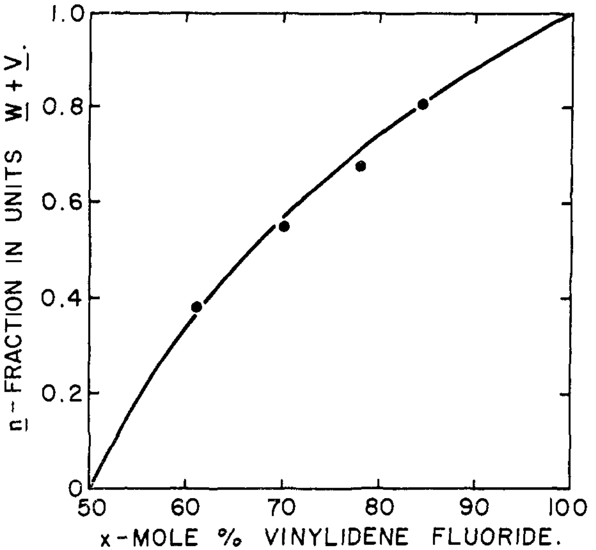

Fig. 2.—Fraction of vinylidene fluoride in units W + V *vs.* mole %: —, calculated; •, observed.

The relative concentrations of 1:1 copolymer and poly-(vinylidene fluoride) units were strongly dependent on the monomer ratio. Several intensity relationships could be used to calculate the ratios, with good consistency. The ratio of CF_3 line b *vs.* CF_2 line c appeared to give the greatest probable accuracy. However, the more general relationship $n = (c + g)/[c + g + {}^1/_2(d + e + f + h)]$ was preferred, since it required no assumption in regard to the relative concentration head-to-tail and head-to-head repeat units; n is defined as the fraction of vinylidene fluoride in units W + X.

Assuming no hexafluoropropylene–hexafluoropropylene repeat units occur, $n = (x - 50)/x$, where x is the mole % vinylidene fluoride. The calculated and observed relationships between n and x are shown in Fig. 2. The agreement was within experimental error. As a result of this analysis the structure of the copolymer can be expressed as $(U_{0.93}V_{0.07})_{1-n}(W_{0.95}X_{0.05})_{n/2}$.

Discussion

Analysis of the spectra of the vinylidene fluoride-hexafluoropropylene copolymers has shown (1) that certain modes of addition of the monomers to the propagating chain are highly preferred, (2) that little or no homopolymerization of hexafluoropropylene occurs, (3) that little or no chain branching occurs, and (4) that the four basic repeat units are randomly distributed. The second and third conclusions must be qualified, since the sensitivity of the nuclear resonance method was inadequate to detect homopolymer units, branches or unsaturation spaced at intervals greater than 10 to 20 monomer units.

A highly random arrangement of the four basic repeat units is required to account for the mole ratio-dependent line shapes of the CF_2 lines. These effects have been attributed to small chemical shifts due to β-carbon substituents, which can arise only at junctions between different repeat units. A block polymer of the type UUU...WWW..., etc., would have too few junctions to affect the line shapes measurably.

Two methods of analysis for the monomer ratios of the copolymers have been employed. The most general method uses the integrated CF_3 and CF_2 line intensities, and the relationship, mole % vinylidene fluoride = $(3\Sigma CF_2 - 2\Sigma CF_3)/3\Sigma CF_2$. This is an absolute method, provided that appropriate precautions against systematic intensity errors are taken.[4] A second method, used more routinely because of its simplicity, employs empirical calibration of the peak height ratios of lines b and c or h and c. With appropriate care, the mole % vinylidene fluoride can be obtained with a standard deviation of about 1%.

Acknowledgment.—The author extends his thanks to Dr. S. Dixon who prepared the copolymers studied and to Drs. R. E. Naylor and T. E. Beukelman for reference data and helpful discussions.

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(4) H. S. Gutowsky in W. G. Berl's "Physical Methods in Chemical Analysis," Academic Press, Inc., New York, N. Y., 1956, p. 370.

[CONTRIBUTION NO. 1588 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

Ion-pairing in Aqueous Ethanolic Solutions of Sulfonium Salts

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RECEIVED OCTOBER 16, 1959

The ionic association constants of trimethylsulfonium iodide in ethanol–water mixtures have been measured from 0 to 0.94 mole fraction ethanol by the static conductance method of Fuoss, *et al.* The degree of association to ion-pairs changes from slight ($K_A = 5$) in water-rich solvents to appreciable ($K_A = 120$) to ethanol-rich solvents. The results indicate that in ethanol-rich media the ion-pair equilibrium may be of importance in formulating the mechanism of sulfonium salt solvolysis.

Introduction

Interest in the kinetics of the neutral solvolysis of sulfonium salts has derived largely from the fact that such systems represent the case where the formal charge of the initial state is presumably dispersed on moving to the transition state of the rate determining step. Consequently it would be

$$R_2\text{–}S^+\text{–}R \longrightarrow (R_2\text{–}\overset{\delta_+}{S}\ldots\overset{\delta_+}{R}) \longrightarrow R_2S + R^+$$

expected that the transition state would be more favored as the solvent dielectric constant decreased and an increase in reaction rate observed. Behavior of this type was observed by Ingold and

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co-workers[3] in earlier investigations and more recently by Swain and co-workers.[4] In discussing the solvolysis mechanism, Swain and Kaiser[5] considered the possibility of an ion-pair contribution to the rate determining step as the dielectric constant of the solvent medium was reduced. In order to determine whether such an ion-pairing phenomenon was of importance, Swain and Kaiser attempted to detect ion-pair formation in the tribenzylsulfonium chloride system in 90% acetone–water ($D = 27$) by standard conductance determination methods. The salt concentration range employed was 5×10^{-2} to 4×10^{-4} molar. Analysis of the conductance data on the basis of the Onsager equation for strong electrolytes led these authors to the conclusion that the tribenzylsulfonium chloride in 90% acetone–water showed negligible ion-pairing in the concentration range studied. Our interest in this conclusion arose from the fact that although the rate of neutral solvolysis of sulfonium salts (I^-, Cl^-, Br^-, C_6H_5-So_3^-) is independent of the nature of the anion in highly aqueous media, the solvolysis rate appears to show a dependence on anion character as the dielectric constant of the medium is lowered below 30.[6] Subsequent to the work of Swain and Kaiser, Fuoss[7] reported a much improved method of detecting ion-pairing and measuring association constants (K_A), which recently has been applied to the tetraethylammonium picrate system in methanol–water mixtures.[8]

Attempts to reanalyze the conductance data of Swain and Kaiser by the newer Fuoss method revealed that the data were of insufficient accuracy to meet the precise requirements of the Fuoss analysis and no conclusion regarding the degree of association could be made.

We report here a reinvestigation of the problem through measurement of the conductance behavior of trimethylsulfonium iodide in aqueous ethanol mixtures and conclude from an analysis of the data by the Fuoss method that ion association is appreciable in media of dielectric constant less than 30.

Experimental

Materials.—Good distilled water was boiled for several hours with simultaneous passage of pure nitrogen and allowed to cool with continued nitrogen passage; conductance of the water was never greater than 10^{-6} mho.

Ethanol was distilled from sodium ethoxide and diethyl phthalate and used immediately in the preparation of working solutions.

Trimethylsulfonium iodide was prepared from dimethyl sulfide and methyl iodide in nitromethane solution and recrystallized twice from ethanol, m.p. 206–207°.

Conductance Determinations.—A calibrated standard type AC conductance bridge with oscilloscope balance point detection was used to measure resistances of solutions in a modified version of the stirred cell (Fig. 1) previously reported by Hyne and Robertson.[9] The cell constant, determined using aqueous KCl solutions, was 1.3755 ± 0.0005 (average of 5 determinations). Oil thermostat temperature was controlled at 25.000 ± 0.005°. The usual precautions were observed in establishing cell cleanliness. The main body of the cell was completely immersed in the thermostat fluid, the narrow inlet port and exhaust vent being the only parts of the solvent compartment above the level of the fluid. Solvent condensation was not a problem.

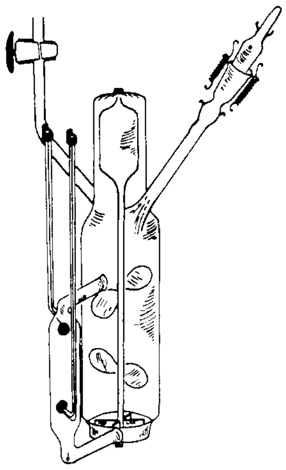

Fig. 1.—Conductance cell; detachable pear-shaped flask not shown.

Preparation of Working Solutions.—Bulk quantities (2 l.) of each solvent composition were prepared by weight and conductance determined. The most concentrated salt solution of each series was prepared by weight in an auxiliary pear-shaped flask which could be attached by a ground glass joint to the conductance cell for delivery of solution. The cell and contents then were weighed. Subsequent dilutions were made by returning the contents of the cell to the attached auxiliary flask containing a weighed amount of pure solvent and mixing thoroughly. The cell was flushed several times with the new solution and then refilled to the same level as in the previous determination. Cell and contents then were reweighed. By repetition of this procedure the series of salt concentrations obtained could be calculated from the various weighings and each conductance determination was made on the same volume of solution in the cell. Stirring was used in the cell to ensure thorough temperature equilibration but was stopped several minutes prior to each conductance determination. Successive resistance readings considered acceptable were constant to 0.05%

Results

Attempts were made initially to carry out a conductance study using dimethyl *tert*-butyl sulfonium iodide since the solvolysis of this salt is of particular kinetic interest. Even at 25°, however, the solvolysis reaction was sufficiently rapid to be detectable conductimetrically and to introduce conductance changes beyond the tolerances permitted in the Fuoss method of analysis. Consequently trimethylsulfonium iodide was chosen as a suitable model sulfonium salt; no conductance changes attributable to reaction at 25° could be detected over a period of several days.

The conductance data for a series of salt concentrations (c) in the ethanol–water mixtures studied are given in Table I. Since the purpose of this work was to establish the existence and degree of ion-pairing in the system under study, the range of solvent compositions in which ion-pairing was not appreciable was not studied in detail.

Evaluation of Association Constant K_A.—The method of Fuoss[7] was applied directly and is summarized below in so far as it applies to the evalua-

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[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953.

[4] C. G. Swain, L. E. Kaiser and T. E. C. Knee, THIS JOURNAL, **80**, 4092 (1958).

[5] C. G. Swain and L. E. Kaiser, *ibid.*, **80**, 4089 (1958).

[6] J. B. Hyne, to be published.

[7] R. M. Fuoss, THIS JOURNAL, **81**, 2659 (1959).

[8] F. Accascina, A. D'Aprano and R. M. Fuoss, *ibid.*, **81**, 1058 (1959).

[9] J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **35**, 623 (1957).

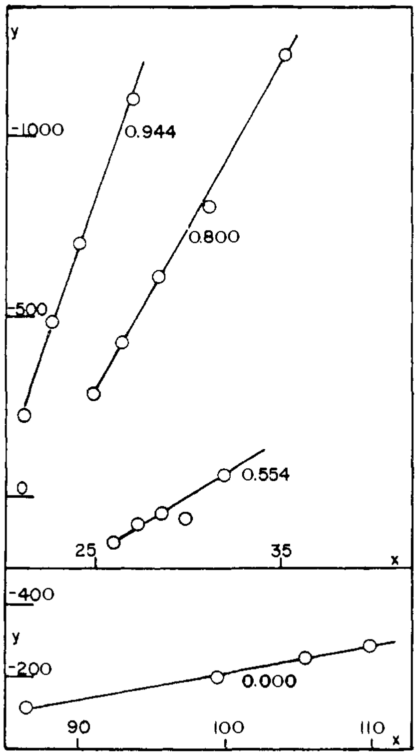

Fig. 2.—*y vs. x* function plot for various solvent compositions identified by mole fraction of ethanol.

tion of K_A. The basic conductance equation

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

where the symbols have the usual significance [see ref. 8] can be rewritten

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

where

$$\Lambda' = \Lambda_0 + Jc\gamma - K_A c\gamma f^2\Lambda - F\Lambda_0 c \quad (3)$$

Under conditions where the dielectric constant of the medium is relatively low and association is significant only the last term of equation 3 may be neglected as a first approximation. Equation 3 may then be rearranged to give

$$(\Lambda' - \Lambda_0)/c\gamma = J - K_A f^2\Lambda \quad (4)$$

which in turn gives

$$y = J - K_A x \quad (5)$$

where

$$y = (\Lambda' - \Lambda_0)/c\gamma \text{ and } x = f^2\Lambda$$

Plots of *y versus x* should therefore be linear (see Fig. 2) the slopes giving the value of K_A for each solvent composition. The critical unknown in the evaluation of the *y* terms is Λ_0. The linearity of plots of equation 5 is critically dependent upon the Λ_0 value [see ref. (8)] and the best value of Λ_0 can be obtained by successive refinement of the initial trial value obtained by back extrapolation of the simple Onsager plot of Λ *versus* $c^{1/2}$; Λ' for the *y* term evaluation is obtained from equation 2 using the Arrhenius approximation for $\gamma = \Lambda/\Lambda_0$ and employing the same Λ_0 trial value throughout. The *x* term is found using *f* values derived by the method of Fuoss.[10]

TABLE I

THE CONDUCTANCE OF TRIMETHYLSULFONIUM IODIDE IN ETHANOL–WATER MIXTURES AT 25° (SOLVENT COMPOSITION IN MOLE FRACTION ETHANOL)

$c \times 10^3$	Λ	$c \times 10^3$	Λ
EtOH = 0.0000		EtOH = 0.8001	
6.4553	111.479	3.8516	36.508
3.1829	114.597	3.0720	37.663
1.5746	116.818	2.2941	39.074
0.82567	118.204	1.5181	40.930
		0.74669	43.356
EtOH = 0.5546		EtOH = 0.9446	
4.9510	36.913		
3.9915	37.530	5.3915	33.094
3.1857	38.259	4.3544	34.331
2.5456	38.997	3.4743	35.782
1.6963	39.876	2.3247	38.232

TABLE II

COLLECTED CONSTANTS FOR TRIMETHYLSULFONIUM IODIDE IN VARIOUS ETHANOL–WATER MIXTURES

Mole fraction ethanol	D[a]	$\eta \times 10^3$[b]	Λ_0	K_A[c]	a[d]
0.0000	78.5	8.937	121.05	6.6	9.1
.5546	34.8	1.866	44.2	32	8.3
.8001	27.7	1.385	48.5	90	8.7
.9446	25.1	1.175	50.7	148	9.7

[a] Solvent dielectric constant interpolated from data of G. Akerlof [THIS JOURNAL, **54**, 4125 (1932)]. [b] Solvent viscosity interpolated from data of "International Critical Tables." [c] Association constant by Fuoss method [see ref. 7]. [d] Center to center distance of spheres electrostatically equivalent to ions in ion-pairs, Å. units.

The K_A values obtained are shown for each solvent composition in Table II together with other relevant constants for the system.

Discussion

The data in Table II show that above a solvent dielectric constant of 35 (approx. 0.6 mole fraction ethanol) the K_A does not exceed 40 which, for an arbitrary salt concentration of 10^{-3} molar, is equivalent to an association to ion-pairs of approximately 2%. The effect of such a degree of association might not be easily detectable by even the most precise kinetic methods although at higher salt concentrations the degree of association would be correspondingly greater. However, even at 10^{-3} molar the degree of association when $K_A = 120$ is 10%. Association of this order of magnitude could make a considerable contribution to the kinetic behavior of a reacting system of the sulfonium salt type and should be readily detectable.

The justification for concluding that the ion-pair behavior in the trimethylsulfonium iodide case is similar to that in the tribenzylsulfonium chloride system studied by Swain and Kaiser[5] merits attention. Since the macroscopic dielectric constant of the medium has been shown, in most cases studied, to be the major factor determining the effect of the medium on the degree of ion-pairing, it seems justifiable to conclude that acetone–water and ethanol–water mixtures having the same bulk dielectric constant can be compared. The ion-pairing model considered in the Fuoss treatment is that of the sphere in a continuum and consequently the extent of ion-pairing depends upon

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[10] R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

the proximity of the equivalent sphere centers attainable in the ion-pair configuration. We observe that in the tribenzylsulfonium chloride the cation is larger than that in the trimethylsulfonium iodide but that the anion is smaller. To some extent, therefore, the differences will be compensatory at least in so far as the radii of the equivalent spheres is concerned. Turning now to the more detailed point of the effect of the relative symmetries of the two cations on ion-pairing, there can be little difference in the two salts. In both cases there would be a symmetrical disposition of organic groups about the central sulfur atom affording approximately similar screening of the centrally located charge. On rather tentative grounds, however, it might be suggested that the three benzyl groups can delocalize the positive charge to a somewhat greater extent than the three methyl groups so enhancing the tendency to form ion-pairs in the former case. It seems reasonable to conclude that in the tribenzylsulfonium chloride system ion-pairing behavior would be at least similar to that in the trimethylsulfonium iodide case.

In Table II are shown values for the center-to-center distance of the spheres electrostatically equivalent to the ions in the ion-pairs (a). Although these values are not pertinent to the main conclusion of this paper attention has been drawn[11] to the unrealistically large values resulting from the application of the Fuoss treatment to this system. The values are "unrealistic" in so far as they exceed, by several ångström units, the values to be expected on the basis of a model of unsolvated, uniformly charged spheres in contact for the ion-pair configuration. Ions of the type under consideration, however, are neither spherical (on a microscopic scale) nor uniformly charged especially in the ion-pair configuration. Considerable difficulty always has been encountered in giving true physical significance to the value (a) as determined by conductance methods and Sadek and Fuoss[12] have stated that "so many unknown quantities are lumped together into the 'ion-size' that it has no clear physical meaning." Until such time as it is possible to determine the value of the center-to-center distance by methods free from complicating factors no real physical significance can be attached to the absolute values obtained by methods so far applied.

A further interesting point, not wholly unrelated to the explanation of the (a) values, concerns the applicability of the complex formalism of the Fuoss analysis to a system where the dielectric constant is varied by changing the composition of a binary mixture of relatively efficient solvating species. Here we are focussing attention on the "continuum" assumption of the ion-pair model. There is now ample evidence in the literature to suggest the reality of a "sorting" process in arranging the molecular composition of the immediate environment of an ion in a mixed solvent. The existence of such a "specific solvation" phenomenon clearly casts doubt on the validity of using the bulk dielectric constant (*D*) as a measure of the microdielectric in the immediate vicinity of the ion. It is indeed possible that the lack of recognition of such an effect in the model upon which the Fuoss treatment is based may, in part, be responsible for the high (a) values obtained. Until such time as it is possible to measure, directly or indirectly, the microdielectric constant there seems little choice but to use the value for the bulk dielectric constant and acknowledge its limitations.

It does not appear, however, that this criticism materially affects the major conclusion to be drawn from this study, namely, that the possibility of an ion-pair mechanism cannot be eliminated as being an important contributor to the over-all mechanism of the sulfonium salt solvolysis in media of dielectric constant less than or equal to 30.

Acknowledgments.—The authors wish to express their indebtedness to Prof. R. M. Fuoss and Dr. E. Hirsch for their helpful interest in this work and to Research Corporation for a grant-in-aid.

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[11] Comment of referee.

[12] H. Sadek and R. M. Fuoss, THIS JOURNAL, **76**, 5902 (1954).