mixture of known composition in a sealed tube was determined in a special rocker-heating apparatus by slowly raising the temperature. Supercooling phenomena prevented a check of these data by the cooling method.

Solid phase analyses were obtained by direct sampling of the solid in equilibrium with the saturated solution. The sample was then dried between filter paper, weighed, and ignited to ThO_2.

The thermometers used in the analytical determinations were standardized against a Bureau of Standards platinum resistance thermometer. The temperature readings of data obtained by the synthetic method were measured with an iron–constantan thermocouple.

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RECEIVED MARCH 12, 1951

On the Nature of the Reaction between Gelatin and Some Copper(II) Complexes

BY LOUIS MEITES

During the course of some earlier work on the polarographic effects of gelatin and other maximum suppressors, it was noted that pronounced changes in the colors of some of the solutions occurred at or near the polarographic critical concentration of the surface-active material.[1] The present note describes the results of a spectrophotometric investigation of some typical systems containing gelatin and a colored metal complex.

Experimental

Spectrophotometric measurements were made with a Beckman Model B spectrophotometer, using band widths of 4 millimicrons or less. Absorbancy measurements were generally reproducible to ±0.003 unit or ±1%, whichever was greater.

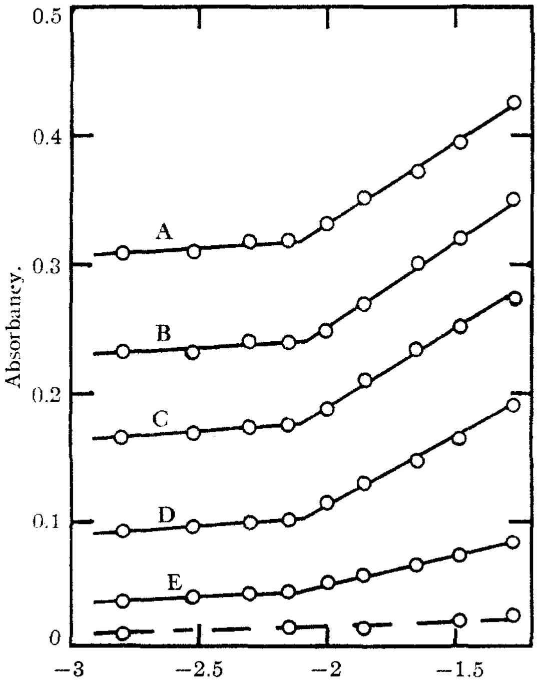

Fig. 1.—Spectrophotometric titration of 0.80 mM copper(II) in 1.0 F potassium hydroxide–0.50 F potassium citrate with gelatin at (A) 320, (B) 325, (C) 330, (D) 340 and (E) 360 mμ. The dashed line represents the absorbancies at 330 mμ of copper-free 1.0 F potassium hydroxide–0.50 F potassium citrate solutions containing various concentrations of gelatin.

The gelatin was identical with that used in the earlier study,[1] and its solutions were prepared in the same manner. They were always used within 8 hours of preparation. Other materials were ordinary reagent grade. As the polarographic characteristics of aged solutions of the copper complexes differ in some respects from those of fresh solutions, indicating a slow deterioration (precipitates of cupric oxide are frequently observed after long standing), no solution was used after standing for more than 30 hours.

Data and Discussion

Figure 1 shows the effect of gelatin on the absorbancy of a solution of copper(II) in F potassium hydroxide–0.5 F potassium citrate at wave lengths between 325 and 360 mμ. Similar curves are obtained at other wave lengths where the extinction of the solution is sufficiently high to permit accurate measurements. Although the addition of 10^{-4}% gelatin increases the absorbancy at any given wave length very slightly over that in the original solution, no further detectable change occurs as the gelatin concentration is increased to about 5×10^{-3}%. However, at the "optical critical concentration" (whose definition and measurement are clear from Fig. 1), the absorbancy begins to increase, and continues to rise in every case up to the highest gelatin concentration used (sometimes as high as 0.7%).

This behavior is very like the previously described effects of gelatin on the interfacial tension between mercury and an electrolyte solution and on various polarographic phenomena. Moreover, the optical and polarographic critical concentrations are in excellent agreement in every case where data on both are available. For example, in F potassium hydroxide–F potassium citrate the values of pC [$= -\log$ (critical concentration)] are 2.22 (2 mM copper) and 2.31 (0.5 mM copper) from optical measurements, and 2.28 from polarographic

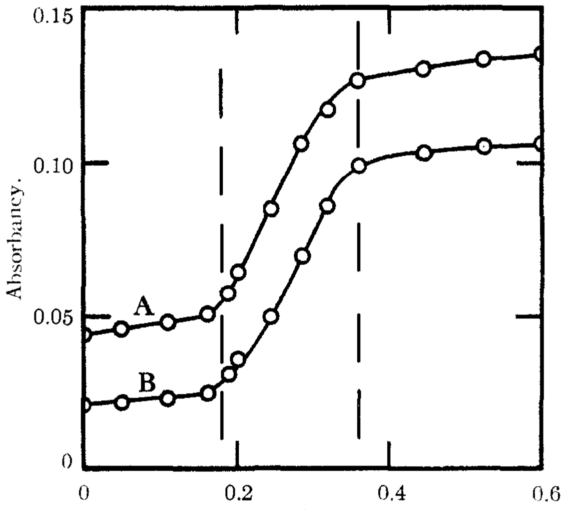

Fig. 2.—Spectrophotometric titration of 3.00 ml. of 1.20 mM copper(II) in 1.0 F potassium hydroxide with 20.0 mM potassium citrate–1.0 F potassium hydroxide containing 1.20 mM copper(II). The dashed vertical lines correspond to the consumption of one and two citrate ions per copper atom. Measurements were made at (A) 320 and (B) 340 mμ.

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[1] L. Meites and T. Meites, THIS JOURNAL, **73**, 177 (1951).

data. In F potassium hydroxide alone the optical value is 2.50 and the polarographic value is 2.49.[2] Other values of pC found from spectrophotometric measurements are reported in Table I.

TABLE I

OPTICAL CRITICAL CONCENTRATIONS OF GELATIN IN VARIOUS MEDIA

Supporting electrolyte	Copper (II), millimolar	pC
1 F KOH–1 F K_3Cit	5.0	2.16
	1.0	2.19
1 F KOH–0.5 F K_3Cit	5.0	2.20
	2.0	2.11
	0.80	2.09
1 F KOH–0.1 F K_3Cit	2.0	2.22
	0.50	2.31
0.1 F KOH–1 F K_3Cit	0.50	2.11
0.1 F KOH–0.5 F K_3Cit	0.50	2.14
1 F KOH–0.5 F Na_2Tart	2.0	2.39
	1.0	2.37
1 F KOH	1.0	2.50
5 F KOH	2.0	2.74

This phenomenon might be thought to be due to the successive formation of two complexes between gelatin and the complex metal ion. Of these two complexes, the one formed at lower gelatin concentrations would have to have an absorption curve substantially identical with that of the original metal complex, while the other, formed above the optical critical concentration, must have an absorption curve differing from that of the original complex only in having much higher extinction coefficients.

Such a combination of characteristics is improbable but by no means impossible, an actual example being shown by Fig. 2. This represents the data secured in the spectrophotometric titration of copper(II) (as cuprate) with potassium citrate in F potassium hydroxide. The breaks in this curve correspond to the successive formation of complexes containing one and two citrates per copper atom, and there is little evident difference between this curve and those of Fig. 1. However, the positions of the end-points in titrations like those of Fig. 2 depend in the expected stoichiometric fashion on the amount of copper present, while there is no such dependence in the gelatin experiments. Thus, in F potassium hydroxide–0.5 F potassium citrate the optical critical concentration is independent of the copper concentration between 0.8 and 5 mM within about ±10%, which is approximately the experimental error.

Therefore the optical critical concentration must represent the point at which binding of copper begins, rather than the point at which a second type of complex begins to form. It seems probable that the reaction above the optical critical concentration consists essentially of the binding of the complex metal ions at loci of attachment (presumably the carboxylate groups) on the gelatin micelles which appear near the critical concentration. There is little or no evidence that gelatin at concentrations below the critical concentration is capable of binding any of these complexes.

In view of the marked effect on pH on the binding of cupric ions by bovine serum albumin demonstrated by Klotz and Curme,[3] it is of interest that at pH values near 7, Klotz[4] found no effect of even as much as 1% gelatin on the spectra of the methyl orange or azosulfathiazole anions, while in the present study no spectra alterations were produced by the addition of gelatin to the anionic carbonate, citrate, oxalate or tartrate complexes of copper(II) at pH values between 9 and 11.5.

It should be mentioned that the increasing absorbancy above the optical critical concentration is not due to the slight turbidity of the stock gelatin solution used, as shown by the dashed line in Fig. 1. Nor is it due to the formation of a turbidity in the solutions containing copper(II) and gelatin, for the absorbancy at 475 mμ invariably remained constant at 0.002 ± 0.003 up to the highest concentration of gelatin used: this could not have been the case if any significant amount of dispersed solid had been formed.

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[2] E. L. Colichman, THIS JOURNAL, **72**, 4036 (1950).

[3] I. M. Klotz and H. G. Curme, THIS JOURNAL, **70**, 939 (1948).

[4] I. M. Klotz, *ibid.*, **68**, 2299 (1946).

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RECEIVED APRIL 11, 1951

Concerning the Reduction of α-Bromoketones by Hydrogen Bromide

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It is known that the reaction of bromine with a ketone to yield α-bromoketone and hydrogen bromide is reversible.[1]

$$RCOCH(R)_2 + Br_2 \rightleftarrows RCOC(R)_2Br + HBr$$

It has been shown that the equilibrium constant ($K_{eq} = [RCOC(R)_2Br]\,[HBr]/[RCOCH(R_2)][Br_2]$ is quite small when the hydrogen replaced in the ketone is acidic,[1d] but considerably larger in ketones such as acetophenone.[1c] It has also been shown that the rate of acid-catalyzed bromination is independent of the bromine concentration and that the bromination proceeds through the enol form.[2] There has been little discussion of the way in which bromine reacts with the enol form to yield bromoketone, possibly because the rate is too fast to measure.[2] Addition of bromine to an olefin is commonly represented by the formation of an intermediate cyclic bromonium ion,[3] and, in the absence of an alternate explanation, this mechanism might be assumed to apply to the bromination of an enol. However, it is possible to write a cyclic intermediate involving a six atom ring, I, which will account for the bromination of the enol form and also a similar six atom ring, II, which will picture the reduction of a bromoketone by hydrogen bromide.

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[1] (a) A. Lapworth, *Mem. Manchester Phil. Soc.*, **64**, ii, 8 (1920); (b) R. Robinson, *Ann. Reports Chem. Soc.*, 1922, p. 100 ff; (c) F. Kröhnke and H. Timmler, *Ber.*, **69**, 614 (1936); F. Kröhnke, *ibid.*, **69**, 921 (1936); (d) R. Altschul and P. D. Bartlett, *J. Org. Chem.*, **5**, 623 (1940).

[2] The evidence is summarized in L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 231 ff.

[3] The evidence is summarized in ref. 2, p. 147 ff.