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# Effect of Pressure on Conductance. IV. Ionic Association

## and Walden Products in Ethanol<sup>1</sup>

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The conductance at 30° of sodium bromide in methanol and in ethanol, under pressures up to 500 atm, were measured in the concentration range  $3 \leq 10^4 c \leq 20$ . Confirming previous results,<sup>2</sup> the association constant in methanol increases with increasing pressure. In ethanol, the association constant is indistinguishable from zero. Solvation of bromide ions by hydrogen bonds to alcohol molecules is suggested. The conductances of tetramethylammonium bromide and tetrabutylammonium bromide and tetraphenylboride in ethanol were measured over the same range of variables. The net conductance of the three salts decreases with increasing pressure, corresponding to the increase of viscosity (relative viscosity at 5000 atm is 5.2). The association constants decrease with increasing pressure, due to the increase by 27% in dielectric constant. The association constant of Bu<sub>4</sub>N·BPh<sub>4</sub> (about 300 at 30° and 1 atm) is larger than that of Me<sub>4</sub>NBr (about 200), presumably because the excluded volume factor in the association constant is so large for the former.

The conductance of an electrolytic solution is a very complicated function of pressure, because every variable and parameter (except temperature and valence) in the conductance function is an implicit function of pressure. Viscosity usually increases with pressure: limiting mobility and the electrophoretic term therefore decrease. Dielectric constant also increases with pressure: electrostatic association constant and relaxation field decrease, the former exponentially and the latter as  $D^{-3/2}$ . Even the concentration is pressure dependent; due to compression, the volume concentration of a solution of fixed weight concentration increases with pressure. A collection of  $\Lambda(P; c)$  data therefore is not very informative; it is necessary to analyze the isobaric phoreograms in order to isolate the fundamental parameters and then to study their dependence on pressure.

In a previous paper,<sup>2</sup> we reported the conductance of sodium bromide, tetramethylammonium bromide, tetrabutylammonium bromide, and tetrabutylammonium tetraphenylboride in methanol. As expected, the main effect of increasing pressure was to reduce conductance in such a way that the Walden product remained constant for  $Bu_4N \cdot BPh_4$  and increased somewhat for the other three salts. The association constant  $K_{\rm A}$  of sodium bromide appeared to increase with pressure (contrary to expectation); the effect was small, and on account of the many interpolations involved in the calculations, it was practically impossible to assess the uncertainty in  $K_A$ . We have therefore repeated the measurements on the system NaBr-MeOH, using a method which required no interpolations of conductance The previous result is confirmed. Furtherdata. more, in ethanol, which has a much lower dielectric constant, the association constant of sodium bromide turns out to be very small; in fact, within our experimental error,  $K_{\rm A}$ (NaBr, EtOH) is indistinguishable from zero. Solvation of bromide ions is suggested as the cause of these effects.

As expected from the lower dielectric constant of ethanol, the association constants of the quarternary salts are found to decrease with increasing pressure, corresponding to the 17% increase in dielectric con-

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<sup>(2)</sup> J. F. Skinner and R. M. Fuoss, J. Phys. Chem., 70, 1426 (1966).

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stant at 5000 atm. Just as in methanol, association at a given pressure was greater for  $Bu_4N \cdot BPh_4$  than for the bromide. The association constant is the product of a sequence of factors: one of these is the volume exclusion term which increases as the cube of ionic dimensions, and another is the Boltzmann factor  $\exp(\epsilon^2/aDKT)$  which decreases with increasing contact distance a. The function has a minimum for  $a_M = \epsilon^2/3DkT$ ; our results for the tetraphenylboride in methanol and in ethanol suggest that the contact distance for this salt is greater than  $a_M$ , and therefore the salt is more highly associated than the bromide, for which the contact distance is less than  $a_M$ .

### **Experimental Section**

The salts used have already been described.<sup>2</sup> Reagent grade ethanol (U. S. Industrial Chemicals) was used as received; periodic checks on random samples with an F and M Model 700 chromatograph always showed less than 0.05% water and 0.01% other impurities. The specific conductance of the ethanol (at the relevant pressure) was subtracted from the observed solution conductance; the correction was always less than 1%. Methanol, which was purified by slow distillation from anhydrous calcium sulfate, had a specific conductance of less than  $10^{-7}$  mho; this correction was negligible. Acetonitrile (used in the cell calibration) was dried in the same way. The specific conductance of the acetonitrile was about  $2 \times 10^{-7}$ ; the maximum correction was 0.3%. Solutions were prepared by weight, using a Model M Mettler microbalance for the solutes. Solutions were assumed to have the solvent density at a given pressure.

The high-pressure generating system and autoclavethermostat have been described previously.<sup>3</sup> The operating temperature was  $30.0 \pm 0.4^{\circ}$ . The highpressure conductance cell described previously, recalibrated with Bu<sub>4</sub>NBr in freshly distilled acetonitrile at 25°, had a cell constant of  $0.1605 \pm 0.0002$  cm<sup>-1</sup>. (The electrodes had been jarred since their previous calibration.) A similar cell, with  $2.0 \times 2.8$  cm electrodes 1 mm apart, was used for the dilute solutions. Its constant was  $0.0390 \pm 0.0001$  cm<sup>-1</sup>. The cell constants were assumed independent of pressure and temperature. Butyl rubber O-rings, which had been boiled three times in ethanol, were used to seal the conductance cells.

Measurements were made using the same technique and equipment as before,<sup>2</sup> with one change. Previously, measurements were made at random pressures between atmospheric and our maximum of about 5000 atm, a procedure which subsequently necessitated interpolation to round values of pressure in order to simplify calculations of parameters, and which therefore obscured experimental errors by the smoothing thereby involved. In the present work, conductances were measured at round values of pressure gauge readings. These were chosen to give approximately equal increments of conductance; they were 0 (atmospheric pressure), 5000, 10,000, 15,000, 25,000, 40,000, and 70,000 psig. (Our gauges read psi, not metric units.) After measuring at atmospheric pressure, and at the above sequence of increasing pressures, pressure was slowly released, and the conductance at 1 atm was remeasured: the final value usually checked the initial value within 0.5%. Increasing pressure naturally raised the temperature in the autoclave; resistance was measured at intervals after reaching a predetermined pressure, and restoration of the original temperature of 30° was indicated by constancy of the resistance within 0.2% for at least 15 min. Small adjustments were made, of course, to hold the desired pressure as the contents of the autoclave cooled after initial compression.

The properties of ethanol and of methanol are summarized in Table I; they were obtained from literature values<sup>4-6</sup> by interpolation at the pressures listed above. Densities were used to convert weight concentrations into volume concentrations at the relevant pressures; viscosities and dielectric constants were used to calcu-

Table I:	Properties	of Ethanol	and Methanol a	t 30°
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		-Ethanol-		Methanol				
$10^{3}P$	ρ	100η	D	ρ	100η	D		
0	0.781	1.00	23.2	0.782	0.512	31.7		
5	0.807	1.21	24.2	0.808	0.599	33.0		
10	0.827	1.41	24.8	0.829	0.681	34.0		
15	0.845	1.62	25.3	0.847	0.753	34.9		
25	0.875	2.12	26.2	0.876	0.916	36.2		
40	0.908	3.04	27.2	0.911	1.167	37.7		
70	0.960	5.20	29.4	0.963	1.725	40.1		

late the Onsager coefficients. Pressures are given in  $lb/in.^2$ ; "zero" means atmospheric pressure, of course. Conductances are summarized in Table II, where pressures are given at the head of each pair of  $10^4c-\Lambda$  columns. Each line in Table II corresponds to a single run; that is, data were taken at a sequence of pressures for a given initial weight concentration.

<sup>(3)</sup> J. F. Skinner and R. M. Fuoss, J. Phys. Chem., 69, 1437 (1965).
(4) P. W. Bridgman, Proc. Am. Acad. Arts Sci., 49, 3 (1913); 61, 57 (1926).

<sup>(5)</sup> R. Danford, Phys. Rev., 38, 1224 (1931).

<sup>(6)</sup> H. Hartman, A. Neuman, and G. Rinck, Z. Physik. Chem. (Frankfurt), 44, 204, 218 (1965).

Table II: Conductance at 30° under Pressure

	-0		00	10,	000	15,	000		000	<i>—</i> 40,	000	70.	. 000
$10^4c$	Λ	$10^{4}c$	Λ	$10^{4}c$	Λ	$10^{4}c$	Δ	$10^{4}c$ -	Λ	$10^{4}c$	Λ	$10^{4}c$	Λ
					Sodi	um Bromi	de in Eth	nanol					
2.87	44.5	2.97	38.7	3.04	34.8	3.11	31.6	3.22	26.5	3.34	20.6	3.53	14.3
4.25	44.2	4.39	38.0	4.50	34.0	4.60	30.6	4.76	25.8	4.94	20.3	5.22	13.8
5.67	44.0	5.86	38.2	6.00	34.3	6.13	30.7	6.35	26.0	6.59	20.8	6.97	13.9
7.73	42.7	7.99	37.2	8.18	33.2	8.36	30.3	8.65	25.6	8.98	20.1	9.50	13.6
9.14	42.4	9.45	36.9	9.68	33.0	9.89	30.0	10.24	25.1	10.63	20.0	11.24	13.6
13.78	41.2	14.25	35.9	14.60	32.3	14.92	29.4	15.43	24.8	16.02	19.7	16.94	13.5
20.00	39.7	20.68	34.3	21.18	31.2	21.65	28.3	22.40	23.8	23.25	18.6	24.59	12.8
				Tet	ramethyl	ammoniun	n Bromid	e in Ethan	lol				
2.71	53.7	2.81	46.4	2.88	41.7	2.94	37.8	3.04	31.5	3.16	24.0	3.34	16.1
4.02	52.9	4.16	45.9	4.26	40.9	4.35	37.0	4.51	30.6	4.68	23.7	4.95	15.5
5.77	51.3	5.97	44.4	6.12	39.7	6.25	36.0	6.47	29.2	6.71	23.3	7.10	15.4
8.21	49.9	8.49	43.3	8.70	38.5	8.89	35.2	9.20	28.9	9.55	22.6	10.09	14.9
11.94	46.2	12.35	40.8	12.65	36.8	12.92	33.5	13.37	28.1	13.89	21.7	14.70	14.5
18.31	44.1	18.93	38.9	19.40	35.0	19.82	31.7	20.51	26.6	21.29	21.0	22.51	14.0
23.63	42.6	24.42	37.9	25.02	34.2	25.25	30.7	26.45	25.7	27.46	20.2	29.04	13.5
				Te	trabutyla	mmonium	Bromide	e in Ethano	ol				
1.86	45.6	1.92	39.3	1.97	34.2	2.01	29.7	2.08	25.1	2.16	19.2	2.29	12.7
2.46	44.9	2.54	38.2	2.60	33.9	2.66	30.4	2.75	25.0	2.86	19.6	3.02	12.9
3.54	44.2	3.66	37.4	3.75	33.1	3.83	29.5	3.96	24.2	4.12	18.8	4.35	12.2
6.11	41.8	6.32	35.9	6.47	31.6	6.61	28.8	6.84	23.5	7.10	18.0	7.51	12.0
8.62	41.3	8.91	34.8	9.13	30.5	9.33	27.4	9.65	22.6	10.02	17.6	10.60	11.5
12.51	39.2	12.93	34.0	13.25	29.8	13.54	26.5	14.01	22.1	14.55	17.2	15.38	11.2
14.79	37.7	15.29	32.6	15.67	28.9	16.01	26.1	16.56	21.6	17.20	16.9	18.18	11.3
				Tetrabu	itylammo	nium Tetr	aphenylb	oride in E	thanol				
1.92	39.6	1.99	32.2	2.04	27.6	2.08	23.7	2.15	18.7	2.24	13.6	2.36	7.96
3.20	37.8	3.30	30.6	3.39	26.7	3.46	23.2	3.58	18.1	3.72	13.0	3.93	7.50
3.31	38.4	3.42	31.8	3.51	27.3	3.58	23.6	3.71	18.5	3.85	13.5	4.07	8.05
4.78	36.6	4.94	30.2	5.06	25.7	5.17	22.6	5.35	17.7	5.55	12.9	5.87	7.44
5.70	36.2	5.90	29.9	6.04	25.6	6.17	22.3	6.39	17.4	6.63	12.6	7.45	7.46
7.65	34.9	7.90	29.0	8.10	24.7	8.27	21.5	8.56	16.5	8.89	12.0	9.40	7.14
					Sodiu	m Bromid	e in Metl	hanol					
3.03	103.7	3.13	94.1	3.22	86.6	3.29	80.4	3.40	71.0	3.54	59.4	3.74	44.6
4.64	104.0	4.79	93.6	4.92	86.0	5.02	79.7	5.20	69.6	5.41	58.6	5.72	44.0
6.77	103.0	7.00	92.5	7.18	85.0	7.34	78.9	7.59	69.1	7.90	58.2	8.35	43.8
9.25	101.0	9.55	91.1	9.80	83.9	10.02	78.0	10.37	66.8	10.78	56.3	11.40	42.5
11.71	100.4	12.10	90.1	12.41	83.1	12.70	77.4	13.12	67.9	13.65	55.6	14.43	42.3
14.95	99.9	15.45	90.0	15.85	82.6	16.19	77.0	16.76	68.2	17.43	57.7	18.43	43.0

#### Discussion

In a general sort of way, the data of Table II can be summarized by saying that, for these systems, conductance decreases with increasing pressure. In order to give a quantitative description, however, it is necessary to consider the dependence on pressure of all the parameters which appear in the conductance function. To an approximation sufficient for data of the precision of those reported here, conductance depends on two parameters, the limiting conductances  $\Lambda_0$  and the association constant  $K_{\Lambda}$ ; these in turn depend on viscosity and dielectric constant, which vary with pressure. Concentration-dependent effects of pressure are eliminated by extrapolation to infinite dilution, using the equations<sup>7</sup>

$$\Lambda = \gamma (\Lambda_0 - Sc^{1/2} \gamma^{1/2}) \tag{1}$$

$$1 - \gamma = K_{\rm A} c \gamma f^2 \tag{2}$$

The derived constants are summarized in Table III. In order to estimate the uncertainty in the values of the

<sup>(7)</sup> R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959; eq XVII.12 and 15.

Table III: I	Perived Constants						
				10 <sup>-3</sup> P	Marine Street		
	0	5	10	15	25	40	70
			Sodium Bron	nide in Ethanol			
$\Lambda_0$	47.4	41.0	36.8	33.4	27.9	21.6	14.6
$\Lambda_0\eta$	0.475	0.495	0.518	0.540	0.590	0.656	0.760
KA	0	3	4	2	5	0	5
$\Delta K$	10	10	10	10	10	10	10
		Tet	ramethylammoni	um Bromide in E	thanol		
$\Lambda_0$	59.5	50.5	45.2	40.8	33.8	25.6	16.6
$\Lambda_0\eta$	0.597	0.610	0.635	0.660	0.715	0.776	0.864
KA	200	150	150	145	130	90	65
$\Delta K$	40	30	20	20	20	10	10
		Te	trabutylammoniu	m Bromide in Et	thanol		
$\Lambda_0$	48.8	41.3	36.6	32.7	26.6	20.2	13.2
$\Lambda_{0}\eta$	0.490	0.498	0.515	0.529	0.562	0.614	0.686
KA	170	140	140	130	100	80	70
$\Delta K$	30	20	20	15	15	10	10
		Tetrabu	tylammonium Te	etraphenylboride	in Ethanol		
$\Lambda_0$	43.5	35.1	29.8	26.0	20.5	14.6	8.58
$\Lambda_{0\eta}$	0.437	0.423	0.419	0.420	0,433	0.443	0.447
KA	290	200	180	170	160	180	150
$\Delta K$	40	40	30	30	30	20	20
			Sodium Brom	ide in Methanol			
$\Lambda_0$	110.4	98.5	90.3	83.5	72.9	62.3	46.5
$\Lambda_0\eta$	0.565	0.606	0.615	0.629	0.668	0.727	0.802
KA	10	10	5	0	0	25	35
$\Delta K$	20	20	20	20	20	20	20

association constants, the  $F/\Lambda$  vs.  $c\Lambda f^2/F$  plots were deliberately shifted by changing the ordinates by  $\pm 1.0\%$  and recalculating the slopes. The resulting changes in association constant are listed in Table III as  $\Delta K$ . The column heading are pressures in lb/in.<sup>2</sup>. The Walden products  $\Lambda_{0\eta}$  for sodium bromide, tetramethylammonium bromide, and tetrabutylammonium bromide in ethanol agree within our experimental error with the values 0.486, 0.592, and 0.484 found<sup>8</sup> at  $25^{\circ}$ .

We consider first the association constants. In an earlier paper,<sup>2</sup> it was reported that the association constant of sodium bromide in methanol increased with pressure. This change is in the opposite direction to that which would follow from an increase in dielectric constant. Due to the multiple interpolations made in the earlier work, it was impossible to estimate the error in  $K_A$ ; for this reason, the system NaBr-MeOH was reinvestigated, this time at the same gauge pressures for each concentration. As seen in Table III, even with a pessimistic estimate of  $\pm 20$  in association constant, there is a distinct upward trend of  $K_{\rm A}$  with increasing pressure, which matches in magnitude the previously reported increase. In ethanol, however, which has a

much lower dielectric constant than methanol, the association constant of sodium bromide is practically zero. Hydrogen bonding between alcohol molecules and the bromide ion to give a solvated ion which retains solvate in the ion pair would account for the lower association in ethanol compared to methanol, because  $Br^{-} \cdot (HOC_2H_5)_n$  obviously is larger than  $Br^{-} \cdot (HO^{-})_n$  $(CH_3)_n$ . Solvation of bromide ion by alcohol is consistent with the observation that addition of methanol to bromide and iodide in the aprotic solvents nitrobenzene<sup>9</sup> and nitromethane<sup>10</sup> sharply reduces the limiting conductance. Furthermore, the association of tetrabutylammonium bromide in nitrobenzene is strongly decreased by the addition of methanol. More study of alcohol-ion interaction in aprotic solvents is clearly needed in order to understand this behavior, which is completely unexpected. On the basis of the simple sphere-in-continuum model, one would predict

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<sup>(8)</sup> R. L. Kay and D. F. Evans, J. Phys. Chem., 70, 2325 (1966). (9) H. Sadek and R. M. Fuoss, J. Am. Chem. Soc., 72, 301, 5803 (1950).

<sup>(10)</sup> M. A. Coplan and R. M. Fuoss, J. Phys. Chem., 68, 1177 (1964).



Figure 1. Dependence of association constants on dielectric constant in ethanol: curve 1,  $(1.0 + \log K_A)$  for Bu<sub>4</sub>N·BPh<sub>4</sub>; curve 2,  $(0.5 + \log K_A)$  for Bu<sub>4</sub>NBr; curve 3, log  $K_A$  for Me<sub>4</sub>NBr.

that sodium bromide would be much more associated than tetrabutylammonium tetraphenylboride, in a given solvent, while the results of Table III show that precisely the opposite sequence is correct.

The association of the quaternary salts is as expected, as far as the direction and magnitude of the change in association constant with pressure is concerned: association decreases with increasing pressure, corresponding to an increase in dielectric constant. As shown in Figure 1, the logarithm of association constant is linear  $D^{-1}$ , as required by the equation<sup>11</sup>

$$K_{\rm A} = (4\pi N a^3/3000) \exp(\epsilon^2/aDkT) \tag{3}$$

Also, the slopes (proportional to 1/a) decrease in the expected sequence  $Bu_4NBPh_4 < Bu_4NBr < Me_4NBr$ , consistent with a values of about 9, 6, and 5 A. The interesting feature here is the absolute values of the association constants. The values for Me\_4NBr and  $Bu_4NBr$  are nearly equal, and unmistakably *smaller* than for the much bulkier  $Bu_4N \cdot BPh_4$ . The function of eq 3, as a function of a for fixed D, has a minimum at  $a_M = \epsilon^2/3DkT$ , which in ethanol at 1 atm and 30° is at about 8 A. The increased association of  $Bu_4N$ -BPh<sub>4</sub> compared to that of  $Bu_4NBr$  is on this basis a consequence of the larger target area offered by the  $BPh_4^-$  ion; in other words, here the  $a^3$  in the excluded volume factor has a greater effect than the 1/a in the exponential factor.

Finally, we consider the dependence of mobility on



Figure 2. Dependence of Walden products on pressure in ethanol: 1, Me<sub>4</sub>NBr; 2, NaBr; 3, Bu<sub>4</sub>NBr; 4, Bu<sub>4</sub>NBPh<sub>4</sub>.



Figure 3. Variation of Stokes radius with dielectric constant in ethanol: 1,  $Bu_4N^+$ ; 2,  $Na^+$ ; 3,  $Br^-$ ; 4,  $Me_4N^+$ .

pressure. For Bu<sub>4</sub>N · BPh<sub>4</sub>, the Walden product (Figure 2, curve 4) is substantially independent of pressure, showing that the ions of this salt behave like Stokes spheres in ethanol. For the other three salts, the Walden product increases with increasing pressure. For the two quaternaries, this presumably is due to the bromide ion, since the plot for Bu<sub>4</sub>N · BPh<sub>4</sub> is flat. Using the value 1.073 for the ratio of the single-ion conductances<sup>12</sup> of Bu<sub>4</sub>N <sup>+</sup> and BPh<sub>4</sub><sup>-</sup>, the other single-ion conductances can be calculated, and from these, the Stokes radii  $R_{\pm}$  are obtained from the equation

$$R_{+} = 0.819 \times 10^{-8} / \lambda^{0}_{+} \eta \tag{4}$$

As shown in Figure 3, these radii decrease with increasing dielectric constant. Part of this change<sup>13</sup> is

<sup>(11)</sup> R. M. Fuoss, J. Am. Chem. Soc., 80, 5059 (1958).

<sup>(12)</sup> J. F. Coetzee and G. P. Cunningham, *ibid.*, 87, 2529 (1965).
(13) R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S.*, 45, 807 (1959); Figure 5B.

caused by a relaxation effect between ions and solvent dipoles; as was observed in methanol and in other

examples, the slope in hydrogen-bonding solvents is considerably larger than in aprotic solvents.