Metal Ammine Formation in Solution. XXIV. The Copper(II)– and Some Other Metal(II)–Mono- and Diethanolamine Systems

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This paper reports a potentiometric and spectrophotometric study of the copper(II)–mono- and diethanolamine systems. Stability constants in these systems and in the zinc(II), cadmium(II) and cobalt(II) systems were determined in 0.5 and 2 M amHClO$_4$ at 25 °C (see Table 3). The amine complex formation was disturbed by hydrolysis in the copper(II) systems, but only to a negligible extent in 2 M amHClO$_4$. The consecutive stability constants in this medium for the copper(II)–monoethanolamine system were found to be: $K_1=10^{4.90}$, $K_2=10^{3.95}$, $K_3=10^{2.85}$, $K_4=10^{1.03}$, and for the copper(II)–diethanolamine system: $K_1=10^{4.74}$, $K_2=10^{3.90}$, $K_3=10^{1.66}$. It was also possible to calculate the acidity constants for the copper(II) complexes from data on media with varying ethanolammonium concentrations in 0.5 M (amH,Na)ClO$_4$. For the acidity constants of the first three Cu(II)–monoethanolamine complexes the values: $K_{1,a}=10^{-6.2}$, $K_{2,a}=10^{-6.8}$ and $K_{3,a}=10^{-7.5}$ were estimated and similar values were obtained for the first two Cu(II)–diethanolamine complexes: $K_{1,a}=10^{-6.2}$, $K_{2,a}=10^{-6.8}$. Polymerization reactions play only a minor role in these systems. It was shown by spectrophotometric measurements that Cu(mea)$_4^{2+}$ is transformed into a penta-amine complex at very high monoethanolamine concentrations. For the diethanolamine complexes it was shown that Cu(dea)$_3^{2+}$ is the dominating complex for [dea]$\gtrsim$1 M and up to the highest attainable amine concentrations.

Copper(II) and other metal(II) complexes of mono-, di- and triethanolamine (in the following

abbreviated to mea, dea and tea) have been known since 1932[1] and have been studied in solid state by IR spectroscopic methods.[2-4] The composition and stability of the complexes in solution has been investigated by polarographic,[5-8] potentiometric and spectrophotometric methods.[9-22] These studies have shown that simple monodentate metalamine complex formation is dominant in aqueous ethanolammonium solutions but for copper(II) the solutions are subject to hydrolysis at pH-values higher than 5. The formation of the hydroxo complexes is accompanied to greater or lesser extent by polymerization.[20,21] The tendency of the alcohol groups of the ethanolamines to release protons followed by chelating coordination of the ethoxide groups, is not very pronounced in aqueous solutions.[19]

Comprehensive studies of the copper(II)– and nickel(II)–triethanolamine systems have been made previously,[20,21] and the present paper reports similar studies on copper(II) and some other metal(II)–mono and diethanolamine systems.

EXPERIMENTAL

Reagents and solutions. The metal(II) perchlorate reagents used were all of analytical grade. Monoethanolamine (Fluca, *puriss*) was distilled under atmospheric pressure and the main fraction boiling at 165 °C was used without further purification. Diethanolamine (Fluca, *puriss*) was distilled at ~10 mmHg and the main fraction boiling at 160−163 °C was used without further purification. The various solutions were prepared in volumetric flasks by weighing or pipetting from analyzed stock solutions. 2.50 M stock solutions

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Table 1. Selected results of glass electrode measurements on copper(II)-, cobalt(II)-, zinc(II)- and cadmium(II)-monoethanolamine solutions at 25 °C.
pK_{meaH^+}=9.54±0.01 in 0.5 M (meaH, Na)ClO$_4$, and 9.80±0.01 in 2 M meaHClO$_4$.

No.	C_{meaH^+}	C_{Cu}	C_{mea}	pH	p[mea]	$\bar{n}_{exp}$	$\bar{n}_{calc.(I)}$	$\bar{n}_{calc.(II)}$
1	2.00	0.04036	0.01546	4.322	5.178	0.384		
2	2.00	0.04036	0.0551	5.446	4.054	1.363		
3	2.00	0.004036	0.00561	5.381	4.119	1.373		
4	2.00	0.004036	0.01356	6.958	2.542	2.651		
5	2.00	0.02018	0.0573	7.049	2.451	2.666		
6	2.00	0.02018	0.0970	8.000	1.500	3.241		
7	0.500	0.02018	0.00767	4.950	4.890	0.380		
8	0.500	0.02018	0.0276	5.896	3.944	1.363	1.424	1.373
9	0.500	0.02018	0.0324	6.082	3.752	1.596	1.626	1.585
10	0.500	0.02018	0.0374	6.291	3.549	1.838	1.823	1.809
11	0.500	0.004036	0.00950	6.654	3.186	2.193	2.146	2.170
12	0.500	0.02018	0.0572	7.240	2.600	2.711	2.798	2.691
13	0.500	0.004036	0.01940	7.665	2.175	3.147	3.220	3.012
		C_{Co}						
14	2.00	0.0344	0.00794	6.441	3.059	0.205		
15	2.00	0.0344	0.01985	6.907	2.593	0.503		
16	2.00	0.0344	0.0397	7.319	2.181	0.963		
17	0.500	0.0344	0.00992	7.071	2.769	0.239		
18	0.500	0.0344	0.01985	7.399	2.441	0.472		
19	0.500	0.0344	0.0397	7.735	2.105	0.926		
		C_{Zn}						
20	2.00	0.01552	0.00397	6.173	3.327	0.226		
21	2.00	0.0621	0.0278	6.410	3.090	0.435		
22	2.00	0.01552	0.00794	6.517	2.983	0.445		
23	0.500	0.01550	0.00397	6.671	3.169	0.213		
24	0.500	0.01550	0.00595	6.843	2.997	0.319		
25	0.500	0.003104	0.00238	6.928	2.912	0.374		
		C_{Cd}						
26	2.00	0.00401	0.001985	6.356	3.144	0.316		
27	2.00	0.00401	0.00397	6.724	2.776	0.572		
28	2.00	0.02004	0.0397	7.408	2.092	1.577		
29	2.00	0.02004	0.0992	8.200	1.300	2.449		

of ethanolammonium perchlorate were prepared by neutralizing 1 l of 5.00 M HClO$_4$ with the amine and diluting to a volume of 2 l. Complete equivalence between amine and perchloric acid was ensured as described previously.[24]

Spectrophotometric measurements (UV and Vis) were made with a Cary 118 spectrophotometer at room temperature (22–23 °C). Cells of path-length 0.1 to 2 cm were used, the reference cells being filled with a corresponding metal(II)-free solution.

pH=−log[H$^+$] was determined by glass electrode measurements at 25 °C as described previously.[24]

Estimation of the stability constants. The exponent of the free amine concentration p[am] and ligand number

$$\bar{n}=(C_{am}-[am]+[H^+])/C_{Me}$$

were determined from pH-measurements at constant ethanolammonium ion concentrations in the usual manner.[25] The acidity constants of the ethanolammonium ions pK_{amH^+} were also determined. Part of the data is shown in Tables 1 and 2. All concentrations are in mol/l, and C_X represents the stoichiometric concentrations of the species X. The formation curves for 0.5 M (amH,Na)ClO$_4$ and 2 M amHClO$_4$ media are

Table 2. Selected results of glass electrode measurements on copper(II)-, cobalt(II)-, zinc(II)- and cadmium(II)-diethanolamine solutions at 25 °C.
$pK_{deaH^+}=8.93\pm0.01$ in 0.5 M (deaH,Na)ClO$_4$, and 9.33 ± 0.01 in 2 M deaHClO$_4$.

No.	C_{deaH^+}	C_{Cu}	C_{dea}	pH	p[dea]	$\bar{n}_{exp}$	$\bar{n}_{calc.(I)}$	$\bar{n}_{calc.(II)}$
1	2.00	0.02018	0.00593	3.886	5.144	0.325		
2	2.00	0.01998	0.01304	4.377	4.653	0.654		
3	2.00	0.004036	0.00416	4.706	4.324	1.023		
4	2.00	0.02018	0.0302	5.243	3.787	1.487		
5	2.00	0.004036	0.00630	5.289	3.741	1.519		
6	2.00	0.02015	0.04094	6.223	2.807	1.955		
7	2.00	0.02018	0.05165	6.887	2.143	2.203		
8	2.00	0.02018	0.0838	7.523	1.507	2.611		
9	0.500	0.02018	0.01866	5.294	3.936	0.922	0.913	0.905
10	0.500	0.02076	0.01866	5.266	3.964	0.896	0.881	0.874
11	0.500	0.02077	0.02804	5.640	3.590	1.338	1.305	1.295
12	0.500	0.02075	0.03210	5.803	3.427	1.528	1.482	1.472
13	0.500	0.02044	0.04038	6.245	2.985	1.923	1.931	1.903
14	0.100	0.004036	0.00275	5.672	4.268	0.669	0.691	0.650
15	0.100	0.004036	0.00328	5.880	4.060	0.925	0.969	0.936
16	0.100	0.004036	0.004895	6.062	3.878	1.179	1.233	1.187
17	0.100	0.02053	0.04060	6.656	3.284	1.953	1.940	1.916
		C_{Co}						
18	2.00	0.0344	0.00429	5.828	3.202	0.106		
19	2.00	0.0344	0.0129	6.364	2.666	0.312		
20	2.00	0.0344	0.0429	7.111	1.919	0.895		
21	0.500	0.0344	0.0150	6.686	2.344	0.304		
22	0.500	0.0344	0.0322	7.082	1.948	0.608		
		C_{Zn}						
23	2.00	0.0155	0.00429	5.875	3.155	0.232		
24	2.00	0.0155	0.00858	6.238	2.792	0.453		
25	0.500	0.0155	0.00858	6.728	2.502	0.350		
		C_{Cd}						
26	2.00	0.02004	0.01290	6.351	2.679	0.539		
27	2.00	0.02004	0.0429	7.138	1.892	1.501		
28	2.00	0.02004	0.0858	7.685	1.345	2.027		
29	0.500	0.02004	0.01290	6.833	2.397	0.444		
30	0.500	0.02004	0.0417	7.484	1.746	1.185		
31	0.500	0.02004	0.1250	8.177	1.053	1.821		

shown in Figs. 1 and 2. The formation curves for the nickel(II) systems taken from our previous paper[22] are also plotted. The data and figures show that the formation curves are unchanged for a 5−10-fold variation in the metal(II) concentration within the experimental uncertainty. The formation curves for 0.5 M (amH,Na)ClO$_4$ medium are also, with the exception of those for copper(II), unaltered by a change in the ethanolammonium ion concentration. From these results it follows that only mononuclear metal-amine complex formation takes place in the solutions.

Furthermore, the dependence of the ethanolammonium concentrations show that hydrolysis interferes with metal amine complex formation in the copper(II) solutions. The hydrolysis is negligible in 2 M amHClO$_4$ and the stability constants in this medium could therefore be calculated in the same way as for the other metal(II) ions. The estimated stability constants are given in Table 3, and the calculated full curves in Figs. 1 and 2 show how well these constants reproduce the experimental data. Stability constants for the metal(II) ethanolammine complexes mentioned
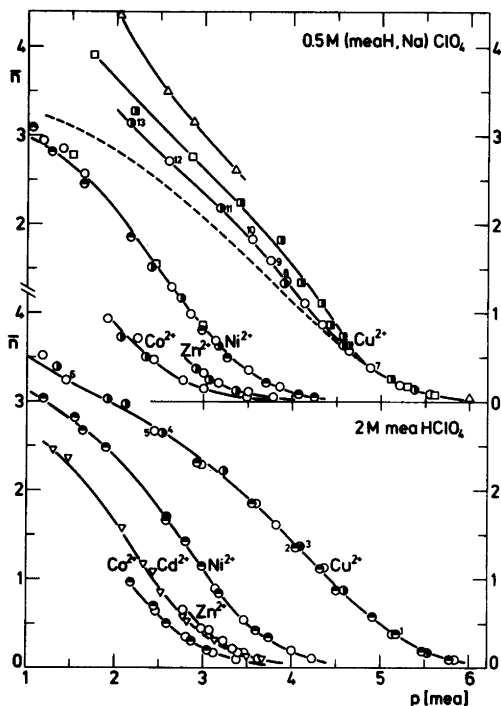
Fig. 1. Formation curves ($\bar{n}$ *versus* p[mea]) at 25 °C for copper(II)−and the other metal(II)−monoethanolamine complexes studied in this paper. For comparison purposes the formation curves for nickel(II) taken from a previous paper[22] are also shown. The different points in 0.50 M meaHClO$_4$ and 2.00 M meaHClO$_4$ at the particular metal concentration are as follows: ◉ ($C_{Me}\sim0.04$ M), ○ ($C_{Me}\sim0.02$ M), ◑ ($C_{Me}\sim0.004$ M) and for cadmium ▽ ($C_{Cd}\sim0.02$ M) to distinguish from the zinc points. The points in the 0.50 M (meaH,Na)ClO$_4$ solutions with $C_{meaH^+}=0.10$ M are denoted: □($C_{Me}\sim0.02$ M), ◪ ($C_{Me}\sim0.004$ M) and in the solutions with $C_{meaH^+}=0.02$ M; △ ($C_{Cu}\sim0.02$ M). The solid formation curves are calculated by means of the estimated stability constants. The points numbered 1−13 on the copper curves refer to the solutions described in Table 1. The dotted curve for copper(II) in 0.5 M meaHClO$_4$ is that estimated for the pure copper(II)-amine complex formation in this medium.

in Table 3 have also been estimated by other authors[5-8,12-18] and most of these values can be found in Tables of Stability Constants.[23] Some of the data in the literature are not very reliable.

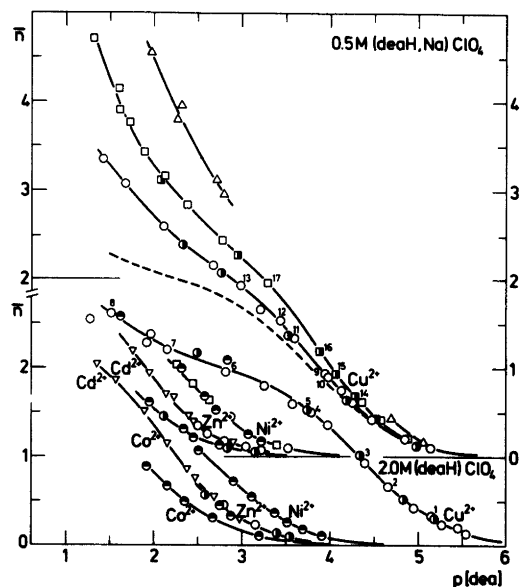Table 3 shows that pK_{amH^+} and log K_n increases when the salt concentration is changed

Fig. 2. Formation curves ($\bar{n}$ *versus* p[dea]) at 25 °C for copper(II)− and the other metal(II)−diethanolamine complexes studied in this work. For comparison purposes the formation curves for nickel(II) from a preceding paper[22] are also shown. The plotted points in the figure and all other symbols are the same as those in the legend for Fig. 1. The points numbered 1−17 on the copper curves refer to the solutions described in Table 2.

from 0.5 to 2 M. The influence of the salt concentration increases from the nickel(II) mea to the tea systems,[22] and is higher in the copper(II)- than in the other metal(II) systems. It seems to be a general rule[25] that the consecutive constants in a metal amine complex system change uniformly with the salt medium when hydrolysis is insignificant. It will be seen that the data in Table 3 are reasonably consistent with this rule. In the copper(II) mono- and diethanolamine systems the influence of hydrolysis can be neglected, not only in 2 M amHClO$_4$ but also for the first of the constants in 0.5 amHClO$_4$. The rule can therefore be used to estimate the subsequent constants in 0.5 M amHClO$_4$ (those in brackets). The copper(II) formation curve corrected for hydrolysis is plotted in Figs. 1 and 2.

The hydroxyl groups in the ethanolamines cause a considerable steric effect; the larger values of the ratios between successive stability constants than in the corresponding ammonia systems[22,25] show this directly. The ethanol-

Table 3. Stability constants for ethanolamine and diethanolamine complexes of copper(II) and some other metal(II) ions in 0.5 and 2 M ethanolammonium solutions at 25 °C.

Ethanolamine	Copper(II)				Nickel(II)	
	0.5^a	$2\ M^a$	0.5^b	$2\ M^c$	0.5^d	$2\ M^d$
pK_{meaH}	9.54	9.80	9.60		9.54	9.80
$\log K_1$	4.60	4.90	4.53	4.78	3.12	3.32
$\log K_2$	(3.65)	3.95	(3.75)	4.18	2.56	2.78
$\log K_3$	(2.55)	2.85	–	2.89	1.80	2.00
$\log K_4$	0.75	1.03	–	1.65	(0.32)	(0.40)

	Cobalt(II)		Zinc(II)		Cadmium(II)	
	0.5^a	$2\ M^a$	0.5^a	$2\ M^a$	0.5	$2\ M^a$
$\log K_1$	2.23	2.43	2.50	2.70	–	2.65
$\log K_2$	1.56	1.80	2.28	2.48	–	2.17
$\log K_3$	–	–	–	–	–	1.40

Diethanolamine	Copper(II)			Nickel(II)	
	0.5^a	$2\ M^a$	0.5^b	0.5^d	$2\ M^d$
pK_{deaH}	8.93	9.32	9.00	8.93	9.32
$\log K_1$	4.20	4.74	4.15	2.60	3.00
$\log K_2$	(3.35)	3.90	–	1.87	2.27
$\log K_3$	(1.11)	1.66	–	–	–

	Cobalt(II)		Zinc(II)		Cadmium(II)	
	0.5^a	$2\ M^a$	0.5^a	$2\ M^a$	0.5^a	$2\ M^a$
$\log K_1$	1.88	2.24	2.13	2.52	2.10	2.47
$\log K_2$	1.19	1.42	(1.40)	1.88	1.71	2.05
$\log K_3$	–	–	–	–	–	0.78

[a] Values determined in this paper for 0.5 M (amH,Na)ClO₄ and 2 M amHClO₄. The uncertainties are of the order ±0.03. [b] Values estimated by Bjerrum and Refn[9] for 0.5 M amHNO₃. [c] Values for 2 M meaHNO₃ estimated in our department in 1968 by Dr. Hans Peter Jensen. [d] Values determined by Bjerrum and Djurdjevic[22] for 0.5 M (amH,Na)ClO₄ and 2 M amHClO₄.

amines coordinate to the metal through the nitrogen atom[26] and it is possible that part of the steric effect is due to a weak chelate coordination of the hydroxyl groups in competition with the solvated water molecules.

Estimation of hydrolysis constants. Confining ourselves to study the hydrolysis reactions at relatively high ethanolammonium ion concentrations it is reasonable to assume that the species $Cuam(OH)^+$, $Cuam_2(OH)^+$ and $Cuam_3(OH)^+$ are the dominating hydrolysis products. Defining the corresponding hydrolysis constants as follows:

$$K_{1,a}=[Cuam(OH)^+][H^+]/[Cuam^{2+}]$$

$$K_{2,a}=[Cuam_2(OH)^+][H^+]/[Cuam_2^{2+}]$$

$$K_{3,a}=[Cuam_3(OH)^+][H^+]/[Cuam_3^{2+}]$$

one can write for the average formation function:

$$\bar{n}=\sum_0^n n[Cuam_n]+2[Cuam(OH)]+3[Cuam_2(OH)]$$
$$+4[Cuam_3(OH)]/\sum_0^n [Cuam_n]+[Cuam(OH)]+$$
$$[Cuam_2(OH)]+[Cuam_3(OH)]$$

This expression can be transformed to an equation of the form:

$$a_1K_{1,a}+a_2K_{2,a}+a_3K_{3,a}=b \tag{1}$$

where

$$a_1=\{(2-\bar{n})\beta_1[am]\}/[H^+] \tag{2}$$

$$a_2=\{(3-\bar{n})\beta_2[am]^2\}/[H^+] \tag{3}$$

$$a_3=\{(4-\bar{n})\beta_3[am]^3\}/[H^+] \tag{4}$$

$$b=\bar{n}\sum_0^n \beta_n[mea]^n-\sum_0^n n\beta_n[mea]^n \tag{5}$$

and

$$\beta_n=K_1K_2...K_n$$

This means that the problem of determining the hydrolysis constants is reduced to that of solving a set of linear equations with three unknowns. For the integer n a value of four has to be inserted in eqn. (5) for the monoethanolamine system and three for the diethanolamine system.

In other words the complexes $Cu(mea)_4^{2+}$ and $Cu(dea)_3^{2+}$ have been considered not to contribute to the hydrolysis. A small influence of the Cu(II)-aqua ion has also been neglected. The calculation of the hydrolysis constants in the 0.5 M (amH,Na)ClO$_4$ medium has been carried out with the estimated stability constants for this medium. The solutions 8−13 (see Table 1) and solutions 10−17 (Table 2) were used for this purpose. The points corresponding to these solutions in Figs. 1 and 2 are marked by figures. The sets of linear equations, eqn. (1), calculated from these data have been solved by the least squares method using a simple computer program. Sets I in Table 4 show the results of this calculation. In another calculation of the hydrolysis constants using a larger computer program the sum of the squares of the differences $\Sigma(\bar{n}_{calc}-\bar{n}_{obs})^2$ was minimized using Gauss-Newton algorithm.[27] For this calculation all data for the 0.5 M amHClO$_4$ media with values of $\bar{n}$ between 0.8 and 3.2 were used, as well as data for $[meaH^+]=0.1$ M in 0.5 M (meaH,Na)ClO$_4$. Sets II in Table 4 show the results of the calculation. Hydrolysis was so pronounced for $[amH^+]=0.02$ M that the data could not be used in the calculations. The values of $\bar{n}$ which can be calculated using the two sets of hydrolysis constants are compared in the last columns of Tables 1 and 2 with the experimental values. Both sets of constants approach the experimental data about equally well. When solving eqns. (1) it was assumed in the computer program that the uncertainty in b was 10 %. Recalculation with the constants obtained shows that the uncertainty is higher, being on average about 17 %. The uncertainty in the pK-values can be assumed to be of the order $\pm 0.05-0.10$.

In the mono- and diethanolamine systems polymerization of the hydrolysis products was found to be negligible in the range of copper
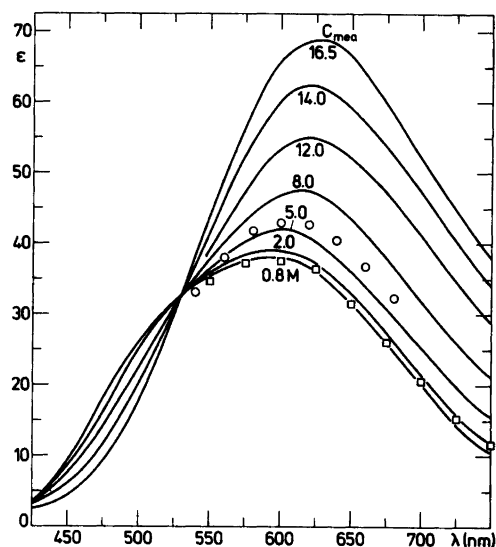
concentrations employed. This is different from the behaviour in the triethanolamine system (cf. Table 4). In the latter system there is steric hindrance to the uptake of more than one amine ligand, but it is noteworthy that the values of $pK_{1,a}$ for the mono-, di- and triethanolamines are approximately the same. $pK_{2,a}$ for $Cu(mea)_2^{2+}$ and $Cu(dea)_2^{2+}$ are also similar. Table 4 also shows that the acidity of the complexes decreases with the number of coordinated amine molecules: $pK_{1,a}<pK_{2,a}<pK_{3,a}$. There is evidence that the copper(II) aqua-ammine ions are weaker acids than the copper(II) aqua ion.[25,28] The first hydrolysis product of these ions are more or less dimerized.[28] The aqua ion itself has $pK_a\sim 8$ and log $K_{ass}\sim 5.1$.[29,30] The fact that the copper(II) ethanolamine ions are more acidic than the copper(II) ammonia ions can be explained by a strong steric influence of the hydroxyl groups of the amino alcohols on the coordinated water molecules.

Spectrophotometric results. Fig. 3 shows

Table 4. Calculated acidity constants of the copper(II)-ethanolamine complexes in 0.5 M (amH,Na)ClO$_4$.

| | Mea[a] | | Dea[a] | | Tea[b] |
	I	II	I	II	Bjerrum et al.[20]
$pK_{1,a}$	6.09	6.40	6.29	6.35	6.41±0.05
$pK_{2,a}$	6.87	6.72	6.75	6.81	
$pK_{3,a}$	7.39	7.77			

[a] the uncertainties in the pK-values are estimated to be of the order ±0.05–0.10. [b] The first hydrolysis product Cu(tea)(OH)$^+$ is dimerized, with log K_{ass}=3.15±0.15.

Fig. 3. Spectra (ε,λ) of aqueous copper(II)-monoethanolamine perchlorate solutions with $C_{Cu}\sim 0.01$ M and C_{mea} varying from 0.8 M up to pure mea (99 %). The nearly constant absorption in the range with C_{mea} between 0.8 and 2 M approaches the spectrum of $Cu(mea)_4^{2+}$. The curves with increasing C_{mea} up to 16.5 M show the formation of $Cu(mea)_5^{2+}$. The □-points indicate the spectrum of a strongly alkaline solution with C_{NaOH}=2.0 M, and C_{mea}=2.0 M. The ○-points show similarly the spectrum of a solution with C_{mea}=8.0 M and C_{NaOH}=2.0 M.

absorption (ε,λ) curves in the visible region for Cu(II)–monoethanolamine solutions with C_{mea} varying from 0.8 M up to the pure amine. The spectrum is nearly unchanged for ethanolamine concentrations between 0.8 and 2 M. In this concentration range formation of the tetra-kis(ethanolamine) species is nearly complete. This follows from the value for the fourth consecutive stability constant log $K_4 \sim 0.7$ and the formation curves given in Fig. 1. The solutions used for the spectrophotometric measurements were prepared without ethanolammonium salt, but this has only a slight influence on the spectra when [mea]$>\sim$1 M. Between 2 M and up to the pure ethanolamine the spectra are shifted to-wards the red with an isosbestic point at 530 nm. In the concentration range where the curves pass through the isosbestic point there exists an equilibrium between a tetrakis and a penta-kis(ethanolamine) ion as in other copper(II)–amine systems.[28,31] The extent to which the wavelengths at the absorption maxima, assumed to be those of the tetra- and penta-amine ions, agree with those of the analogous copper(II)-ammonia complexes is shown in Table 5. Com-plexes with aliphatic amines have usually a higher intensity of the ligand field band than those of the corresponding ammonia complexes. It is there-fore remarkable that ε_{max} of Cu(mea)$_4^{2+}$ is lower than that of Cu(NH$_3$)$_4^{2+}$ (see Table 5). The tetrammine copper(II)-ion contains at least one strongly coordinated water molecule.[28,34,35] This water molecule is perpendicular to the plane in the square pyramidal configuration and is re-sponsible for the relatively high intensity of the absorption band.[37,38] It is therefore reasonable to assume that steric strain due to the hydroxyl groups in Cu(mea)$_4^{2+}$ weakens the bonding of the water molecule (as well as of the fifth amine
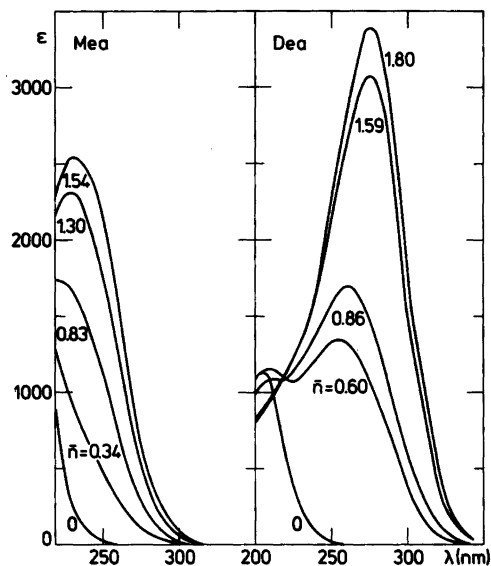

Fig. 4. The UV (ε,λ) spectra of some Cu(II)-mono- and diethanolamine solutions in 2 M amHClO$_4$. The figures on the curves indicate the values of the ligand number $\bar{n}$ of the solutions examined.

ligand in Cu(mea)$_5^{2+}$), which explains the weak intensity of the absorption bands of these com-plexes.

The influence of hydroxide ions on the tetra- and penta-amine equilibrium are shown in Fig. 3. As in the ammonia[28] and methylamine[31] systems the penta-amine complex shows some tendency to exchange the fifth amine ligand with a hydrox-ide ion with formation of Cuam$_4$(OH)$^+$. In the systems studied until now[28,31] the hydroxotetra-amine ions have a somewhat weaker absorption band which is slightly more shifted towards the red than the corresponding tetrammine ion. However, in our case the results in Fig. 3 are not sufficient to a quantitative treatment.

The UV (ε,λ) absorption spectra of some Cu(II)-mea and Cu(II)-dea solutions with 2 M amHClO$_4$ are shown in Fig. 4. The ligand number varies from 0 to 1.54 in the mea solutions and from 0 to 1.80 in the dea solutions. Since they are electron transfer spectra they have ε_{max}-values of several thousand. As in the analogous Cu(II)-tea system,[20] the absorption band in-creases in intensity and is shifted towards the visible with increasing ligand number. The UV absorption is practically negligible at wavelengths above $\sim$320 nm in the mea system and $\sim$360 nm in the dea system. It was therefore possible with
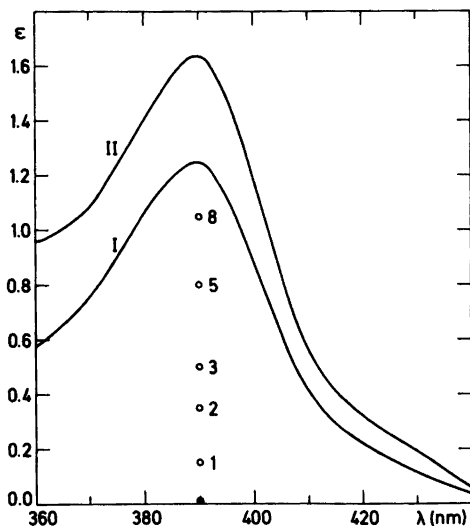
Table 5. Comparison of absorption maxima for copper(II)-amine complexes.

Complex	λ(nm)	ε_{max}	
CuNH$_3^{2+}$	745	22	Ref. 33
Cudea^{2+}	750	30	estim.
Cutea^{2+}	755	32	Ref. 20
Cu(NH$_3$)$_2^{2+}$	635	41	Refs. 32, 33
Cu(dea)$_2^{2+}$	625	52	[dea]$>$1M
Cu(NH$_3$)$_4^{2+}$	590	53	Refs. 32, 33
Cu(CH$_3$NH$_2$)$_4^{2+}$	580	85	Ref. 31
Cu(mea)$_4^{2+}$	589	39	[mea]=2 M
Cu(NH$_3$)$_5^{2+}$	640	83	Refs. 32, 33
Cu(CH$_3$NH$_2$)$_5^{2+}$	640	124	Ref. 31
Cu(mea$_5$)$^{2+}$	630	61	99 % mea

Fig. 5. Formation of a small absorption band at 390 nm in two solutions of the following composition:

deaHClO₄	C_{Cu}	C_{dea}	p[dea]	$\bar{n}$
I 2.00	0.02018	0.00379	5.441	0.200
II 2.00	0.02018	0.00593	5.144	0.325

Curve I and II show the final spectra of the solutions after more than 10 d. The absorption of solution I was followed with time after its preparation.

Time in d	0	1	2	3	5	8
ε_{max} at 490 nm	0.01	0.16	0.35	0.50	0.80	1.05

These data are plotted in the figure.

the Cu(II)–dea system to detect a very weak absorption band at 390 nm. The band is not seen with freshly prepared solutions, but develops during the following days (*cf.* Fig. 5). Similar weak bands in Cu(II)-ammonia solutions at 317 nm[28] and in Cu(II)-methylamine solutions at 328 nm[31] have shown to be caused by the formation of small amounts of di-μ-hydroxo complexes. However, the position of the band at 390 nm and especially the slowness of its formation suggest that other explanations must also be considered. The formation of the band is not accompanied by any change in pH and has therefore no disturbing influence on the calculations we have made for these solutions.

The (ε,λ) spectra of aqueous copper(II)-dea solutions at high amine concentrations are shown in Fig. 6. The only very slight changes in the

spectra show that the same complex dominates in the entire range of concentrations from [dea]~1 M and up to the pure amine. The value of the third consecutive stability constant (log K_3~1.11) as well as the formation curves in Fig. 2 show that this complex is the tris(diethanolamine) complex. The observation of the absorption maxima at ~625 nm $(Cu(NH_3)_3^{2+}$ shows λ_{max}~635 nm) supports this assumption (*cf.* Table 5). The values of λ_{max} for the three mono-amine complexes $Cu(NH_3)^{2+}$, $Cudea^{2+}$ and $Cutea^{2+}$ at ~750 nm, are also shown in Table 5 and provide further evidence that λ_{max} is determined mainly by the number of copper-nitrogen bonds in the complex.

As a result of our studies on the copper(II)-ethanolamines it can be concluded that the steric influence of the hydroxyl group in the monoethanolamine is not greater than it is possible for the Cu(II) ion to coordinate the amino groups of four ligands with a considerable strength and even to form a penta-amine complex at very high ethanolamine concentrations. On the other hand, in the copper(II)-diethanolamine system the steric effect of the hydroxyl groups is so great that the Cu(II) ion is unable to coordinate the amino groups of more than three ligands. Finally, in the copper(II) triethanolamine system the steric influence of the ligand is so great that the mono complex shows greater tendency towards uptake of hydroxide ions and deprotonation of the ligand, followed by chelation, than towards binding a second triethanolamine molecule.

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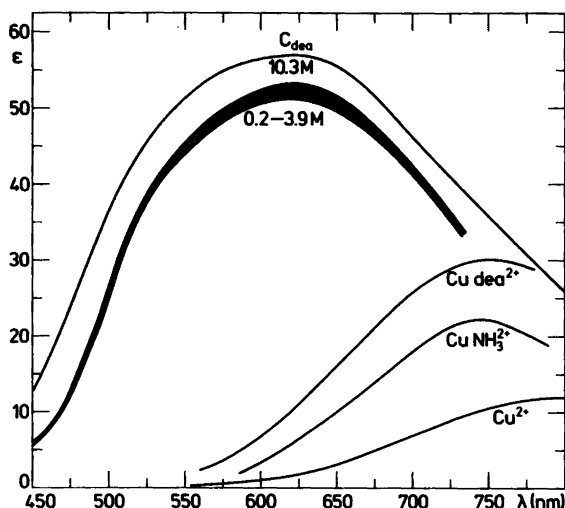5. Flannery, R. J., Ke, B., Grieb, M. W. and Trivich, J. *J. Am. Chem. Soc.* 77 (1955) 2996.

Fig. 6. Spectra (ε,λ) of aqueous copper(II)-diethanolamine solutions at high amine concentrations. Four curves with $C_{Cu}\sim0.01$ M and [dea]=0.19, 0.46, 1.44, and 3.85 M are situated close to each other within the hatched area in the figure. In these solutions the dominating complex is $Cu(dea)_3^{2+}$ and further increase of the amine concentration up to 10.3 M (99 % amine) causes only a slight change in the spectra. In the lower part of Fig. 6 the monoamine spectrum of $Cu(dea)^{2+}$ in 2 M deaHClO$_4$ is compared with those of $Cu(NH_3)^{2+}$ in 2 M NH$_4$NO$_3$[33] and of $Cu(tea)^{2+}$ in 2 M teaHClO$_4$.[20]

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