Electrolyte–Solvent Interaction. II. Quaternary Salts in Methanol–Nitromethane and Methanol–Benzene Mixtures

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Conductances at 25° were measured in the following systems: tetrabutylammonium bromide in methanol–nitromethane and in methanol–benzene mixtures, and tetramethylammonium bromide in methanol–benzene mixtures. Both salts are somewhat associated in methanol, but addition of small amounts of nitromethane or benzene reduces association markedly, and decreases the mobility. With more than about 10 mole % nitromethane, the conductance curves approach the Onsager tangent from above, indicating practically complete absence of association. These results show that specific interaction between solute and solvent must occur, because they cannot be explained on the basis of a continuum model. Other workers have concluded that methanol is polymeric and is partially depolymerized by the addition of other solvents. Solvation of anions by monomeric methanol in the mixtures will account for the observed conductance, because the effective ion size (both hydrodynamic and electrostatic) will therefore be greater in the mixtures than in pure methanol.

Introduction

In the approximately isodielectric system methanol–nitrobenzene, the Walden product for tetrabutylammonium bromide increases by about 16% as the mole fraction of nitrobenzene increases from zero to unity. The salt shows some association in both pure solvents, but acts like an unassociated electrolyte in the mixtures.[1] The conventional model (rigid charged spheres in a continuum) of electrolytic solutions is therefore at best a fair hydrodynamic representation and a poor one electrostatically. Our conclusion was that specific interaction between solute and solvent must be considered in any real system, because the properties in the mixed solvent were so different from those in the pure solvents. We present herewith several more examples of similar failures of the model: tetrabutylammonium bromide in methanol–nitromethane and methanol–benzene, and tetramethylammonium bromide in methanol–benzene mixtures. The first system is isodielectric, and its properties resemble those of the methanol–nitrobenzene system. Surprisingly enough, the initial addition of benzene to methanol solutions of electrolytes has qualitatively the same effect as the addition of nitro compounds, despite the profound difference in polarity. This observation suggests an explanation of the phenomena. Methanol is the common component of the various systems. It has been proposed[2] that methanol exists chiefly as a polymer in the pure solvent, and that addition of other liquids causes it to depolymerize partially. If we assume that monomeric methanol is much more effective in solvating ions than is the polymer, then the lower mobility and decreased association of electrolytes in mixtures of methanol with other solvents relative to the values in methanol can easily be accounted for. We assume that the sphere equivalent to the ion is larger in the mixtures; that is, we retain the conventional model, and allow for the interaction with solvent by making the radius in general dependent on solvent composition. In some systems, such as water–dioxane,[3] this dependence is negligible, while in others, such as those described in this paper, the dependence is marked.

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

(2) R. Mecke, *Discussions Faraday Soc.*, **9**, 161 (1950).

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

Experimental

Materials.—Tetrabutylammonium bromide was from the supply prepared by Sadek.[1] Tetramethylammonium bromide was prepared by bubbling methyl bromide into a 10% solution of trimethylamine in a 2:1 ethanol–methanol mixture. The crude salt which separated was recrystallized once from a 1:1 ethanol–methanol mixture. Methanol was purified by the procedure of Hartley and Raikes[4]; the specific conductance was of the order of 10⁻⁷. Nitromethane was distilled twice from phosphorus pentoxide, the middle fraction being retained for use. The latter was water-white and had a specific conductance of the order of 10⁻⁷. The conductance of this solvent increases on standing; in order to avoid uncertainties from this source, conductance runs were always completed within 8 hr. of the second distillation. Benzene was dried over calcium hydride.[5]

Apparatus and Method.—The conductance cell was similar to Sadek's; the constant was found to be 0.05288 by comparison with a cell which was calibrated using precise data[6] for potassium chloride solutions. Adsorption errors were minimized by leaving the electrodes bright. Salt was weighed into mixed solvent in a weight buret; successive portions of the solution were then added to the same mixed solvent in the conductance cell, after first determining the solvent conductance. All measurements were made at 25.00 ± 0.02°. The bridge has been described elsewhere[7,8]; measurements were made at several audiofrequencies in order to eliminate polarization errors.

Properties of Solvents.—Densities of the methanol–nitromethane mixtures were determined in 20-ml. pycnometers at 25.00°. Since all our salt concentrations were small, densities of the solvents were used in computing normalities c from the observed weight concentrations. For the methanol–benzene mixtures, densities were interpolated from literature values.[9] Viscosities were measured in an Ostwald viscometer, using $\eta = 0.005460$ as the calibrating datum for methanol at 25°. Dielectric constants of the methanol–nitromethane mixtures were determined in a cell with platinum electrodes, using a General Radio Type 716C bridge at 200 kc. The value $D = 32.63$ for methanol at 25° was used as the calibrating datum[10]; the data were smoothed by interpolation on a deviation plot of δ against mole fraction, where $\delta = D$ (ideal) $- D$ (obs.) and D (ideal) $= (x_1 V_1^0 D_1 + x_2 V_2^0 D_2)/V_{12}$. A plot of dielectric constant against mole fraction for the methanol–nitromethane mixtures is monotone, and does not exhibit a minimum near pure methanol as did the nitrobenzene mixtures,[1] because the molar volume of nitromethane is much smaller than that of nitrobenzene. For the methanol–benzene

(4) H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

(5) A. S. Brown, P. M. Levin and E. W. Abrahamson, *J. Chem. Phys.*, **19**, 1226 (1951).

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

(7) T. Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

(8) D. Edelson and R. M. Fuoss, *J. Chem. Ed.*, **27**, 610 (1950).

(9) G. Scatchard, S. E. Wood and J. M. Mochel, THIS JOURNAL, **68**, 1957 (1946).

(10) A. A. Maryott and E. R. Smith, *Natl. Bur. Standards Circular*, **514**, 5 (1951).

mixtures, literature values[11] were used; a slight correction was made to make the value for methanol consistent with the Bureau of Standards recommendation for this solvent.

The properties of the solvents are summarized in Table I where w_2 is weight % nitromethane (or benzene), x_2 is the corresponding mole %, ρ is the density, η is the viscosity, D is the dielectric constant and κ_0 is the solvent conductance. The code numbers in the first column will be used to identify the mixtures.

TABLE I

PROPERTIES OF MIXED SOLVENTS AT 25°

No.	w_2	x_2	ρ	$100\,\eta$	D	$10^6\,\kappa_0$
		Methanol–Nitromethane				
1	0.00	0.00	0.7865	0.5460	32.63	0.131
2	1.85	0.98	.7920	.5437	32.66	0.174
3	3.93	2.10	.7965	.5412	32.70	0.288
4	29.63	18.10	.8664	.5111	33.06	1.043
5	57.38	41.41	.9546	.4974	33.42	1.773
6	81.70	70.09	1.0437	.5218	34.01	0.703
7	100.00	100.00	1.1251	.6275	35.94	0.080
		Methanol–Benzene				
8	1.09	0.49	0.7874	0.5466	32.05	0.097
9	3.99	1.68	.7897	.5482	31.40	.146
10	7.33	3.15	.7924	.5506	30.18	.127
11	11.20	5.22	.7961	.5536	29.02	.235
12	22.33	10.55	.8047	.5606	25.88	.114
13	23.52	11.20	.8057	.5613	25.50	.177
14	52.96	31.59	.8306	.5758	15.70	.087

Results

Conductance data for the various systems studied are summarized in Table II, where the equivalent conductance Λ is given as a function of concentration c in equivalents per liter. Composition of solvent is given by reference to the first column of Table I; salt is indicated by a suffix, so that "4-Bu" indicates, for example, data for tetrabutylammonium bromide in solvent mixture No. 4. For completeness, we have included several of Hartley's data[12] for Me$_4$NBr in methanol under the heading 1-Me.

Discussion

The conductance curves divide themselves into two distinct categories: concave-down and concave-up, with respect to the limiting tangent in the range of concentrations where approach to this tangent is theoretically meaningful. The former corresponds to strong electrolytes in which ion association occurs, and the latter to electrolytes exhibiting negligible (or more precisely, undetectable) association. This criterion will serve as the basis for a qualitative discussion of the results, which is presented as introduction to the consideration of numerical values. In methanol, Bu$_4$NBr gives a concave-down curve (Fig. 1, in order to prevent confusion due to crossing, the Λ-$c^{1/2}$ curves are displaced 10 Λ-units vertically from each other). Addition of a little nitromethane brings the curve much nearer the limiting tangent, and from about 10 mole % nitromethane, the curves are concave-up, the maximum positive departure from the tangent being at around 15–20%. Toward the

(11) J. H. LaRochelle and A. A. Vernon, THIS JOURNAL, **72**, 3293 (1950).

(12) T. H. Mead, O. L. Hughes and H. Hartley, *J. Chem. Soc.*, **125**, 1207 (1923).

TABLE II

CONDUCTANCES OF TETRABUTYL- AND TETRAMETHYLAMMONIUM BROMIDES IN METHANOL–NITROMETHANE AND METHANOL–BENZENE MIXTURES

$10^4\,c$	Λ	$10^4\,c$	Λ	$10^4\,c$	Λ
1-Bu		6-Bu		14-Bu	
1.818	93.36	1.803	97.79	0.399	75.10
2.118	93.03	3.746	96.11	0.754	73.28
2.675	92.62	6.248	95.85	1.751	69.80
3.218	92.22	11.104	94.02	3.166	67.26
5.887	90.60	16.128	93.03	5.608	62.77
7.003	90.02	7-Bu		8-Me	
2-Bu		1.920	84.06	0.554	121.37
2.481	92.36	4.505	82.70	1.063	120.12
4.602	91.04	8.833	81.09	2.070	118.90
8.332	89.17	13.354	79.90	3.992	117.35
13.404	87.48	9-Bu		7.545	115.00
3-Bu		2.239	90.46	10-Me	
2.767	93.10	4.544	89.06	1.573	117.43
5.056	91.62	9.081	86.99	2.503	115.94
9.021	89.98	11-Bu		4.814	113.56
13.377	88.38	1.148	88.40	9.795	109.38
4-Bu		2.423	87.38	12-Me	
0.855	98.91	4.982	85.64	0.487	112.80
1.929	98.38	8.346	84.07	1.006	110.51
4.199	97.24	11.953	82.64	2.076	108.24
5.834	96.67	13-Bu		4.061	105.97
8.770	95.47	0.941	85.14	6.910	103.14
5-Bu		1.944	83.97	1-Me	
1.529	101.19	4.187	82.07	1.008	122.38
2.963	100.05	7.366	79.90	1.884	121.22
5.894	98.65	11.008	78.02	3.779	119.27
9.500	97.47			7.754	116.16

nitromethane end of the scale, the curves again approach nearer to the limiting tangent; in pure nitromethane, the points lie on the tangent over our working range of concentration. These results show that Bu$_4$NBr is somewhat associated in
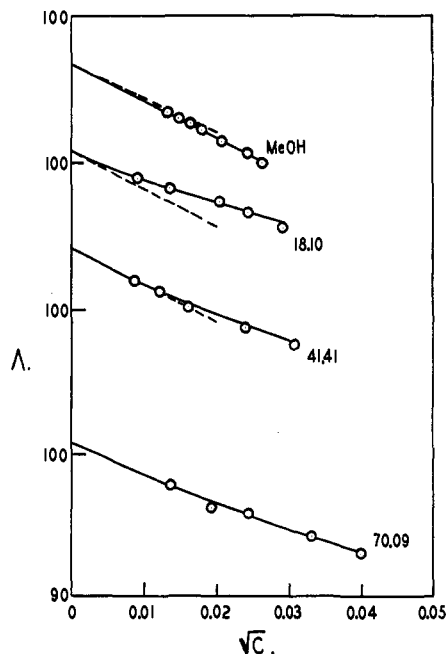

Fig. 1.—Conductance of Bu$_4$NBr in methanol–nitromethane mixtures. (Curves displaced 10 units vertically).

methanol, and that addition of nitromethane prevents and eventually eliminates association, giving in fact conductance curves which resemble those of many salts in water, despite the fact that the dielectric constant has increased by only 10%. A still more striking result is obtained by the addition of benzene to solutions of Bu$_4$NBr in methanol: *lowering* the dielectric constant of as olvent initially *decreases* association: at 1.7 mole % benzene, association is barely detectable (Fig. 2) and only at about 5.2% has the decrease in dielectric constant succeeded in restoring the extent of association found in pure methanol. The effect of benzene on
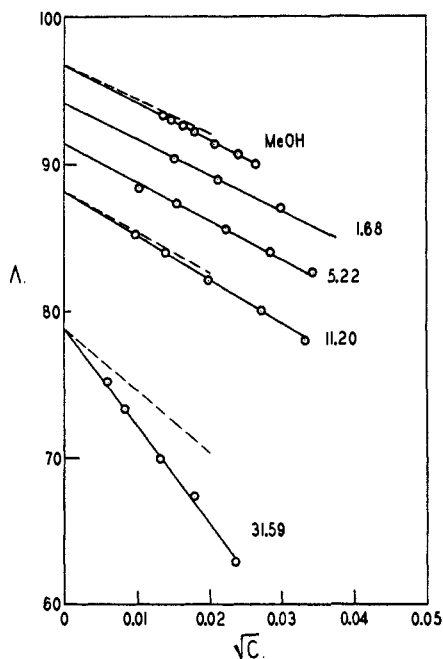

Fig. 2.—Conductance of Bu$_4$NBr in methanol–benzene mixtures.

ion association in methanol is also shown convincingly by the curves (Fig. 3) for Me$_4$NBr: addition of only 0.5% benzene cuts association to about one half and brings the curve nearly into coincidence
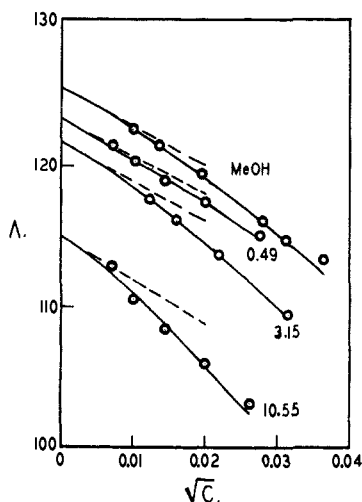

Fig. 3.—Conductance of Me$_4$NBr in methanol–benzene mixtures.

with the limiting tangent. All of these facts may be summarized by saying that addition of nitromethane (nitrobenzene[1]) or benzene to methanol solutions of quaternary salts increases the size of the sphere which is electrostatically equivalent to one or both of the ions, relative to the size of the sphere which is characteristic in methanol. In other words, specific interaction between solute and solvent must occur and the sphere-continuum model for the solute–solvent system is, in these cases at least, inadequate to account for experimental results.

The curves which approach the limiting tangent from above can be reproduced by the function[6]

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)c^{1/2} + Bc \log c + Dc$$

where α and β are the Onsager coefficients and B and D are semi-theoretical constants,[13,14] which can best be determined[15] from the data. For systems 4, 5 and 6, the constants B and D have, respectively, the values -4810 and $-12,000$, 950 and 3960, and 780 and 3170. The negative values for system 4 are unusual; the other pairs have the same sign and magnitude as is found in aqueous solutions.

If the $c \log c$ term is missing, a concave-down Λ-$c^{1/2}$ curve results; the equation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)c^{1/2} - \Lambda_0 c/K$$

has been used[13] to estimate K when the degree of association is small. But since we have sound theoretical reasons to expect a $c \log c$ term to be present, it is obviously hazardous to place too much reliance on numerical values of K calculated from curves which lie just under the limiting tangent. It is entirely possible that there may be some ion association in electrolytes which give concave-up curves, but the then large $c \log c$ term masks the linear term, only part of which can be due to association ("only part," because if the $c \log c$ term is visible, linear terms from the same source must also be and they usually have the opposite sign from the linear association term). Conversely, when association begins to appear (for example, with decreasing dielectric constant) as a down-concavity, we must grant that part of the observed linear term is compensated by the c and $c \log c$ terms from mobility and the K-value computed from the linear term is therefore too large.

With this caution in mind, we next consider the reciprocal association constants K for the various systems measured. They were obtained, for the concave-down curves, by Shedlovsky's extrapolation method[16] and are summarized in Table III. The value of 0.055 for Bu$_4$NBr in methanol agrees fairly well with Sadek's value of 0.038. There is a sharp rise in K on the initial addition of nitromethane, and regardless of numerical values, there can be no doubt that association is much diminished. As mentioned above, beyond about 10% nitromethane, association is negligible. The methanol–benzene systems permit a more careful analysis, because association is more pronounced, although again the initial addition of the foreign

(13) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

(14) R. M. Fuoss, *ibid.*, **35**, 59 (1935).

(15) E. G. Baker and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **37**, 726 (1951).

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

solvent markedly decreases association. If we plot log K against x_2, the mole % of benzene, it actually appears (cf. Fig. 6) as if there is a discontinuity at the limit $x_2 = 0$. A somewhat paradoxical situation arises if we consider methanol with a trace of benzene in it: as salt concentration is decreased, there will be a range of concentration where the (salt/benzene) ratio decreases through unity. In this range, K will depend on salt concentration, because the salt will change from the higher to the lower associated type and its conductance curve could conceivably cross the limiting tangent. The change in salt type is very nicely shown if we calculate effective electrostatic radii a from the K-values of Bu$_4$NBr in the methanol–benzene mixtures by the method of Fuoss and Kraus.[3] In methanol $a = 4.7 \times 10^{-8}$ cm.; at 1.7% benzene, it jumps to 8.2×10^{-8} and then slowly decreases again on further addition of benzene. Similarly, Me$_4$NBr has $a = 3.2 \times 10^{-8}$ in methanol, and with 0.5% benzene in the methanol, a has increased to 5.2×10^{-8}.

TABLE III

CONSTANTS DERIVED FROM CONDUCTANCE DATA

No.	Λ_0	K	$10^8 a$	$\Lambda_0 \eta$
Bu$_4$NBr–MeOH–MeNO$_2$				
1	96.7	0.055	4.70	0.528
2	96.2	.11	6.41	.523
3	96.9	.16	7.08	.524
4	100.6	∞	..	.514
5	104.2	∞	..	.518
6	101.0	∞	..	.527
7	86.8	∞	..	.545
Bu$_4$NBr–MeOH–C$_6$H$_6$				
9	94.1	0.31	8.22	0.516
11	91.3	.11	7.87	.506
13	88.1	.032	6.68	.494
14	78.6	.0024	5.45	.453
Me$_4$NBr–MeOH–C$_6$H$_6$				
1	125.3	0.031	3.24	0.684
8	123.2	.063	5.22	.674
10	121.7	.017	2.88	.670
12	114.9	.010	3.18	.644

The hydrodynamic properties likewise vary with solvent composition. If the sphere-continuum model were applicable here, then the Walden product $\Lambda_0 \eta$ would be a constant. As shown in Fig. 4,
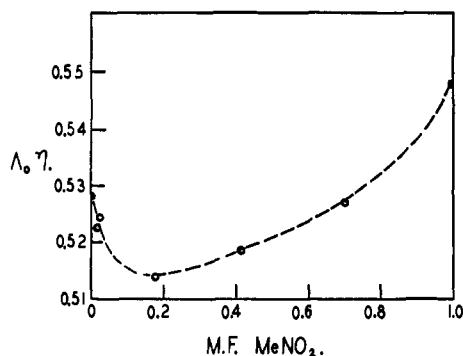

Fig. 4.—Walden product $\Lambda_0 \eta$ for Bu$_4$NBr in methanol–nitromethane mixtures.

the product for Bu$_4$NBr in methanol–nitromethane goes through a minimum at a somewhat lower mole fraction of nitromethane than where the viscosity of the mixture (cf. Fig. 5) has its minimum.
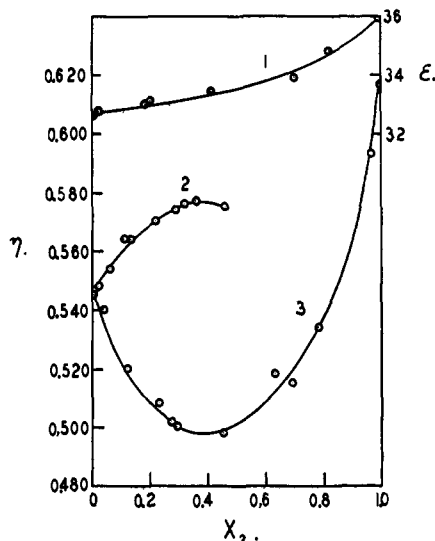

Fig. 5.—Properties of mixed solvents: curve 1, dielectric constants of methanol–nitromethane; curve 2, viscosity of methanol–benzene; curve 3, viscosity of methanol–nitromethane.

The change is considerably less than the change in viscosity, i.e., there is a rough approximation to Stokes hydrodynamics, but the ions move somewhat faster than they should in nitromethane relative to their speed in methanol, although the initial ef-
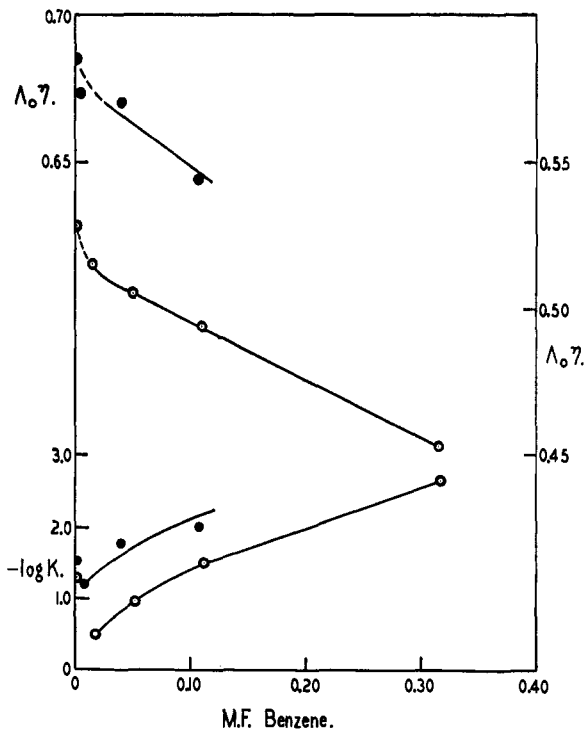

Fig. 6.—Properties in methanol–benzene mixtures: Walden products: Me$_4$NBr, top; ● Bu$_4$BNr, O top. Reciprocal association constants; Me$_4$NBr, ● bottom, Bu$_4$NBr, O bottom.

fect of adding nitromethane is to decrease relative mobility. In nitrobenzene,[1] Bu$_4$NBr also has a high conductance relative to the methanol value; in this solvent pair, however, addition of a little nitrobenzene to methanol did not cause a drop of mobility although it did produce an increase in K. In the benzene mixtures, the opposite effect on solvent viscosity appears: addition of benzene *raises* the viscosity of methanol; nevertheless, both the mobilities of Bu$_4$NBr and Me$_4$NBr are *decreased* relative to their values in methanol more than corresponds to the increase in hydrodynamic friction as measured by the macroscopic viscosity. The fact that both Me$_4$NBr and Bu$_4$NBr are changed in a parallel fashion (see Fig. 6) suggests that the anion is different in methanol and in mixtures of methanol with other solvents. We have just seen that the association phenomena could be interpreted as an increase in the electrostatic radius of the ions as nitromethane or benzene is added to methanol; this behavior is paralleled by the hydrodynamic model, in that the kinetic units appear to be larger in the mixtures.

The behavior of the electrolyte in pure nitromethane and in pure nitrobenzene, however, cannot be predicted from a knowledge of the properties in methanol and in mixtures of these solvents with methanol. This statement is based on the facts that the ratios $\Lambda_0\eta(C_6H_5NO_2)/\Lambda_0\eta$ (CH$_3$OH) = 1.16 and $\Lambda_0\eta$ (CH$_3$NO$_2$)/$\Lambda_0\eta$ (CH$_3$OH) = 1.03, while the values of K are K(MeOH) = 0.04, $K\cdot$(C$_6$H$_5$NO$_2$) = 0.02 and K(CH$_3$NO$_2$) = ∞. That is, the ions move relatively more rapidly in the nitro compounds, while the association is greater in one and less in the other than in methanol. These results flatly contradict the usual pairing of high Λ_0 with small K, and *vice versa*.

A given solute is thus seen to behave like two or three different substances, depending on whether it is in solvent A, solvent B, or a mixture of the two. This seeming absurdity can only be accounted for by postulating that the actual solute particles are different in the three cases; this can only occur if there is specific interaction between solute and solvent. When methanol is one of the components of the mixture, some speculation can be made regarding the mechanism. Methanol–nitromethane mixtures show very large deviations from ideal

behavior, as demonstrated by vapor pressure measurements.[17] Methanol–benzene mixtures show similar deviations[9]; it was in fact for this reason that we decided to investigate benzene–methanol mixtures. The viscosity–composition curves of Fig. 5 also show that there is strong interaction between methanol and the added solvents. Mecke[2] has summarized a considerable body of experimental evidence which suggests that in pure methanol the molecules are associated into polymers, and that the addition of certain other liquids causes partial dissociation into monomeric methanol. We are indebted to Dr. P. L. Lyons of this Laboratory for a measurement of the Raman spectrum of methanol–nitromethane mixtures; he found that the band associated with free OH-groups appeared when nitromethane was added to methanol. We would expect monomeric methanol to be a more efficient solvating agent for anions than the polymer, because the OH-dipole fields are shielded in the latter. The fact that both nitromethane and benzene, despite their complete polar dissimilarity, produce the same effect on the association of electrolyte dissolved in their mixtures with methanol supports the idea that monomeric methanol is the active component as far as interaction with electrolytic solute is concerned. All of our results can be accounted for on the basis of this hypothesis. If addition of nitromethane or benzene to methanol releases monomeric methanol, which in turn solvates the electrolyte, the effective size of the ions is increased, and consequently they should move more slowly in a given field, and should be less associated at a given concentration in the mixed solvent than in pure methanol. Likewise, addition of a little methanol to nitromethane should give a solvent containing mostly methanol monomer, and we indeed observe a decrease of mobility and of association. Tetrabutylammonium bromide thus shows three distinct patterns of behavior, one in pure methanol, another in methanol–nitromethane mixtures, and still another in pure nitromethane.

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(17) N. I. Joukovsky. *Bull. soc. chim. Belg.*, **43**, 397 (1934).