

Metal Ammine Formation in Solution. XXI. On the Formation of Di(triethanolamine)di- μ -hydroxodicopper(II) and other Complexes in the Copper(II)–Triethanolamine System

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This paper reports a potentiometric and spectrophotometric study of the copper(II)–triethanolamine system. The formation curves (\bar{n} , $p[L]$) at different triethanolammonium concentrations (for $\bar{n} \leq 2$) are analyzed and constants determined for the formation of Cu tea^{2+} , Cu tea(OH)^+ and $\text{Cu}_2 \text{tea}_2(\text{OH})_2^{2+}$ ($\text{tea} = \text{N}(\text{C}_2\text{H}_4\text{OH})_3$) corresponding to equations (1)–(3) at 25 °C in 0.5 M (teaH_3K) NO_3 ($\log K_1 = 4.22 \pm 0.01$, $pK_{1a} = 6.42 \pm 0.05$, $\log K_{\text{ass}} = 3.15 \pm 0.15$) and in 2 M teaHClO_4 ($\log K_1 = 4.99 \pm 0.02$, $pK_{1a} = 6.31 \pm 0.10$, $\log K_{\text{ass}} = 2.70 \pm 0.25$).

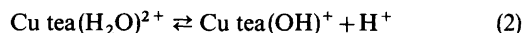
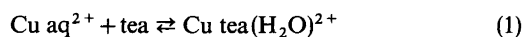
Analysis of the spectra show that at higher amine concentrations this system of complexes is converted at least partially to the inner complex $\text{Cu}(\text{tea}')_2$ ($\text{tea}' = \text{N}(\text{C}_2\text{H}_4\text{OH})_2\text{C}_2\text{H}_4\text{O}^-$), which in strong alkaline solution with uptake of hydroxide ions again loses one of its amine ligands.

The complex formation of triethanolamine with copper(II) ions in solution has been studied by several authors.^{1–7} In 1947 Bjerrum and Refn¹ determined the formation constant for the 1:1 complex $\text{Cu}(\text{tea})^{2+}$ [$\text{tea} = \text{N}(\text{C}_2\text{H}_4\text{OH})_3$] and showed that at $\text{pH} \geq 5$ this complex begins to hydrolyze with dimerization. Values for the dimerization constant and for the acidity constant were determined.

Hall and coworkers^{2,3} determined the first formation constant and studied the hydrolysis of the $\text{Cu}(\text{tea})^{2+}$ complex by various methods assuming

only monomeric complexes up to high pH-values. They found that in basic solution the complex deprotonated with formation of neutral and even negatively-charged hydroxo complexes for $\text{pH} > 10$. Cadiot-Smith⁴ studied the system by potentiometric methods and reports a variety of complexes including $\text{Cu}(\text{tea})^{2+}$ and $\text{Cu}_2(\text{tea})_2(\text{OH})_2^{2+}$. Davies and Patel⁷ in a potentiometric study examined whether hydroxo- or alcoholate complexes are formed during the hydrolysis of $\text{Cu}(\text{tea})^{2+}$. In the case of uptake of hydroxide ions they expected to find diol formation, but their measurements gave no evidence for dimerization, and for this reason they assumed that it was the hydroxyl groups in triethanolamine that gave off protons in basic solution with formation of bidentate and tridentate monoamine complexes $\text{Cu}(\text{tea}')^+$ and $\text{Cu}(\text{tea}'')^0$.^{*} In agreement with Hall and coworkers^{2,3} they found no evidence for formation of higher complexes, except perhaps at high concentrations of amine.

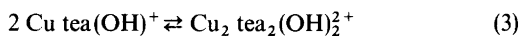
Theory and procedure for analyzing the Cu(II)–tea system from measurements of the hydrogen ion concentration. The main purpose of this paper is to show that the behaviour of the Cu(II)–tea system in weakly acidic solutions can be accounted for quantitatively by the set of equilibria (1)–(3);



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* tea' and tea'' denote tea in which one and two hydroxyl groups, respectively, have become deprotonated.



in the concentration range for which the apparent ligand number \bar{n} is given by eqn. (4).

$$\bar{n} = \frac{C_{\text{tea}} - [\text{tea}] + [\text{H}^+] - [\text{OH}^-]}{C_{\text{Cu}}} \lesssim 1.7 \text{ and} \\ [\text{H}^+] \gg [\text{OH}^-] \quad (4)$$

The equilibrium constants corresponding to equations (1)–(3) are denoted in eqns. (5)–(7).

$$K_1 = \frac{[\text{Cu tea}^{2+}]}{[\text{Cu}^{2+}][\text{tea}]} \quad (5)$$

$$K_{1a} = \frac{[\text{Cu tea}(\text{OH})^+][\text{H}^+]}{[\text{Cu tea}^{2+}]} \quad (6)$$

$$K_{\text{ass}} = \frac{[\text{Cu}_2 \text{tea}_2(\text{OH})_2^{2+}]}{[\text{Cu tea}(\text{OH})^+]^2} \quad (7)$$

We also define eqn. (8).

$$\beta_{2,2}^* = \frac{[\text{Cu}_2 \text{tea}_2(\text{OH})_2^{2+}][\text{H}^+]^2}{[\text{Cu tea}^{2+}]^2} = K_{1a}^2 K_{\text{ass}} \quad (8)$$

C_X denotes the stoichiometric molar concentrations of X and [X] the individual concentrations of the species in question.

With the assumptions made here the stoichiometric concentrations of copper(II) and triethanolamine can be expressed as eqns. (9) and (10).

$$C_{\text{Cu}} = [\text{Cu}^{2+}] + [\text{Cu tea}^{2+}] + [\text{Cu tea}(\text{OH})^+] + 2[\text{Cu}_2 \text{tea}_2(\text{OH})_2^{2+}] \quad (9)$$

$$C_{\text{tea}} - [\text{tea}] + [\text{H}^+] = [\text{Cu tea}^{2+}] + 2[\text{Cu tea}(\text{OH})^+] + 4[\text{Cu}_2 \text{tea}_2(\text{OH})_2^{2+}] \quad (10)$$

By eliminating eqn. (11) from equations (9) and (10) by subtraction and employing eqn. (5) we obtain

$$C'_{\text{Cu}} = [\text{Cu tea}(\text{OH})^+] + 2[\text{Cu}_2 \text{tea}_2(\text{OH})_2^{2+}] \quad (11)$$

$$[\text{Cu}^{2+}] = \frac{2C_{\text{Cu}} - (C_{\text{tea}} - [\text{tea}] + [\text{H}^+])}{2 + K_1[\text{tea}]} \quad (12)$$

eqn. (12), K_1 can be calculated independently of the hydrolysis products from the more acid solutions when $\bar{n} < 0.5$. For this reason C'_{Cu} is directly accessible for calculation from a knowledge of $[\text{H}^+]$ and

$K_{\text{teaH}^+} = [\text{tea}][\text{H}^+]/[\text{teaH}^+]$ in solutions with a known concentration of the triethanolammonium ion. This is then sufficient to calculate values for K_{ass}, K_{1a} and $\beta_{2,2}^*$.

A representative part of the experimental data is given in Tables 1 and 2. The data in Table 1a and Table 2a show that the first formation constant (5) can be calculated with sufficient accuracy from the relation

$$K_1 = \frac{\bar{n}}{(1-\bar{n})[\text{tea}]}$$

when $\bar{n} \lesssim 0.5$.

The value of $\text{p}K_{\text{teaH}^+}$ given in Table 1a for the 0.5 M (K, teaH)-nitrate medium has been determined previously by Bjerrum and Refn⁸ and the value in 2M teaHClO₄ is found by the same procedure to be 8.42 ± 0.01 . It will be observed that $\text{p}K_{\text{teaH}^+}$ as well as $\log K_1$ are considerably larger in the medium with a high concentration of the triethanolammonium ion than in the 0.5 M (K, teaH)-nitrate medium ($\log K_1 = 4.99$ in contrast to 4.22). For comparison purposes it can be mentioned that $\log K_1$ in the copper(II)–ammonia system has values of the same order of magnitude⁹ (4.22 in 2 M NH₄NO₃ and 4.10 in 0.5 M NH₄NO₃ at 25 °C).

Tables 1b and 2b show experimental data for values of \bar{n} varying from ~ 1 to ~ 1.6 . Using the values obtained for K_1 and the relations (5) and (12) values for $[\text{Cu}^{2+}]$, $[\text{Cu tea}^{2+}]$ as well as the residual copper concentration C'_{Cu} , which according to our assumptions is equal to $[\text{Cu tea}(\text{OH})^+] + 2[\text{Cu}_2 \text{tea}_2(\text{OH})_2^{2+}]$, have been calculated and are given in Tables 1b and 2b. It will be noticed that in some cases in Table 1b it has been necessary to correct for the change in the ammonium concentration caused by the formation of the hydroxo complexes.

The entire experimental material is plotted in Fig. 1. In the figure \bar{n} is plotted *versus* $\text{p}[\text{tea}]$ instead of *versus* pH, so as to separate the formation curves for the different triethanolammonium concentrations. The dependence of the curves on the copper concentration show qualitatively that complexes with more than one copper atom are present.

The formation curves show, especially at high teaH⁺-concentrations, a tendency to converge towards $\bar{n}=1$ and again towards $\bar{n}=2$, but they exceed this value and become steeper and steeper with increasing \bar{n} -values. This seems to indicate comparing with the copper(II)–pyridine system¹⁰

Table 1a. Glass electrode measurements of copper(II)–triethanolamine solutions at 25 °C. $C_{\text{teaHNO}_3} + C_{\text{KNO}_3} = 0.50 \text{ M}$. $\text{p}K_{\text{teaH}^+} = 7.90 \pm 0.01$.

No.	$C_{\text{teaH}^+}^{\circ}$	C_{Cu}	C_{tea}	pH	p[tea]	[tea]	\bar{n}	log K_1
1	0.020	0.00980	0.00254	4.922	4.678	0.0000210	0.258	4.218
2	0.050	0.00982	0.00349	4.729	4.471	0.0000338	0.355	4.212
3	0.100	0.01991	0.00751	4.484	4.416	0.0000384	0.377	4.198
4	0.400	0.01975	0.00991	4.072	4.228	0.0000591	0.501	4.230
5	0.100	0.01964	0.01115	4.775	4.125	0.0000750	0.565	4.238
								4.22 ± 0.01

Table 1b. Calculations with log $K_1 = 4.22$.

No.	C_{teaH^+}	C_{Cu}	C_{tea}	pH	p[tea]	\bar{n}	$[\text{Cu}^{2+}]$	$[\text{Cu tea}^{2+}]$	C'_{Cu}
6	0.400	0.01977	0.02120	5.085	3.215	1.041	0.001565	0.01585	0.0238
9	0.400	0.02001	0.04163	6.051	2.249	1.799	0.0000526	0.00492	0.01504
10	0.050	0.01035	0.01001	5.420	3.780	0.951	0.00628	0.00628	0.00180
	0.052 ^a				3.764	0.950	0.00223	0.00638	0.00174
11	0.050	0.01028	0.01532	5.821	3.379	1.449	0.000633	0.00440	0.00525
	0.055 ^a				3.337	1.446	0.000590	0.00452	0.00517
12	0.050	0.001950	0.003015	5.886	3.314	1.297	0.0001363	0.00110	0.000714
14	0.050	0.000500	0.001394	6.063	3.137	1.329	0.0000238	0.000288	0.000188
15	0.0050	0.009877	0.01045	5.853	4.347	1.054	0.003295	0.00276	0.00382
	0.0083 ^a				4.128	1.049	0.00287	0.00363	0.00338
17	0.0050	0.003191	0.001998	5.787	4.413	0.615	0.00167	0.00109	0.00043
	0.0054 ^a				4.380	0.613	0.00163	0.00116	0.00040
20	0.0050	0.003244	0.005456	6.379	3.820	1.637	0.0000258	0.000662	0.00232
	0.0072 ^a				3.663	1.615	0.0000219	0.000808	0.00221

^a Corrected for hydrolysis ($C_{\text{teaH}^+} = C_{\text{teaH}^+}^{\circ} + C'_{\text{Cu}}$).

Table 1c. Estimation of the hydrolysis constants with log $K_{\text{ass}} = 3.15 \pm 0.15$.

No.	C'_{Cu}	$[\text{Cu tea}(\text{OH})^+]$	$[\text{Cu}_2 \text{ tea}_2 (\text{OH})_2^{2+}]$	$\text{p}K_{1a}$	$\text{p}\beta_{2,2}^*$	$\bar{n}_{\text{calc.}}^a$	$\text{pH}_{\text{calc.}}$
6	0.00238	0.000757	0.000813	6.406	9.662	1.041	5.092
9	0.01504	0.00214	0.00645	6.413	9.676	1.750	6.093
10	0.00174	0.000629	0.000555	6.427	9.704	0.952	5.414
11	0.00517	0.00119	0.00199	6.401	9.652	1.446	5.833
12	0.00714	0.000356	0.000179	6.376	9.062	1.296	5.908
14	0.000188	0.00136	0.0000261	6.389	9.628	1.329	6.068
15	0.00338	0.000932	0.001225	6.444	9.738	1.052	5.842
17	0.000400	0.000239	0.0000805	6.473	9.796	0.614	5.771
20	0.00221	0.000726	0.000744	6.426	9.702	1.613	6.378
				Average	6.41 ± 0.05	9.68 ± 0.05	
				Using all nos. 6–20	6.42 ± 0.05	9.69 ± 0.05	(log $K_{\text{ass}} = 3.15 \pm 0.15$)

^a $\bar{n}_{\text{calc.}} = ([\text{Cu tea}^{2+}] + 2C'_{\text{Cu}})/C_{\text{Cu}}$.

Table 2a. Glass electrode measurements of copper(II)–triethanolamine solutions in 2 M teaHClO₄ at 25°C. pH + [tea] = 8.12 ± 0.01.

No.	C _{Cu}	C _{tea}	p[tea]	pH	[tea]	\bar{n}	log K ₁
21	0.01964	0	5.651	2.469	0.00000223	0.173	4.972
22	0.04912	0.01524	5.301	2.819	0.00000500	0.331	4.994
23	0.04913	0.01997	5.143	2.977	0.00000720	0.428	5.017
24	0.01964	0.00952	4.969	3.151	0.00001075	0.520	5.00
25	0.00480	0.00285	4.719	3.401	0.0000191	0.673	5.03
							4.99 ± 0.02

Table 2b. Calculations with log K₁ = 4.99.

No.	C _{Cu}	C _{tea}	p[tea]	pH	\bar{n}	[Cu ²⁺]	[Cu tea ²⁺]
26	0.04911	0.06490	2.844	5.276	1.293	0.000244	0.0342
27	0.04912	0.07440	2.609	5.511	1.465	0.000106	0.02597
28	0.04911	0.08445	2.384	5.736	1.636	0.0000413	0.01747
29	0.01962	0.02476	2.886	5.234	1.196	0.0001218	0.01550
31	0.01965	0.03346	2.373	5.747	1.487	0.0000241	0.01000
34	0.00482	0.01199	2.295	5.825	1.436	0.00000545	0.00271
35	0.00491	0.01654	2.038	6.082	1.503	0.00000271	0.002435

Table 2c. Estimation of the hydrolysis constants with log K_{ass} = 2.93 ± 0.25.

No.	C _{Cu}	[Cu tea(OH) ⁺]	[Cu ₂ tea ₂ (OH) ₂ ²⁺]	pK _{1a}	pβ _{2,2} [*]	$\bar{n}_{\text{calc.}}$	pH _{calc.}
26	0.01466	0.00266	0.00600	6.386	9.842	1.300	5.289
27	0.02304	0.00340	0.00980	6.394	9.858	1.466	5.515
28	0.03160	0.00402	0.01379	6.374	9.818	1.643	5.749
29	0.00400	0.00127	0.001365	6.322	9.714	1.198	5.291
31	0.00963	0.00210	0.003765	6.424	9.918	1.489	5.732
34	0.00211	0.000856	0.000627	6.325	9.720	1.436	5.842
35	0.00247	0.000946	0.000762	6.493	10.056	1.503	6.069
				Average	6.38 ± 0.10	9.84 ± 0.10	
Using all nos. 26–36				"	6.31 ± 0.10	9.92 ± 0.10	(log K _{ass} = 2.70 ± 0.25)

$$^a \bar{n}_{\text{calc.}} = ([\text{Cu tea}^{2+}] + 2C_{\text{Cu}}) / C_{\text{Cu}}$$

that the activity coefficient of the amine decreases with increasing concentration of the amine, and for this reason, and owing to the method of calculation the calculated points in Fig. 1 are not reliable for $\bar{n} \geq 2.5$. The points numbered 6–20 and 26–35 for $\bar{n} < 2$ are all employed in the calculations, but only for some of them are full details given in the tables.

In order to calculate K_{1a} and β_{2,2}^{*} [eqns. (6) and (8)] from a knowledge to C_{Cu}, [Cu tea²⁺] and [H⁺], a computer programme has been constructed which searches for the value of K_{ass} which gives the best fit of the data. The results of the computer calcu-

lations are shown in Table 3. The calculations were made with the data in Table 1 b and Table 2b as well as with the data corresponding to all the numbered points in Fig. 1. It will be seen from Table 3 that the sum of the squares of the deviations from the average values of pK_{1a} (calculated with varying values of log K_{ass}) obtained using either the complete set of data or only those in Tables 1 and 2 shows a distinct minimum for nearly the same values of log K_{ass}. In Tables 1c and 2c the values of [Cu tea(OH)⁺], [Cu₂ tea₂(OH)₂²⁺], pK_{1a} and β_{2,2}^{*} for the single measurements are tabulated that are

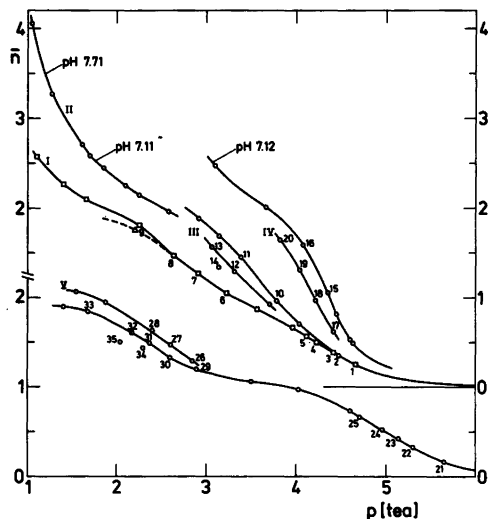


Fig. 1. Formation curves \bar{n} versus $p[\text{tea}]$. The curves are drawn through points with the same initial triethanolammonium- and approximately the same copper(II) concentration. The numbers in the figure refer to the solutions specified in Tables 1 and 2. For $\bar{n} \leq 0.5$ the points (1–5) in 0.5 M (K, teaH)NO₃ and (21–25) in 2 M teaHClO₄ fell on the same curve independently of the copper(II) concentration. Curve I has $C_{\text{teaHNO}_3} = 0.400$ M, $C_{\text{Cu}} \sim 0.02$ M (6–9); curve II $C_{\text{teaHNO}_3} = 0.100$, $C_{\text{Cu}} \sim 0.02$; curves III $C_{\text{teaHNO}_3} = 0.050$, $C_{\text{Cu}} \sim 0.01$ (10–11), $C_{\text{Cu}} \sim 0.003$ (12–13) and $C_{\text{Cu}} \sim 0.0005$ (14); curves IV $C_{\text{teaHNO}_3} = 0.0050$, $C_{\text{Cu}} \sim 0.01$ (15–16) and $C_{\text{Cu}} \sim 0.003$ (17–20). Finally curves V referring to Table 2 (with changed ordinate) have $C_{\text{teaHClO}_4} = 2.00$, $C_{\text{Cu}} \sim 0.04$ (26–28), $C_{\text{Cu}} \sim 0.02$ (29–33) and $C_{\text{Cu}} \sim 0.002$ (34–35). For sol. 9 with $\bar{n} \sim 1.8$ \square indicates the experimental point and Δ the point recalculated by means of the computed constants. In all cases for $\bar{n} \leq 1.6$ the experimental and recalculated points differ so little that they are indistinguishable in the Figure (cf. Tables 1 and 2).

calculated from the values for K_{ass} obtained in this way. The uncertainties quoted for pK_{1a} and $\beta_{2,2}^*$ are estimated from assumed uncertainties for $\log K_{\text{ass}}$ (± 0.15 in Table 1c and ± 0.25 in Table 2c).

In order to test the quality of the calculated constants the hydrogen ion concentration (which is the basis for all the calculations) has been recalculated using a special computer programme written by Morten Jannik Bjerrum. The computed values of pH are shown in the last column of Table 1c and Table 2c. The agreement with the experimentally determined values is seen to be excellent

with the exception of the value for sol. 9 which had an \bar{n} -value too close to the limiting value ($\bar{n}=2$) for a good agreement to be expected (cf. Fig. 1). Further support of the correctness of our results is provided by the fact that the sum of the squares of the deviations from the computed pH-values $\Sigma \Delta^2$ (pH) calculated with varying values of K_{ass} has a minimum (cf. Table 3) for nearly the same values of $\log K_{\text{ass}}$ as $\Sigma \Delta^2$ (pK_{1a}).

Results of analysis of the absorption spectra. Table 4 shows values of the molar extinction coefficients for some of the solutions mentioned in Table 2. From those data the values for the extinction coefficients of Cu tea²⁺ (ϵ_1) and for the equilibrium mixtures of Cu tea(OH)⁺ and Cu₂ tea₂(OH)₂²⁺ (ϵ_x) as shown in the table have been calculated. The data are plotted in Fig. 2 together with the spectra of two solutions with $\bar{n} \approx 1.82$ (curve I) and $\bar{n} \approx 1.98$ (curve II).

The values calculated for ϵ_x with the average association factor x varying from 1.42 to 1.77 are seen to differ only slightly indicating that the spectra of monomer and dimer are quite similar. Furthermore, the solution with $\bar{n} \sim 2$ (curve II) has a spectrum situated very close to that calculated for ϵ_x .

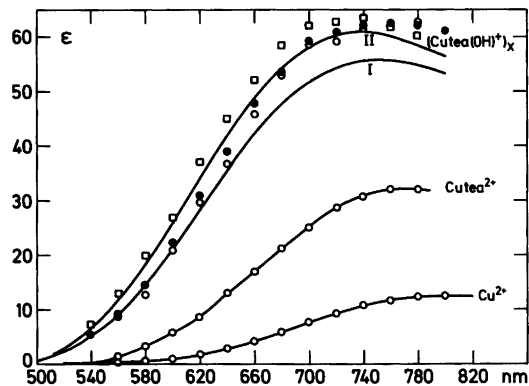


Fig. 2. Visible absorption spectra (ϵ, λ) of Cu aq²⁺, Cu tea²⁺ (from data in Table 4), and molar extinction coefficients for the equilibrium mixture of Cu tea(OH)⁺ and Cu₂ tea₂(OH)₂²⁺ calculated from data for solutions 26 with $C_{\text{Cu}} = 0.0491$, $\bar{n} = 1.293$ (\circ), 28 with $C_{\text{Cu}} = 0.0491$, $\bar{n} = 1.636$ (\bullet) and 34 with $C_{\text{Cu}} = 0.00482$, $\bar{n} = 1.436$ (\square) in Table 2. Curve I is the spectrum of a solution with $\bar{n} \approx 1.82$ ($C_{\text{teaHClO}_4} = 2.00$, $C_{\text{Cu}} = 0.00958$, $C_{\text{tea}} = 0.0304$) and curve II of one with $\bar{n} \approx 1.98$ ($C_{\text{teaHClO}_4} = 2.00$, $C_{\text{Cu}} = 0.00959$, $C_{\text{tea}} = 0.0570$).

Table 3. Results of computer calculations.

$\log K_{\text{ass}}$	$\text{p}K_{1a}$	$\Sigma\Delta^2(\text{p}K_{1a})$	$\text{p}\beta_{2,2}^*$	$\log K_{\text{ass}}$	$\text{p}K_{1a}$	$\Sigma\Delta^2(\text{p}K_{1a})$	$\Sigma\Delta^2(\text{pH})$
Data from Table 1				With all Nos. 6–20 in Fig. 1			
3.50	6.553	0.01227	9.606	3.50	6.558	0.02847	0.000179
3.30	6.474	0.00825	9.647	3.30	6.477	0.02276	0.000160
3.20	6.435	0.00716	9.670	3.20	6.437	0.02099	0.000156
3.10	6.398	0.00695	9.696	3.10	6.398	0.02030	0.000159
3.00	6.362	0.00783	9.724	3.00	6.361	0.2097	0.000162
2.90	6.327	0.01005	9.754	2.90	6.325	0.02331	0.000189
2.70	6.261	0.01934	9.823	2.70	6.256	0.03430	0.000258
3.15	6.41	min.	9.68	3.10	6.40	min	
				3.18	6.43		min.
Data from Table 2				With all Nos. 26–35 in Fig. 1			
3.10	6.458	0.02126	9.816	3.10	6.476	0.03044	0.000186
3.00	6.415	0.02107	9.829	3.00	6.432	0.02975	0.000179
2.90	6.372	0.02101	9.844	2.90	6.389	0.02916	0.000173
2.80	6.330	0.02114	9.860	2.80	6.347	0.02872	0.000168
2.70	6.289	0.02153	9.879	2.70	6.306	0.02851	0.000165
2.60	6.249	0.02226	9.898	2.60	6.265	0.02861	0.000164
2.50	6.211	0.02342	9.922	2.50	6.226	0.02913	0.000166
2.40	6.173	0.02513	9.946	2.40	6.187	0.03017	0.000172
2.93	6.38	min.	9.84	2.67	6.29	min	
				2.65	6.28		min.

Table 4. Estimation of the spectra in the visible region of Cu tea^{2+} and of the equilibrium mixture of $\text{Cu tea}(\text{OH})^+$ and $\text{Cu}_2 \text{ tea}_2(\text{OH})_2^{2+}$ calculated from some of the measured solutions in 2 M teaHClO_4 .

No.	C_{Cu}	ϵ	540	580	620	660	700	740	780 nm
	0.0488	$\epsilon_0(\text{Cu aq})^a$	0.20	0.61	1.74	4.20	7.68	10.65	12.19
23	0.0491	$\bar{n}=0.331$	0.25	1.53	4.07	8.40	13.48	17.30	18.83
24	0.0491	$\bar{n}=0.428$ $\epsilon_1(\text{Cu tea}) \text{ av.}^b$	0.25	1.78	4.58	9.67	15.01	19.08	20.61
			0.33	3.37	8.53	16.94	25.0	30.54	32.06
26	0.0491	$\bar{n}=1.293$ $\epsilon_x(x=1.69)^c$	2.04	6.11	14.76	25.45	34.92	39.71	41.03
			5.6	12.6	29.6	45.7	58.6	61.6	62.5
28	0.0491	$\bar{n}=1.636$ $\epsilon_x(x=1.77)$	3.56	10.69	22.91	36.65	46.83	50.91	51.41
			5.4	14.7	30.9	47.7	59.0	62.3	62.3
34	0.00482	$\bar{n}=1.436$ $\epsilon_x(x=1.42)$	3.37	10.48	21.01	32.42	41.23	45.02	44.35
			7.1	19.9	37.0	52.1	62.1	63.5	60.2

^a Measured in 0.05 M acid solution. ^b $\epsilon_1 = (\epsilon_{\bar{n}} - (1-\bar{n})\epsilon_0)/\bar{n}$ ($\bar{n} \lesssim 0.5$). ^c $\epsilon_x = (\epsilon_{\bar{n}} C_{\text{Cu}} - \epsilon_1 [\text{Cu tea}^{2+}] - \epsilon_0 [\text{Cu}^{2+}])/C_{\text{Cu}}$ ($\sim 1 < \bar{n} < 2$); $x = C'_{\text{Cu}}/([\text{Cu tea OH}^+] + [\text{Cu}_2 \text{ tea}_2(\text{OH})_2^{2+}])$ is the average association factor.

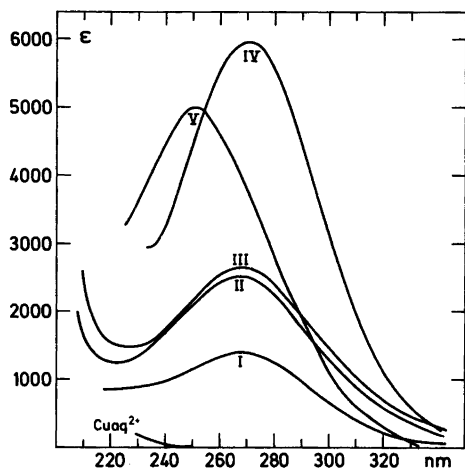


Fig. 3. UV absorption spectra of copper(II)-triethanolamine perchlorate solutions. Curve I shows the spectrum of sol. 25 in Table 2a with $\bar{n}=0.673$, II of sol. 34 ($\bar{n}=1.436$) and III of sol. 35 ($\bar{n}=1.503$). Curve IV is the spectrum of a solution with $C_{\text{Cu}}=0.00207$, $C_{\text{teaHClO}_4}=0$, $C_{\text{tea}}=2.92$ M, and V of a strongly alkaline solution with $C_{\text{Cu}}=0.00199$, $C_{\text{tea}}=2.89$ and $C_{\text{NaOH}}=2.00$ M.

The UV absorption spectra (ϵ , λ) for three of the solutions mentioned in Table 2 (curves I, II and III with $\bar{n}=0.673$, 1.436 and 1.503, respectively) are shown in Fig. 3. It can be seen that these solutions have an absorption maximum at the same wavelength (267 nm). As electron transfer bands they are much more intense than the ligand field bands of similar solutions in the visible region, and using the data given in Table 2 it can be estimated that Cu tea^{2+} has $\epsilon_{\text{max}} \sim 2000$ and that $(\text{Cu teaOH})_x$ with $x \sim 1.5$ has $\epsilon_{\text{max}} \sim 4500$.

Fig. 4 (lower part) shows the spectra in the visible region of species existing at higher amine concentrations than those present for values of $\bar{n} \leq 2$. It will be seen that the absorption starts to increase for increasing values of \bar{n} (curve II is estimated from the data given in Fig. 1 to correspond to $\bar{n} \sim 2.8$ and curve III to $\bar{n} \sim 3$) at the same time as λ_{max} shifts towards lower wavelengths. This shift of λ_{max} towards lower wavelengths continues with increasing amine concentration but with decreasing absorption. For amine concentration between 0.238 and 7.38 M the curves IV to VIII form a system with an isosbestic point at 606 nm. A new band appears at 560 nm and the limiting curve VIII for the system in pure amine ($\sim 97\%$) as solvent

still has a flat maximum approaching a shoulder at 630 nm. The large shift (~ 150 nm) of λ_{max} from curve III to the new band at 560 nm indicates the uptake of a second amine molecule, and considering that $\text{pH} > 11$ it is reasonable to assume that the complex responsible for the band at 630 nm is the inner complex $\text{Cu}(\text{tea})_2^\circ$, for which $\bar{n}=4$. The complex corresponding to $\bar{n}=3$ (\sim curve III) is possibly $\text{Cu tea}(\text{OH})^\circ$, which like $\text{Cu tea}(\text{OH})^+$ may be dimerized to some extent. This assumption is supported by the fact that curve III nearly coincides with that for the much more strongly basic solution (curve IIa).

Fig. 4 (upper part) shows the influence of sodium hydroxide in high concentrations on the spectra of

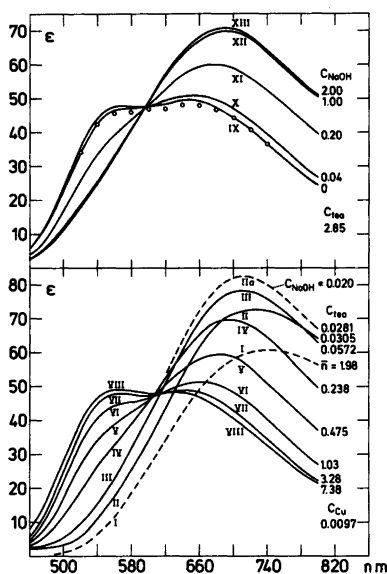


Fig. 4. Visible absorption spectra (ϵ , λ) of the $\text{Cu}(\text{II})$ -tea complexes formed at higher amine and hydroxyl ion concentrations ($\bar{n} > 2$). Lower part. Curve I (the same as curve II in Fig. 2) shows the spectrum of $(\text{Cu teaOH})_x$ in 2 M teaHClO_4 and II-VIII are the absorption curves of aqueous solutions (without added triethanolammonium salt) with $C_{\text{Cu}}=0.0097$ M and increasing concentrations of triethanolamine from 0.0305 to 7.38 M as shown on the figure. Curve IIa is the spectrum of an alkaline solution with $C_{\text{Cu}}=0.00981$, $C_{\text{tea}}=0.0281$ and $C_{\text{NaOH}}=0.02$ M. Upper part. Five absorption curves (IX-XIII) with $C_{\text{Cu}} \sim 0.01$ M, $C_{\text{tea}}=2.85$ M and increasing concentrations of NaOH from 0 to 2 M as shown on the figure. The o-points situated close to curve IX are for a solution with a 5 times higher copper(II) concentration ($C_{\text{Cu}}=0.05$ M, $C_{\text{tea}}=2.85$ M).

solutions with $[\text{tea}] = 2.85 \text{ M}$. Curve IX (no addition of NaOH) is very little different from the limiting spectrum in the pure amine (curve VIII), and does not change very much on increasing pH from ~ 11 to 12.6 (curve X with $C_{\text{NaOH}} = 0.04 \text{ M}$). The o-points close to curve IX correspond to $C_{\text{Cu}} = 0.05 \text{ M}$ whereas the full drawn curve is for $C_{\text{Cu}} = 0.01 \text{ M}$. This shows that Beer's law applies which is in agreement with our assumption that the major complex in these solutions is the monomeric inner-complex $\text{Cu}(\text{tea})_2$ with two chelating ligands. On increasing the hydroxide concentration $\text{Cu}(\text{tea})_2$ is transformed to a new complex with $\epsilon_{\text{max}} = 70$ at 690 nm. The system of curves IX to XIII has an isobestic point at 697 nm and the formation of the new complex is complete in $\sim 1 \text{ M}$ NaOH. The large shift of λ_{max} ($\sim 130 \text{ nm}$) back towards the red makes it reasonable to assume that the new complex is a monoamine complex in which the second amine molecule is replaced by hydroxide ions. This is most likely also when one considers the difficulty with which the second amine molecule is taken up, even in the pure amine as solvent. The complex in 1 M NaOH probably has a constitution corresponding to $\bar{n} = 5$, such as $\text{Cu tea}''(\text{OH})_2^{2-}$ with a tridentate ligand or perhaps even $\text{Cu tea}''(\text{OH})_3^{2-}$. In both cases the presence of five bound ligand groups is assumed as in other copper(II)-amine systems at high amine and hydroxide concentrations.^{11,12}

Curves IV and V in Fig. 3 show the UV spectra of solutions stabilized with a high concentration of amine ($C_{\text{tea}} \sim 2.9 \text{ M}$), and with and without added NaOH (2 M). It will be observed that the effect of the hydroxide concentration is to shift λ_{max} towards lower wavelengths, viz. from 270 to 250 nm. It has further some interest in this connection that a strongly basic solution with a much smaller amine concentration ($C_{\text{Cu}} = 0.00098$, $C_{\text{tea}} = 0.062$, $C_{\text{NaOH}} = 1.00 \text{ M}$) although with a considerable background of colloidal character was found to have a distinct shoulder also at 250 nm.

EXPERIMENTAL

Reagents and solutions. The reagents were of analytical grade. The triethanolamine used by Agarwala was Merck *pro analysi* with less than 1% diethanolamine. The triethanolamine used by Mrs. Refn was purified as described previously.⁸ The various solutions were prepared in volumetric flasks by weighing or pipetting from stock solutions.

Spectrophotometric measurements (UV and Vis) were performed with a Cary 118 spectrophotometer at room temperature. Cells of pathlength 0.1 to 2 cm were used, the reference cells being filled with a corresponding copper-free solution.

$\text{pH} = -\log[\text{H}^+]$ was determined by glass electrode measurements at 25 °C as described previously.^{8,11}

The present study was begun by J.B. in 1947¹ with S.R. who performed all the glass electrode measurements in the 0.5 M (teaH,K)-nitrate medium. The pH-measurements in the 2 M teaHClO₄ medium and all the spectrophotometric measurements were made by B.V.A. in 1978.

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