92. *Complex Formation in Salt Solutions. Part I.*

By R. W. Money and Cecil W. Davies.

It is well known that a salt is normally less soluble in a solution of a salt having an ion in common than it is in pure water. If, as is frequently done, it is assumed that both salts are completely dissociated into ions, a quantitative treatment becomes possible on the basis of the Debye–Hückel activity theory, and leads to results such as those illustrated in Curves 2 and 3 of Fig. 1. Consider a solution of the salt BA which is saturated with the sparingly soluble binary salt CA. From the solubility-product principle, $f^2m_Cm_A = S$, where in dilute solutions S is a constant for a given temperature, m is the molar concentration of an ion, and f is the mean ion activity coefficient of the salt CA; f can be calculated from the equation $\log f = -0{\cdot}5\, z^2\sqrt{\mu} + B\mu$, where z is the ionic charge, μ the ionic strength, and the numerical value of B depends on the nature of the two salts. Curve 2 has been calculated for a bi-bivalent salt of solubility $0{\cdot}001M$ in pure water, using the value $B = 2$, and Curve 3 applies to manganese oxalate on the same assumptions. The main effect of increasing the concentration of the solvent salt BA is to increase m_A and reduce m_C, thus lowering the solubility. All salts should give a curve of this type, individual differences being governed merely by the individual values of S and B. Eventually, the solubility curve may show a minimum and a slight tendency to rise at high ionic strengths, but this can only occur where the solubility of the salt is very low, and when B has a very small value.

Fig. 1.

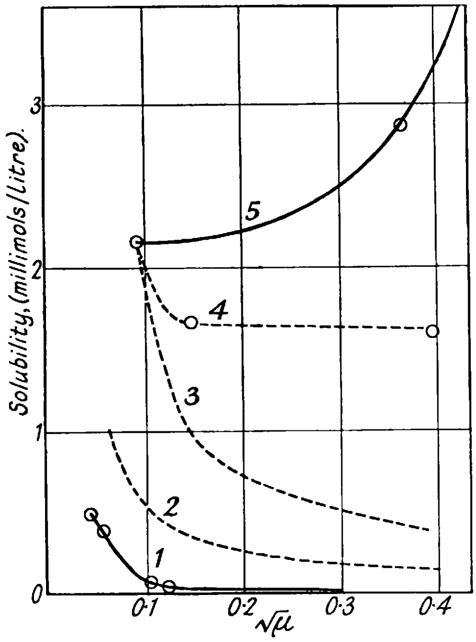


Fig. 1 shows experimental results for the two salts studied in this paper, the dihydrates of barium and manganous oxalate. Barium oxalate (Curve 1) gives a curve of the normal type, although quantitative agreement with the complete dissociation hypothesis is not to be expected in view of the conductivity figures for this salt. The curves for manganous oxalate are quite abnormal; for its solutions in manganous chloride (Curve 4) the deviation from the standard curve (Curve 3) is very great, and this is accounted for by the incomplete dissociation of the oxalate; the solubility measurements lead to a dissociation constant for this salt which agrees with that previously found from conductivity measurements. The behaviour of manganous oxalate in solutions of other oxalates (Curve 5) is obviously influenced by a further complicating factor, and we attribute the rising solubility to the formation of a complex ion, $Mn(C_2O_4)_2''$, the instability constant of which can be calculated from the measurements. Work on other salts is in progress, and it is hoped that a quantitative study of the two stages of association $C + A \rightleftharpoons CA$, $CA + A \rightleftharpoons CA_2$ for a number of radicals will throw light on the underlying processes.

EXPERIMENTAL.

Materials.—The barium oxalate dihydrate was prepared by Scholder's method (*Ber.*, 1927, **60**, 1510), and the manganous oxalate dihydrate by that of Scholder and Linstrom (*Ber.*, 1930, **63**, 2832). The solvent salts were A.R. chemicals. All were analysed by the method described below.

Method.—The apparatus was a modification of that described by Brönsted and LaMer (*J. Amer. Chem. Soc.*, 1924, **46**, 560); the bulb and column of saturating salt were connected by capillary tubing to a second, parallel, arm in which the saturated liquid collected, and the whole was immersed in a thermostat at 25° ± 0·02°. Experiment showed that 100 c.c. of liquid became fully saturated if the time of flow through the column of salt was not less than one hour, and errors from evaporation into the upper part of the collecting tube were avoided by withdrawing and analysing the solution not more than 3 hours after the beginning of the experiment. In making a determination, about 400 c.c. of the stock solution were run through the saturator and discarded, and two consecutive samples were then collected by means of a pipette calibrated to deliver 20 c.c. (100 c.c. for the barium oxalate solutions) at 25°. The sample was run into a conical flask, excess sulphuric acid added, and the whole heated to 80°. A weighed slight excess of 0·1N-potassium permanganate was slowly run in and the solution cooled, 1 g. potassium iodide added, and the liberated iodine titrated by means of 0·005N-sodium thiosulphate. Samples of the stock solution were analysed for oxalate content in the same way, and the amount of the sparingly soluble salt that had gone into solution was thus obtained by difference. The method gave results which were reproducible to within 0·1 c.c. of 0·005N-thiosulphate.

The 0·1N-permanganate was standardised by A.R. sodium oxalate using the same procedure. The 0·005N-thiosulphate was made as required from a 0·1N-stock solution, and was standardised by titration against a known weight of permanganate.

Results.—The results are given in Fig. 1 and below; col. 1 shows the concentration of the solvent salt (in g.-mol./l.) and col. 2 that (s) of the saturating salt (in millimols./l.), col. 3 gives the stoicheiometric ionic strength (complete dissociation being assumed), and col. 4 the square root of this.

Barium oxalate dihydrate; solubility in water: 0·4826 *millimol./l.*

Solvent salt.	s.	μ.	$\sqrt{\mu}$.	Solvent salt.	s.	μ.	$\sqrt{\mu}$.
0·00054M-$(NH_4)_2C_2O_4$	0·3930	0·00319	0·0565	0·00491M-$(NH_4)_2C_2O_4$	0·0499	0·01493	0·1222
0·00258 ,,	0·0700	0·01054	0·1025				

The solubility in 0·0493M- and 0·0986M-solution was very small.

Manganous oxalate dihydrate; solubility in water: 2·160 *millimols./l.*

0·005M-$MnCl_2$	1·672	0·02169	0·1473	0·07806M-$Na_2C_2O_4$	4·624	0·2447	0·4947
0·05 ,,	1·6	0·156	0·395	0·1600 ,,	7·708	—	—
0·0405M-$K_2C_2O_4$	2·869	0·1330	0·3648	0·2411 ,,	10·97	—	—
0·1198 ,,	6·065	—	—				
0·1994 ,,	9·529	—	—				

The figures for barium oxalate require no quantitative treatment; the curve is of the normal type, and shows clearly that barium oxalate has no appreciable tendency to form complex anions.

The points for manganous oxalate in the presence of manganous chloride are abnormal in that the solubility is much greater than that calculated from the complete dissociation theory, as shown by Curve 3 of Fig. 1. This behaviour is in keeping with conductivity results which show the salt to be weak, and give the dissociation constant, $K_1 = 1{\cdot}3 \times 10^{-4}$ (Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609). On the basis of this value, the saturated solution in water is over 70% undissociated, and since the depressing effect of added manganous ion on the solubility is restricted to the remaining 30%, the solubility of the salt in the presence of the common ion remains abnormally large. Curve 4 of Fig. 1 has been calculated by using the dissociation constant quoted and assuming that the activity coefficient (and therefore the concentration) of undissociated manganese oxalate in a saturated solution is unaffected by changes in the ionic strength. The line is in close agreement with the experimental points, which confirms the dissociation constant found from conductivities. The measurement in 0·1N-manganous chloride is approximate only, since the temperature of the thermostat varied beyond the specified limits; its agreement with theoretical requirements is sufficiently close, however, to show that no complex cations are formed in the mixture.

The enhanced solubility in the oxalate solutions contrasts with the results in manganous chloride, and shows that the oxalate ion combines with manganous oxalate. For a limited concentration range the main reaction may be written : $MnC_2O_4 + (n-1)C_2O_4 \rightleftharpoons Mn(C_2O_4)_n$, since complex products involving more than one molecule of manganous oxalate will not be expected to occur. The value of n may be determined as follows. For concentrations of added oxalate greater than 0·02*M*, it can readily be shown from the mass-action expression, or by direct reference to Curve 4 of Fig. 1, that the simple dissociation of the manganous oxalate is completely suppressed owing to the common-ion effect. The species present in more concentrated solutions are therefore the cation of the solvent salt, Ox″, MnOx, and $MnOx_n$ and these are related by the equation $F \cdot m_{MnOx} \cdot m_{Ox}{}^{(n-1)}/m_{MnOx_n} = K_2$, where K_2 is the instability constant of the complex ion, and F is an activity factor which corrects for possible changes in the ionic environment. If A is the molar concentration of solvent salt, and s is the solubility of manganous oxalate, the concentrations of oxalate ion and complex ion are given by :

$$\begin{aligned} m_{MnOx_n} &= s - m_{MnOx} \\ m_{Ox} &= A + s - m_{MnOx} - nm_{MnOx_n} \\ &= A - (n-1)(s - m_{MnOx}) \end{aligned}$$

Hence,
$$\frac{K_2}{F \cdot m_{MnOx}} = \frac{m_{Ox}{}^{(n-1)}}{m_{MnOx_n}} = \frac{\{A-(n-1)(s-m_{MnOx})\}^{n-1}}{(s-m_{MnOx})},$$

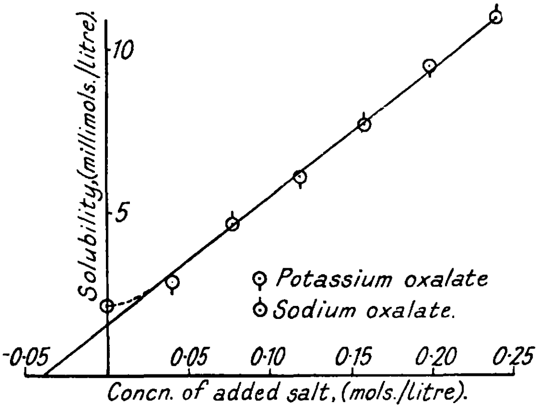
and, rearranging, $A = (n-1)(s - m_{MnOx}) + \left\{\frac{K_2(s - m_{MnOx})}{Fm_{MnOx}}\right\}^{1/(n-1)}$;

for these saturated solutions, it will be remembered, m_{MnOx} can be regarded as constant. Reference to Fig. 2 shows that up to the highest concentrations studied a linear relationship exists between A and s. This is only possible if $n - 1$, in the above equation, is equal to unity. The formula of the complex ion is therefore $Mn(C_2O_4)_2''$, and F in the equation will also be unity, as a close approximation, since the expression for K_2 contains one bivalent ion in both numerator and denominator. The equation now becomes :

$$A = (s - m_{MnOx})(1 + K_2/m_{MnOx}),$$

and gives, for $A = 0,\ s = m_{MnOx}$,
for $s = 0,\ -A = m_{MnOx} + K_2$.

Fig. 2.



The values of the intercepts read off from Fig. 2 are : $s = 0·00155$, $-A = 0·0385$. Hence the concentration of undissociated manganous oxalate in a saturated solution at 25° is 0·00155 g.-mol./l., and this fixes the extent of the simple dissociation of the salt in water; actually, it leads to a dissociation constant $K_1 = 1·5 \times 10^{-4}$, which is in satisfactory agreement with the value $K_1 = 1·3 \times 10^{-4}$ found from the conductivity of the salt at 18° (see p. 401). Further, the value of K_2, the instability constant of the complex ion is $0·0385 - 0·00155 = 0·037$.

In deriving a value of K_1 from conductivity measurements (Money and Davies, *loc. cit.*), it was mentioned that the result was slightly uncertain owing to the possible presence of a small proportion of complex ions. The value of K_2 just reported makes it possible to calculate the extent to which autocomplex-formation occurs; in the saturated solution approximately 1% of the manganese exists in the form of complex anion, and if the mobility of this is assumed to be two-thirds that of the oxalate ion, K_1 becomes $1·22 \times 10^{-4}$.

SUMMARY.

Solubility measurements on barium oxalate and manganous oxalate in the presence of salts having an ion in common demonstrate that the former, which conductivity measurements have already shown to be one of the strongest bi-bivalent salts, shows no appreciable tendency to form complex ions. Manganous oxalate, on the other hand, gives abnormal

results which show the salt to be a relatively weak one, and confirm the value of the dissociation constant previously found by conductivity methods. The results further show that manganous oxalate forms no complex cations but readily forms a complex anion, $Mn(C_2O_4)_2''$, the instability constant of which is 0·037.

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[*Received, February 5th,* 1934.]