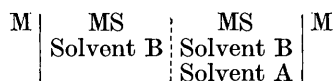


CXCI.—*An Electrochemical Method for the Approximate Determination of the Constitution of Complexes in Solution. Application to Some Complex Ions of Copper and of Nickel.*

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IN a previous communication (J., 1930, 2053) a simple electrochemical method for the simultaneous determination of the constitution and the equilibrium constant of complex ions in solution was described and applied to some complex silver ions. For electrodes which, unlike the silver electrode, do not give constant and reproducible potentials, the method cannot be used, and the equilibrium constant cannot therefore be determined electrometrically. The constitution of the complex ion (or of a molecular complex) can, however, be approximately determined electrometrically by the method described below.

Consider the cell (compare *loc. cit.*, p. 2054)



where MS is a salt of the metal M. If it be assumed that the electromotive activity of the A complex ions may be neglected compared with that of the B-solvated ions in the mixed solvent, and if the

concentration of the salt MS is the same on both sides of the cell, then the *E.M.F.* (*E*) of this cell is given (*loc. cit.*, p. 2057) by the equation

$$E - e = (RT/nF) \cdot \log_e K_m - x(RT/nF) \cdot \log_e m \quad . \quad (1)$$

where *e* is the liquid-junction potential; *K<sub>m</sub>* is the constant for the equilibrium between the A complex ions, the B-solvated ions, and the two solvents A and B; *x* is the number of molecules of the complex-forming solvent A taken up by a single metal ion; and *m* is the concentration (in g.-mols./l.) of free solvent A.

Let it now be supposed that a concentration of *c* g.-mols./l. of a new substance, which also forms complexes with solvent A, be added to the mixed solvent. If it be assumed that the only effect of the addition of the latter substance is to alter the position of the equilibrium by removing a quantity of solvent A equal to (*m - m'*) g.-mols./l., then the new *E.M.F.* (*E'*) will be given by the equation

$$E' - e' = (RT/nF) \cdot \log_e K_m - x(RT/nF) \cdot \log_e m' \quad . \quad (2)$$

where *e'* is the new liquid-junction potential.

Hence by (1) and (2)

$$(E' - E) - (e' - e) = \Delta E - \Delta e = x(RT/nF) \cdot \log_e (m/m') \quad . \quad (3)$$

Now the number of molecules (*z*) of solvent A taken up by a single molecule of the added substance is

$$z = (m - m')/c \quad . \quad . \quad . \quad . \quad (4)$$

Eliminating *m'* between (3) and (4), we have

$$- \Delta E + \Delta e = x(RT/nF) \cdot \log_e (1 - cz/m) \quad . \quad . \quad (5)$$

In the last equation all the necessary quantities (except  $\Delta e$ , see below) can be determined experimentally, and therefore *z* can be calculated.

If, in a special case, *cz/m* be small compared with unity, then on expanding the right-hand side of (5) and neglecting terms higher than the first, we have the simplified form

$$z = (nF/RT) \cdot (m/xc) \cdot (\Delta E - \Delta e) \quad . \quad . \quad . \quad (6)$$

The liquid-junction potential *e* may be regarded as negligibly small compared with *E* because the concentration of the salt MS is the same on both sides of the cell. On account of the addition of the new substance to the mixed solvent (especially if this be an electrolyte) the new liquid-junction potential *e'* can, however, no longer be regarded, in general, as negligibly small compared with the new *E.M.F.* (*E'*). Since  $\Delta e$  cannot be determined experimentally, it must be neglected and an uncertainty is thus introduced into the value of *z*. Although the method can therefore only be approximate, it appeared to merit investigation because it may prove useful when

other more exact methods cannot be applied. For the cases here examined, the error in  $x$  is of the order of 15%.

The method has been applied to the cases where the metal M is silver, the salt MS is silver nitrate, solvent B is water, solvent A is ammonia or pyridine, and the added substance is copper sulphate or nickel sulphate.

The apparatus and purification of the materials have been previously described (*loc. cit.*). The copper sulphate and nickel sulphate were recrystallised and air-dried.

The values of  $z$  have been calculated from equation (4), using equations (1), (2), and (3) and taking  $x = 2$ ,  $K_m = 6.3 \times 10^{-8}$  for the ammonia-water mixtures, and  $K_m = 7.1 \times 10^{-5}$  for the pyridine-water mixtures as previously found (*loc. cit.*, p. 2061). The concentration of silver nitrate was 0.01 g.-mol./l. on each side of the cell in all cases, and  $m$  is therefore the total concentration of ammonia or pyridine in g.-mols./l. minus 9.02.

$c.$	$m.$	$E'$	$E.$	Free solvent A ( $m'$ ).	$z.$
CuSO <sub>4</sub> .	NH <sub>3</sub> .				
0.0250	0.160	0.302	0.325	0.10	2.3
0.0500	0.340	0.342	0.363	0.22	2.3
0.0500	0.520	0.367	0.385	0.37	3.1
0.100	0.880	0.390	0.411	0.58	3.0
CuSO <sub>4</sub> .	C <sub>5</sub> H <sub>5</sub> N.				
0.0247	0.169	0.128	0.151	0.11	2.5
0.0506	0.404	0.166	0.195	0.23	3.5
0.100	0.765	0.188	0.227	0.37	4.1
0.100	0.788	0.190	0.229	0.39	4.2
NiSO <sub>4</sub> .	C <sub>5</sub> H <sub>5</sub> N.				
0.0315	0.235	0.154	0.168	0.17	1.8
0.0785	0.476	0.178	0.203	0.32	2.3
0.109	0.593	0.189	0.214	0.37	2.1

Reychler (*Bull. Soc. chim.*, 1895, **13**, 387; *Ber.*, 1895, **28**, 555) found that no appreciable effect was produced on the freezing points or specific conductivities of aqueous copper sulphate solutions until after somewhat less than 4 mols. of ammonia per mol. of copper sulphate had been added to the solution. Similar conclusions were drawn by Konowalov (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910) and Gaus (*Z. anal. Chem.*, 1900, **25**, 236) from measurements of the partial vapour pressures of ammonia over ammoniacal copper sulphate solution in water. Dawson and McCrae (*J.*, 1901, **79**, 496, 1072) showed from the distribution of ammonia between chloroform and aqueous copper sulphate solutions that, under varying conditions, 4, or less than 4, mols. of ammonia were taken up per mol. of copper sulphate: values lower than 4 were attributed to the dissociation of the complex ion  $\text{Cu}(\text{NH}_3)_4^{++}$ . It will be observed that the same phenomenon occurs in the case of the ion  $\text{CuPy}_4^{++}$ .

Some results now obtained for the distribution of pyridine between benzene and aqueous solutions of copper sulphate and nickel sulphate (carried out as previously described, *loc. cit.*, p. 2060) are given below, concentrations being expressed as g.-mols./l. The total available pyridine is 57.5 and 11.5 mols. per mol. of salt for the 0.02 and 0.10*N*-solutions respectively.

CuSO <sub>4</sub> (in water).	C <sub>5</sub> H <sub>5</sub> N,		Free C <sub>5</sub> H <sub>5</sub> N (in water).	z.
	water.	benzene.		
0	0.303	0.847	0.30	—
0.02	0.360	0.790	0.28	3.9
0.10	0.534	0.616	0.23	3.0
NiSO <sub>4</sub> (in water).				
0.02	0.334	0.815	0.29	2.0
0.10	0.453	0.697	0.25	2.0

The agreement of the values of *z* found by the electrochemical method with those obtained by the distribution-coefficient method is as good as can be reasonably expected.

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