

Table II: Conductance at 30° under Pressure

0		5,000		10,000		15,000		25,000		40,000		70,000	
10 ⁴ c	Λ	10 ⁴ c	Λ	10 ⁴ c	Λ	10 ⁴ c	Λ	10 ⁴ c	Λ	10 ⁴ c	Λ	10 ⁴ c	Λ
Sodium Bromide in Ethanol													
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
Tetramethylammonium Bromide in Ethanol													
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
Tetrabutylammonium Bromide in Ethanol													
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
Tetrabutylammonium Tetraphenylboride in Ethanol													
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
Sodium Bromide in Methanol													
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 Λ_0 and the association constant K_A ; 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 equations⁷

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

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

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

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

Table III: Derived Constants

	$10^{-3}P$						
	0	5	10	15	25	40	70
Sodium Bromide in Ethanol							
Λ_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
K_A	0	3	4	2	5	0	5
ΔK	10	10	10	10	10	10	10
Tetramethylammonium Bromide in Ethanol							
Λ_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
K_A	200	150	150	145	130	90	65
ΔK	40	30	20	20	20	10	10
Tetrabutylammonium Bromide in Ethanol							
Λ_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
K_A	170	140	140	130	100	80	70
ΔK	30	20	20	15	15	10	10
Tetrabutylammonium Tetraphenylboride in Ethanol							
Λ_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
K_A	290	200	180	170	160	180	150
ΔK	40	40	30	30	30	20	20
Sodium Bromide in Methanol							
Λ_0	110.4	98.5	90.3	83.5	72.9	62.3	46.5
$\Lambda_0\eta$	0.535	0.606	0.615	0.629	0.668	0.727	0.802
K_A	10	10	5	0	0	25	35
ΔK	20	20	20	20	20	20	20

association constants, the F/Λ vs. $c\Delta f^2/F$ 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 ΔK . The column heading are pressures in lb/in.². 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 found⁸ at 25°.

We consider first the association constants. In an earlier paper,² 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 ± 20 in association constant, there is a distinct upward trend of K_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 $\text{Br}^-(\text{HOC}_2\text{H}_5)_n$ obviously is larger than $\text{Br}^-(\text{HOCH}_3)_n$. Solvation of bromide ion by alcohol is consistent with the observation that addition of methanol to bromide and iodide in the aprotic solvents nitrobenzene⁹ and nitromethane¹⁰ 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

(8) 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).

(10) M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1177 (1964).