for measured lengths of time. The V(II) solution was the final solution shown in Table IV. The least squares slope for Table V was 0.1434 in exact agreement with the theoretical value which was used in Table V. The least squares slope of log concentration ratio *versus* measured potential for Table VI was 0.1516 with a standard error of 0.0001 as compared with the theoretical value of 0.1434 which was used in Table VI.

TABLE VI

POTENTIAL OF CELL C, V(III), V(II), Pt(II)(1 *M*), Pt

Anodization[a] time, sec.	Concn. V(III)[b] concn. V(II)	*E*, v., *vs.* Pt. ref.[c]	E^0_M, v.
180.00	0.1108	−0.7824	−0.7516
360.00	.2491	− .7330	− .7526
540.00	.4269	− .6895	− .7517
720.00	.6635	− .6680	− .7487
900.00	.9945	− .6414	− .7473
1080.00	1.490	− .6135	− .7445
1260.00	2.312	− .5830	− .7414
		Av.	−0.7483
		Stand. dev.	0.0042

[a] Electrode anodized at 20.00 ma. [b] Total concentration of V was 0.09447 *M*. Volume of solvent was 3.96 ml. [c] Concentration Pt(II) was 0.0330 *M*. Temperature of operation 450°. Equilibration time was 20 minutes.

Polarograms taken after each anodization of the V(II) solution and during the equilibration time are illustrated in Fig. 5. In accordance with expected behavior the anodic wave at potentials less negative than −0.9 v. decreased and the cathodic wave between −0.9 and −1.5 v. increased as the concentration of V(II) decreased and the concentration of V(III) increased.

Vanadium(II) probably could have been oxidized at a platinum surface as easily as it was done at a graphite surface. No indication of oxidation states higher than III for vanadium was found. If V(IV) is stable in this solvent, the standard potential of V(IV), V(III) is positive to the platinum dissolution potential.

Standard potentials E^0_M, E^0_m and E^0_X, extrapolated to unit concentration on the molarity, molality and mole fraction scales, are listed in Table VII. The conversion factors for concentrations are $m = m/1.648$ and $X = N/29.60$ where 1.648 is the density of the melt at 450° and 29.60 is the number of moles of solvent per liter of solvent. From the Nernst equation and the conversion factors, the correction terms from E^0_M to E^0_m and E^0_X are, respectively, $0.0311/n$ and $0.2110/n$, where n is the number of electrons involved in the electrode process. The correction term must be applied to both the electrode system in question and the platinum reference electrode. Whether the correction is added or subtracted depends upon whether the concentration of oxidant or reductant is being extrapolated. Precautions in the use of these values have been discussed previously.[2]

TABLE VII

STANDARD POTENTIALS

Electrode system	E^0_M, v.	E^0_M, v.	E^0_X, v.
V(II)–V(0)	−1.533	−1.533	−1.533
Fe(II)–Fe(0)	−1.172	−1.172	−1.172
V(III)–V(II)	−0.748	−0.764	−0.854
I_2–I^-	− .207	− .254	− .524
Pt(II)–Pt(0)	.000	.000	.000
Fe(III)–Fe(II)	+ .086	+ .070	− .020
Br_2–Br^-	+ .177	+ .130	− .140
Cl_2–Cl^-	+ .322	+ .306	+ .216

URBANA, ILLINOIS

[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA-FISICA OF THE UNIVERSITY OF ROME]

The Conductance of Tetraethylammonium Picrate in Methanol–Water Mixtures at 25°

BY FILIPPO ACCASCINA, ALESSANDRO D'APRANO AND RAYMOND M. FUOSS[1]

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The conductance of tetraethylammonium picrate in mixtures of methanol and water was measured, in order to study the transition from the case of negligible ionic association ($K_A = 0.8$) in water to that of moderate association ($K_A = 18.9$) in methanol. The data conform to the Fuoss equation for associated electrolytes, which is based on the Fuoss–Onsager equation for unassociated electrolytes, and on the hypothesis that any pair of ions in contact must be considered as not contributing to conductance for the duration of the contact. For the diameter of the sphere electrostatically equivalent to the ions, $å$ equals 5.31. The conductance data show the effect of the presence of the dipole in the picrate ion. The Einstein viscosity term leads to an average hydrodynamic radius of 4.27.

Introduction

Ionophores[2] (substances comprised of ions in the crystal form) in water show very slight association and their conductance curves can be reproduced by the Fuoss–Onsager equation[3] which neglects association. In solvents of dielectric constant below 20–25, association occurs to so great an extent that the modified[4–6] Ostwald dilution law can be used to analyze the data, because the Onsager square root term[7] is a satisfactory approximation to the effects of long range electrostatic forces on conductance; the higher terms in the Fuoss–Onsager equation become nearly negligible compared to the effects of pairwise association. By replacing the Bjerrum[8] definition of ion pairs by a physically more realistic one, according to which any two ions in contact are to be counted as a pair (regardless of the magnitude of their potential energy), it was possible to modify[9,10] the Fuoss–Onsager equation and to obtain a

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[1] On sabbatical leave from Yale University, spring semester 1958. Grateful acknowledgment is made for a Fulbright Grant.

[2] R. M. Fuoss, *J. Chem. Educ.*, **32**, 527 (1955).

[3] R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

[4] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933).

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

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

[7] L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

[8] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[9] R. M. Fuoss, THIS JOURNAL, **79**, 3301 (1957).

[10] R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957).

generalized conductance equation which transforms in a continuous fashion from the original equation (applicable only to the case of negligible association) to the modified Ostwald equation (applicable only to the case of marked association). The artificial discontinuity in association constant as a function of dielectric constant, which was a consequence of the Bjerrum cut-off distance, does not occur in the new theory. By means of the latter, conductance data in the intermediate range of dielectric constants, where the transition from negligible association to pronounced association occurs, can now be analyzed in terms of three arbitrary constants: Λ_0, the limiting conductance a, the center-to-center distance between anion and cation at contact in a pair and K_A, the association constant. Assuming only charge-charge forces to be acting, the latter two constants are related[11,12] by the simple equation

$$\ln K_A = \alpha + \epsilon^2/aDkT \qquad (1)$$

where e^α is the association constant for unchanged particles (or for ions in a hypothetical medium of infinite dielectric constant) and the other symbols have their usual meanings.

The purpose of this paper is to present conductance data for tetraethylammonium picrate in mixtures of methanol and water, together with a theoretical analysis of the experimental results. The system was chosen with the requirements of the theory in mind. Since the theory is based on a model which represents the solvent as a continuum, a salt with ions large compared to solvent molecules was selected. Methanol has a low enough dielectric constant (32.66) to induce moderate association ($K_A = 18.9$) and with addition of a little water, gives a range of solvents where all three constants (Λ_0, K_A and a) can be derived directly from the data. Larger amounts of water reduce association ($K_A = 0.8$ in water) and give a series of systems which permit an exploration of the transition from the case of moderate association to that of nearly negligible association. As required by the sensitivity of the theory to experimental error, precautions were taken to obtain good precision ($\pm 0.02\%$). Since the theory is not applicable for values of κa greater than 0.2, only the lower range of concentrations was studied; our highest concentration corresponds to $\kappa a = 0.14$.

Experimental

Materials.—Water was purified by the method of Kraus and Dexter[13]; the conductance varied from 0.2 to 0.4 × 10^{-6} mho.

Methanol was treated as recommended by Hartley and Raikes[14]: it was first distilled from silver nitrate to remove traces of aldehydes and ketones. After sufficient treatment with silver nitrate, as shown by a negative test[14] for carboxylic impurities, it was then distilled twice from successive portions of aluminum amalgam (from mercuric chloride and aluminum turnings). The middle cut was used; conductance 1–3 × 10^{-8} mho.

Tetraethylammonium picrate was prepared by neutralizing a hot aqueous solution of 25% tetraethylammonium hydroxide (analytically pure grade from FLUKA Chemische Fabrik) with a hot alcoholic solution of 20% picric acid (analytically pure grade from British Drug Houses, Ltd.). The product, which separated on cooling, was recrystallized eight times from methanol. Traces of solvent were removed by drying for 12 hr. under high vacuum, and then by 36 hr. at 45° at about 10^{-4} mm., m.p. 256–258°. Recrystallization was repeated until successive samples gave identical conductances in methanol.

Apparatus.—A Jones bridge was used for the conductance measurements, using an oscilloscope[15] to determine the balance point. The cells were held at constant temperature in an oil-bath equipped with a Leeds and Northrup photoelectric regulator. Temperatures were measured with a platinum resistance thermometer, using a Mueller bridge. The bath temperature was 25.000 ± 0.003°.

The cell design followed that of Daggett, Bair and Kraus,[16] except for the leads. In place of mercury contacts, platinum wires were welded to the electrode posts and extended to the tops of the cell arms. The bridge leads were clamped to the platinum wires for measurements. The electrodes were lightly platinized. The cell constant was determined, using aqueous potassium chloride solutions.[17] The final value of the cell constant was 0.1550 ± 0.0003 (average of 0.1551, 0.1553, 0.1549, 0.1552, 0.1551, 0.1554, 0.1546, 0.1552, 0.1550, 0.1545, 0.1550; the cell constant was determined before a microbalance became available and therefore is much less precise than the conductance data. Since, however, it is a multiplicative constant in all the equivalent conductances, the uncertainty of 0.2% in absolute values will not affect our conclusions). Before each run, the cell was cleaned with fuming nitric acid, rinsed thoroughly with conductivity water, steamed out for about 2 hr., dried at 110° for 2–3 hr. and allowed to cool in an evacuated desiccator.

Method.—The methanol–water mixtures (about 700 cc.) were prepared by weight in the conductance cell. First, water was pumped into the weighed empty cell by means of nitrogen pressure; after weighing, the amount of methanol to give the desired solvent mixture was calculated and added in a similar way. The final weight of cell plus contents gave the exact composition of the solvent. The cell plus solvent was placed in the thermostat to permit determination of solvent conductance. Then successive portions (at least 50 mg.) of salt (weighed on the microbalance) were added, using the technique described by Daggett, Bair and Kraus.[16] A magnetic stirrer assured uniform mixing of the contents of the cell. One hour was allowed for attainment of temperature equilibrium; cell resistances were read at intervals of 10 min. until successive readings checked to 0.01%. When room temperature was less than 25°, the cap of the cell was kept warm by a lamp, to prevent condensation of solvent.

Results

The properties of the solvent mixtures are summarized in Table I. Dielectric constants (D) were interpolated from the data of Gosting and Albright[18] and viscosities (η) from the data of Dunstan and Thole.[19] The last column gives the value c_0 of con-

TABLE I

PROPERTIES OF METHANOL–WATER MIXTURES AT 25°

No.	Wt. % MeOH	D	$10^3\eta$	$10^4 c_0$
1	100.00	32.66	5.52	60
2	97.93	33.90	6.02	64
3	90.75	37.53	7.84	70
4	74.73	44.96	11.48	82
5	49.96	56.28	15.60	106
6	25.01	68.50	14.98	126
7	0.00	78.48	8.91	145

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(11) J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).

(12) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

(13) C. A. Kraus and W. B. Dexter, *ibid.*, **44**, 2468 (1922).

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

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

(16) H. M. Daggett, Jr., E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

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

(18) L. J. Gosting and P. S. Albright, THIS JOURNAL, **68**, 1061 (1946).

(19) A. E. Dunstan and F. B. Thole, *J. Chem. Soc.*, **95**, 1559 (1909).

centration corresponding to $\kappa a = 0.2$, using the round value $\mathring{a} = 5$. This concentration is the highest concentration at which the theoretical equations may be applied; our highest concentration was about $c_0/2$.

The conductance data are given in Table II for the seven solvents; for the last four, data for two separate series are included. (It is in general not necessary to make check runs when working with mixed solvents; a criterion of reliability is provided by a plot of derived constants, such as $\Lambda_0\eta$, K_A, etc., against composition of solvent or against a variable such as D^{-1} which depends on composition.)

TABLE II

CONDUCTANCE OF Et_4NPi IN $MeOH-H_2O$ AT 25°

10^4c	Λ	10^4c	Λ
100% MeOH		75% MeOH	
2.7355	102.849	1.8626	56.271
5.4550	100.872	3.2580	55.804
9.3487	98.763	3.7321	55.723
17.098	95.716	6.4168	55.110
28.795	92.140	6.4942	55.120
98% MeOH		11.126	54.351
		11.764	54.220
2.6209	95.828	19.773	53.252
5.2026	94.146	24.995	52.784
8.8662	92.375		
14.398	90.381	50% MeOH	
20.847	88.476	2.8045	41.762
91% MeOH		3.3059	41.638
2.5158	77.947	5.7362	41.403
6.3989	76.344	6.2889	41.273
11.899	74.736	9.4154	40.997
18.183	73.347	11.308	40.867
26.233	71.965	16.760	40.435
		25.425	39.964
25% MeOH		27.815	39.802
2.4453	41.721		
3.0086	41.652	0% MeOH	
5.2280	41.392	2.8065	61.678
5.9845	41.312	5.1247	61.194
8.4673	41.940	8.7864	60.671
10.259	40.940	16.085	59.999
24.532	40.040	17.557	59.857
		27.041	59.173
		29.512	59.017

Discussion

The revised[20] conductance equation for associated electrolytes is

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_A c\gamma f^2\Lambda - F\Lambda_0 c \quad (2)$$

where the symbols have the following meaning: Λ = observed equivalent conductance, Λ_0 = limiting equivalent conductance, S = the Onsager coefficient, c = concentration in equivalents per liter, γ = fraction of salt present as free ions, E = the Fuoss–Onsager coefficient, J = an explicit function[20] of a (the ion size), K_A = association constant, f = activity coefficient and F = the Einstein coefficient $(5\varphi/2)c$, where φ is volume fraction of solute. This equation can be rearranged as follows, to define a quantity Λ'

$$\Lambda' = \Lambda + Sc^{1/2}\gamma^{1/2} - Ec\gamma \log c\gamma \quad (3)$$

or

$$\Lambda' = \Lambda_0 + Jc\gamma - K_A c\gamma f^2\Lambda - F\Lambda_0 c \quad (4)$$

The variable Λ', for the case of slight association where γ is approximately unity, reduces to

$$\Lambda' = \Lambda + Sc^{1/2} - Ec \log c \quad (5)$$

or

$$\Lambda' = \Lambda_0 + Jc - K_A cf^2\Lambda - F\Lambda_0 c \quad (6)$$

In the form (5), Λ' serves as a test variable to detect the extent of association; it is a much more useful dependent variable than the conductance itself, because it includes the known[21] square root and transcendental terms and permits the effect of the other terms of (2) to be seen. If K_A is small, (6) reduces to

$$\Lambda' = \Lambda_0 + Jc - F\Lambda_0 c \quad (7)$$

Consequently, when association is slight, Λ' calculated by (5) becomes linear in concentration.

The data of Table II show quite clearly the transition from negligible association to moderate association with decreasing dielectric constant, when they are treated as outlined above. In Fig. 1, Λ' (minus an arbitrary constant), defined by (5), is plotted against concentration. Systems 7–4 (0–75% MeOH inclusive) give linear plots; system 3 (90.75% MeOH, $D = 37.53$) begins to show curvature, which becomes more pronounced as the dielectric constant is reduced to that of methanol. The curvature originates from two sources: first, Λ' as calculated from (5) becomes too large, because γ begins to decrease from unity; and second, the non-linear term $K_A c\gamma f^2\Lambda$ in Λ' becomes steadily more significant as K_A increases with decreasing dielectric constant.

In systems 1–3, association is sufficient to permit determination of Λ_0, J and K_A by the $y - x$ method.[9,20] To a first approximation, the viscosity term $F\Lambda_0 c$ is neglected compared to the much larger association term; then

$$y = (\Lambda' - \Lambda_0)/c\gamma \quad (8)$$

$$= J - K_A f^2 \Lambda \quad (9)$$

In (8), Λ' has the value given by (3) and the Arrhenius approximation $\gamma = \Lambda/\Lambda_0$ is used to calculate the terms $Sc^{1/2}\gamma^{1/2}$ and $Ec\gamma \log c\gamma$. (For details, see ref. 10 and 20.) If the limiting conductance Λ_0 were known, y as defined by (8) would be a linear function of $x = f^2\Lambda$. This condition suggests the method of solving the problem: trial values of Λ_0 are used to calculate y and then y is plotted against x. As shown in Fig. 2, the y *vs.* x plot is concave-up if the trial value of Λ_0 is too small, and concave-down if it is too large. The function y, which has the limiting form (0/0), is extraordinarily sensitive to the trial value of Λ_0 used in the calculations; as shown in the figure a change of only 0.02% suffices to change the y *vs.* x plot from concave-up to concave-down. Hence the true value of Λ_0 can be determined with high precision, provided data of precision comparable with the sensitivity of the method are available. The sensitivity is due, of course, to the fact that y will approach $\pm \infty$ in-

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(20) R. M. Fuoss, THIS JOURNAL, **80**, 3163 (1958).

(21) A value of Λ_0 sufficiently accurate for the preliminary calculation of E and S can be obtained from the data by a Shedlovsky extrapolation.

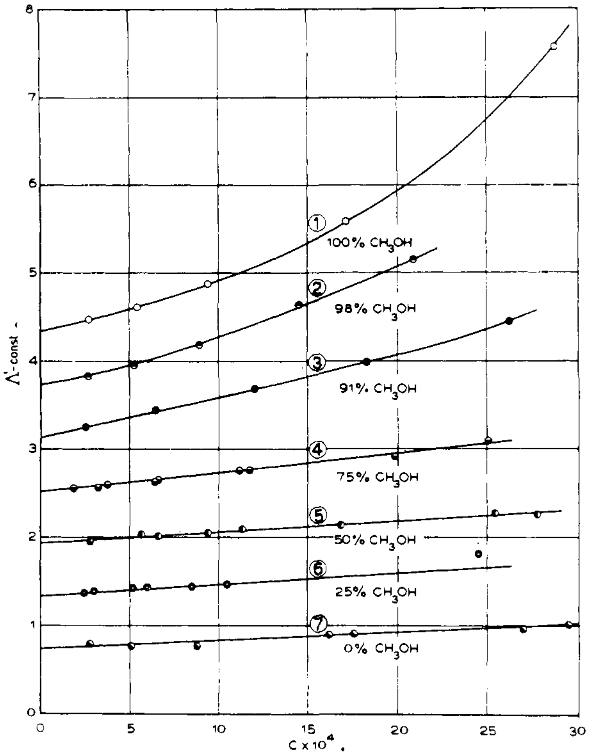

Fig. 1.—Dependence of Λ' on concentration of Et_4NPi and on composition of solvent.

stead of a constant $(J - K_A\Lambda_0)$ at zero concentration if the incorrect value of Λ_0 is used in (8).

From the lines of Fig. 2, values of K_A and J are obtained from the slope and the relation

$$J = y + K_A x \tag{10}$$

Then from a plot of J against a values of the parameter a (center-to-center distance at contract of the spheres which are electrostatically equivalent to the ions) are interpolated. The results of these calculations are summarized in Table III. The value of a shows a slight trend with solvent composition; when the correction for the neglected term $F\Lambda_0 c$ is made (see below), the spread is somewhat reduced. The last column of Table III gives the final corrected values of $\mathring{a}$. The association constant in pure methanol is about 20; at a concentration of 3×10^{-3}, the decrease in conductance due to the formation of ion pairs therefore amounts to about 6%. With increasing water content, the association constant decreases, as will be noted in Fig. 2 from the slope which decreases in the sequence of increasing dielectric constants.

TABLE III

CONSTANTS FOR Et_4NPi IN MeOH-RICH SYSTEMS

No.	D	Λ_0	K_A	J(prelim.)	$\mathring{a}$(prelim.)	$\mathring{a}$
1	32.66	107.37	18.9	1940	5.10	5.47
2	33.90	99.71	15.5	1590	4.92	5.28
3	37.53	80.59	9.4	960	4.72	5.18

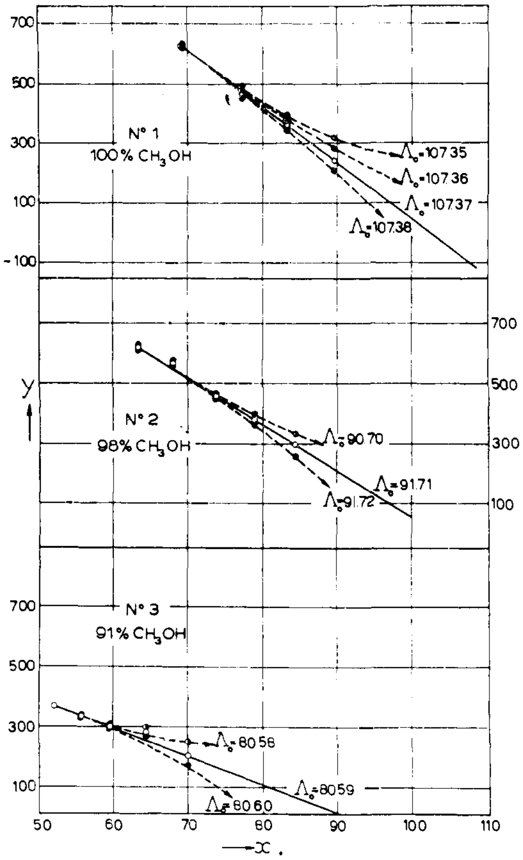

Fig. 2.—Determination of limiting conductance, association constant and $J(a)$ for systems 1–3.

The y *vs.* x plots for systems 7 to 4 are so nearly horizontal that it is impossible to obtain a reliable value of K_A from the slope. A different method was therefore used to analyze the data. A plot of log K_A against reciprocal dielectric constant is shown in Fig. 3; the three points available from Systems 1–3 lie quite precisely on a straight line. We shall therefore assume that the association constant satisfies equation 1 (or its equivalent) and that we may extrapolate from the values for the methanol-rich systems to obtain values of K_A in the water-rich systems. This is equivalent to assuming that a is independent of solvent composition. The values obtained are given in Table IV. Now if we may consider K_A as known, equation 2 can be rearranged to define a new variable Λ_J

$$\Lambda_J = \Lambda + Sc^{1/2} - Ec \log c + K_A cf^2\Lambda \tag{11}$$

or

$$\Lambda_J = \Lambda_0 + (J - \Lambda_0 F)c \tag{12}$$

where, since $K_A < 10$ for Systems 7–4, the approximation $\gamma \approx 1$ over our working range of concentrations is justified. Now Λ_J, as defined by (11), becomes the new dependent variable which replaces (and includes) the observed conductance. According to (12), Λ_J should be a linear function of concentration in the range of variables where the approximation $\gamma \approx 1$ is justified. A test of the equation is shown in Fig. 4, for systems 7–4; as will be noted, the Λ_J *vs.* c plots are linear as expected. The intercepts give the limiting conductances listed in Table IV, while the slopes evaluate the constants

$$H = J - \Lambda_0 F \tag{13}$$

In order to separate H into its components, we use the round value $\mathring{a} = 5.0$ obtained from the data for

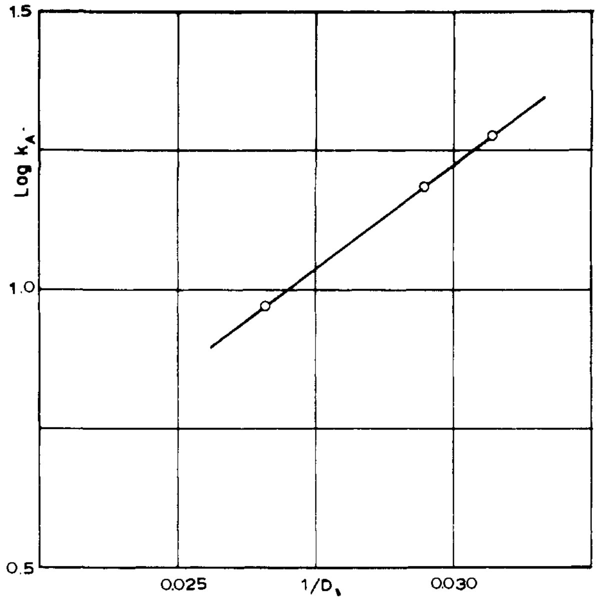

Fig. 3.—Dependence of association constant on dielectric constant of solvent.

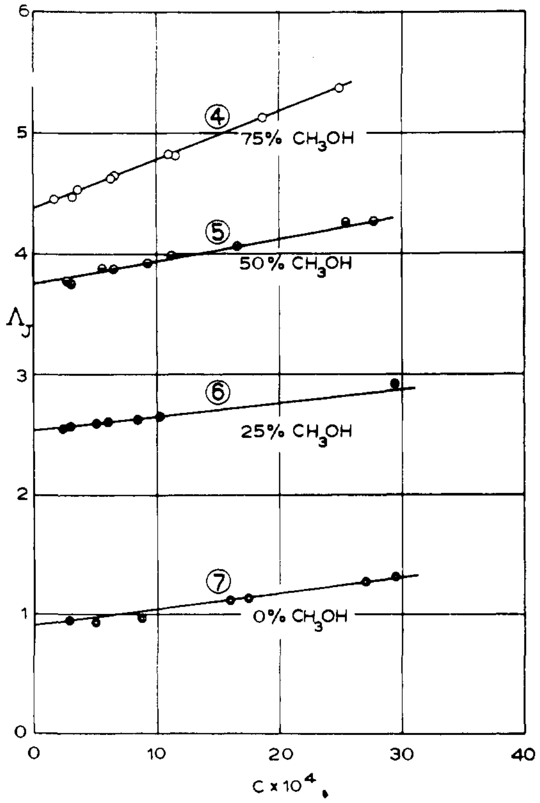

Fig. 4.—Determination of Λ_0 and H for systems 4–7.

Systems 1–3 to calculate $J(a)$; then (13) gives F, the Einstein coefficient. The values found for F are also included in Table IV; the constancy observed in F is a rigorous test both of the theory and of the precision of the data. The average value of F is 1.0; at a concentration of 3×10^{-3}, the viscosity term amounts to about 0.3% of the total conductance. Our precision, which is of the order of 0.02%, therefore can establish F to about ±7%.

TABLE IV

CONSTANTS FOR 0–75% METHANOL

No.	D	K_A	Λ_0	H	F
4	44.96	4.27	57.566	400	1.16
5	56.28	1.96	42.762	173	0.91
6	68.50	1.13	42.535	106	0.92
7	78.48	0.82	62.950	120	0.91

If we assume that both species of ions contribute equally to F, then the corresponding hydrodynamic radius R can be calculated by means of the equation

$$F = (5/2)(4\pi N/3000)(2R^3) \qquad (14)$$

whence

$$\mathring{R} = 4.27F^{1/3} \qquad (15)$$

Our average of $F = 0.99$ gives $R = 4.27 \times 10^{-8}$ cm. which is an acceptable value. The value of F obtained from the data for systems 7–4 may now be used to correct the preliminary results of the y *vs.* x extrapolation for systems 1–3. The values of J (prelim.) given in Table III are actually values of $(J - F\Lambda_0)$; adding $F\Lambda_0$ to the preliminary J values gives J (a) and then interpolation on the J *vs.* a plots gives the final values of $\mathring{a}$ listed in Table III. It will be noted that the spread has been somewhat reduced in the corrected values, which average to $\mathring{a} = 5.31$.

The viscosity of methanol–water mixtures changes quite rapidly with composition, reaching a maximum of nearly three times the viscosity of methanol at about 40% methanol. The limiting conductances change correspondingly but not quite enough to hold the Walden product $\Lambda_0\eta$ constant; as shown in Fig. 5, the product has a maximum at about 60% methanol.[22] This system therefore furnishes another example of the interaction between the ions and the solvent. Even at the limit of extreme dilution, there must be a braking effect somewhat similar to the relaxation term in the mobility. As an ion moves through the solution, it

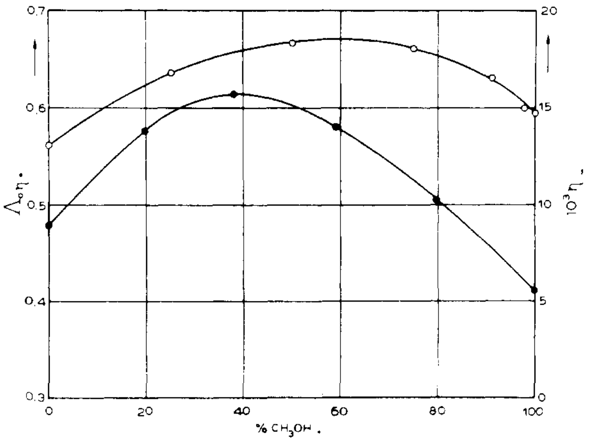

Fig. 5.—Dependence of viscosity (●, ordinates right) and Walden product (O, ordinates left) on composition of solvent.

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[22] The maximum was also observed by N. G. Foster and E. S. Amis, *Z. physik. Chem.* (*Frankfort*), **7**, 360 (1956). These authors extrapolated their data by the empirical Kohlrausch square root scale and neglected ionic association. Consequently no convenient comparison of results is feasible.

must orient dipoles in its vicinity. There will be an orientation of solvent molecules in front of the moving ion and a relaxation to random orientation behind it. The steady state will correspond to a net excess of oriented dipoles behind the moving ion and a deficiency in front, due to the non-zero viscosity of the medium, and the ion therefore carries an electrostatic brake with itself in any polar solvent. This effect is at least part of the reason why $\Lambda_0\eta$ is not a true constant, as it would be if the Stokes model were valid.

Finally, a suspected property of the picrate ion can be deduced from the conductance data. The ion is electrically asymmetrical; to first approximation, we may neglect (as a mutually cancelling vector sum) the dipole moments of the three nitrogroups. The net negative charge is, of course, distributed over the entire structure, but it must be an unsymmetrical distribution, leaving a fairly strong dipole with the negative end at the oxygen atom at position 1. From the J values of systems 1–3, we found $\mathring{a} = 5.31$. From the slope of Fig. 3, we obtain the smaller value of 3.18, if we assume that K_A is given by equation 1. If, however, a dipole field is also involved, (1) should be replaced[23] by

$$\ln K_A = \alpha + e^2/DkTa + \mu e/DkTd^2 \quad (16)$$

where μ is the dipole moment of the picrate ion and d is the distance parameter in the dipole term in the potential energy at contact of anion and cation. The slope of the log K_A *vs.* $1/D$ plot then is

$$d \log K_A/dD^{-1} = 0.4343(e^2/akT + \mu e/d^2kT) \quad (17)$$

Using the experimental value of 176 for the slope from Fig. 3 and $\mathring{a} = 5.31$, equation 17 gives 0.61 for the ratio $\mu_D/d^2{}_A$ (moment in debyes, distance in Å.). This ratio appears to be quite reasonable; if the distance from the center of the cation to the center of the dipole in the picrate ion is set equal to 2 Å., for example, we obtain a moment of 2.4 for the latter.

[23] See discussion of sodium bromate, ref. 10.

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The Influence of Solvent on the Rate of Aromatic Chlorination

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In ethylene dichloride the rate of toluene chlorination is extremely slow at room temperature unless a polar catalyst is present. In the presence of added hydrogen chloride the reaction is first order with respect to each reactant and to the catalyst. The rate of simple bimolecular nuclear chlorination of toluene at 25° varies with solvent in the order, $ClCH_2CH_2Cl \ll (CH_3CO)_2O \sim CH_3COOH \sim CH_3CN < CH_3NO_2$. The activation energies, excluding that for ethylene dichloride which must be very large, fall off in the order $CH_3COOH > (CH_3CO)_2O > CH_3CN > CH_3NO_2$. The activation entropy for the reaction in the hydroxylic solvent, acetic acid, is much less negative than in more polar non-acidic media. The reaction is actually more rapid in acetic acid than in acetic anhydride. The activation energy for aromatic hydrocarbon chlorination in a given solvent varies in the order, benzene > toluene > *m*-xylene. The variation in the entropies of activation in this series is very small.

The activated complex for electrophilic halogenation of the aromatic nucleus is presumed to be an aggregate of molecules of the benzenoid compound, the halogen and an additional substance. The primary function of this additional substance is to assist rupture of the bond between the two atoms of the halogen molecule.[1] In a medium of low polarity, such as carbon tetrachloride, the halogen or hydrogen halide may serve as the third member of the aggregate as evidenced by the fact that the reactions are of higher than first order in halogen or are autocatalytic.[2] When, alternatively, a polar medium is used, the order with respect to halogen may drop to unity and the sensitivity of the reaction to catalysis by extraneous polar substances is reduced. In this case the solvent itself may serve as the third component of the activated complex.

To obtain more detailed information concerning the contribution of a polar solvent to the activation process for aromatic halogenation the energies and entropies of activation for the chlorination of toluene in several different media of widely varying polarity have been determined. Chlorine, rather than another of the halogens, has been used since its reactions with aromatic hydrocarbons are usually first order in halogen and are, except in carbon tetrachloride,[2] insensitive to hydrogen halide.[3] A few measurements to determine the influence of temperature changes on the rate of chlorination of *p*- and *m*-xylenes have been conducted. Comparative values for the activation energies and entropies of halogenation of the entire series of methylbenzenes are potentially of considerable theoretical interest.[4] Because of extreme variations in reactivity of these hydrocarbons, a complete set of such constants was not obtainable by the methods of this investigation.

Experimental

Materials.—The aromatic hydrocarbons were obtained from commercial sources and were purified as described previously.[5] Procedures used in preparing hydrogen chloride and dry acetic acid have been reported earlier.[3a]

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[1] For recent pertinent discussions see (a) P. W. Robertson, *J. Chem. Soc.*, 1267 (1954); (b) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953); (c) R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956); (d) E. Berliner and M. C. Beckett, *ibid.*, **79**, 1425 (1957).

[2] See, for example, L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 1412, 5169 (1957).

[3] (a) R. M. Keefer and L. J. Andrews, *ibid.*, **79**, 4348 (1957); (b) H. C. Brown and L. M. Stock, *ibid.*, **79**, 5175 (1957).

[4] *Cf.* F. E. Condon, *ibid.*, **70**, 1963 (1948).

[5] N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 2210 (1956).