733. *The Conductivity of Some Salts in Ethanol–Water Mixtures.*

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The conductivities of cobaltous chloride and sulphate, magnesium sulphate, potassium bromate, silver nitrate, and zinc perchlorate in some ethanol–water mixtures at 25° c are reported and discussed.

The equivalent conductances at 25° c are reported for magnesium and cobaltous sulphates in a series of ethanol–water mixtures; some results of James [1] for zinc and copper sulphates are available for comparison. In addition measurements have been made with cobaltous chloride, potassium bromate, silver nitrate, and zinc perchlorate in 50%(w/w) ethanol.

Results

The results for 50% ethanol–water mixtures are in Table 1. To save space, the conductances of magnesium and cobaltous sulphates in other solvents are given at round concentrations in Table 2.* The results are the mean of two or more (usually four) independent runs. The solvent correction (2—4 × 10^{-7} ohm^{-1}) has been subtracted.

Table 1. *Conductances in 50% ethanol–water at 25°.*

	$MgSO_4$			$CoSO_4$			$CoCl_2$	
Run	10^4C	Λ	Run	10^4C	Λ	Run	10^4C	Λ
1	2·3375	29·01	1	1·3821	29·74	1	2·1272	43·68
2	3·2040	26·99	2	1·4680	29·65	1	2·8092	43·42
1	4·0615	25·29	2	2·2025	26·75	2	3·1009	43·28
2	4·8856	24·12	1	2·5729	25·49	1	3·9848	42·98
1	6·0615	22·62	2	3·2028	24·19	2	4·4474	42·89
2	8·3810	20·49	1	3·3806	23·61	1	6·3074	42·36
1	8·6090	20·36	2	4·4621	21·84	2	8·0239	41·97
2	11·286	18·73	1	6·5017	19·32	2	11·943	41·20
1	13·243	17·76	2	7·0107	18·97			
1	16·388	16·56	1	9·1482	17·44		$Zn(ClO_4)_2$	
2	17·258	15·97	1	12·921	15·66	Run	10^4C	Λ
1	24·750	14·42	3	18·698	13·54	1	2·3010	44·82
3	33·653	13·71	3	36·320	10·63	2	2·7121	44·73
4	43·581	11·80	4	44·894	9·73	2	3·7358	44·56
3	50·910	11·46	3	57·515	8·96	1	4·5556	44·35
4	70·249	10·02	4	69·132	8·44	2	5·2114	44·28
3	94·732	8·81	3	76·206	8·11	2	7·4790	43·88
			4	90·843	7·61	1	7·7885	43·79
						1	11·244	43·41
						2	14·050	42·96

			$KBrO_3$						$AgNO_3$		
Run	10^4C	Λ	Run	10^4C	Λ	Run	10^4C	Λ	Run	10^4C	Λ
1	1·5667	46·66	2	7·8058	45·75	1	2·6973	47·74	2	17·165	46·42
2	1·5838	46·62	3	10·674	45·41	2	3·1634	47·59	3	18·989	46·27
1	2·1401	46·51	4	11·030	45·31	1	3·4641	47·57	4	20·959	46·19
2	2·2936	46·47	3	12·287	45·26	2	4·0411	47·52	3	22·710	46·06
1	2·5126	46·42	4	15·424	45·02	1	4·8578	47·42	4	33·306	45·51
2	2·9334	46·31	3	23·909	44·39	2	6·4953	47·27	3	49·810	44·83
1	3·6594	46·19	4	37·904	43·71	1	8·4177	47·06	4	57·874	44·49
2	4·3081	46·13	3	50·874	43·02	1	11·938	46·77	3	86·180	43·58
1	5·8162	45·89	3	63·622	42·51				4	113·16	42·89
1	6·1361	45·80	4	78·710	41·95						

When the results for the sulphates are plotted against the square root of the concentration slopes much steeper than the limiting Onsager slope are given. This is attributed to ion-pair formation, and Owen's method [2] was used for determining Λ_0. At ethanol concentrations of 20% or more the method was unsatisfactory, and for these solutions the Λ_0 values in Table 2

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* Full results are reported by G. O. Thomas, Thesis, University of Wales, 1955.

[1] James, *J.*, 1951, 153.

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

are those which, by trial and error, give the most constant K values when applied to the measurements below $C = 1 \times 10^{-3}$ (g.-equiv./l.).

TABLE 2.

	Ethanol, wt. %									
	5	10	15	20	30	40	50	10	30	50
10^4C				$MgSO_4$					$CoSO_4$	
0	112·6	95·5	81·8	71·1	55·2	48·50	43·50	95·2	57·50	42·50
1	108·4	92·0	78·2	67·2	51·2	42·48	33·20	91·2	51·7	31·50
2	106·2	89·8	76·0	65·1	49·25	39·45	30·00	88·9	48·9	27·49
3	104·3	88·1	74·4	63·6	47·75	37·42	27·53	87·0	46·75	24·49
5	101·6	85·3	71·7	61·2	45·4	34·02	24·01	84·1	43·3	21·15
7	99·4	83·2	69·7	59·2	43·45	31·70	21·72	81·8	40·95	18·89
10	96·6	80·6	67·1	56·8	40·95	29·10	19·45	78·8	38·0	16·92
20		74·6	61·5		35·3	24·26	15·22	72·1	32·45	13·17
40					29·7	19·90	12·36	64·7	27·15	10·20
70					25·0	16·77	10·00	57·9	23·25	8·36
100							8·60	53·9	21·1	7·33

Dissociation constants for comparison with the known values[3] in aqueous solution were obtained from the equation: $K = f_{\pm}^2\alpha^2C/2(1 - \alpha)$ by successive approximations. $f_{\pm}$ is the mean ion-activity coefficient and α the fraction of salt present as free ions, and it was assumed that the limiting equations of Debye and Hückel and Onsager can be applied to the very dilute solutions studied. These assumptions cannot be separately justified, but it has been shown in previous work that in the conductivity method of determining dissociation constants the

FIG. 1.

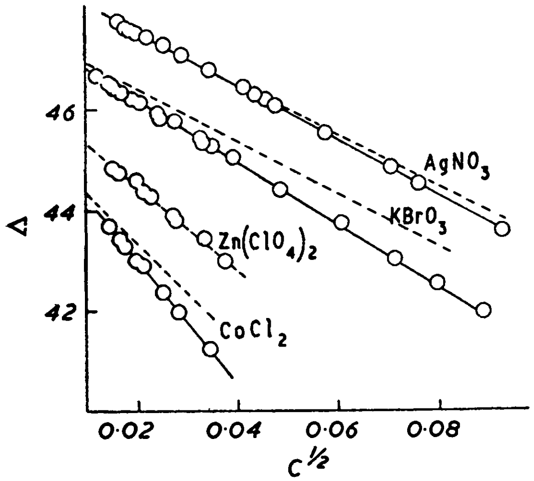

TABLE 3.

Ethanol (wt. %)	Ethanol (mole fraction)	Density[5] (g./ml.)	Viscosity[6] (millipoise)	Dielectric constant[7]	pK $MgSO_4$	pK $CoSO_4$
0	0	0·99708	8·95	78·54	—	—
5	0·0202	0·98817	10·8	75·80	2·41 ± 0·01 (9)	—
10	0·0417	0·98043	13·2	72·80	2·47 ± 0·01 (10)	2·58 ± 0·01 (10)
15	0·0646	0·97334	16·0	69·90	2·63 ± 0·01 (7)	—
20	0·0891	0·96864	18·0	67·00	2·76 ± 0·02 (8)	—
30	0·1436	0·95067	22·0	61·10	2·97 ± 0·02 (6)	3·245 ± 0·003(9)
40	0·2069	0·93148	23·7	55·00	3·416 ± 0·005 (10)	—
50	0·2812	0·90985	23·7	49·00	3·86 ± 0·01 (7)	3·98 ± 0·01 (7)

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[3] Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609; Dunsmore and James, *J.*, 1951, 2925.
For refs. 5–7 see p. 3662.

effects of higher terms neglected in the limiting equations cancel out rather exactly; and it is believed that the K values reported are as reliable as can be obtained at the present time.[4] Table 3 gives the constants used, and the values of pK ($= -\log_{10} K$) derived from the data. The figure following the pK value gives the average deviation of the separate determinations from the mean, and the number in parentheses is the number of determinations.

The remaining salts were studied in 50% ethanol only, and the results are shown in Fig. 1. The broken lines are the limiting Onsager slopes. Of the bi-univalent salts, zinc perchlorate conforms with the theoretical slope extremely well, and clearly contains few, if any, ion-pairs at these concentrations. By direct extrapolation $\Lambda_0 = 46{\cdot}10$. Cobaltous chloride is weaker, and by Onsager's method [8] of plotting ($\Lambda + bC^{\frac{1}{2}}$) against C (where b is the Onsager slope) we obtain $\Lambda_0 = 45{\cdot}30$. It can be assumed that in the concentration range studied ion association does not go beyond the first stage: $Co^{2+} + Cl^- = CoCl^+$, and an approximate idea of the dissociation constant of the $CoCl^+$ ion may be obtained by the method previously applied to aqueous solutions.[9] For this purpose the equivalent conductances of all three ions are needed, and we have assumed (*a*) that the transport numbers at zero concentration are the same in 50% ethanol–water as in water, and (*b*) that the mobility of $CoCl^+$ is one-half that of the Co^{2+} ion. The values used are not very critical; an alteration of 30% in the mobility adopted for $CoCl^+$ alters the derived K value by only 5%. The mean pK value obtained for the $CoCl^+$ ion from eight determinations is $1{\cdot}63 \pm 0{\cdot}02$.

Of the uni-univalent salts, potassium bromate appears to be appreciably associated. Extrapolation by Onsager's method gives $\Lambda_0 = 47{\cdot}40$, and calculations of the kind applied to the bi-bivalent salts lead to a value pK = $1{\cdot}216 \pm 0{\cdot}006$ (7 points). With this uni-univalent salt only the conductances below $C = 4 \times 10^{-4}$ could be used in the calculation; thereafter K showed a definite upward trend. Silver nitrate is a stronger salt, and direct extrapolation in conformity with the limiting Onsager equation gives $\Lambda_0 = 48{\cdot}55$. The salt probably contains ion-pairs, for the experimental line lies below the Onsager slope at all concentrations.

DISCUSSION

Walden's rule is not obeyed in ethanol–water mixtures. If the Walden product $\Lambda_0\eta$ for magnesium sulphate is plotted against the percentage of alcohol in the solvent, the curve rises to a maximum at 15% ethanol and then falls steadily away. This is just what has been found by Bateman and Ewing [10] for strontium chloride and bromide in ethanol–water mixtures, and by Longsworth and MacInnes [11] for salts in water–methanol mixtures. It follows that if Stokes's law were used to estimate the mean ionic radius of a salt in these mixtures, the values on adding alcohol would first become smaller than that calculated for an aqueous medium and would then rise again. The same facts are shown in a different way in Fig. 2, where the fluidity ratio and the Λ_0 ratio in different solvent mixtures are compared. The fluidity ratio, ϕ(water)/ϕ(solvent), is shown by the continuous line. It is unlikely that the changes are really due to changes in the ionic radii, and it may not be without significance that the divergence first becomes serious at a solvent structure where the initial decrease in fluidity is being halted and reversed.

When the pK values of Table 3 are plotted against the reciprocal of the dielectric constant, the points are found to lie on straight lines. That of cobalt sulphate has the slope required by Bjerrum's ion-association theory; [12] that is, the mean ionic diameter of 3·78 Å derived from this theory for aqueous solutions also fits the pK results in ethanol–water mixtures. For magnesium sulphate the experimental line has a markedly steeper slope than the theoretical; the mean ionic diameters calculated from Bjerrum's equation

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[4] Cf. Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1957, **79**, 3310.
[5] " Internat. Critical Tables," Vol. 3, p. 116.
[6] Interpolated from " Internat. Critical Tables," Vol. 5, p. 22.
[7] Interpolated from Åkerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4132.
[8] Onsager, *Physikal. Z.*, 1927, **28**, 277.
[9] Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592.
[10] Bateman and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 2137.
[11] Longsworth and McInnes, *J. Phys. Chem.*, 1939, **43**, 239.
[12] Bjerrum, *Kgl. danske Vidensk. Selskabs*, 1926, **7**, no. 9.

for this salt fall steadily from 5·1 Å in water to 4·0 Å in 50% ethanol. James has found similar trends for zinc and copper sulphates, and has suggested that the cause may lie not in variations in effective radii, but in a divergence of the dielectric constant effective for encounters from the value measured for the solvent. Another explanation of the discrepancy, which recognises the discrete nature of the solvent, is that the free energy of ion-pair formation contains a contribution from solvent-interaction energy changes in addition to that calculated from Coulomb's law.

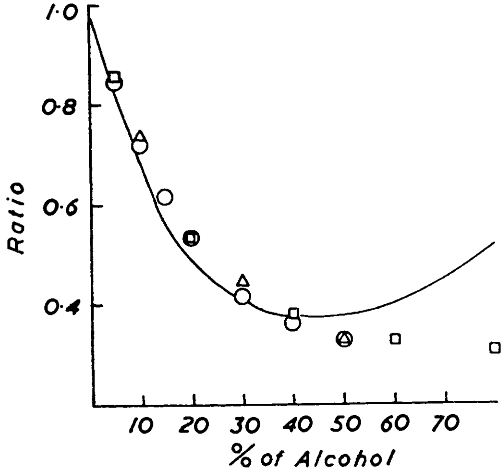

FIG. 2. *The experiment points give the plot of Λ_0 ratio, the continuous line the plot of the fluidity ratio, both against % of alcohol in the solvent.*

○ $MgSO_4$. △ $CoSO_4$. □ $SrCl_2$.

EXPERIMENTAL

Solvent mixtures. Absolute ethyl alcohol was shaken for several hours with freshly burnt quicklime. Immediately before use it was distilled and collected under nitrogen, the first and the last portion (each 10%) being rejected. The water was prepared by mixed-bed deionisation. Solvent mixtures were made up by weight and kept under nitrogen, and the composition of each was checked by a density determination.

Salts. Zinc perchlorate was prepared by heating " AnalaR " zinc oxide with the calculated quantity of " AnalaR " perchloric acid to dissolution. The crystals obtained on cooling were washed and recrystallised from aqueous alcohol. The other salts were " AnalaR " specimens that had been recrystallised from conductivity water. Stock solutions were made up by weight, when possible, and their concentrations were checked by analysis.

Measurements. The apparatus has been described previously, and was freshly calibrated. The oil thermostat maintained a temperature of 25° ± 0·01°. The cell was of the Hartley–Barrett type with greyed electrodes, and a stream of purified nitrogen passed through it whilst additions from a weight-burette were made. The resistance readings showed no tendency to drift with time.

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