A New Principle for the Investigation of Complex Equilibria and the Determination of Complexity Constants

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The main methods for potentiometric determination of the complexity constants of a complex system are founded on measurements of the concentration of free ligand or of free central group. Such methods have been described by J. Bjerrum [1] and Leden [2]. In a previous treatise [3], the present author has developed methods of these two kinds and furthermore a third method, based on the use of cells without liquid junction. These three methods are suited for a determination of the complexity constants of the mononuclear complexes, irrespective of whether or not polynuclear complexes are formed, and in this respect they are general. Under favourable circumstances the constants of some of the dinuclear complexes can also be determined.

In practice, the choice of a measurement method will depend on the possibility of finding a suitable electrode. Many complex systems cannot be investigated by any of the methods mentioned, because there is no electrode of the first or second order, by means of which the concentration of free ligand or free central group can be determined. So *e. g.* the complex formation between Cu^{2+} and Cl^- cannot be investigated potentiometrically by means of a copper amalgam electrode or a silver chloride electrode, as both of them reduce Cu^{2+} to Cu^+ in the presence of Cl^-. In such a case it would be desirable that the measurements could be made via a second ligand, employing a non-reducing electrode.

The basic principle of the new method, described below, is the use of a three component complex system. Thus the solutions contain a central group M and two competing ligands A and B. It is thus possible to have the formation of complexes with A or B as ligands, and furthermore the formation of mixed complexes with both A and B as ligands. The affinity of M for B must

be greater than that of M for A, so that B will finally completely displace A as ligand, if the concentration of A is kept constant, while that of B is increased within a limited range. When the measurements give a direct determination of the concentration of free ligand [B] in the solutions, it will be shown below that it is possible to calculate the complexity constants of the mononuclear complexes MA, MA_2, ..., MA_N. The complexity constants of mixed complexes of the type MA_jB $(j = 1,2, ...)$ can also be determined. Naturally the constants of the B-complexes MB_j $(j = 1,2, ...)$ can be calculated too, in the manner described in the previous treatise.[3, p. 14]

This method of determining the complexity constants of the A-complexes by means of another ligand will be called the "method of ligand displacement".

Deduction of the equations necessary for the calculation of the complexity constants

For the sake of brevity, we postulate that in the solutions, containing the central group M and the ligands A and B, only mononuclear complexes of the general type MA_jB_k are formed. As will be seen below, our equations easily can be generalized, so that they are also valid, when polynuclear complexes are formed.

For the known total concentrations of M and B we have the following expressions:

$$C_M = [M] + \sum_{j+k=1}^{N} [MA_jB_k]; \quad j, k \geqq 0 \tag{1}$$

$$C_B = [B] + \sum_{j+k=1}^{N} k[MA_jB_k] \tag{2}$$

We apply the law of mass action to the dissociation equilibria of the complexes and obtain *:

$$\beta_{j,k} = [MA_jB_k] [M]^{-1}[A]^{-j}[B]^{-k} \tag{3}$$

As the measurements are performed at a constant ionic strength, we may presume that the complexity "constants" $\beta_{j,k}$ remain approximately constant, when the total concentrations C_M, C_A and C_B are varied within limited ranges. By substituting eq. (3) in (1) and (2), we obtain the expressions:

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* The constants that we in the first place intend to determine are $\beta_{j, 0}$, for which the notation β_j is used when the solutions contain only one sort of ligand.

$$C_M = [M] \left(1 + \sum_{j+k=1}^{N} \beta_{j,k} [A]^j [B]^k\right) \tag{4}$$

$$C_B = [B] + [M] \sum_{j+k=1}^{N} k\beta_{j,k} [A]^j [B]^k \tag{5}$$

For the sake of brevity we use the notation:

$$X([A], [B]) = 1 + \sum_{j+k=1}^{N} \beta_{j,k} [A]^j [B]^k \tag{6}$$

In the following we shall sometimes write only X in place of $X([A], [B])$. By partial differentiation of X we get:

$$\frac{\partial X}{\partial [B]} = \sum_{j+k=1}^{N} k\beta_{j,k} [A]^j [B]^{k-1} \tag{7}$$

The ligand number $\bar{n}$, with respect to the ligand B, is defined in the usual way:

$$\bar{n} = \frac{C_B - [B]}{C_M} \tag{8}$$

Combining eq. (4—8) we obtain:

$$\frac{\partial \ln X}{\partial [B]} = \frac{\bar{n}}{[B]} \tag{9}$$

Here $\bar{n}$ is a function of [A] and [B]. Eq. (9) is deduced under the assumption that only mononuclear complexes exist. If polynuclear complexes are also formed, the expression for $\bar{n}$ will contain terms with [M], $[M]^2$ etc. as factors (cf. Fronæus [3, p. 19]). Then $\bar{n}$ will be a function of [A], [B] and C_M. But if we allow $C_M \to 0$ (that is $[M] \to 0$) these terms cancel, and we have the quite *general* equation:

$$\frac{\partial \ln X}{\partial [B]} = \left(\frac{\bar{n}}{[B]}\right)_{C_M = 0} \tag{10}$$

For the sake of clarity we put $(\bar{n})_{C_M=0} = \bar{n}([A], [B])$. By $\Delta \bar{n}$ we mean the difference between the ligand numbers of two solutions, the first of which has [A] = 0, while [B] and C_M are the same in both solutions. Then we have: $\bar{n}(0, [B]) - \bar{n}([A], [B]) = (\Delta \bar{n})_{C_M=0}$. If [A] is kept at a constant value $[A]_n$, we obtain by integration of (10) with respect to [B]:

$$ln \frac{X([A]_n, [B]_n)}{X([A]_n, 0)} = \int\limits_0^{[B]_n} \frac{\bar{n}([A]_n, [B])}{[B]} \cdot d[B] \qquad (11)$$

For $[A]_n = 0$ this equation is reduced to:

$$lnX(0, [B]_n) = \int\limits_0^{[B]_n} \frac{\bar{n}(0, [B])}{[B]} \cdot d[B] \qquad (12)$$

Eq. (12) is identical with the eq. (24) of the previous treatise [3, p. 15]. From eq. (11) and (12) we derive:

$$ln\, X([A]_n, 0) - ln \frac{X([A]_n, [B]_n)}{X(0, [B]_n)} = \int\limits_0^{[B]_n} \left(\frac{\Delta\bar{n}}{[B]}\right)_{C_M = 0} \cdot d[B] \qquad (13)$$

The term of the polynomial $X([A], [B])$ which is of the highest degree with respect to $[B]$ is $\beta_{0, N} \cdot [B]^N$. Then we have presumed that the saturated complex MB_N, which cannot take up an additional ligand B, cannot take up a ligand A either. Hence it follows that:

$$\lim_{[B]_n \to \infty} \frac{X([A]_n, [B]_n)}{X(0, [B]_n)} = 1$$

As already mentioned, this means that if C_A is kept constant but C_B is increased, the higher M—B complexes become the predominant complexes in the solutions. Thus B will completely displace A as ligand, and the stronger a complex former (with respect to M) B is than A, the faster this displacement will proceed. The validity of this assumption can be examined experimentally, for if we choose a ligand B with the proper affinity for M, it will be possible to find a value b, within an appropriate concentration range, so that when $[B] \geqq b$ the function $(\Delta\bar{n}/[B])_{C_M = 0}$ is $= 0$, the random errors considered. If b is taken as the upper limit of integration in eq. (13), we consequently obtain:

$$ln\, X([A]_n, 0) = \int\limits_0^b \left(\frac{\Delta\bar{n}}{[B]}\right)_{C_M = 0} \cdot d[B] \qquad (14)$$

It is evident that the greater the value of $[A]_n$ is, the greater becomes the value of b which must be taken.

Determination of corresponding values

of [B] and $\left(\dfrac{\Delta\,\bar{n}}{[\mathrm{B}]}\right)_{c_{\mathrm{M}}\,=0}$

The calculation method is based on an experimental determination of [B] in the complex solutions. The measurements are arranged in the following way. In a series of measurements C_{A} and C_{M} are kept constant *, and C_{B} is varied. From the ligand measurement (regarding [B]) we obtain $\bar{n}/[\mathrm{B}]$ which can be plotted against [B] with C_{M} (or its starting value in the series) and C_{A} as parameters. By repeating the measurements at different values of C_{M}, but still at the same value of C_{A}, the limiting function $(\bar{n}/[\mathrm{B}])c_{\mathrm{M}}\,{=}\,0 = \bar{n}\,([\mathrm{A}]_n,$ [B])/[B] can be obtained by extrapolation. At $C_{\mathrm{M}} = 0$, $[\mathrm{A}]_n$ is also constant and $= C_{\mathrm{A}}$ at varying [B]. The function $\bar{n}\,(0,\,[\mathrm{B}])/[\mathrm{B}]$ at $C_{\mathrm{A}} = 0$ is determined in the same way (cf. Fronæus [3, p. 16]). From the difference we get the function $(\Delta\bar{n}/[\mathrm{B}])c_{\mathrm{M}}\,{-}\,0$, and then the integration in eq. (14) is performed graphically and will give us a pair of values of $[\mathrm{A}]_n$ and $X\,([\mathrm{A}]_n,\,0)$. After a sufficient number of corresponding values have been obtained in this way, the complexity constants of the complexes MA_j $(j = 1,2,\,\ldots)$ can be calculated from the eq.:

$$X([\mathrm{A}]_n,\,0) = 1 + \sum_{j=1}^{N} \beta_j\,[\mathrm{A}]_n^{j} \qquad (15)$$

In (15) the complexity constants have been denoted by β_j instead of $\beta_{j,\,0}$ as no confusion is to be feared here.

If the complexity constants of the complexes MB_j are not known in advance, they can be computed from eq. (12).

Calculation of the complexity constants of mixed
complexes of the type $\mathrm{MA}_j\mathrm{B}$

By combining eq. (6) and (10), we obtain the relation:

$$\lim_{[\mathrm{B}]\,\to\,0}\left(\frac{\bar{n}}{[\mathrm{B}]}\right)_{c_{\mathrm{M}}\,=\,0} = \frac{\displaystyle\sum_{j\,=\,0}^{N-1}\beta_{j,\,1}\,[\mathrm{A}]^{j}}{X\,([\mathrm{A}],\,0)} \qquad (16)$$

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* In order to reduce the number of titration solutions necessary, we may also allow C_{M} to vary in the series. Then C_{M} must be a known function of C_{B} (see eq. (18)).

At different values of [A], the limiting values of the left member of eq. (16) are estimated by graphical extrapolation of $(\overline{n}/[B])_{c_M = 0}$ to [B] = 0. The corresponding values of the polynomial $X([A], 0)$ have already been calculated, and $\beta_{0,1}$, the constant of the complex MB, is determined in advance. Thus from eq. (16) we can compute as many of the constants $\beta_{1,1}$, $\beta_{2,1}$, $\beta_{N-1,1}$, as the concentration range of [A] will admit.

Estimation of the random errors

From the reproducibility obtained in the measuring of [B], the maximum random errors in the values of the functions $\overline{n}(0, [B])/[B]$ and $\overline{n}$ $([A]_n$, [B])/[B] can be estimated as well as the corresponding maximum error in their difference. If the last-mentioned error is denoted by ε, and is considered to be practically constant at different values of [B], as it was in the measurements described below, the maximum error of $lnX([A]_n, 0)$, computed from (14), will be $\varepsilon \cdot b$.

Another error may arise from the fact that in eq. (14) we have a finite range of integration (0 to b instead of 0 to ∞). From the algebraical expression for the function $(\Delta\overline{n}/[B])_{c_M = 0}$, it is easily seen that the function, at great values of [B], can be approximated by $\varphi([A]) \cdot [B]^{-2}$, as no mixed complex with N B-ligands exists. If no mixed complexes with $N-1, \ldots, N-k$ B-ligands are formed, we can use, at great values of [B], the approximation $\varphi([A]) \cdot [B]^{-k-2}$, and at increasing values of b the integral in eq. (14) then converges more rapidly. Thus, in the most disadvantageous case, we have as an approximate expression of the omitted integral R:

$$R = \int\limits_{b}^{\infty} \frac{\varphi([A])}{[B]^2} \cdot d\,[B] = \frac{\varphi([A])}{b} \tag{17}$$

When [B] = b, the integrand is ~ 0 according to our measurements. Then on the basis of the estimated random errors, the true value can be ε at most.

$$\frac{\varphi([A])}{b^2} \leqq \varepsilon \;\; ; \;\; (R)_{\text{max.}} = \varepsilon \cdot b$$

Thus, the total maximum error of $lnX([A]_n, 0)$ is $2\,\varepsilon \cdot b$.

It is rather difficult to decide how the product $\varepsilon \cdot b$ depends on the strength of the M—B complexes. However, in order to secure approximately constant activity coefficients it is necessary that the value of b be considerably smaller than the chosen ionic strength.

A POTENTIOMETRIC INVESTIGATION OF THE $Cu^{2+}-SO_4^{2-}$ SYSTEM WITH Ac^-* AS THE DISPLACING LIGAND

In order to examine the applicability of the method described, it has been applied to the cupric sulphate system, which the present author has investigated in a previous work [3, p. 57] by potentiometric and spectrophotometric methods. In the latter work the potentiometric investigation was a central ion measurement, that did not presuppose anything regarding the composition of the complex system. These previous measurements proved that Cu^{2+} forms considerably weaker complexes with SO_4^{2-} than with Ac^-, and therefore the last-mentioned ion has been taken as the displacing ligand. In order to be able to compare the results, we have used the same ionic strength, 1 C (mols/litre), with sodium perchlorate as a neutral salt.

Chemicals used. The same preparations of cupric perchlorate, sodium perchlorate, perchloric acid, sodium sulphate, sodium acetate, acetic acid and quinhydrone were used as in the earlier investigations [3, p. 31]. The cupric perchlorate, however, was further purified by recrystallisation from water, so that the excess of perchloric acid in the preparation was negligble.

The measurements for the determination of $[Ac^-] = [B]$ were carried out with the quinhydrone electrode, as this gives great reproducibility and its applicability for this purpose has been examined in the previous work [3, p. 36]. The cells, the emf:s of which have been measured, were of the following type:

$$+ \text{ RE} \quad \left\| \begin{array}{c} \text{quinh. (s)} \\ \text{complex} \\ \text{solution} \end{array} \right\| \quad \text{Au} -$$
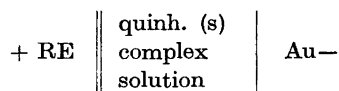
The reference electrode RE had the same composition as before [3, p. 34], and the salt bridge consisted of 1 000 mC $NaClO_4$. The solution of the right half-cell was obtained by mixing two solutions S_1 and S_2, both of them of an ionic strength of 1 C.

$$S_1 = \begin{cases} a \text{ mC } Cu(ClO_4)_2 \\ C_A \text{ mC } Na_2SO_4 \\ (1000-3a-3C_A) \text{ mC } NaClO_4 \end{cases} \qquad S_2 = \begin{cases} C_A \text{ mC } Na_2SO_4 \\ 500 \text{ mC } NaAc \\ 250 \text{ mC } HAc \\ (500-3C_A) \text{ mC } NaClO_4 \end{cases}$$

Then for the measuring solution we have the following relation between C_M and C_B in mC:

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* Ac^- = acetate ion.

$$C_M = a \left(1 - \frac{C_B}{500} \right) \qquad (18)$$

The mixing was carried out in the electrode vessel, and good stirring was brought about by a stream of nitrogen gas, released from oxygen and led through 1 C $NaClO_4$ in order to obtain the correct water pressure. The cells were placed in a thermostat at 20.00 $\pm$ 0.02 °C. The emf:s measured were very steady and reproducible within 0.1—0.2 mV.

The emf in mV of the cell, given above, is denoted by E. At the same values of C_A and C_B, but at $C_M = 0$, the emf is called E_0. The value of E_0 is practically independent of C_B within the concentration range used, but varies somewhat with C_A (see Table 1). The difference $E_0 - E = E_B$ is the emf of a concentration cell, and we have

$$E_B = 58.16 \ log \frac{[H^+]}{[H^+]_0} \qquad (19)$$

if we neglect the effect of somewhat different liquid junction potentials and activity coefficients in the two halves of the concentration cell. $[H^+]_0$ denotes the concentration of H^+ in the solution with $C_M = 0$. The concentration of undissociated acetic acid is:

$$0.500 \cdot C_B - [HSO_4^-] - [H^+] = 0.500 \cdot C_B - \vartheta$$

The correction term ϑ is calculated from the relation $\vartheta = [H^+]([SO_4^{2-}]/K_2 + 1)$, where K_2 is the secondary dissociation constant of the sulphuric acid. At $C_M = 0$, the correction term is called ϑ_0. For the calculation of ϑ and ϑ_0, we may put $[SO_4^{2-}] \simeq C_A$. For the dissociation of the acetic acid we have:

$$\frac{[H^+] \ [B]}{0.500 \cdot C_B - \vartheta} = \frac{[H^+]_0 \ (C_B + \vartheta_0)}{0.500 \cdot C_B - \vartheta_0}$$
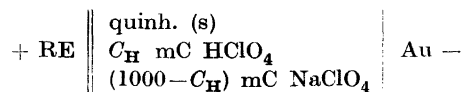
or approximately:

$$\frac{[H^+]}{[H^+]_0} = \frac{C_B - 2 \ \vartheta + 3 \ \vartheta_0}{[B]} \qquad (20)$$

For the ligand number $\bar{n}$ (regarding B) the expression is:

$$\bar{n} = \frac{C_B + \vartheta - [B]}{C_M} \qquad (21)$$

where $C_B + \vartheta$ is the corrected value of the total concentration of B. In order to compute the correction terms ϑ and ϑ_0, it is necessary to make an approximate determination of the dissociation constant K_2. For this reason the emf of the cell

$$+ \text{ RE } \left\| \begin{array}{c} \text{quinh. (s)} \\ C_H \text{ mC } HClO_4 \\ (1000-C_H) \text{ mC } NaClO_4 \end{array} \right| \text{ Au } -$$

was measured and gave a calibration curve, representing the relationship between the emf and $[\text{H}^+] = C_H$. A new series of measurements were then carried out, when the solution of the right half-cell had the composition C_A mC Na_2SO_4, C_H mC $HClO_4$, $(1\,000-3C_A-C_H)$ mC $NaClO_4$, and with the relation $8\,C_A + 3\,C_H = 1\,000$ mC. From the emf, measured at different C_H, and the calibration curve, $[\text{H}^+]$ in these solutions was calculated without the liquid junction potentials influencing the measurements essentially. K_2 could then be computed, and at $C_H \leqq 100$ mC the value of K_2 was fairly constant and equal to $(8.4 \pm 0.5) \cdot 10^{-2}$ C. Thus we know all data that are necessary for the determination of [B] and $\bar{n}/[\text{B}]$ from eq. (19—21) and the values of E_0.

Table 1. Determination of $[\text{H}^+]_0$ *and* ϑ_0 *at different* C_A.

C_A mC	E_0 mV	$[\text{H}^+]_0$ mC	ϑ_0 mC
0	169.6	0.012	0.01
50	169.0	0.012	0.02
100	168.5	0.013	0.03
150	167.3	0.013	0.04

The values obtained from the potentiometric measurements of the cupric sulphate system are shown in Table 2. In the first four measurement series in the table (nos. 1—13) the factor a in eq. (18) has a value of 100 mC, and in the remaining four measurement series (nos. 14—27) a value of 50 mC. Every value of E_B is a mean value from at least two parallel measurements.

To obtain further proof of the applicability of the quinhydrone electrode, a measurement series $(C_A = 0)$ was repeated with a glass electrode (Radio meter, type G 100), combined with a valve potentiometer (Radiometer, type PHM 3 h). The cells measured were of the following type:
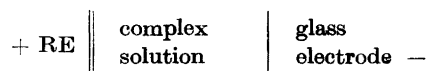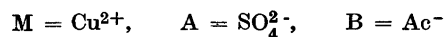
$$+ \text{ RE } \left\| \begin{array}{c} \text{complex} \\ \text{solution} \end{array} \right| \begin{array}{c} \text{glass} \\ \text{electrode } - \end{array}$$

Table 2. Potentiometric measurements on the cupric sulphate system with the acetate ion as a displacing ligand.

$$M = Cu^{2+}, \quad A = SO_4^{2-}, \quad B = Ac^-$$

No.	C_M mC	C_B mC	$C_A = 0$ mC	$C_A = 50$ mC	$C_A = 100$ mC	$C_A = 150$ mC
				E_B	mV	
1	97.4	12.99	43.2	39.7	36.7	33.4
2	96.2	19.23	42.0	38.6	35.8	32.3
3	93.8	31.3	39.8	36.6	34.1	30.5
4	90.9	45.5	37.4	34.4	31.8	28.5
5	88.2	58.8	35.1	32.1	29.8	26.8
6	83.3	83.3	30.6	28.2	26.2	23.5
7	75.0	125.0	23.8	22.0	20.8	18.8
8	68.2	159.1	18.9	17.9	16.9	15.3
9	60.0	200.0	14.3	13.8	13.2	11.9
10	50.0	250	10.1	9.9	9.6	8.7
11	37.5	313	6.5	6.6	6.3	5.9
12	25.9	370	4.1	4.1	4.0	3.8
13	13.04	435	2.0	1.9	2.0	2.0
14	49.3	6.58	29.6	26.8	23.9	21.3
15	48.7	12.99	28.4	25.6	23.0	20.2
16	48.1	19.23	27.1	24.4	21.8	19.2
17	46.9	31.3	24.7	22.2	20.1	17.7
18	45.4	45.5	22.2	20.0	18.2	16.1
19	44.1	58.8	20.1	18.0	16.4	14.6
20	41.7	83.3	16.6	15.0	14.0	12.5
21	37.5	125.0	12.0	11.1	10.5	9.6
22	34.1	159.1	9.3	8.8	8.4	7.7
23	30.0	200.0	7.1	6.8	6.5	6.0
24	25.0	250	4.9	4.9	4.8	4.4
25	18.75	313	3.2	3.3	3.3	3.1
26	13.00	370	2.2	2.1	2.2	2.1
27	6.52	435	1.1	1.0	1.2	1.2

Concerning the determination of the slope of the glass electrode and experimental details, the reader is referred to the previous treatise[3, p. 40]. E_0 was determined before, as well as after, the measurement of E, in order to control that the asymmetry potential was a constant during a measurement series. Within the limits of the random errors, the measurements with the glass electrode gave the same values of E_B as the measurements with the quinhydrone electrode.

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Table 3. Determination of $\bar{n}/$ [B] as a function of [B] at different values of the parameters C_A and a.

No.	$C_A = 0$			$C_A = 50$ mC			$C_A = 100$ mC			$C_A = 150$ mC		
	ϑ	[B]	$\dfrac{\bar{n}}{[B]}$	ϑ	[B]	$\dfrac{\bar{n}}{[B]}$	ϑ	[B]	$\dfrac{\bar{n}}{[B]}$	ϑ	[B]	$\dfrac{\bar{n}}{[B]}$
	mC	mC	C⁻¹	mC	mC	C⁻¹	mC	mC	C⁻¹	mC	mC	C⁻¹
1	0.07	2.33	47.3	0.09	2.67	40.0	0.12	3.00	34.6	0.14	3.41	29.3
2	0.07	3.62	45.0	0.08	4.15	38.0	0.11	4.62	33.1	0.13	5.30	27.6
3		6.47	40.9	0.08	7.33	35.0	0.1	8.06	30.7	0.1	9.30	25.3
4		10.35	37.4		11.65	31.9		12.92	27.7		14.72	23.0
5		14.65	34.2		16.50	29.1		18.07	25.6		20.4	21.4
6		24.8	28.3		27.3	24.7		29.5	21.9		32.9	18.4
7		48.7	21.0		52.3	18.5		54.9	17.0		59.4	14.7
8		75.2	16.3		78.4	15.1		81.5	14.0		86.8	12.2
9		113.5	12.7		115.9	12.1		118.7	11.5		125.0	10.0
10		168	9.8		169	9.6		171	9.2		177	8.2
11		242	7.8		242	7.8		244	7.6		248	7.0
12		315	6.8		315	6.8		315	6.8		319	6.3
14	0.04	2.02	46.2	0.06	2.25	39.5	0.07	2.51	33.4	0.09	2.80	28.0
15	0.04	4.20	43.3	0.05	4.69	36.6	0.07	5.19	31.1	0.08	5.80	25.7
16	0.04	6.57	40.2	0.05	7.30	34.1	0.07	8.08	28.9	0.08	8.96	24.0
17		11.77	35.3		13.00	30.0		14.13	25.9		15.53	21.6
18		18.88	31.0		20.6	26.6		22.1	23.2		24.1	19.6
19		26.5	27.6		28.8	23.6		30.7	20.8		33.0	17.7
20		43.2	22.3		46.0	19.5		47.9	17.7		50.8	15.4
21		77.7	16.2		80.6	14.6		82.5	13.7		85.6	12.3
22		110.1	13.1		112.3	12.2		114.1	11.6		117.3	10.5
23		150.9	10.8		152.8	10.3		154.6	9.8		157.8	8.9
24		206	8.6		206	8.6		207	8.3		210	7.6
25		276	7.2		276	7.2		276	7.2		276	7.2

From Table 2 it is obvious that the values of E_B, at different C_A, gradually coincide when C_B is increased. In Table 3, [B] and $\bar{n}/$[B] of the solutions measured have been calculated. It is only necessary to compute the correction term ϑ at the smallest values of C_B, and it is evident that [HSO$_4^-$] is quite negligible, compared with C_A.

Fig. 1 represents the measurements graphically at [B] $\leqq$ 55 mC. The function $\bar{n}/$[B] is dependent on the factor a in eq. (18). The reason for this is that in two solutions with the same values of C_A and [B] but with different values of C_M (that is of a), [A] is greatest in the solution that has the smallest
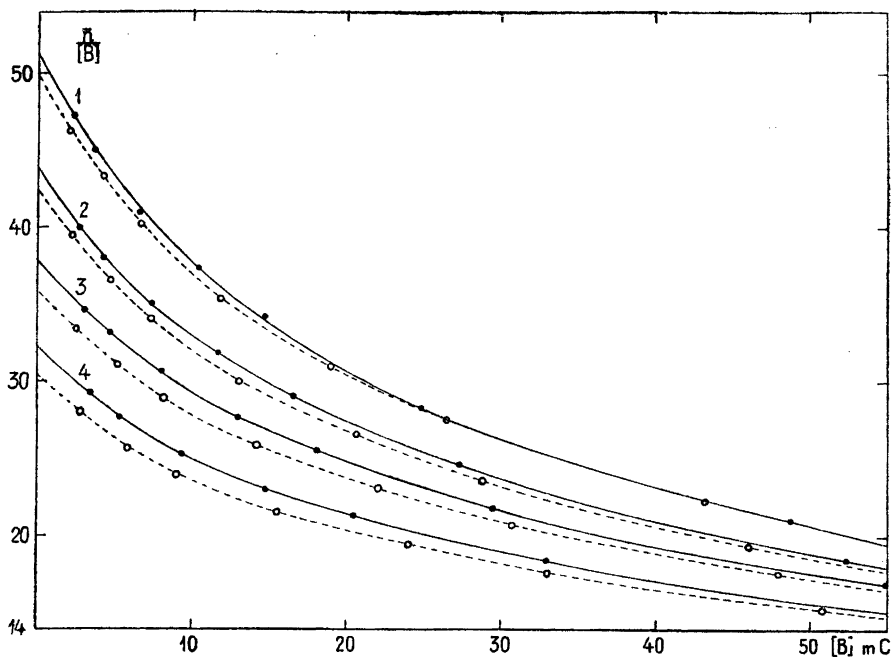
Fig. 1. $\bar{n}/[B]$ *as a function of* $[B]$. *1.* $C_A = 0$; *2.* $C_A = 50$ mC; *3.* $C_A = 100$ mC; *4.* $C_A = 150$ mC. — *Fulldrawn curves are valid at* $a = 100$ mC (*see eq.* (18)); *dashed curves at* $a = 50$ mC.

concentration C_M. Polynuclear complexes also may contribute to the dependence on a.

The definition of $\Delta\bar{n}$ has been given above (p. 74). In Table 4 the function $\Delta\bar{n}/[B]$ has been calculated at different values of $[B]$. The values in the columns 2—7 have been obtained from the graphical representation of $\bar{n}/[B]$. As potentiometric measurements have been performed at only two values of the parameter a, it has been presumed from the extrapolation of $\Delta\bar{n}/[B]$ to $a = 0$ (that is $C_M = 0$), that $\Delta\bar{n}/[B]$ is a linear function of a at a constant value of $[B]$. From Table 4 it will be seen that the dependence on a is rather small, and therefore this approximation is justified. In the columns 8—10 in Table 4, the extrapolated values of $(\Delta\bar{n}/[B])_{C_M} = 0$ at $[A]_n = 50$, 100, and 150 mC are to be found.

As an upper limit of integration in eq. (14) for the three values of $[A]_n$ we may choose $b = 0.200$, 0.250, and 0.300 C, which appears from Table 4. The values of ln X ($[A]_n$, 0) have been calculated by graphical integration and are given in Table 5.

Table 4. Determination of $(\Delta\bar{n}/[B])_{C_M=0}$ as a function of [B] at different values of the parameter $C_A = [A]_n$.

[B] mC	$C_M = 100-\dfrac{C_B}{5}$ mC			$C_M = 50-\dfrac{C_B}{10}$ mC			$C_M = 0$		
	$C_A=50$ mC	$C_A=100$ mC	$C_A=150$ mC	$C_A=50$ mC	$C_A=100$ mC	$C_A=150$ mC	$C_A=50$ mC	$C_A=100$ mC	$C_A=150$ mC
	$\dfrac{\Delta\bar{n}}{[B]}$ C^{-1}			$\dfrac{\Delta\bar{n}}{[B]}$ C^{-1}			$\dfrac{\Delta\bar{n}}{[B]}$ C^{-1}		
0	7.2	13.3	19.0	7.5	14.1	19.5	7.8	14.9	20.0
5.0	5.9	10.3	15.2	6.1	11.0	15.9	6.3	11.7	16.6
10.0	4.7	8.5	12.7	4.9	9.1	13.3	5.1	9.7	13.9
15.0	3.9	6.9	10.7	4.2	7.6	11.5	4.5	8.3	12.3
20.0	3.3	5.8	9.2	3.6	6.6	10.0	3.9	7.4	10.8
30.0	2.5	4.6	7.3	3.0	5.3	8.0	3.5	6.0	8.7
50.0	1.8	3.0	4.9	2.3	3.6	5.3	2.8	4.2	5.7
75.0	1.0	1.8	3.2	1.3	2.1	3.4	1.6	2.4	3.6
100	0.6	1.2	2.4	0.9	1.5	2.6	1.2	1.8	2.8
150	0.3	0.6	1.6	0.5	1.0	1.8	0.7	1.4	2.0
200	0.1	0.4	1.0	0.1	0.4	0.9	0.1	0.4	0.8
250	0	0.2	0.6	0	0.1	0.4	0	0	0.2
300	0	0	0.4	0	0	0	0	0	0

The values of the function $\Delta\bar{n}/[B]$ at $C_A = 50$ mC are, on the average, 0.3 C^{-1} greater at $a = 50$ mC than at $a = 100$ mC within the main part of the range of integration (see Table 4). The greatest deviation from this average value is 0.2 C^{-1}. This means that the maximum error in the values of the function is about 0.1 C^{-1} in the two series of measurements. Then the values of the function at $a = 0$ may have a maximum error $\varepsilon = 0.2$ C^{-1}. The same value of ε is obtained at the other concentrations C_A. Thus according to the

Table 5. Corresponding values of $[A]_n$, $X([A]_n, 0)$ and $(\bar{n}/[B])_{C_M=0}$.

$[A]_n$ mC	$lnX([A]_n, 0)$	$X([A]_n, 0)$	$(\bar{n}/[B])_{\substack{C_M=0 \\ [B]=0}}$ C^{-1}	$\sum\limits_{j=0}^{N-1}\beta_{j,\,1}[A]_n^j$ C^{-1}
0			48.2	48.2
50	0.37 ± 0.08	1.45	40.8	59.2
100	0.65 ± 0.10	1.92	33.8	64.9
150	0.97 ± 0.12	2.64	28.6	75.5

calculation of errors, given above (p. 77), the maximum random error of $ln \ X$ is $= 0.4 \cdot b$.

From corresponding values of [A] and X ([A], 0) in Table 5, the constants of the mononuclear sulphate complexes have been computed from eq. (15), and the following values have been obtained:

$$\beta_1 = 9 \pm 2 \ C^{-1}; \ \beta_3 = 80 \ C^{-3}$$

We get a small value for β_2, but since the uncertainty is great it is not justifiable to assign a numerical value. In the calculation of β_3 we may therefore put $\beta_2 \simeq 0$. It is hardly possible to mention an upper limit of the random error in the computed value of β_3. At an ionic strength of 1 C and with Ac^- as a displacing ligand, the sulphate concentration C_A cannot be increased materially above 150 mC, and therefore the value of $\beta_3 \cdot [A]^3$ is small compared with the value of the polynomial $X([A], 0)$. This fact is the cause of the difficulty in determining β_3 accurately.

The fourth column of Table 5, gives values of $(\bar{n}/[B])_{C_M = 0}$ at [B] = 0. They have been obtained from Fig. 1 by linear extrapolation to $C_M = 0$ of the intercepts on the $\bar{n}/[B]$-axis, that correspond to a constant concentration C_A. The values of $\sum_{j=0}^{N-1} \beta_{j, 1} [A]_n^j$, in the fifth column, have been calculated from eq. (16) The complexity constant of the mixed complex $CuSO_4Ac^-$ is:

$$\beta_{1,1} = 190 \pm 50 \ C^{-2}$$

The measurements admit no determination of the remaining constants $\beta_{j, 1}$.

Discussion

In the previous measurements by the present author[3, p. 62] with an amalgam electrode, the following values of the complexity constants of the mononuclear sulphate complexes were obtained at an ionic strentth of 1 C: $\beta_1 = 10.6 \ C^{-1}$, $\beta_2 = 10$—17 C^{-2}, and $\beta_3 = 200 \ C^{-3}$. The value of β_1 has been confirmed in the present investigation, and the agreement shows the applicability of the new method. The divergence between the values of β_3 may be caused partly by the random errors, and partly by medium changes, since in the present measurements part of the sodium perchlorate must be exchanged for acetate buffer.

The complex formation in cupric sulphate solutions has been studied several times (Mecke and Ley [4], Ley and Heidbrink [5], Rouyer [6], Plake [7], Brintzinger

and Osswald [8], Davies [9], Owen and Gurry [10]). These investigations have been discussed in the previous treatise [3, p. 57]. Later Näsänen[11] made a spectrophoto-metric study of cupric perchlorate — litium sulphate solutions. It was assu-med that only the complex $CuSO_4$ was formed, and by means of a Debye-Hückel equation the variation of β_1 with the ionic strength was investigated. At $I = 1$ C the value $\beta_1 = 4$ C^{-1} was obtained. However, a neglecting of the complex $Cu(SO_4)_2^{2-}$ must give too low values of β_1 in such measurements even at small concentrations of SO_4^{2-} (cf. Olerup [12, p. 60], Fronæus [3, p. 91]). In addition it must be emphasized that from the variation of β_1 with the ionic strength it is not justifiable to draw any conclusions about the variation when only the composition is changed but the ionic strength is kept constant by addition of sodium perchlorate.

SUMMARY

A new method for the investigation of the complex formation between a central group M and a ligand A is described. The method is based on the use of an auxiliary ligand B, the concentration of which can be measured in the complex solutions.

A competition for the central group arises between the ligands A and B, and B must form such strong complexes, that by increasing the concentration of B, the ligand A can be completely displaced.

The theoretical treatment shows that it is possible to calculate from the measurements the complexity constants of the mononuclear complexes MA_j ($j = 1, 2, \ldots, N$), irrespective of whether or not mixed complexes and poly-nuclear complexes are formed. The method also admits a determination of the complexity constants of the mixed complexes of the type MA_jB ($j = 1, 2, \ldots$).

In order to examine the method it has been applied to the cupric sulphate system with the acetate ion as the displacing ligand B. The ionic strength of the solutions has been kept constant at 1 C by addition of sodium perchlorate. As an acetate buffer has been used, it has been possible to determine [B] in the solutions by potentiometric measurements, employing the quinhydrone electrode. The measurements have been carried out at 20° C and the com-plexity constants of $CuSO_4$, $Cu(SO_4)_3^{4-}$ and $CuSO_4Ac^-$ have been computed and found to be

$$\beta_1 = 9 \pm 2 \text{ C}^{-1}; \qquad \beta_3 = 80 \text{ C}^{-3}; \qquad \beta_{1,1} = 190 \pm 50 \text{ C}^{-2}$$

The complexity constant β_2 of $Cu(SO_4)_2^{2-}$ is too small to be calculated from these measurements.

The results are in rather good agreement with previous measurements by the present author, and prove the applicability of the new method.

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