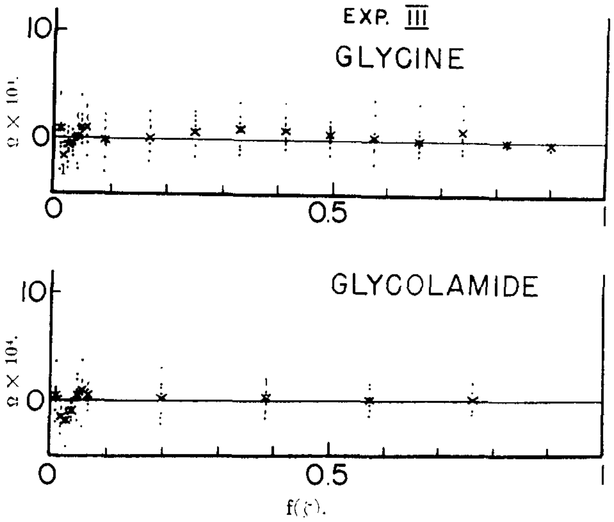

Fig. 2.—Relative fringe deviation graphs for glycine and glycolamide. The glycolamide deviation graph is for an experiment (ref. 4) in which the mean concentration was $\bar{C} = 0.1249_9$ and the difference in concentration across the boundary was $\Delta C = 0.2499_8$.

two or three microns in δ. Calculated and experimental values of j_m are in good agreement while those for D_A differ by 0.4%.

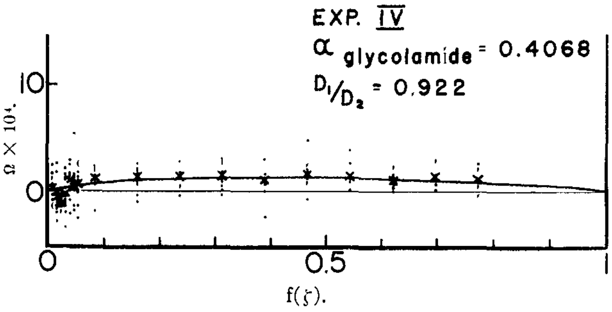

Fig. 3.—Relative fringe deviations for the glycine–glycolamide mixture, $\alpha_{\text{glycolamide}} = 0.4068$.

It should be noted that, for three component systems in which r_2 is close to unity, as α_2 varies from one to zero the experimental D_A values vary from D_2 to D_1 even though the relative fringe deviation graph remains close to zero in all cases (see Fig. 3). For example, at the same mean concentration, $\bar{C}$, used in experiment IV, equation 10[1] indicates that D_A values will range from 1.048 ($\alpha_{\text{glycine}} = 1$) to 1.136 ($\alpha_{\text{glycolamide}} = 1$). It is important that this point be remembered when using relative fringe deviation graphs to study heterogeneity in proteins, since in the range $0.92 < r_2 < 1.08$ the presence of impurities cannot be detected without still greater experimental accuracy. For this case it is thus impossible to know whether the diffusion coefficient measured experimentally represents a value for a single-solute or is a "height–area average."

That the calculated values of D_A for both the above mixtures differ a little from the experimental values could be due to two factors which have been assumed negligible.[1] Firstly, the solute flows in three-component systems may interact slightly, and secondly, the differential diffusion coefficient of a solute, measured for a two-component system, could differ from the value obtained when that solute diffuses in a system of three components. In the absence of interaction between the solute flows the correct values of the differential diffusion coefficients, D_k, to use in equation 10 should be measured by experiments in which all solutes, except the diffusing component "k," are at the same concentration in both solutions forming the initial boundary. However the experiments described in this paper and those previously reported[1] show that, when Fick's first law[10] is sufficient to describe the flows of solutes in dilute solution, the differential diffusion coefficients, obtained from two component systems, are adequate to a first approximation for computing height–area average diffusion coefficients from equation 10. Further experiments with other three component systems are planned to investigate the case when the solute flows interact.

Acknowledgments.—The author would like to acknowledge the very valuable aid and advice of Professor L. J. Gosting throughout the course of this study. He is also indebted to Dr. R. L. Baldwin for his kind and helpful interest.

This research was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(10) Adolf Fick, *Pogg. Ann.*, **94**, 59 (1855).

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Polarographic Study of Copper(II) Complexes with Ethanolamine and Some Derivatives

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RECEIVED JANUARY 25, 1955

The literature[1] records several studies of complexes of copper(II) with ethanolamine and its derivatives, usually involving analysis of precipitates. In some of these studies it has been suggested that both the hydroxyl and the amino groups are coördinated to the copper(II) ion. The present research was undertaken to determine the formulas of some of the complexes and their formation constants by a polarographic method.

Experimental Method

Chemicals.—Solutions for electrolysis were prepared from reagent chemicals, used without further purification, with the exception of the ethanolamines which were of the best commercial grades and were vacuum distilled just before use. The diethanolamine and the ethylethanolamine were supplied by Carbide and Carbon Chemicals Company and the monoethanolamine was provided by Sharples Chemicals, Incorporated.

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(1) (a) F. Garelli, *Atti accad. sci. Torino, Classe sci. fis., mat. e nat.*, **68**, 398 (1933); F. Garelli and A. Tettamanzi, *Gazz. chim. ital.*, **63**, 570 (1933); H. Brintzinger and B. Hesse, *Z. anorg. allgem. Chem.*, **252**, 293 (1944); **248**, 351 (1941); W. Hieber and E. Levy, *ibid.*, **219**, 225 (1934); J. C. Duff and E. H. Steer, *J. Chem. Soc.*, 2861 (1932); J. M. Bolling and J. L. Hall, THIS JOURNAL, **75**, 3953 (1953); L. A. Nikolaev, *Vestnik, Moskov. Univ.*, No. 6, 115 (1947); (b) J. L. Harvey, C. I. Tewksbury and H. M. Haendler, THIS JOURNAL, **71**, 3641 (1949).

Apparatus.—Polarograms were recorded on a Sargent Model XXI polarograph. All electrolyses were performed with the solutions in an H-cell at constant temperature. A bottle type saturated calomel electrode, with a saturated potassium chloride–agar salt bridge, was employed as the reference electrode. Nitrogen used for the deäeration of solutions was freed of oxygen with a gas scrubbing train containing an acidic chromous sulfate solution. Measurements of potential were made with a Leeds and Northrup student type potentiometer.

Procedure.—Appropriate quantities of stock solutions were combined and diluted so that the concentration of $Cu(NO_3)_2$ was 0.001 *M;* that of KNO_3, the supporting electrolyte, was 0.5 *M;* and that of gelatin, the maximum suppressor, was 0.005% for all experimental solutions. The concentration of the ethanolamines was varied between 0.01 and 0.1 *M*.

The solutions were flushed with oxygen-free nitrogen for ten minutes and electrolyzed at 25 ± 0.05°. Each polarogram was calibrated by making two potentiometric readings of voltage applied. The galvanometer sensitivity setting of the polarograph was 0.04 μa./mm. and the voltage span was 0.5 volt. No damping was used. For the capillary in the dropping mercury electrode, m was 2.32 mg./sec. and t was 3.2 sec. at 40 cm. reservoir height in 0.1 *N* KCl with open circuit. The mercury height was maintained at 40 cm. for all electrolyses.

A plot of $\log (i_d - i)/i$ *versus* E_{dme} was made for each polarogram. This plot was used to determine the half-wave potential and to test for reversibility.[2]

Results

The polarograms recorded showed a single wave with a height substantially equal to that obtained with copper(II) in absence of coördinating agent, corresponding to a two electron reduction. The plots $\log (i_d - i)/i$ *versus* E_{dme} were linear and gave the reciprocal slope values recorded in Table I. It was assumed that the reduction was reversible.

Table I also gives the half-wave potentials for each concentration of the solutions of the ethanolamines. Figure 1 is a composite of the plots of $E_{1/2}$ *versus* $\log C_x$ values for the ethanolamines. The formation constants, K_f, the slopes of the $E_{1/2}$ *versus* $\log C_x$ plots and the number, p, of bound coördinating molecules per copper(II) unit are given in Table II.

TABLE I

POLAROGRAPHIC DATA FOR SOLUTIONS COMPOSED OF VARIOUS CONCENTRATIONS OF COÖRDINATING AGENT, 0.001 *M* $Cu(NO_3)_2$, 0.5 *M* KNO_3 AND 0.005% GELATIN

	Ethanolamine		Diethanolamine		Ethylethanolamine	
Cx	$E_{1/2}$, v. *vs.* S.C.E.	Recip. slope	$E_{1/2}$, v. *vs.* S.C.E.	Recip. slope	$E_{1/2}$, v. *vs.* S.C.E.	Recip. slope
0.000	0.016	0.034	.....	...	.....	...
.01	− .226	.051	−0.209	0.051	.....	...
.02	− .267	.041	− .254	.055	−0.267	0.042
.023	− .270	.041	.....	...	.....	...
.03	− .282	.048	− .279	.050	− .300	.040
.04	− .303	.036	− .297	.048	− .315	.040
.05	− .316	.039	− .309	.047	− .329	.037
.06	− .325	.038	− .317	.048	− .340	.044
.07	.....	...	− .326	.045	− .344	.043
.08	− .336	.041	− .329	.045	.....	...
.081	.....	...	.....	...	− .353	.039
.09	− .338	.042	− 334	.042	.....	...
.10	− .348	.041	.....	...	− .365	.040

TABLE II

STABILITY CONSTANT, SLOPE $E_{1/2}$ *vs.* LOG C_x, AND p VALUES FOR THE COPPER(II) COMPLEXES

Complex	K_f	Slope $E_{1/2}$ *vs.* log C_x	p
Ethanolamine	3×10^{16}	−0.120	4
Diethanolamine	1×10^{16}	− .118	4
Ethylethanolamine	6×10^{15}	− .123	4

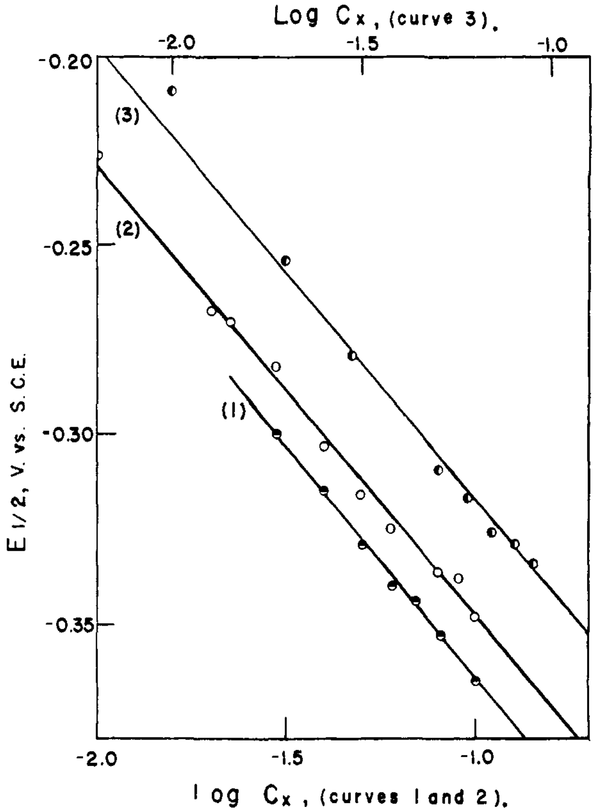

Fig. 1.—Plots of $E_{1/2}$ *versus* $\log C_x$ for (1) ethylethanolamine and (2) monoethanolamine, employing the lower $\log C_x$ scale, and for (3) diethanolamine employing the upper $\log C_x$ scale.

For p equal to four and n equal to two, $-0.0591p/n$, the theoretical slope value, should be −0.118.

Discussion

In the presence of complexing agent, the polarographic wave shifts to more negative values, and this shift is a function of the concentration of the complexing agent. At 25° [3]

$$\Delta E_{1/2} = \frac{-0.0591}{n} \log K_f - p\,\frac{0.0591}{n} \log C_x - \frac{0.0591}{n} \log \frac{f_s k_c f_x^p}{f_c k_s} \quad (1)$$

where the subscripts c, s and x refer to the complex metal ions, the simple metal ions and the ethanolamine, respectively; K_f is the formation constant of the complex ion; f is the activity coefficient; k is the proportionality coefficient between the concentration and the diffusion currents in the Ilkovic equation; C_x is the concentration of complexing agent; and p is the number of ligands bound per metal ion. The last term of equation 1 was neglected. The formation constant, K_f, is defined as

$$K_f = \frac{[CuX_4^{++}]}{[Cu^{++}][X]^4} \quad (2)$$

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[2] J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

[3] *Cf.* I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 214.

where the brackets indicate molar concentration and X corresponds to the ethanolamine used.

The reciprocal slope values given in Table I have a wide range of values and this causes some uncertainty in the determination of the values of K_f. Therefore, the K_f values in Table II are given to only one significant figure.

For each of the ethanolamines studied, the value of p obtained was four which indicates that the complexes contain four ligand molecules. Since copper(II) ordinarily has a coördination number of four, this shows that the coördinating molecules are monodentate. It is assumed that the coördinate bond occurs through the amine nitrogen.

The diethanolamine complex found was quite similar in behavior to the monoethanolamine and ethylethanolamine complexes, and this points to the likelihood of amino coördination. Diethanolamine has one more hydroxyl than either monoethanolamine or ethylethanolamine. Hence, for hydroxyl coördination, diethanolamine should behave differently from the latter two compounds. All three compounds should act in a similar manner in the formation of complexes through the amine nitrogen. The fact that it was found that four molecules of the ethanolamines were coördinated in all three cases substantiates the assumption that the linkage is through the amine nitrogen.

Some further studies with diethylethanolamine and triethanolamine in this Laboratory indicate that the corresponding complexes are not formed in the same concentration range as the others given here, but show a tendency toward coördination of only two or three molecules per copper(II). The square-planar configuration of copper(II) complexes might produce steric hindrance if the coordination occurs through the tertiary amine nitrogen. This would not be the situation if it were the hydroxyl group which coördinates. This is in agreement with the beliefs of other authors. Breckenridge and Hodgins[4] and Mann[5] have described complexes of 1,3-diamino-2 propanol with copper(II) for which they believe the coördination took place through the amino groups only. Breckenridge[6] states that for N-hydroxyethylethylenediamine the hydroxyl group does not coördinate. Harvey, *et al.*,[1b] describe a number of complexes of N-hydroxyethylethylenediamine studied spectrophotometrically. Among the structures mentioned is $[Cu(HOC_2H_4NHC_2H_4NH_2)_4]^{++}$ for which they reason that only the primary amino group is coördinated. They also give evidence for the existence of a complex of diethanolamine with copper(II) in which the amine group, rather than the hydroxyl group, is coördinated.

If the difference in coördinating ability of the amino and hydroxyl groups is substantially different, then one should expect to find only one type of group coördinated when an excess of the complexing agent is present. This assumes that there are no complications such as steric effects. Thus the experimental conditions of this research favored the formation of the $[CuX_4]^{++}$ complex. However in the presence of a limited amount of the ethanolamines, particularly in non-aqueous solutions where water does not compete, it is possible that one may find chelates formed with both the amino and hydroxyl groups being coördinated. One can find support for this hypothesis in the results of earlier workers based on analyses of compounds prepared under these conditions.

It would be of interest to compare the formation constants for the ethanolamine complexes of copper(II) with the corresponding simple amine complexes, but the data on these do not appear to be available. However the silver complexes have been reported and it has been found that two moles of the complexing agent are coördinated per atom of silver(I). The formation constants reported[7] for the monoethanolamine, diethanolamine, ethylamine and diethylamine complexes of silver are, respectively, 4.8×10^6, 0.30×10^6, 0.2×10^6 and 1.6×10^6. These values indicate that the simple amines and the hydroxy substituted amines are not very different in coördinating ability.

It is suggested that the water solubility of these ethanolamine complexes is enhanced by the presence of the hydroxyl groups extending into solution. This may explain the fact that certain N-hydroxyethylethylenediaminetriacetic acid complexes are more soluble than the corresponding complexes with ethylenediaminetetraacetic acid.

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(4) J. G. Breckenridge and J. W. R. Hodgins, *Can. J. Research*, **B17**, 331 (1939).

(5) F. G. Mann, *J. Chem. Soc.*, 2904 (1927).

(6) J. G. Breckenridge, *Can. J. Research*, **B26**, 11 (1948).

(7) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

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On the Mechanism of the Acid-catalyzed Rearrangement of Siloxane Linkages in Organopolysiloxanes

BY DALLAS T. HURD

RECEIVED JANUARY 3, 1955

It has been well established that the active agent in the base-catalyzed rearrangement of siloxane linkages in polydimethylsiloxanes is the oxygen atom, or ionic form derived therefrom, which acts as an electron donor to silicon in the siloxane linkage exchange mechanism.[1,2] Since the rate of siloxane rearrangement depends on the effective strength of the oxygen as an electron donor, determined in turn by the nature of the group or groups attached to it, it seems improbable that the acid-catalyzed rearrangement of siloxane linkages would follow a course entirely analogous to that of base-catalyzed rearrangement.

It is known that, like basic catalysts, protonic acid catalysts do react with siloxane molecules in the course of the rearrangement reaction and the products formed are formally analogous to those formed with basic catalysts.[3-5] The reaction, either with base or acid, involves a cleavage of the siloxane

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(1) D. T. Hurd, R. C. Osthoff and M. L. Corrin, THIS JOURNAL, **76**, 249 (1954).

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(3) F. P. Price, *ibid.*, **70**, 871 (1948).

(4) L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, *ibid.*, **68**, 156 (1946).

(5) C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Revs.*, **41**, 139 (1947).