

SPECTROPHOTOMETRIC AND POTENTIOMETRIC INVESTIGATIONS OF COPPER (II)-ETHANOLAMINE COMPLEXES

PART III. DIETHANOLAMINE

(Gaussian Analysis of Electronic Spectra in Mono and Diethanolamine Systems)

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Received December 12, 1970

(Communicated by Prof. M. R. A. Rao, F.A.Sc.)

ABSTRACT

Spectrophotometric and potentiometric investigations have been carried out on copper-diethanolamine system. Job plots at 900, 900 and 580 $m\mu$ have indicated the formation of CuD^{++} , CuD_2^{++} and CuD_3^{++} . The \bar{n} - pA curves obtained indicate the formation of CuD^{++} , CuD_2^{++} , CuD_3^{++} , $CuDOH^+$, CuD_2OH^+ and CuD_3OH^+ . The \bar{n} - pA curves have been analyzed to obtain the stability constants of these complexes. Absorption curves of pure complexes have been computed by a graphical method. Gaussian analysis of the absorption curves of pure and hydroxy complexes show the presence of a second band, indicating that the structure is that of a distorted octahedron.

INTRODUCTION

SUBRAHMANYA¹ and Fisher and Hall^{2,3} have studied the copper-diethanolamine system polarographically and obtained evidence for the formation of hydroxy complexes. In the present work this system is studied by spectrophotometric and potentiometric methods to determine the equilibria involved in the formation of hydroxy complexes. The absorption spectra of the complexes in copper-ethanolamine systems (mono- and di-) have been subjected to Gaussian analysis to understand the nature of electron transitions. Although the polarograms indicated qualitatively the formation of hydroxy complexes, yet quantitative interpretation was not possible due to the complicated nature of the polarographic waves.

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EXPERIMENTAL

Experimental procedure for this work has already been described in a previous paper.⁴ Suitable correction has been applied for the free acid in cupric salt solutions employing the method of Brosett.⁵ The notations are the same as in Part I of this series. In the present paper 'D' is used for diethanolamine. The temperature of potentiometric measurements has been $30^\circ \pm 0.1^\circ \text{C}$ and spectrophotometric measurements $30^\circ \pm 2^\circ \text{C}$.

RESULTS

(1) *Characteristics of $\bar{n} - pA$ and $E_m - pA$ curves under Bjerrum conditions.*—The $\bar{n} - pA$ curves at various concentrations of diethanolammonium ion (DEA ion) are given in Fig. 1. The values of \bar{n} calculated both by the potentiometric method and the method of corresponding solutions agree as in copper-monoethanolamine system. Due to the presence of high (and constant) concentration of DEA ion, the formula $pA = -\log A_t + pH_0 - pH_{\text{comp}}$ can be used for calculating pA even when the pH value approaches pK and also in presence of hydroxy complexes.⁶

Figure 1 indicates that curves 1 to 4 practically intersect at A. Curves 4 and 5 obtained with 0.1 M DEA ion and 0.1 M DEA ion + 0.9 M KNO_3 do not coincide indicating slight ionic strength dependence of the stability constant. The slight non-coincidence of the curves below A is due to ionic strength effect. The non-coincidence above point A is obviously due to the formation of hydroxy complexes as in copper-monoethanolamine system.^{4,6}

Another interesting feature that has been noticed is that the $\bar{n} - pA$ curves at all metal concentrations studied in each set of experiments containing the same amount of DEA ion coincide, till the value of \bar{n} reaches 2.6. Beyond this value, the $\bar{n} - pA$ curves obtained with higher metal concentrations are slightly lower (32, 16, 8 and 8 mm cupric ion solutions in 1.0, 0.5, 0.2 and 0.1 M DEA ion solutions respectively; marked by broken lines in Fig. 1).

(2) *Vosburgh and Copper's method⁷ for the determination of complexes in copper-diethanolamine system.*—Absorption curves with the metal/ligand ratio of 1, 1/2 and 1/3 indicated that at $900 m\mu$ $E_1 \simeq E_2E_3 = E_3$ ($E_1 = 18.5$, $E_2 = 21.3$, $E_3 = 21.1$) and at $580 m\mu$, $E_0 = 0$, $E_3 > E_2$. These data have been used to choose the wavelengths for the Job plots.⁴ It is assumed that the formation of hydroxy complexes could be neglected in the region where the peaks for 1:1, 1:2 and 1:3 complexes occur.

Total absorbance $Y = E_0 [M] + E_1 [MA] + E_2 [MA_2] + E_3 [MA_3]$.
Expressing $[M]$ in terms of M_t , MA , MA_2 and MA_3 , rearranging and taking derivatives with respect to A_t , one gets

$$\begin{aligned} \frac{d}{dA_t} (Y - E_0 M_t) \\ = \frac{dY_1}{dA_t} = (E_1 - E_0) \frac{d}{dA_t} [MA] + (E_2 - E_0) \\ \left\{ \frac{d}{dA_t} [MA_2] + \frac{d}{dA_t} [MA_3] \right\}. \end{aligned}$$

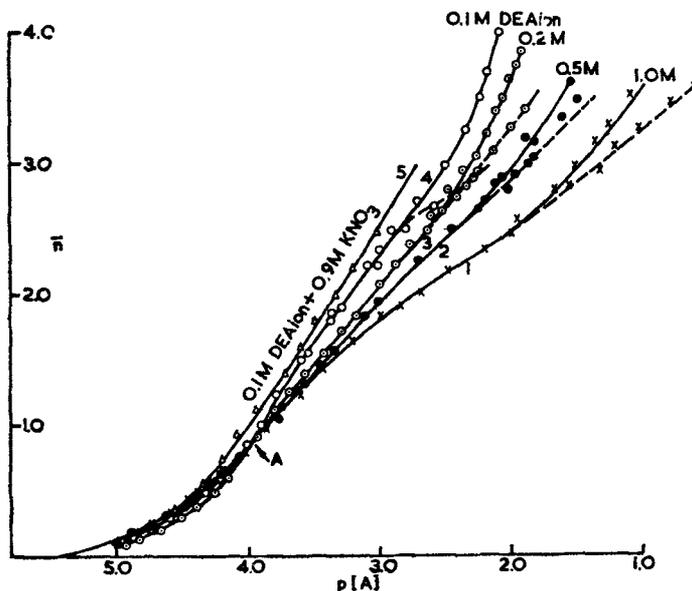


FIG. 1. Cu (II) - DEA System. η - pA Curves

Since at $900 \text{ m}\mu$, $E_1 \simeq E_2 = E_3$, the concentration of MA_2 and MA_3 is very small in the region where 1 : 1 peak appears, and the stability of MA is greater than MA_2 and MA_3 , the plot of Y_1 vs. $A_t/(A_t + M_t)$ should show a peak at 1 : 1 and this is found to be the case.

Expressing $[MA]$ in terms of M_t , $[M]$, $[MA_2]$ and $[MA_3]$ and noting that on either side where the Job peak is expected to appear, $[M]$ is very small the following equation can be written.

$$Y_2 = Y - E_1 M_t = (E_2 - E_1) \{ [MA_2] + [MA_3] \}$$

Since $E_2 = E_3$ at 90μ .

$$\frac{dY_2}{dA_t} = (E_2 - E_1) \left\{ \frac{d}{dA_t} [MA_2] + \frac{d}{dA_t} [MA_3] \right\}.$$

If the stability of MA_2 is greater than MA_3 a peak should appear at metal to ligand ratio 1 : 2 in the Job plot

Y_2 vs. $A_t/(A_t + M_t)$.

At 580μ , $E_0 = 0$, $E_3 > E_2$ and $[MA]$ is quite low in the region where 1 : 3 is expected to appear. Expressing $[MA_2]$ in terms of M_t and $[MA_3]$, the following equations can be written

$$Y_3 = Y - E_2 M_t = (E_3 - E_2) [MA_3]$$

$$\frac{dY_3}{dA_t} = (E_3 - E_2) \frac{d}{dA_t} [MA_3].$$

The plot of Y_3 vs. $A_t/(A_t + M_t)$ should give a peak at metal to ligand ratio 1 : 3 and this is found to be the case.

The Job plots are not fully symmetrical due to the approximations regarding the absorbance in the wavelength chosen for the Job plot and also due to the formation of the hydroxy complex (at higher pH values).

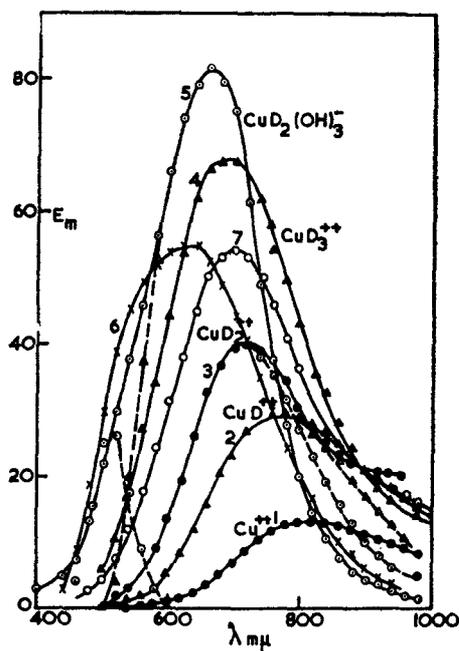


FIG. 2. Spectra of Copper (II)--DEA Complex (with Gaussian analysis).

(3) *Absorption spectra of CuD^{++} , CuD_2^{++} and CuD_3^{++} in 1MDEA ion solutions.*—Absorption spectra (between 500 and 900 $m\mu$ at intervals of 20 $m\mu$) of fifty solutions at different \bar{n} values (0 to 2.7) indicated that the E_m vs. λ curves at different metal concentrations coincide indicating the presence of only mononuclear complexes. A few typical values concerning copper-di and monoethanolamine are given in Table I. Such data have been used to compute the absorption spectra of pure complexes by the method already described.⁴ The absorption spectra of pure complexes obtained in the case of copper-diethanolamine system are given in Fig. 2. In the region $0.5 < \bar{n} < 1.2$, MA and MA_2 exist and in the region $1.6 < \bar{n} < 2.3$ MA, MA_2 and MA_3 exist. The following equations hold.

$$\frac{E_m - E_0 a_0}{a_2} = E_1 \frac{a_1}{a_2} + E_2$$

TABLE I

Typical data on the molar extinction coefficients of copper-ethanolamine complexes at various wavelengths

\bar{n}	E_m at various wavelengths in $m\mu$									
	500	560	620	680	740	800	860	920	940	960 ($m\mu$)
(a) Copper-diethanolamine system										
0	..	0.30	1.60	5.00	10.30	13.00	12.40	10.40	..	8.30
0.5	0.12	1.10	4.80	12.60	18.70	20.00	17.70	14.50	..	11.60
1.0	0.40	2.20	9.10	20.20	26.30	25.30	21.30	17.60	..	14.70
1.5	0.65	3.90	14.60	28.70	33.40	28.80	23.20	19.90	..	18.00
2.4	3.15	13.90	32.90	48.90	47.00	34.90	24.50	19.70	..	17.50
2.7	5.15	20.00	42.00	56.10	50.80	36.30	24.70	18.20	..	14.50
(b) Copper-monoethanolamine system										
0.5	0.51	1.50	5.12	11.80	17.12	18.00	15.45	..	11.25	..
1.0	1.05	3.25	10.33	19.00	23.30	22.00	18.00	..	11.90	..
1.4	1.62	5.50	16.05	25.80	23.25	24.62	19.30	..	12.20	..
2.0	3.02	12.00	27.12	36.50	33.62	26.00	18.85	..	11.65	..
2.6	5.62	22.00	42.35	45.25	36.25	24.80	16.10	..	9.50	..

and

$$\frac{E_m - E_1 a_1}{a_3} = E_2 \frac{a_2}{a_3} + E_3$$

The absorption spectra of pure complexes in the case of copper-monoethanolamine system⁴ are presented in Fig. 3.

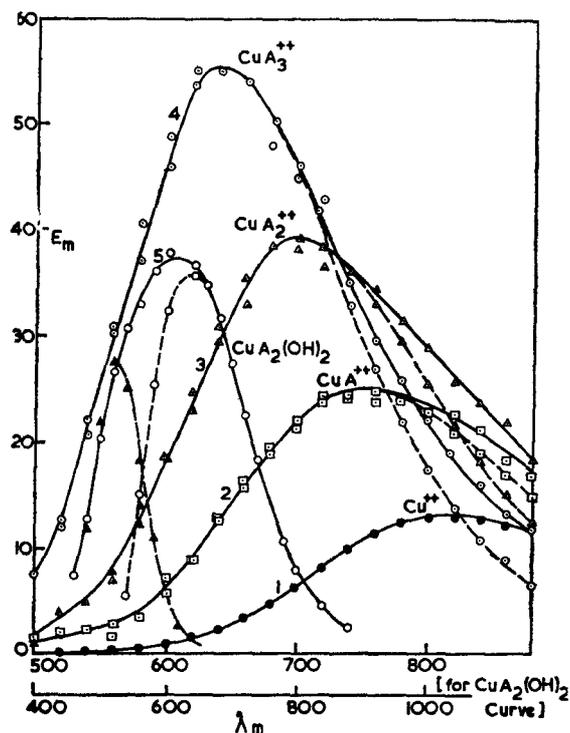


FIG. 3. Spectra of pure and Hydroxy Copper (II)-MEA Complexes. (With gaussian analysis)

DISCUSSION

(1) *Analysis of \bar{n} -pA curves: Stability constants of pure and hydroxy complexes in 0.1 to 1 M DEA ion solutions.*—The method of analysis is the same as already described.⁴ The details pertaining to the analysis are given in Table II.

In 1.0 M DEA ion solutions only pure complexes exist till \bar{n} attains a value of 2.3. The question is whether CuD_4^{++} or CuD_3OH^+ is present above $\bar{n} = 2.3$. If it is assumed that CuD_4^{++} is formed and not CuD_3OH^+ one gets a value of 10.67 for $\log \beta_{14}$. On the other hand, if it is assumed that only CuD_3OH^+ and not CuD_4^{++} is formed one gets a value of 15.5 for $\log \beta_{130\text{H}}$. It may, however, be pointed out, that this value is a bit too

TABLE II

Conc. of DEA ion	Range of \bar{n}	Species assumed (M stands for Cu^{++})	Plot used for analysis	$\log \beta$
0.1 M to 1.0 M	$0.3 < \bar{n} < 0.8$ (pH < 5.5)	MD^{++} and MD_2^{++}	$\frac{\bar{n}}{(1-\bar{n})} \frac{1}{[\text{A}]}$ vs. $\frac{(\bar{n}-2)}{(\bar{n}-1)} [\text{A}]$	$\log \beta_{1,1} = 3.99, 3.99, 4.11$ and 4.20 and $\log \beta_{1,2} = 7.72, 7.67, 7.71$ and 7.71 in $0.1, 0.2, 0.5$ and 1.0 M DEA ion solutions
1.0 M	$1.2 < \bar{n} < 2.2$ (pH < 5.5)	$\text{MD}^{++}, \text{MD}_2^{++}$ and MD_3^{++}	$\frac{\bar{n}}{(3-\bar{n})} \frac{1}{[\text{A}]^3} + \frac{1}{(3-\bar{n})} \frac{1}{[\text{A}]^2}$ vs. $\frac{1}{(\bar{n}-2)} + \frac{1}{(\bar{n}-3)} \frac{1}{[\text{A}]}$	$\log \beta_{1,2} = 7.72$ $\log \beta_{1,3} = 9.72$
0.1 M	$1.24 < \bar{n} < 1.68$	$\text{MD}^{++}, \text{MD}_2^{++}, \text{MD}_3^{++}$	Equation (2)	MDOH ⁺ not formed as the plot passes through origin
	$2.2 < \bar{n} < 2.8$	MD_2OH^+ and MD_3OH^+	Reference 6	$\log \beta_{1,2} \text{ OH} = 14.34$
	$2.20 < \bar{n} < 2.8$	$\text{MD}^{++}, \text{MD}_2^{++}, \text{MD}_3^{++}$	Equation (3)	$\log \beta_{1,2} \text{ OH} = 14.37$
0.2 M	$2.20-2.80$	$\text{MD}_2\text{OH}^+, \text{MD}_3\text{OH}^+$	Reference 6	$\log \beta_{1,3} \text{ OH} = 16.72$
	$2.20-2.80$	$\text{MD}^{++}, \text{MD}_2^{++}, \text{MD}_3^{++}$	Equation (3)	$\log \beta_{1,2} \text{ OH} = 14.19$
	$2.20-2.80$	$\text{MD}_2\text{OH}^+, \text{MD}_3\text{OH}^+$	Reference 6	$\log \beta_{1,3} \text{ OH} = 16.54$
0.5 M	$2.20-2.80$	$\text{MD}^{++}, \text{MD}_2^{++}, \text{MD}_3^{++}$	Equation (3)	$\log \beta_{1,2} \text{ OH} = 14.37$
	$2.20-2.80$	$\text{MD}_2\text{OH}^+, \text{MD}_3\text{OH}^+$	Reference 6	$\log \beta_{1,3} \text{ OH} = 16.16$

low for $\log \beta_{1,30H}$. Hence, it may be concluded that above $\bar{n} = 2.3$, in addition to other pure species both CuD_4^{++} and CuD_3OH^+ might be formed. It has already been pointed out⁶ that the present technique cannot be used if the solution contains a mixture of CuD_4^{++} and CuD_3OH^+ .

The stability constants of CuD^{++} , CuD_2^{++} , CuD_3^{++} , CuD_2OH^+ and CuD_3OH^+ have been used to calculate the values of \bar{n} , not covered in the above analysis and the results of such calculations indicate that the agreement between the calculated and the experimental values is quite good.

TABLE III
Characteristics of the first band

Complex	λ_{max} . (m μ)	Half-width $\times 10^3$	ν_0 cm ⁻¹	E_{mo}
Cu (MEA) ⁺⁺ ..	750	2.292	13,333	25.0
Cu (MEA) ₂ ⁺⁺ ..	700	2.271	14,285	39.25
Cu (MEA) ₃ ⁺⁺ ..	640	2.425	15,625	55.5
Cu (DEA) ⁺⁺ ..	764	2.201	13,089	29.4
Cu (DEA) ₂ ⁺⁺ ..	713	2.052	14,025	39.6
Cu (MEA) ₂ (OH) ₂ ..	524	1.577	19,084	27.5
Cu (DEA) ₂ (OH) ₃ ⁻ ..	512	1.302	19,531	27.0

(2) *Electronic transition of the absorption bands in the spectra of pure and hydroxy complexes in copper-mono- and diethanolamine systems.*—Absorption spectra taken (i) at pH 10.98 containing 2.0 M diethanolamine and 1.0 M potassium nitrate solution and 4 mM cupric ion and (ii) with a mixture of 4 mM cupric ion, 8 mM DEA ion and 0.2 M sodium hydroxide are, however, entirely different (Fig. 2, curves 6 and 5 respectively). Hence the composition of the complex under condition (ii) is not the same as under condition (i). Under condition (i) the composition has been established as $CuD_2(OH)_2$ by Srinivasan and Subrahmanya⁸ by polarographic-redox potential method. The composition of the complex in (ii) cannot be expected to be $CuD(OH)_2$ since a mixture of 4 mM cupric ion, 4 mM DEA ion and 0.2 M sodium hydroxide precipitates. Hence it is reasonable to expect the composition to be $CuD_2(OH)_3^-$. It has not been possible to obtain the spectrum of pure CuD_3OH^+ or CuD_2OH^+ . The spectra obtained at *pA* 2.3 and different pH values can be regarded as due to a mixture of pure and the above monohydroxy complexes. The spectra obtained at *pA* 2.3 and various pH values are qualitatively similar

and a typical curve is included in Fig. 2 (curve 7, taken in presence of 0.5 M DEA ion, pH being 6.87).

Gaussian analysis⁹ of pure and hydroxy complexes of copper-mono and diethanolamine systems have been carried out using the following Gaussian formula:

$$E_m = E_{m0} 2^{-(\nu-\nu_0/\delta)^2}$$

where,

E_m = molecular extinction coefficient corresponding to frequency ν .

E_{m0} = molecular extinction coefficient corresponding to the maximum

δ = half-width.

A few typical Gaussian analysed curves of pure and hydroxy complexes are given in Figs. 2 and 3 and the parameters describing the first band in all cases are given in Table III. The presence of a second band is apparent in all cases though it is very weak. If the complexes had only regular octahedral configuration one would have expected only one absorption band corresponding to the transition $E_g \rightarrow T_{2g}$.¹⁰ The presence of the second band is a sufficient proof to indicate the distorted octahedral configuration of the complexes. Since we cannot expect CuD_3^{++} to behave differently it is likely that the second transition is far too weak.

ACKNOWLEDGEMENT

The authors wish to thank Professor M. R. A. Rao for helpful discussions.

REFERENCES

1. Subrahmanya, R. S. .. *Proc. Ind. Acad. Sci.*, 1957, **46 A**, 377.
2. Fisher, J. F. and Hall, J. L. .. *Anal. Chem.*, 1962, **34**, 1094.
3. ——— and ——— .. *Ibid.*, 1967, **39**, 1950,
4. Mahapatra, S. and Subrahmanya, R. S. .. *Proc. Ind. Acad. Sci.*, 1963, **58 A**, 161.
5. Brosset, C. .. *Acta Chem. Scand.*, 1952, **6**, 810.
6. Mahapatra, S. and Subrahmanya, R. S. .. *Proc. Ind. Acad. Sci.*, 1964, **59 A**, 299.
7. Vosburgh, W. C. and Cooper, G. R. .. *J. Am. Chem. Soc.*, 1941, **63**, 437.
8. Srinivasan, K. and Subrahmanya, R. S. .. *J. Electroanaly. Chem.* (in press).
9. Jorgensen, C. K. .. *Acta Chem. Scand.*, 1954, **8**, 1495.
10. Bjerrum, J., Ballhausen, C. J. and Jorgensen, C. K. .. *Ibid.*, 1954, **8**, 1275; C. J. Ballhausen, *Mat. Fys. Medd. Dan. Vid. Selskab.*, 1954, **29**, 4.