Absorption Spectra and Catalytic Behavior of the Copper(II) Chelates of Some Alkylated Ethylenediamines

By Heijirô OJIMA and Kôzô SONE

(Received July 12, 1961)

The copper chelates of various alkylated ethylenediamines were studied first by Pfeiffer and Glaser(1), and then by Irving and Griffiths(2), and especially by Basolo and his collaborators(3). Comparative studies of the absorption spectra of some of these chelates have been carried out recently by the present authors, together with some experiments on their activities to catalyze the chemiluminescent reaction of luminol with hydrogen peroxide in alkaline solution. The results of these experiments will be described and discussed in the present paper.

Experimental

Materials. — The samples of $[\mathrm{Cu\,en_2}](\mathrm{ClO_4})_2$, $[\mathrm{Cu\,pn_2}](\mathrm{ClO_4})_2$ and $[\mathrm{Cu}(N,N\text{-diethyl-en})_2](\mathrm{ClO_4})_2$ were prepared and purified according to the methods of the literature(1), while those of $[\mathrm{Cu(tetramethyl\text{-}en)_2}]\mathrm{I_2}$, $[\mathrm{Cu}(N\text{-propyl-en})_2]\mathrm{Br_2}$ and $[\mathrm{Cu}(N,N'\text{-dipropyl-en})_2](\mathrm{NO_3})_2$ were kindly presented by Prof. Fred Basolo of Northwestern University (Evanston, Ill., U. S. A.) to one of the authors (K. S.). The spectrum of $[\mathrm{Cu}(N\text{-hydroxyethyl-en})_2]^{2+}$ was measured with a solution containing $\mathrm{CuSO_4}(5\times10^{-3}\,\mathrm{M})$ and purified ligand amine in the molar ratio of 1 : 2 (ionic strength : 0.5 with $\mathrm{KNO_3}$).

Absorption Spectra.—A Shimadzu QR-50 quartz spectrophotometer with cells 10 mm. in thickness

---

1) P. Pfeiffer and H. Glaser, *J. prakt. Chem.*, **151**, 134 (1938).

2) H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, **1954**, 213.

3) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952); **76**, 211 (1954); F. Basolo, Y. T. Chen and R. K. Murmann, ibid., **76**, 956 (1954).

was used throughout this study. 5×10^{-3} M solutions of the chelates were used in the spectral measurements; their ionic strength was kept at 0.5 by adding potassium nitrate. The measurements were mostly carried out at approx. 27°C.

Paper Electrophoresis.—Filter paper strips (6×22 cm^2) were dipped in electrolyte solutions containing various amounts of NaOH up to 5×10^{-2} M (ionic strength: 5×10^{-2} with potassium nitrate for 10 hr., and small amounts of aqueous solutions of the chelates (approx. 10^{-7} mol.) were spotted at their centers. Electrophoresis experiments with these strips were then carried out by means of the horizontal open strip method, with a potential of 10 V./cm. and at 25°C for 30 min. The migration distances of the spots were measured, and corrections were made of the flow of the liquid phase caused by electroösmosis and evaporation effects, by comparing the data with those of *o*-nitroaniline obtained under the same conditions. The corrected data were plotted against the alkali concentration (cf. Fig. 5).

Catalytic Activity for the Chemiluminescence of Luminol.—Seven milliliters portions of various sodium hydroxide solutions ($0\sim5\times10^{-2}$ M; ionic strength: 0.1 with potassium nitrate) containing luminol (10^{-5} mol.) and each one of the chelates (5×10^{-6} mol.) were kept in a thermostat at 25°C, and 0.5 ml. portion of a hydrogen peroxide solution (containing 1.6×10^{-4} mol.) was poured rapidly into each of them. The intensities of the chemiluminescence emitted by these mixtures were measured by means of a selenium photocell-galvanometer circuit, and the maxima of the galvanometer readings, which were obtained several seconds after the addition of the hydrogen peroxide solution, were plotted against the alkali concentration (cf. Fig. 6).

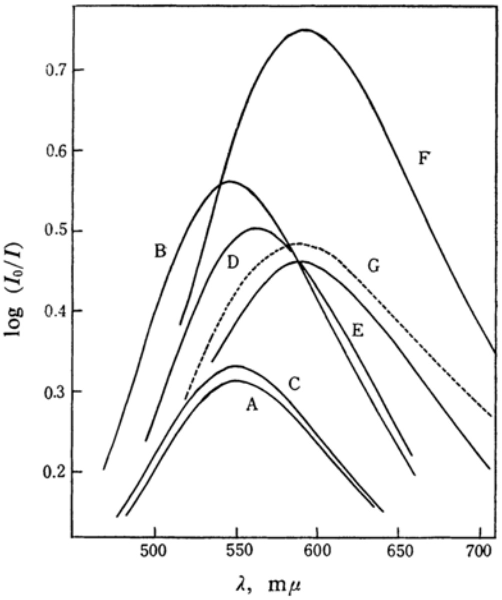


Fig. 1. Absorption spectra of the chelates. A, B,......, G: cf. Table I. Concn.: 5×10^{-3} M.

Results and Discussion

Visible Absorption Spectra.—The visible absorption spectra of the chelates in their aqueous solutions are shown in Fig. 1, and the maximum frequencies and molar extinction coefficients ($\nu_{\max}$ and $\varepsilon_{\max}$) calculated from these curves are shown in Table I, together with the values of their stability constants taken from the literature[2,3]. It can be seen that there is an approximately linear relationship between $\nu_{\max}$ and log k_1k_2 (or log k_2), so that the more stable a chelate is, the larger is its $\nu_{\max}$ value, in accord with the general trend observed in many Co(III) and Cr(III) complexes as well as in certain complexes of

TABLE I

	Chelates	$\nu_{\max}$ (10^{13} sec^{-1}) in H_2O ( ): $\varepsilon_{\max}$*	$\nu_{\max}$ (10^{13} sec^{-1}) in EtOH	log k_1	log k_2**
(A)	$[\mathrm{Cu\,en_2}]^{2+}$	54.5 (64)	54.5	10.76	9.37[3]
(B)	[Cu(tetramethyl-en)$_2$]$^{2+}$	55.0 (112)	52.6	11.63	10.24[3]
(C)	$[\mathrm{Cu\,pn_2}]^{2+}$	54.5 (66)	—	10.78	9.28[3]
(D)	[Cu(*N*-propyl-en)$_2$]$^{2+}$	53.2 (101)	50.0	9.98	8.16[3]
(E)	[Cu(*N*, *N*′-dipropyl-en-$_2$]$^{2+}$	50.8 (93)	51.8	8.79	5.55[3]
(F)	[Cu(*N*, *N*-diethyl-en)$_2$]$^{2+}$	50.6 (150)	53.0	8.17	5.55[2]
(G)	[Cu(*N*-hydroxyethyl-en)$_2$]$^{2+}$	50.9 (97)	—	—	—

* The $\varepsilon_{\max}$ values in this table are those calculated from the curves of Fig. 1; the exact values of the more unstable chelates may be somewhat higher than these. In fact, while the addition of an excess of ethylenediamine (Cu : en=approx. 1 : 10) to a solution of $[\mathrm{Cu\,en_2}]^{2+}$ has almost no effect on its spectra, the addition of *N*, *N*-diethyl-ethylenediamine to a solution of [Cu(*N*, *N*-diethyl-en)$_2$]$^{2+}$ causes a small but noticeable increase in the intensity (up to approx. 15% when Cu : amine=1 : 8) of its absorption band, indicating the partial dissociation of the latter chelate in its solution.

** The log k values are all those at 25°C and at an ionic strength of 0.5, except in (F), where the ionic strength is 0.1. The log k values of [Cu(*N*, *N*′-dimethyl-en)$_2$]$^{2+}$ in Fig. 2 are those of Basolo et al.[3], which were obtained under the same conditions.

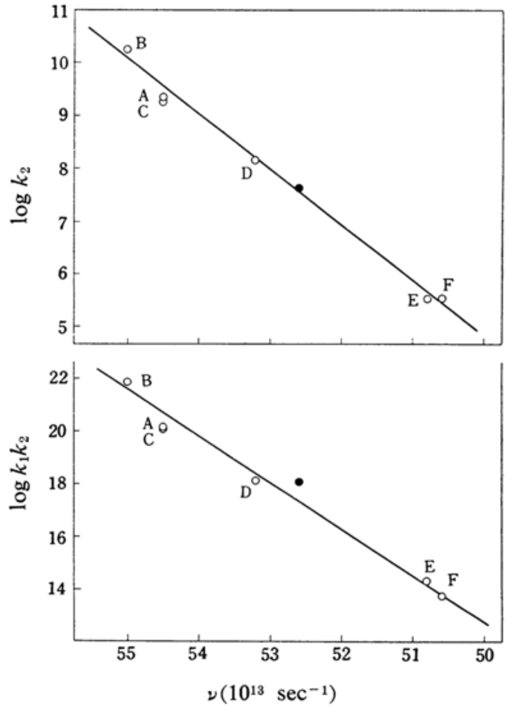


Fig. 2. Relation between $\nu_{\max}$ and log k values of the chelates. A, B,$\cdots$, F: cf. Table I. Black circles correspond to $[\mathrm{Cu}(N,N'\text{-dimethyl-en})_2]^{2+}$, the value of which were taken from the literature[2,3] (cf. Footnote of Table I).

Ni(II) and Cu(II)[4] (cf. Fig. 2). It can also be seen that the absorption intensities of the alkylated chelates are generally much higher than that of $[\mathrm{Cu\,en_2}]^{2+}$.

It was formerly observed by Sone and Kato[5] that a striking color change from blue-violet to yellow took place when the alcoholic solutions (or aqueous solutions containing sodium perchlorate) of $[\mathrm{Ni\,en_2}]^{2+}$ and $[\mathrm{Ni\cdot pn_2}]^{2+}$ were heated, and this change was ascribed to the existence of the equilibrium

$$\underset{\text{blue-violet}}{[\mathrm{Ni\,en_2A_2}]^{2+}} \rightleftarrows \underset{\text{yellow}}{[\mathrm{Ni\ en_2}]^{2+}} + 2\mathrm{A} \quad (\mathrm{A:\ H_2O\ or\ EtOH})$$

in these media[5]. On the other hand, no such drastic spectral change was observed when the copper chelates studied here were treated in the same manner; only small shifts and intensity changes in their absorption curve occurred. Some data on the absorption bands in alcoholic solutions are given in Table I. It may be of interest that the bands of the two unstable chelates shift to shorter wavelengths in alcohol, while the bands of the other chelates generally shift in the opposite direction. The natures of these shifts were not studied in greater detail, however, partly because some of these chelates were sparingly soluble in such media, and also because of the lack of sufficient quantities for such a study.

It is also of some interest to compare the absorption curve of the chelate $[\mathrm{Cu}(N\text{-propyl-en})_2]^{2+}$ with that of $[\mathrm{Cu}(N\text{-hydroxyethyl-en})_2]^{2+}$, the ligand of which contains an $-\mathrm{OH}$ group instead of $-\mathrm{CH_3}$ at the end of the N-substituent radical. It has already been shown by Harvey, Hall et al.[6,7] that the latter complex is formed predominantly in a solution containing $\mathrm{Cu^{2+}}$ and N-hydroxyethyl-ethylenediamine in the ratio of 1:2; the absorption curve of such a mixture measured by the present authors (curve G, Fig. 1) agreed well with the data of these earlier investigators, showing a band at 590 mμ which lies at a much longer wavelength than the band of the N-propyl chelate, This difference is very probably due to the 5- (or possibly 6-) coordinated structure of the N-hydroxyethyl chelate, in which also the $-\mathrm{OH}$ group is taking part in coordination, since a number of instances showing that the formation of a 5- or 6-coordinated structure in a copper complex is generally accompanied by a shift of its absorption band to a longer wavelength is already known in the literature[8-11]. For example, Rosenblatt[8] found that the addition of a large quantity of $\mathrm{NH_3}$ to a solution of $[\mathrm{Cu\cdot en_2}]^{2+}$ produced a shift of its band at 550 mμ to ~610 mμ, owing to the formation of the complex $[\mathrm{Cu\,en_2NH_3}]^{2+}$, and Jonassen et al.[9] observed a similar shift in solutions containing $[\mathrm{Cu\,en_2}]^{2+}$ and NaOH, owing to the formation of $[\mathrm{Cu\,en_2OH}]^{+}$ in such media.

Effect of Added Alkali on the Spectra.—In their study of copper complexes of N-alkylated ethanolamines, the present authors found that the spectral data indicate the presence of at least two types of complexes, a chelate and a non-chelate, in their solutions containing various amounts of ligand and sodium hydroxide[12].

---

[4] Cf. e. g., R. Tsuchida, "Color and Structure of Metallic Compounds", Zoshindo, Osaka (1947); H. Ito, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1383 (1956).

[5] K. Sone and M. Kato, *Z. anorg. u. allgem. Chem.*, **301**, 277 (1959).

[6] J. L. Harvey, C. I. Tewksbury and H. M. Haendler, *J. Am. Chem. Soc.*, **71**, 3641 (1949).

[7] J. L. Hall and W. E. Dean, ibid., **80**, 4183 (1958).

[8] F. Rosenblatt, *Z. anorg. u. allgem. Chem.*, **204**, 351 (1932).

[9] H. B. Jonassen, R. E. Reeves and L. Segal, *J. Am. Chem. Soc.*, **77**, 2748 (1955).

[10] S. Yamada and R. Tsuchida, This Bulletin, **29**, 289 (1956).

[11] H. Ito, Ref. 4.

[12] H. Ojima and K. Sone, *Z. anorg. u. allgem. Chem.*, **309**, 110 (1961).

The effect of added alkali on the spectra of the alkylated ethylenediamine chelates, which were studied in a manner similar to that of Jonassen et al. cited above, is now shown in Figs. 3 and 4; it can be seen that the situation is quite different here from that in ethanolamine complexes, owing to the increased stability of the chelate rings formed by the diamine molecules[13].

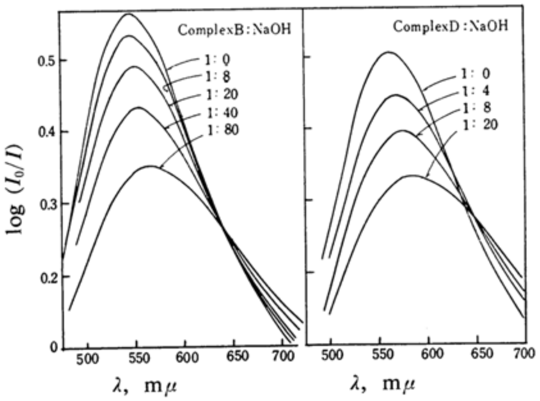


Fig. 3. Effect of added alkali on the spectra of $[Cu(\text{tetramethyl-en})_2]^{2+}$ (B) and $[Cu\cdot(N\text{-propyl-en})_2]^{2+}$ (D).

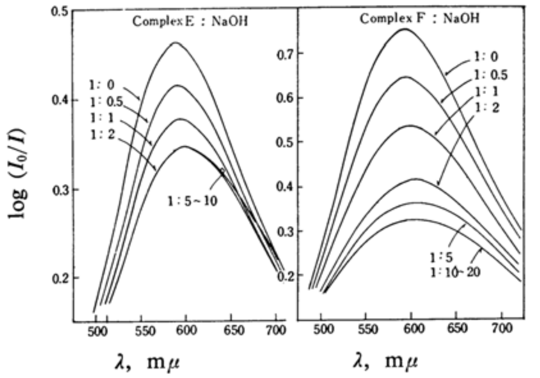
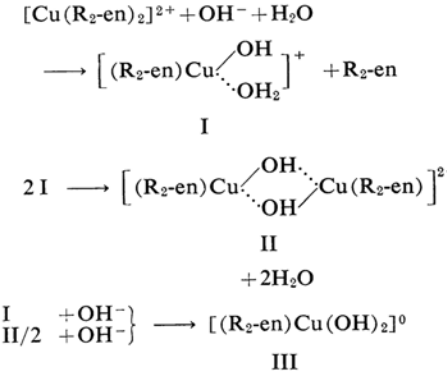


Fig. 4. Effect of added alkali on the spectra of $[Cu(N,N'\text{-dipropyl-en})_2]^{2+}$ (E) and $[Cu(N,N\text{-diethyl-en})_2]^{2+}$ (F).

In the case of tetramethyl and *N*-propyl chelates (Fig. 3), it can be seen that the appearance of the spectral changes is very similar to that of $[Cu\,en_2]^{2+}$ described by Jonassen et al.; this indicates the gradual formation of the complexes of the type $[Cu\,en_2\cdot OH]^+$ with an increasing OH^- concentration. Approximate values of their formation constants can be estimated at ~2 and 15 respectively from analysis of the curves in Fig. 3.

On the other hand, the situation is somewhat different in the case of *N, N'*-dipropyl and *N, N*-diethyl chelates. The curves in Fig. 4 show that even relatively small amounts of sodium hydroxide can cause a great decrease in their absorption intensities; as soon as only two moles of OH^- ions are added to one mole of the chelate, the change seems to become more or less complete.

Now the drastic spectral changes of these chelates can be explained in the following manner: because there are so many and such large alkyl groups around the coordination center, it is to be expected that the formation of the $[Cu\,en_2OH]^+$-type complexes would be strongly hindered in these chelates; however, the steric interactions of these groups make these chelates themselves unstable (cf. log *k* values in Table 1), so that they are easily decomposed by relatively small amounts of OH^- ions, probaly through the following successive steps:



$$[Cu(R_2\text{-en})_2]^{2+}+OH^-+H_2O \longrightarrow \left[(R_2\text{-en})Cu\begin{matrix}OH\\OH_2\end{matrix}\right]^+ +R_2\text{-en}$$

I

$$2\,\text{I} \longrightarrow \left[(R_2\text{-en})Cu\begin{matrix}OH\\OH\end{matrix}Cu(R_2\text{-en})\right]^{2+}$$

II

$$+2H_2O$$

$$\left.\begin{matrix}\text{I} & +OH^-\\ \text{II}/2 & +OH^-\end{matrix}\right\} \longrightarrow [(R_2\text{-en})Cu(OH)_2]^0$$

III

In fact, Pfeiffer and Glaser[1] obtained binuclear complexes like II by using *N, N'*-trialkylated ethylenediamines as ligands, and Martell et al.[14] recently studied the equilibria involving chelates of types I, II and III by using ligands which are very similar to those in this study.

Therefore, it seems probable that the spectral changes in Fig. 4 are due to these decomposition reactions, which lead eventually to the complexes of the type $[Cu\,en(OH)_2]$ with no electric charge. Experimental data supporting this point of view are also obtained from the studies of the behaviors of these chelates in paper electrophoresis.

Paper Electrophoresis Studies.—It was found by Maki[15] and also Ojima[16] that there is a marked parallel between the migration velocities

---

[13] The precipitation of $Cu(OH)_2$, which frequently occurs in mixtures containing OH^- ions and *N*-alkylated ethanolamine complexes (cf. Ref. 12), is not observed in the solutions of the compositions shown in Figs. 3 and 4.

[14] A. E. Martell, S. Chaberek, R. Courtney, S. Westerback and H. Hyytiainen, *J. Am. Chem. Soc.*, **79**, 3036 (1957); R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr. and A. E. Martell, ibid., **81**, 519 (1959); R. L. Gustafson and A. E. Martell, ibid., **81**, 525 (1959).

[15] M. Maki, *Japan Analyst* (*Bunseki Kagaku*), **4**, 217 (1955).

[16] H. Ojima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1331 (1957).

of ionic complexes in paper electrophoresis experiments and the magnitudes of their electric charges, if complexes with similar structures are used for comparison. The results of such experiments on the chelates studied here, carried out in solutions containing various amounts of sodium hydroxide, are shown in Fig. 5. In solutions containing no sodium hydroxide, the mobilities of the alkylated chelates are all smaller than that of $[Cu\cdot en_2]^{2+}$ and are not very different from one another, although it seems that the mobility becomes smaller with the increase in substituted alkyl groups. The mobilities of the more stable chelates of ethylenediamine and tetramethyl- and *N*-propyl-ethylenediamines do not change very much with the addition of OH^- ions, and they gradually decrease when the alkali concentration becomes large, probably owing to the formation of $[Cu\,en_2OH]^+$-type complexes. On the other hand, the mobilities of the two other chelates begin to drop quickly and approach zero with an increasing alkali concentration, indicating the final formation of uncharged complexes. The color of the spots indicates, however, that there is no precipitation of $Cu(OH)_2$, and the tailing of the spots observed when the alkali concentration is $5\sim25\times10^{-4}$ N suggests the coexistence of two or more complex species in solution. All these findings are in accord with the foregoing considerations based on the spectral changes of these chelates.

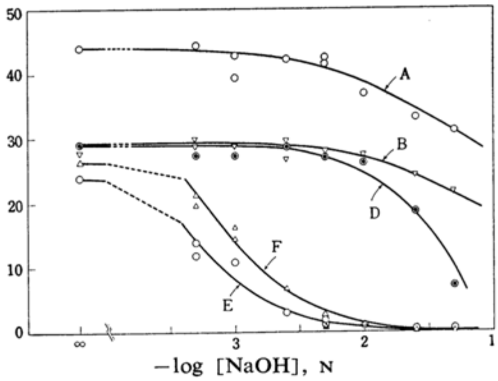


Fig. 5. Relation between migration distance and alkali concentration. A, B,⋯, F: cf. Table I.

Catalytic Behavior in the Chemiluminescence of Luminol.—It was shown earlier by Ojima[17,18] that the chemiluminescence emitted in the reaction between luminol (5-aminophthalaz-1, 4-dione) and hydrogen peroxide in alkaline solution is remarkably intensified by various amine complexes of copper. The mode of this catalytic action depends strongly on the nature of the amine used; NH_3, pyridine, and primary aliphatic amines are all effective, but complex solutions containing these ligands in a great excess (Cu: amine=1: several hundreds when the concentration of Cu^{2+} is 5×10^{-6} g. ion/7 ml.) must be used to obtain the maximum effect. On the other hand, only a small quantity of ethylenediamine (Cu : en = approx. 1 : 2) is sufficient to create an effect of similar magnitude, and the luminescence is markedly hindered when ethylenediamine is added in excess.

On the basis of these and other results, Ojima postulated the formation of an intermediate complex $[Cu\cdot en\cdot(\text{luminolate anion})]^+$ in such media, which reacts more easily with hydrogen peroxide than free luminol, emitting a stronger luminescence than that of the latter.

It was found that all the chelates studied here show the same catalytic effect; the relation between the observed luminescent intensities and alkali concentrations are shown in Fig. 6, and the relation between the maximum intensities in this figure and the chelate stabilities is shown in Fig. 7. It is clear from these data that the catalytic activity increases with the decreasing chelate stability; this fact is also in conformity with the mechanism postulated above, since the formation of the complex $[Cu\cdot en\cdot(\text{luminolate anion})]^+$ will be facilitated by the instability of the original chelate.

It is certain that many further studies are

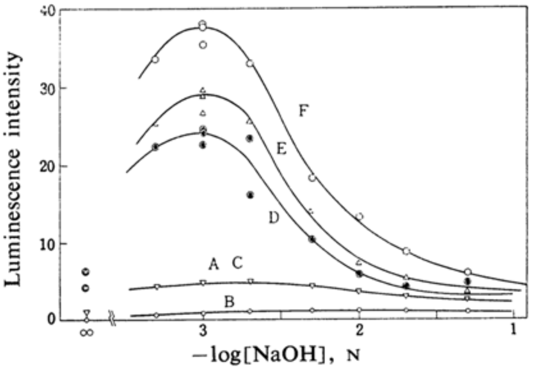


Fig. 6. Relation between chemiluminescence intensity and alkali concentration in the reaction mixture. A, B,⋯, F: cf. Table I.

---

[17] H. Ojima, ibid., **79**, 1076 (1958); **80**, 965, 1371 (1959); **81**, 1785 (1960).

[18] Recently, the authors found that the data of B. Kirson (*Bull. soc. chim. France*, **1956**, 1793; **1957**, 257) on the catalytic decomposition of H_2O_2 by copper complexes are of special interest in connection with this problem. Some data on the absorption spectra of Cu-ammine complexes are also given in his papers. However, the possible relation of his results to those of the authors will be discussed more fully elsewhere.

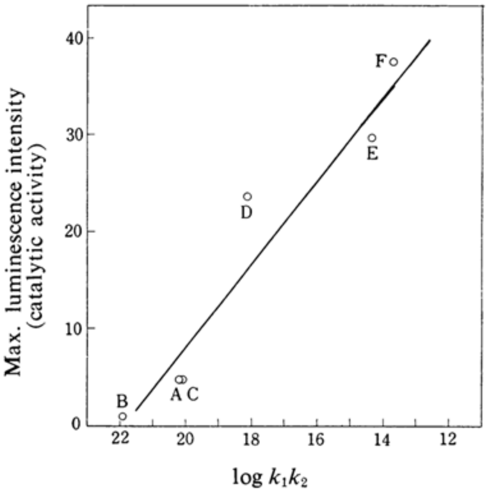


Fig. 7. Relation between catalytic activity and chelate stability. A, B,···, F: cf. Table I.

needed to get a clear understanding of this complicated reaction; however, even apart from the discussions of the reaction mechanism, the data in Figs. 6 and 7 are of practical interest, because they suggest a new method of estimating chelate stabilities with the aid of chemiluminescence measurements, although its application will be limited to certain favorable cases like the present ones.

Summary

The absorption spectra of the copper chelates of ethylenediamine and several alkylated ethylenediamines were studied in their aqueous solutions, and an approximately linear relationship was found between the frequencies of their absorption maxima and the logarithms of their stability constants. The spectral changes caused by the addition of a strong base (sodium hydroxide) to these solutions, and the activities of these chelates to catalyze the chemiluminescent reaction of luminol with sodium peroxide in an alkaline solution, were also studied; it was shown that the chelates with smaller stabilities show, in general, more drastic spectral changes and higher catalytic activities than those with larger stabilities.

The authors are grateful to Professor Fred Basolo of Northwestern University, Evanston, Ill., U. S. A., for his invaluable gift of chelate samples, and also to Professor Hatsusaka Kato of their University for his encouragement throughout this study.

Aichi Gakugei University
Chemical Laboratories
Okazaki and Nagoya