E.M.F. STUDIES OF ELECTROLYTIC DISSOCIATION

PART 2.—MAGNESIUM AND LANTHANUM SULPHATES IN WATER

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The cell $H_2 \mid HCl, X \mid AgCl—Ag$, where X is $MgSO_4$ or $La_2(SO_4)_3$ has been used to examine ion-association between Mg^{2+} or La^{3+} and SO_4^{2-} ions from 20° to 35° C. The results are compared with those which have been obtained by the conductivity method.

Hitherto, the deviations of the conductivities of dilute solutions of sulphates from the values predicted by the appropriate limiting forms of the theoretical Onsager equation have provided practically all the available information concerning the dissociation of these salts. Thus Davies,[1] using this method, derived $K = 0.0061$ for the dissociation constant of $MgSO_4$ at 18° C, and Dunsmore and James,[2] using the same method, obtained $K = 0.0062$ at 25° C. The other ion-pair considered in the present paper, i.e. $LaSO_4^+$ has by this treatment a dissociation constant [3] of 1.8×10^{-4} at 18° C, while conductivity measurements [14] at 25° C yield the value of 2.0×10^{-4}. In this second example we have one of the few independent checks on the extent of interaction between SO_4^{2-} and metallic cations since the strongly enhanced solubility of $La(IO_3)_3$ in K_2SO_4 solutions at 25° C, as reported by La Mer and Goldman,[4] was shown by Davies [3] to be explicable if $LaSO_4^+$ ions form under such conditions. A quantitative treatment gave the dissociation constant as 2.2×10^{-4}.

These two electrolytes, $MgSO_4$ and $La_2(SO_4)_3$, since they are derived from an acid which does not fully ionize, should be capable of study by the method suggested in part 1 of this series,[5] namely, by addition of them to the cell $H_2 \mid HCl \mid AgCl—Ag$. As it happens, very precise measurements are required to obtain accurate information concerning the extent of interaction (the reasons are discussed later), but the results reported here do indicate the value of the method.

The magnitude of the dissociation constants of the ion-pairs $MgSO_4$ and $LaSO_4^+$ are derived from the e.m.f. measurements as follows. If α represents the concentrations of HSO_4^- ions, and β_1 and β_2 represent the concentrations of $MgSO_4$ and $LaSO_4^+$ ion-pairs respectively when the molalities are $m_1 = HCl$, $m_2 = MgSO_4$, $m_3 = La_2(SO_4)_3$, then the concentrations of H^+ ions are derived from the e.m.f. relation

$$F(E - E°)/(2.3026\,RT) + \log f_H f_{Cl} + \log m_1 = -\log m_H, \qquad (1)$$

so the differences between these and m_1 gives α, and the substitution of these in the dissociation constant expression for HSO_4^- gives the concentrations of free SO_4^{2-} ions, i.e.,

$$\log m_{SO_4} = \log K_2 + \log \alpha - \log f_H f_{SO_4}/f_{HSO_4} - \log m_H. \qquad (2)$$

The concentrations of the ion-pairs are thus obtained by difference:

$$\beta_1 = m_2 - \alpha - m_{SO_4} \text{ and } \beta_2 = 3m_3 - \alpha - m_{SO_4}. \qquad (3)$$

Successive approximations are needed to obtain the true values of these concentrations. The activity coefficient expression referred to in part 1 [5] and the

values of K_2 in that paper were used. The appropriate expressions for the ionic strengths are:

$$I = m_1 + 4m_2 - 2\alpha - 4\beta_1 \text{ for the MgSO}_4 \text{ solutions,}$$

and
$$I = m_1 + 15m_3 - 2\alpha - 6\beta_2 \text{ for the La}_2(SO_4)_3 \text{ solutions,}$$

and the dissociation constants have been computed from

$$K_{MgSO_4} = (m_2 - \beta_1)(m_2 - \alpha - \beta_1)f_{Mg}f_{SO_4}/\beta_1$$

and
$$K_{LaSO_4^+} = (2m_3 - \beta_2)(3m_3 - \alpha - \beta_2)f_{La}f_{SO_4}/\beta_2 f_{LaSO_4}.$$

EXPERIMENTAL

A.R. quality $MgSO_4$ was recrystallized 3 times from conductivity water, heated for 3 h at 140° C, then ground and an appropriate amount heated to constant weight at 320° C. Hirano [6] has shown that this temperature renders the salt anhydrous. The weighing bottle was then added to a solution of HCl of known molality. The preparation of the HCl has been described [5] in part 1. $La_2(SO_4)_3, 9H_2O$ crystals were prepared from pure $La(NO_3)_3$ (B.D.H.) and A.R. grade H_2SO_4 solutions. These crystals were recrystallized 3 times from conductivity water and dried by the method of Nathan, Wallace and Robinson.[7] A sample was heated to 650° C and this showed the crystals to have the given formula to within 0·02 %. A strong aqueous solution of these had a pH of 5·5, but this slight hydrolysis was considered to be suppressed in the presence of HCl. Stock solutions were made by adding weighed amounts to HCl solutions and stirring with a stream of N_2 for about 12 h in order to obtain the crystals in solution. The e.m.f. system has been described [5] in part 1.

DISCUSSION

The experimental results and the derived data are given in tables 1 and 2.

TABLE 1.—E.M.F.S OF THE CELL H_2 (1 ATM) | HCl (m_1), $MgSO_4$ (m_2) | AgCl—Ag
$10^3 m_1$: (a) 7·762, (b) 5·893, (c) 5·294, (d) 7·666.
$10^3 m_2$: (a) 3·795, (b) 4·596, (c) 5·762, (d) 6·933.

soln.	E(V)	$10^4\alpha$	$10^4\beta_1$	$10^3 I$	10^3K	E (V)	$10^4\alpha$	$10^4\beta_1$	10^3I	$10^3 K$
			20° C					25° C		
a	0·4806	8·28	5·35	19·15	5·06	0·4821	8·99	5·84	18·81	4·33
b	0·4952₅	7·65	7·75	19·65	5·09	0·4970₅	8·30	8·61	19·08	4·26
c	0·5017	8·10	11·46	22·14	4·89	0·5037	8·82	12·37	21·63	4·26
d	0·4839₅	12·57	13·17	27·62	5·33	0·4857	13·59	14·30	26·96	4·57
			30° C					35° C		
a	0·4834₅	9·68	6·57	18·38	3·54	0·4846₅	10·46	6·98	18·06	3·09
b	0·4988	9·08	9·08	18·79	3·82	0·5003₅	9·83	9·56	18·49	3·40
c	0·5056₅	9·64	12·91	21·25	3·87	0·5073	10·40	13·97	20·67	3·31
d	0·4872	14·51	16·16	26·06	3·67	0·4886	15·59	17·21	25·40	3·19

For several reasons the results obtained do not represent the most accurate that should be obtainable by this method. The chief of these is due to the potentiometer being a type where the e.m.f.s could only be read to ± 0·1 mV, and an error of this order would produce a variation of 10 to 20 % in the dissociation constants calculated from the most dilute solutions studied. Such large variations lie in the fact that H_2SO_4 itself is comparatively strong; where the acid of the associating anion is weaker, the reliability of the results is less dependent on the accuracy of the measured e.m.f.s. In spite of this drawback, our results are of sufficient value to demonstrate the value of this treatment. A second experimental weakness lies in the reproducibility of the AgCl electrodes. Although these were carefully checked against the HCl data of Harned and Ehlers,[8] they do appear to be subject to small inaccuracies. This point has been discussed

by Hills and Ives,[9] and has been commented upon in part 1 of this series.[5] Taking these factors into consideration, the agreement between the average figures (table 3), and those derived by conductivity measurements (which were reviewed at the beginning of this paper) is sufficiently close to examine in detail.

In both cases the e.m.f. results are lower than those which have been obtained by the conductivity method, and it is worth examining the theoretical bases of both methods to see if these can account for the discrepancies. Taking firstly conductivities, these are based on a treatment which uses a limiting form of Onsager's conductivity theory, i.e. it is only strictly valid at extremely low concentrations. As Davies has commented,[10] where $\Lambda^\circ - \Lambda$ is 10 % of Λ°, the

TABLE 2.—E.M.F.S OF THE CELL H_2 (1 ATM) | HCl (m_1), $La_2(SO_4)_3$ (m_3) | AgCl—Ag

$10^3 m_1$: (a) 6·037, (b) 5·901, (c) 6·036, (d) 6·030.
$10^4 m_3$: (a) 5·865, (b) 7·618, (c) 9·803, (d) 29·90.

soln.	E (V)	$10^4 \alpha$	$10^4 \beta_2$	$10^3 I$	$10^4 K$	E (V)	$10^4 \alpha$	$10^4 \beta_2$	$10^3 I$	$10^4 K$
		20° C						250° C		
a	0·4899	2·57	7·08	10·07	1·54	0·4914₅	2·85	6·96	10·09	1·54
b	0·4915	3·10	9·69	10·89	1·62	0·4931	3·43	9·71	10·82	1·53
c	0·4909₅	3·87	12·83	12·27	1·77	0·4925₅	4·23	13·06	12·16	1·60
d	0·4944₅	8·37	48·06	20·37	1·56	0·4963₅	9·14	48·68	19·85	1·40
		30° C						35° C		
a	0·4928₅	3·13	7·13	9·93	1·38	0·4941	3·48	6·98	9·95	1·39
b	0·4944₅	3·76	9·83	10·69	1·42	0·4958₅	4·17	9·74	10·65	1·40
c	0·4939₅	4·59	13·41	11·77	1·37	0·4952₅	5·04	13·34	11·67	1·32
d	0·4981	10·03	48·86	19·56	1·32	0·4996₅	10·32	49·48	19·02	1·17

second order terms which are neglected in the Onsager equation probably amount to a 1 % correction. This means that the calculated conductivity of a fully ionized electrolyte is 1 % too low, and if this is taken into consideration the calculated extent of dissociation of electrolytes such as those considered here becomes somewhat greater. For this reason the method used by Davies, which was also used [5] in part 1, namely, plotting log K' against $I^{\frac{1}{2}}$, where K' is the concentration dissociation constant, and then using the theoretical Debye-Hückel slope to decide where the extrapolation to $I = 0$ should lie, has much in its favour. This approach should eliminate most of the uncertainties in the conductivity treatment, and was essentially the means whereby the previously quoted figure of

TABLE 3.—AVERAGE VALUES OF THE DISSOCIATION CONSTANTS

°C	$MgSO_4$	$LaSO_4^+$
20	0·0051	0·00016₂
25	0·0044	0·00015₂
30	0·0037	0·00013₇
35	0·0032₅	0·00013₃

0·0061 for $MgSO_4$ at 18° C was obtained. Taking our e.m.f. figures, an approximate extension from 20° C to 18° C would give $K = 0·0054$, so that the discrepancy is less than appears upon a first consideration. Dunsmore and James,[2] as mentioned earlier, give $K = 0·0062$ at 25° C, but this was the result of averaging the results over a concentration range, using the Debye-Hückel activity coefficient expression to correct for ionic strength effects. It may be observed, however, that a plot of their pK data against concentration has a distinct drift towards a lower K value. The extrapolation method of Davies has therefore been applied ; the calculations are given in table 4 and are plotted in fig. 1, using the theoretical Debye-Hückel slope in the extrapolation. This method points to K being 0·0054

at 25° C, so that at this temperature also the difference between the conductivity and e.m.f. results is narrowed down.

The preceding remarks concerning the useful range of the Onsager treatment naturally apply also to our second example, $La_2(SO_4)_3$, but in addition another complication arises since the ion-pair formed has a residual charge. In deducing dissociation constants from conductivity data where charged ion-pairs arise, some assumption has to be made concerning their mobilities. It is usual to multiply that of the parent ion by the ratio of the charges carried by the two. The

TABLE 4.—CALCULATIONS BASED ON CONDUCTIVITY DATA [2] FOR $MgSO_4$ AT 25° C

$10^4 C$	Λ	α	$10^2 I^{\frac{1}{2}}$	$-\log K'$	$10^4 C$	Λ	α	$10^2 I^{\frac{1}{2}}$	$-\log K'$
1·6196	127·31	0·9890	1·79	2·142	8·5946	117·85	0·9561	4·05	2·048
1·7021	127·11	0·9880	1·82	2·160	11·194	115·50	0·9476	4·48	2·042
3·2672	124·27	0·9790	2·53	2·124	12·011	114·92	0·9458	4·77	2·002
3·9871	123·13	0·9750	2·79	2·130	14·393	113·14	0·9391	5·20	1·982
5·3847	121·34	0·9685	3·23	2·096	16·759	111·61	0·9329	5·60	1·956
6·1798	120·33	0·9649	3·39	2·070	17·692	111·02	0·9318	5·74	1·949
8·5401	117·89	0·9563	4·04	2·049					

uncertainty thus introduced decreases as the valencies of the associating ions increases, since the extent of ion-association rapidly increases with their valency product, and should not be serious in the present case. On the other hand, attempts to overcome the approximations in the Onsager treatment become much more difficult since a plot of log (concentration) dissociation constant against $I^{\frac{1}{2}}$ is very steep and is difficult to extrapolate, especially if data for very dilute solutions are not available. This occurs with our present example. Although the conductivity measurements extend down to 0·0004 equiv./l., it is impossible
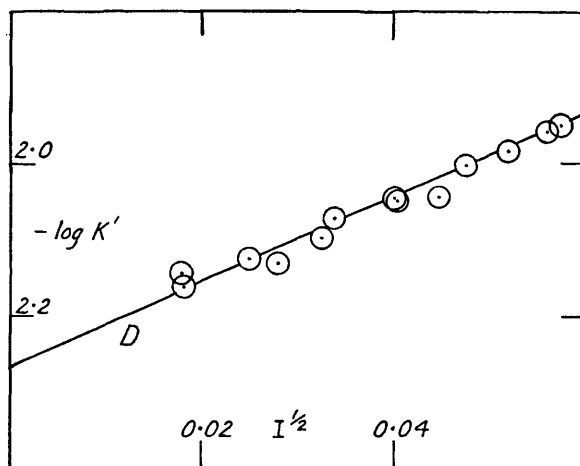

FIG. 1.—Plot of log (concentration) dissociation constant for $MgSO_4$ from conductivities. D, theoretical Debye-Hückel slope.

to extend the curve to zero ionic strength with any certainty. Furthermore the slope is less steep than that required by the Debye-Hückel theory. All one can say on this basis is that it is highly probable that $K = 2·0 \times 10^{-4}$ is too high and that the difference between this and the lower e.m.f. result of $1·52 \times 10^{-4}$ is more apparent than real.

In reviewing the possible errors in the e.m.f. method (apart from the experimental limitations mentioned earlier), there appear to be two distinct types. Firstly, the ion activity coefficient expression used [5] is of a general nature. Any errors

arising from this should be manifest by trends in the derived constants over a range of ionic strengths. Our measurements have been confined to rather low ionic strengths of a limited range but the drifts in the values of K do not appear to be significant. It would be profitable to extend the measurements with more refined apparatus to still lower ionic strengths to clear up this point; extension to higher ionic strengths would not be useful since they would not only multiply any uncertainties arising from the activity coefficient expression but would also increase the errors arising from the second source of errors. This second factor arises in that we are dealing with solutions containing several ionic species. Accordingly other types other than those considered here, may possibly occur. In the $MgSO_4$ solutions for instance, we have not considered any association that may develop between Mg^{2+} and HSO_4^- ions. A somewhat similar case, namely the interaction between Mg^{2+} and NO_3^- ions, has been examined by Righellato and Davies,[12] who estimate the dissociation constant of $MgNO_3^+$ to be $1 \cdot 0$. If this is taken as a criterion, it is evident that provided the concentration product of Mg^{2+} and HSO_4^- ions is kept low (as it was in the solutions studied here), any resultant association will be of little significance. It is, nevertheless, another argument in favour of using solutions of low rather than of high ionic strengths.

The $La_2(SO_4)_3 + HCl$ solutions cannot be discussed with as much certainty. Interaction between La^{3+} and HSO_4^-, and between $LaSO_4^+$ and SO_4^{2-} ions are both reasonable possibilities, and while on general grounds they may not have much influence on the general result they may partly account for the discrepancy between the conductivity and e.m.f. results, and are worthy of experimental investigations in themselves.

Even if our e.m.f. results are to be considered as somewhat approximate, it is possible to extract some thermodynamic data from them. The plots of log K against $1/T$ permit reasonable values of $\Delta H°$, the heat of ionization, to be found. Using the data at $25°$ C then gives values of $\Delta G°$ and $\Delta S°$; these are collected below.

	$MgSO_4$	$LaSO_4^+$	$LaFe(CN)_6$
$\Delta H°$ (kcal)	$- 5 \cdot 7$	$- 2 \cdot 5$	$- 2 \cdot 02$
$\Delta G°$ (kcal)	$3 \cdot 2$	$5 \cdot 2$	$5 \cdot 09$
$\Delta S°$ (kcal)	$-31 \cdot 0$	$-26 \cdot 0$	$-23 \cdot 9$

For comparison, similar figures for $LaFe(CN)_6$ are given.[13] The two $\Delta H°$ and $\Delta S°$ data for lanthanum are of the same order (clearly since $\Delta G°$ depends on the dissociation constant these are not comparable), while those for $MgSO_4$ are quite different. It is hoped to discuss this point, in conjunction with further figures, in a later paper.

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