282. *Conductivity Studies of Some Thiosulphates in Aqueous Methanol and in Aqueous Ethanol.*

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The conductivities of sodium, potassium, magnesium, calcium, and strontium thiosulphates have been measured in 44% aqueous ethanol,* and the sodium salt in 20%, 50%, and 80% aqueous methanol. The dissociation constants of the ion-pairs have been calculated.

In order to consider the effect of incomplete dissociation of some thiosulphates in reaction rates involving these salts, their dissociation constants have been obtained by Davies's conductivity methods.[1] The conductivity measurements and the resultant calculations

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* In this and the following two papers, *e.g.*, 44% aqueous alcohol denotes 44 parts by wt. of alcohol contained in 100 parts of solution.

[1] Davies, *Trans. Faraday Soc.*, 1927, **23**, 351.

are given in Tables 1, 2, and 3, where c = equivs./l., Λ = equivalent conductivity, K = dissociation constant of the ion-pairs, and b, b_1, and b_2 are the Onsager factors referred to later.

TABLE 1. *Conductivity of sodium thiosulphate in aqueous methanol at 25°.*

20% (w/w) Methanol; $\Lambda_0 = 92{\cdot}56$; $b_1 = 111{\cdot}3$; $b_2 = 58{\cdot}6$.

10^4c	4·2116	5·0219	6·3985	6·6299	9·2036	10·972	14·121
Λ	89·60	89·31	88·88	88·79	88·10	87·61	86·89
K	0·12	0·12	0·12	0·11	0·12	0·11	0·10

50% (w/w) Methanol; $\Lambda_0 = 72{\cdot}65$; $b_1 = 118{\cdot}1$; $b_2 = 60{\cdot}9$.

10^4c	3·0415	4·1464	5·0964	6·4248	7·8016	10·299	16·184
Λ	69·68	69·13	68·70	68·12	67·63	66·79	65·14
10^2K	2·52	2·62	2·48	2·47	2·54	2·54	2·52

80% (w/w) Methanol; $\Lambda_0 = 81{\cdot}20$; $b_1 = 206{\cdot}9$; $b_2 = 107{\cdot}4$.

10^4c	3·0159	3·9043	4·7769	5·4463	6·4692	7·8324	9·5171
Λ	74·41	73·32	72·68	71·68	70·72	69·56	68·32
10^3K	4·40	4·44	4·47	4·48	4·47	4·48	4·52

TABLE 2. *Conductivity of potassium thiosulphate in* 20% *(w/w) methanol at* 25°.

$\Lambda_0 = 106{\cdot}96$; $b_1 = 116{\cdot}5$; $b_2 = 62{\cdot}5$.

10^4c	2·9152	3·7230	4·6076	5·2215	6·1791	7·4172	10·942
Λ	104·29	103·91	103·53	103·26	102·92	102·54	101·45
10^2K	6·8	6·9	6·8	6·2	6·5	7·1	6·8

TABLE 3. *Conductivities of magnesium, calcium, strontium, sodium, and potassium thiosulphates in* 44·05% (w/w) *ethanol.*

Magnesium: 20°; $\Lambda_0 = 43{\cdot}05$; $b = 116{\cdot}5$.

10^4c	2·7791	3·5083	4·9022	6·9794	9·2837	9·8065
Λ	34·67	33·59	32·01	29·94	28·25	27·97
10^4K	4·95	4·96	4·95	4·95	4·93	4·94

Magnesium: 25°; $\Lambda_0 = 50{\cdot}55$; $b = 139{\cdot}4$.

10^4c	2·3981	2·6037	3·0742	3·6590	3·7591	6·0142	7·6791
Λ	41·24	40·86	39·88	38·92	38·73	35·76	34·08
10^4K	4·68	4·72	4·67	4·70	4·68	4·70	4·63

Magnesium: 30°; $\Lambda_0 = 59{\cdot}24$; $b = 166{\cdot}7$.

10^4c	2·4998	3·4686	3·6801	5·3954	7·0260	7·6633	9·9301
Λ	47·75	45·41	45·17	42·12	40·23	39·33	37·41
10^4K	4·43	4·35	4·38	4·40	4·41	4·38	4·39

Calcium: 25°; $\Lambda_0 = 52{\cdot}25$; $b = 142{\cdot}3$.

10^4c	1·8578	2·5581	3·0154	3·6191	4·0461	4·9162	6·0350
Λ	42·20	40·24	39·20	37·90	37·15	35·82	34·18
10^4K	3·26	3·25	3·26	3·23	3·25	3·26	3·20

Strontium: 25°; $\Lambda_0 = 52{\cdot}15$; $b = 142{\cdot}1$.

10^4c	1·9432	2·1851	2·5653	3·0052	3·0830	4·1010	5·2311
Λ	40·51	39·77	38·68	37·62	37·39	35·39	33·55
10^4K	2·60	2·61	2·60	2·61	2·59	2·61	2·60

Sodium: 25°; $\Lambda_0 = 51{\cdot}30$; $b_1 = 82{\cdot}6$; $b_2 = 42{\cdot}6$.

10^4c	2·6246	3·5295	4·2758	6·8994	7·9731	9·6160
Λ	49·20	48·78	48·52	47·60	47·25	46·80
10^2K	1·47	1·43	1·49	1·46	1·42	1·42

Potassium: 25°; $\Lambda_0 = 57{\cdot}50$; $b_1 = 86{\cdot}0$; $b_2 = 45{\cdot}1$.

10^4c	2·3407	2·8582	4·1840	4·9764	5·0228	6·0654
Λ	55·31	55·05	54·39	54·05	53·98	53·62
10^2K	1·18	1·21	1·16	1·15	1·14	1·16

Approximate values of Λ_0 were obtained by extrapolation of the plots of Λ against $\sqrt{c}$. For the sodium and potassium salts, except in 80% methanol, more precise values of Λ_0 were then found by Onsager's method,[2] *i.e.*, by plotting $(\Lambda + b\sqrt{c})$ against c, where b is

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[2] Onsager, *Phys. Z.*, 1927, **28**, 277.

the calculated coefficient of Onsager's conductivity expression, $\Lambda = \Lambda_0 - bI^{\frac{1}{2}}$, I being the ionic strength. For these extrapolations it was assumed that $I = c$. The physical constants used were taken from recent data,[3] and the dielectric constants [4] D, the viscosities [5] η, and the densities [6] d used in working out the results are :

Solvent	Temp.	D	$10^3\eta$	d	Solvent	Temp.	D	$10^3\eta$	d
20% Methanol	25°	69·2	13·90	0·9641	44·05% Ethanol	20°	53·95	28·71	0·9267
50% Methanol	25	54·8	15·42	0·9134	,,	25	52·50	23·85	0·9229
80% Methanol	25	40·7	10·12	0·8433	,,	30	51·12	20·06	0·9189

For the other examples the methods of Davies [1] and of Owen [7] were used in obtaining Λ_0.

The dissociation constants of the alkaline-earth thiosulphates were derived by first inserting Λ_0 for Λ_x on the right-hand side of

$$\Lambda_x = \Lambda_0 - b(\Lambda_c/\Lambda_x)^{\frac{1}{2}}$$

where Λ_x represents the conductivity at an ionic concentration of $\alpha c = \Lambda c/\Lambda_x$ and where α is the degree of dissociation. Values of Λ_x were successively tried in the equation until constant figures were reached. The dissociation constants were then calculated from :

$$K = \alpha^2 c f_{\mathrm{M}} f_{\mathrm{S_2O_3}}/(1 - \alpha)$$

for which the mean ion activity coefficients were obtained from the limiting form of the Debye–Hückel expression :

$$-\log f_{\mathrm{i}} = 1{\cdot}8246 \times 10^6 z_{\mathrm{i}}^2 (DT)^{-\frac{3}{2}} I^{\frac{1}{2}}$$

Here z_{i} is the ion valency, and the ionic strength $I = 2\alpha c$.

The sodium and potassium data were treated similarly. We have

$$\Lambda = (\beta/2)(\Lambda_{0,1} - b_1 I^{\frac{1}{2}}) + (1 - \beta)(\Lambda_{0,2} - b_2 I^{\frac{1}{2}})$$

where $\Lambda_{0,1}$ is the sum of the mobilities of the M^+ and the $MS_2O_3^-$ species, $\Lambda_{0,2}$ is the sum of the M^+ and $S_2O_3^{2-}$ mobilities, and b_1 and b_2 are the respective Onsager factors. The fraction of salt present as ion-pairs is represented by β and $I = c(1{\cdot}5 - \beta)$. The mobility of the $MS_2O_3^-$ ion-pair is rather uncertain and we have estimated it as follows. In water the mobility [8] of the thiosulphate ion is 87·4; and from the figures for the alkaline-earth cations in water [9] and the values of Λ_0 for their thiosulphates in 44% ethanol the ratio Λ_0 (44% ethanol)/Λ_0 (water) = 0·36. We have therefore taken Λ_0 for the thiosulphate ion to be 87·4 × 0·36 = 31·3 and thus assumed $NaS_2O_3^-$ and $KS_2O_3^-$ to have the value of 16·0. Calculation shows that an error of 1 unit has little effect on the value of K. By similar comparisons we deduce 29·0 for the $NaS_2O_3^-$ ion-pair in 20% methanol, 23·0 in 50% methanol, and 26·0 in 80% methanol. The average dissociation constants are given in Table 4.

Among the numerous factors which influence the extent to which ions associate in solution is their effective size. Where essentially electrostatic interaction occurs, Bjerrum[10] has proposed a quantitative relation between the dissociation constant and the effective radius of the ion pair. These values (a in Å) are given in Table 4, together with the corresponding figures for water as solvent. Except for $KS_2O_3^-$ in 44% ethanol, the effective radii of the ion-pairs in water are bigger, implying that in mixed solvents ion-hydration tends to decrease.

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[3] Rossini, Gucker, Johnston, and Pauling, and Vinal, *J. Amer. Chem. Soc.*, 1952, **74**, 2699.

[4] Akerlöf, *ibid.*, 1932, **54**, 4125; Broach and Amis, *J. Chem. Phys.*, 1954, **22**, 39.

[5] (*a*) " International Critical Tables," Vol. V, p. 22; (*b*) Tammann and Pillsburg., *Z. anorg. Chem.*, 1928, **172**, 250.

[6] Ref. 5*a*, Vol. III, pp. 111—116.

[7] Owen, *J. Amer. Chem. Soc.*, 1939, **61**, 1393.

[8] Denney and Monk, *Trans. Faraday Soc.*, 1951, **47**, 992.

[9] Harned and Owen, " Physical Chemistry of Electrolytic Solutions," Reinhold, New York, **1950**, p. 172.

[10] Bjerrum, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1926, **7**, No. **9**.

TABLE 4. *Collected data.*

Ion-pair	Solvent	10^4K (solvent)	10^4K (water)	a (solvent)	a (water)	R
$NaS_2O_3^-$	44% EtOH	144	2100	3·84	5·5	0·999
$KS_2O_3^-$	44% EtOH	117	1200	3·41	3·9	0·957
MgS_2O_3	44% EtOH	4·67	145	4·47	8·5	0·963
CaS_2O_3	44% EtOH	3·25	104	4·15	7·1	0·952
SrS_2O_3	44% EtOH	2·60	92	4·00	6·4	0·951
MgS_2O_3 (20°) ...	44% EtOH	4·95	—	—	—	—
MgS_2O_3 (30°) ...	44% EtOH	4·39	—	—	—	—
$KS_2O_3^-$	44% EtOH	680	1200	4·46	3·9	1·029
$NaS_2O_3^-$	20% MeOH	1100	2100	5·32	5·5	1·042
$NaS_2O_3^-$	50% MeOH	243	2100	4·69	5·5	0·913
$NaS_2O_3^-$	80% MeOH	45	2100	4·07	5·5	0·669

A semiquantitative relation between ion mobilities and their radii is expressed by Stokes's law, which in terms of limiting mobilities becomes

$$r_i = 8{\cdot}197 \times 10^{-9} z_i/\lambda_0\eta$$

where r_i is the ion radius, z_i is its valency, and λ_0 is its limiting mobility. In terms of anion and cation this may be written

$$\eta(\lambda_{0,1} + \lambda_{0,2}) = \eta\Lambda_0 = 8{\cdot}197 \times 10^{-9}(z_1/r_1 + z_2/r_2)$$

When the radii remain constant we have the familiar Walden's rule,[11] $\Lambda_0\eta$ = constant, whence, $\Lambda_0\eta$ (water) = $\Lambda_0\eta$ (solvent). The ratio of these two is given in Table 4 under R. Except for 50% and 80% methanol these are all within 5% of unity implying that no real change takes place in the effective radii of the ions until the alcohol content becomes high. This is in contrast to the deductions made above on the basis of Bjerrum's treatment, and seems to imply that in solvents of lower dielectric constant where the dissociation constants become much smaller the forces of ion-association are no longer purely electrostatic.

When the conventional thermodynamic functions are applied to the data for magnesium thiosulphate in 44% ethanol the following figures emerge where $\Delta H°$ is the heat of dissociation and $\Delta S°$ is the corresponding entropy change:

$$\Delta H° \text{ (20—25°)} = -2{\cdot}16,\ \Delta H° \text{ (25—30°)} = -2{\cdot}10 \text{ kcal./mole};\ \Delta S° \text{ (25°)} = -22{\cdot}0$$

The $\Delta S°$ value is very close to that found for several thiosulphates in aqueous solution.[12]

EXPERIMENTAL

The conductivity apparatus has been described elsewhere.[13] The conductivity water was prepared by a mixed ion-exchange resin column.[14] Pure ethanol and methanol were prepared by shaking the commercial alcohols with quicklime, allowing the whole to stand several days, and then distilling under nitrogen. The solvents were made up by weight and stored under nitrogen.

" AnalaR " sodium thiosulphate was recrystallised from water below 80° and dried at 35°. The equivalent weight was found for each batch by titration against standard potassium iodate. Potassium thiosulphate of B.D.H. Laboratory Reagent grade was recrystallised four times. Magnesium thiosulphate was made by adding magnesium sulphate solution dropwise to a stirred suspension of barium thiosulphate in slight excess. After filtration the solution was evaporated under a vacuum at 35° till crystals were formed. The solution was filtered and most of the remaining barium thiosulphate precipitated by alcohol. The magnesium salt crystallised from the filtrate after evaporation at 25°, and was recrystallised 3 times from alcohol–water. Determinations of equivalent weight showed the crystals to be $MgS_2O_3,6H_2O$. Strontium thiosulphate crystallised when concentrated sodium thiosulphate and strontium chloride

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[11] Walden, *Z. phys. Chem.*, 1912, **78**, 257.

[12] Gimblett and Monk, *Trans. Faraday Soc.*, 1955, **51**, 793.

[13] Davies, *J.*, 1937, 432; Davies and Monk, *J.*, 1949, 413.

[14] Davies and Nancollas, *Chem. and Ind.*, 1950, 129.

solutions were dripped into a small volume of ice-water; the crystals were washed with aqueous ethanol and recrystallised three times from water; they proved to be $SrS_2O_3,5H_2O$. Alcohol was added to a saturated solution of B.D.H. calcium thiosulphate until about 10% had been precipitated; this was filtered off and discarded; most of the remainder was precipitated by alcohol, then redissolved, and the procedure was repeated thrice; the crystals obtained were $CaS_2O_3,5H_2O$.

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