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Electrolyte–Solvent Interaction. I. Tetrabutylammonium Bromide in Methanol–Nitrobenzene Mixtures

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Introduction.—In a general sort of way, the behavior of a given electrolyte in a given solvent is predictable; thus, ion association increases with decreasing dielectric constant of the solvent and size of the solute ions, and mobility increases with decreasing viscosity of the solvent and ion size. Above a certain value of dielectric constant, critical for a given ion size, ion pairs become unstable with respect to thermal motion, and ion association is negligible in solvents of higher dielectric constant. The theoretical treatment under lying these generalizations is based on a model in which ions are approximated as spheres and the solvent as a continuum. Now ions are not actually spheres, of course, nor is the solvent a continuum. Consequently, when we examine experimental data for any specific system, we expect and find deviations from conformity to the idealized model, which are characteristic of the particular system under investigation. We have therefore planned a systematic survey of a series of electrolytic solutions with the hope that regularities among the exceptions and correlations between the latter and structure might appear.

As a starting point, we are presenting herewith a study of a simple 1-1 electrolyte with spherically symmetric ions, tetrabutylammonium bromide, in mixtures of a pair of solvents, methanol and nitrobenzene, which have about the same dielectric constant, but which otherwise are quite different. The former is a small molecule, with a fairly high dipole moment, where the positive end of the dipole is in an exposed position. It is a protonic basic solvent, and can be expected to form hydrogen bonds with itself and with solutes. Nitrobenzene, on the other hand, is an aprotonic solvent, with a large molecule, and with the negative charge of the dipole exposed. To a first approximation, we would expect the salt to have about the same strength in the two solvents, because the dielectric constants are nearly equal, and the limiting conductance should increase regularly as we go from nitrobenzene to the less viscous methanol. As we shall see, tetrabutylammonium bromide acts as a much stronger electrolyte in mixtures of nitrobenzene and methanol than it does in either solvent alone. Furthermore, the mobility change is quite imperfectly compensated by the viscosity change in the mixtures. We are of the opinion that both of these effects are due to specific interactions between the two solvents and the two ions involved, with the result that the first approximation expectations must be modified.

Experimental

Tetrabutylammonium bromide was prepared by heating 37.0 g. (0.20 mole) of redistilled (101–104° at 20 mm.) tri-*n*-butylamine, 27.4 g. (0.20 mole) of redistilled (b. p. 102°) *n*-butyl bromide and 25.4 g. (0.55 mole) of ethanol at 83° for twenty-three hours. Potentiometric titrations for bromide ion showed that the conversion was then 80.3% complete. Sufficient water (210 ml.) was added to give a 20% solution of salt; unreacted reagents were extracted with petroleum ether. The solution was chilled to −15° and the salt (22.0 g.) was filtered off on a cold Buchner funnel and immediately transferred to an evacuated desiccator over phosphorus pentoxide. The mother liquor was titrated and then concentrated to 20% by vacuum evaporation for recovery of a second crop. The salt was twice recrystallized from benzene (5 ml./g.) plus sufficient petroleum ether to produce turbidity in the hot solution. Gravimetric analysis gave 24.91% Br; potentiometric titration, 24.60%; theoretical 24.79%; m. p. 119.4°. Ethyl acetate[1a] has also been used to recrystallize tetrabutylammonium bromide; this procedure is hazardous, especially in humid weather, because a trace of water in the ethyl acetate leads to contamination of the salt with tetrabutylammonium acetate, and the acetate and bromide seem to be unusually difficult to separate by recrystallization.

Methanol was purified as recommended by Hartley[2]; the specific conductance was 4–20 $\times 10^{-8}$, and was always determined just before use in conductance experiments. Nitrobenzene was purified by the procedure of Witschonke and Kraus[3]; its conductance was in the range 0.3–0.5 $\times 10^{-8}$. Both solvents were stored in flasks protected by drying tubes, and were pumped into other containers (cells, dilution flasks, weight burets, etc.) by means of dry air pressure.

The conductance cell consisted of an Erlenmeyer flask to which was sealed a capsule containing bright platinum electrodes 2 × 2.5 cm., space 3 mm. apart. The electrode leads were brought through the glass by the Hnizda and Kraus[4] platinum–707–332–Pyrex tube seals. A long (20 × 1.0 cm.) glass-stoppered neck was sealed to the flask to minimize diffusion of moisture into the cell. The cell constant was 0.05277 ± 0.02%, as determined by comparison with a cell calibrated against 0.01 demal[5] potassium chloride solution. Conductances were measured on a bridge essentially of the design recommended by Shedlovsky[6]; small polarization effects were eliminated[7] by extrapolation from data at several frequencies in the audiorange. All solutions were made up by weight, and volume concentrations in equivalents per liter were calculated, using the densities of the solvents (Table I); since our highest weight concentration was about 0.3 g./l. the error so introduced is negligible.

Results

Properties of Solvent Mixtures.—Densities of the mixtures were determined in 20-ml. pycnometers at 25.00 ± 0.02°. Viscosities were

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[1a] N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

[2] H. Hartley and H. R. Raikes, *Trans. Chem. Soc.*, **127**, 524 (1925).

[3] C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

[4] V. F. Hnizda and C. A. Kraus, *ibid.*, **71**, 1565 (1949).

[5] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

[6] T. Shedlovsky, *ibid.*, **52**, 1793 (1930).

[7] G. Jones and S. M. Christian, *ibid.*, **57**, 272 (1935).

measured at average velocity gradients of 2500–6000 sec.$^{-1}$ in a Bingham[8] viscometer at 25.00°. Dielectric constants were measured at 60 cycles and 25.00° in a cell similar to that described by Mead and Fuoss,[9] using a resistance bridge.[10] The physical constants of the solvent mixtures are summarized in Table I, where ρ is density in g./ml., η is viscosity in centipoises and ϵ is dielectric constant. For compactness in later discussion, the solvents are identified by the code numbers of the first column of Table I. Concentrations in Table I are given as weight per cent. (w_1) and mole fraction (x_1) of methanol in the mixtures.

TABLE I

MEASURED PROPERTIES OF METHANOL–NITROBENZENE MIXTURES AT 25°

No.	w_1	x_1	ρ	η	ϵ	$10^6\ \kappa_0$
1	100.00	1.0000	0.7865	0.5460	30.6[a]	17.4
2	94.55	0.9852	.8025	.5642	30.4_5	19.9
3	77.47	.9296	.8562	.6279	29.9	26.3
4	61.39	.8593	.9127	.7113	30.1	21.7
5	44.36	.7539	.9794	.8366	30.71	8.7
6	27.16	.5889	1.0556	1.0357	31.18	6.0
7	19.29	.4788	1.0939	1.1607	31.71	3.0
8	8.44	.2616	1.1506	1.4159	32.61	1.82
9	1.98	.0719	1.1867	1.6976	33.64	1.00
10	0.00	.0000	1.1983	1.8602	34.72	0.52

[a] Previous values for the dielectric constant of methanol at 25° include: ϵ = 32.8, Kyropoulos, *Z. Physik*, **40**, 507 (1927); ϵ = 34.0, Astin, *Phys. Rev.*, **36**, 300 (1927); ϵ = 30.5, Gundermann, *Ann. phys.*, **6**, 545 (1930); ϵ = 30.0, Farkas, *Z. Elektrochem.*, **38**, 654 (1932); ϵ = 31.52, Åkerlöf, THIS JOURNAL, **53**, 4126 (1932); ϵ = 31.5, Le Fevre, *Trans. Faraday Soc.*, **34**, 1127 (1938); ϵ = 32.61, Jones and Davies, *Phil. Mag.*, **28**, 307 (1939). Åkerlöf's value of 31.52 is probably the best; our lower value is due to errors arising from the high conductive component in the cell admittance at 60 cycles. For the present discussion, we prefer to use our values, however, because relative rather than absolute values are more important here.

TABLE II

DERIVED PROPERTIES OF METHANOL–NITROBENZENE MIXTURES AT 25°

No.	V_{12}	$-\Delta$	f_1	P_{12}	ϵ (calcd.)
1	40.74	0.00	1.0000	272.4	30.63
2	41.61	.05	0.9647	276.8	30.51
3	44.94	.19	.8427	293.4	30.11
4	49.14	.33	.7125	323.1	30.13
5	55.59	.40	.5524	373.0	30.54
6	65.82	.41	.3645	448.5	31.23
7	72.68	.38	.2684	503.9	31.67
8	86.28	.24	.1236	615.4	32.61
9	98.22	.06	.0298	723.0	33.71
10	102.74	.00	.0000	781.0	34.68

In Table II are given several derived properties of the solvent mixtures. The second column gives the observed molar volumes

$$V_{12} = (x_1M_1 + x_2M_2)v \qquad (1)$$

where x_1 is mole fraction of methanol, M_1 = 32.04 and v is the observed specific volume. Partial molal volumes were calculated by the formula

$$V = (V_{12} - x_jM_jv^0{}_j)/x_j \qquad (2)$$

and plotted against mole fraction. We find 40.0 cc./mole as the limiting molar volume of methanol at zero concentration in nitrobenzene and 99.5 cc./mole as the limiting molar volume of nitrobenzene in methanol. The maximum deviation from linear addition of volumes appears at 60 mole % methanol, as is shown by the quantity Δ in Table II, where

$$\Delta = V_{12} - (x_1M_1v_1^0 + x_2M_2v_2^0) \qquad (3)$$

The viscosities of the mixtures are no simple function of any of the conventional variables; plots of viscosity or fluidity ($\phi = 1/\eta$) are concave-up on both mole fraction and volume fraction ($f_1 \approx v_{01}x_1M_1/V_{12}$) scales, while the logarithm of fluidity gives a concave-up plot on a mole fraction scale and a concave-down one on a volume fraction scale. Closest approaches the linearity are given by ϕ–f and by η–x plots. The log ϕ curves are nearly linear in the methanol-rich half of the log ϕ–f plot and in the nitrobenzene-rich half of the log ϕ–x plot. In order to save space, these graphs are not shown.

Molar polarizations were calculated from the observed dielectric constants by Kirkwood's[11] formula

$$P_{12} = (\epsilon - 1)(2\epsilon + 1)V_{12}/9\epsilon \qquad (4)$$

and are given in the fifth column of Table II. While a minimum appears in the methanol-rich end of the ϵ–x_1 curve, the P_{12}–x_1 curve is monotone; in other words, addition of nitrobenzene (with the higher dielectric constant) depresses the dielectric constant of the methanol initially because the volume of the nitrobenzene molecule is so large compared to that of methanol. Any "explanations" of this minimum on the basis of dipole interaction would therefore be fallacious. Since we are interested in the dielectric constant as one of our fundamental independent variables, and since the observed dielectric constants scattered somewhat due to the inherent difficulty of measuring capacities at 60 cycles in moderately well conducting solutions, the data were smoothed as follows. First the quantity

$$P_{12}^0 = x_1P_1^0 + x_2P_2^0 \qquad (5)$$

was calculated, where P_1^0 and P_2^0 are the molar polarizations of methanol and nitrobenzene, respectively; *i. e.*, P_{12}^0 is the hypothetical polarization of a mixture in which no molecular interaction occurred. We then plotted δP where

$$\delta P = P_{12}^0 - P_{12}\ (\text{obsd.}) \qquad (6)$$

against x_1 and interpolated values of $\delta P'$ at the experimental concentrations from a smooth curve drawn through the experimental δP points.

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(8) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922.

(9) D. J. Mead and R. M. Fuoss, THIS JOURNAL, **61**, 2047 (1939).

(10) R. M. Fuoss, *ibid.*, **60**, 451 (1938).

(11) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

Finally, using these values of $\delta P'$, smoothed values of P_{12} were calculated and dielectric constants were computed by the formula

$$\epsilon_{\text{calcd.}} = 1 + 4.432\, P_{12}\,(\text{calcd.})/V_{12}\,(\text{obsd.}) \qquad (7)$$

The smoothed values of dielectric constant are given in Table II; these numbers are used in all subsequent calculations in this paper, on the assumption that they represent better relative values of this parameter than the individually observed experimental quantities. In Fig. 1, the top curve is the function of eq. (7) and the open circles represent the observed points.

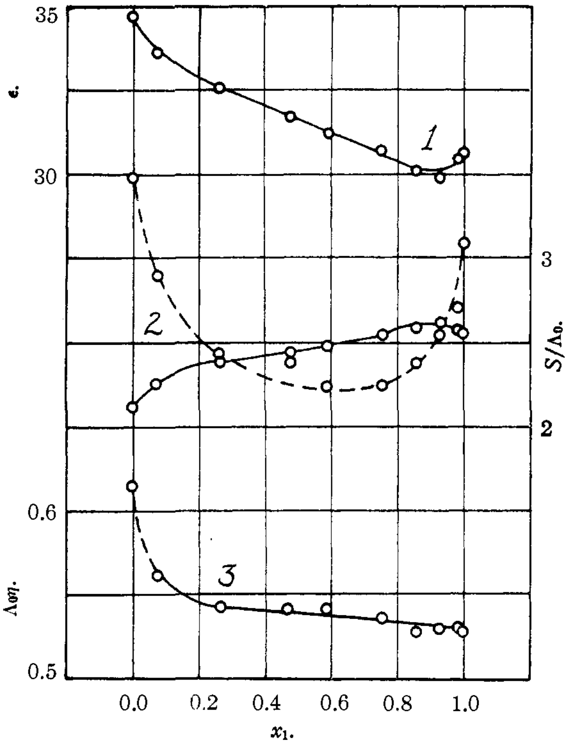

Fig. 1.—Properties of tetrabutylammonium bromide and methanol–nitrobenzene mixtures: 1, dielectric constants ϵ as function of mole fraction x_1 of methanol; 2, dotted, empirical $\Lambda/\Lambda_0 - \sqrt{c}$ slopes, S'/Λ_0; 2, solid, theoretical $\Lambda/\Lambda_0 - \sqrt{c}$ slopes, S/Λ_0; 3, Walden products, $\Lambda_0\eta$.

The transmission of a series of methanol–nitrobenzene mixtures was measured by means of a Beckman spectrophotometer (model DU) in the visible range. Quartz cells with 1.00-cm. solvent thickness were used; slit width was 0.045 to 0.025 mm. The absorption edge near λ 4300, characteristic of nitrobenzene, gradually shifts to shorter wave lengths as methanol is added. In Fig. 2, optical density $(-D = \log_{10} I/I_0)$ is plotted against concentration $N_2 = 1000\, w_2\rho/M_2$ = moles nitrobenzene per liter of solution (in pure nitrobenzene, $N_2 = 9.73$). It will be observed that the graphs are linear in the range λ 4240–4340; the mixtures thus satisfy Beer's law and we may conclude that there is no specific interaction between the protons of the methanol and the electrons of the nitro-group. The extinction coefficient α, defined by the familiar relationship

$$D = \log I_0/I = \alpha l N \qquad (8)$$

increases rapidly with increasing frequency in this region as shown by the α–λ curve superimposed on the absorption data in Fig. 2. The numerical values of the slopes are as follows: λ 4240, $\alpha = 0.244$; 4260, 0.185; 4280, 0.129, 4300, 0.092; 4320, 0.065; 4340, 0.048.

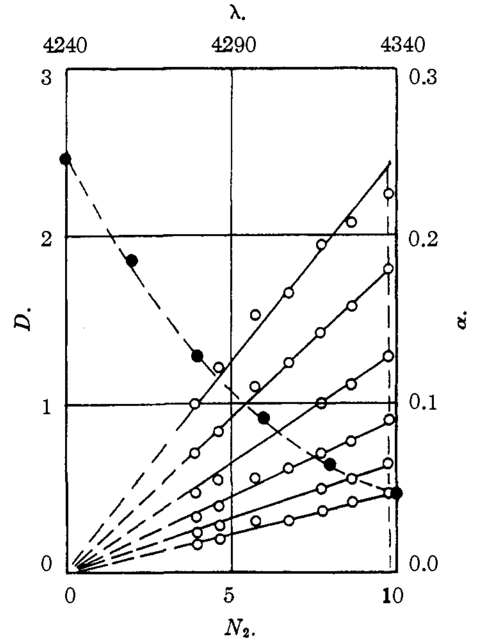

Fig. 2.—Transmission of methanol–nitrobenzene mixtures: optical density D at λ 4240 (top curve), λ 4260, λ 4280, λ 4300, λ 4320 and λ 4340 as function of N_2, normality of nitrobenzene. Dotted curve, ordinates right-extinction coefficient α as function of λ.

Conductance data for tetrabutylammonium bromide in methanol–nitrobenzene mixtures are given in Table III. Here concentrations c of salt are given as equivalents per liter. The equivalent conductance was calculated from the observed specific conductance after subtracting the conductance of the solvent. The latter figures are given as the last column of Table I; the correction varied from about 0.1% in the most dilute solution in nitrobenzene to a maximum of nearly 3% in methanol. All data were obtained by concentration runs: solvent was pumped into the clean, dry cell and its conductance measured Then successive portions of increasing size of concentrated solution (of the order of 0.002 N) of salt in the same solvent mixture were added from a weight buret. Adsorption errors[1] appeared to be negligible, because the cell resistance (after temperature equilibrium had been established, of course) remained unchanged on tipping the cell to replace the liquid between the electrodes in the cell capsule with a fresh sample from the bulk of solu-

TABLE III

CONDUCTANCE OF TETRABUTYLAMMONIUM BROMIDE IN METHANOL–NITROBENZENE MIXTURES AT 25°

$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
100 MeOH		61.39 MeOH		19.29 MeOH	
0.650	94.65	0.736	72.59	0.809	45.76
1.618	93.37	2.812	71.29	1.839	45.16
2.097	92.75	5.474	70.09	4.190	44.41
2.716	92.17	7.751	69.31	6.403	43.92
3.995	91.37	44.36 MeOH		8.833	43.41
4.493	90.80	0.646	62.63	8.44 MeOH	
6.145	89.80	1.851	62.04	0.863	37.48
94.55 MeOH		5.232	60.58	1.660	37.16
1.182	91.33	7.277	59.93	3.947	36.48
3.383	89.21	9.793	59.30	6.193	36.01
6.235	87.65	27.16 MeOH		8.612	35.64
9.059	86.35	1.007	50.90	1.98 MeOH	
77.47 MeOH		2.178	50.54	0.417	32.82
0.580	82.05	4.171	49.86	1.009	32.33
1.295	81.30	6.536	49.18	2.684	31.72
3.129	80.44	8.306	48.88	5.746	31.08
5.109	79.80			9.139	30.52
6.432	78.81			0.00 MeOH	
				1.294	32.18
				1.511	32.03
				2.422	31.70
				4.708	31.04
				8.255	30.24

tion in the main compartment of the Erlenmeyer cell.

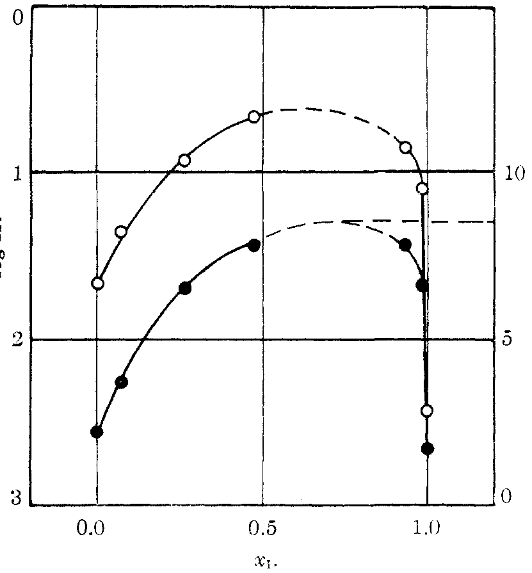

Fig. 3.—Dissociation constants (upper curve, ordinates left) and ion sizes (lower curve, ordinates right) for tetrabutylammonium bromide in methanol (x_1)–nitrobenzene mixtures.

Discussion.—When the observed equivalent conductances were plotted against the square root of concentration, straight lines were obtained for all of the systems reported in Table III. As is well known, the Debye–Hückel[12] theory predicts that Λ–$\sqrt{c}$ curves should approach linearity at low concentrations with a slope S which has the value computed by Onsager[13] for 1–1 salts at 25° in a solvent of dielectric constant

$$S = 158.6\,\Lambda_0/\epsilon^{3/2} + 4.75/\eta\epsilon^{1/2} \qquad (9)$$

ϵ and viscosity η. The quantity S/Λ_0 is much less sensitive to salt and solvent than S, on account of the approximate constancy of the Walden–Stokes product $\Lambda_0\eta$. The experimental values of the slopes over Λ_0 are plotted in Fig. 1 as (dotted) curve 2; it will be observed that the Λ–$\sqrt{c}$ curves are steepest in the pure solvents and that the empirical slope S'/Λ_0 decreases markedly as we go over to the mixed solvents. For comparison, the theoretical slopes of eq. (9), based on the experimental Λ_0, η and ϵ values are shown on the same plot as the (solid) curve 2. It will be immediately noted that the observed empirical slopes S' vary with solvent composition in a way which is in flat contradiction to the behavior expected on the basis of theory; the differences are qualitative as well as quantitative.

Ion association[14] will account for the Λ–$\sqrt{c}$ curves steeper than theoretical, while as yet unknown higher terms in the conductance equation produce slopes less than theoretical in the range of finite concentrations. Obviously both influences are operating in these systems. The net results of interionic terms in mobility and activity coefficients combined with ion association produces a Λ–$\sqrt{c}$ curve which has an inflexion point, and this inflexion region leads to a fictitious linear conductance curve over a limited range of concentration. Some authors have used this inflexion slope to extrapolate conductance date in order to obtain limiting equivalent conductances; the Λ_0 values thus obtained are necessarily incorrect.

We have analyzed the data of Table III by Shedlovsky's[15] modification of the Fuoss and Kraus[16] conductance equation, in which ion association as well as the dependence of both activity coefficient and ionic mobilities on ionic strength are explicitly brought into the calculation. The resulting $1/\Lambda S(z)$–$c\Lambda f^2 S$ plots were all linear and need not be reproduced here. The limiting conductances obtained by extrapolation to zero concentration and the values of the dissociation constants K so obtained are given in Table IV for each of the systems studied. It should be emphasized that the theoretical slopes of eq. (9) were used in this calculation; for activity coefficients, we used the Debye–Hückel limiting formula which, for 1–1 electrolytes at 25°, reduces to

$$-\log_{10} f = 352.4\sqrt{c}/\epsilon^{3/2} \qquad (10)$$

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(12) P. Debye and E. Hückel, *Physik. Z.*, **24**, 305 (1923).

(13) L. Onsager, *ibid.*, **28**, 277 (1926).

(14) R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

(15) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(16) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933), R. M. Fuoss, *ibid.*, **57**, 488 (1935); R. M. Fuoss and T. Shedlovsky, *ibid.*, **71**, 1496 (1949).

TABLE IV

CONSTANTS DERIVED FROM CONDUCTANCE DATA OF TETRABUTYLAMMONIUM BROMIDE IN METHANOL–NITROBENZENE MIXTURES AT 25°

No.	Λ_0	K	$\Lambda_0\eta$	a	S/Λ_0	S'/Λ_0
1	96.6_6	0.0038	0.5278	1.74	2.56	3.09
2	93.9_0	$.08_1$	.5298	6.65	2.58	2.71
3	84.3_9	.14	.5299	7.89	2.62	2.55
4	74.2_9	∞	.5284	(8+)	2.59	2.38
5	64.0_4	∞	.5358	(8+)	2.55	2.25
6	52.3_6	∞	.5423	(8+)	2.48	2.24
7	46.7_1	0.22	.5422	7.83	2.44	2.38
8	38.3_4	.12	.5429	6.58	2.38	2.44
9	33.1_1	.045	.5621	3.72	2.26	2.90
10	33.0_7	.022	.6152	2.28	2.12	3.48

Let us first consider the limiting conductances, which vary from 96.7 in methanol to 33.1 in nitrobenzene, *i. e.*, in the ratio 2.92. Most of this change is due to the increase in viscosity as the nitrobenzene content of the solvent increases; as Walden pointed out long ago, if ions were Stokes spheres in a continuum describable hydrodynamically by the macroscopic viscosity, the product $\Lambda_0\eta$ would be constant for a given electrolyte in a series of solvents. Curve 3 of Fig. 1 shows that their product is indeed approximately constant in the methanol-rich mixtures, but is significantly higher in nitrobenzene. In other words, addition of a small amount of methanol to nitrobenzene, causes a sharp decrease in ionic mobility, despite the fact that this addition produces a *decrease* in the viscosity of the solvent. We must therefore conclude that some specific interaction between methanol and the solute takes place, such that the mobile hydrodynamic unit in methanol–nitrobenzene mixtures offers greater resistance to motion than in pure nitrobenzene. Tentatively, we ascribe this decrease to solvation of the anions by the methanol, due to electrostatic interaction between the charge on the anion and that on the hydroxyl proton in methanol. We may not assume that a bond as strong as a hydrogen bond is formed, because the $\Lambda_0\eta$-x_1 curve exhibits gradual (although sharp) curvature at the nitrobenzene end; if a bond of potential energy large compared to kT were formed, a discontinuity would appear on the initial addition of methanol to nitrobenzene. (We recall that the figures under discussion are limiting values for zero ion concentration and hence even a trace of methanol in the solvent is in molar excess with respect to solute electrolyte.) But on an average, a certain fraction of anions carry methanol molecules through the solvent; or taking the equivalent statistical point of view, all the anions drag along methanol molecules part of the time, and part of the time migrate as unsolvated bromide ions. The probability of this occurrence must depend on the geometry of the solvent molecules and on the instaneous configurations of ion–solvent groups; it therefore seems worthwhile to investigate other alcohols to see, for example, whether larger alkyl groups would give a smaller relative decrease in the $\Lambda_0\eta$ product than methanol, due to lower probability of favorable orientation for solvation or whether this effect would be compensated by the larger hydrodynamic resistance which should appear when solvation occurs with a larger molecule. The remaining small change in the $\Lambda_0\eta$ product after the initial drop is probably due to the overall relaxation effect between moving ions and solvent dipoles which was studied in a preliminary way by Born.[17]

The dissociation constants likewise indicate interaction between solvent and solute of a nature which requires more than continuum theory for its interpretation. We note first that the solute is a much weaker electrolyte in methanol than in nitrobenzene, and that the difference is much greater than can be accounted for on the basis of the somewhat lower dielectric constant of methanol. If we compute ion sizes[18] a from the dissociation constants, assuming spherical ions and a coulomb continuum, we find 1.74×10^{-8} cm. for the salt in methanol and 2.28×10^{-8} in nitrobenzene. These figures would be the same if the equivalent sphere representing the salt were independent of solvent. The result seems reasonable if we remember that the nitrobenzene molecule is much larger than the methanol molecule, and that the a-parameter measures the probability of approach of two ions of opposite charge. In a real solvent, as opposed to a continuum, large molecules will interfere more with ion contact than small molecules with the same macroscopic dielectric constant, and thus lead to a larger calculated value for the contact distance for the equivalent spheres.

This conclusion seems to be borne out by the striking effect which appears on the addition of a little nitrobenzene to methanol; an enormous increase in K, despite the small decrease in dielectric constant, results. Then with increasing nitrobenzene content, the dissociation constant systematically increases. In the middle three mixtures, the $1/\Lambda S$-$c\Lambda Sf^2$ curves were horizontal within the limit of experimental error, showing complete absence of association. In Table IV, we have indicated this by writing the infinity sign in the K-column, although any K greater than unity would give the same result. The ion size above which association becomes negligible for dielectric constants in this range is about 9×10^{-8} cm.; a plot of a against mole fraction of methanol gives a smooth curve which has a maximum of 8.6×10^{-8} cm. at about 75 mole % methanol.

The sudden rise in K on addition of nitrobenzene suggests that a structure in which a bromide ion (carrying a methanol molecule) associated with a cation carrying a nitrobenzene molecule is more stable than a simple ion pair. Specific interaction

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[17] M. Born, *Z. Physik.*, **1**, 221 (1920); H. Schmick, *ibid.*, **24**, 56 (1924).

[18] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

between the nitrobenzene dipole, with its negatively charged protuberance, and the tetrahedral cation does not seem unreasonable. But apparently a $Bu_4N^+\cdot(^-O_2N^+C_6H_5)\cdot Br^-(^+HO^-CH_3)$ structure is stable, while the cation–nitrobenzene grouping alone is not, because nothing unusual appears in the $\Lambda_0\eta$–x_1 curve at the methanol-rich end. It will be noted that the rise in K on the addition of methanol to nitrobenzene is gradual, as contrasted to the abrupt rise at the other end. The variation of equivalent ion size with solvent composition in an approximately isodielectric mixture can only mean that we should consider short range interaction between solvent and solute, in which the detailed structure of both must be taken into account. Again, we realize that further work with systematically varied solvent and solute geometries will be necessary to clarify some of the puzzles suggested by this work. In any case, it is significant to note that tetrabutylammonium bromide is a much stronger electrolyte in mixtures of nitrobenzene and methanol than it is in either solvent alone. The conclusion that interaction between anions and methanol on the one hand and between cations and nitrobenzene on the other, seems inescapable.

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Summary

1. Densities, light absorption (λ 4000–4600), viscosities and dielectric constants of methanol–nitrobenzene mixtures have been determined at 25°.

2. The conductance of tetrabutylammonium bromide in these mixtures has been measured at concentrations below 0.001 N. Dissociation constants and limiting conductances were obtained by extrapolation to zero concentration.

3. Tetrabutylammonium bromide is a much stronger electrolyte in methanol–nitrobenzene mixtures than in either solvent alone. The mobility is markedly decreased by addition of methanol to nitrobenzene and the dissociation constant is abruptly increased by addition of nitrobenzene to methanol.

4. Neither hydrodynamic nor electrostatic properties of the electrolyte in the mixtures can be described by means of a continuum theory; rather, specific interaction, presumably determined by structural details of both solvent and solute, must be involved.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

A Contrast between Polyelectrolytes[1] and Simple Electrolytes[2]

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Introduction

Concentrated solutions of simple electrolytes such as sodium chloride are characterized, from the theoretical point of view, by the large fluctuations in charge density which occur in the neighborhood of a given test ion. As a consequence, it is impossible to describe the behavior of such solutions in terms of a time average potential of an ionic atmosphere; the latter simply does not exist. It is the purpose of this paper to present some experimental data on solutions of another type of electrolyte, in which the local charge distribution resembles that in a concentrated solution of a one–one electrolyte, *regardless of the stoichiometric concentration of the salts in question.*

Chain polymers, such as polystyrene, in which some hundreds or thousands of atoms are held by primary valence bonds into single molecules, are quite familiar. Flory[3] has called attention to the fact that locally no dilute solution of a polymer exists, in the sense that a small exploring element of volume will either contain pure solvent or else concentrated polymer solution, depending on whether the element is "far" from a polymer molecule or "near" one. If an electrolyte with a skeleton structure similar to polystyrene is considered, we see that an analogous situation must obtain. If, for example, alkyl halide is added to polyvinylpyridine, we have a macromolecule in which every other carbon atom of a long chain carries a positive pyridonium ion; it is at once realized that these charges in the polycation can diffuse no farther apart than would correspond to maximum extension of the carbon backbone of the molecule, no matter how dilute the solution may be in terms of grams per unit volume. As a consequence of the high positive charge density localized in the polycation, we would expect a relatively large number of anions to accompany the polymeric ion, much as gegen ions accompany a protein molecule or soap micelle—with the important difference, however, that the gegen ions in the present case can diffuse into and through the coil of the poly-

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(1) Project NR 054-002 of the Office of Naval Research.

(2) Presented at the 116th meeting of the American Chemical Society at Atlantic City, September 20, 1949, Symposium on Concentrated Electrolytes and Fused Salts.

(3) P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945).