

The Second Dissociation Constant of Sulfuric Acid in Acetonitrile and in Dimethyl Sulfoxide¹

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Abstract: From potentiometric $p\text{a}_\text{H}$ measurements with the glass electrode in mixtures of tetraethylammonium sulfate and bisulfate the second dissociation constant at 25° of sulfuric acid, denoted as $pK^{\text{d}}_{\text{HSO}_4^-}$, has been calculated to be 25.9 in acetonitrile (AN) and 14.5 in dimethyl sulfoxide (DMSO). Because of electrostatic repulsion the formation constant of the homoconjugation reaction $\text{SO}_4^{2-} + \text{HSO}_4^- \rightleftharpoons \text{H}(\text{SO}_4)_2^-$ in AN is only of the order of 30, while in DMSO, in which the bisulfate ion is strongly hydrogen bonded to the solvent, it is negligibly small. A previously reported value⁶ of $pK^{\text{d}}_{\text{HSO}_4^-}$ of 9.1 in DMSO as derived from $p\text{a}_\text{H}$ measurements in very dilute equimolar mixtures of sodium bisulfate and sulfate is some 5.5 units smaller than the value derived from the $p\text{a}_\text{H}$ of tetraethylammonium salts. This is due to the highly incomplete dissociation: $\text{NaSO}_4^- \rightleftharpoons \text{Na}^+ + \text{SO}_4^{2-}$. The dissociation constant of tetraethylammonium bisulfate in AN has been found to be 3×10^{-2} . At concentrations smaller than $1 \times 10^{-2} M$ the first dissociation of tetraethylammonium sulfate is virtually complete in AN, while $K_2 = [\text{Et}_4\text{N}^+][\text{SO}_4^{2-}]f_{\text{Et}_4\text{N}^+}f_{\text{SO}_4^{2-}}/[\text{Et}_4\text{NSO}_4^-]f_{\text{Et}_4\text{NSO}_4^-} = 5 \times 10^{-3}$. In DMSO both salts are practically completely dissociated at concentrations smaller than $1 \times 10^{-2} M$. From potentiometric $p\text{a}_\text{H}$ data in sulfuric acid-tetraethylammonium bisulfate mixtures in AN values of $pK^{\text{d}}_{\text{H}_2\text{SO}_4}$ and $K^{\text{f}}_{\text{H}(\text{SO}_4)_2^-}$ have been redetermined⁷ and found equal to 7.8 and 4×10^3 , respectively.

Numerous analytical papers have been published in which diprotic acids were titrated potentiometrically with the glass electrode as pH electrode in aprotic protophobic (*e.g.*, acetone) or aprotic protophylic (*e.g.*, pyridine or dimethylformamide) solvents with tetrabutylammonium hydroxide as titrant. From these studies it is clear that $pK_1 - pK_2$ in such solvents should be much greater than in water. For example, $pK_1 - pK_2$ of succinic acid in water is only 1.4 units and no inflection occurs at the first equivalence point in the potentiometric titration curve in water. On the other hand, a pronounced break was observed at the first equivalence point in solvents like acetone² or pyridine.³⁻⁵ The two dissociation constants of diprotic acids cannot be calculated from such studies, because the glass electrode had not been calibrated in the aprotic solvents. Moreover, as we will see in a subsequent paper, the pH of a mixture of the tetraalkylammonium salt of the monoprotic and the divalent sulfate anion is greatly affected by water, methanol, and other alcohols. The tetraalkylammonium hydroxide used as titrant always contains some alcohol; in addition water is formed during the titration.

We have instigated a study involving the determination of pK_1 and pK_2 of diprotic acids in the aprotic protophobic solvent acetonitrile (AN) and the aprotic protophylic solvent dimethyl sulfoxide (DMSO). The word aprotic solvent is used advisedly in a loose sense; it designates a solvent the acid properties of which are too weak to be measured quantitatively, even though solutions of alkali metal salts of the protophylic solvent DMSO have been prepared.

This paper deals with the determination of the second dissociation constant $K^{\text{d}}_{\text{HSO}_4^-}$ of sulfuric acid in AN and DMSO. $K^{\text{d}}_{\text{HSO}_4^-}$ was calculated from $p\text{a}_\text{H}$ values de-

termined with the glass electrode and also spectrophotometrically with phenol red and thymol blue as indicators in mixtures of tetraethylammonium bisulfate and sulfate. The dissociation constants of these salts were derived from conductance measurements in the two solvents.

In the exploratory study⁶ $K^{\text{d}}_{\text{HSO}_4^-}$ in DMSO was calculated from the spectrophotometrically determined ratio of the concentrations of the acid (yellow) and basic (blue) forms of dibromo-*o*-cresolbenzein in a mixture which supposedly was 0.0005 *M* in both sodium sulfate and bisulfate. In order to find the discrepancy with the data in the present paper we have determined the solubility of anhydrous sodium sulfate in DMSO and have titrated the saturated solution with sulfuric acid. Because of the slight solubility of the salt in DMSO we have determined the $p\text{a}_\text{H}$ of extemporaneously prepared highly dilute mixtures which were equimolar in sodium sulfate and bisulfate.

In our first paper⁷ the first dissociation constant of sulfuric acid, $K^{\text{d}}_{\text{HSO}_4^-}$, and the homoconjugation constant $K^{\text{f}}_{\text{H}(\text{HSO}_4)_2^-}$ were calculated from conductance and spectrophotometric data. At that time the glass electrode had not been calibrated and used for $p\text{a}_\text{H}$ measurements in AN. Values of the homoconjugation constant $K^{\text{f}}_{\text{H}(\text{HSO}_4)_2^-}$ and of $K^{\text{d}}_{\text{H}_2\text{SO}_4}$ as calculated from potentiometric $p\text{a}_\text{H}$ measurements in mixtures of sulfuric acid and tetraethylammonium bisulfate are more accurate than those obtained from the previous type of measurements. Hence, such $p\text{a}_\text{H}$ measurements have been carried out in the present work.

In mixtures of an unchanged monoprotic acid, HA, and its tetraalkylammonium salt $pK^{\text{d}}_{\text{HA}}$ was calculated from the $p\text{a}_\text{H}$ at the midpoint⁸ designated as $p\text{a}_{\text{H}^{1/2}}$

$$pK^{\text{d}}_{\text{HA}} = p\text{a}_{\text{H}^{1/2}} - \log f_{\text{A}^-}$$

(1) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-1223-67.

(2) J. Fritz and S. Yamamura, *Anal. Chem.*, **29**, 1079 (1957).

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(6) I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 89 (1962).

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In mixtures of a normal and acid tetraalkylammonium salt derived from a diprotic acid, H_2A , it is easily shown that

$$pK_{HA}^d = p_{a_{H^{1/2}}} - \log f_{A_2^-}/f_{HA^-}$$

where $K_{HA}^d = a_{H^+}a_{A_2^-}/a_{HA^-}$. The homoconjugation constants $K_{HA_2^-}^f$ and $K_{HA \cdot A_2^-}^f$ (the latter defined as $a_{HA \cdot A_2^-}/(a_{HA^-}a_{A_2^-})$) are calculated from the difference in $p_{a_{H^+}}$ from a given point on the titration curve and the midpoint, using the relation previously derived⁷

$$K_{HA_2^-}^f = [C_s r^2 - r(C_a + C_s) + C_a]/r(C_s - C_a)^2 \quad (1)$$

where C_a and C_s denote the analytical concentrations of HA and A^- and $r = a_{H^+}/a_{H^{1/2}}$. It is easily shown that in systems of R_4NHA and $(R_4N)_2A$ the expression similar to eq 1 for $K_{HA_2^-}^f$ has a factor f in the denominator, f being $f_{HA^-}f_{A_2^-}/f_{HA_2^{2-}}$.

Activity coefficients in AN and DMSO solutions when $\mu \geq 1 \times 10^{-2}$ for monovalent ions and $\geq 2 \times 10^{-3}$ for divalent ions were calculated using the partially extended Debye-Hückel expression $-\log f = Az^2\mu^{1/2}/(1 + Ba\mu^{1/2})$. In AN A and B are 1.51 and 4.8×10^7 , and in DMSO 1.12 and 3.9×10^7 . The crystallographic diameter of 3.10 \AA was taken for the unsolvated sulfate ion⁹ in both solvents, while values equal to 4 \AA for bisulfate¹⁰ and 6 \AA for the tetraethylammonium ions¹⁰ were taken from Kielland's tabulation in aqueous media and assumed to be the same in DMSO and AN. The ionic diameter of the homoconjugate ion, $HSO_4 \cdot SO_4^{2-}$, and the mono- and divalent forms of thymol blue and phenol red are also assumed to be 6 \AA in both solvents.

Experimental Section

Chemicals. Acetonitrile⁷ and dimethyl sulfoxide⁶ were purified and dispensed as described previously. The water contents of the above solvents were 3×10^{-3} and $7 \times 10^{-3} M$, respectively.

Anhydrous sulfuric acid,⁷ tetraethylammonium bisulfate,⁷ thymol blue,¹¹ and phenol red¹¹ were products used previously. Tetraethylammonium sulfate (normal salt) was prepared in the same way as the bisulfate salt and was recrystallized from petroleum ether "B" (bp $60-80^\circ$)-ethyl acetate mixture. Assay by titration to a sharp end point in AN with perchloric acid (in acetic acid) using α -naphtholbenzein as indicator gave 99.5%. Sodium sulfate was Merck Reagent Grade product, recrystallized once from water and dried *in vacuo* at 100° . A deaerated aqueous solution $2 M$ in the salt and $1 \times 10^{-5} M$ in brom thymol blue was green; the above solution turned blue in the presence of $3 \times 10^{-5} M$ sodium hydroxide and yellow in $3 \times 10^{-5} M$ hydrochloric acid, indicating the presence of $<10^{-3}\%$ acid impurity in the salt.

Solubility of Sodium Sulfate in DMSO. Purified DMSO (25 ml) was shaken overnight with 500 mg of anhydrous sodium sulfate and filtered through a fine porosity filter funnel. A 5-ml aliquot was titrated to a bisulfate end point with $0.0015 M$ sulfuric acid in DMSO using neutral red indicator. A blank was run at the same time. The $0.05 M$ stock solution of sulfuric acid solution in DMSO was standardized by flooding 1 volume with 25 volumes of water and titrating with aqueous sodium hydroxide. Brom cresol green served as indicator.

Conductometric,⁷ potentiometric,⁸ and spectrophotometric⁶ techniques and instrumentation have been described previously. All experiments have been carried out at $25.0 \pm 0.1^\circ$.

Results

Ionic Mobilities and Dissociation Constants of Salts. Conductivity data in AN of tetraethylammonium bisulfate and tetraethylammonium sulfate are presented

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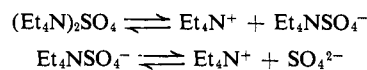
(10) J. Kielland, *J. Amer. Chem. Soc.*, **59**, 1675 (1937).

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Table I. Conductivity in Acetonitrile

Tetraethylammonium bisulfate		Tetraethylammonium sulfate	
$C_{(Et_4N)HSO_4}$, $M \times 10^3$	Λ	$C_{(Et_4N)_2SO_4}$, $M \times 10^3$	Λ
1.57	161	0.192	176
2.59	157.5	0.334	169
4.08	149.5	0.476	167
5.04	144	0.660	159
6.44	141	0.935	148
7.35	137.5	0.15	144
8.67	134	1.36	140.5
9.57	130.5	1.80	132.5
13.6	122	2.20	129
	$\Lambda_0 = 185$	2.80	119
		3.18	116.5
		3.71	114
		4.06	108.5
		4.73	104
		5.02	101
		5.65	98.5
			$\Lambda_0 = 205$

in Table I. From Λ_0 values and the values of $\lambda_0(Et_4N^+)$ of 85.05^{12} the following ionic mobilities were found: $\lambda_0(HSO_4^-) = 100$ and $\lambda_0(SO_4^{2-}) = 120$. The dissociation constant of tetraethylammonium bisulfate equal to 3×10^{-2} was found from a Fuoss and Kraus treatment of the data in Table I. Tetraethylammonium sulfate was found to dissociate into two steps, the first ionization



$K_{d_2} = [Et_4N^+][SO_4^{2-}]/[Et_4N^+][SO_4^{2-}]/[Et_4NSO_4^-]f_{Et_4NSO_4^-}$ constant, K_{d_1} , being very large. The Shedlovsky relation as modified by Dawson¹³ was used in the treatment

$$FA = \Lambda_0 - (1.5/K\Lambda_0)C_{(Et_4N)_2SO_4}f_{SO_4^{2-}} \times [(FA)^2 - 0.111\Lambda_0^2]$$

of the conductivity data and a plot of FA vs. $[(FA)^2 - 0.111\Lambda_0^2]$ entered in Figure 1. A value of K_{d_2} in AN equal to 5×10^{-3} was obtained.

From the conductance data in DMSO in Table II it

Table II. Conductivity of Tetraethylammonium Sulfate in DMSO

$C_{(Et_4N)_2SO_4}$, $M \times 10^3$	Λ
0.143	36.5
0.239	34.5
0.474	33.3
1.35	33.3
2.16	32.0
3.58	30.4
4.74	29.8
7.08	27.5
8.72	26.6
	$\Lambda_0 = 37.1$

is concluded that tetraethylammonium sulfate at concentrations less than $0.01 M$ behaves as a completely dissociated univalent electrolyte. The observed and

(12) J. F. Coetzee and C. P. Cunningham, *J. Amer. Chem. Soc.*, **87**, 2529 (1965).

(13) L. Dawson and M. Golben, *ibid.*, **74**, 4134 (1952).

calculated Onsager slopes of the Δ vs. $(N_{(\text{Et}_4\text{N})_2\text{SO}_4})^{1/2}$ plot are 78 and 110, respectively, while a value of $\Delta_0((\text{Et}_4\text{N})_2\text{SO}_4)$ equal to 37.1 was obtained from the intercept.

Potentiometric Determination of $pK^{\text{d}}_{\text{H}_2\text{SO}_4}$ in AN and $pK^{\text{d}}_{\text{HSO}_4^-}$ in AN and DMSO. In the calculation of $pK^{\text{d}}_{\text{H}_2\text{SO}_4}$ in AN and $pK^{\text{d}}_{\text{HSO}_4^-}$ from potentiometric data in both solvents both tetraethylammonium bisulfate and sulfate are assumed to be completely dissociated in the concentration range studied.

Sulfuric acid was previously found to be a strong uni-univalent electrolyte in DMSO.⁶ Values of pa_{H} in mixtures of tetraethylammonium bisulfate and sulfuric acid in AN as measured with the glass electrode are recorded in Table III. From this table $pK^{\text{d}}_{\text{H}_2\text{SO}_4}$ in AN

Table III. Glass Electrode pa_{H} Values in Sulfuric Acid-Tetraethylammonium Bisulfate Mixtures in AN

$C_{\text{H}_2\text{SO}_4}$, $M \times 10^3$	$C_{\text{Et}_4\text{NHSO}_4}$, $M \times 10^3$	pa_{H}	f	$K^{\text{f}}_{\text{H}_2\text{A}^{2-}}$ $\times 10^{-3}$
2.81	0.476	5.98	0.93	4.7
2.75	0.935	6.43	0.91	4.85
2.60	2.18	7.43	0.85	5.0
2.47	3.39	8.27	0.80	
2.26	4.98	8.95	0.77	4.8
1.95	7.61	9.56	0.74	3.9
0.935	0.476	7.12	0.93	4.3
0.920	0.935	7.82	0.89	
0.867	2.18	8.87	0.85	5.2
0.820	3.39	9.30	0.82	4.0
0.744	4.94	9.72	0.77	4.3
0.935	5.15	9.46	0.76	(2.8)
11.2	0.907	4.98	0.91	5.4
0.560	5.43	10.10	0.76	5.6
Av				5

was found to be 7.8 and $pK^{\text{f}}_{\text{H}(\text{HSO}_4)_2^-}$ equal to -3.6 . Potentiometric data obtained in tetraethylammonium bisulfate-sulfate mixtures in AN and DMSO are entered in Tables IV and V. Values of $pK^{\text{d}}_{\text{HSO}_4^-}$ equal to 25.9 and

Table IV. Glass Electrode pa_{H} in Tetraethylammonium Bisulfate-Tetraethylammonium Sulfate Mixtures in AN, $pK^{\text{d}}_{\text{HSO}_4^-} = 25.9$ (from $pa_{\text{H}^{1/2}}$)

$C_{\text{Et}_4\text{NHSO}_4}$, $M \times 10^3$	$C_{(\text{Et}_4\text{N})_2\text{SO}_4}$, $M \times 10^3$	pa_{H}	$f_{\text{HA}^{\text{f}}\text{A}^{2-}}/$ $f_{\text{HA}^{\text{d}}\text{A}^{2-}}$	$K^{\text{f}}_{\text{HA}^{\text{f}}\text{A}^{2-}}$ $\times 10^{-1}$
0.348	0.97	26.30		
0.692	0.97	25.90		
1.38	0.96	25.63		
2.76	0.94	25.35		
4.96	0.91	24.92	3.3	2.3
7.97	0.88	24.53	4.3	3.3
12.1	0.86	24.10	5.7	3.6
Av				3

Table V. Glass Electrode pa_{H} Values in Tetraethylammonium Bisulfate-Tetraethylammonium Sulfate Mixtures in DMSO

$C_{\text{Et}_4\text{NHSO}_4}$, $M \times 10^3$	$C_{(\text{Et}_4\text{N})_2\text{SO}_4}$, $M \times 10^3$	pa_{H}	f_{HA^-}	$f_{\text{A}^{2-}}$	$pK^{\text{d}}_{\text{HSO}_4^-}$
0.56	3.88	15.00	0.80	0.41	14.47
1.40	3.88	14.57	0.79	0.39	14.44
2.82	3.88	14.30	0.785	0.38	14.48
4.80	3.88	14.08	0.78	0.37	14.47
7.90	3.88	13.80	0.764	0.34	14.37
12.7	3.88	13.53	0.744	0.31	14.37
Av					14.45

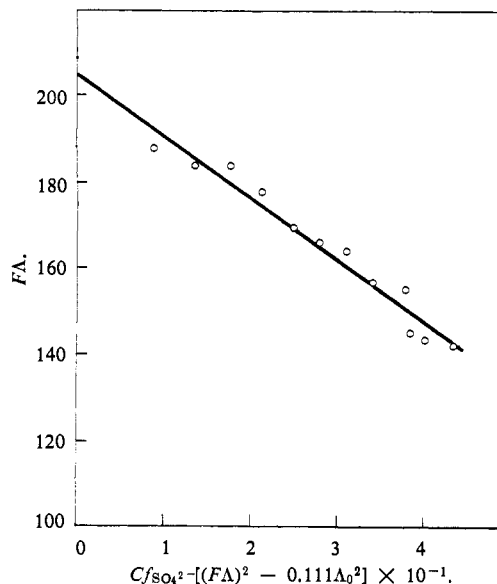


Figure 1. FA vs. $C_{\text{fSO}_4^{2-}} - [(FA)^2 - 0.111\Delta_0^2]$ plot of tetraethylammonium sulfate in AN: slope = 1.42; $\Delta_0 = 205$ from intercept).

14.45 were found in AN and DMSO, respectively, while the homoconjugation constant, $K^{\text{f}}_{\text{H}(\text{SO}_4)_2^-}$, was approximately equal to 3×10^1 in AN. No evidence of homoconjugation was found in DMSO.

Spectrophotometric Determination of $pK^{\text{d}}_{\text{HSO}_4^-}$ in DMSO. A few spectrophotometric measurements in DMSO have been made in dilute solutions of $1.3 \times 10^{-3} M$ tetraethylammonium sulfate and 1×10^{-4} to $6.8 \times 10^{-3} M$ bisulfate using both thymol blue and phenol red as indicators. The $pK^{\text{d}}_{\text{HT}}$ of these indicators has been reported¹⁴ to be 15.3 and 13.7, respectively. A value of $pK^{\text{d}}_{\text{HSO}_4^-}$ found with these indicators was equal to 15.1. Even in mixtures with considerably greater ionic strength, which varied between 0.013 and 0.05, the same value of $pK^{\text{d}}_{\text{HSO}_4^-}$ was found, even though values of activity coefficients are much smaller and less certain than in the above dilute solutions. No explanation can be offered for the relatively large difference in $pK^{\text{d}}_{\text{HSO}_4^-}$ values found potentiometrically and colorimetrically.

Solubility of Sodium Sulfate and pa_{H} of Mixtures of Sodium Sulfate-Bisulfate in DMSO. The concentration of sodium sulfate in its saturated solution in DMSO was found to be of the order of $3 \times 10^{-5} M$. To the saturated solution was added an approximately isohydric solution of phenol red in DMSO. The indicator adopted an intermediate color, indicating a pa_{H} of the order of 14. This pa_{H} is considerably smaller than that observed in a $3 \times 10^{-5} M$ tetraethylammonium sulfate solution in carbon dioxide free DMSO, so the indicator was completely in its basic form in the latter. A trace of bisulfate in the sulfate might have been responsible for this result.

In order to verify the previously reported value⁶ of $pK^{\text{d}}_{\text{HSO}_4^-}$ equal to 9.1 as calculated from the spectrophotometrically determined value of pa_{H} in a mixture which reportedly was $5 \times 10^{-4} M$ both in sodium sulfate and bisulfate, a mixture was prepared in carbon dioxide free DMSO which was $1.4 \times 10^{-4} M$ in both tetraethyl-

(14) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *J. Amer. Chem. Soc.*, **90**, 23 (1968).

ammonium sulfate and bisulfate and $4 \times 10^{-4} M$ in sodium perchlorate. The $p\alpha_H$ of this solution was measured immediately after preparation using dibromothymolbenzein as indicator¹⁴ and found equal to 10 ± 0.2 . In order to exclude any possible precipitation of sodium sulfate a similar solution was prepared which was five times as dilute in the reagents as above. The $p\alpha_H$ was found to be of the same order of magnitude as that in the more concentrated mixture.

Discussion

It is of interest that the difference in $pK_{\text{HSO}_4^-}^d$ in AN and DMSO is $25.9 - 14.5 = 11.4$ as compared to a difference of 9.7 for monoprotic acids, the anions of which have a localized charge, and of about 11.5 for monoprotic acids, the undissociated form of which have intramolecular hydrogen bonding in AN. Using values for $r_{\text{HS}^+} = 5 \text{ \AA}$, $r_{\text{HSO}_4^-} = 4 \text{ \AA}$, and $r_{\text{SO}_4^{2-}} = 4 \text{ \AA}$ the Born correction would yield a value of $\Delta pK_{\text{HSO}_4^-}^d$ of $11.4 - 0.6 = 10.8$. Using $r_{\text{SO}_4^{2-}} = 1.6 \text{ \AA}$ $\Delta pK_{\text{HSO}_4^-}^d$ would become $11.4 - 1.5 = 9.9$. It seems doubtful whether the bisulfate ion in AN has intramolecular hydrogen bonding.

The difference between $pK_{\text{HSO}_4^-}^d$ of 2 in water and that in AN of 25.9 and DMSO of 14.45 is very large. In addition to the difference in basicity of the solvents,¹⁴ it must be attributed to a major extent to the fact that the sulfate ion is virtually unsolvated in DMSO and AN, indicating that the logarithm of the medium activity coefficient of SO_4^{2-} as referred to water as the standard state is large. In spite of the nakedness of the sulfate ion in the two organic solvents the homoconjugation in DMSO is negligible, while in AN it is small ($K_{\text{H}(\text{SO}_4)_2}^f = 30$ in AN). DMSO hydrogen bonds the bisulfate ion and thus competes with the sulfate ion. The electrostatic repulsion between the univalent bisulfate and the divalent sulfate ion in both solvents strongly interferes with the hydrogen bonding between the two ions, thus accounting for the fact that the homoconjugation constant $K_{\text{H}(\text{SO}_4)_2}^f$ is so small. As will be shown in a subsequent paper association in AN of sulfate with bi-

sulfate ion and BH^+ (B is an amine) is extremely pronounced when the charge of the sulfate ion is neutralized by BH^+ in the form of slightly dissociated $(\text{BH}_2)\text{SO}_4$. It may be added here that conjugation of the sulfate ion in AN with uncharged proton donors which does not involve a charge effect is much stronger than that with univalent ions.

In DMSO ion-dipole interaction between sulfate and solvent is hardly possible, as the positive center of the solvent dipole is hidden by the methyl groups. The fact that the Walden product $\eta\Lambda_{0(\text{Et}_4\text{N})_2\text{SO}_4}$ in AN and DMSO is found in this paper to be 70.7 and 72.8, respectively, even though the viscosity, η , of DMSO is approximately six times as large as that of AN indicates that also in AN the sulfate ion as well as the tetraethylammonium ion are virtually unsolvated.

At concentration less than 0.01 M tetraethylammonium sulfate the salt can be considered to be completely dissociated in DMSO; in AN the first dissociation is virtually complete and even the constant for the second dissociation is large (5×10^{-3}).

The solubility of sodium sulfate in AN is immeasurably small and it is only of the order of $10^{-5} M$ in DMSO. By working with extemporaneously prepared mixtures which were extremely dilute and equimolar in sodium bisulfate and sodium sulfate (see Results) the previously low value of $p\alpha_H$ of the order of 9.6–10 has been confirmed, whereas in the same mixtures with tetraethylammonium instead of sodium as the cation a value of 14.5 is found. Assuming that the first dissociation in DMSO of sodium sulfate is complete it may be inferred that the dissociation $\text{NaSO}_4^- \rightleftharpoons \text{Na}^+ + \text{SO}_4^{2-}$ is extremely small, even though the sodium ion is considerably solvated in DMSO.

The value of the over-all constant ($pK_{2(\text{HA})}$) of 4.2 of sulfuric acid in AN is in good agreement with the value of 4.2 found previously,⁷ from spectrophotometric data with indicators. The values for the constants of the first dissociation of sulfuric acid, $pK_{\text{H}_2\text{SO}_4}^d = 7.8$, and of the homoconjugation, $pK_{\text{H}(\text{SO}_4)_2}^f = -3.6$, are considered more reliable than the values of 7.2 and -3.4 derived previously⁷ from conductometric data.