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Electrolyte–Solvent Interaction. IV. Tetrabutylammonium Bromide in Methanol–Carbon Tetrachloride and Methanol–Heptane Mixtures

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The conductance of tetrabutylammonium bromide in methanol–carbon tetrachloride mixtures (up to 33 mole % CCl_4 where the dielectric constant is 15.31) and in three methanol–*n*-heptane mixtures (up to 5.5 mole % C_7H_{16}, $D = 26.67$) has been measured. Densities, dielectric constants, viscosities and indices of refraction of the solvent mixtures are included. The initial effect of adding another solvent to methanol is to decrease the degree of association of the electrolyte, despite the accompanying decrease in dielectric constant. Eventually association increases when the dielectric constant drops below about 25. The results cannot be accounted for quantitatively in terms of a sphere-in-continuum model for the electrolytic solution.

Introduction

Previous studies of the conductance of quaternary salts[1-3] in mixtures of methanol with other solvents have shown that the properties of the electrolyte in the mixtures cannot be predicted from a knowledge of the properties in the pure components of the solvent mixture. Restated, this means that the bulk dielectric constant and viscosity do not suffice to describe a liquid as far as detailed molecular processes are concerned. The kernel of a cation which we have used frequently is a positively charged nitrogen atom covalently bonded to four butyl groups; the structure is describable as a point charge embedded in a sphere of paraffin. The bromide ion likewise has spherical symmetry; here the charge is uniformly distributed over the peripheral volume. We might therefore optimistically expect[4] that the radii of the corresponding spheres would permit prediction of electrical and hydrodynamic properties, but experience has shown that this approach is at best a rough approximation, reliable only within an order of magnitude in K, the reciprocal association constant. The obviously necessary correction must be allowance for the fact that the solvents are not continuous media; disregard of this feature of real structure appears arithmetically as a variation in the values of radii calculated from K's in various solvents. Our program consists in studying various solvent combinations with the expectation that correlations will eventually be found between the changes in apparent ion size for a given electrolyte and specific properties of the solvent molecules.

In one of the preceding papers[2] of this series, it was reported that initial addition of benzene to methanol caused tetrabutylammonium bromide to act like a stronger (*i.e.*, less associated) electrolyte, despite the attendant decrease in dielectric constant. We decided to investigate the effect of addition of other solvents of low dielectric constant; results for carbon tetrachloride and *n*-heptane are presented in this paper. Their effect is the same as that of benzene. We believe that the effect supports the hypothesis that methanol exists predominantly as a hydrogen bonded polymer which is dissociated by the addition of another liquid.[5] Two mechanisms can be suggested. Release of monomeric methanol would give small molecules with intense dipole fields, which could be attracted and held by anions especially; the effective increase in ion size would then decrease association. Alternatively, the ion size could remain the same, and the decrease in association could be ascribed to an increase in local dielectric constant produced by the presence of free monomeric molecules, which would be expected to concentrate themselves into the regions of high field intensity near the ions. In last analysis, this alternative can be considered a sort of long range solvation, in the sense that the

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* Du Pont Postdoctoral Research Fellow, 1953–1954 at Yale; on academic study leave from the University of Alexandria, Egypt. Grateful acknowledgment is made for a travel grant by the Fulbright Exchange Program.

(1) H. Sadek and R. M. Fuoss, THIS JOURNAL, **72**, 301 (1950); correction, *ibid.*, **72**, 5803 (1950).

(2) R. C. Miller and R. M. Fuoss, *ibid.*, **75**, 3076 (1953).

(3) F. M. Sacks and R. M. Fuoss, *ibid.*, **75**, 5172 (1953).

(4) For a discussion of solvation, see the first paragraph of ref. 3.

(5) R. Mecke, *Discs. Faraday Soc.*, **9**, 161 (1950).

solvent dipoles electrostatically shield the ions and distribute their fields.

Experimental

Materials.—Tetrabutylammonium bromide from laboratory stock was recrystallized from benzene–petroleum ether, and titrated potentiometrically for bromide: found, 24.84, 24.80% Br′; theoretical, 24.79%. Methanol (Baker's absolute analyzed reagent grade) was treated as before by Hartley's method[6]; refluxing for at least 12 hr. over aluminum amalgam gives methanol with solvent conductance κ_0 less than 3×10^{-8}. Carbon tetrachloride (Baker's analyzed reagent grade) was shaken with solid sodium bicarbonate (15 g./l.) for 2 hr. and left standing over calcium chloride for about 18 hr. It was then distilled through an 80-cm. column packed with glass beads; b.p. 75.7° at 758.2 mm. Heptane was distilled from Drierite; b.p. 98° at 754 mm.

Care must be taken in the preparation of mixtures of methanol with other solvents, on account of the exothermic heat of mixing. (Mecke[5] calculates 4.73 kcal./mole as the mean association energy of methanol.) The index of refraction serves as a rapid and convenient control of composition.

Apparatus and Method.—An erlenmeyer type conductance cell was used; its constant was 0.08405 ± 0.00005, as determined by comparison with a cell standardized against Shedlovsky's conductance data[7] for potassium chloride. The bridge has been described previously.[8] All solutions were made up by weight (usually 10–15 mg. salt, weighed on a semi-microbalance, were added to about 50 ml. of solvent in the cell, and then diluted stepwise to approximately 250 ml.). Volume concentrations were calculated using solvent densities. All data were obtained in cells, etc., thermostated to 25.00 ± 0.01°.

Densities of the mixtures of methanol and carbon tetrachloride (or heptane) were determined in a 20-ml. pyknometer. Viscosities were measured in a modified Ubbelohde suspended level viscometer; the average flow time for methanol at 25° was 371.2 sec. Dielectric constants were obtained from capacity measurements at 100 or 200 kilocycles made on a General Radio 716C Bridge equipped with Guard Circuit 716-P4. The value of $D = 32.63$ for the dielectric constant of methanol at 25° was used as the calibrating datum.[9]

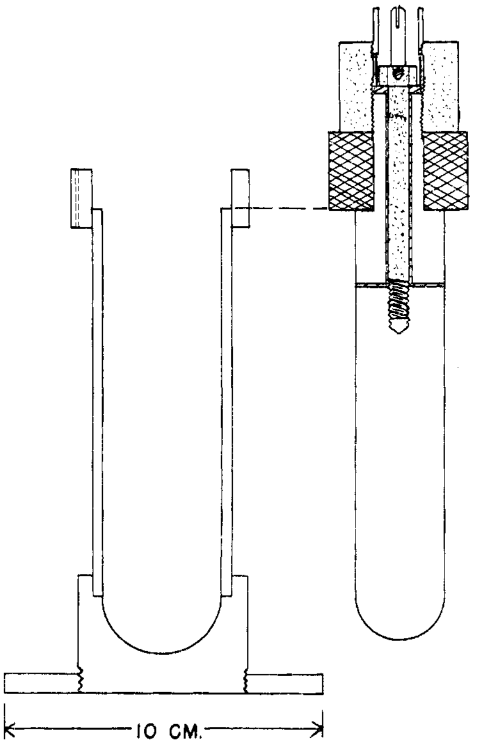

Fig. 1.—Guarded capacitor for dielectric constant measurements.

The dielectric cell, shown in Fig. 1, has an air capacity of 22.78 $\mu\mu$f. The electrodes are brass, polished and heavily gold plated (2 coats, the first one buffed). The test electrode is insulated from the guard electrode by a Teflon sleeve (0.025 in. wall) and Teflon washers at top ($^3/_{32}$ in. thick) and bottom ($^1/_{16}$ in. thick). The guard-test assembly is held together by a stainless steel post with a hexagonal shoulder as shown; the top of the post is threaded to take a standard General Radio 874B inner connector. A Teflon bushing is locked onto the shoulder of the guard electrode by a knurled stainless steel nut; the latter is tapped to take the external connector of the bridge cable. This bushing sets in the annular space at the top of the outer (grounded) electrode and serves to insulate guard from ground and simultaneously to center the guard-test assembly with respect to the grounded container. Rotation of the inner electrodes and/or removal and replacement of the inner electrodes produced a maximum variation of 0.1 $\mu\mu$f. in capacity of the cell when filled with methanol (total capacity 743.2 $\mu\mu$f.). A small groove in the Teflon bushing permitted air to escape. One precaution in using the cell at temperatures above 25° should be mentioned: Teflon has a much larger coefficient of expansion than brass, and therefore no attempt should be made to take a hot cell apart, because the bushing will seize.

Properties of solvents are summarized in Tables I–IV, where w_2 represents weight % carbon tetrachloride, x_2 mole fraction, ρ density, n_D index of refraction for sodium light, 100 η viscosity in centipoises and D dielectric constant.

TABLE I

DENSITIES OF METHANOL–CARBON TETRACHLORIDE MIXTURES

w_2	x_2	ρ	$10^4\,\delta$
0.00	0.0000	0.7864	0.0
4.67	.0101	.8055	−1.8
4.97	.0108	.8068	−2.6
9.06	.0203	.8243	−4.1
10.49	.0238	.8307	−6.8
17.54	.0424	.8626	−1.1
30.16	.0825	.9278	−7.0
41.29	.1278	.9936	−8.0
50.15	.1733	1.0530	−8.3
57.93	.2228	1.1114	−9.4
67.59	.3029	1.1931	−7.1
79.50	.4469	1.3121	−4.8
83.63	.5154	1.3582	+1.0
90.28	.6592	1.4410	3.7
94.97	.7973	1.5057	5.8
100.00	1.0000	1.5839	0.0

TABLE II

VISCOSITIES OF METHANOL-CARBON TETRACHLORIDE MIXTURES

x_2	100 η	x_2	100 η
0.0000	0.5445	0.1790	0.7001
.0108	.5557	.3029	.7746
.0238	.5692	.3600	.8002
.0424	.5856	.4603	.8377
.0589	.6023	.5154	.8498
.0712	.6120	.6592	.8643
.0825	.6255	.7973	.8658
.1269	.6607	1.0000	.9107

Deviations δ from volume additivity were calculated by the equation

$$1/\rho = w_1/100\rho_1 + w_2/100\rho_2 + \delta \qquad (1)$$

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

(7) T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

(8) H. Eisenberg and R. M. Fuoss, THIS JOURNAL, **75**, 2914 (1953).

(9) A. A. Maryott and E. R. Smith, National Bureau of Standards Circular No. 514, p. 1 (1951).

TABLE III

DIELECTRIC CONSTANTS AND REFRACTIVITIES OF METHANOL–CARBON TETRACHLORIDE MIXTURES

x_2	D	n_D	V_{12}	R_{12}	P_{12}
0.0000	32.63	1.3266	40.75	8.24	290.7
.0112	31.88	1.3290	41.36	8.41	288.3
.0265	30.91	1.3340	42.25	8.72	285.4
.0375	30.21	1.3368	42.83	8.90	282.7
.0644	28.43	1.3442	44.36	9.40	275.1
.0917	26.80	1.3520	45.89	9.93	268.0
.1335	24.53	1.3620	48.19	10.69	256.0
.1613	23.02	1.3674	49.76	11.19	248.8
.2023	20.97	1.3756	52.11	11.95	236.8
.2367	19.40	1.3821	54.01	12.57	226.6
.3253	15.52	1.3966	59.08	14.22	196.8
.4527	10.95	1.4145	66.25	16.57	153.3
.6491	5.75	1.4332	77.37	20.12	88.9
1.0000	2.25	1.4572	97.13	26.46	32.9

TABLE IV

PROPERTIES OF METHANOL–HEPTANE MIXTURES

x_2	w_2	ρ	D	$100\ \eta$	$10^6\ \kappa_0$
0.0155	4.69	0.7793	30.83	0.5405	0.212
.0307	9.01	.7730	29.21	.5365	.122
.0551	15.41	.7641	26.67	.5304	.129

Partial molal volumes were also calculated. There is an initial contraction on the addition of carbon tetrachloride to methanol which produces a minimum in δ near $w_2 = 50$, and an initial expansion on the addition of methanol to carbon tetrachloride which leads to a maximum near $w_2 = 95$. Data in the literature[10] were combined with those of Table I to give a deviation plot ($\delta - w_2$) from which interpolated values were taken to compute densities of the mixtures used in the conductance runs.

The viscosity curve is quite complicated (see Fig. 2), but we believe the structure shown is real, because the curve (unpublished observations) for ethanol–carbon tetrachloride shows a similar pattern. The data show a systematic deviation from those of W. J. Jones and co-workers[11]; their value for carbon tetrachloride (0.902) is about 1% lower than ours, while for methanol (0.552), this value is about 1% higher. Our methanol figure (which was the datum used to calibrate the viscometer[12]) agrees much better than this with other literature values: 0.5457,[13] 0.5450[14] and 0.5444.[15] Viscosities for the solvent mixtures used in the conductance determinations were obtained from a large scale plot of the deviation between observed viscosities and a linear mixture formula

$$\eta = 0.5445 + 0.3662\ x_2 + \delta'$$

Dielectric constants are given in Table III, together with indices of refraction and the following derived quantities

$$V_{12} = (x_1M_1 + x_2M_2)/\rho \qquad (2)$$

$$R_{12} = V_{12}(n^2 - 1)/(n^2 + 2) \qquad (3)$$

and

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

Equation 4 may be rearranged to the form

$$D = 1 + 9P_{12}/2V_{12}\ (1 + 1/2D) \qquad (5)$$

For interpolation, we define δD as the difference

$$\delta D = D - D^0 \qquad (6)$$

where

$$D^0 = 1 + 2(x_1P_1{}^0 + x_2P_2{}^0)/9\,V_{12}(1 + 1/2D) \qquad (7)$$

In equation 7, $P_1{}^0$ and $P_2{}^0$ are the molar polarizabilities of methanol and carbon tetrachloride obtained by substituting the appropriate values in equation 4. The value of D in the correction term in the denominator can be interpolated with sufficient accuracy from a plot of D against x_2. A plot of δD against x_2 shows a maximum of +0.13 at $x_2 = 0.075$ and a minimum of −1.82 at $x_2 = 0.65$; as expected, the mixture rule (4) describes the polarization best over the methanol-rich range of concentrations.

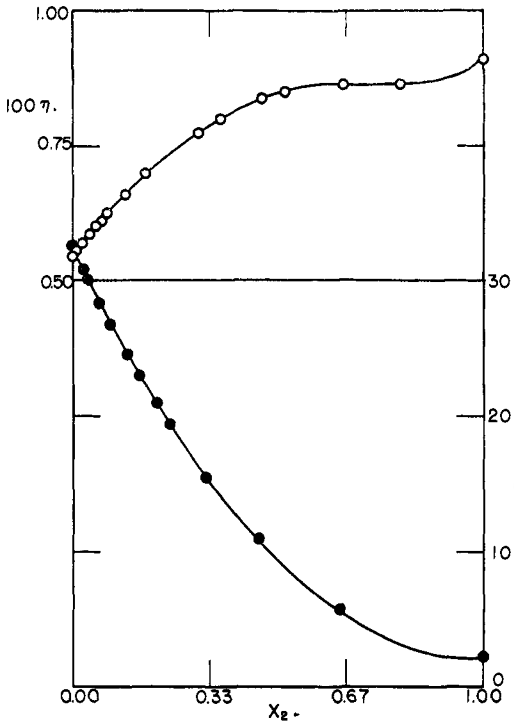

Fig. 2.—Properties of methanol–carbon tetrachloride mixtures: ○, viscosity; ●, dielectric constant.

Measurements were also made in three methanol–n-heptane mixtures, whose properties are summarized in Table IV, where x_2 is mole fraction of hydrocarbon.

Results

Conductance data are summarized in Table V,

TABLE V

CONDUCTANCES OF TETRABUTYLAMMONIUM BROMIDE IN METHANOL–CARBON TETRACHLORIDE AND METHANOL–n-HEPTANE MIXTURES

10^4c	Λ	10^4c	Λ	10^4c	Λ
0.00		45.19		70.83	
1.809	92.86	1.619	71.21	3.189	47.32
2.212	92.54	2.595	70.07	4.487	45.14
3.002	91.94	3.519	69.20	6.031	43.19
4.167	91.10	4.829	68.14	8.674	40.68
6.292	89.97	6.256	67.18	11.789	38.50
18.02		50.78		4.69 H	
2.664	84.27	1.330	69.04	1.613	92.87
3.942	83.35	2.247	67.74	2.353	92.26
5.319	82.49	3.042	66.81	3.734	91.38
7.031	81.61	4.047	65.80	5.784	90.06
9.241	80.64	5.275	64.77	9.01 H	
33.25		57.53		2.627	89.61
2.656	77.18	2.449	62.74	4.139	88.23
3.881	76.10	3.421	61.46	6.217	86.44
5.334	75.09	4.568	60.26	15.41 H	
7.528	73.88	6.011	58.94	0.673	91.59
10.047	72.75	7.742	57.56	1.602	89.77
				2.265	88.98
				3.573	87.65

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(10) G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **68**, 1960 (1946).

(11) W. J. Jones, S. T. Bowden, W. W. Yarnold and W. H. Jones, *J. Phys. Chem.*, **52**, 753 (1948).

(12) W. N. Maclay, Thesis, Yale University, 1950.

(13) J. R. Lewis, THIS JOURNAL, **47**, 626 (1925).

(14) F. K. Ewart and H. R. Raikes, *J. Chem. Soc.*, 1907 (1926).

(15) G. Jones and H. J. Fornwalt, THIS JOURNAL, **60**, 1683 (1938).

where the equivalent conductance Λ is given as a function of concentration c in equivalents per liter. Each group of figures is headed by the corresponding value of w_2, the weight % of the non-polar component. For compactness in presentation, mixtures of methanol with carbon tetrachloride and with n-heptane are included in the table; the heptane data are identified by H following w_2.

Discussion

The data of Table V were extrapolated[16] to zero concentration in order to obtain values of the limiting conductance Λ_0 and of the reciprocal association constant K. These quantities are given in Table VI. In order to eliminate the (first order) effects of variable viscosity from mixture to mixture and to permit focussing attention first on the effect of variable dielectric constant, the conductances of Table V were divided by the appropriate values of Λ_0 and Λ/Λ_0 was then plotted against the square root of concentration in Fig. 3. The limiting tangents are shown at the left. (In order to simplify the diagram, each curve is displaced vertically while the ordinate scale is the same for all except the lowest one, where the scale is halved.) Over the concentration range centering around 4 × 10^{-4} N, the conductance curve for methanol as solvent lies a little below the limiting tangent; this deviation represents a combination of the effects of ion association and of higher terms in the mobility equation. If the entire negative deviation is ascribed to ion association, we find K = 0.069. Addition of carbon tetrachloride (w_2 = 18.02) lowers the dielectric constant to 29.74, and this decrease of 10% should make the limiting tangent steeper and simultaneously increase association, provided the size of the spheres electrostatically equivalent to the ions does not change. But the conductance curve for this system lies nearer to its limiting tangent than does the methanol curve; the formal K calculates to 0.069. Since the dielectric constant is now smaller, the failure of K to decrease can be interpreted as an increase in ion size on addition of carbon tetrachloride. The next addition of carbon tetrachloride (w_2 = 33.25) causes a significant departure of the conductance curve from the limiting tangent in this range of concentration, and the deviation now steadily increases as the content of carbon tetrachloride is increased. The shape of the curves changes in a systematic way as w_2 increases: near w_2 = 0, the curves are parabolic and concave down; as w_2 increases, the curves approach linearity in this range of concentration with an inflection slope significantly higher than the limiting slope. Finally the inflection points move to quite low concentrations while the curve becomes concave-up in our working range.

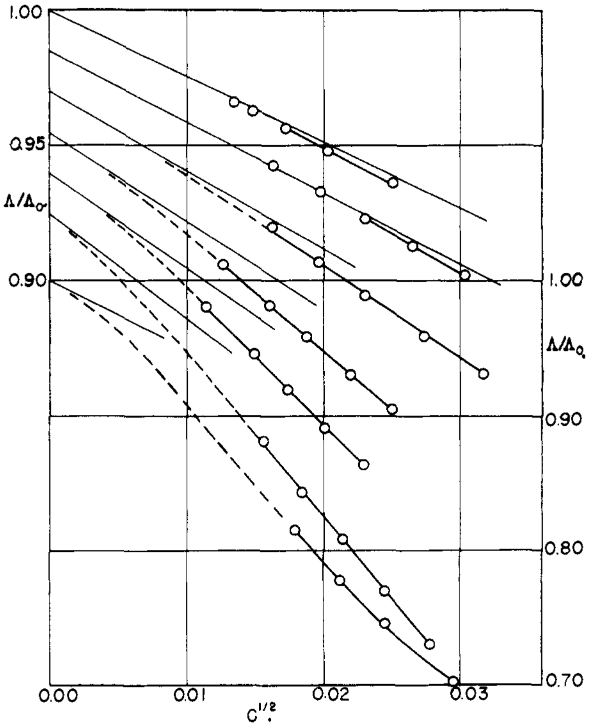

Fig. 3.—Reduced conductance as a function of concentration. Ordinate scale for bottom curve (w_2 = 70.83) to right.

TABLE VI

CONSTANTS DERIVED FROM CONDUCTANCE DATA

$Bu_4NBr-MeOH-CCl_4$

x_2	D	100 η	Λ_0	10^3K	10^8a	$\Lambda_0\eta$
0.0000	32.63	0.5445	96.15	69.4	5.28	0.5236
.0438	29.74	.5895	87.99	69.4	6.63	.5187
.0940	26.72	.6349	81.27	35.2	6.08	.5160
.1466	23.80	.6762	74.90	13.7	4.83	.5064
.1769	22.23	.6973	72.66	9.1	4.57	.5067
.2200	20.13	.7261	68.54	5.85	4.60	.4977
.3311	15.31	.7867	58.14	1.40	4.61	.4574

There is admittedly considerable ambiguity in the interpretation of the deviations from the limiting law in the methanol-rich mixtures, because mobility terms in c and $c \log c$ are evidently of the same order as the negative c terms due to ion association. There is, however, no doubt that the initial addition of carbon tetrachloride brings the curve nearer to the limiting tangent at a given concentration: this could occur if the mobility terms become smaller as D decreases which seems unlikely on general grounds, because DkT to some power is the ubiquitous denominator in the Debye–Hückel theory. The only alternative therefore appears to be a decrease of association on initial addition of carbon tetrachloride. This behavior was also observed when benzene[2] or heptane was added to methanol, as well as when nitrobenzene,[1] nitromethane[2] or methyl ethyl ketone[3] was added.

One significant difference between the behavior with added non-polar solvent as contrasted with that with polar is observed: initial addition of any liquid, polar or non-polar, to the methanol decreased ion association. With further addition of polar solvent, association usually goes through a shallow minimum (for example, nitrobenzene, nitromethane and methyl ethyl ketone). Further addition of non-polar solvent, on the other hand, eventually increases ion association sharply. The striking fact is not the mere increase; qualitatively one expects increased ion association with decrease in dielectric constant. Actually ion association in-

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[16] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); H. M. Daggett, Jr., THIS JOURNAL, **73**, 4977 (1951).

creases faster than one would calculate on the basis of the behavior in the methanol rich systems: in other words, the equivalent electrostatic sphere goes through a maximum as a function of added non-polar solvent, and the value beyond the maximum is considerably smaller than the value computed from the K's in the methanol-rich systems. The three solvents benzene, carbon tetrachloride and heptane are compared in their effect on ion size a in Fig. 4. The decrease with heptane is especially abrupt. Another way of stating the result is that the same electrolyte shows a different dissociation constant in different mixtures which have the same dielectric constant: it is therefore clear that a continuum described by a macroscopic dielectric constant is inadequate to represent these systems electrostatically.

Part of the complications shown in the variation of a with x_2 for a given system may be only apparent, and simply the consequence of the already mentioned ambiguity in the calculation of K for systems which exhibit only a slight degree of association. According to the data for the methanol–carbon tetrachloride system, the value of a is nearly constant beyond $x_2 \approx 0.15$, $K \approx 0.01$. If we use the average value $\mathring{a} = 4.60$ obtained for the range $x_2 > 0.15$ to compute K's for the mixtures for which $x_2 < 0.15$, we obtain the dotted curve shown in Fig. 4. This curve seems intuitively to be preferable to the solid one which is based on the K's calculated from the conductance data, and lends support to our feeling that K values numerically greater than 0.01 have little direct physical meaning when calculated by our present method. For larger values of x_2 than 0.15, K rapidly decreases, and therefore the uncertainty due to the contribution of the unknown mobility terms becomes relatively unimportant. Furthermore, the difference between K as calculated[17] by the Shedlovksy or by the Fuoss–Kraus functions becomes imperceptible. But the significant fact remains unchallenged: in the range of K values where we may place confidence in the numerical values, the equivalent ion size calculated from K for a given electrolyte depends specifically on the molecular structure of the components of the solvent.

The observed mobility likewise conflicts with conclusions based on a viscous continuum as the model for the solvent. The viscosity increases as x_2 increases, but Λ_0 decreases at a more rapid rate, with the consequence that $\Lambda_0\eta$ decreases. Except for the case of nitrobenzene, a decrease of $\Lambda_0\eta$ with added other solvent to methanol has been the general pattern of behavior, regardless of whether viscosity increases or decreases when the solvents are mixed. Individual effects still persist, however; for example, a plot of $\Lambda_0\eta$ against x_2 is concave down for the carbon tetrachloride–methanol mixtures and concave up for benzene–methanol.

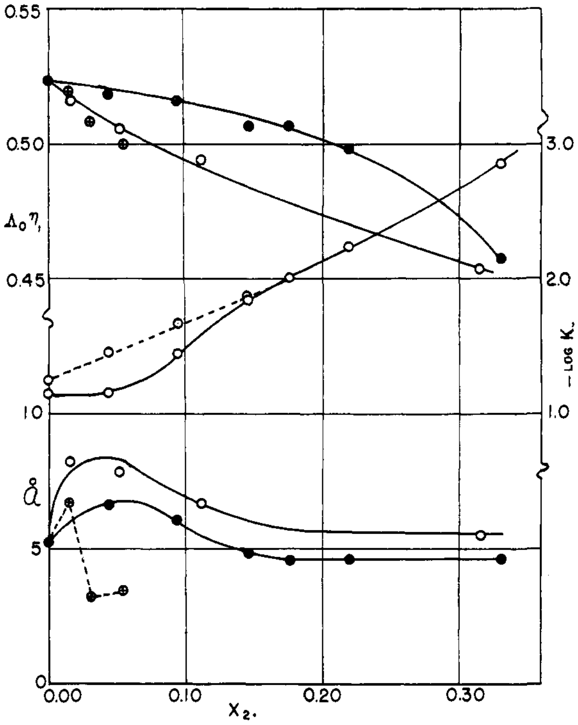

Fig. 4.—Derived properties of Bu_4NBr in mixed solvents: top curves, Walden products for Bu_4NBr in $MeOH–CCl_4$ (solid), $MeOH–C_6H_6$ (open) and $MeOH–C_7H_{16}$ (crossed); middle curves, dissociation constants in $MeOH–CCl_4$; bottom curves, ion size calculated from K (same code as top).

The methanol–carbon tetrachloride system provides an excellent example of the fact that there is no necessary correlation between radii calculated from K by application of Coulomb's law and those calculated from Λ_0 by Stokes hydrodynamics. Disregarding the uncertain range of high K values, we shall consider only the range beyond $x_2 = 0.15$. Here, the electrostatic radius is practically constant, while the $\Lambda_0\eta$ product decreases by approximately 10% as x_2 increases from 0.15 to 0.33. Strictly interpreted, this would mean that the ions in a pair have a constant solvate shell (which may, of course, be zero), while the individual ions in free motion carry a solvate shell of variable average thickness, which depends on the composition of the solvent, both qualitative and quantitative. A more realistic interpretation is to consider the variability of radius as evidence that the model is too highly over-simplified. We must therefore look for additional parameters which will permit inclusion of specific characteristics of the components of the system. To be of any value in an understanding of molecular interaction, these parameters may not be empirical constants (whose use is merely a demonstration of patience) but rather must be physically definable quantities such as dipole moments, electron densities, energies of interaction and the like.

Acknowledgment.—Part of the materials and apparatus used in this work were purchased with funds made available by a contract with the Office of Naval Research.

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[17] R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).