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### Conductance of Tetraalkylammonium Bromides in Formamide-Water Mixtures at 25°C\*

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Conductance data of tetraethylammonium bromide (TEAB) and tetrabutylammonium bromide (TBAB) in formamide-water mixtures at 25°C ± 0.005° in concentration range 0.01 to 0.10N are being reported. The experimental data have been analysed on the basis of Fuoss equation [*J. phys. Chem.*, **79** (1975), 525]. The parameters  $\Lambda_0$ ,  $K_A$  and  $R$  have been calculated for each system. Walden product ( $\Lambda_0\eta$ ) passes through an ill-defined minimum as formamide content increases in the solvent mixture. Association constant,  $K_A$ , is almost negligible for TEAB and is slightly more than unity in the case of TBAB. For a given solvent mixture  $\Lambda_0$  is less for TBAB as compared to that for TEAB.

**S**TUDIES on different physico-chemical properties like density, viscosity and dielectric constant of amide-water mixtures have been undertaken<sup>1-3</sup> with a view to throwing light on ion-solvent interactions and molecular association. Singh *et al.*<sup>4</sup> have determined the viscosities of solutions of sodium and magnesium sulphates in acetamide-water mixtures and the data were analysed in terms of intermolecular association in aqueous acetamide. However, a survey of literature reveals that the study of conductance of electrolytes in amide-water mixtures, which is basic to the elucidation of structure of electrolyte solutions, is lacking. We report here conductance data on tetraethylammonium bromide (TEAB) and tetrabutylammonium bromide (TBAB) in formamide-water mixtures. The data have been analysed in terms of conductance-concentration equation due to Fuoss based on a new model for ionic association<sup>5</sup>.

Tetraethylammonium bromide (AR, BDH) and tetrabutylammonium bromide (Purum, Fluka) were further purified by Harkness's method<sup>6</sup>. Triply

distilled water (sp. cond. 0.4-0.9 × 10<sup>-6</sup> mho cm<sup>-1</sup>) was used for preparing different solvent mixtures. KCl (AR, BDH) was recrystallized as suggested by Hawes and Kay<sup>7</sup>. Formamide (LR, BDH) was purified by the method of Dawson *et al.*<sup>8</sup> and the purified sample had a conductivity of 0.3-1.1 × 10<sup>-5</sup> mho cm<sup>-1</sup>.

A conductivity bridge (Cambridge, model No. L-370873) was used for conductance measurements. All the measurements were carried out at 25°C ± 0.005° under N<sub>2</sub> atmosphere. Variation of the temperature was checked using a Beckmann thermometer with an accuracy of ± 0.002°. Two conductivity cells of the type suggested by Daggett *et al.*<sup>9</sup> were used. Electrodes were slightly platinized. Cells were calibrated by determining the conductance of KCl solutions in water at 25°C in concentration range 0.01-0.10N and using Fuoss equation<sup>10</sup>. Cell constants were found to be 0.3044 ± 0.0002 and 0.6132 ± 0.0003/cm. All the solvent mixtures were prepared by weight. Viscosity and density of the solvents were determined at 25°C ± 0.1° using a Cannon Ubbelohde viscometer (50/A703) and a calibrated pycnometer of 20 ml capacity respectively. Time of flow was reproducible within 0.1 sec. Dielectric constants of the solvent-mixtures were taken from literature<sup>3</sup>.

The equivalent conductance of tetraethyl- and tetrabutyl-ammonium bromides at different concentrations and in various formamide-water mixtures are given in Table 1.

The three adjustable parameters,  $\Lambda_0$ ,  $K_A$  and  $R$ , were obtained by solving Eqs. (1-3).

$$\Lambda = \gamma[\Lambda_0(1 - \Delta X/X) - \Delta\Lambda_e] \quad \dots(1)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad \dots(2)$$

$$\ln f = -\beta K/2(1 + KR) \quad \dots(3)$$

where  $R$  is cosphere diameter<sup>5</sup> and other terms have their usual meanings. Expressions for  $\Delta X/X$  and  $\Delta\Lambda_e$  and the method of analysis adopted here were the same as given by Fuoss<sup>5</sup>. All computations were performed on IBM 7044 computer. Computer programmes were kindly supplied by Prof. R. M. Fuoss and these were used after making minor corrections to suit the computer. In most of the cases SCAN or PKV-SCAN programme was used. Calculated values of  $\Lambda_0$ ,  $K_A$  and  $R$  are given in Table 2.

Viscosity of the solvent-mixtures increases progressively with an increase in the formamide content of the solvent. No minimum or maximum was observed indicating the absence of strong structure-breaking or structure-forming effects as well as possible loose association<sup>3</sup> of formamide with water molecules which will lead to increased viscosity. Decrease in  $\Lambda_0$  with increase in formamide content of the solvent (Table 2) is attributable mainly to change in viscosity of solvent; influence of simultaneous increase in dielectric constant can be neglected as dissociation is almost complete in all the compositions. Walden product ( $\Lambda_0\eta$ ) passes through an ill-defined minimum and then increases with increase in formamide content of the solvent. For a given solvent mixture,  $\Lambda_0$  for TBAB is less

\*Dedicated to (late) Dr D. Singh.

TABLE 1 — CONDUCTANCE DATA IN FORMAMIDE-WATER MIXTURES AT 25°

Formamide conc. (mole %)									
10		25		40		50		70	
[TEAB] × 10 <sup>4</sup>	Λ	[TEAB] × 10 <sup>4</sup>	Λ	[TEAB] × 10 <sup>4</sup>	Λ	[TEAB] × 10 <sup>4</sup>	Λ	[TEAB] × 10 <sup>4</sup>	Λ
951.90	78.69	946.60	67.34	949.80	58.18	949.25	52.48	948.20	41.84
901.80	79.09	896.77	67.66	899.81	58.28	899.28	52.66	898.28	41.90
846.13	79.18	841.42	68.16	844.26	58.36	843.77	52.72	842.84	41.98
783.91	79.57	779.55	68.40	782.18	58.58	781.73	53.05	780.87	42.06
713.92	80.15	709.95	68.56	712.35	58.88	711.93	53.27	711.15	42.15
634.60	80.90	631.06	68.83	633.20	59.14	632.83	53.43	632.13	42.25
543.94	81.34	540.91	69.83	542.74	59.35	542.42	53.85	541.82	42.62
439.33	83.36	436.89	70.15	438.36	59.73	438.11	54.17	437.63	43.35
380.76	84.86	378.64	70.86	379.92	60.30	379.50	54.69	379.28	43.54
317.30	85.86	315.53	71.88	316.60	61.52	320.36	55.90	316.06	44.14
248.32	87.78	246.93	74.20	247.77	62.44	247.63	56.71	247.35	44.92
173.07	90.02	172.10	76.41	172.69	64.10	172.59	58.15	172.40	45.65
[TBAB] × 10 <sup>4</sup>	Λ	[TBAB] × 10 <sup>4</sup>	Λ	[TBAB] × 10 <sup>4</sup>	Λ	[TBAB] × 10 <sup>4</sup>	Λ	[TBAB] × 10 <sup>4</sup>	Λ
951.45	63.15	951.12	55.75	950.65	47.74	950.45	43.52	954.85	34.61
901.37	63.65	900.61	56.29	900.61	48.14	900.42	43.76	904.59	34.79
845.73	64.49	845.02	56.45	845.02	48.44	844.84	43.90	848.75	34.96
783.54	64.69	782.88	56.99	782.88	48.78	782.72	44.07	786.34	35.20
713.58	65.55	712.98	57.30	712.98	49.14	712.83	44.19	716.13	35.51
634.30	66.48	633.76	57.85	633.76	49.42	633.63	44.49	636.56	35.95
543.68	68.21	543.22	58.51	543.22	49.95	543.11	45.21	545.62	36.99
439.13	69.42	438.76	59.82	438.76	51.41	438.66	46.25	440.70	46.38
480.58	70.78	380.26	60.48	380.26	52.08	380.18	47.39	381.94	37.96
317.15	72.28	316.88	62.14	316.88	53.42	316.81	48.20	318.28	38.96
248.20	75.00	247.99	63.61	247.99	54.68	247.94	48.90	249.09	39.93
172.99	77.02	172.84	65.40	172.84	55.82	172.81	50.16	173.61	40.82

TABLE 2 — VALUES OF DIFFERENT PARAMETERS DERIVED FOR TBAB AND TEAB

[Formamide], mole %	<i>D</i>	$\beta/R$	$\sigma$	$\Lambda_0$	$K_A$	$10^8 R$	$\Delta\sigma_f$
TETRABUTYLAMMONIUM BROMIDE							
10	88.03	2.300	0.413	87.67	2.813	2.768	0.8718
25	98.17	2.004	0.468	72.25	1.480	2.854	0.8589
40	105.28	1.904	0.400	61.69	1.620	2.796	0.8810
50	108.40	1.872	0.405	55.08	1.350	2.761	0.8865
70	111.18	1.900	0.341	45.04	2.079	2.653	0.9487
TETRAETHYLAMMONIUM BROMIDE							
—	88.03	2.568	0.545	99.10	0.730	2.479	0.9855
—	98.17	2.338	0.759	82.01	0.360	2.442	0.9749
—	105.28	2.066	0.508	68.34	—	2.577	0.9759
—	108.40	2.421	0.443	62.05	—	2.135	0.9988
—	111.18	2.221	0.270	48.77	—	2.269	1.0274

than that for TEAB in agreement with the earlier observations in the case of other solvents<sup>12,13</sup>. The increase may be attributed to the larger ionic size of  $Bu_4N^+$ . A similar conclusion can be drawn on the basis of ion-solvent interaction also.  $Bu_4N^+$  ion is more structure-forming compared to  $Et_4N^+$  ion<sup>14,16</sup>, so in the former case mobility of ions will be less giving a smaller value of conductance. Cosphere diameter, *R*, for both the compounds remains practically unchanged ( $2.76 \pm 0.10$  for TBAB and  $2.35 \pm 0.22$  for TEAB) with change of amide con-

centration in the solvent mixture (Table 2) indicating the absence of any appreciable change in ionic association. This is supported by the fact that value of  $K_A$  never exceeds 3.0 (Table 2).

With the limited data it is not possible to give any rational explanation for low value of *R* (viz. 2.76 Å for TBAB and 2.35 Å for TEAB) in aq. formamide mixtures compared to the value 6.8 Å reported in aqueous systems<sup>5</sup>.

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## Phenol as a Non-aqueous Solvent

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Organic tertiary bases form 1:1 and 1:2 adducts with phenol. Tetrachlorides of tin and titanium form  $\text{SnCl}_4(\text{OC}_6\text{H}_5)_2 \cdot \text{C}_6\text{H}_5\text{OH}$  and  $\text{TiCl}_4(\text{OC}_6\text{H}_5)_2 \cdot \text{C}_6\text{H}_5\text{OH}$  when dissolved in phenol. Acid-base titrations of tetraphenoxides of tin and titanium against pyridine and sodium phenoxide have been carried out to establish the autoionization of phenol as  $2\text{C}_6\text{H}_5\text{OH} \rightleftharpoons \text{C}_6\text{H}_5\text{OH}_2^+ + \text{C}_6\text{H}_5\text{O}^-$ .

ORGANIC polar solvents have been extensively investigated as non-aqueous solvents. However, no such studies with phenol are available in literature though some phenoxides of the metals have been prepared by the solvolysis of metal chlorides in phenol<sup>1-3</sup>.

Phenol is slightly acidic in nature ( $pK_a = 1.0 \times 10^{-10}$ ). Its physical properties like dielectric constant (9.78 at 45°), dipole moment (1.76 D) and specific conductance ( $1.8 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) are comparable to those of acetic acid (dielectric constant, 6.0; dipole moment, 1.76 D). It has been shown<sup>4-6</sup> that, in fluorosulphuric acid, phenol is protonated at the ring rather than at the oxygen while in disulphuric acid, it gets sulphonated<sup>7</sup>. It is amphoteric in nature. It is, therefore, of interest to investigate its solution chemistry and explore the possibility of isolation of its adducts with Lewis acids and bases and characterize them.

TABLE 1 — SPECIFIC CONDUCTANCES OF SOME SOLUTES IN PHENOL AT 50°

Compound	Conc. (mole/litre)	Sp. conductance $\times 10^6$ ( $\text{ohm}^{-1} \text{ cm}^{-1}$ )
Sodium phenoxide	0.012	7.67
$\alpha$ -Picoline	0.020	1.96
Pyridine	0.039	1.47
Tin(IV) chloride	0.034	2.52
Antimony(V) chloride	0.031	2.38
Titanium(IV) phenoxide	0.021	2.81
Tin(IV) phenoxide	0.038	3.09

Phenol was purified by distilling it twice and collecting the fraction boiling at 179°. It was crystallized twice by cooling in ice-water. Any traces of moisture were removed by keeping it *in vacuo* over  $\text{P}_2\text{O}_5$  for 48 hr. Samples of phenol having m.p. 43° and specific conductance  $1.8 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  at 50° were used in this investigation. The conductance measurements were carried out using a Toshniwal conductivity bridge Sr No. 447. All the solutions were prepared in moisture-free atmosphere. IR spectra were recorded in nujol on a Perkin-Elmer spectrophotometer No. 337.

Dilute solutions of organic tertiary bases and alkali metal phenoxides in phenol are far more conducting than either of the components. Though the specific conductance values of these solutions are not very high (Table 1), yet these are quite significant in view of the low conductances of the components and the low dielectric constant of the medium. This suggests that bases form complexes with phenol, and at lower concentrations these are ionized. No solid compound of these bases with phenol could be isolated under the present experimental conditions suggesting weak interaction between the two components. Nevertheless, conductometric studies on the mixture of the two components show breaks in the conductance-composition curves at the molar ratio (base: phenol) of 1:1 and 2:1.

IR spectral studies of the 1:1 liquid compound show that the spectral bands of the pure components undergo similar changes as are observed in the case of pyridinium chloride<sup>8</sup> complexes of tertiary bases with tellurium tetrachloride<sup>9</sup>, acetyl chloride<sup>10</sup> and selenium tetrachloride<sup>11</sup>. The bands at 1622, 1608, 1503, 1480, 1385 and 1322  $\text{cm}^{-1}$  are due to pyridinium ion. A new band observed at 1432  $\text{cm}^{-1}$ , not present in the pure components, may be assigned to  $\nu\text{-N-H}$ . The bands at 1250, 1204, 1165, 1080, 993, 890, 750 and 680  $\text{cm}^{-1}$  also support the formation of pyridinium ion. The broad band present at 3360  $\text{cm}^{-1}$  in phenol, assigned to hydrogen-bonded OH group, shifts to 3160  $\text{cm}^{-1}$  in these compounds. The O-C stretching mode present at 1350  $\text{cm}^{-1}$  in the phenol shifts to 1400  $\text{cm}^{-1}$ . These observations suggest that OH group in phenol is retained and is hydrogen-bonded to the nitrogen atom of the tertiary base<sup>12</sup>. The spectral changes in the compounds of