ACTA CHEMICA SCANDINAVICA 5 (1951) 139–156

A Potentiometric and Extinctiometric Study of the Cupric Nitrite Complex System

STURE FRONÆUS

Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Lund, Sweden

In the literature several investigations of cupric nitrite solutions are to be found, but the purpose has chiefly been to study the decomposition of the solutions. References to such investigations can be found in a paper by Gallais and Vives [1]. These authors have studied cupric nitrite solutions by several methods in order to establish which complexes are formed. The investigation is essentially of a qualitative nature and gives no information about the strength of the complexity. The only quantitative investigation, found in the literature, is an extinctiometric investigation by Kossiakoff and Sickman [2]. At the calculation of the complexity constants, however, certain assumptions have been made that render the estimation of the results rather difficult.

Previously no potentiometric investigation of this complex system seems to have been carried out, presumably due to the fact that copper and copper amalgam cannot be used to determine the cupric ion concentration in cupric nitrite solutions. The present author found that such solutions are rapidly reduced by copper amalgam with the formation of nitrite oxide.

The investigation methods chosen

The method of ligand displacement, developed by the present author in a previous paper [3], was used in this investigation for a potentiometric determination of the complexity constants of the mononuclear complexes. In this case ammonia was chosen as a displacing ligand. Then the measurements could be performed at such values of $p[H^+]$ * that the decomposition of the nitrite ion proceeded slowly and did not disturb the measurements. Besides ammonia forms so strong complexes with the cupric ion that the nitrite ion can be completely displaced as ligand even at rather low values

* $p[H^+] = -\log [H^+]$.

of the concentration of free ammonia, and this is essential for the applicability of the method (see Fronæus [3, p. 75]).

As in the earlier investigations of the present author the measurements were carried out at a constant ionic strength I = 1 C. In order to prevent the formation of hydroxo complexes the ionic medium consisted of ammonium perchlorate (0.500 C) and sodium perchlorate. Then, as the complex solutions contained an ammonia buffer, the concentration of free ammonia could be determined by emf measurements with the use of a glass electrode.

As a different method of investigating the cupric nitrite system the extinctiometric method was selected. Also these measurements were carried out at the ionic strength I = 1 C with sodium perchlorate as the neutral salt. In this case it was not possible to let ammonium perchlorate form part of the ionic medium, for in the absence of ammonia the p[H^+] in the solutions then would have become too low. Naturally such a difference in the composition of the ionic medium may cause some discrepancy between the potentiometrically and the extinctiometrically determined complexity constants.

CHEMICALS USED

Sodium nitrite, p. a. Stock solutions were prepared from calculated amounts of the dried preparation. The concentration was checked by oxidation with ceric sulphate in excess, strongly acidified with sulphuric acid. During stirring the nitrite solution was added from a pipette, put down into the ceric sulphate solution. Then the surplus of ceric sulphate was titrated with ferrous sulphate, the *o*-phenanthroline ferrous complex being used as oxidation-reduction indicator.

Ammonium perchlorate, p. a. The concentration of the stock solutions was checked by Kjeldahl distillation and titration of the ammonia obtained. From ammonium perchlorate and carbon dioxide-free ammonia a buffer was prepared.

The *other chemicals* were the same as before [4, p. 31].

THE POTENTIOMETRIC INVESTIGATION

Summary of notation and equations used

As in a previous paper (cf. Fronæus [3]) the following notation is used:

C_M, C_A, C_B = total concentrations of the central group M and the ligands A and B.

a = a quantity, defined by eq. (1) below.

$\beta_{j,k}$ = the complexity constant of the complex MA_jB_k ($j, k \geqq 0$)

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

$\bar{n}$ = the ligand number with respect to the ligand B.

$\Delta\bar{n}$ = the difference between the ligand numbers of two solutions, the first of which has [A] = 0, while [B] and a are the same in both solutions.

At the measurements described below C_M was a function of C_B:

$$C_M = a \cdot f(C_B) \tag{1}$$

Here the value of the parameter a was kept constant in a series of measurements. If we allow $a \to 0$ (that is $C_M \to 0$), the limiting function $(\Delta\bar{n})_{C_M=0}$ will be a function of $[A] = C_A$ and $[B]$. Corresponding values of $[A]$ and $X([A],0)$ can be calculated from eq. (14) in the previous paper [3, p. 75]. When the integration is performed graphically, it is often advantageous to use the following equivalent eq:

$$\log X([A],0) = 0.4343 \cdot \int_0^{b'} \left(\frac{\Delta\bar{n}}{[B]}\right)_{C_M=0} \cdot d[B] + \int_{\log b'}^{\log b} (\Delta\bar{n})_{C_M=0} \cdot d \log[B] \tag{2}$$

The upper limit of integration b must be selected in such way that $(\Delta\bar{n})_{C_M=0} = 0$, when $[B] \geqq b$ [3, p. 75]. Then the complexity constants $\beta_{j,0}$ of the mononuclear complexes MA_j can be computed from corresponding values of $[A]$ and $X([A],0)$ according to the methods described before [4, p. 28].

For the calculation of the complexity constants $\beta_{j,1}$ of the mixed complexes MA_jB we have the eq: [3, p. 76]

$$\lim_{\substack{C_M \to 0 \\ [B] \to 0}} \left(\frac{\bar{n}}{[B]}\right) = \frac{\sum_{j=0}^{N-1} \beta_{j,1} [A]^j}{X([A],0)} \tag{3}$$

The measurements and calculations

The emf measurements that tended to a determination of $[NH_3] = [B]$ in the complex solutions, were performed, as already mentioned, with a glass electrode (Radiometer, type G 100). The cells measured were of the following type:

$$+ \text{ RE} \;\|\; \begin{matrix}\text{complex} \\ \text{solution}\end{matrix} \;|\; \begin{matrix}\text{glass} \\ \text{electrode}\end{matrix} \; -$$

The reference electrode RE and the salt bridge had the same composition as before [4, p. 34]. In a measurement series the solution of the right half-cell was obtained by mixing two solutions S_1 and S_2 of the composition:

$$S_1 = \begin{cases} a & \text{mC } Cu(ClO_4)_2 \\ C_A & \text{mC } NaNO_2 \\ 500 & \text{mC } NH_4ClO_4 \\ (500 - 3\,a - C_A) & \text{mC } NaClO_4 \end{cases} \qquad S_2 = \begin{cases} C_A & \text{mC } NaNO_2 \\ 252 & \text{mC } NH_3 \\ 500 & \text{mC } NH_4ClO_4 \\ (500 - C_A) & \text{mC } NaClO_4 \end{cases}$$

Then the relation (1) between C_M and C_A in mC takes the following form:

$$C_M = a \cdot \left(1 - \frac{C_B}{252}\right)$$

To a known volume of the solution S_1 in the electrode vessel portions of the solution S_2 were added from a burette. Stirring in the cell solution was arranged by a stream of nitrogen gas. A valve potentiometer (Radiometer, type PHM 3 h) was used and the measurements were carried out in an air thermostat at 20.0° C. Concerning experimental details, the reader is referred to a previous treatise [4, p. 40]. The reproducibility of the emf was 0.3—0.4 mV. All measurements were repeated at least once.

After the last emf measurement in each series the nitrite concentration in the measuring solution and in S_1 and S_2 was determined. The determination was performed by oxidation with ceric sulphate in the manner described above (p. 140). In the solution S_1 the decrease in C_A was < 1 % (at $a = 20$ mC) after about one hour. The solution S_2 and the last measuring solutions in each series, which had higher p[H^+] -values, were rather stable, so that no decrease in C_A could be detected after twenty-four hours. Thus, as a measurement series could be performed fairly rapidly, the instability of the solutions did not affect the emf measurements.

The emf E in mV of the cell above is given by

$$E = E_k - s \cdot log\,[H^+] \tag{4}$$

Here E_k is a constant, as long as the asymmetri potential of the glass electrode, the liquid junction potential and the activity coefficient of H^+ has not changed, and s is the slope of the glass electrode.

At $C_M = 0$ but at the same values of C_A and C_B as in (4) we use the notations E_0 and $[H^+]_0$. Then, as the ionic medium is approximately unchanged, we have:

$$E_0 = E_k - s \cdot log\,[H^+]_0 \tag{4 a}$$

For the concentration $[H^+]_0$ it holds:

$$\frac{[H^+]_0 \cdot C_B}{[NH_4^+]} = K_c \tag{5}$$

K_c is the dissociation constant of the ammonium ion in the salt medium used and $[NH_4^+] = 500$ mC. At C_B varying between 3 and 125 mC E_0 was measured and graphically represented as a function of $log\ C_B$. The result was

a practically stright line with the slope $s = 57.5$ mV. The variation of E_0 with C_A is quite slight at $C_A \leqq 300$ mC which seems to justify the assumption that the partial exchange of sodium perchlorate for sodium nitrite does not affect the activity coefficients very much.

Combining eq. (4) and (4a) we obtain the expression of $E_B = E_0 - E$ in mV

$$E_B = 57.5 \; log \frac{[H^+]}{[H^+]_0} \tag{6}$$

A measurement series (with constant values of a and C_A) was started with the determination of the E_0-values, and then the emf:s E were measured. The reproducibility of the E_B-values was used as a control that the asymmetri potential had not changed perceptibly during the measurements of E_0 and E.

For the dissociation of the ammonium ion it holds:

$$\frac{[H^+] \cdot [B]}{500 - \vartheta} = \frac{[H^+]_0 \cdot C_B}{500} \tag{7}$$

Here $\vartheta = [HNO_2]$ is a quantity quite negligible.

Thus we have:

$$\frac{[H^+]}{[H^+]_0} = \frac{C_B}{[B]} \tag{7a}$$

The expression for the ligand number in respect of B is:

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

At a constant value of $[A] \simeq C_A$ the correction term ϑ is fixed by the value of $[H^+]$ only. Therefore ϑ could be determined in an acetate buffer with a low value of C_{HAC}, which had the same value of $[H^+]$ (measured with the glass electrode) as the complex solution. The solutions I and II below with known values of C_{HAC} and C_{AC} were measured.

I $\begin{cases} C_{HAC} \text{ mC HAc} \\ C_{AC} \text{ mC NaAc} \\ C_A \text{ mC } NaNO_2 \\ (1\,000 - C_{AC} - C_A) \text{ mC } NaClO_4 \end{cases}$ II $\begin{cases} C_{HAC} \text{ mC HAc} \\ C_{AC} \text{ mC NaAc} \\ (1\,000 - C_{AC}) \text{ mC } NaClO_4 \end{cases}$

From the difference ΔE between the emf:s ϑ could be computed:

$$\Delta E = 57.5 \; log \frac{(C_{AC} + \vartheta) \cdot C_{HAC}}{(C_{HAC} - \vartheta) \cdot C_{AC}} \tag{9}$$

Table 1. Emf measurements on the three component complex system $Cu^{2+} - NO_2^- - NH_3$.

No.	C_M mC	C_B mC	$C_A = 0$ mC	$C_A = 100$ mC	$C_A = 200$ mC	$C_A = 300$ mC
			E_B mV			
1	19.48	6.56	137.6	131.5	127.7	123.0
2	19.24	9.71	136.1	130.3	126.3	122.1
3	18.76	15.81	131.2	125.3	121.8	117.6
4	18.16	23.0	123.5	117.2	114.3	109.4
5	17.64	29.7	114.4	108.2	104.7	99.5
6	16.68	42.1	93.3	87.4	83.2	79.3
7	15.00	63.1	49.7	47.1	45.7	42.9
8	13.64	80.3	27.7	27.2	27.0	26.0
9	12.00	101.0	15.6	15.9	15.8	16.0
10	10.00	126.3	8.9	8.5	8.8	8.9
11	9.74	6.56	117.5	111.5	107.3	103.0
12	9.62	9.71	112.6	106.3	102.5	97.9
13	9.38	15.81	100.0	93.0	89.4	85.4
14	9.08	23.0	81.0	73.8	70.7	66.9
15	8.82	29.7	60.9	55.8	53.2	50.4
16	8.34	42.1	33.9	31.8	30.7	30.5
17	7.50	63.1	15.9	15.4	15.2	16.0
18	6.82	80.3	10.4	10.1	9.8	10.3
19	6.00	101.0	6.6	6.6	6.8	7.0

The values of E_B, obtained at the emf measurements on the complex system are shown in Table 1. For the solutions with nos. 1—10 the parameter a in eq. (1) has a value of 20 mC and for the solutions nos. 11—19 a value of 10 mC.

In Table 2, [B] and $\bar{n}/[B]$ or $\bar{n}$ of the solutions measured have been calculated. At greater values of C_B the correction term ϑ is quite negligible. Though the relative random error in $\bar{n}$ is rather great for the solutions with nos. 10, 18 and 19, it is evident that at $[B] \simeq 50$ mC $\bar{n}$ has attained the "characteristic" co-ordination number $N = 4$ in every measurement series. Then A is completely displaced as ligand.

In Figs- 1 and 2, the measurements are graphically represented. As the measurements could be performed at so small values of the parameter a, owing to the fact that ammonia forms rather strong complexes, the difference C_A—[A] is comparatively small. The consequence of this is that the curves, corresponding to the same value of C_A but different values of a, coincide within the

Table 2. Determination of corresponding values of [B] and $\bar{n}/[B]$ or $\bar{n}$ at different C_A and a.

No.	$C_A = 0$		$C_A = 100$ mC			$C_A = 200$ mC			$C_A = 300$ mC		
	[B] mC	$\frac{\bar{n}}{[B]}$ C^{-1}	ϑ mC	[B] mC	$\frac{\bar{n}}{[B]}$ C^{-1}	ϑ mC	[B] mC	$\frac{\bar{n}}{[B]}$ C^{-1}	ϑ mC	[B] mC	$\frac{\bar{n}}{[B]}$ C^{-1}
1	$2.65 \cdot 10^{-2}$	12 650	0.16	$3.39 \cdot 10^{-2}$	10 100	0.29	$3.94 \cdot 10^{-2}$	8 900	0.37	$4.76 \cdot 10^{-2}$	7 400
2	$4.17 \cdot 10^{-2}$	12 050	0.09	$5.26 \cdot 10^{-2}$	9 650	0.17	$6.13 \cdot 10^{-2}$	8 300	0.24	$7.31 \cdot 10^{-2}$	7 050
3	$8.26 \cdot 10^{-2}$	10 150	0.03	0.105	8 000	0.05	0.120	6 700	0.07	0.142	5 900
4	0.164	7 650		0.211	5 950		0.237	5 300		0.288	4 340
		$\bar{n}$			$\bar{n}$			$\bar{n}$			$\bar{n}$
5	0.304	1.667		0.390	1.661		0.449	1.661		0.553	1.650
6	1.00	2.46		1.27	2.45		1.50	2.43		1.76	2.42
7	8.62	3.63		9.57	3.57		10.1	3.53		11.3	3.45
8	26.5	3.94		27.0	3.91		27.2	3.89		28.3	3.81
9	54.1	3.91		53.4	3.97		53.6	3.95		53.2	3.98
10	88.4	3.80		89.9	3.64		88.8	3.75		88.4	3.80
		$\frac{\bar{n}}{[B]}$ C^{-1}			$\frac{\bar{n}}{[B]}$ C^{-1}			$\frac{\bar{n}}{[B]}$ C^{-1}			$\frac{\bar{n}}{[B]}$ C^{-1}
11	$5.94 \cdot 10^{-2}$	11 250	0.07	$7.55 \cdot 10^{-2}$	8 900	0.10	$8.93 \cdot 10^{-2}$	7 550	0.13	0.106	6 400
12	0.107	9 350	0.02	0.138	7 200	0.02	0.160	6 200	0.02	0.193	5 150
		$\bar{n}$			$\bar{n}$			$\bar{n}$			$\bar{n}$
13	0.288	1.655		0.382	1.645		0.441	1.639		0.517	1.630
14	0.897	2.43		1.20	2.40		1.36	2.38		1.58	2.36
15	2.59	3.07		3.18	3.00		3.53	2.97		3.95	2.91
16	10.8	3.75		11.8	3.63		12.3	3.57		12.4	3.56
17	33.4	3.96		34.1	3.87		34.3	3.84		33.2	3.99
18	52.9	4.02		53.6	3.92		54.3	3.81		53.2	3.97
19	77.5	3.92		77.5	3.92		76.9	4.02		76.3	4.11

limits of experimental errors. Thus the limiting curves at $a = 0$ (that is $C_M = 0$) are obtained directly.

In Table 3 the functions $(\Delta\bar{n}/[B])_{C_M=0}$ and $(\Delta\bar{n})_{C_M=0}$ have been calculated at different [B] and [A] = 100, 200, and 300 mC. The values of the functions have been obtained from the curves in Fig. 1 and Fig. 2.

From Table 3 it is obvious that $b = 50.0$ mC can be taken as an upper limit of integration in eq. (2). The values of *log X* ([A],0), given in Table 4, have been computed by graphical integration and with $b' = 0.20$ mC.

The complexity constants $\beta_{j,0}$ of the mononuclear nitrite complexes MA_j have been calculated from corresponding values of [A] and X([A],0) in Table 4.

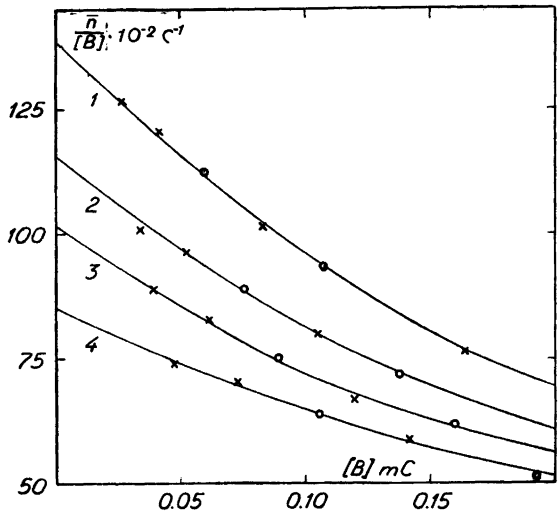

Fig. 1. $\bar{n}/[B]$ as a function of $[B]$. 1. $C_A = 0$; 2. $C_A = 100$ mC; 3. $C_A = 200$ mC; 4. $C_A = 300$ mC. ——— × : $a = 20$ mC; ○: $a = 10$ mC.

The determination was performed graphically (*cf.* Fronæus [4, p. 28—29]). The estimation of the maximum random errors was carried out in a similar way as before [3, pp. 77 and 84]. But in this case we neglect the error that the finite

Table 3. Determination of $(\Delta\bar{n}/[B])_{C_M=0}$ and $(\Delta\bar{n})_{C_M=0}$ as functions of $[B]$ at different values of the parameter $C_A = [A]$.

[B] mC	$C_A = 100$ mC	$C_A = 200$ mC	$C_A = 300$ mC	$C_A = 100$ mC	$C_A = 200$ mC	$C_A = 300$ mC
	$(\Delta\bar{n}/[B])_{C_M=0}$ C^{-1}			$(\Delta\bar{n})_{C_M=0}$		
0	2 200	3 650	5 300			
0.02	2 150	3 450	4 900			
0.05	1 900	3 050	4 200			
0.10	1 450	2 400	3 100	0.145	0.240	0.310
0.15	1 100	1 750	2 300	0.165	0.260	0.345
0.25	700	1 100	1 500	0.180	0.275	0.380
0.50				0.190	0.285	0.420
1.00				0.19	0.31	0.42
2.50				0.18	0.29	0.41
5.00				0.16	0.25	0.36
10.0				0.12	0.20	0.27
25.0				0.05	0.10	0.15
50.0				0	0	0
75.0				0	0	0

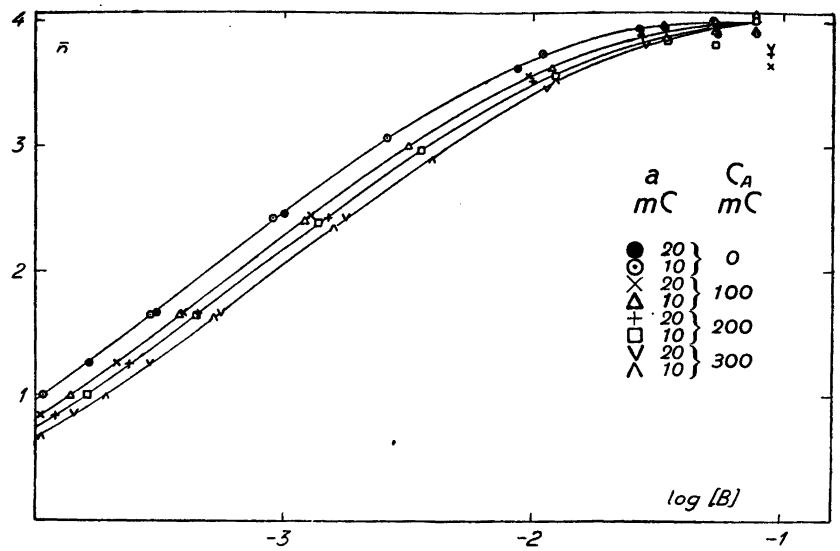

Fig. 2. $\bar{n}$ as a function of log [B] at different values of a and C_A.

range of integration in eq. (2) instead of an infinite may cause, as the ligand number with respect to ammonia attains the limiting value 4 within the concentration range of [B] used. The values of the constants obtained are:

$$\beta_{1,0} = 17 \pm 2\ \mathrm{C}^{-1} \quad ; \quad \beta_{2,0} = 30 \pm 8\ \mathrm{C}^{-2}$$

The $X([A],0)$ -value at [A] = 300 mC indicates that also the complex MA_3 is formed to some extent, but it seems too delicate to determine the constant $\beta_{3,0}$ from these measurements.

Table 4. Corresponding values of [A], $X([A], 0)$ and $(\bar{n}/[B])_{\substack{C_M=0 \\ [B]=0}}$.

[A] mC	*log* $X([A]), 0)$	$X([A], 0)$	$(\bar{n}/[B])_{\substack{C_M=0 \\ [B]=0}}$ C^{-1}	$\sum_{j=0}^{N-1} \beta_{j,1}\,[A]^j$ C^{-1}
0		1.00	13 900	13 900
100	0.473	2.97	11 600	34 500
200	0.759	5.74	10 200	58 500
300	1.053	11.3	8 500	96 000

With the constants obtained, the ligand number and the composition of the two component system $Cu^{2+} - NO^{2-}$ has been computed in Table 5. For the calculation the eq. (39—41) of a previous treatise [4, p. 29] were used.

The values in the fourth column of Table 4 have been obtained by extrapolation to [B] = 0 of the curves in Fig. 1. From corresponding values of [A] and $\sum_{j=0}^{N-1} \beta_{j,1}\,[A]^j$ in the same table the complexity constants of the complexes MB, MAB and MA_2B have been calculated.

$$\beta_{0,1} = (1.40 \pm 0.05) \cdot 10^4\ C^{-1}, \quad \beta_{1,1} = (1.9 \pm 0.2) \cdot 10^5\ C^{-2};$$
$$\beta_{2,1} = (1.6 \pm 0.5) \cdot 10^5\ C^{-3}$$

From the investigation of J. Bjerrum [5, p. 127] one gets $\beta_{0,1} = 1.6 \cdot 10^4\ C^{-1}$ at 20° C and in 1 C ammonium nitrate.

Assuming that we may disregard the mutual forces between the ammonia molecule and the nitrite ions taken up as ligands, we should by purely statistical reasons expect the following relation to hold for the thermodynamical complexity constants:

$$\beta_{j,1} = \frac{N-j}{N} \cdot \beta_{j,0} \cdot \beta_{0,1} \tag{10}$$

If we further assume that the taking up of an ammonia molecule does not change the activity coefficient of the complex ion very much, that is $f_{MA_jB} \simeq f_{MA_j}$ and $f_{MB} \simeq f_M$, eq. (10) can be used also at the ionic strength I = 1 C. With the values of $\beta_{1,0}$, $\beta_{2,0}$, and $\beta_{0,1}$ obtained and with N = 4 eq. (10) gives $\beta_{1,1} \simeq \beta_{2,1} \simeq 2.0 \cdot 10^5\ C^{-2}\ (C^{-3})$ in good agreement with the values calculated above.

Table 5. The ligand number $\bar{n}_A$ with respect to A and the composition of the two component system $Cu^{2+} - NO_2^-$ as calculated at different [A] with the constants obtained.

$\beta_1 = 17 \pm 2\ C^{-1}$ $\beta_2 = 30 \pm 8\ C^{-2}$

[A] mC	$\bar{n}_A$	100 α_0	100 α_1	100 α_2
10	0.155	85.0	14.5	0.5
50	0.520	52.0	44.0	4.0
100	0.765	33.5	56.5	10.0
200	1.035	18.0	60.5	21.5
300	1.190	11.5	58.0	30.5

THE EXTINCTIOMETRIC INVESTIGATION

The equations for the calculation of the complexity constants

At the calculations in this section the following notation is used (*cf.* Fronæus [4]):

E = the extinction of the complex solution.
d = the thickness of the absorbing layer.
$e = E/d$.
ε_M^0, ε_A^0, ε_j = the molar extinctions of M, A and the complex MA_j.
$\varepsilon_M = (e - \varepsilon_A^0 \cdot C_A)/C_M$.
β_i and $X([A])$ = the quantities denoted $\beta_{i,0}$ and $X([A],0)$ at the potentiometric measurements.
$X_1 = (X-1)/[A]$, $X_2 = (X_1-\beta_1)/[A]$.
$\bar{n}$ = the ligand number with respect to A.

The determination of the ligand number extinctiometrically is possible, only if mononuclear complexes are formed exclusively (*cf.* Olerup [6, p. 70] Fronæus [4, p. 90]). The calculation method has been described in a previous treatise [4, p. 87], so we shall only give a summary of the main points here.

Assuming that Beer's law can be applied to the complex solutions, we obtain the exprssion for e:

$$e = \varepsilon_M^0 [M] + \sum_{j=1}^{N} \varepsilon_j [MA_j] + \varepsilon_A^0 [A] \tag{11}$$

Introducing the complexity constants, we get:

$$\varepsilon_M = \frac{\varepsilon_M^0 + \sum_{j=1}^{N} (\varepsilon_j - j \cdot \varepsilon_A^0)\, \beta_j [A]^j}{X\ ([A])} \tag{12}$$

In every measurement series (with a constant value of d) we have a relation between C_M and C_A of the kind, given in eq. (1). Then ε_M can be graphically represented as a function of C_A and with a as a parameter. From eq. (12) it is obvious that a constant value of ε_M corresponds to a constant value of [A] and thus of $\bar{n}$. From the relation $C_A = [A] + \bar{n} \cdot C_M$ we consequently obtain:

$$\left(\frac{\partial C_A}{\partial C_M}\right)_{\varepsilon_M} = \bar{n} \tag{13}$$

Then, if C_A is plotted against C_M at a constant value of ε_M, a straight line with the intercept [A] on the C_A-axis and with the slope $\bar{n}$ should be obtained. The values of C_A are taken from the (ε_M, C_A)-diagram, mentioned above, and the values of C_M are calculated from the relations (1). When the ($\bar{n}$/[A], [A])-curve has been determined in this way, pairs of values (X([A]), [A]) are calculated in the manner, described before (see Fronæus [4, pp. 14 and 110]).

In the previous treatise [4, p. 90] it has been shown that extinctiometric measurements give a false "ligand number", when also dinuclear complexes are formed. The expression for $(\partial C_A/\partial C_M)_{\varepsilon_M}$ in this case contains [M] and the molar extinctions of the different complexes. So the derivative may depend on C_M and at a constant value of the intercept on the C_A-axis the calculated value of the "ligand number" may depend on the wave length λ used. At $C_M = 0$ the derivative is made up of the real ligand number $\bar{n}$ and a term depending on the wave length.

If possible, extinctiometric measurements should be carried out at different wave lengths in different absorption bands of the extinction curve. Of course the dependence on C_M and λ sometimes may be so small that it falls within the limits of the experimental random errors, and yet the calculated values f $\bar{n}$ may be wrong.

The measurements and calculations

The extinctiometric investigation was carried out with a Beckman Quartz Spectrophotometer (Model DU). In order to make measuring at a constant temperature (20.0° C) possible the apparatus had been altered in the manner described by Adell [7, p. 3]. Concerning other experimental details and the arranging of the measurements the reader is referred to a previous treatise [4, p. 93].

In order to select convenient wave lengths, at which the measurements could be carried through, the extinction curve *log* (e/C_M) of a solution of the composition 25 mC $Cu(ClO_4)_2$ + 925 mC $NaNO_2$ was determined and is represented in Fig. 3. At 725 mμ the curve has a relative maximum and differs considerably from the extinction curve of Cu^{2+}. As the systematic error in the extinction E, that not strictly monochromatic light may cause, vanishes, where the curve has a horizontal tangent, it was advisable to select this wave length. The other wave lengths chosen were 465 and 430 mμ. From Fig. 3, curve 3 it is evident that *log* ε_A^0 is very small at these wave lengths.

In a measurement series, corresponding to a constant value of d, the measuring solution was obtained by mixing two solutions of the composition a mC $Cu(ClO_4)_2$ + (1000—3 a) mC $NaClO_4$ and 1000 mC $NaNO_2$. In the manner,

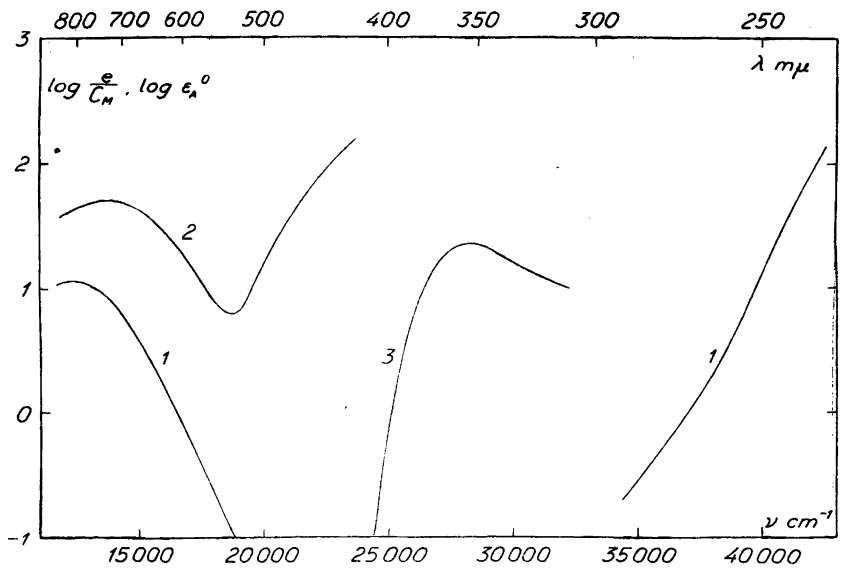

Fig. 3. Extinction curves of: 1. the cupric ion; 2. a complex solution with C_M = 25 mC and C_A = 925 mC; 3. the nitrite ion.

described above, it was checked that the nitrite concentration had not altered during the measurement. For the relation between C_M and C_A in mC we have:

$$C_M = a\left(1 - \frac{C_A}{1000}\right) \tag{14}$$

In the different measurement series the product $d \cdot a$ was kept constant and equal to 22.5 cm.mC. Thus at a constant concentration C_A the product $d \cdot C_M$ had the same value in different series. In order to avoid systematic errors in $\bar{n}$, caused by imperfect monochromaticity of the light and its partial reflection at the end-plates of the absorption cell, solutions with the same value of ε_M should be measured at approximately the same value of E that is of $d \cdot C_M$ (see Fronæus [4, p. 98], Olerup [6, p. 50]). From Table 7 it is evident that this condition is fulfilled.

Table 6 contains the values obtained of the function ε_M. The reproducibility was about 0.5 %. In Fig. 4 the fulldrawn curves represent the measurements at 725 mμ. The quotient $\varepsilon_M(430)/\varepsilon_M(465)$ is practically constant for all the solutions measured and the mean value is 2.42 ± 0.02. Thus $\varepsilon_{j+1}/\varepsilon_j$ (j = 1,2,...) is independent of the wave length within this wave length range. From the

Table 6. Extinction measurements on the complex system $Cu^{+2}-NO_2^-$.

d cm	C_M mC	C_A mC	$\lambda = 725$ mμ	$\lambda = 465$ mμ	$\lambda = 430$ mμ	$\lambda = 725$ mμ	$\lambda = 465$ mμ	$\lambda = 430$ mμ
			$(e-\varepsilon_A^0 \cdot C_A)$ cm^{-1}			ε_M $cm^{-1} \cdot C^{-1}$		
3	7.40	13.2	0.0945	0.0247	0.0603	12.75	3.34	8.15
3	7.35	19.6	0.106	0.0353	0.0867	14.4	4.80	11.80
3	7.26	32.3	0.125	0.0537	0.136	17.2	7.40	18.0
3	7.16	44.6	0.139	0.0693	0.168	19.4	9.68	23.5
3	7.03	62.5	0.158	0.0883	0.211	22.5	12.55	30.0
3	6.82	90.5	0.177	0.110	0.266	26.0	16.1	39.0
3	6.62	117.6	0.188	0.127	0.306	28.4	19.2	46.2
3	6.25	166.7	0.200	0.149	0.355	32.0	23.8	56.8
3	5.92	211	0.206	0.161	0.384	34.8	27.2	64.9
3	5.63	250	0.207	0.167	0.400	36.8	29.7	71.0
3	5.12	318	0.203	0.172	0.413	39.6	33.6	80.7
3	4.50	400	0.190	0.169	0.406	42.2	37.6	90.2
1	22.2	13.2	0.267	0.062	0.150	12.05	2.80	6.75
1	22.1	19.6	0.297	0.090	0.218	13.45	4.07	9.86
1	21.8	32.3	0.346	0.137	0.338	15.9	6.28	15.5
1	21.5	44.6	0.391	0.186	0.440	18.2	8.65	20.5
1	21.1	62.5	0.442	0.233	0.567	20.9	11.05	26.9
1	20.5	90.9	0.497	0.302	0.731	24.2	14.7	35.7
1	19.8	117.6	0.547	0.355	0.863	27.6	17.9	43.6
1	18.8	166.7	0.585	0.423	1.02	31.1	22.5	54.3
1	17.8	211	0.605	0.464	1.13	34.0	26.1	63.5
1	16.9	250	0.608	0.485	1.18	36.0	28.7	69.8
1	15.3	318	0.600	0.505	1.22	39.2	33.0	79.7
1	13.5	400	0.570	0.499	1.20	42.2	37.0	88.9
0.3	74.0	13.2	0.790	0.123	0.307	10.70	1.66	4.15
0.3	73.5	19.6	0.867	0.187	0.460	11.80	2.54	6.26
0.3	72.6	32.3	0.990	0.300	0.743	13.65	4.13	10.25
0.3	71.6	44.6	1.09	0.403	0.997	15.2	5.63	13.90
0.3	70.3	62.5	1.24	0.543	1.34	17.6	7.72	19.1
0.3	68.2	90.9	1.44	0.759	1.85	21.1	11.15	27.1
0.3	66.2	117.6	1.58	0.926	2.25	23.9	14.0	34.0
0.3	62.5	166.7	1.76	1.18	2.82	28.2	18.9	45.1
0.3	59.2	211	1.84	1.33	3.23	31.1	22.5	54.6
0.3	56.3	250	1.86	1.45	3.50	33.0	25.8	62.2
0.3	51.2	318	1.90	1.55	3.73	37.1	30.3	72.9
0.3	45.0	400	1.81	1.57	3.77	40.2	34.9	83.8

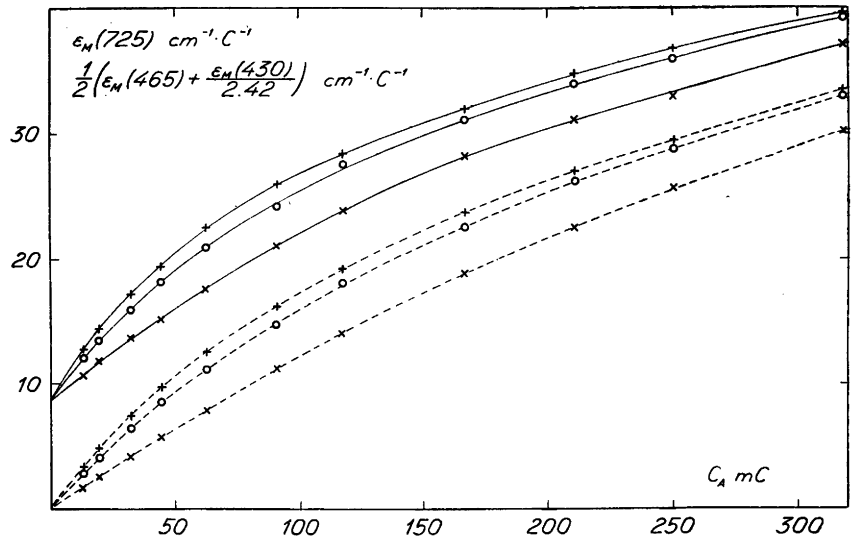

Fig. 4. Fulldrawn curves: $\varepsilon_M(725)$ as a function of C_A at different a. Dashed curves: 0.5 $\{\varepsilon_M(465) + \varepsilon_M(430)/2.42\}$ as a function of C_A at different a. —— +: *a = 7.5 mC;* ○: *a = 22.5 mC;* ×: *a = 75 mC (see eq. (14)).*

calculation method it is evident that the measurements at 430 mμ give the same ($\bar{n}$/[A], [A])-curve as the measurements at 465 mμ. In order to reduce the calculations but make use of all ε_M-values obtained, the mean values 0.5 (ε_M (465) + ε_M (430)/2.42) are represented in Fig. 4, the dashed curves.

Table 7 contains a number of selected ε_M-values. The corresponding concentrations C_A and C_M are taken from Fig. 4 and eq. (14). The connection between C_M and C_A at a constant ε_M proves to be linear and, as already mentioned, this is a necessary condition for the computation of $\bar{n}$.

In Fig. 5 the function $\bar{n}$/[A] is represented graphically. It is obvious that the measurements at 725 mμ within the limits of experimental random errors give the same $\bar{n}$/[A]-curve as the measurements at 465 and 430 mμ. This indicates that only mononuclear complexes are formed.

In Table 8 values of the functions X, X_1, and X_2 have been calculated at different [A]. By extrapolation of X_1 and X_2 to [A] = 0 we get the following values of the complexity constants β_1 and β_2:

$$\beta_1 = 20 \pm 1 \text{ C}^{-1}; \quad \beta_2 = 45 \pm 5 \text{ C}^{-2}$$

At the higher nitrite concentrations there is some indication that also the complex MA_3 is formed, but the tendency is so weak that β_3 cannot be determined.

Table 7. Determination of corresponding values of [A] and $\bar{n}/[A]$ from the extinction measurements.

ε_M (725) $cm^{-1} \cdot C^{-1}$	d = 0.3 cm		d = 1 cm		d = 3 cm		$C_M = 0$	$\bar{n}$	$\frac{\bar{n}}{[A]}$ C^{-1}
	C_M mC	C_A mC	C_M mC	C_A mC	C_M mC	C_A mC	$C_A = [A]$ mC		
12.0	73.4	21.7	22.2	13.2	7.43	10.4	9.3	0.169	18.2
14.0	72.3	35.6	22.0	22.6	7.37	18.0	16.4	0.267	16.3
17.0	70.7	57.5	21.6	38.0	7.27	31.0	28.6	0.410	14.3
20.0	68.9	82.0	21.2	56.5	7.15	48.0	44.5	0.545	12.2
23.0	66.9	108.0	20.7	77.5	7.00	67.0	63.0	0.675	10.7
26.0	64.5	140	20.1	105.0	6.82	91.0	87	0.82	9.4
29.0	61.6	179	19.4	139	6.57	125	120	0.96	8.0
32.0	58.0	227	18.5	180	6.25	167	159	1.17	7.4
35.0	54.0	280	17.3	230	5.89	215	207	1.35	6.5
37.0	51.2	317	16.4	270	5.59	255	247	1.37	5.55
$\frac{1}{2}\{\varepsilon_M(465) + \frac{\varepsilon_M(430)}{2.42}\}$									
3.00	73.3	23.2	22.2	14.3	7.41	11.7	10.4	0.175	16.8
5.00	72.1	39.2	21.9	24.6	7.34	20.5	18.2	0.291	16.0
8.00	70.2	64.4	21.6	41.5	7.24	35.3	31.5	0.470	14.9
11.0	68.3	89.5	21.1	62.0	7.10	52.5	49.0	0.595	12.1
14.0	66.2	117.5	20.6	84.5	6.95	73.5	69.0	0.730	10.6
17.0	63.9	148	20.0	110	6.77	98.0	92.0	0.875	9.5
21.0	60.6	192	19.1	149	6.48	136	130	1.02	7.8
25.0	56.9	242	18.1	195	6.13	183	174	1.20	6.9
28.0	53.6	286	17.1	238	5.81	226	217	1.29	5.9
30.0	51.4	315	16.4	269	5.56	259	250	1.26	5.0

Table 8. The functions $X([A])$, $X_1([A])$, and $X_2([A])$ at different [A].

[A] mC	$X([A])$	$X_1([A])$ C^{-1}	$X_2([A])$ C^{-2}
10	1.20	20	
25	1.53	21.2	
50	2.13	22.6	
75	2.79	23.9	52
100	3.53	25.3	53
150	5.26	28.4	56
200	7.43	32.2	61
250	9.98	35.9	64

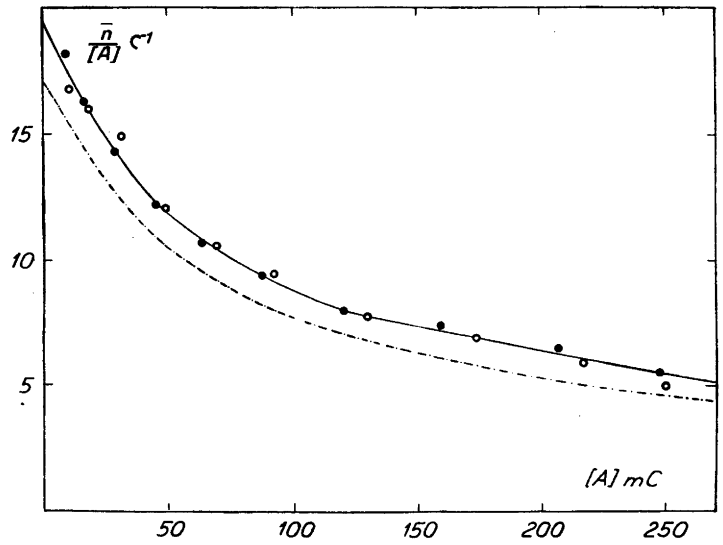

Fig. 5. Fulldrawn curve: the extinctiometrically determined $\bar{n}/[A]$ as a function of $[A]$. ——— ●: λ = 725 mμ; ○; λ = 465 and 430 mμ. Dashed curve: $\bar{n}/[A]$ calculated from the potentiometrically determined complexity constants.

Thus there is a good agreement between the results from the potentiometric and the extinctiometric investigations, and the constants obtained may be considered as true complexity constants. The small divergence between the two sets of constants may be caused, as mentioned before, by the difference in the composition of the ionic mediums in the two cases.

SUMMARY

The complexity of the cupric nitrite system has been investigated potentiometrically and extinctiometrically.

The method of ligand displacement was used, as it is the only potentiometric method, applicable on this system. Ammonia was the displacing ligand and the measurements were carried out with a glass electrode.

The extinctiometric investigation was performed in two different absorption bands at the wave lengths 725, 465, and 430 mμ. Consistent results have been obtained at the different wave lengths, showing that only mononuclear complexes are formed.

According to both methods the complexity constants β_j ($j = 1,2$) of the complexes $Cu(NO_2)_j^{2-}$ have been determined at 20° C and at the ionic strength 1 and found to be:

	β_1 C^{-1}	β_2 C^{-2}
pot. method	17 ± 2	30 ± 8
ext. method	20 ± 1	45 ± 5

The complex $Cu(NO_2)_3^-$ is formed in so small amounts within the nitrite concentration range used that β_3 cannot be computed.

From the potentiometric investigation the complexity constants $\beta_{j,1}$ ($j = 1,2$) of the mixed complexes $Cu(NO_2)_j\ NH_3^{2-j}$ have been calculated:

$$\beta_{1,1} = (1.9 \pm 0.2) \cdot 10^5\ C^{-2};\quad \beta_{2,1} = (1.6 \pm 0.5) \cdot 10^5\ C^{-3}$$

The author wishes to thank Professor S. Bodforss for the facilities, put at my disposal.

REFERENCES

1. Gallais, F., and Vives, J. P. *Bull. soc. chim. France* **1948**, 702.
2. Kossiakoff, A., and Sickman, D. V. *J. Am. Chem. Soc.* **68** (1946) 442.
3. Fronæus, S. *Acta Chem. Scand.* **4** (1950) 72.
4. Fronæus, S. Diss. Lund (1948).
5. Bjerrum, J. Diss. Copenhagen (1941).
6. Olerup, H. Diss. Lund (1944).
7. Adell, B. *Acta Chem. Scand.* **4** (1950) 1.

Received September 15, 1950.