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Studies of Ionic Association. I. Alkali Halide and Sodium Nitrate in the Butyl Alcohol-Water System

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It has previously been reported that the dissociation of alkali halide and sodium nitrate between butanol and water phases could be explained reasonably if they were dissociated into free ions in each phase. The present investigation was undertaken to see to what extent dissociation occurs in the butanol phase. Conductometric measurements were carried out on solutions of LiBr, NaBr, NaCl, KCl, RbCl, and $NaNO_3$ in the *n*-butanol-water system and on the solution of NaCl in the *t*-butyl alcohol-water system at 20°C or 25°C. These data were analyzed by using the Fuoss-Onsager equation for associated electrolytes, and the association constants were calculated to be as follows: NaBr 250, NaCl 600, KCl 610, RbCl 1850, $NaNO_3$ 180, and NaI 220 in the *n*-butanol-water (11 wt%) system at 25°C (except NaBr), and NaCl; 590, 160, and 75 for water wt% 30, 45, and 60 in the *t*-butyl alcohol-water system at 25°C, respectively. The association constants of NaCl in the *t*-butyl alcohol-water system were explained in terms of the simple electrostatic theory. The results were discussed briefly in comparison with conductance data reported in the literature.

The solvent extraction of various species has been widely investigated and reviewed by Marcus and by Diamond and Tuck.[1,2] However, the investigations have been restricted to systems involving a distribution of the species between aqueous and organic solvents immiscible with water. These distributions have, in general, been interpreted in terms of the association of ions in organic solvents. We reported previously that the distribution of alkali halide and sodium nitrate between *n*-butanol and water phases could be explained most reasonably if they were treated as dissociating into free ions.[3] The present investigation was undertaken to see to what extent dissociation occurs in the butanol–water system. Many authors have studied the conductometric behavior of strong electrolytes in binary mixtures of solvents in order to establish the effect of ion-solvent interaction.[4] However, there is insufficient information on the behavior of electrolytes in the butanol–water system. Butanol, which is an associated solvent with a low vapor pressure and with a moderate value of the dielectric constant at 25°C, offers an interesting solvent for the study of ion-ion and ion-solvent interactions.

Experimental

Materials. The conductivity water used in the present study was prepared by the passage of distilled water through mixed-bed ion exchange resin. The specific conductance of this water was below 5×10^{-7} ohm^{-1} cm^{-1}. We treated *n*-butanol with a sodium bisulfite solution, then we boiled it for 4 hours with a 10% solution of NaOH, washed the separated butanol with water, and neutralized it to remove any NaOH. The butanol was boiled with fresh lime for 3 hr. The butanol was decanted from the lime and refluxed with magnesium turning. Then, we collected the middle of a distillation under an atmospheric pressure.[5] The salts and t-butanol were of a reagent grade and were used without further purification. The salts were dried at 110°C before use.

Procedure. The electric equipment, conductance cell (flask type), and general techniques were essentially the same as had been previously described[6] except for the conductance bridge, which was of a YOKOGAWA BV-Z-103B type. A quartz flask cell with lightly platinized electrodes was used. The cell constant was determined by means of an aqueous KCl solution to be 0.1893 cm^{-1}. The solvents and solutions were prepared by weight. All the measurements were carried out in a thermostat of 25±0.01°C or 20±0.01°C. The conductance of the solution was determined by subtracting the conductance of the solvent. Since the specific conductance of solvent was below 10^{-6} ohm$^{-1}\cdot$cm^{-1} at 25°C, no solvent correction was necessary even for the most dilute solution. Relative viscosity measurements were made by using an Ostwald viscometer immersed in a thermostat of 25±0.01°C or 20±0.01°C.

Results and Discussion

Alkali Halide in n*-Butanol–Water System.* The properties of *n*-butanol–water solvents are listed in Table 1. The conductances were determined in the range of salt concentration of $0.5—10\times10^{-3}$ mol/l. The salts used in this investigation were LiBr, NaCl, KCl, $NaNO_3$, and NaI. The distributions of these salts have all previously been studied except for $NaNO_3$. The solvent compositions are in the range of the upper phase (rich in *n*-butanol) compositions that correspond to the composition of the separation of the two phases. Because of solubility limitations, many data were not available in the precision required.[7] The addition of salt above the

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[1] Y. Marcus, *Chem. Rev.*, **63**, 139 (1963).

[2] R. M. Diamond and D. C. Tuck, "Progress in Inorganic Chemistry" F. A. Cotton ed., Interscience Publishers Inc., New York (1960), p. 109.

[3] Y. Kurokawa and N. Yui, *Nippon Kagaku Zasshi*, **89**, 487 (1968).

[4] J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **72**, 144 (1968). A. S. Quist and W. L. Marshall, *ibid.*, **72**, 684 (1968). T. C. Wehman and A. L. Popov, *ibid.*, **72**, 4031 (1968). D. F. Evans and T. L. Broadwater, *ibid.*, **72**, 1037 (1968). D. F. Evans and P. Gardam, *ibid.*, **73**, 158 (1969).

[5] J. A. Riddik and E. E. Toops, "Technique of Organic Chemistry Vol VII Organic Solvents" Interscience Publishers, Inc., New York (1955), p. 346.

[6] N. Yui, Y. Kurokawa, M. Sono, and T. Hiramoto, *Nippon Kagaku Zasshi* **89**, 483 (1968); T. Shedlovsky, *J. Amer. Chem. Soc.*, **54**, 1411 (1932).

[7] The solubilities of salts in pure *n*-butanol are all very small except for NaI.

TABLE 1. PROPERTIES OF n-BUTANOL-WATER MIXTURE

Water (wt%)	η (poise)	$\varepsilon^{a)}$	Temp. (°C)
5.0	0.02250	20.0	20
9.0	0.02360	22.3	20
11.0	0.02593	24.0	25
15.0	0.02487	26.0	20

a) They were estimated from the values for pure water and pure n-butanol by assuming that the dielectric constant of mixtures is a linear function of the weight fraction by analogy with the behavior of water-ethanol mixture. H. S. Harned and B. B. Owen, "The Physical Chemistry of electrolytic Solutions" Reinhold Publishing Co. (1964), p. 161.

extent of solubility brought about the separation of the solution into two phases. The values of conductance Λ (ohm^{-1} cm^2), are presented in Table 2. The measurements temperatures were 20 °C for LiBr and NaBr, and 25 °C for the others. Λ $vs.\sqrt{c}$ plots for each salt are shown in Fig. 1. The curves are similar in form and show the same behavior as weak electrolytes. It is considered from these results that the salts are considerably associated.

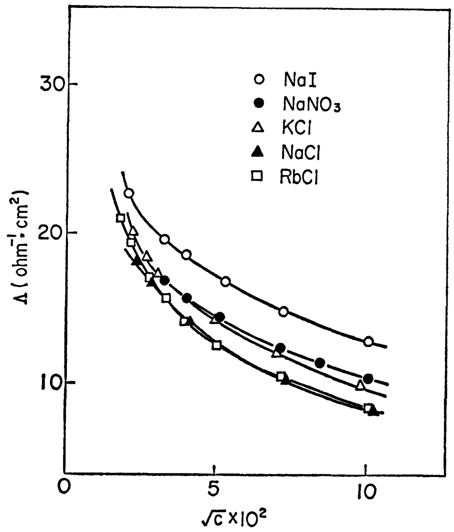

Fig. 1. Conductance $vs.$ square root of concentration for alkali halide in n-butanol-water system at 25 °C.

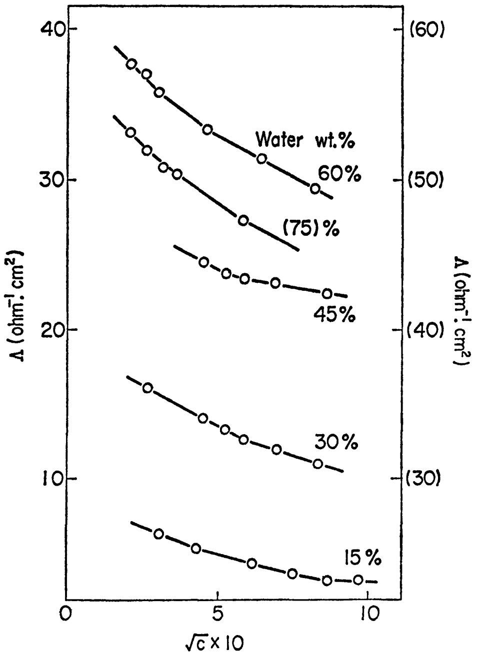

Fig. 2. Conductance $vs.$ square root of concentration for NaCl in t-butyl alcohol-water system at 25 °C.

TABLE 2. CONDUCTANCE OF ALKALI SALTS IN n-BUTANOL-WATER SYSTEM

(A) LiBr; 20 °C	water 11%	(B) NaBr; 20 °C	water 15%	(C) NaBr; 20 °C	water 9%	(D) NaCl; 25 °C	water 11%
$c\times10^3$	Λ	$c\times10^3$	Λ	$c\times10^3$	Λ	$c\times10^3$	Λ
1.542	12.03	1.522	14.97	1.569	17.06	0.4967	17.91
2.348	11.01	2.684	12.98	2.497	15.58	0.6903	16.69
3.504	9.86	3.478	12.39	3.677	14.47	0.9938	15.95
4.778	9.89	5.087	11.14	5.002	13.66	1.492	14.05
5.829	9.44	6.439	10.57	6.261	13.35	2.486	12.40
7.224	9.03	7.483	10.42	7.924	12.51	4.972	10.28
9.396	8.40	10.00	9.50	9.804	11.86	9.945	8.30

(E) KCl; 25 °C	water 11%	(F) NaI; 25 °C	water 11%	(G) NaNO$_3$; 25 °C	water 11%	(H) RbCl; 25 °C	water 11%
$c\times10^3$	Λ	$c\times10^3$	Λ	$c\times10^3$	Λ	$c\times10^3$	Λ
0.472	19.99	0.404	22.61	0.4962	17.24	0.3078	20.88
0.661	18.21	1.009	19.51	0.9925	16.54	0.4104	19.38
0.944	17.21	1.513	18.52	1.489	15.55	0.5130	18.54
1.416	15.84	2.523	16.86	2.481	14.11	0.7183	17.03
2.360	14.00	5.045	14.89	4.962	12.07	1.026	15.52
4.721	11.80	10.09	12.83	6.947	11.12	1.539	14.09
9.443	9.70	100.9	8.19	9.925	10.34	2.565	12.36
						5.130	10.19
						10.66	8.20

NaCl in t-*Butyl Alchohol–Water System.* The other butanols have dielectric constants above 18, while *t*-butyl alcohol has a dielectric constant of 11.8 and yet is the only butanol completely miscible with water at 25°C.[8] Appropriate conductance measurements provides a useful indication of ion-solvent interaction, but conductance studies over the range of solvent composition have not been previously published for the *t*-butyl alcohol–water system at 25 °C. The properties of the solvents are summarized in Table 3.

TABLE 3. PROPERTIES OF *t*-BUTYL ALCOHOL–WATER MIXTURE AT 25°C

Water content (wt%)	η (poise)	ε	Density (g/cm^3)
15	0.04569	14.3	0.8154
30	0.04845	21.4	0.8519
45	0.05105	31.5	0.8869
60	0.03757	43.9	0.9023
75	0.02568	57.1	0.9567
100	0.008937	78.5	0.9971

The viscosity reaches its maximum in the vicinity of a water content of 40%, as in the cases of water–methanol, –ethanol, and –propanol. The values of Λ are represented in Table 4 and show a sharp increase in the conductance with an increase in water content. As shown in Fig. 2, the values of Λ change smoothly with the increase in water content, despite the maximum in viscosity. Obviously, ion mobility is not predominantly controlled by the bulk viscosity.

Calculation. In order to ascertain whether any variation in the conductance could be due to ion-pair formation, the limiting equivalent conductance and the ion-pair formation constants, K_A were calculated by the Fuoss and Fuoss-Onsager methods. The data were initially treated by the method of Fuoss.[9]

$$F(z)/\Lambda = 1/\Lambda^0 + (K_A \cdot c\Lambda f_\pm^2)/(F(z)/\Lambda^{02}) \qquad (1)$$

where $F(z)$ is the Fuoss function and where $f_\pm^2$ is calculated from the Debye-Hückel theory. The initial value of $\Lambda°$ was obtained by the extrapolation of Λ *vs.* $\sqrt{c}$ plot to an infinite dilution. After we had obtained the apparent Λ^0 and value of K_A, the data were analyzed by the Fuoss-Onsager extended equation for associated electrolytes in this form.[10]

$$\Lambda = \Lambda^0 - S(c\gamma)^{1/2} - Ec\gamma \log c\gamma + Jc\gamma - K_A c\gamma \Lambda f_\pm^2 \qquad (2)$$

Here, γ is the degree of dissociation, S is the Onsager limiting slope, and both E and J are the parameters as defined in the Fuoss-Onsager equation. In computing the Λ' defined by the equation:

$$\Lambda' = \Lambda + S(c\gamma)^{1/2} - Ec\gamma \log c\gamma \qquad (3)$$

the following variables are defined thus;

$$\Delta\Lambda = \Lambda' - \Lambda^0 \qquad (4)$$

$$y = \Delta\Lambda / c\gamma \qquad (5)$$

$$x = f_\pm^2 \Lambda \qquad (6)$$

Then, Eq. 2 is transformed into Eq. 7;

$$y = J - K_A x \qquad (7)$$

If $\Lambda°$ was known, y could be calculated, then a plot of y against x should be linear and K_A could be evaluated.[10] The association constans, K_A, obtained by the above two methods are given in Table 5. The values of K_A calculated by the Fuoss method are approximately twice as large as those calculated by the Fuoss-Onsager method.[11] As can be seen in Table 5, K_A increases in the order of NaCl<KCl<RbCl with an increase in the size of the cation, and increases in the order of NaI<NaBr<NaCl with a decrease in the size of the anion. That is, RbCl, in spite of its greater size, is more associated than the others. This means that the cations are hydrated, while halide ions are not. This is in agreement with the order found by Kay and Fuoss for the alkali halide in various hydrogen-bonded solutions.[12,13] That is, the association increases in this order; Li<Na<K<Rb<Cs. Fuoss and his co-workers have found the same order for alkali halides in a dioxane–water system, and Smith has reported that KNO_3 is more associated than $LiNO_3$ in pure ethanol.[14] However, Evans has reported that tetraethyl ammonium salts in alcohol do not exhibit the simple dependence upon the order of association predicted by the electrostatic theory, that is, K_A increases with an increase in the anion size.[4]

TABLE 4. CONDUCTANCE OF NaCl IN *t*-BUTYL ALCOHOL–WATER SYSTEM AT 25 °C

(A) water 15%		(B) water 30%		(C) water 45%		(D) water 60%		(E) water 75%	
$c\times10^3$	Λ	$c\times10^3$	Λ	$c\times10^3$	Λ	$c\times10^3$	Λ	$c\times10^3$	Λ
0.951	6.273	0.712	15.98	1.391	24.96	0.4234	37.68	0.4131	53.14
1.902	5.532	1.423	14.14	2.086	24.27	0.6774	37.30	0.6884	51.95
3.805	4.677	1.993	13.77	2.781	23.73	0.8468	35.88	0.9638	50.76
5.707	3.783	2.135	13.48	3.476	23.29	2.117	33.45	1.377	50.48
7.610	3.414	3.559	12.66	4.867	23.37	4.234	31.72	3.422	47.30
9.512	3.409	4.982	11.91	6.953	22.30	6.774	29.50		
		5.694	11.85						
		7.117	11.23						

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[8] Ref. 5, p. 90.

[9] R. M. Fuoss, *J. Amer. Chem. Soc.*, **57**, 478 (1935).

[10] R. M. Fuoss and F. Accasina, "Electrolytic Conductance" Interscience Publishers, Inc. (1959), p. 225.

[11] E. Kubota and M. Yokoi, *Nippon Kagaku Zasshi*, **86**, 894 (1965).

[12] J. L. Fabry and R. M. Fuoss, *J. Phys. Chem.*, **68**, 971 (1964).

[13] J. L. Hawes and R. L. Kay, *ibid.*, **69**, 2420 (1965).

[14] G. D. Parfitt and A. L. Smith, *Trans. Faraday Soc.*, **59**, 57 (1963).

TABLE 5. ASSOCIATION CONSTANT OF ALKALI HALIDE IN *n*-BUTANOL–WATER SYSTEM

	K_A		Λ^0	Temp. (°C)
	Fuoss	Fuoss-Onsager		
$NaNO_3$	350	180	20.7	25
NaI	490	220	25.5	25
NaCl	1170	600	23.0	25
KCl	1140	610	24.0	25
RbCl	4060	1850	29.0	25
NaBr(1)		250	25.57	20
NaBr(2)		280	20.83	25

(1) and (2) in NaBr indicate 15 and 9 water content (wt%), respectively.

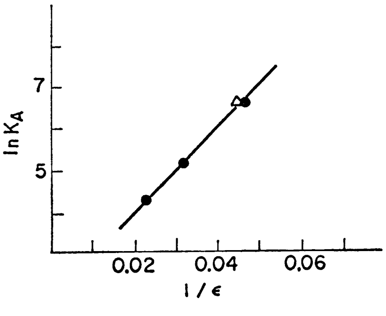

Fig. 3. Logarithm of association constant *vs.* reciprocal of dielectric constant for NaCl in *t*-butyl alcohol-water system at 25°C. △: NaCl in *n*-butanol-water (11 wt%)

The coulombic theory predicts that a plot of log K_A against $1/\varepsilon$ for any given salt will be a straight line with a slope proportional to $1/a_K$.[10] Such a plot

$$K_A = K_A^0 \exp(e^2/a_K \cdot \varepsilon \cdot kT) \qquad (8)$$

for NaCl in the *t*-butanol–water system is shown in Fig. 3. An approximately straight line is obtained, and the value of a_K, 5.6 Å is calculated from the slope of the line. The point for NaCl in the *n*-butanol–water(11 wt%) system seems to fall on the line. Therefore, it seems that the solvent structure plays a negligible role in the association process. Water molecules in the primary solvation shell are not easily replaced by butanol molecules. This hydrated ion is further solvated either by more water molecules or by the butanol molecules through hydrogen-bonding, thus forming the secondary solvation shell.

In conclusion, we can say that the alkali halide is partly associated in the *n*-butanol phase which is equilibrated with the aqueous phase at 20°C or 25°C, and that the Fuoss and Fuoss-Onsager equation describe the behavior of alkali halide.