ened significantly by the polar solvent especially when hydrogen bonding can occur, thus two lines close together often appear as one. Weak lines are difficult to observe in water because of the well-known trouble in getting water free from colloidal matter and motes.

The spectral patterns for H_2SO_4, $H_2PO_4^-$ and silicate ion showed a marked resemblance that has already been pointed out.[21] As one goes from H_2SO_4 to $H_2PO_4^-$ and on to $H_2SiO_4^=$, there is a decrease in sharpness of the spectral lines, however. Since the observed silicate spectrum is consistent with that expected for the $H_2SiO_4^=$ form, the weight of evidence strongly favors this as the structure.

Acknowledgment.—The authors are grateful to the Office of Ordnance Research of the U. S. Army for support.

PROVIDENCE, R. I.

[CONTRIBUTION FROM L'ISTITUTO DI CHIMICA FISICA DELL' UNIVERSITÀ DEGLI STUDI DI ROMA]

The Conductance of Tetrabutylammonium Tetraphenylboride in Acetonitrile-Carbon Tetrachloride Mixtures at 25°

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The conductance of $Bu_4N{\cdot}BPh_4$ was measured in acetonitrile ($D = 36.0$) and in six mixtures of MeCN with CCl_4 with dielectric constants of 33.2, 28.8, 24.9, 15.35, 7.20 and 4.80. Association to ion pairs is slight ($K_A = 14.3$) in MeCN but steadily increases as the dielectric constant decreases; at $D = 4.80$, $K_A = 3.0 \times 10^6$. Triple ion clustering also occurs in the two mixtures of lowest dielectric constants. The system illustrates the transition from almost negligible association in MeCN, where the phoreogram lies above the Onsager tangent, to the case of marked association where $c\Lambda^2$ is approximately constant. Both ions are very large compared to the solvent molecules; nevertheless, the Walden product decreases with increasing CCl_4 content of the solvent. This variation shows that Stokes law must be corrected for the electrostatic interaction between the ions and the dipoles of the polar constituent of the solvent.

Introduction

Recent theoretical work[2] has shown that the conductance of ionophores can be described on the basis of a model in which the ions are represented as charged spheres in a continuum. In solvents of high dielectric constant, the conductance changes with concentration primarily because the long range electrostatic forces between the ions reduce the mobility as the concentration increases; with decreasing dielectric constant, the conductance decreases still more rapidly, because part of the solute is then present as non-conducting ion pairs. Tetrabutylammonium tetraphenylboride[3] is an electrolyte in which both ions are very large compared to ordinary solvent molecules and have centrally located charges. This salt, therefore, conforms quite well to the theoretical model. The purpose of this paper is to present conductance data on $Bu_4N{\cdot}BPh_4$ in acetonitrile ($D = 36.0$) and in a series of mixtures of this solvent with carbon tetrachloride, which cover the dielectric constant range down to 4.80 (95% CCl_4). A continuous transition is observed, from almost negligible association ($K_A = 14.3$) in acetonitrile to marked association ($K_A = 2.96 \times 10^6$) at $D = 4.80$. This system thus supplements work on the system tetraethylammonium picrate-methanol-water[4] which covered the range of moderate to completely negligible association. While the continuum model serves to describe the electrostatic effects, however, it is found to be inadequate for the hydrodynamic properties. Despite the fact that the ions of $Bu_4N{\cdot}BPh_4$ are both much larger than the molecules of either acetonitrile or carbon tetrachloride, the Walden product $\Lambda_0\eta$ is not constant but decreases with increasing carbon tetrachloride in the mixed solvent. A relaxation field between ions and solvent dipoles could account for the inconstancy of $\Lambda_0\eta$.

Experimental

Materials.—Tetrabutylammonium bromide (Eastman, special order, unpurified raw product from tri-*n*-butylamine and *n*-butyl bromide) was dissolved in benzene at 80° (5 cc./g.) and precipitated by adding hot *n*-hexane (15 cc./g.) and allowing to cool. The hygroscopic precipitate was dried over phosphorus pentoxide in an evacuated desiccator for 24 hr. and then kept at 40° and 10^{-4} mm. for a week. This procedure was repeated twice; m.p. 116-117° (or on some batches, a metastable form[5] melting at 101-102° was obtained).

Tetrabutylammonium tetraphenylboride[3] was prepared by metathesis from purified tetrabutylammonium bromide and sodium tetraphenylboride.[6] The latter was dissolved in conductance water (2% solution); after filtration to remove a small amount of insoluble impurities, an equivalent amount of tetrabutylammonium bromide in 2% aqueous solution was slowly added. The bulky white precipitate was washed 5 times by decantation. After drying, the product was recrystallized 4 times from 1:3 water-acetone (200 cc./g. salt) and finally dried for several days at 40° and 10^{-4}, mm.; m.p. 223-225°.

Acetonitrile was treated as recommended by Wawzonek and Runner[7]; b.p., 81.5° at 760 mm. For conductance work, the purified solvent was distilled from P_2O_5, using a conductance cell between the condenser and the receiver to monitor the product; distillate with conductance $5\text{-}9 \times 10^{-8}$ mho was collected. Due to its hygroscopicity, acetonitrile was always transferred from one container to another by dry nitrogen pressure after the final distillation.

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(1) On sabbatical leave from Yale University, second semester 1957-1958. Grateful acknowledgment is made for a Fulbright Grant.

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

(3) R. M. Fuoss, J. B. Berkowitz, E. Hirsch and S. Petrucci, *Proc. Nat. Acad. Sci.*, **44**, 27 (1958).

(4) F. Accascina, A. D'Aprano and R. M. Fuoss, THIS JOURNAL, **81**, 1058 (1959).

(5) H. M. Daggett, E. I. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

(6) G. Wittig and P. Raff, *Ann.*, **573**, 195 (1951); bibliography 1949-1955, A. J. Barnard, Jr., *Chem. Anal.*, **44**, 104 (1955).

(7) S. Wawzonek and M. E. Runner, *Trans. Electrochem. Soc.*, **99**, 457 (1952); see also P. Walden and E. I. Birr, *Z. physik. Chem.*, **144A**, 269 (1929); A. I. Popov and N. E. Skelly, THIS JOURNAL, **77**, 3722 (1955).

Carbon tetrachloride was washed with hot concentrated sodium hydroxide solution to eliminate carbon bisulfide, then washed with water and dried over P_2O_5. The conductance of the final distillate was far below the limit of detectability.

Apparatus and Method.—Two conductance cells were used. The first[4] had a constant of 0.1550 cm.$^{-1}$, as determined by measurements on potassium chloride (5 times recrystallized from conductance water),[8] using Shedlovsky's data.[9] The second cell (lightly platinized electrodes) had a constant of 0.07356, as determined by comparison with the first, using solutions of Bu_4NBPh_4 in acetonitrile. As a control, the conductance of tetramethylammonium picrate in methanol was determined: the results were in satisfactory agreement with those of Evers.[10] Most of the measurements were made using a Jones bridge (Leeds and Northrup); some were made at the Sterling Chemistry Laboratory of Yale University, using a Shedlovsky bridge. All data were extrapolated to infinite frequency in order to eliminate polarization errors. The cells were immersed in a thermostat at 25.00 ± 0.005°, which was monitored by a platinum resistance thermometer and Mueller bridge.

Solvent mixtures were prepared by weight, and volume concentrations were calculated from the densities. All solvent transfers were made with precautions to avoid contamination by atmospheric moisture. The solvent densities d_0 are given in Table I; then final electrolyte concentrations were calculated by use of the equation

$$d = d_0 + 0.225c_0$$

where c_0 is the concentration calculated using d_0 as first approximation. (Within the experimental error, the coefficient 0.225 was the same for solutions in acetonitrile, isobutyronitrile and in a 50-50 mixture of acetonitrile and carbon tetrachloride.) Corrections (maximum, about 0.01%) were made for the amount of solvent in the vapor phase; for the mixtures, we assumed ideal behavior in computing this correction. At least 20 mg., and usually 50 mg., of salt was weighed in a weighed glass cup on the microbalance; then cup and contents were placed in the cell containing solvent (or solution); a magnetic stirrer was used to ensure uniformity of composition of the solution.

TABLE I

PROPERTIES OF ACETONITRILE–CARBON TETRACHLORIDE MIXTURES

Wt. % CCl_4	d	100 η	D
0.00	0.7771	0.3438	35.99
17.63	....	....	33.06
28.20	0.9063	.3822	30.68
44.06	1.0015	.4191	...
44.94	....	.4187	27.94
57.70	1.0998	.4595	...
67.31	1.1841	.4995	19.80
71.91	....	.5376	...
80.37	1.3176	.5942	...
80.97	....	....	11.54
100.00	1.5851	.9017	2.25

Solvent properties are summarized in Table I. The densities were determined, using an Ostwald–Sprengel pycnometer, which is especially convenient for work with mixtures of components of different volatilities, because it can be filled rapidly. Viscosities were measured, using both Ostwald and Ubbelohde viscometers. Dielectric constants were measured, using a General Radio Schering bridge and the cell described by Sadek and Fuoss.[11] For calibration, we used $D = 34.82$ for nitrobenzene and $D = 32.63$ for methanol.[12] The physical constants of the solvents used in the conductance experiments were interpolated graphically from the data of Table I; these values are summarized in Table II, which also gives code numbers for later use. The fifth column of Table II gives the value of κa corresponding the highest stoichiometric concentration at which conductance was measured in a given solvent. Here, κ is the Debye–Hückel parameter, and $\mathring{a}$ was set equal to 9.0. The solvent conductance κ_0 is given in the sixth column. The conductance data are summarized in Table III, where Λ is equivalent conductance and c is concentration (equivalents of salt per liter of solution).

Discussion

The seven systems investigated cover the range $36.0 \geqslant D \geqslant 4.80$; in acetonitrile, only about 0.3% of the solute is present as ion pairs at $c = 2 \times 10^{-4}$, while at the same concentration in the mixture with $D = 4.80$, only about 4% of the solute is present as free ions, the other 96% being associated to pairs and triples. These systems thus serve to illustrate the transition from almost negligible association to marked clustering of ions under the influence of mutual electrostatic forces, as the dielectric constant is decreased. Naturally, different methods must be used to analyze the data, according to the magnitude of the association constant K_A. In acetonitrile and in solvent 2, the conductance curve lies above the Onsager tangent; in solvent 3 ($D = 28.8$), the points are practically on the tangent; then with decreasing dielectric constant, the curves become progressively steeper in our working range of concentrations and all lie below the limiting tangent.

A preliminary analysis of systems 1–5 is shown in Fig. 1 where Λ'_η is plotted against concentration; the variable Λ'_η, defined by the equation

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

represents the observed conductance Λ, corrected for the static viscosity and the theoretically predictable square root and logarithmic terms in mobility.[13] For systems 1 and 2, the fraction of solute associated to pairs is so small that γ in (1) can be replaced by unity; for systems 3–5, we used the approximation

$$\gamma = \Lambda/[\Lambda_0 - S(c\,\Lambda/\Lambda_0)^{1/2}] \quad (2)$$

It will be seen that the plots are linear, with a slope which increases as dielectric constant decreases; the intercepts at $c = 0$ evaluate the limiting conductance Λ_0. Association is so slight in systems 1–4 that the y-x method[2] cannot be used to evaluate the association constants, because the plots are practically horizontal. A different method was therefore used, based on an extrapolation of the association constants which are obtained for systems 5–7.

System 5 ($D = 15.35$) shows marked association. In this case, the term $K_A c\gamma f^2\Lambda$ is very much larger than $(Jc\gamma + Ec\gamma \log c\gamma)$ and the approximate equation

$$\Lambda = \gamma(\Lambda_0 - Sc^{1/2}\gamma^{1/2}) \quad (3)$$

adequately represents the conductance curve; extrapolation by the method of Fuoss and Kraus[14] or of Shedlovsky[15,16] may be used. The Shedlovsky plot is shown in Fig. 2; from slope and intercept, we

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[8] C. A. Kraus and W. B. Dexter, THIS JOURNAL, **44**, 2468 (1922).

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

[10] E. C. Evers, THIS JOURNAL, **73**, 1739 (1951).

[11] H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5897 (1954).

[12] A. A. Maryott and E. R. Smith, *N.B.S. Circular*, **514**, 1 (1951).

[13] The symbols in Eq. 1, as well as those used later in this paper, have the meanings given in ref. 2.

[14] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933); R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

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

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

TABLE II

PROPERTIES OF SOLVENTS FOR CONDUCTANCE EXPERIMENTS

No.	% CCl_4	D	100η	κa at c (max.)	$10^8\,\kappa_0$	Λ_0	K_A	$\Lambda_0\eta$
1	0.00	35.99	0.344	0.18	24.0	119.60	14.3	0.411
2	16.90	33.20	.362	.14	16.0	112.24	17.8	.406
3	40.23	28.20	.406	.09	8.0	98.80	20.0	.401
4	55.25	24.90	.448	.14	12.0	88.30	36.0	.395
5	74.89	15.35	.550	.14	1.7	70.26	146	.386
6	90.26	7.20	.711	.39	0.6	(54.35)	4.09×10^4	(.386)
7	94.97	4.80	.796	.32	0.2	(48.55)	2.96×10^6	(.386)

TABLE III

CONDUCTANCE OF $Bu_4N{\cdot}BPh_4$ IN MeCn–CCl_4 MIXTURES AT 25°

10^4c	Λ	10^4c	Λ
No. 1		No. 4	
2.478	114.5	0.938	84.95
2.494	114.5	2.138	83.25
3.062	113.95	3.708	81.65
3.447	113.6	5.338	80.3
4.278	112.95	6.562	79.4
4.843	112.5	No. 5	
6.783	111.3	0.2905	67.15
7.508	110.85	1.0165	64.8
8.911	110.15	2.2025	62.7
10.139	109.6	4.000	60.25
13.530	108.15	2.045	62.85
16.787	107.0	3.615	60.6
		4.542	59.55
No. 2		No. 6	
3.040	106.5	4.030	19.32
3.883	105.8	6.105	16.54
7.453	103.4	12.626	13.25
9.628	102.25	14.287	12.80
		16.085	12.33
No. 3		No. 7	
0.4535	96.5	0.498	4.61
0.923	95.65	1.501	3.05
2.338	93.75	2.719	2.33
3.489	92.7	4.717	1.95
		6.909	1.74

obtain $K_A = 165$ and $\Lambda_0 = 69.66$. By the $y - x$ method, we find $K_A \approx 120$ and $\Lambda_0 = 69.6$; the points scatter rather badly, and this value of K_A is preliminary. A better value will be obtained in the second approximation by means of equation 11. This system shows the effect of neglecting the higher terms in the conductance equation; the use of the approximation 3 gives too high an association constant.

In systems 6 and 7, association to pairs is so pronounced that (3) practically reduces to the limiting form

$$c\Lambda^2 = \Lambda_0^2/K_A \qquad (4)$$

when combined with the mass action equation, because γ becomes negligible compared to unity. This means that an extrapolation by the modified[14-16] Ostwald dilution law can only evaluate the quotient Λ_0^2/K_A; the plot is so steep that the intercept $1/\Lambda_0$ becomes indistinguishable from zero. Also, in this low range of dielectric constant, it becomes necessary to include the effects of higher clustering. We therefore used the Fuoss and Kraus equation[17]

$$\Lambda c^{1/2}g = \Lambda_0 K_A^{-1/2} + (\lambda_0/kK_A^{1/2})(1 - \Lambda/\Lambda_0)c \qquad (5)$$

to analyze the data for systems 6 and 7. In eq. 5, λ_0 is the limiting conductance of the triple ion double cluster (A_2B^+) (AB_2^-), k is the constant for the triple ion equilibrium and g is a function which approximates the effects of long range electrostatic forces. Figure 3 shows the data for systems 6 and

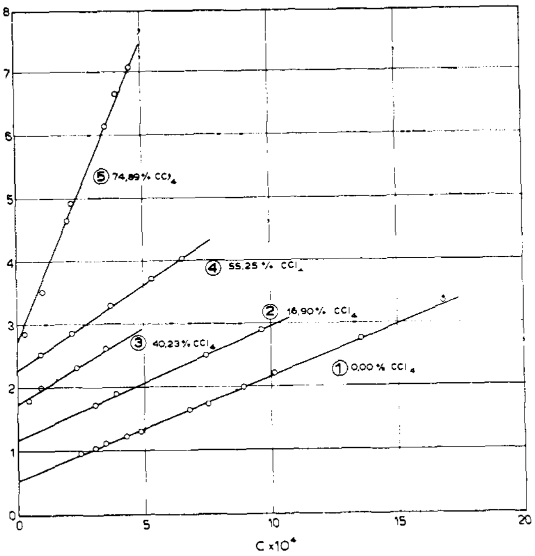

Fig. 1.—Determination of Λ_0 for systems 1–4.

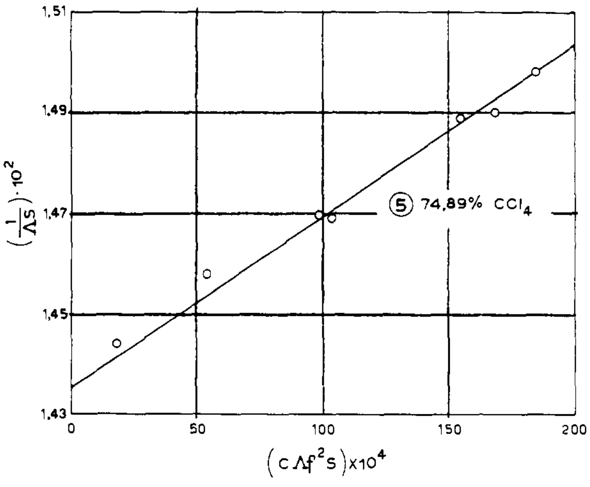

Fig. 2.—Shedlovsky plot for system 5.

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[17] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 2387 (1933).

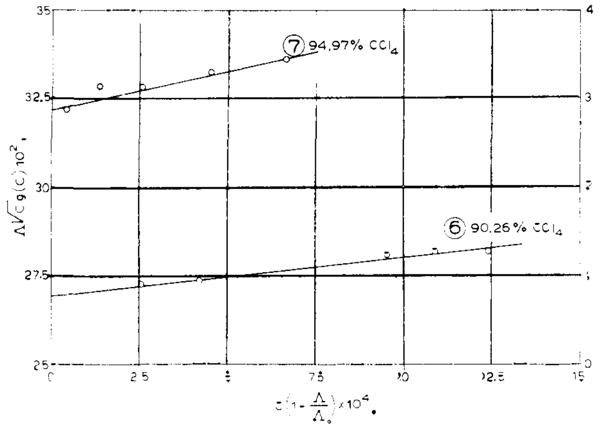

Fig. 3.—Triple ion plot for systems 6–7.

7, plotted according to eq. 5. By using Walden's rule and the value $\Lambda_0\eta = 0.386$ (based on the final value of Λ_0 for system 5), we find from the intercepts at $c = 0$ the values $K_A = 4.09 \times 10^4$ and 2.96×10^6 for systems 6 and 7, respectively. Assuming[17] that $\lambda_0 = \Lambda_0/3$, these values of K_A and the slopes of the lines of Fig. 3 give $k = 7.2 \times 10^{-3}$ and 1.0×10^{-3} for the triple ion constants of the two systems.

In Fig. 4, the logarithms of the pairwise association constants are plotted against reciprocal dielectric constant; the three points for systems 5-6-7 can be approximated by a straight line as shown. Assuming[18] that

$$K_A = K^0{}_A\, e^b \qquad (6)$$

where

$$b = e^2/aDkT \qquad (7)$$

the slope gives $\mathring{a} = 8.5$ for $Bu_4N{\cdot}BPh_4$. This value is, as expected, larger that the preliminary values reported[3] for this salt in several solvents where, for lack of information on the dependence of association on dielectric constant, the approximation $K_A \approx 0$ had to be made.

With the information obtained from systems 5–7, it becomes possible to analyze the data for the solvents of higher dielectric constant. We define a new variable Λ_K by the equations

$$\Lambda_K = \Lambda'_\eta - Jc \qquad (8)$$

$$= \Lambda_0 - K_A c f^2 \Lambda_\eta \qquad (9)$$

which are readily obtained from the general conductance equation by rearrangement. Here γ has been approximated by unity, and the value[3] $F = 2.0$ was used to calculate $\Lambda_\eta = \Lambda(1 + Fc)$. Now J is an explicit function of a; we used $\mathring{a} = 5.0$, 7.0 and 9.0 to calculate $J(a)$ and then Λ_K by means of (8). According to (9), Λ_K should be a linear function of $cf^2\Lambda_\eta$; as shown in Fig. 5, the data give straight lines when so plotted. The terms Jc and $K_A c f^2 \Lambda_\eta$ in the conductance equation oppose each other; therefore a larger a corresponds to a larger K_A. The problem is to solve equations 8 and 9 for J and K_A. No solution is possible without additional information, of course, because these equations actually are parts of the equation

$$\Lambda'_\eta = \Lambda_0 + Jc - K_A\, cf^2\Lambda_\eta \qquad (10)$$

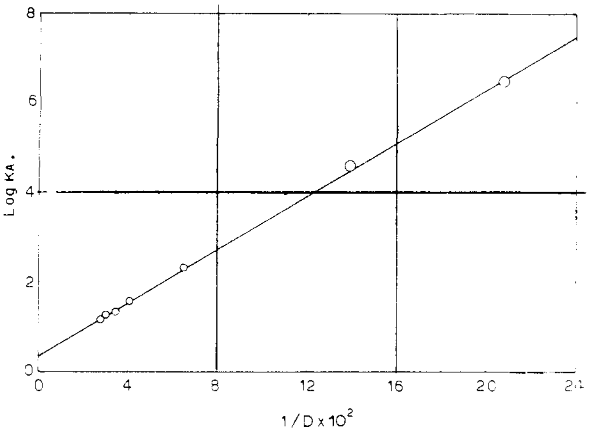

Fig. 4.—Dependence of association constant on dielectric constant.

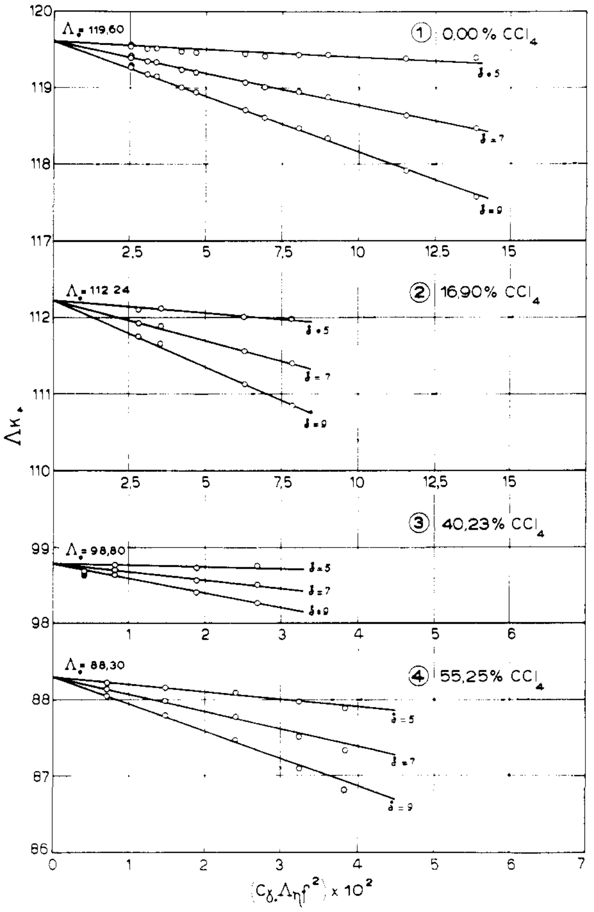

Fig. 5.—Equations 8 and 9 for applied to systems 1–4.

which, for high dielectric constants and low concentrations, is approximately

$$\Lambda'_\eta \approx \Lambda_0 + (J - K_A\Lambda_0)c \qquad (11)$$

In other words, the data serve only to evaluate the difference $(J - K_A\Lambda_0)$. But the information in Fig. 4 provides a method of resolving the difference into its two components. The slopes of the lines of Fig. 5 give $K_A(a)$ as a function of the trial values of $\mathring{a}$ used in computing $J(a)$. If we assume that a is independent of solvent composition, then the cor-

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[18] J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955); R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

rect value of a is the one which will give a set of log $K_A - D^{-1}$ points for systems 1–4 which will lie on the extrapolation of the line through the points for systems 5–7. The four points at the left in Fig. 5 are those obtained using $\mathring{a} = 9.0$ in (8). Within the validity of the various approximations made, this is in satisfactory agreement with the value $\mathring{a} = 8.5$ found from the slope of Fig. 4. The points obtained using J (5.0) and J (7.0) in (8) lie below any reasonable extrapolation of the line approximating the points for systems 5–7. Now $J(a)$ represents the change in mobility due to the higher terms in the conductance equation, while $K_A(a)$ of course describes the ion-pair equilibrium. The agreement between the values of a from J and from K_A shows that charge–charge interaction suffices to describe the behavior of $Bu_4N{\cdot}BPh_4$ in the solvent system CH_3CN–CCl_4. From the viscosity coefficient F, the value of the hydrodynamic radius was found[3] to be 5.4 Å., assuming the two ions to be of equal size. Center-to-center distance at contact, based on viscosity data, then would be 10.8. This is in fair agreement with the electrostatic parameter, $\mathring{a} \approx 9$, considering the completely different physical processes underlying the two results. Molecular models show that the nearest one can possibly bring the boron and nitrogen atoms of $Bu_4N{\cdot}BPh_4$ is about 7 Å.; this must represent the lowest possible bound for $\mathring{a}$. The two ions are, of course, not spheres; the boron–nitrogen distance averaged over random orientations of the two ions at contact must certainly be larger than this minimum figure, as we found above from the conductance (and viscosity) data.

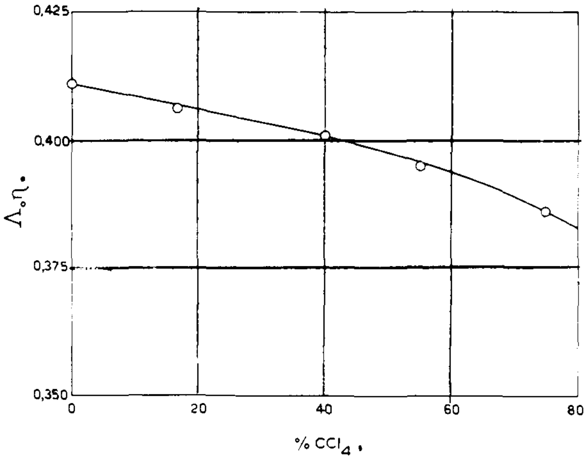

Fig. 6.—Dependence of Walden product on composition of solvent.

Finally, we consider the Walden products shown in Fig. 6. Both ions are much larger than the solvent molecules, and the system therefore should be a fairly good approximation to the Stokes model of a sphere in a continuum, for which the product $\Lambda_0\eta$ would be constant. Nevertheless, the product decreases by about 6% in going from acetonitrile to system 5; *i.e.*, as the viscosity increases from 0.00344 to 0.00550, the limiting conductance decreases faster than would correspond to Stokes friction. This result supports the tentative conclusion[4] that an ion–dipole relaxation force between the moving ion and the dipolar molecules of the solvent must also be considered in the analysis of ionic motion.

Rome, Italy

[Contribution No. 2383 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology]

A Rotor Aperture for the Determination of Optical Density within Rotating Ultracentrifuge Cells

By E. Robkin, M. Meselson and J. Vinograd

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The design and applications of an exponential aperture for analytical ultracentrifuge rotors are described. Images of the rotating aperture and ultracentrifuge cell are recorded side by side on absorption photographs. Photometry of these photographs provides the necessary data for accurate evaluation of optical density within the rotating cell.

The photographic determination of optical density within a cell during the operation of the analytical ultracentrifuge is of importance in many experiments.[1] It is convenient in such work to employ the film within the linear range of its characteristic response to exposure and to measure its optical density with a photometer possessing linear response to film optical density. These two conditions are expressed by the relation

$$\beta \log \text{exposure} = \text{Pen Deflection} + f_1 \qquad (1)$$

where β and f_1, are constants characteristic of the film specimen and the photometer.

Because film characteristics vary with emulsion and conditions of exposure and development, a verification of film linearity must be made whenever accurate work is to be done.

A convenient method for calibrating the response of the film and photometer has been developed through the construction of a special aperture in the rotor. Light passing through this rotating aperture produces a graded blackening on the film alongside the image of the centrifuge cell (Fig. 1). The shape of the aperture is chosen so that the photometric record of the graded blackening will be a straight line whenever the conditions expressed by equation 1 are satisfied. The appropriate aperture shape is given by

$$\theta(r) = \exp(K_1 r + K_2) \qquad (2)$$

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[1] T. Svedberg and K. O. Pederson, "The Ultracentrifuge," The Clarendon Press, Oxford, 1940, pp. 240–253.