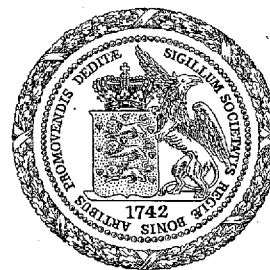


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THE COMPLEX
FORMATION BETWEEN CUPRIC
AND ACETATE IONS

BY

KAI JULIUS PEDERSEN

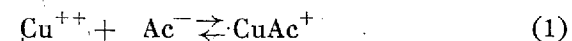


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Our present knowledge of the complex formation between cupric and carboxylate ions is very scanty and mostly of a qualitative nature. Although complex formation in solutions of cupric acetate has been studied by several workers (EWAN⁽¹⁾, CALAME⁽²⁾, SIDGWICK and TIZARD⁽³⁾, GÜNTHER-SCHULZE⁽⁴⁾, FRENCH and LOWRY⁽⁵⁾, BRITTON and MEEK⁽⁶⁾), no satisfactory quantitative information of the problem is to be found in the literature.

The author of this paper has studied the complex formation in solutions containing cupric and acetate ions both by means of the glass electrode and by measurements of light absorption. The following equilibria are found (the acetate ion being denoted by Ac^-):



and



The measurements of light absorption indicate that higher complexes, such as CuAc_3^- and CuAc_4^{--} , and also polynuclear complexes, are formed in sufficiently concentrated solution.

In general, the complex formation between a central group M and ligand groups A may be expressed in one of the following ways:



and



The equilibrium constants are

$$K_n = \frac{(\text{MA}_n)}{(\text{M})(\text{A})^n} \quad (5)$$

and

$$k_n = \frac{(MA_n)}{(MA_{n-1})(A)}, \quad (6)$$

respectively, where

$$K_n = k_1 k_2 \cdots k_n. \quad (7)$$

When only mononuclear complexes are formed, the total concentration of the central group is

$$c = \sum_0^N (MA_n) = \sum_0^N K_n (M) (A)^n, \quad (8)$$

where N is the maximum value of n , and $K_0 = 1$. The total concentration of ligands bound to the central group is

$$x = \sum_0^N n (MA_n) = \sum_0^N n K_n (M) (A)^n. \quad (9)$$

Into the mathematical formula

$$\sum_0^N \left(y_n \sum_0^N n y_n \right) = \sum_0^N \left(n y_n \sum_0^N y_n \right)$$

we insert

$$y_n = K_n (M) (A)^n$$

and use equations 8 and 9. We obtain

$$\sum_0^N K_n (M) (A)^n x = \sum_0^N n K_n (M) (A)^n c,$$

which may also be written as follows:

$$\sum_0^N K_n (nc - x) (A)^n = 0. \quad (10)$$

Glass Electrode Measurements.

The method is similar to that used by J. BJERRUM⁽⁷⁾ in his study of metal ammine formation. The concentration of free acetate ion in a solution of acetic acid, sodium acetate, and cupric nitrate may be found from the equation

$$(Ac^-) = K \frac{(HAc)}{(H^+)}, \quad (11)$$

when the hydrogen ion concentration (H^+) is measured and K , the dissociation constant of acetic acid in the solution, is known.

We make the assumption that the cupric ion concentration is sufficiently small for neglecting the formation of polynuclear complexes, and the acetate ion concentration sufficiently small for neglecting the formation of complexes with more than two acetate ions, that is, we consider only complexes formed according to the equilibria 1 and 2.

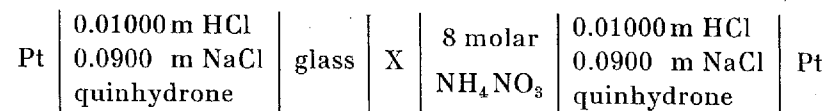
We further assume (1) that K is the same as in a solution in which the ions Cu^{++} and $CuAc^+$ have been replaced by Ba^{++} and Na^+ , respectively, and (2) that we may neglect a possible complex formation between barium and acetate ions. K is therefore determined by measuring the hydrogen ion concentration of solutions whose composition is denoted in the following way:

$$X = \begin{cases} d & \text{molar barium nitrate} \\ (s-b) & \text{molar sodium nitrate} \\ a & \text{molar acetic acid} \\ b & \text{molar sodium acetate.} \end{cases} \quad (12)$$

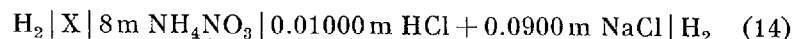
The complexity constants are found by measuring the hydrogen ion concentration of solutions composed as expressed in the following scheme:

$$X = \begin{cases} c & \text{molar cupric nitrate} \\ (s-b) & \text{molar sodium nitrate} \\ a & \text{molar acetic acid} \\ b & \text{molar sodium acetate.} \end{cases} \quad (13)$$

The measurements were carried out at 18.0°C. The procedure was the same as that reported in an earlier paper⁽⁸⁾. The cells measured had the composition:



When a small asymmetry potential (measured daily by substituting for X the solution 0.01000 m HCl + 0.0900 m NaCl) was subtracted, the e.m.f., E volts, of cells of the composition

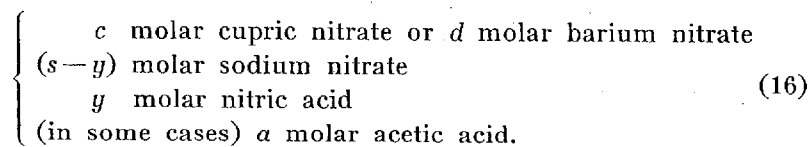


was obtained.

The hydrogen ion concentration (H^+) of the solution X may be found from the measurements when we know A_0 in the equation

$$-\log(\text{H}^+) = A_0 + 17.32 E. \quad (15)$$

A_0 includes the salt effect and the effect of the liquid-liquid junction of the left half cell (scheme 14), together with the whole effect of the right half cell, the latter having the same composition throughout the measurements. As an approximation to A_0 for the solutions of the schemes 12 and 13 we use the values of A_0 found for solutions in which the ions Ac^- and CuAc^+ have been replaced by NO_3^- and Na^+ , respectively. In order to determine these values, E is first measured for solutions of known hydrogen ion concentration of the composition expressed by the following scheme:



$A = -17.32 - \log(\text{H}^+)$ is calculated from the measurements, and A_0 is found by extrapolation to $y = 0$.

Materials. — Acetic acid (glacial, free from higher homologs, for analytical purposes) was purified by partial crystallization and, finally, by distillation in an all-glass apparatus fitted out with a column containing glass beads (freezing point 16.54°). — 1 molar sodium hydroxide was prepared from a clear, satu-

rated solution of sodium hydroxide (for analytical purposes) and carbon dioxide-free water. It was stored in a bottle covered inside with paraffin wax and protected from the carbon dioxide of the air.—Cupric nitrate (purest, Schering-Kahlbaum) was recrystallized from water. 1 molar solutions were stored in silica bottles. They were analyzed for copper by the iodometric titration method of HAGEN⁽⁹⁾. Metallic copper (electrolytically deposited) was used as a standard substance.—Barium nitrate and sodium nitrate (both for analytical purposes) were recrystallized.—Redistilled water was used for all the solutions.

Determination of A_0 . The results are given in Table 1. The acid dissociation of the cupric ion being negligible⁽⁸⁾, $(\text{H}^+) = y$ for all the solutions not containing acetic acid. In calculating (H^+) for the two solutions containing 0.1 and 0.5 m acetic acid, respectively, the dissociation constants of acetic acid given in Table 3 have been used. It is seen that the increase of A_0 , when acetic acid is added, is $0.030 \times (\text{HAc})$.

The dissociation constant of acetic acid. The results of the electrometric measurements in solutions composed as expressed in scheme 12 are given in Table 2. Within each series, consisting of 4 solutions of the same ionic strength μ , d , s , and a are kept constant, while b varies. $-\log(\text{H}^+)$, presented in the 6th column, is computed from E by means of equation 15. For A_0 are used values taken from Table 1 for solutions of the same composition, except that the acetate ions have been replaced by nitrate ions (that is, $b = 0$). Before use, the values are corrected for the influence of acetic acid. The last column but one of Table 2 gives the dissociation constant K of acetic acid found from the measurements. The dependence of $-\log K$ on b , within a series at constant μ may be expressed by the linear relationship given in the 5th column of Table 3. $-\log K$ calculated from this formula is given in the last column of Table 2. The agreement between $-\log K$ found and calculated is always satisfactory.

Table 3 gives a summary of the dissociation constants measured. $-\log K$ for acetate-free solution, obtained by extrapolation to $b = 0$ of the expression in the 5th column of the table, is free of the error introduced by using A_0 for acetate-free solution

Table 1.

$$A = -17.32 E - \log(H^+),$$

where E is the e.m.f. in volts at 18.0°C. of the cell

$$H_2 \left| \begin{array}{c} c \text{ molar } Cu(NO_3)_2 \\ d \text{ molar } Ba(NO_3)_2 \\ (s-y) \text{ molar } NaNO_3 \\ y \text{ molar } HNO_3 \end{array} \right| \begin{array}{c} 8 \text{ molar} \\ NH_4NO_3 \end{array} \left| \begin{array}{c} 0.01000 \text{ molar } HCl \\ 0.0900 \text{ molar } NaCl \end{array} \right| H_2,$$

measured by means of the glass electrode, and (H^+) is the hydrogen ion concentration of the solution in the left half cell. A_0 , the value of A corresponding to $y = 0$, has been found by extrapolation.

c	d	s	A when y =				A ₀
			0.02	0.01	0.005	0.0025	
0.100	0.000	0.100	..	2.009	2.013	2.015	2.017
0.000	0.100	0.100	1.998	2.006	2.015	2.012	2.017
0.050	0.000	0.150	..	2.004	2.007	2.010	2.012
0.000	0.050	0.150	1.993	2.003	2.012	..	2.014
0.000	0.000	0.200	1.991	2.001	2.008	2.006	2.010
0.050	0.000	0.100	..	2.004	2.007	2.010	2.012
0.000	0.050	0.100	1.995	2.003	2.010	2.011	2.013
0.000	0.025	0.125	1.998	2.003	..	2.009	2.011
0.000	0.025	0.125 ¹	2.001	2.006	..	2.012	2.014
0.000	0.025	0.125 ²	2.013	2.018	..	2.023	2.026
0.000	0.000	0.150	1.993	2.001	2.008	..	2.013
0.025	0.000	0.100	..	2.004	2.010	2.012	2.014
0.000	0.025	0.100	1.995	2.003	2.008	2.009	2.012
0.000	0.000	0.125	1.993	2.002	2.010	..	2.015
0.010	0.000	0.100	..	2.004	2.011	2.015	2.019
0.000	0.000	0.100	1.996	2.006	2.013	2.016	2.019
c	d	s	A when y =				A ₀
			0.008	0.004	0.002	0.001	
0.004	0.000	0.040	2.018	2.025	2.032	2.034	2.036
0.000	0.004	0.040	2.019	2.029	2.031	..	2.036
0.000	0.000	0.044	2.019	2.031	2.033	..	2.037

¹ The solution in addition contains 0.100 molar acetic acid.

² The solution in addition contains 0.500 molar acetic acid.

Table 2.

The electromotive force E volts at 18.0°C. of the cell

$$H_2 \left| \begin{array}{c} d \text{ molar } Ba(NO_3)_2 \\ (s-b) \text{ molar } NaNO_3 \\ a \text{ molar } CH_3COOH \\ b \text{ molar } CH_3COONa \end{array} \right| \begin{array}{c} 8 \text{ molar} \\ NH_4NO_3 \end{array} \left| \begin{array}{c} 0.01000 \text{ molar } HCl \\ 0.0900 \text{ molar } NaCl \end{array} \right| H_2,$$

measured by means of the glass electrode. The hydrogen ion concentration (H^+) and the dissociation constant of acetic acid K in the solution of the left half cell.

d	s	a	b	E	$-\log(H^+)$	$-\log K$ found	$-\log K$ calcd.
0.1000	0.1000	0.1000	{	0.09984	0.1420 ₈	4.480	4.481
				0.04000	0.1186 ₈	4.075	4.472
				0.01994	0.1011 ₅	3.772	4.468
				0.00991	0.0843	3.480	4.468
0.0500	0.1500	0.1000	{	0.09984	0.1442	4.515	4.515
				0.04000	0.1205 ₅	4.105	4.502
				0.01994	0.1029	3.799	4.495
				0.00991	0.0858 ₅	3.504	4.493
0.0000	0.2000	0.1000	{	0.09984	0.1463	4.547	4.547
				0.04000	0.1226	4.136	4.533
				0.01994	0.1050	3.832	4.528
				0.00991	0.0878 ₅	3.535	4.525
0.0500	0.1000	0.1000	{	0.09984	0.1443	4.515	4.515
				0.04000	0.1207 ₅	4.107	4.504
				0.01994	0.1032	3.803	4.499
				0.00991	0.0862	3.509	4.498
0.0250	0.1250	0.1000	{	0.09984	0.1456 ₅	4.537	4.537
				0.04000	0.1220 ₅	4.128	4.525
				0.01994	0.1044	3.822	4.519
				0.00991	0.0873	3.526	4.516
0.0250	0.1250	0.5000	{	0.1005	0.1056 ₅	3.856	4.552
				0.04069	0.0823 ₅	3.452	4.538
				0.02065	0.0657	3.164	4.533
				0.01052	0.0507	2.904	4.531
0.0000	0.1500	0.1000	{	0.09984	0.1472	4.566	4.566
				0.04000	0.1231 ₅	4.149	4.546
				0.01994	0.1057	3.847	4.543
				0.00991	0.0885	3.549	4.539

(To be continued)

Table 2 (continued).

<i>d</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>E</i>	$-\log(\text{H}^+)$	$-\log K$ found	$-\log K$ calcd.
0.0250	0.1000	0.1000	0.09984	0.1459	4.542	4.542	4.543
			0.04000	0.1222 ₅	4.132	4.529	4.527
			0.01994	0.1045	3.825	4.521	4.521
			0.00991	0.0874 ₅	3.530	4.519	4.519
0.0000	0.1250	0.1000	0.09984	0.1477	4.576	4.577	4.577
			0.04000	0.1238 ₅	4.163	4.560	4.559
			0.01994	0.1061	3.856	4.552	4.553
			0.00991	0.0890	3.559	4.550	4.550
0.0100	0.1000	0.1000	0.09984	0.1472	4.572	4.572	4.571
			0.04000	0.1232 ₅	4.157	4.554	4.555
			0.01994	0.1058	3.855	4.551	4.550
			0.00991	0.0886	3.557	4.547	4.548
0.0040	0.0400	0.1000	0.03986	0.1250 ₅	4.205	4.603	4.603
			0.01597	0.1019 ₅	3.805	4.597	4.597
			0.00796	0.0851	3.513	4.594	4.595
			0.00406	0.0704	3.258	4.594	4.594
0.0000	0.0440	0.1000	0.03986	0.1258 ₅	4.220	4.618	4.617
			0.01597	0.1025	3.815	4.607	4.608
			0.00796	0.0856 ₅	3.523	4.605	4.605
			0.00406	0.0710	3.270	4.604	4.604

for the computation of $-\log(\text{H}^+)$. The formula at the bottom of the table expresses $-\log K$ (when $b = 0$) as a function of μ and a . The influence of the acetic acid was estimated by comparing the 5th and the 6th series, containing 0.1 and 0.5m acetic acid, respectively. The factor before $\sqrt{\mu}$ follows from Debye-Hückel's theory, while the other constants in the formula have been chosen so as to obtain the best fit. $-\log K$ calculated from the formula is given in the last column of Table 3. A comparison with the values in the last column but one shows that the agreement is fairly good, although small systematic deviations owing to the individual influences of the sodium and barium ions are noticeable. The fact that equal ionic strengths of sodium and barium nitrate have nearly the same influence on the dissociation constant seems to justify the neglect of a possible complex formation between barium

Table 3.

The dissociation constant K at 18.0° C. of acetic acid

in the solution: $\begin{cases} d \text{ molar Ba(NO}_3)_2 \\ (s-b) \text{ molar NaNO}_3 \\ a \text{ molar CH}_3\text{COOH} \\ b \text{ molar CH}_3\text{COONa.} \end{cases}$

<i>d</i>	<i>s</i>	<i>a</i>	μ	$-\log K$	$-\log K$ ($b = 0$) calculated
0.1000	0.1000	0.1000	0.400	$4.466 + 0.15 b$	4.465
0.0500	0.1500	0.1000	0.300	$4.490 + 0.26 b$	4.490
0.0000	0.2000	0.1000	0.200	$4.523 + 0.24 b$	4.516
0.0500	0.1000	0.1000	0.250	$4.496 + 0.19 b$	4.503
0.0250	0.1250	0.1000	0.200	$4.514 + 0.24 b$	4.516
0.0250	0.1250	0.5000	0.200	$4.528 + 0.24 b$	4.530
0.0000	0.1500	0.1000	0.150	$4.536 + 0.29 b$	4.532
0.0250	0.1000	0.1000	0.175	$4.516 + 0.27 b$	4.522
0.0000	0.1250	0.1000	0.125	$4.547 + 0.30 b$	4.543
0.0100	0.1000	0.1000	0.130	$4.545 + 0.26 b$	4.540
0.0040	0.0400	0.1000	0.052	$4.593 + 0.25 b$	4.594
0.0000	0.0440	0.1000	0.044	$4.602 + 0.37 b$	4.602

$$-\log K = 4.759_5 + 0.035a - 0.996\sqrt{\mu} + 1.15\mu - 0.80\mu^2, \text{ when } b = 0.$$

and acetate ions. By extrapolation to infinite dilution, the activity constant $-\log K^\circ = 4.759_5$ is obtained. There is a satisfactory agreement between this result and $-\log K^\circ = 4.757$ found by HARNED and EHLERS⁽¹⁰⁾ from electrometric measurements of cells without liquid junction at the same temperature.

The complexity constants. The results of the electrometric measurements in solutions composed as expressed in scheme 13 are given in Table 4a and b. Within each series consisting of 5 solutions, c , s , and a are kept constant, while b varies. $-\log(\text{H}^+)$, presented in the last column but one of Table 4a, is found from E by means of equation 15. For A_0 is used a value, found by interpolation in Table 1 for a solution containing, instead of the two ions CuAc^+ and Ac^- , the ions Na^+ and NO_3^- , respectively. Its composition may be expressed

Table 4a.

c	s	a	b	E	A ₀	—log(H ⁺)	—log K
0.09978	0.1005	0.1000	0.1005	0.1137	2.015	3.984	4.506
			0.07536	0.1033	2.015	3.804	4.495
			0.5044	0.0908	2.016	3.589	4.486
			0.02023	0.0655	2.018	3.152	4.475
			0.00976	0.0485 ₅	2.019	2.860	4.470
0.04985	0.1005	0.1000	0.1005	0.1291	2.017	4.253	4.543
			0.07536	0.1191	2.016	4.079	4.532
			0.05044	0.1058	2.016	3.848	4.521
			0.02022	0.0783 ₅	2.015	3.372	4.507
			0.00978	0.0600	2.015	3.054	4.502
0.04985	0.1000	0.5000	0.09989	0.0889	2.029	3.569	4.556
			0.07536	0.0789 ₅	2.028	3.395	4.546
			0.04983	0.0653 ₅	2.028	3.160	4.535
			0.01963	0.0392 ₅	2.027	2.707	4.521
			0.00976	0.0254 ₅	2.027	2.468	4.516
0.02492	0.1005	0.1000	0.1005	0.1386 ₅	2.019	4.420	4.567
			0.07535	0.1294	2.019	4.260	4.558
			0.05043	0.1169	2.018	4.043	4.547
			0.02022	0.0893 ₅	2.017	3.565	4.531
			0.00975	0.0702	2.017	3.233	4.524
0.00999	0.1005	0.1000	0.1005	0.1444	2.021	4.522	4.574
			0.07535	0.1360 ₅	2.021	4.377	4.567
			0.05043	0.1246	2.021	4.179	4.560
			0.02022	0.0989	2.022	3.735	4.551
			0.00975	0.0796 ₅	2.022	3.402	4.549
0.003992	0.0398	0.1000	0.03976	0.1229	2.040	4.169	4.614
			0.02970	0.1150	2.040	4.032	4.609
			0.01975	0.1042	2.040	3.845	4.604
			0.00771	0.0801	2.039	3.426	4.598
			0.00393	0.0654	2.039	3.172	4.596

Table 4b.

(Ac ⁻)	x	μ	log K ₁ found	log K ₁ formula	log K ₂ found	log K ₂ formula	E calcd.	Δ10 ⁴
0.03003	0.07057	0.2689	1.646	1.630	2.46	2.44	0.1138	+1
0.02034	0.05518	0.2957	1.639	1.617	2.47	2.43	0.1037	+4
0.01264	0.03806	0.3267	1.607	1.603	..	2.41	0.0909	+1
0.00472	0.01622	0.3686	1.587	1.586	..	2.39	0.0655	0
0.00242	0.00872	0.3840	1.584	1.580	..	2.38	0.0487	+1
..	..	0.400	1.577	1.575	..	..	..	..
0.05129	0.04927	0.1620	..	1.699	2.56	2.54	0.1292	+1
0.03520	0.04024	0.1760	1.678	1.688	2.51	2.52	0.1190	-1
0.02120	0.02938	0.1944	1.651	1.674	2.45	2.50	0.1054	-4
0.00730	0.01334	0.2243	1.653	1.655	..	2.48	0.0783	-1
0.00353	0.00713	0.2368	1.655	1.647	..	2.47	0.0602	+2
..	..	0.240	1.642	1.640	..	..	..	..
0.05149	0.04867	0.1625	..	1.699	2.53	2.54	0.0888	-1
0.03529	0.04047	0.1755	1.692	1.688	2.52	2.52	0.0789	-1
0.02106	0.02946	0.1944	1.661	1.674	2.47	2.50	0.0651	-3
0.00764	0.01395	0.2243	1.658	1.655	..	2.48	0.0393	+1
0.00445	0.00871	0.2358	1.651	1.648	..	2.47	0.0255	+1
..	..	0.240	1.645	1.640	..	..	..	..
0.07127	0.02927	0.1246	..	1.734	2.64	2.59	0.1389	+3
0.05032	0.02509	0.1306	..	1.728	2.61	2.58	0.1296	+2
0.03130	0.01922	0.1396	1.672	1.719	2.52	2.57	0.1167	-2
0.01078	0.00971	0.1564	1.694	1.704	..	2.55	0.0892	-2
0.00509	0.00525	0.1655	1.686	1.696	..	2.54	0.0699	-3
..	..	0.175	1.678	1.689	..	..	..	..
0.08870	0.01183	0.1098	..	1.750	2.52	2.61	0.1442	-2
0.06454	0.01085	0.1113	..	1.749	2.56	2.61	0.1360	0
0.04156	0.00894	0.1142	1.515	1.745	2.53	2.60	0.1244	-2
0.01525	0.00515	0.1207	1.714	1.738	..	2.59	0.0987	-2
0.00710	0.00305	0.1251	1.743	1.734	..	2.59	0.0798	+2
..	..	0.130	1.74	1.728	..	..	..	..
0.03587	0.00396	0.0448	..	1.859	2.87	2.76	0.1231	+2
0.02646	0.00333	0.0457	1.93	1.856	2.80	2.76	0.1151	+1
0.01739	0.00250	0.0471	1.784	1.853	..	2.75	0.1040	-2
0.00670	0.00138	0.0495	1.843	1.848	..	2.74	0.0800	-1
0.00374	0.00086	0.0507	1.838	1.845	..	2.74	0.0654	0
..	..	0.052	1.835	1.842	..	..	..	..

as follows: (Cu^{++}) molar $\text{Cu}(\text{NO}_3)_2 + [s + (\text{CuAc}^+)]$ molar $\text{NaNO}_3 + a$ molar HAc . In order to find this value of A_0 , we must have a rough knowledge of the equilibria in the solution under investigation. The method, therefore, is one of successive approximations. The value of A_0 given in the 6th column of Table 4a is that finally adopted.

(Ac^-) , presented in the first column of Table 4b, is found from (H^+) by means of equation 11 and

$$(\text{HAc}) = a - (\text{H}^+).$$

For K is used a value found by interpolation in Table 3 for a solution containing, instead of the two ions Cu^{++} and CuAc^+ , the ions Ba^{++} and Na^+ , respectively. Its composition may be expressed as follows: (Cu^{++}) molar $\text{Ba}(\text{NO}_3)_2 + [s + (\text{CuAc}^+) - (\text{Ac}^-)]$ molar $\text{NaNO}_3 + a$ molar $\text{HAc} + (\text{Ac}^-)$ molar NaAc . Here also, we must apply successive approximations. The value of $-\log K$, given in the last column of Table 4a, is that finally adopted.

x , the concentration of acetate ion bound to cupric ion, is given in the second column of Table 4b. It has been computed by means of the equation

$$x = b + (\text{H}^+) - (\text{Ac}^-).$$

As already mentioned, we neglect in our computations polynuclear complexes and complexes with more than two acetate ions. We may also neglect the acid dissociation of the cupric ion. It follows from the equilibrium constants reported in an earlier paper⁽⁸⁾ that the decrease in cupric ion concentration owing to acid dissociation is less than 0.1 per cent. at the hydrogen ion concentrations measured here. We therefore only consider the equilibria 1 and 2 with the mass action constants

$$K_1 = \frac{(\text{CuAc}^+)}{(\text{Cu}^{++})(\text{Ac}^-)} \quad \text{and} \quad K_2 = \frac{(\text{CuAc}_2)}{(\text{Cu}^{++})(\text{Ac}^-)^2}. \quad (17)$$

According to the equations 8 and 10, we have

$$c = (\text{Cu}^{++}) + K_1 (\text{Cu}^{++})(\text{Ac}^-) + K_2 (\text{Cu}^{++})(\text{Ac}^-)^2 \quad (18)$$

$$\text{and} \quad x = K_1 (c - x) (\text{Ac}^-) + K_2 (2c - x) (\text{Ac}^-)^2. \quad (19)$$

Equation 19 may also be written as

$$\frac{x}{(c - x)(\text{Ac}^-)} = K_1 + K_2 \frac{(2c - x)(\text{Ac}^-)}{c - x}. \quad (20)$$

From the equations 18, 19, and 17, we obtain

$$(\text{Cu}^{++}) = \frac{2c - x}{2 + K_1 (\text{Ac}^-)} \quad (21)$$

and

$$(\text{CuAc}^+) = \frac{K_1 (\text{Ac}^-)(2c - x)}{2 + K_1 (\text{Ac}^-)}. \quad (22)$$

The concentrations of the cations in the solutions are (Cu^{++}) , (CuAc^+) , $(\text{Na}^+) = s$, and (H^+) . Only univalent anions are present. By means of the equations 21 and 22 we therefore find that the ionic strength is

$$\mu = s + (\text{H}^+) + \frac{3 + K_1 (\text{Ac}^-)}{2 + K_1 (\text{Ac}^-)} (2c - x). \quad (23)$$

When (Ac^-) approaches 0, the last term of equation 20 vanishes. From each of the 6 series of measurements in the table, a preliminary value of K_1 (corresponding to $\mu = 3c + s$) may therefore be found by extrapolation of the term on the left side of equation 20 to $(\text{Ac}^-) = 0$. In this way, values of K_1 at 5 different ionic strengths are obtained. They differ only slightly from those finally adopted. The final values, which are expressed by formula 24, are found by successive approximations, starting from the preliminary values. It is sufficient to describe the last step. We assume that we have obtained formula 24, and we shall show that the next step leads to the same formula.

μ and $\log K_1$, given in the 3rd and 5th column of Table 4b, are calculated from the formulae 23 and 24 by successive approximations. From K_1 obtained in this way and the experimental data, we now compute K_2 by means of formula 19. It follows from this formula that K_2 is the less sensitive to an

error of K_1 the smaller $|c-x|$, while, on the other hand, K_1 is the less sensitive to an error of K_2 the smaller (Ac^-) or x . When $x = c$, K_1 disappears from the equation. K_2 , therefore, has only been computed for solutions where $|c-x| < \frac{c}{2}$. The results are to be found in the 6th column of Table 4b. They are used for developing formula 25. $\log K_2$, calculated from this formula, is given in the 7th column of the table. From the values of K_2 obtained from formula 25 and the experimental data, we now compute K_1 by means of formula 20. $\log K_1$ found in this way is given in the 4th column of Table 4b. For the reason mentioned above, no results are given for the smallest values of $|c-x|$. The accuracy of K_1 increases when x approaches 0, not only because the influence of complexes with two or more acetato-groups vanishes, but also owing to the disappearance of the error introduced by choosing a value of A_0 corresponding to acetate-free solution. The values of $\log K_1$ found for the smallest values of b are therefore considered the most reliable. The values printed in italics in Table 4b have been found by extrapolation to the ionic strengths corresponding to $b = 0$ by means of the dependence on μ expressed in formula 24. When these values are used in developing an interpolation formula, equation 24 is obtained. $-\log K_1$ calculated from this formula is given in the 5th column of the table.

The formulae expressing the two equilibrium constants found from the measurements are

$$\log K_1 = 2.164 - \frac{1.992\sqrt{\mu}}{1 + 1.8\sqrt{\mu}} \quad (24)$$

$$\log K_2 = 3.205 - \frac{2.988\sqrt{\mu}}{1 + 2\sqrt{\mu}} \quad (25)$$

They contain two empirical constants each. The factor before the square root in the numerator has been deduced by the Debye-Hückel theory.

Equilibria 1 and 2 give a satisfactory explanation of the measurements in Table 4a, when the equilibrium constants have the values calculated from formulae 24 and 25. This is seen most directly when E is calculated by means of these

formulae and the system of equations given above, together with the values of A_0 from Table 1 and K from Table 3. In this way, the values of E presented in the last column but one of Table 4b are obtained. The deviation Δ from E observed is given in the last column. The agreement is satisfactory.

By comparison of the second and third series of Table 4a and b, it is seen that an increase of the concentration of acetic acid from 0.1 to 0.5 molar (and, consequently, the corresponding increase of the hydrogen ion concentration) has no influence on the equilibrium constants found. This shows that the acetato-complexes considered have neither split off nor taken up protons to any perceptible degree. Complexes containing hydroxyl ions or acetic acid as ligands are, therefore, of no importance in the solutions measured here.

K_1 of equation 24 has been found by an extrapolation to acetate-free solution. It is, therefore, essentially free of the error due to the neglect of complexes with more than two acetato-groups and to the application of values of A_0 found for acetate-free solutions. On the other hand, we cannot exclude errors due to the formation of polynuclear complexes and to the use of K for solutions containing barium ions instead of cupric ions. Further, formation of nitrate-complexes may have some influence. All these errors, however, vanish when c approaches 0. K_2 of equation 25 is much less accurate than K_1 . None of the errors mentioned can be excluded.

If we extrapolate to $\mu = 0$ by means of the formulae 24 and 25, we obtain

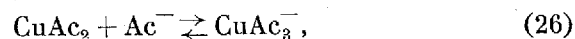
$$K_1^0 = 146 \quad \text{and} \quad K_2^0 = 1600.$$

When the equilibria are written in the form of scheme 4, we find, according to equation 7:

$$k_1^0 = 146 \quad \text{and} \quad k_2^0 = 11.$$

Hence, $k_2^0/k_1^0 = 0.075$. If we assume that a cupric ion can take up altogether 4 acetate ions in 4 uniform co-ordinative positions, k_2^0/k_1^0 should, for statistical reasons only, be $\frac{3}{8} = 0.375$ (cf. J. BJERRUM⁽⁷⁾). A ligand effect is therefore responsible for

a 5 times decrease of the ratio. We may make a very rough estimate of k_3 , the mass action constant of the equilibrium



when we assume that the ligand effects of k_2^0/k_1^0 and k_3^0/k_2^0 are equal. The statistical factor of k_3/k_2 is $\frac{4}{9}$. Hence, we find $k_3^0 \approx \frac{4}{9} \times \frac{1}{5} \times 11 \approx 1$. Owing to the nature of equilibrium 26, k_3 is approximately independent of the salt concentration. Using equation 7, we therefore find $K_3 \approx K_2$. By means of this very rough estimate of K_3 , an attempt was made to correct the determinations of K_1 and K_2 for the influence of the formation of triacetato-complexes. As might be expected, formula 24 was unchanged. The only change of formula 25 was that the constant 3.205 fell to 3.17.

The figure illustrates the complex formation in solutions of sodium acetate containing an infinitesimal amount of cupric nitrate. The fraction of the cupric ions which has combined with n acetate ions (α_n), and the average number of acetate ions bound per atom of copper ($\frac{x}{c}$), have been computed by means of the formulae

$$\alpha_n = \frac{K_n (\text{Ac}^-)^n}{\sum_0^N K_n (\text{Ac}^-)^n}$$

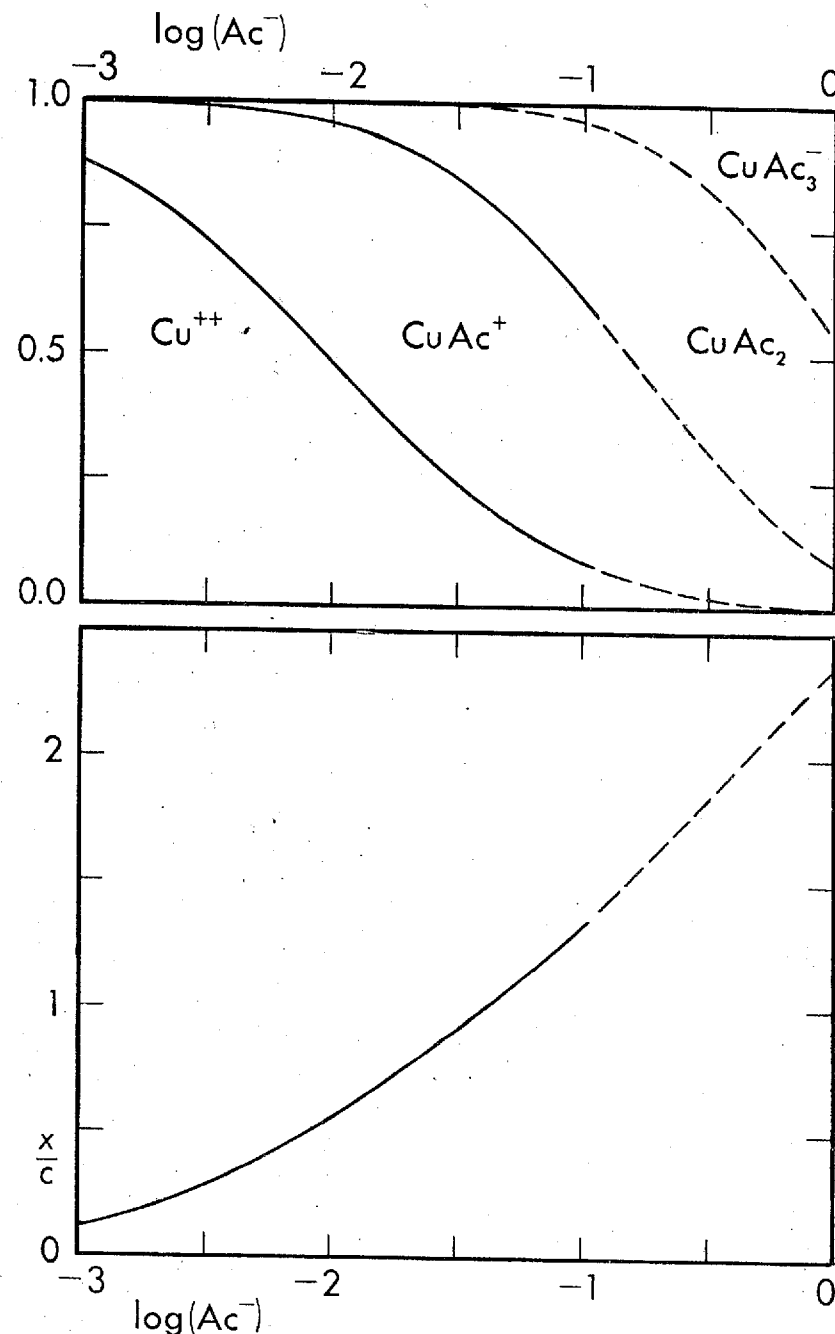
and

$$\frac{x}{c} = \sum_1^N n \alpha_n.$$

It has been assumed that complexes with more than three acetato-groups are not formed ($N = 3$). K_1 has been calculated from equation 24, while both K_2 and K_3 have been found from equation 25 modified as just mentioned.

Measurements of Light Absorption.

When sodium acetate is added to a solution of cupric nitrate, the blue colour intensifies, even when the formation of hydroxo-



Complex formation in solutions of sodium acetate containing a small amount of cupric nitrate. In the upper graph, the parts of the ordinate falling in the areas marked Cu^{++} , CuAc^+ , CuAc_2 , and CuAc_3^- , respectively, represent the

complexes is repressed by the addition of acetic acid together with the sodium acetate. In 0.1 molar sodium acetate the colour intensity was very roughly estimated to be 4, in 1 molar 10, in 2 molar 20, and in 3 molar 40 times as great as in acetate-free solution. This, when compared with the results of the electrometric measurements, shows that complexes with more than 2, presumably with 3 and 4, acetato-groups are formed in concentrated solutions of sodium acetate.

The light absorption of solutions containing cupric nitrate, sodium acetate, and acetic acid was studied more accurately by means of a König-Martens spectrophotometer. The measurements were carried out at room temperature ($20 \pm 1^\circ \text{C}$). The wave-length intervals used were $610 \pm 4 \text{ m}\mu$, $630 \pm 4 \text{ m}\mu$, $650 \pm 5 \text{ m}\mu$, and $670 \pm 8 \text{ m}\mu$. The wave-length adjustment of the apparatus was calibrated by means of a mercury lamp.

The molar extinction coefficient ϵ of the solution was obtained by dividing the extinction coefficient measured by the concentration of cupric nitrate c .

If the absorption is due only to ordinary cupric ions and to mononuclear acetato-cupric complexes, we may write

$$\epsilon = \sum_0^N \alpha_n \epsilon_n, \quad (27)$$

where α_n is the fraction of the copper which has taken up n acetate ions, while ϵ_n is the molar extinction coefficient of the complex formed.

First, ϵ was measured for $0.05 \text{ m Cu(NO}_3)_2 + 0.01 \text{ m HNO}_3$ and for the same solution containing in addition 1.90 m NaNO_3 (see Table 5). The increase, when adding the sodium nitrate, was only about 13 per cent. This shows that nitrate-complexes can only take a slight part in the absorption in the first solution. Its absorption is therefore practically completely due to ordinary cupric ions ($\epsilon = \epsilon_0$).

The results of measurements in solutions of cupric nitrate, sodium acetate, and acetic acid are given in Table 6. The composition of the solutions is to be found in the first section of the table, while ϵ is given in the last four sections. We shall examine to what extent the measurements agree with the as-

Table 5.

Molar extinction coefficients of solutions of cupric nitrate.

	610 m μ	630 m μ	650 m μ	670 m μ
0.0500 m $\text{Cu(NO}_3)_2 + 0.01 \text{ m HNO}_3$..	1.115	1.850	2.880	4.030
Same + 1.90 m NaNO_3	1.257	2.110	3.252	4.514
Percentage increase	13	14	13	12

sumptions (1) that only the reversible reactions 1 and 2 take place, and (2) that their equilibrium constants are given by the formulae 24 and 25. It follows from the first assumption that

$$\epsilon = \alpha_0 \epsilon_0 + \alpha_1 \epsilon_1 + \alpha_2 \epsilon_2. \quad (28)$$

μ , α_0 , α_1 , and α_2 , presented in the table, have been calculated by means of equations 18 and 19. Using these values of α_0 , α_1 , and α_2 , together with ϵ_0 measured in acetate-free solution (Table 5), we compute the values of ϵ_1 and ϵ_2 which, at low concentrations of sodium acetate, best satisfy equation 28. The molar extinction coefficients of the individual complexes obtained in this way are given in Table 7. ϵ is, finally, calculated by means of equation 28 and these values of the extinction coefficients. The results obtained are given in the second column of each of the last four sections of Table 6. The percentage difference between ϵ found and ϵ calculated is given in the third column. The agreement is good for the first 4 or 5 solutions. When $b > 0.1$, systematic deviations are found. This indicates that considerable amounts of complexes with more than two acetato-groups are formed in these solutions.

A comparison of the solutions nos. 6 and 7 (Table 6) suggests that also polynuclear complexes are formed. This is seen in the following way. When c increases, while b is constant, the acetate ion concentration will decrease. According to equation 6, a change in favour of complexes with fewer acetato-groups will, therefore, take place. If only mononuclear complexes were possible, a decrease of the deviation would follow; but actually an increase is found.

The same is seen from the measurements in Table 8. The concentration of cupric nitrate is $\frac{5}{2}$ times as great in solution X as in solution Y, while the concentrations of sodium acetate

Table 6.

The molar extinction coefficients ϵ of cupric nitrate solutions containing:
 c molar $\text{Cu}(\text{NO}_3)_2 + b$ molar $\text{CH}_3\text{COONa} + 0.100$ molar CH_3COOH .

No.	c	b	μ	α_0	α_1	α_2
1	0.04976	0.02000	0.1424	0.7344	0.2538	0.0118
2	0.05035	0.04002	0.1427	0.5397	0.4169	0.0434
3	0.05035	0.07031	0.1490	0.3392	0.5428	0.1180
4	0.05035	0.0999	0.1629	0.2257	0.5729	0.2014
5	0.1003	0.04002	0.2808	0.7068	0.2765	0.0167
6	0.02042	0.1998	0.2123	0.0563	0.4407	0.5030
7	0.05035	0.1998	0.2370	0.0834	0.4888	0.4278
8	0.05035	0.2998	0.3262	0.0440	0.3941	0.5619

No.	ϵ at 610 $m\mu$			ϵ at 630 $m\mu$		
	found	calcd.	Percentage diff.	found	calcd.	Percentage diff.
1	2.071	2.074	-0.1	3.412	3.413	0
2	2.912	2.900	+0.4	4.737	4.726	+0.2
3	3.967	3.975	-0.2	6.364	6.384	-0.3
4	4.804	4.804	0	7.622	7.623	0
5	2.219	2.194	+1.1	3.639	3.602	+1.0
6	7.072	6.986	+1.2	10.90	10.76	+1.3
7	6.763	6.493	+4.0	10.53	10.06	+4.5
8	8.077	7.342	+9.1	12.46	11.26	+9.6

No.	ϵ at 650 $m\mu$			ϵ at 670 $m\mu$		
	found	calcd.	Percentage diff.	found	calcd.	Percentage diff.
1	5.208	5.201	+0.1	6.954	6.925	+0.4
2	7.072	7.086	-0.2	9.230	9.288	-0.6
3	9.344	9.366	-0.2	12.14	12.17	-0.2
4	11.02	10.99	+0.3	14.29	14.23	+0.4
5	5.473	5.471	0	7.380	7.264	+1.6
6	15.35	14.83	+3.4	19.60	19.17	+2.2
7	14.86	14.00	+5.8	18.70	18.10	+3.2
8	17.41	15.41	+11.5	21.78	19.92	+8.6

Table 7.

Molar extinction coefficients of the individual complexes.

		610 $m\mu$	630 $m\mu$	650 $m\mu$	670 $m\mu$
Cu^{++}	ϵ_0	1.115	1.850	2.880	4.030
CuAc^+	ϵ_1	4.49	7.41	11.26	14.46
CuAc_2	ϵ_2	9.83	14.7	19.3	25.0

are the same. The sodium nitrate is added in order to keep the ionic strength nearly constant. The difference between the extinctions of 2 cm. of solution X and 5 cm. of solution Y was measured directly, and the difference between the molar extinction coefficients of the solutions, $\epsilon_X - \epsilon_Y$, was evaluated. When passing from solution X to solution Y, a change in favour of

Table 8.

Measurements of the difference between the molar extinction coefficients ϵ_X and ϵ_Y of the cupric nitrate solutions X and Y at the wave-length 630 $m\mu$. All the solutions contain 0.200 m acetic acid.

Solution X			Solution Y			$\epsilon_X - \epsilon_Y$
$\text{Cu}(\text{NO}_3)_2$	CH_3COONa	NaNO_3	$\text{Cu}(\text{NO}_3)_2$	CH_3COONa	NaNO_3	
0.0760	0.500	1.35	0.0304	0.500	1.44	0.158
0.0760	0.750	1.10	0.0304	0.750	1.19	0.399
0.0512	0.750	1.15	0.0205	0.750	1.21	0.237

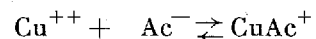
complexes with a greater number of acetato-groups will take place. If only mononuclear complexes were formed, $\epsilon_X - \epsilon_Y$ would therefore be negative; but actually positive values are found.

I wish to express my cordial thanks to the head of the laboratory, Professor NIELS BJERRUM, for advice and kind interest in my work.

Summary.

The hydrogen ion concentration of solutions containing cupric nitrate, sodium nitrate, acetic acid, and sodium acetate was measured at 18.0° C. by means of the glass electrode.

The acetate ion concentration of the solutions was calculated from the hydrogen ion concentration and the dissociation constant of acetic acid. The mass action constants of the equilibria



and



were evaluated.

The dissociation constant of acetic acid was determined from measurements of the hydrogen ion concentration of solutions containing barium nitrate instead of cupric nitrate.

Spectrophotometric measurements were carried out on solutions containing cupric nitrate, acetic acid, and sodium acetate. Although they do not allow an independent calculation of the complexity constants, they agree with the electrometric measurements at concentrations where a comparison is possible. They further indicate that both complexes with more than two acetate-groups and polynuclear complexes are formed in more concentrated solution.

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