

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

Part II. Monoethanolamine (Analysis of Mixed Hydroxy Complexes with Polarographic Evidence)

BY S. MAHAPATRA AND R. S. SUBRAHMANYA

(Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-12, South India)

Received January 14, 1964

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

INTRODUCTION

In a previous communication¹ it was pointed out that the \bar{n} -pA curves for copper (II)-monoethanolamine system indicated the formation of hydroxy complexes. The analysis of \bar{n} -pA curves for hydroxy complexes are presented in this paper. Additional evidence for the formation of hydroxy complexes both by the spectrophotometric and polarographic measurements has also been indicated.

EXPERIMENTAL AND RESULTS

The \bar{n} -pA curves¹ for the copper (II) in 0.1, 0.2, 0.5 and 1.0 M MEA ion solutions have been employed to get the corresponding values of \bar{n} and pA given in Table I.

In Fig. 1, the absorption curves obtained at three typical pA values are given. For purposes of comparison the absorption curves for CuA_3OH^+ (A = monoethanolamine) and for a mixture of 4 mM cupric copper, 8 mM MEA ion and 0.2 M sodium hydroxide are given. It is assumed that the spectra obtained with the latter solution corresponds to $\text{CuA}_2(\text{OH})_2^2$. It is obvious that the absorption curves obtained at pA 4.80, coincide both in 0.1 and 1.0 M MEA ion solutions while those obtained at pA 1.81 and 2.78 deviate. The curves, obtained in 0.1 M MEA ion solutions are nearer to the curves corresponding to the pure hydroxy complexes indicating the presence of a larger proportion of the hydroxy complex.

TABLE I

* Values of \bar{n} at various values of pA and pH in the presence of different concentrations of MEA ion

\bar{n}	pA and pH at different concentrations of MEA ion							
	1.0 M		0.5 M		0.2 M		0.1 M	
	pA	pH	pA	pH	pA	pH	pA	pH
0.2	5.10	4.30	5.10	4.68	5.10	5.12	5.10	5.43
0.4	4.80	4.68	4.80	5.04	4.80	5.44	4.80	5.75
0.6	4.54	4.91	4.54	5.29	4.54	5.70	4.54	5.97
0.8	4.34	5.12	4.34	5.50	4.34	5.88	4.39	6.14
1.0	4.16	5.31	4.16	5.68	4.16	6.04	4.26	6.28
1.2	4.00	5.49	4.00	5.83	4.03	6.19	4.12	6.42
1.4	3.82	5.68	3.82	6.00	3.89	6.33	3.99	6.54
1.6	3.63	5.84	3.66	6.16	3.74	6.46	3.85	6.68
1.8	3.44	6.03	3.50	6.32	3.60	6.59	3.72	6.81
2.0	3.24	6.23	3.36	6.51	3.45	6.73	3.60	6.93
2.2	3.02	6.43	3.15	6.68	3.31	6.86	3.46	7.05
2.4	2.78	6.65	2.96	6.86	3.16	7.01	3.31	7.19
2.6	2.53	6.90	2.75	7.06	2.99	7.19	3.15	7.34
2.8	2.28	7.16	2.51	7.28	2.78	7.38	2.97	7.53
3.0	1.99	7.44	2.25	7.54	2.55	7.65	2.74	7.76

* The values of \bar{n} are given in intervals of 0.2 units read out from the enlarged \bar{n} -pA and \bar{n} -pH curves. The values of pK_w used to calculate the hydroxyl ion concentration determined potentiometrically are 13.67, 13.64, 13.62 and 13.64 in 0.1, 0.2, 0.5 and 1.0 M potassium nitrate solutions respectively.

Polarograms have been taken employing Radiometer polariter PO₄ with the usual precautions.³ The value of 'm' is 1.175 mg. per sec. and the

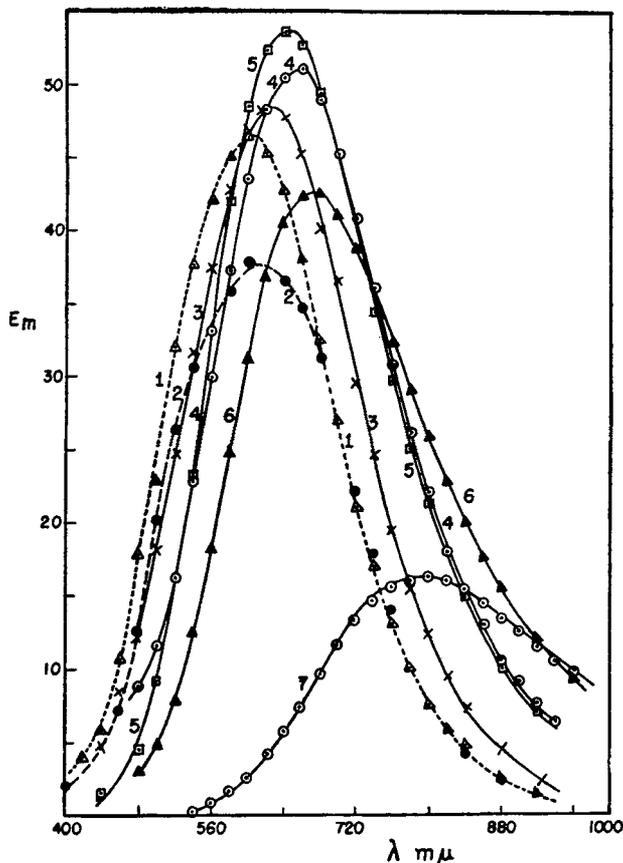


FIG. 1. Absorption spectra of copper-monoethanolamine complexes (pure and hydroxy).
 Curve 1: is obtained in 1.0 M potassium nitrate + 2.0 M monoethanolamine (CuA_2OH^+).
 Curve 2: obtained for copper: monoethanolamine as 1:2 with 0.2 M sodium hydroxide and 1M potassium nitrate [$\text{CuA}_2(\text{OH})_2$].
 Curves 3 and 5 are obtained at pA 1.81 ± 0.02 in presence of 0.1 M MEA ion (pH 8.69) and 1.0 M MEA ion (pH 7.67) respectively.
 Curves 4 and 6 are obtained at pA 2.78 ± 0.02 in presence of 0.1 M MEA ion (pH 7.74) and 1.0 M MEA ion (pH 6.68).
 Curve 7: Identical Curves are obtained at pA 4.81 ± 0.01 in 0.1 M (pH 5.70) and in 1.0 M (pH 4.68) MEA ion.

drop-time is 3.9 sec. a drop in 1N potassium chloride. The polarograms obtained are given in Fig. 2. The conditions under which these polarograms are taken (legend to Fig. 2) correspond to the region where \bar{n} is between 3 and 4. It is not possible to conduct polarographic experiments at lower values of \bar{n} (say 2) since the condition of the swamping concentration of the ligand cannot be satisfied.

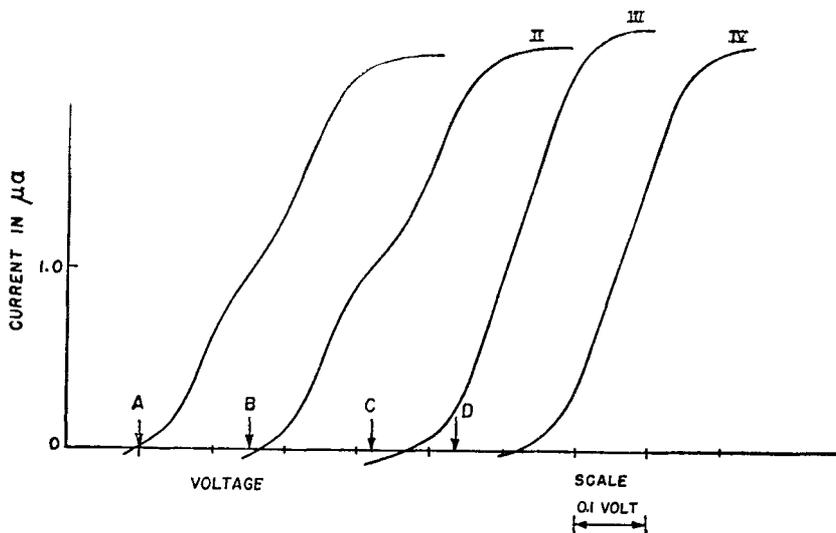


FIG. 2. Polarograms (peak current contours) for copper (0.38 millimolar) monoethanolamine complexes in 0.1 and 1.0 M MEA ion solutions.

Curves 1 and 2 are obtained with 1.0 M MEA ion containing 0.0192 M and 0.0384 M monoethanolamine (pH 7.71 and 8.02) respectively.

Curves 3 and 4 are obtained with 0.1 M MEA ion containing 0.0192 M and 0.0384 M monoethanolamine (pH 8.82 and 9.11) respectively.

The letters A, B, C and D correspond to 0.0 V vs. S.C.E. of the polarograms 1, 2, 3 and 4 respectively.

DISCUSSION

(1) Polarographic Evidence for the Formation of Hydroxy Complexes in 0.1 M MEA Ion Solutions

The polarograms obtained (Fig. 2) in 1 M MEA ion solutions contain two waves which can be taken to be very nearly as 1:1. The values of $E_4 - E_4$ are of the order of 0.060 V indicating the reversibility of the electrode process. The half-wave potentials cannot be taken accurately from the polarograms since the separation between the two waves is not well defined. Consequently the half-wave potentials have been read out from the derivative polarograms. The value of ΔE_4 for the first wave is 0.018 V and for the second wave is 0.034 V, when the concentration of monoethanolamine is changed from 0.0192 M to 0.0384 M. Application of Lingane's equation⁴ indicates that the formula of the cuprous complex is CuA_2^+ and that of the cupric complex CuA_3^{++} . Working in MEA ion solutions containing 0.1 to 1.0 M amine, Srinivasan and Subrahmanya⁵ obtained a value of 2 for

($p - q$) indicating that CuA_4^{++} might have been produced. They have however pointed out that the formation of CuA_3OH^+ cannot be ruled out at such high pH values (8.75 to 9.75).

In 0.1 M MEA ion solutions the first and the second waves (Fig. 2) are so close that only one wave is formed. Hence a different complex may be expected in these solutions. If it is assumed that there is not much interference from the second wave at potentials corresponding to E_1 of the first wave, an approximate estimate of the shift due to the change in concentration of the amine can be obtained. The shift in this case has been found to be of the order of 0.030 V instead of 0.018 V obtained in 1 M MEA ion solutions. Application of Ligane's equation gives a value of 1.7 for ($p - q$). Since Srinivasan and Subrahmanya⁵ have shown that the cuprous complex has no tendency to form hydroxy complexes, one can take the formula of the cuprous complex to be CuA_2^+ in this medium also. This indicates that the most predominating cupric complex is CuA_4^{++} . One cannot, however, expect, in the same range of concentration of the amine, the formation of CuA_3^{++} in 1 M MEA ion solutions and CuA_4^{++} in 0.1 M MEA ion solutions. The shift of 30 millivolts could only be ascribed to the formation of a large proportion of the hydroxy complex CuA_3OH^+ (due to higher pH) in addition to CuA_3^{++} . Thus in 1 M MEA ion solutions the predominant cupric species is CuA_3^{++} while in 0.1 M MEA ion solutions, for the same concentration range of the amine, the predominant cupric species is CuA_3OH^+ . It can therefore be stated that the conclusion reached previously¹ regarding the formation of hydroxy complexes from the non-coincidence of \bar{n} -pA curves is borne out by an independent evidence. It is also obvious that, since the first wave moves close to the second wave due to the formation of CuA_3OH^+ , an apparently single wave is formed.

(2) Analysis of Bjerrum Formation Curves for Hydroxy Complexes

In the analysis of Bjerrum formation curves for the hydroxy complexes the following special features have to be taken into account:—

(i) Since the concentration of the ethanolanmonium ion is high as compared to the concentration of the metal ion, the ethanolanmonium ion produced consequent to the formation of the hydroxy complex is negligible and does not upset the determination of the free ligand calculated by the equation

$$pA = -\log A_t + pH_p - pH_{\text{comp.}}$$

(ii) The introduction of either the amine group or the hydroxy group into the complex has the same effect on the free ligand concentration. Both remove the same amount of the ligand and produce the same drop in pH. It is because of this, Cadiot Smith⁶ concluded that Bjerrum formation curves cannot be used for the analysis of hydroxy complexes.

(iii) The higher value in \bar{n} obtained when the value of pA is maintained constant, in presence of 0.5, 0.2 and 0.1 M MEA ion solutions is due to the conversion of MA to MAOH, MA₂ to MA₂OH, MA₃ to MA₃OH. The formation of higher hydroxy complexes can be neglected due to the low pH of the solutions (< 8).

(iv) It is not possible to distinguish between MAOH and MA₂, MA₃ and MA₂OH, and MA₄ and MA₃OH since the two complexes in each set produce the same drop in pH and have the same effect on \bar{n} .

(v) The formation of hydroxy complexes decreases the concentration of free metal ion and the pure metal complexes at the same value of pA since the ratios [M]/[MA], [MA]/[MA₂] and [MA₂]/[MA₃] have to remain constant when the system contains only the mononuclear complexes.

(a) *Analysis of \bar{n} -pA curves in 0.1 M MEA ion solutions.*—Examination of the distribution curves (Fig. 5, Ref. 1, where α 's are plotted against \bar{n} instead of pA), in 1 M MEA ion solutions indicates that when $1.1 < \bar{n} < 1.5$, MA, MA₂ and MA₃ are present. It may be concluded, for qualitative purposes, that similar distribution of complexes is present even in 0.1 M MEA ion solutions. The hydroxy complexes that can be expected in 0.1 M MEA ion solutions are MAOH, MA₂OH and MA₃OH. Since the concentration of MA₃ is below 4%, one can neglect the formation of MA₃OH. The complexes that can be expected are limited to the following species: MA, MA₂, MA₃, MAOH and MA₂OH.

The following equation gives the relationship between the experimentally determined \bar{n} ($\bar{n} = \{A_t - [A]\}/M_t$) and the concentrations of the different species (pure and hydroxy) present in the solution:

$$\bar{n} = \frac{[MA] + 2[MA_2] + 3[MA_3] + 2[MAOH] + 3[MA_2OH]}{[M] + [MA] + [MA_2] + [MA_3] + [MAOH] + [MA_2OH]} \quad (1)$$

In the above equation the terms [MAOH] and [MA₂OH] in the numerator are multiplied by 2 and 3, since in the formation of MAOH and MA₂OH, the same amount of the ligand is consumed as in the formation of MA₂ and MA₃. Expressing the concentrations of the complex species in terms of the stability constants and the concentration of the ligand and hydroxy group the following equation can be written:

$$\bar{n} = \frac{\beta_{1,1} [A] + 2\beta_{1,2} [A]^2 + 3\beta_{1,3} [A]^3 + 2\beta_{1,1,OH} [A] [OH] + 3\beta_{1,2,OH} [A]^2 [OH]}{1 + \beta_{1,1} [A] + \beta_{1,2} [A]^2 + \beta_{1,3} [A]^3 + \beta_{1,1,OH} [A] [OH] + \beta_{1,2,OH} [A]^2 [OH]}$$

or

$$\bar{n} + (\bar{n} - 1) \beta_{1,1} [A] + (\bar{n} - 2) \beta_{1,2} [A]^2 + (\bar{n} - 3) \beta_{1,3} [A]^3 + (\bar{n} - 2) \beta_{1,1,OH} [A] [OH] + (\bar{n} - 3) \beta_{1,2,OH} [A]^2 [OH] = 0.$$

On rearranging one gets

$$\begin{aligned} & \frac{1}{(2 - \bar{n}) [OH]} \left\{ \frac{\bar{n}}{[A]} + (\bar{n} - 1) \beta_{1,1} \right\} - \frac{[A]}{[OH]} \left\{ \beta_{1,2} + \frac{(3 - \bar{n})}{(2 - \bar{n})} [A] \beta_{1,3} \right\} \\ & = \beta_{1,1,OH} + \beta_{1,2,OH} \frac{(3 - \bar{n})}{(2 - \bar{n})} [A]. \end{aligned} \quad (2)$$

The plot of L.H.S. vs. $(3 - \bar{n}) [A]/(2 - \bar{n})$ (equation 2) should be a straight line the intercept giving $\beta_{1,1,OH}$ and the slope giving $\beta_{1,2,OH}$. The values of $\beta_{1,1}$ and $\beta_{1,2}$ required to compute the value of L.H.S. are taken from the analysis of \bar{n} -pA curves below \bar{n} 0.8 (Ref. 1). Since the same value for $\beta_{1,1}$ ($10^{4.54}$) and $\beta_{1,2}$ ($10^{9.30}$) are obtained in presence of 0.1, 0.2, 0.5 and 1.0 M MEA ion, it is reasonable to assume that the value of $\beta_{1,3}$ ($10^{11.09}$) obtained in 1.0 M MEA ion solutions can be used for the present analysis without any error. The plot corresponding to equation (2) is given in Fig. 3. The values of $\beta_{1,1,OH}$ and $\beta_{1,2,OH}$ are $10^{10.97}$ and $10^{14.84}$ respectively.

In the region $2.3 < \bar{n} < 2.8$ one can expect the formation of MA_3OH also. The formation of MA_3OH instead of MA_4 has been assumed in the present case since the \bar{n} values (till $\bar{n} = 2.7$) obtained in 1 M MEA ion solutions agree with the theoretical values of \bar{n} calculated assuming the formation of only MA , MA_2 and MA_3 (Table II). Proceeding in the same way as described above the following equation can be obtained:

$$\begin{aligned} & \frac{1}{(4 - \bar{n}) [A]^2 [OH]} \left\{ \frac{\bar{n}}{[A]} + (\bar{n} - 1) \beta_{1,1} + (\bar{n} - 2) \beta_{1,2} [A] \right. \\ & \quad \left. + (\bar{n} - 3) \beta_{1,3} [A]^2 + (\bar{n} - 2) \beta_{1,1,OH} [OH] \right\} \\ & = \beta_{1,3,OH} + \frac{(3 - \bar{n})}{(4 - \bar{n})} \frac{1}{[A]} \beta_{1,2,OH}. \end{aligned} \quad (3)$$

The value of the L.H.S. is evaluated making use of the value of $\beta_{1,1,OH}$ determined previously. The plot of the L.H.S. vs. $(3 - \bar{n})/(4 - \bar{n}) 1/[A]$ is a straight line (Fig. 4) from which values of $10^{17.16}$ and $10^{14.86}$ are obtained for $\beta_{1,3,OH}$ and $\beta_{1,2,OH}$ respectively. It is interesting that the value of $\beta_{1,2,OH}$

obtained in the region $2.3 < \bar{n} < 2.8$ agrees very well with the value of $10^{14.84}$ obtained in the region $1.1 < \bar{n} < 1.5$. This agreement is indicative of the validity of the assumptions involved.

TABLE II
Experimental and calculated values of \bar{n} in various concentrations of MEA ion solutions

\bar{n} (expt.)	pA at			\bar{n} (calc.) at			\bar{n} (expt.) pA \bar{n} (calc.)		
	0.50 M	0.20 M	0.10 M	0.50 M	0.20 M	0.10 M	(1.0 M. ion)		
1.60	3.66	3.74	3.85	1.61	1.61	1.62	2.40	2.78	2.43
1.70	3.58	3.67	3.79	1.71	1.70	1.71	2.50	2.66	2.53
1.80	3.50	3.60	3.72	1.80	1.81	1.82	2.60	2.53	2.61
1.90	3.43	3.53	3.66	1.89	1.91	1.90	2.70	2.40	2.69
2.00	3.36	3.45	3.60	1.98	2.02	2.00	2.80	2.28	2.75
2.10	3.25	3.39	3.52	2.09	2.10	2.08	2.90	2.13	2.81
2.20	3.15	3.31	3.46	2.21	2.18	2.20	3.00	1.99	2.86

(b) \bar{n} -pA curves in 0.2 M monoethanolammonium ion solutions.—

(i) $1.25 < \bar{n} < 1.75$.

The plot corresponding to equation (2) is given in Fig. 3. The plot passes through the origin indicating the non-existence of MAOH. The slope gives a value of $10^{14.76}$ for $\beta_{1,2,\text{OH}}$.

(ii) $2.35 < \bar{n} < 2.90$.

The plot of equation (3) (Fig. 4) gives a value of $10^{16.93}$ for $\beta_{1,3,\text{OH}}$ and $10^{14.75}$ for $\beta_{1,2,\text{OH}}$. The term corresponding to MAOH is deleted when applying equation (3) for these experimental results since MAOH has not been found to exist.

(c) \bar{n} -pA curves in 0.5 M monoethanolammonium ion.— $2.25 > \bar{n} < 2.90$.

Since MAOH is not formed in 0.2 M MEA ion solutions it is reasonable to conclude that MAOH is not present even in these solutions. Application

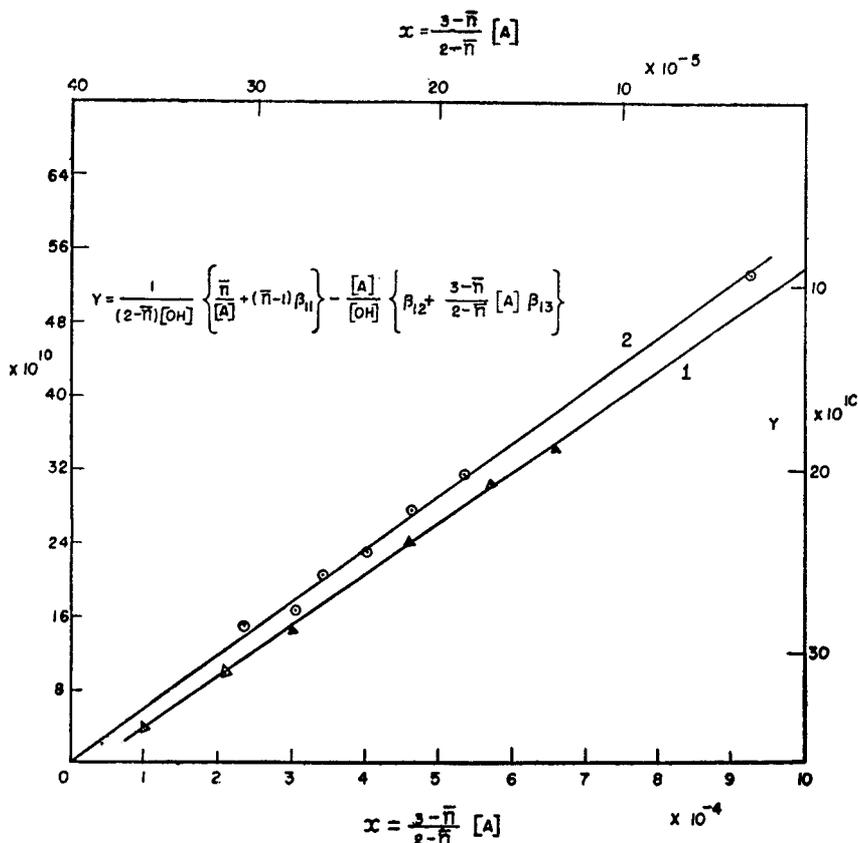


FIG. 3. Plot corresponding to equation (2) for the determination of $\beta_{1,1,OH}$ and $\beta_{1,2,OH}$.

Curve 1: The plot of equation (2) in 0.1 M MEA ion ($1.1 < \bar{n} < 1.5$).

The zero of the axis start at the right hand top of the figure.

Curve 2: The plot of equation (2) in 0.2 M MEA ion ($1.25 < \bar{n} < 1.75$).

The zero of the axis start at the left hand bottom of the figure. The line passes through the origin indicating the non-existence of CuAOH^+ .

of equation 3 (Fig. 4) without the term corresponding to MAOH to the experimental data gives a value of $10^{16.60}$ for $\beta_{1,3,OH}$ and $10^{14.50}$ for $\beta_{1,2,OH}$.

(d) \bar{n} - pA curves in 1.0 M monoethanolammonium ion.—It has been concluded previously that in 1 M MEA ion solutions, the amount of the hydroxy complex formed is negligibly small even when \bar{n} is 2.4. Calculation of \bar{n} employing the constants for MA, MA_2 and MA_3 indicates good agreement between the theoretically calculated and experimentally observed values even when \bar{n} is 2.7 (Table II). Deviations occur only thereafter. It can therefore be concluded that the hydroxy complexes occur if at all, in very

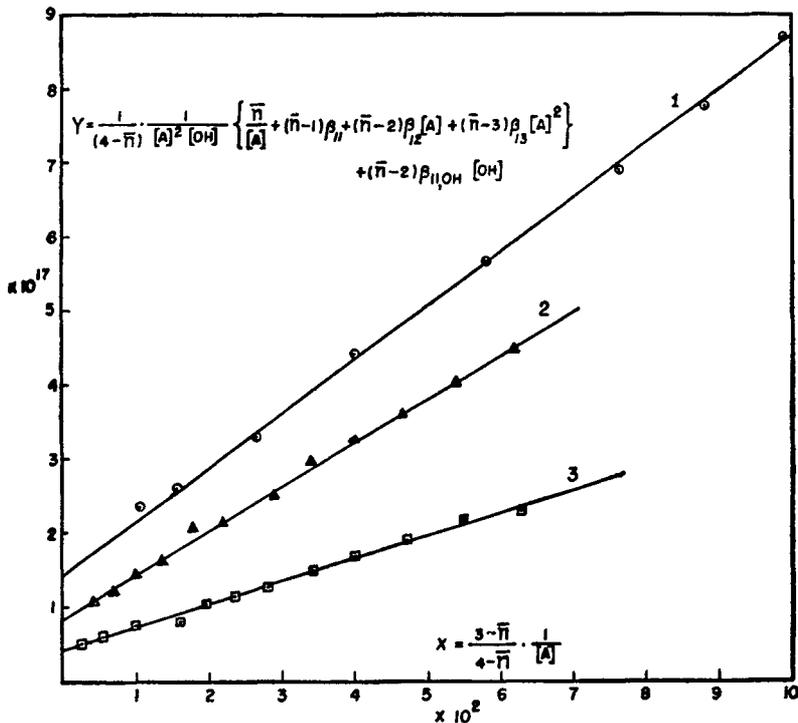


FIG. 4. Plot of equation (3) for the determination of $\beta_{1, s, \text{OH}}$ and $\beta_{1, z, \text{OH}}$ at different MEA ion concentrations.

Curve 1: The plot of equation (3) in 0.1 M MEA ion ($2.30 < \bar{n} < 2.80$).

Curve 2: The plot of equation (3) in 0.2 M MEA ion ($2.35 < \bar{n} < 2.90$).

Curve 3: The plot of equation (3) in 0.5 M MEA ion ($2.25 < \bar{n} < 2.90$).

While plotting curves 2 and 3 the term corresponding to CuAOH^+ is omitted.

small quantities below $\bar{n} 2.7$. Even above $\bar{n} 2.7$ the amount formed is quite small. This is borne out by polarographic experiments conducted between pA 1.5 and 1.8, where the cupric complex is shown to be predominantly CuA_3^{++} .

(3) Validity of the Stability Constants

The stability constants that have been determined for CuA^{++} , CuA_2^{++} , CuA_3^{++} , CuAOH^+ , CuA_2OH^+ , and CuA_3OH^+ have been used to calculate the theoretical values of \bar{n} in the region not covered in the analysis described above (Figs. 3-4). The results are given in Table II. It is obvious that the agreement between the theoretical and the experimental values are quite good.

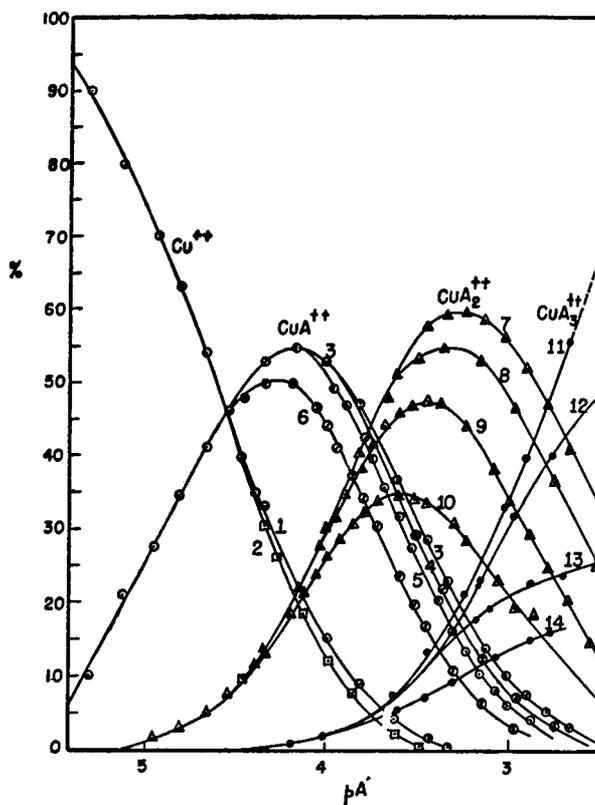


FIG. 5. Percentage distribution of pure complexes of copper (II)-monoethanolamine system at various pA values.

Curves 1 and 2 give the % free cupric ion in 1.0 and 0.1 M MEA ion solutions respectively.

Curves 3, 4, 5 and 6 give the % of CuA^{++} in 1.0, 0.5, 0.2 and 0.1 M MEA ion solution respectively.

Curves 7, 8, 9 and 10 give the % of CuA_2^{++} in 1.0, 0.5, 0.2 and 0.1 M MEA ion solution respectively.

Curves 11, 12, 13 and 14 give the % CuA_3^{++} in 1.0, 0.5, 0.2 and 0.1 M MEA ion solution respectively.

(4) Distribution of Pure and Hydroxy Complexes at Various pA Values in Presence of 0.1, 0.2, 0.5 and 1.0 M MEA Ion Solutions

The values of α 's, i.e., fractions of the free metal ion or any complex species present in the solution to the total concentration of all species at any pA value are calculated as follows. The value of $\alpha_{1,OH}$ is calculated by the following equation:

$$\alpha_{1,OH} = \frac{[MAOH]}{M_t}$$

$$= \frac{\beta_{1,1,OH} [A] [OH]}{1 + \beta_{1,1} [A] + \beta_{1,2} [A]^2 + \beta_{1,3} [A]^3 + \beta_{1,1,OH} [A] [OH] + \beta_{1,2,OH} [A]^2 [OH] + \beta_{1,3,OH} [A] [OH]}$$

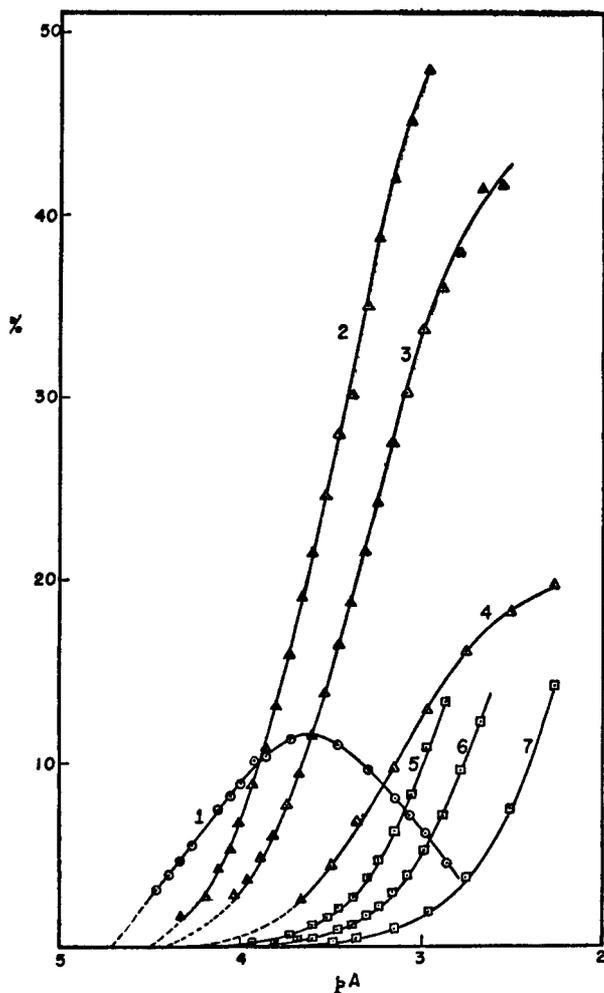


FIG. 6. Percentage distribution of hydroxy complexes of copper (II)-monoethanolamine system at various pA values.

Curve 1: % distribution of $CuAOH^+$ in 0.1 M MEA ion solutions.

Curves 2, 3 and 4: % distribution of CuA_2OH^+ in 0.1, 0.2 and 0.5 M MEA ion solution respectively.

Curves 5, 6 and 7: % distribution of CuA_3OH^+ in 0.1, 0.2 and 0.5 M MEA ion solution respectively.

Similar expressions can be written for other cases. The values of the α 's multiplied by 100 gives the percentage distribution of the various complexes. The distribution curves of the pure and the hydroxy complexes are given in Figs. 5 and 6 respectively. Examination of these figures indicate that, when pA is maintained constant in the region where hydroxy complexes are formed.

(i) The percentage of pure complexes decreases with a decrease in the concentration of the MEA ion which results in an increase of pH. This is due to the fact that at higher pH values more of the hydroxy complexes are produced, decreasing the total amount of the pure complexes formed. Since the ratios of $[M]/[MA]$, $[MA]/[MA_2]$ and $[MA_2]/[MA_3]$ have to be constant when pA is maintained constant, it is obvious that the percentage of these complexes will decrease.

(ii) The percentage of the various hydroxy complexes decreases with an increase in the concentration of MEA ion (which results in a decrease of pH) at the same value of pA.

The hydroxy complexes in copper-monoethanolamine system investigated by previous workers are limited mostly to the polarographic method. Srinivasan and Subrahmanya⁵ have determined the stability constant of CuA_3OH^+ by the 'polarographic-redox potential method' and obtained a value of 10^{18} .

Analyzing the data of Fisher and Hall,⁷ Sturrock⁸ obtained a value of $10^{16.4}$ for the stability constant of CuA_2OH^+ . This value appears to be a bit too high for CuA_2OH^+ . The present authors have obtained a value of $10^{14.6}$ for CuA_2OH^+ . The stability constant for CuA_3OH^+ obtained in the present work ($10^{17.1}$) is in greater agreement with the value (10^{18}) reported by Srinivasan and Subrahmanya.⁵ It is usual to find such differences when the stability constants are determined by such widely differing techniques.

SUMMARY

Potentiometric, spectrophotometric and polarographic evidence has been presented for the formation of mixed hydroxy complexes in copper-monoethanolamine system. A method has been developed for the analysis of Bjerrum formation curves taken in presence of 0.1, 0.2, 0.5 and 1.0 M monoethanolammonium ion with respect to hydroxy complexes. The formation of $CuAOH^+$, CuA_2OH^+ and CuA_3OH^+ is shown and the corresponding stability constants are calculated at different concentrations of MEA ion. Curves showing the distribution of pure and hydroxy complexes at various

pA values in solutions containing different concentrations of MEA ion have also been given.

ACKNOWLEDGEMENT

The authors wish to thank Professor M. R. A. Rao for helpful discussions. One of us (S. Mahapatra) wishes to thank the C.S.I.R. for the award of a Fellowship.

REFERENCES

1. Mahapatra, S. and Subrahmanya, R. S. *Proc. Ind. Acad. Sci.*, 1963, **58 A**, 161.
2. Ojima, H. and Sone, K. .. *Z. anorg. allg. Chem.*, 1961, **309**, 110.
3. Subrahmanya, R. S. .. *Proc. Ind. Acad. Sci.*, 1956, **43 A**, 133.
4. Kolthoff, I. M. and Lingane, J. J. *Polarography*, 1952, **1**, 222.
Chem. Revs., 1941, **29**, 1.
5. Srinivasan, K. and Subrahmanya, R. S. Unpublished.
6. Cadot, M. Smith .. *J. Chim. Phys.*, 1963, **60**, 957.
7. Fisher, J. F. and Hall, J. L. *Anal. Chem.*, 1962, **34**, 1094.
8. Sturrock, P. E. ... *Ibid.*, 1963, **35**, 1092.