$. The radioactivity of each electrode was measured by means of a proportional counter. The usual corrections for deadtime losses, backgrounds counts, and decay were applied to the counting rates.

The rate of exchange, R , was calculated by means of the McKay equation⁵ using the method of least squares.

RESULTS AND DISCUSSION

According to the Acree hypothesis,⁶ the overall exchange reaction studied may be separated into the following two reactions,



where k_i and k_m are the rate constants for the two different exchange reactions involving free and paired bromide ions, respectively.

The Acree equation for the observed second-order rate constant, k , may be expressed,

$$k = k_i\alpha + k_m(1 - \alpha) \quad (1)$$

where α is the degree of dissociation of the ion-pairs. Hence, application of eqn. (1) to the kinetic data requires access to ion-pair association constants, K_A , of lithium bromide in the various acetone-water solvent mixtures investigated.

The association constants listed in Table 1 were evaluated from electrical conductance data^{7,8} using the conductance equation of Fuoss and Hsia^{9,10} in the form of Fernández-Prini.¹¹ The Debye-Hückel equation¹² for the mean activity coefficient of free ions was used. The method of calculating K_A has been described.¹³

Table 1, in which ϵ is the permittivity of the solvent and q is the Bjerrum radius,¹⁴ reveals that the association constant is rather insensi-

Table 1. Association constants for lithium bromide in acetone-water mixtures.⁸

water conc. wt.-%	ϵ	$q \times 10^{10}$ m	K_A/M^{-1} $r=q$	$r=q/2$
15 °C				
0.005	21.62	13.41	3424	3344
0.055	21.66	13.39	2990	2905
0.106	21.69	13.37	2814	2739
1.505	22.45	12.92	1697	1635
25 °C				
0.005	20.7	13.54	4160	4073
0.055	20.75	13.51	3695	3610
0.106	20.8	13.47	3413	3334
1.505	21.3	13.16	1758	1698
35 °C				
0.005	19.65	13.80	4513	4404
0.055	19.67	13.79	4168	4080
0.106	19.68	13.78	3918	3830
1.505	20.40	13.29	1852	1780

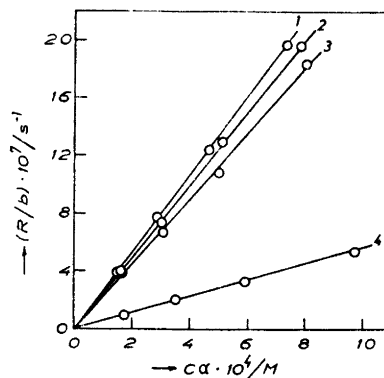


Fig. 1. Graphs of R/b vs. $c\alpha$ for the isotopic exchange between lithium bromide and butyl bromide in acetone-water mixtures at 15 °C. The curves 1-4 represent data for solvent mixtures containing 0.005, 0.055, 0.106 and 1.505 wt.-% water, respectively.

tive to the value of the distance parameter, r , the maximum centre-to-centre distance between the ions in the ion-pair. For a given solvent mixture the values of K_A corresponding to $r=q$ and $r=q/2$, respectively, differ only slightly. Because of this fact, and because the rate constant, k_i , is rather insensitive to moderate changes in K_A , as will be shown below, the distance parameter may be set equal to the Bjerrum radius.

The total rate of exchange, R , may be written

$$R = k_1b + kbc \quad (2)$$

where k_1 is the first-order rate constant, b is the concentration of the organic bromide and c is the concentration of the inorganic bromide.

According to eqns. (1) and (2) a plot of R/b vs. $c\alpha$ should yield a straight line with intercept k_1 and slope k_i , if $\alpha=1$ and/or if $k_m=0$. A straight line was fitted to the experimental points by means of the relative deviation least squares method.¹⁵ Representative graphs of R/b vs. $c\alpha$ are illustrated in Fig. 1. Within experimental errors all curves pass through the origin, indicating no observable contribution of S_N1 exchange to the reaction rate. Hence, the term k_1b in eqn. (2) may be omitted and the observed second-order rate constant k represented by the expression,

$$k = R/(bc) \quad (3)$$

Table 2. Kinetic data for exchange of ^{82}Br between lithium bromide and butyl bromide in acetone-water mixtures at 15.0 °C.

$b \times 10^3$ 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				
5.649	20.18	11.116	9.751	0.3658
5.752	10.20	7.0874	12.08	0.4598
5.740	5.014	4.4610	15.50	0.5686
6.101	2.116	2.3870	18.49	0.7033
0.055 wt-% water				
5.674	20.51	11.056	9.500	0.3843
5.117	10.96	6.5785	11.73	0.4721
5.677	5.195	4.1554	14.09	0.5870
5.697	2.236	2.3018	18.07	0.7171
0.106 wt-% water				
5.694	20.48	10.459	8.969	0.3939
5.708	10.20	6.1540	10.57	0.4932
5.690	5.070	3.7676	13.06	0.6015
5.701	2.266	2.1948	16.99	0.7248
1.505 wt-% water				
5.737	20.36	3.0498	2.611	0.4761
5.739	10.21	1.8762	3.201	0.5801
5.711	5.134	1.1763	4.012	0.6854
5.722	2.133	0.55032	4.509	0.8059

The results of the kinetic measurements are summarized in Tables 2–3, in which the degree of dissociation, α , of the ionic reactant is included.

In accord with eqn. (1) rate constants, k_i and k_m , were evaluated by fitting straight lines to the experimental points of k/α vs. $(1-\alpha)/\alpha$ using the relative deviation least squares method. Calculations of this kind were performed using values of K_A corresponding to $r=q$ and $r=q/2$, respectively. The results are listed in Table 4.

The values of k_i at 25 °C in Table 4, reevaluated from kinetic data previously reported,¹ deviate by less than 1 % from the corresponding values of k_i in Ref. 1, in which α values according to the Fuoss-Onsager equation¹⁶ from 1957 were used. The compilation in Table 4 reveals that the values of k_i obtained using association constants, K_A , corresponding to $r=q$ and $r=q/2$, respectively, differ insignificantly.

The derived values for the ion-pair rate constant, k_m , have not been tabulated. In all in-

stances the k_m values are close to zero. The maximum value of k_m/k_i , obtained for acetone containing 0.055 wt-% water at 25 °C with r set equal to q , amounts to 4 %. Hence the lithium bromide ion-pairs might be regarded as non-reactive species although some reservation should be attached to this statement because it has not been possible to correct for the presence of any (small) kinetic salt effect.

From the data in Table 4 and from Table 3 in Ref. 1 it is apparent that the S_N2 exchange of bromide between lithium bromide and butyl bromide is much faster in anhydrous acetone than in the acetone-water solvent mixtures. The major reason for this retarding effect on the free ion-molecule reaction, when the protic component is added to the system, would be the property of water as a hydrogen-bond donor. Since the bromide ion behaves like a Lewis base (nucleophile) it forms a hydrogen bond with the protic component. This interaction would be stronger than the interaction between the bromide ion and acetone molecules.

For a reaction like (A) in a mixed solvent of acetone and water it would be a competition

Table 3. Kinetic data for exchange of ^{82}Br between lithium bromide and butyl bromide in acetone-water mixture at 35.0 °C.

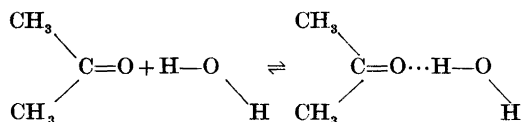
$b \times 10^2$ M	$c \times 10^4$ M	$R \times 10^8$ M s $^{-1}$	$k \times 10^4$ M $^{-1}$ s $^{-1}$	α
0.005 wt-% water				
5.161	19.61	68.730	67.91	0.3309
5.165	9.905	43.557	85.14	0.4201
5.178	4.869	27.329	108.4	0.5261
5.221	2.052	15.095	140.9	0.6629
0.055 wt-% water				
5.153	19.78	67.169	65.90	0.3411
5.118	4.929	26.437	104.8	0.5381
5.144	2.066	14.251	134.1	0.6753
0.106 wt-% water				
5.111	9.936	42.211	83.12	0.4428
5.092	4.995	25.765	101.3	0.5469
5.144	2.116	13.932	128.0	0.6821
1.505 wt-% water				
5.163	19.79	22.949	22.46	0.4675
5.164	9.919	13.814	26.97	0.5711
5.198	4.987	8.5803	33.10	0.6766
5.193	2.082	3.9863	36.87	0.7981

Table 4. Rate constants, k_i , for the exchange of bromine between lithium bromide and butyl bromide in acetone–water mixtures at 15, 25 and 35 °C.^a

Water conc. wt.-%	$k_i \times 10^4 / s^{-1}$ 15 °C	25 °C	35 °C
	$r = q$		
0.005	26.62 ± 0.65	78.15 ± 0.40	212.1 ± 4.3
0.055	24.77 ± 0.71	70.37 ± 1.65	199.0 ± 2.2
0.106	22.66 ± 1.30	68.04 ± 1.51	186.7 ± 3.3
1.505	5.772 ± 0.187	16.61 ± 0.21	46.83 ± 1.46
	$r = q/2$		
0.005	26.57 ± 0.65	78.00 ± 0.40	211.5 ± 4.3
0.055	24.72 ± 0.71	70.22 ± 1.63	198.7 ± 2.3
0.106	22.64 ± 1.29	67.92 ± 1.49	186.4 ± 3.3
1.505	5.762 ± 0.186	16.59 ± 0.21	46.74 ± 1.45

^a The values of k_i at 25 °C were evaluated from the experimental data reported in Ref. 1.

between the different components of the reaction mixture for the hydrogen bonds donated by water. These interactions, *e.g.* that between acetone and water,¹⁷



would be of importance for the rate of the exchange reaction studied. The competition between acetone and water molecules for the bromide ions may be represented by the solvation equilibrium (*cf.* Ref. 1),



according to which we assume that each bromide ion is solvated by either n molecules of acetone ("A") or by $(n-m)$ molecules of acetone and m molecules of water ("W").

According to a spectroscopic investigation of Parker and Brody,¹⁸ the solvation of anions by hydrogen-bond donating solvents has more the character of a general interaction than a specific interaction involving stoichiometric hydrogen-bonded species. In contrast, investigations of Kolthoff and Chantooni^{19,20} on the hydration of ions in aqueous acetonitrile indicate that there are specific 1:1 and 1:2 interactions between ions and water.

Whatever the true picture of the solvation of ions, we will use the equilibrium (C) to cal-

culate overall values of the solvation equilibrium constant, K , and the solvation number m . Following the derivation in Ref. 1 the thermodynamic equilibrium constant, K_{th} , for the equilibrium (C) may be written,

$$K_{\text{th}} = \frac{[\text{Br}^- \text{A}_{n-m} \text{W}_m] [\text{A}]^m}{[\text{Br}^- \text{A}_n] [\text{W}]^m} \times \Phi \quad (4)$$

where square brackets denote molar concentrations and Φ is the activity coefficient ratio for the species involved. On the assumption that the activity coefficient ratio, Φ , does not vary with the composition of the solvent we have,

$$K_{\text{th}}/\Phi = K = \frac{[\text{Br}^- \text{A}_{n-m} \text{W}_m] [\text{A}]^m}{[\text{Br}^- \text{A}_n] [\text{W}]^m} \quad (5)$$

in which the constant, K , may be estimated from our kinetic data.

Using the results of eqns. (1–2), which indicate that both k_1 and k_m may be omitted, and using the stoichiometric condition for bromide ions we obtain the following equation¹

$$\frac{k_A - k_i}{k_i - k_{\text{AW}}} = K \left(\frac{[\text{W}]}{[\text{A}]} \right)^m \quad (6)$$

where k_A is the second-order rate constant for the exchange of bromide and k_{AW} is the rate constant for the corresponding exchange reaction involving $\text{Br}^- \text{A}_{n-m} \text{W}_m$.

For low concentrations of water in the solvent mixture, $k_i \gg k_{\text{AW}}$. Hence, eqn. (6) may be expressed,

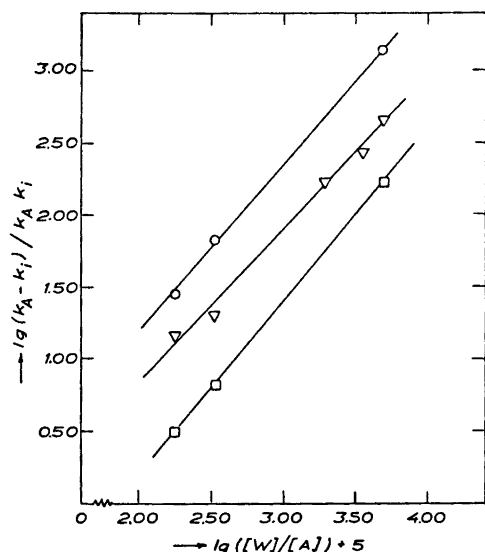


Fig. 2. Graphs according to eqn. 7 for the isotopic exchange between lithium bromide and butyl bromide in acetone-water mixtures at 15 °C (O), 25 °C (∇) and 35 °C (□). Data at 25 °C are obtained from Ref. 1. In the computation of m and K at 25 °C one point (acetone containing 0.3 wt-% water) was omitted.

$$\lg \frac{k_A - k_i}{k_i k_A} = m \lg \frac{[W]}{[A]} + \lg \frac{K}{k_A} \quad (7)$$

Using the method of least squares, eqn. (7) was applied to the kinetic data in Table 4 and in Table 3 of Ref. 1. Graphical representations of eqn. (7) are shown in Fig. 2.

From the slopes and intercepts of the three lines in this figure values of m and K , for solvation of the bromide ion in the acetone-water mixtures investigated at 15, 25 and 35 °C, were obtained. The results are summarized in Table 5, where errors quoted are standard deviations.

Table 5. Over-all solvation constants, K , and over-all solvation numbers, m , for the equilibria (C) and (D) at different temperatures.

t °C	m	K (C)	(D)
15	1.16 ± 0.03	119	5.8
25	1.09 ± 0.06	92	5.4
35	1.20 ± 0.02	132	5.9

If water as a hydrogen bond donor is assumed to solvate the bromide ion much more strongly than acetone, the solvation equilibrium (D) may be used to calculate m and K .



On the assumption expressed by (D), the following equation may be deduced,

$$\lg \frac{k_A - k_i}{k_i k_A} = m \lg [W] + \lg \frac{K}{k_A} \quad (8)$$

As may be seen from Table 5, the values of K calculated by means of eqn. (8) are lower than the K -values obtained by means of eqn. (7), but the values of m are unchanged.

According to Table 5 the overall number of water molecules associated to the bromide ion is close to 1.

With $m=1$, eqn. (7) may be rewritten,

$$\frac{1}{k_i} = \frac{1}{k_A} + \frac{K [W]}{k_A [A]} \quad (9)$$

Application of this expression to the kinetic data in Table 4 using the relative deviation least squares method yields $K=76$, 73, and 75 at 15, 25, and 35 °C, respectively. Comparison of these values with the corresponding figures in Table 5 indicates that the value of the equilibrium constant, K , is rather sensitive to the value of the overall solvation number, m .

Equilibrium (D) with $m=1$, yields $K=5.7$, 5.1 and 5.7 at 15, 25, and 35 °C, respectively.

According to the transition state theory²¹⁻²³ the temperature dependence of the rate constant, k_i , in eqn. (1) may be written

$$\ln k_i = \ln \frac{kT}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (10)$$

where k is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, R is the gas constant, ΔH^\ddagger is the standard enthalpy of activation, and ΔS^\ddagger is the standard entropy of activation. By means of the definition of the Arrhenius activation energy, E_a , eqn. (10) may be written in the form

$$\ln k_i = \ln \frac{kT}{h} + 1 + \frac{\Delta S^\ddagger}{R} - \frac{E_a}{RT} \quad (11)$$

Eqn. (11) was fitted to the kinetic data, referring to $r=q$ in Table 4, according to the method of least squares. Graphs of $\ln k_i$ vs. T^{-1}

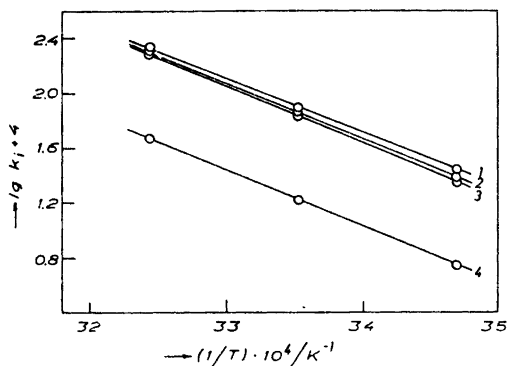


Fig. 3. Temperature dependence of k_i on solvent composition according to eqn. (11). The curves 1–4 represent data for solvent mixtures containing 0.005, 0.055, 0.106 and 1.505 % water by weight, respectively.

are shown in Fig. 3. From the equation of these straight lines we obtain the activation parameters summarized in Table 6, where errors quoted are estimated standard deviations.

When considering the effect of increasing concentration of protic component on the reaction rate, one must consider the changes in solvation of the reactants and the transition state, *i.e.* the changes in Gibbs' free energy of each of these species with solvent composition. According to Table 6, the increase in ΔG^\ddagger amounts to 3.8 kJ mol⁻¹ when the concentration of water in the solvent mixture is increased from 0.005 to 1.5 wt-%. This implies that the solvation of the reactants increases as compared with the solvation of the activated complex.

It seems reasonable to assume that the solvation of butyl bromide should decrease rather than increase with increasing water concentra-

tion of the solvent mixture. Hence, the increase in solvation of the reactants would depend almost entirely on solvation of the anion.

In the activated complex, the negative charge originally located on one bromide ion is distributed on two bromide ions. Hence, formation of the activated complex is accompanied by a reduction in the charge density reducing the ability to form hydrogen bonds. For the acetone–water mixtures with water concentration ≤ 0.1 wt-% (Table 6), $-\Delta S^\ddagger \approx 34-37$ J K⁻¹ mol⁻¹, *i.e.* approximately constant. At 1.5 wt-% water, the activation entropy has decreased to -47 J K⁻¹ mol⁻¹. These data indicate that, for the solvent mixture containing 1.5 wt-% water, the activated complex represents a higher order relative to the reactants than does the transition state in pure acetone.

Comparison of the values of ΔH^\ddagger and ΔS^\ddagger in Table 6 reveals that the entropy of activation is of major importance for the increase in Gibbs' free energy of activation, when the water content of the solvent mixtures is increased from 0.005 to 1.5 wt-%.

Several authors have demonstrated that in reactions of type (A) substitution of a protic solvent for an aprotic one decreases the specific reaction rate. There is strong evidence²⁴⁻²⁵ that an increase in the enthalpy of activation, rather than a decrease in the entropy of activation, is responsible for this change. Comparison with the results of the present investigation suggests that the relative importance of ΔH^\ddagger and ΔS^\ddagger in protic-aprotic solvent mixtures changes gradually with the composition of the solvent.

The influence of ionic strength on the rate of reaction (A) may be represented by the Brønsted-Bjerrum equation,

$$k = k^\circ \frac{(\gamma_{\text{Br}^-})(\gamma_{\text{BuBr}})}{\gamma^\ddagger} \quad (12)$$

where γ is the activity coefficient and \ddagger stands for the activated complex.

In discussing solvation the following type of activity coefficient has been defined, *cf.* Refs. 27–28 and references therein,

$$(\mu_i^\circ)_S = (\mu_i^\circ)_R + RT \ln \gamma_{t,i} \quad (13)$$

where S stands for any solvent or mixture of solvents, R stands for a selected reference sol-

Table 6. Thermodynamic data for the exchange of ⁸²Br between lithium bromide and butyl bromide in aqueous acetone at 25.0 °C.

Water conc. wt-%	ΔG^\ddagger kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹
0.005	85.0	74.1 ± 0.2	-36.7 ± 0.1
0.055	85.3	74.4 ± 1.4	-36.4 ± 0.8
0.106	85.4	75.4 ± 0.4	-33.7 ± 0.2
1.505	88.9	74.8 ± 1.0	-47.2 ± 0.8

vent, and $\gamma_{t,i}$ is the transfer activity coefficient, which reflects the change in chemical potential of a solute, i , on transfer from a reference solvent to another solvent. When transfer activity coefficients are applied to reaction rates by means of the absolute rate theory, an equation similar to eqn. (12), but in terms of transfer activity coefficients, is obtained.

If we use transfer activity coefficients for the systems investigated in this research, the effect of solvent on the rate of the exchange reaction studied may be written,²⁸

$$(k_i)_{AW} = (k_i)_A \frac{(\gamma_{t,Br^-})(\gamma_{t,BuBr})}{\gamma_{t,\ddagger}} \quad (14)$$

where AW and A denote aqueous and pure acetone, respectively.

Upon application of eqn. (13) to reaction (A), the difference in chemical potential between transition state and reactants may be written,

$$(\Delta G^\ddagger)_{AW} = (\Delta G^\ddagger)_A + RT \ln \frac{\gamma_{t,\ddagger}}{(\gamma_{t,Br^-})(\gamma_{t,BuBr})} \quad (15)$$

According to eqns. (14) and (15) we have,

$$(\Delta G^\ddagger_t)_{A \rightarrow AW} = -RT \ln \frac{(k_i)_{AW}}{(k_i)_A} \quad (16)$$

where $(\Delta G^\ddagger_t)_{A \rightarrow AW}$ is the difference in Gibbs' free energy of activation for reaction (A) in aqueous and pure acetone, respectively.

Application of a thermodynamic cycle to reaction (A) in pure acetone and in aqueous acetone yields,

$$\begin{aligned} (\Delta G^\ddagger_t)_{A \rightarrow AW} &= (\Delta G^\ddagger_{t,\ddagger})_{A \rightarrow AW} - \\ &(\Delta G^\ddagger_{t,BuBr})_{A \rightarrow AW} - (\Delta G^\ddagger_{t,Br^-})_{A \rightarrow AW} \end{aligned} \quad (17)$$

Eqn. (17) may be reduced to,

$$(\Delta G^\ddagger_t)_{A \rightarrow AW} = -(\Delta G^\ddagger_{t,Br^-})_{A \rightarrow AW} \quad (18)$$

if we assume that $(\Delta G^\ddagger_{t,\ddagger})_{A \rightarrow AW} = (\Delta G^\ddagger_{t,BuBr})_{A \rightarrow AW}$

which may be a crude approximation because butyl bromide is a neutral molecule but the activated complex is negatively charged. Since the activated complex would be more strongly solvated than the butyl bromide reactant molecule, the effect of solvation on the transfer activity coefficients listed for the bromide ion (Table 7), would be underestimated, which may be seen from eqn. (14).

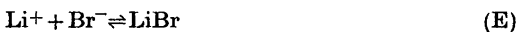
Using the above-mentioned approximation, comparison of eqns. (15-18) reveals that,

$$(\Delta G^\ddagger_{t,Br^-})_{A \rightarrow AW} = RT \ln \frac{(k_i)_{AW}}{(k_i)_A} = RT \ln \gamma_{t,Br^-} \quad (19)$$

If we further assume that the solvation of bromide ions due to hydrogen bond formation is of major importance²⁸ for the retardation of the observed reaction rate, eqn. (19) gives an estimate of the transfer activity coefficient, γ_{t,Br^-} , referring to hydrogen-bond formation.

Transfer activity coefficients derived from kinetic data may be used together with ion-pair association constants, K_A , to obtain some information concerning changes in solvation of the lithium bromide ion-pairs when transferred from pure acetone to a mixture of acetone and water.

From the equilibrium



in pure and aqueous acetone, respectively, we may write,

$$\begin{aligned} (\mu^\circ_{LiBr})_A - (\mu^\circ_{Li^+})_A - (\mu^\circ_{Br^-})_A = \\ -RT \ln (K_A)_A \end{aligned} \quad (20 a)$$

$$\begin{aligned} (\mu^\circ_{LiBr})_{AW} - (\mu^\circ_{Li^+})_{AW} - (\mu^\circ_{Br^-})_{AW} = \\ -RT \ln (K_A)_{AW} \end{aligned} \quad (20 b)$$

Table 7. Estimated values of transfer activity coefficients according to eqns. (19) and (21).

Water conc. wt.-%	$(\gamma_{t,Br^-})_{A \rightarrow AW}$	$(K_A)_{AW}/(K_A)_A$	$\frac{(\gamma_{t,Li^+})_{A \rightarrow AW}}{(\gamma_{t,LiBr})_{A \rightarrow AW}}$
0.005	1	1	1
0.055	0.89	0.89	1
0.106	0.80	0.82	1
1.505	0.22	0.42	2

which, according to eqn. (13), yields,

$$\frac{(K_A)_{AW}}{(K_A)_A} = \frac{(\gamma_{t, Li^+})(\gamma_{t, Br^-})}{\gamma_{t, LiBr}} \quad (21)$$

where $(K_A)_{AW}$ and $(K_A)_A$ are the ion-pair association constants of lithium bromide in aqueous and anhydrous acetone, respectively.

Using the values of K_A at 25 °C in Table 1 and values of k_i/k_A according to eqn. (9) with $K=73$, the data in Table 7 were derived from eqns. (19) and (21). According to these data the activity coefficient ratio, $\gamma_{t, Li^+}/\gamma_{t, LiBr}$, is approximately equal to unity for water concentrations of 0.1 wt-% or less. At 1.5 wt-% water the ratio has increased by a factor of 2. One reason for this effect may be an increased solvation of lithium bromide ion-pairs in the aqueous solvent mixture as compared with the pure solvent.

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