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# Electrolyte-Solvent Interaction: Conductance of Lithium Bromide in Acetone-Water Mixtures at Different Temperatures

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The conductance of lithium bromide in acetone-water mixtures has been measured at different temperatures (25—40°C) in the dielectric constant range from 17.80 to 61. The association constants and centre-to-centre cation-anion distances have been calculated by a modified Fuoss-Onsager equation applicable to $2<b<15$, where $b$ is the Bjerrum parameter. The increase in ion size and the decrease in association constants with the addition of water have been interpreted in terms of the solvated dipoles which contain both solvent molecules in the sheath of solvation. The variation in Walden products and in association constants with the change in the composition of the solvent and the temperature is well represented on this model.

Recently there seems to be revived interest in studies of electrolytic conductance in mixed solvents, especially when one component is highly polar.[1-7] In such systems, remarkable changes have been observed in the presence of small amounts of polar solvents. It may be supposed that the decrease in conductance is due to a sufficiently strong electrostatic attraction between ions and dipoles, an attraction which stabilizes the ion-dipole pair as a kinetic unit. This hypothesis assigns a dual role to the more polar component of the mixture. First, the macroscopic dielectric constant of the polar component controls long-range interaction, and, second, the sufficiently high potential energy of the ion-dipole at contact brings about a short-range interaction which causes a diminution in mobility and effectively diminishes the association constants. This paper will report our findings on the interaction of lithium bromide in acetone-water mixtures at various temperatures. The electrolyte, lithium bromide, was chosen because of its intense ionic field, while water was chosen as one component of the mixed solvent because of its high polarity.

## Experimental

Acetone was purified[8] and stored in amber-coloured bottles; its conductance varied from 0.3 to $0.5\times10^{-6}$ ohm$^{-1}$. The conductance water used was examined frequently for the constancy of its specific conductivity, which was between 0.6 and $0.8\times10^{-6}$ ohm$^{-1}$. Lithium bromide was recrystalised twice from the conductance water.

A Cambridge conductivity bridge with visual indication was used for these measurements. The conductivity cell was fitted with two circular, platinum-foil electrodes separated by 0.45 cm and a stirrer. The cell constant was checked before and after each set

TABLE 1. PROPERTIES OF ACETONE-WATER MIXTURES

| Wt% of $CH_3COCH_3$ | $\eta\times10^3$ | | | | $D$ | | | |
|---|---|---|---|---|---|---|---|---|
| | 25° | 30° | 35° | 40° | 25° | 30° | 35° | 40° |
| 100 | 3.09 | 2.95 | 2.82 | 2.75 | 19.10 | 18.67 | 18.23 | 17.80 |
| 97 | 3.37 | 3.22 | 3.00 | 2.89 | 20.53 | 20.01 | 19.51 | 19.06 |
| 95 | 3.56 | 3.29 | 3.13 | 3.00 | 21.50 | 21.42 | 20.98 | 20.48 |
| 90 | 4.19 | 4.00 | 3.78 | 3.33 | 23.96 | 23.38 | 22.76 | 22.32 |
| 70 | 7.47 | 6.86 | 6.45 | 5.85 | 35.70 | 34.75 | 33.90 | 33.03 |
| 30 | 10.75 | 9.50 | 8.40 | 7.53 | 61.04 | 59.47 | 58.20 | 56.77 |

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TABLE 2. CONDUCTANCE OF LITHIUM BROMIDE IN ACETONE-WATER MIXTURES

(A) Temperature 25°C

| $C\times10^4$ | $\Lambda$ | $C\times10^4$ | $\Lambda$ |
|---|---|---|---|
| (a) 100% $CH_3COCH_3$ | | (b) 97% $CH_3COCH_3$ | |
| 10.3 | 93.2 | 3.5 | 124.8 |
| 11.7 | 91.0 | 4.2 | 121.6 |
| 12.9 | 89.2 | 5.0 | 119.3 |
| 14.8 | 86.6 | 5.7 | 117.6 |
| 16.2 | 84.7 | 6.2 | 115.7 |
| | | 7.1 | 113.7 |
| | | 8.0 | 111.1 |
| (c) 95% $CH_3COCH_3$ | | (f) 30% $CH_3COCH_3$ | |
| 4.1 | 113.2 | 2.1 | 74.8 |
| 5.2 | 110.8 | 3.2 | 74.5 |
| 6.2 | 109.2 | 4.4 | 74.2 |
| 7.1 | 108.7 | 5.3 | 74.1 |
| 8.0 | 107.1 | 6.4 | 73.9 |
| 8.9 | 105.7 | 7.5 | 73.7 |
| 9.7 | 104.6 | | |

(B) Temperature 30°C

| $C\times10^4$ | $\Lambda$ | $C\times10^4$ | $\Lambda$ |
|---|---|---|---|
| (a) 100% $CH_3COCH_3$ | | (b) 97% $CH_3COCH_3$ | |
| 31.5 | 63.2 | 35.3 | 70.1 |
| 32.9 | 62.3 | 36.5 | 69.1 |
| 34.5 | 61.4 | 37.8 | 68.2 |
| 36.2 | 60.2 | 40.6 | 67.0 |
| 37.5 | 59.6 | 42.1 | 66.1 |
| 38.8 | 58.7 | 43.8 | 65.4 |
| 41.8 | 57.2 | 45.6 | 64.6 |
| (c) 95% $CH_3COCH_3$ | | (d) 90% $CH_3COCH_3$ | |
| 34.1 | 73.5 | 36.4 | 72.7 |
| 35.8 | 72.2 | 37.6 | 72.5 |
| 37.0 | 71.7 | 39.0 | 72.4 |
| 38.3 | 71.3 | 40.4 | 72.0 |
| 39.7 | 70.4 | 42.0 | 71.5 |
| 41.3 | 70.6 | 43.6 | 70.5 |
| 42.9 | 69.2 | 45.5 | 70.5 |
| (e) 70% $CH_3COCH_3$ | | (f) 30% $CH_3COCH_3$ | |
| 22.9 | 65.1 | 30.7 | 71.2 |
| 25.1 | 64.7 | 32.3 | 70.9 |
| 27.3 | 64.5 | 33.4 | 71.0 |
| 28.2 | 64.5 | 34.6 | 71.1 |
| 29.3 | 64.1 | 35.9 | 71.2 |
| 30.4 | 64.0 | 37.2 | 70.9 |
| 31.6 | 63.9 | 38.7 | 71.2 |

(C) Temperature 35°C

| $C\times10^4$ | $\Lambda$ | $C\times10^4$ | $\Lambda$ |
|---|---|---|---|
| (a) 100% $CH_3COCH_3$ | | (b) 97% $CH_3COCH_3$ | |
| 31.9 | 63.1 | 29.6 | 74.4 |
| 34.9 | 61.7 | 30.8 | 73.5 |
| 36.6 | 60.5 | 32.1 | 72.9 |
| 39.1 | 59.3 | 33.6 | 71.8 |
| 40.5 | 59.4 | 35.1 | 71.0 |
| 42.0 | 57.8 | 36.8 | 70.1 |
| 43.6 | 57.7 | 38.0 | 69.6 |
| (c) 95% $CH_3COCH_3$ | | (d) 90% $CH_3COCH_3$ | |
| 31.5 | 78.6 | 35.2 | 77.7 |
| 32.9 | 77.5 | 36.4 | 77.1 |
| 36.1 | 75.6 | 37.6 | 76.6 |
| 39.9 | 73.7 | 39.0 | 76.4 |
| 41.4 | 72.9 | 40.4 | 75.8 |
| 43.0 | 72.2 | 42.0 | 75.8 |
| 44.7 | 71.6 | 43.6 | 75.2 |
| (e) 70% $CH_3COCH_3$ | | (f) 30% $CH_3COCH_3$ | |
| 23.2 | 70.0 | 27.7 | 78.1 |
| 23.9 | 69.8 | 29.3 | 77.8 |
| 24.7 | 69.8 | 31.2 | 77.9 |
| 25.5 | 69.6 | 34.6 | 78.0 |
| 26.3 | 69.3 | 35.9 | 77.8 |
| 27.2 | 69.2 | 37.2 | 77.7 |
| 28.2 | 69.1 | 38.7 | 77.6 |

(D) Temperature 40°C

| $C\times10^4$ | $\Lambda$ | $C\times10^4$ | $\Lambda$ |
|---|---|---|---|
| (a) 100% $CH_3COCH_3$ | | (b) 97% $CH_3COCH_3$ | |
| 26.7 | 71.0 | 29.2 | 77.7 |
| 27.9 | 70.0 | 31.8 | 76.1 |
| 29.2 | 68.9 | 36.5 | 73.0 |
| 33.4 | 65.8 | 40.6 | 70.5 |
| 34.7 | 65.1 | 42.1 | 69.6 |
| 37.5 | 63.2 | 43.8 | 68.8 |
| 39.0 | 62.5 | 45.6 | 67.8 |
| (c) 95% $CH_3COCH_3$ | | (d) 90% $CH_3COCH_3$ | |
| 28.6 | 85.3 | 32.1 | 84.5 |
| 29.8 | 84.3 | 33.1 | 84.2 |
| 32.5 | 82.3 | 36.4 | 82.7 |
| 37.0 | 79.9 | 37.6 | 82.2 |
| 38.3 | 78.8 | 39.0 | 81.9 |
| 39.7 | 78.4 | 40.4 | 80.9 |
| 44.7 | 75.2 | 43.5 | 79.9 |
| (e) 70% $CH_3COCH_3$ | | (f) 30% $CH_3COCH_3$ | |
| 22.5 | 74.0 | 27.7 | 91.8 |
| 23.2 | 74.0 | 28.5 | 92.0 |
| 23.9 | 74.1 | 31.2 | 91.6 |
| 24.7 | 74.2 | 32.3 | 92.1 |
| 25.5 | 73.6 | 33.4 | 91.6 |
| 26.3 | 72.7 | 34.6 | 91.5 |
| 28.2 | 74.1 | 37.2 | 91.7 |

of experiments; it was 0.37335±0.00008. The temperature was maintained to within ±0.05°C using a water bath thermostat with a toluene-mercury regular and a relay.

Acetone-water mixtures were prepared by weight. The cell containing the electrolytic solution was kept in the thermostat, and the solvent was added from a semimicroburet reading to 0.01 m*l*; the electrolytic solution was stirred, and its conductance was measured at least twice at regular, usually ten-minute, intervals.

The dielectric constants, $D$, and the viscosities, $\eta$, of the acetone-water mixtures are given in Table 1; the former have been interpolated from the data of Åkerlöf,[9] while the latter have been measured with a Tuan-Fuoss[10] type viscometer with a flow time of 2735 seconds for water at 25°C.

## Results and Discussion

The conductance data are summarized in Table 2, in which the equivalent conductance, $\Lambda$, is given as a function of the concentration, $C$, in equivalents per liter. Each group of data is headed by the weight % of the less-polar component of the solvent, *viz.*, acetone.

The Fuoss-Onsager generalized conductance equation[11-13] for pair-wise association is:

$$\Lambda = \Lambda_0 - SC^{1/2}\gamma^{1/2} + E'C\gamma \log C\gamma + JC\gamma - K_A C\gamma f^2 \Lambda \qquad (1)$$

where $\Lambda$ and $\Lambda_0$ are the observed and the limiting equivalent conductance respectively; $S$, the Onsager coefficient; $C$, the concentration in equivalents per litre; $\gamma$, the fraction of salt present as free ions; $E'$, the Fuoss-Onsager coefficient; $J$, an explicit function of the ion size; $K_A$, the association constant, and $f$, the activity coefficient (Debye-Hückel limiting equation). This equation has been applied to a variety of electrolytes[14,15] in mixed solvents with $D<20$; it gives a rapid increase in the value of $J$ and, hence, in the ionic diameter. Similarly, the ion sizes calculated from Eq. (3) using the value of $K_A$ from Eq. (1) yield abnormal values for $K_A<10$, and the plot of $\log K_A$ against $D^{-1}$ runs concave to the $D^{-1}$ axis with an increase in the dielectric constant.[16-20] Fuoss and Onsager[21] have presented the following equation in order to get rid of these difficulties:

$$\Lambda = \Lambda_0 - SC^{1/2}\gamma^{1/2} + E'C\gamma \ln \tau^2\gamma + LC\gamma - K_A C\gamma f^2 \Lambda \qquad (2)$$

where

$$\tau^2 = 6E_1'C$$
$$f^2 = e^{-2\tau}$$
$$K_A = 4\pi N a^3 \exp(b)/3000 \qquad (3)$$

and

$$b = \varepsilon^2/aD\cdot \boldsymbol{k}T$$

where $\varepsilon$ is the electronic charge, $a$, the ion size; $D$, the dielectric constant; $\boldsymbol{k}$, the Boltzmann constant, and $T$, the absolute temperature. The terms in the conductance equation have been revised[22] assuming the same "sphere-in-continuum" model. The coefficients, $S$ and $E'$, have their usual significance.[23] The linear coefficient, $L$, is given by:

$$L = E_1'\Lambda_0 H(b) - E_2'G(b)$$

where $H(b)$ and $G(b)$ may be computed in the range $15>b>2$ and where the empirical formulae are:

$$H(b) = 3.936 + 329.5 \exp(-3.344 b^{1/2})$$

and

$$G(b) = 10.583 - 21.10 b^{1/2}$$

For the purpose of calculation, the $L$ coefficient has been taken as the sum of two functions expressed as:

$$L = L_1 + L_2(b) \qquad (4)$$

where $L_1$ is not a function of the ion size and where $L_2(b)$ is dependent on the ion size. Their values are given by the equations:

$$L_1 = 3.202 E_1'\Lambda_0 - 3.420 E_2' + \alpha\beta_0$$

where

$$\alpha\beta_0 = 67.68\times 10^6/\eta D^2 T^2$$

and

$$L_2(b) = 2E_1\Lambda_0(2b^2 + 2b - 1)/b^3 + 44E_2'/3b - 2E' \ln b$$

where

$$E' = 6.775\times 10^{12}/(DT)^3$$

In order to simplify Eq. (2), $\Lambda'$ may be defined as:

$$\Lambda' = \Lambda + SC^{1/2}\gamma^{1/2} - E'C\gamma \ln \tau^2\gamma + K_A C\gamma f^2 \Lambda \qquad (5)$$

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[22] R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **66**, 1722 (1962); **67**, 621, 628 (1963); **68**, 1 (1964).

[23] J. E. Lind, Jr., J. J. Zwolanik and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).

Hence,

$$\Lambda' = \Lambda_0 + LC\gamma \tag{6}$$

Equation (6) is used to evaluate $\Lambda_0$ and $L$, and then the ion size and the association constants. In practice, the $\Lambda_0$ value used for calculating $S$ and $E'$ is obtained from a plot of $\Lambda$ *versus* $C^{1/2}$. The known value of the ion size obtained from other data is used to calculate $K_A$ to a first approximation, and then $\Lambda'$ is plotted against $C\gamma$. The intercept at the Y axis gives the value of $\Lambda_0$. The process is then continued, adjusting the value of $\Lambda_0$ and $K_A$ until the slope of the straight line gives the same value of the ion size as that used for obtaining $K_A$. The intercept at the Y axis then gives the correct value of $\Lambda_0$. In the present studies, this method has been used for calculating the association constant of the (a), (b) and (c) systems of Table 2 at various temperatures. For the (d) system of (B), (C) and (D) (Table 2), an approximate value of $K_A$ was obtained from a plot of log $K_A$ against $D^{-1}$, it was then adjusted according to the method of successive approximation described above.

TABLE 3. CONSTANTS FOR LiBr IN $CH_3COCH_3$-$H_2O$ MIXTURES AT DIFFERENT TEMPERATURES

Temperature 25°C

| $D$ | $K_A$ | $\Lambda_0$ | $L$ | $a°$, Å | $\Lambda_0\eta$ |
|---|---|---|---|---|---|
| 19.10 | 635.3 | 137.8 | −7916.4 | 3.32 | 0.426 |
| 20.53 | 163.9 | 143.8 | −6530.5 | 3.90 | 0.484 |
| 21.50 | 41.7 | 129.7 | −4481.8 | 5.92 | 0.462 |
| 61.04 | — | 75.9 | +579.7 | 2.74 | 0.816 |

Temperature 30°C

| $D$ | $K_A$ | $\Lambda_0$ | $L$ | $a°$, Å | $\Lambda_0\eta$ |
|---|---|---|---|---|---|
| 18.67 | 585.0 | 124.0 | −7792.4 | 3.40 | 0.366 |
| 20.01 | 62.8 | 119.7 | −5955.1 | 5.51 | 0.385 |
| 21.42 | 7.6 | 117.2 | −4891.2 | 6.54 | 0.386 |
| 23.38 | 0.65 | 109.2 | −3125.0 | 3.71 | 0.437 |
| 34.75 | — | 78.5 | −824.2 | 3.63 | 0.539 |
| 59.47 | — | 75.1 | +588.2 | 2.75 | 0.715 |

Temperature 35°C

| $D$ | $K_A$ | $\Lambda_0$ | $L$ | $a°$, Å | $\Lambda_0\eta$ |
|---|---|---|---|---|---|
| 18.23 | 701.4 | 129.5 | −8783.8 | 3.32 | 0.365 |
| 19.51 | 66.8 | 123.4 | −5302.9 | 5.66 | 0.370 |
| 20.98 | 6.24 | 121.2 | −4444.4 | 7.28 | 0.379 |
| 22.76 | 1.00 | 115.5 | −3437.5 | 6.24 | 0.437 |
| 33.90 | — | 83.2 | −833.4 | 3.22 | 0.537 |
| 58.20 | — | 82.2 | +650.4 | 2.75 | 0.690 |

Temperature 40°C

| $D$ | $K_A$ | $\Lambda_0$ | $L$ | $a°$, Å | $\Lambda_0\eta$ |
|---|---|---|---|---|---|
| 17.80 | 798.4 | 146.4 | −13888.9 | 3.30 | 0.402 |
| 19.06 | 95.1 | 130.8 | −7352.9 | 4.82 | 0.378 |
| 20.48 | 47.9 | 130.9 | −5153.5 | 5.52 | 0.393 |
| 22.32 | 2.29 | 117.0 | −2525.4 | 6.33 | 0.390 |
| 33.03 | — | 78.4 | −3000.0 | 3.78 | 0.458 |
| 56.77 | — | 96.0 | +750.0 | 3.04 | 0.660 |

For unassociated-electrolytic solutions, (e) and (f) of Table 2, Eq. (2) is used, putting $\gamma=1$ and $K_A=0$, and so defining another quantity:

$$\Lambda_L' = \Lambda + SC^{1/2} - E'C\ln\tau^2 \tag{7}$$

This quantity is plotted against $C$, and the method of successive approximation is applied to find the $a$ and $\Lambda_0$ constants. These results have been summarized in Table 3.

As required by theory, the plot of the logarithm of the association constant against the reciprocal dielectric constant is linear. However, it has been reported that similar plots calculated on the basis of Eq. (1) in the case of alkali halides in dioxan-water mixtures at 25°C are not linear.[16–20] The decrease in $K_A$ with an increase in the amount of water may be attributed to an increase in the dielectric constant as well as in the ion size and to a decrease in the mobilities due to strong electrostatic forces between the ions and dipoles. It is evident from the results in Table 3 that short-range interaction predominates, even in a solution containing 10% water, and that the dipole solvate formed is fairly stable even at higher temperatures. These results follow from the high solvation number[24] of the lithium ion and from the formation of solvates[25] of lithium bromide in acetone and water:

$$Li^+ + l\mathrm{Ac} \rightleftharpoons (Li^+\cdot \mathrm{Ac}_l) \tag{8}$$

$$(Li^+\cdot \mathrm{Ac}_l) + Br^- \rightleftharpoons (\mathrm{Ac}_m\cdot Li^+)\cdot Br^- \tag{9}$$

In the presence of water, a solvated pair results:

$$\begin{aligned}&(\mathrm{Ac}_m\cdot Li^+)\cdot Br^- + xH_2O\\ &\qquad \rightleftharpoons [\mathrm{Ac}_n\cdot Li^+\cdot (H_2O)_x]\cdot Br^-\end{aligned} \tag{10}$$

The pairs are transformed with the further addition of water as follows:

$$\begin{aligned}&[\mathrm{Ac}_n\cdot Li^+\cdot (H_2O)_x]\cdot Br^- \rightleftharpoons\\ &\qquad [(H_2O)_y\cdot Li^+]\cdot Br^- + n\mathrm{Ac}\\ &\qquad\qquad \Big\updownarrow{\scriptstyle H_2O}\\ &\qquad Li^+\cdot (H_2O)_z + Br^-\cdot (H_2O)_p\end{aligned} \tag{11}$$

where Ac represents acetone and where $l$, $m$, $n$, $x$, $y$, $z$, and $p$ are the numbers of the molecules of the solvents.

The lithium ion polarizes acetone molecules and forms a dipole solvate according to Eq. (8). The bromide ion also exists in the solvated form, $Br^-(\cdots C_3H_6{=}O)$,[25] however, it would appear that the molecules of the solvent are squeezed

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[25] H. Ulich, *Trans. Faraday Soc.*, **23**, 392 (1927).

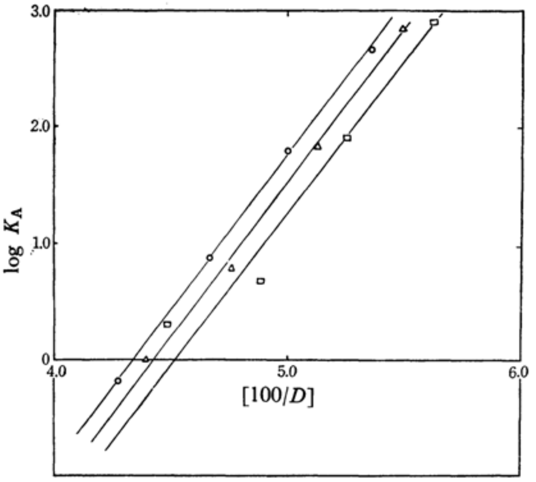

Fig. 1. Dependence of association constant on dielectric constant of solvent.
○ 30°C △ 35°C □ 40°C

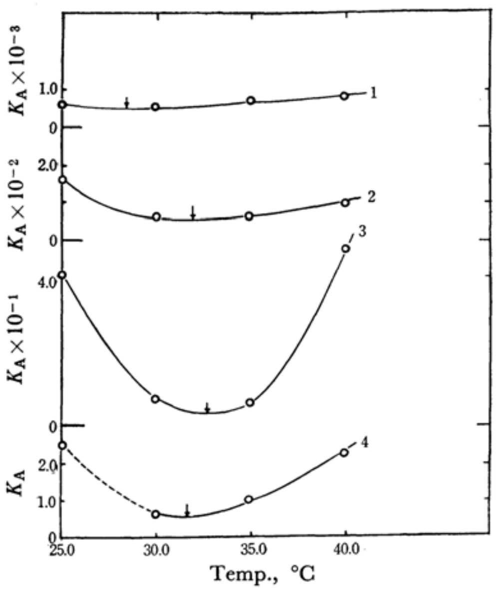

Fig. 2. Temperature dependence of association constant of LiBr in $CH_3COCH_3$-$H_2O$ mixtures.
1. 100% $CH_3COCH_3$ 2. 97% $CH_3COCH_3$
3. 95% $CH_3COCH_3$ 4. 90% $CH_3COCH_3$

out due to the intense ionic fields operating between $Li^+$-$Br^-$ pairs. It is obvious from the molecular structure of acetone that the positive end of the dipole of the molecule will be less able to approach the attracting bromide ion and will, moreover, claim more space than the negative end of the molecule. On the other hand, the solvent molecules are rigidly held by the lithium ion and are unaffected in ion pairing (Eq. (9)). This assumption derives support from the reported solvate of lithium bromide, $LiBr \cdot 2(CH_3)_2CO$.[24,26] The addition of water results in an increase in ion size in accordance with Eq. (10), and yields a solvated dipole in which the lithium ion is shielded by both acetone and water molecules. The further addition of water replaces the acetone molecules and a decrease in ion size follows; the ion size becomes almost constant as the amounts of water increase (Table 3, Fig. 3). Fuoss and Accascina,[27] analysing the conductance data of Owen and Zeldes[28] for aqueous potassium halides solutions, computed the ion size of potassium bromide as 3.26 Å, a value which is in excellent agreement with the sum (3.28 Å) of the crystallographic radii for these ions. This shows that in aqueous solutions of potassium bromide the contact occurs between bare ions and not between their cospheres. This

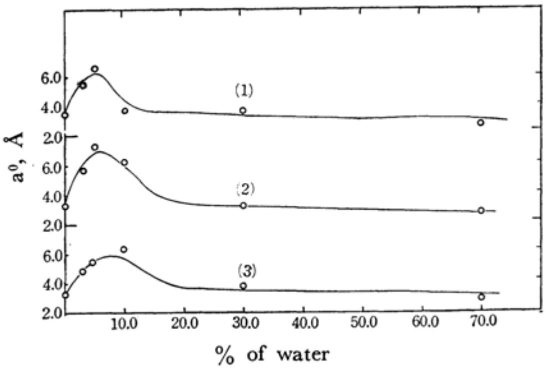

Fig. 3. Ion size of LiBr in $CH_3COCH_3$-$H_2O$ mixtures at different temperatures.
(1) 30°C (2) 35°C (3) 40°C

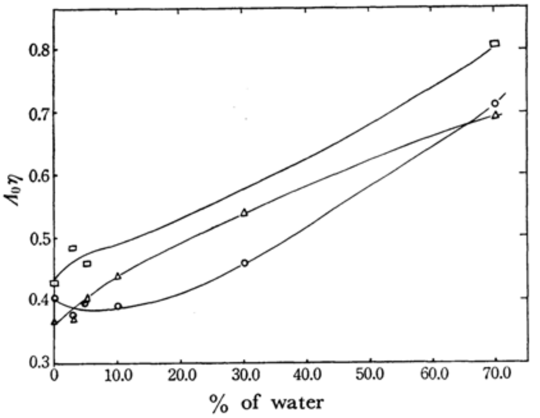

Fig. 4. Walden product: LiBr in $CH_3COCH_3$-$H_2O$ mixture at different temperatures.
□ 25°C △ 30°C ○ 40°C

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[26] P. Walden and E. J. Birr, *Z. Physik. Chem. (Leipzig)*, **A163**, 321, 337 (1933).

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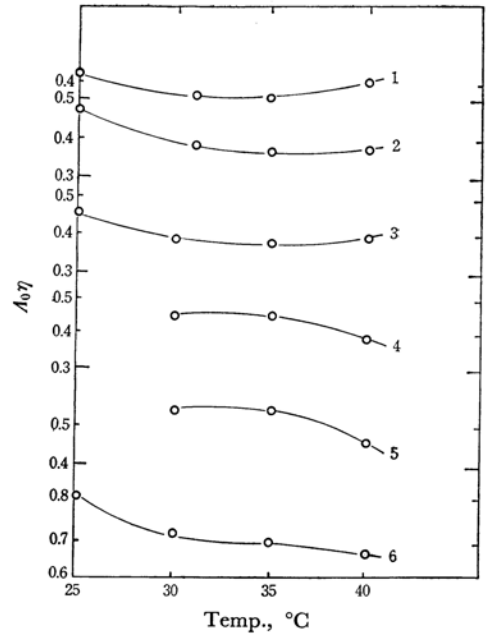

Fig. 5. Temperature dependence of Walden-product of LiBr in $CH_3COCH_3$-$H_2O$ mixtures.
1. 100% $CH_3COCH_3$ 2. 97% $CH_3COCH_3$
3. 95% $CH_3COCH_3$ 4. 90% $CH_3COCH_3$
5. 70% $CH_3COCH_3$ 6. 30% $CH_3COCH_3$

deduction is in good agreement with our supposition that the bromide ion remains unsolvated in the pair. We may, therefore, conclude from the reported hydrates[29-31] of lithium bromide, $LiBr\cdot 5H_2O$, $LiBr\cdot 3H_2O$, $LiBr\cdot 2H_2O$ and $LiBr\cdot H_2O$, that the water molecules in the $[(H_2O)_y\cdot Li^+]\cdot Br^-$ dipole exist in the hydration sheath of the lithium ion and not in that of the bromide ion. The same circumstance may be responsible for the almost constant ion size of the electrolyte in media containing higher percentages of water when both the hydrated ions come in contact with each other. On the basis of this structure, it is quite possible to interpret the results in Figs. 2—5. The results (Fig. 2) show that the decrease in the association constant with an increase in the temperature attains a minimum (arrow in Fig. 2) and then increases thereafter with any further rise in the temperature. The diminution is pronounced with an increase in the percentage of water in the solution, and the minimum moves towards higher temperatures; accordingly, an increase in the ion size and a decrease in the Walden product have been observed (Table 3). This indicates that, depending upon the composition of the solvent, an increase in the temperature in the range from 27.5 to 33°C facilitates solvation.

The effect of adding the highly polar water is shown in Fig. 4, in which the Walden porduct is plotted against the concentration of water at different temperatures. At 40°C, the Walden product decreases initially, showing that the addition of water causes a diminution in the mobility of the ions. As the percentage of water is further increased, however, the $\Lambda_0\eta$-$W$ curves pass through a minimum and the Walden product increases in the region of the higher dielectric constant. Two effects are involved: as the dielectric constant increases, the short-range ion-dipole interaction decreases and, hence, the initial decrease in mobility, which has been ascribed to dipole solvation, disappears. Then, the long-range relaxation[32] effect produced by the motion of ions in a polarizable dielectric takes control and the Walden product increases with an increase in the dielectric constant, according to the relationship:

$$\Lambda_0\eta = (\boldsymbol{F}\varepsilon/1800\pi)\varepsilon_{i=1,2}R_i^{-1}(1 + A_i/DR_i^2)^{-1} \quad (12)$$

where $\boldsymbol{F}$ is the Faraday charge; $A_i$, the constant, and $R_1$ and $R_2$, the hydrodynamic radii of the cation and the anion respectively. As $D$ increases, the denominator in Eq. (12) decreases; hence, the sum of the two terms increases. This disppearance of minima at lower temperatures may be understood as a result of the appreciable increase in the dielectric constant, which increases the Walden product, since the ion size and the hydrodynamic radius remain almost constant (Eq. (12)).

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