398. *The Solubility of Barium Oxalate in Aqueous Salt Solutions.*

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

The solubility of barium oxalate dihydrate has been measured at 25° in potassium chloride and nitrate solutions at concentrations extending up to 0·1M, and in dilute manganous chloride solutions. The results with the first two salts have been used to calculate an equation for the mean ionic activity coefficient of barium oxalate. The increase in solubility produced by manganous chloride is about ten times as

great as with a potassium chloride solution of the same ionic strength, and is in good agreement with the dissociation constant of manganous oxalate previously found from conductivity measurements.

In previous papers (see this vol., p. 273) it has been shown that the discrepancies between experimental solubility figures and the requirements of the Debye–Hückel theory disappear when allowance is made for ionic association. The present paper extends the work to a bi-bivalent salt, and reports solubility measurements on barium oxalate dihydrate at 25° in potassium chloride and nitrate, and manganese chloride solutions.

The barium oxalate dihydrate was prepared, and its solubility measured, by methods already described (J., 1934, 400). The results are shown in the following table, where m is the concentration of the solvent salt, and s the corresponding solubility of barium oxalate, both in millimoles per litre.

Solubility of Barium Oxalate Dihydrate at 25°.
Water : $s = 0.483$.
KCl solutions.

m	0.960	4.80	7.47	9.94	20.0	50.0	100.0
s	0.496	0.563	0.588	0.616	0.700	0.891	1.118

KNO₃ solutions.   MnCl₂ solutions.

m	0.984	4.93	9.92	49.66	100.0		m	0.500	2.25	5.12
s	0.509	0.558	0.643	0.938	1.226		s	0.698	1.350	2.103
							$10^4 . K_{MnOx}$ ...	1.00	1.10	1.13

From the first two series of measurements mean ionic activity coefficients (mol./l.) were calculated for barium oxalate in the following way. Dissociation constants previously reported for barium oxalate (*Trans. Faraday Soc.*, 1932, **28**, 609), potassium oxalate (*ibid.*, 1931, **27**, 621), potassium nitrate (*ibid.*, 1927, **23**, 351), and barium nitrate (*ibid.*, 1930, **26**, 592) were used to calculate the small quantities present of the species BaOx, KOx′, KNO₃ and BaNO₃˙, and by subtraction the concentrations of the free barium and oxalate ions were obtained. The product [Ba˙˙][Ox″] was then plotted against the square root of the ionic strength, and the results of the two series of measurements were found to fall, within experimental error, on a common curve, showing that for these two series the mean ionic activity coefficient of barium oxalate is independent of the nature of the added salt. The activity coefficients were then evaluated from the solubility product equation : $f_{\pm}^2[Ba˙˙][Ox″] = s_0$, on the assumption that for the solubility in pure water (ionic strength 0.00182) the mean ionic activity coefficient is given by the standard equation of Guggenheim (*Phil. Mag.*, 1935, **19**, 629) : $-\log f_{\pm} = 2\sqrt{I}/(1 + \sqrt{I})$. They are shown in the following table for round values of the ionic strength.

I	0.01	0.0225	0.04	0.0625	0.09	0.1225
$\sqrt{I}$	0.10	0.15	0.20	0.25	0.30	0.35
$f_{\pm}$, expt.	0.666	0.558	0.478	0.418	0.374	0.341
$f_{\pm}$, calc.	0.664	0.560	0.482	0.422	0.375	0.339

The figures in the last line are obtained from the empirical equation :

$$-\log f_{\pm} = 2\sqrt{I}/(1 + \sqrt{I}) - 0.40I,$$

which clearly expresses the results satisfactorily up to an ionic strength of 0.1.

The measurements in manganous chloride solutions were made to check the dissociation constant of manganous oxalate previously found from conductivity measurements (*Trans. Faraday Soc.*, 1932, **28**, 609 ; J., 1934, 400). It will be seen from the first table that manganous chloride increases the solubility of barium oxalate by a very much greater amount than does a potassium chloride solution of the same ionic strength. If we attribute the anomaly to the formation of undissociated manganous oxalate, the amount of this can be calculated as follows. We assume that the ionic concentration product, [Ba˙˙][Ox″], has the same value as in a potassium chloride or nitrate solution of the same ionic strength ; [Ba˙˙] is given by the solubility, less a small constant correction for undissociated barium oxalate, and [Ox″] is therefore known ; subtraction gives the amount of oxalate in the

form of undissociated manganese oxalate. The dissociation constant of manganous oxalate is now found from the equation : $f_{\pm}^2[Mn^{\cdot\cdot}][Ox''] / [MnOx] = K$, in which the concentrations are all known, and $f_{\pm}$ is assumed to be given by the same equation as holds good for barium oxalate. The results are in the first table. The agreement with the previously reported value $K = 1\cdot2 \times 10^{-4}$ is satisfactory, and illustrates rather strikingly how abnormal conductivities and abnormal solubilities may be correlated on the basis of the postulated mass-action equilibria. Manganous oxalate in $0\cdot005$N-solution has about one-quarter of the conductivity to be expected of a completely dissociated salt; barium oxalate in manganous chloride solution shows an increase in solubility about ten times as great as would be anticipated from the simple interionic attraction theory; and both results are quantitatively explained by the low dissociation constant found for manganous oxalate.