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Electrolyte-Solvent Interaction. V. Tetrabutylammonium Bromide in Ethanol-Carbon Tetrachloride Mixtures

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The conductance of tetrabutylammonium bromide in ethanol-carbon tetrachloride mixtures (up to 15.3 mole % CCl_4 , where the dielectric constant $D = 19.7$) has been measured. Densities, viscosities, dielectric constants and indices of refraction of the solvent mixtures are also reported. Addition of carbon tetrachloride to ethanol increases ion association sharply; the effect is greater than corresponds to the change in dielectric constant if calculation is based on the sphere-in-continuum model. This behavior is the opposite of that found in methanol-carbon tetrachloride mixtures. A slow reaction between ethanol and carbon tetrachloride, which produced hydrogen chloride and carbon monoxide (and possibly other compounds), was observed.

Introduction

In our previous investigations² of the behavior of electrolytes in solvent mixtures, methanol has usually been one of the components. Two tentative generalizations have been made: initial addition of another liquid (polar or non-polar) to methanol decreases the extent of ion association compared to that in pure methanol, and decreases the Walden product. In terms of the sphere-in-continuum model, these results can be restated by saying that the radius of the average sphere equivalent either electrostatically or hydrodynamically to the ions is increased when other liquids are added to methanol.

In order to learn whether this behavior was a general characteristic of solvents containing alcohols, we decided to investigate ethanol-carbon tetrachloride as a mixed solvent system, using tetrabutylammonium bromide as the reference electrolyte. Ethanol appeared also to offer an advantage over methanol for further work: due to its lower dielectric constant, ion pair equilibrium constants would be smaller, and therefore susceptible of more reliable determination. This hope proved illusory, however, because an unexpected reaction between ethanol and carbon tetrachloride produced conducting impurities whose presence precluded work at concentrations below $2 \times 10^{-4} N$. Measurements were made in mixtures containing up to nearly 40% carbon tetrachloride by weight (mole fraction = 0.1534). These were sufficient to show that the properties of the ethanol-carbon tetrachloride system were quite different from those of the corresponding methanol systems, as we shall point out in the discussion. It is therefore not even safe to use the sphere-in-continuum model to generalize within a class of solvents since methanol and ethanol exhibit properties as electrolyte solvents which differ more than can be accounted for on the basis of dielectric constant and viscosity. It is becoming increasingly more certain that R. H. Fowler's description³ of the ion size as an *omnium gatherum* was most apt.

Experimental

Absolute ethanol was distilled from aluminum amalgam⁴

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(2) H. Sadek and R. M. Fuoss, *THIS JOURNAL*, **76**, 5897 (1954) and other papers cited there.

(3) R. H. Fowler, "Statistical Mechanics," Cambridge University Press, 1929, p. 322.

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

and then redistilled from freshly ignited calcium oxide. Its conductance varied from 0.7 to 3.0×10^{-8} . Carbon tetrachloride was shaken with sodium bicarbonate and then distilled. One lot was distilled from calcium chloride, and one from activated aluminum oxide. The conductance was too small to permit measurement.

Mixtures of carbon tetrachloride with ethanol showed a considerably higher conductance than either of the starting liquids; furthermore, this conductance increased on standing, and with the concentration of carbon tetrachloride. For example, a mixture containing 29.15% of the first batch of carbon tetrachloride had an initial conductance of only 7×10^{-8} ; on standing 228 hr., the conductance rose to 2.06×10^{-6} . A similar mixture prepared with the second batch increased in conductance from 4.5×10^{-8} to 1.20×10^{-6} in 231 hr. The rate of increase in conductance was apparent zero order: a plot of $\log(\kappa - \kappa_0)$ against the logarithm of time was linear for both of the above mixtures, with a slope approximately unity. (Here, κ is conductance at time t and κ_0 is initial conductance at time zero.) Assuming that ethanol and carbon tetrachloride react to produce an electrolyte, presumably hydrogen chloride, the amount of reagents consumed is so small that the zero order is easy to understand: the final conductance corresponds to an electrolyte concentration of the order of only $10^{-4} N$. The actual reaction probably is rather complicated, and time did not permit a detailed study of the problem. A small bubble of gas slowly collected in the electrode compartment, which suggests that phosgene might have been an intermediate; it could decompose into carbon monoxide and chlorine. One mixture of ethanol and carbon tetrachloride was exposed in a special Pyrex vessel to the radiation from an H4 mercury vapor lamp for several days. The vessel was designed so that the gas which formed could be collected; after removing ethanol and carbon tetrachloride by chilling a side arm of the gas chamber in liquid nitrogen, the residual gas was examined in the mass spectrometer. It gave a strong peak at mass 28, a result which supports the suggestion that carbon monoxide is one of the end products. (There was a slight leakage of air, as shown by a small peak at 32, but the peak at 28 was at least six times higher than that due to nitrogen from air in amount estimated from the oxygen peak. Ethanol also gives a peak at 28, but again comparison with other ethanol peaks ruled it out as a source of the strong peak at 28. We are indebted to Dr. J. H. Wang for the spectrometer observations.) The system undoubtedly merits further investigation. Incidentally, there is a marked contrast in the behavior of methanol and ethanol with carbon tetrachloride; the methanol mixture increases only a few per cent. in conductance on standing several hours while the ethanol mixture better than doubles its conductance in the same time.

The following properties of the ethanol-carbon tetrachloride mixtures were measured at 25.00°: density ρ , dielectric constant D , index of refraction n_D and viscosity η . These measurements are summarized in Table I where w_2 is weight % of carbon tetrachloride and x_2 is its mole fraction. Figure 1 shows the dependence of dielectric constant and viscosity on mole fraction of carbon tetrachloride. Methanol has a viscosity of less than half that of ethanol, so the viscosity curve for MeOH- CCl_4 mixtures rises as x_2 increases, while that for EtOH- CCl_4 falls. The structure of the curves is nevertheless quite similar: near $x_2 = 0$, both curves are concave-down (with a maximum in the EtOH- CCl_4 system) and near $x_2 = 1$, both curves are concave-up (with a minimum in the MeOH- CCl_4 system).

TABLE I
PROPERTIES OF ETHANOL-CARBON TETRACHLORIDE MIXTURES

w_2	x_2	ρ	D	n_D	100 η
0.00	0.0000	0.7859	24.91	1.3594	1.1036
17.59	.0601	.8632	22.69	1.3688	1.1064
27.57	.1023	.9136	21.20	1.3745	1.0994
37.03	.1498	.9675	19.67	1.3815	1.1002
46.82	.2086	1.0300	17.80	1.3886	1.0832
59.81	.3082	1.1266	14.60	1.4012	1.0527
69.27	.4030	1.2082	11.76	1.4109	1.0208
79.17	.5323	1.3076	8.12	1.4231	0.9626
88.91	.7060	1.4228	4.45	1.4369	.9030
96.77	.8998	1.53228833
100.00	1.0000	1.5839	2.25	1.4572	.9107

Deviation functions similar to those used in previous papers of this series were used to interpolate for the constants of the mixtures used in the conductance experiments. The volume deviation $\delta = 1/\rho - w_1/\rho_1 - w_2/\rho_2$ of methanol and ethanol mixtures with carbon tetrachloride is shown at the top of Fig. 1. Like the viscosity curve, the volume curve exhibits a quite complicated structure: on initial addition of carbon tetrachloride to either alcohol, contraction occurs, while initial addition of alcohol to carbon tetrachloride produces expansion.

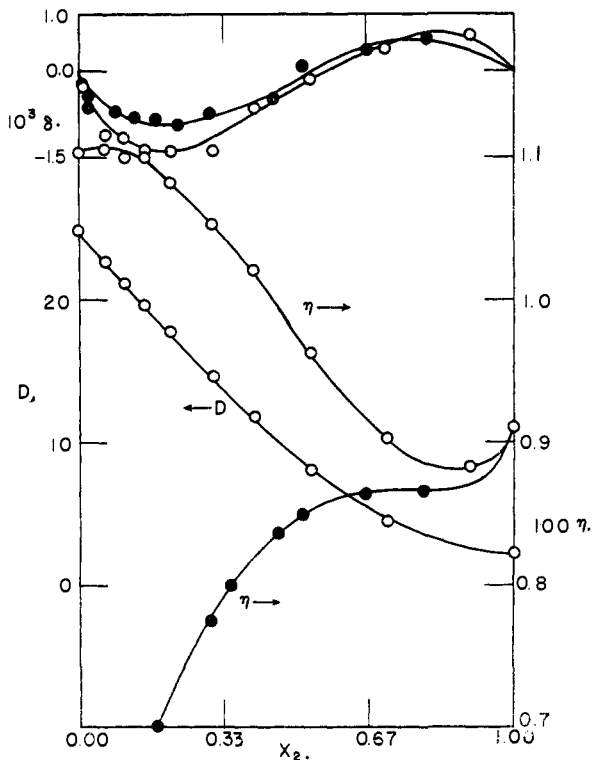


Fig. 1.—Properties of solvent mixtures: O, EtOH- CCl_4 ; ●, MeOH- CCl_4 .

Tetrabutylammonium bromide was from laboratory stock. Solutions were made up by weight. All runs were made by the concentration method, so that conductances of the most dilute solutions of electrolyte were measured immediately after determination of the solvent conductance. We hope in this way to have minimized the uncertainty due to the changing solvent conductance which was described above. Cells, bridge and other equipment were the same as those used in the work on the methanol-carbon tetrachloride system.² Table II summarizes the conductance data: equivalent conductance Λ is given as a function of concentration c in equivalents per liter at 25°. The various systems are identified by the value of w_2 above each set of data.

TABLE II
CONDUCTANCE OF TETRABUTYLAMMONIUM BROMIDE IN ETHANOL-CARBON TETRACHLORIDE MIXTURES AT 25°

$10^4 c$	Λ	$10^4 c$	Λ
0.00		15.21	
2.216	40.50	2.908	38.68
3.164	39.91	4.066	37.64
4.336	39.27	5.791	36.55
6.454	38.24	7.726	35.66
9.685	37.01	17.906	31.80
4.55		19.36	
2.803	39.75	4.547	35.82
3.818	39.07	6.626	35.01
5.503	38.12	9.516	33.82
7.548	37.24	13.780	32.39
17.901	33.85	24.38	
10.45		2.613	38.64
2.382	40.25	3.593	36.90
3.242	39.47	5.211	35.39
4.618	38.47	7.342	34.11
6.144	37.68	18.083	29.80
17.901	32.80	37.69	
		3.978	36.68
		5.679	33.28
		7.914	31.27
		18.050	25.10

Discussion

The system ethanol-carbon tetrachloride, superficially at least, appears to be simpler than the system methanol-carbon tetrachloride. Figure 2 is a plot of Λ/Λ_0 against $c^{1/2}$; values of the limiting conductances Λ_0 were obtained by extrapolation⁵

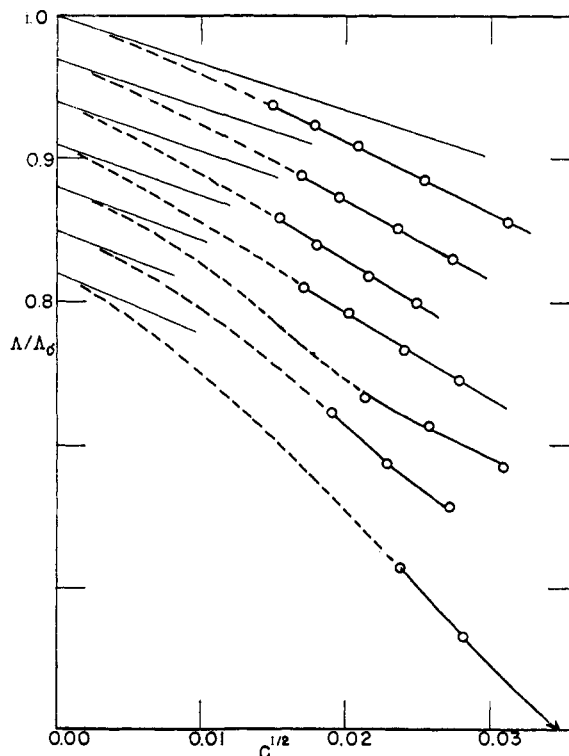


Fig. 2.—Reduced conductance curves in EtOH- CCl_4 mixtures; sequence same as in Table II with ethanol at top.

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

of the data of Table II. As a result of the lower dielectric constants of the ethanol mixtures, association is more pronounced than in the mixtures of methanol with carbon tetrachloride, and consequently the values of K given in Table III are more reliable. The uncertainty due to the effects of neglected linear and $c \log c$ terms in the mobility equation is much reduced, and the effect of choice⁶ of extrapolation function is likewise decreased; α^2/Λ_0^2 is 11% of K^{-1} in ethanol and only 2.6% in the mixture with $x_2 = 0.1534$. As the dielectric constant of the solvent mixture decreases, association increases, as shown in Fig. 2 by the steadily increasing steepness of the curves. The approach to the limiting tangent lies far below our working range of concentrations.

TABLE III

CONSTANTS DERIVED FROM CONDUCTANCE DATA						
x_2	D	100η	Δ_0	$\Delta_{0\eta}$	10^3K	\bar{a}
0.0000	24.91	1.104	43.22	0.477	10.05	3.54
.0141	24.40	1.108	43.29	.480	6.44	3.01
.0337	23.68	1.110	43.80	.486	5.17	2.98
.0510	23.05	1.110	42.64	.473	5.06	3.11
.0671	22.50	1.109	42.02	.467	4.18	3.08
.0880	21.77	1.107	42.28	.468	3.39	3.08
.1534	19.70	1.096	41.9	.460	1.46	2.93

If we assume that the ions may be represented as spheres, radii can be computed⁷ from the values of K . The values obtained for the six mixtures investigated are reasonably constant ($2.93 \leq \bar{a} \leq 3.11$) and show no trend with dielectric constant, which runs from 24.40 to 19.70. The conventional model therefore appears to be fairly satisfactory for ethanol-carbon tetrachloride mixtures. But the average value (3.0) of a in the mixtures is smaller than the value of 3.54 obtained from the data in pure ethanol and also considerably smaller than the

average (4.6) value obtained in the same range of dielectric constant in methanol-carbon tetrachloride.

Another contrast between the alcohols also should be emphasized: initial addition of other solvents to methanol has in our experience always produced a decrease in ionic association which can be described in terms of an increased equivalent ion size. With ethanol, on the other hand, initial addition of carbon tetrachloride produces an immediate increase in association, which corresponds to a decrease in size, even after allowing for the change in dielectric constant. As shown in Fig. 3, where $\log K$ is plotted against dielectric constant for the two solvent mixtures MeOH- CCl_4 and EtOH- CCl_4 , tetrabutylammonium bromide is considerably more associated in the ethanol mixtures at a given dielectric constant than in methanol mixtures. The only conclusion which can be drawn at the present time is that the parameter a is specific for a given electrolyte-solvent system; this statement is, of course, a paraphrase of the admission that so many unknown quantities are lumped together into the "ion size" that it has no clear physical meaning.

The reaction between ethanol and carbon tetrachloride to give a conducting product placed a two-fold limitation on this work. The solvent conductance was so high that reliable measurements could not be made below $2 \times 10^{-4} N$, and this limitation in turn restricted the range of solvent mixtures which could be measured, because data at increasingly higher dilutions become necessary for extrapolation as the dielectric constant decreases. Over our range ($0 \leq x_2 \leq 0.1534$), the viscosity of the mixtures did not change very much, so the approximate constancy of the Walden product is not surprising. The direction of the change in $\Delta_{0\eta}$, however, calls for comment. The product increases when carbon tetrachloride is added to ethanol; *i.e.*, the hydrodynamic radius decreases. While this parallels the change in electrostatic radius, the net effect is much smaller. Finally, the contrast between methanol and ethanol also appears in the Walden product: addition of other liquids to methanol usually decreases $\Delta_{0\eta}$ while addition of carbon tetrachloride to ethanol results in the slight increase mentioned above.

One might be tempted to consider the values of the Walden products for tetrabutylammonium bromide in methanol ($\Delta_{0\eta} = 0.524$) and in ethanol ($\Delta_{0\eta} = 0.477$) as favorable evidence for solvation, arguing that solvation by the bulkier ethanol molecule is responsible for the lower product in that solvent. But opposing this deduction is the fact that the product in the MeOH- CCl_4 mixtures eventually becomes smaller than that for the EtOH- CCl_4 mixtures. With respect to ions as small as the bromide ion, it is evident that the solvent cannot be quantitatively approximated by a hydrodynamic continuum describable by a macroscopic viscosity. Specific details of structure of both solute and solvent molecule must eventually be included in any theory which aspires to generality.

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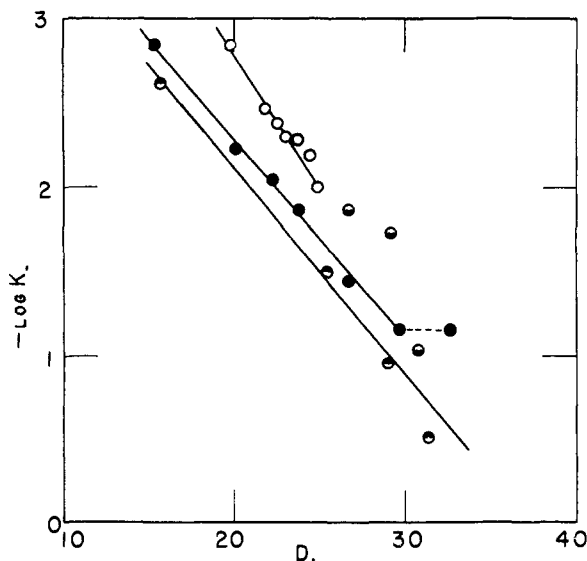


Fig. 3.—Dependence of equilibrium constant on dielectric constant; O, EtOH- CCl_4 ; ●, MeOH- CCl_4 ; ⊙, MeOH- C_6H_6 ; ⊖, MeOH- C_7H_{16} .

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

(7) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 1019 (1933); equations 5 and 6.