[JOINT CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY AND THE DEPARTMENT OF AGRICULTURAL CHEMISTRY OF PURDUE UNIVERSITY]

Complex Formation with High Molecular Weight Amines. II.[1] A Spectrophotometric Study of the Dodecylamine–Cupric Acetate System

BY F. K. BROOME, A. W. RALSTON AND M. H. THORNTON[2]

In the first paper,[3] it was mentioned that no complex compounds of high molecular weight amines and metal salts containing a ratio of amine to metal greater than 2:1 could be obtained. However, it has been noted that a solution of a 2:1 complex containing copper becomes a deeper blue upon the addition of an excess of the corresponding amine. With the thought that compounds other than the 2:1 complex might exist in solution, we have here attempted to apply the Method of Continuous Variations as expanded by Vosburgh and Cooper[4] to the dodecylamine–cupric acetate system.

Experimental

Starting Materials.—Dodecylamine and cupric acetate were prepared as described earlier.[3] Reagent-grade trichloromethane and absolute ethanol were used throughout.

Instrument.—The optical density measurements were performed in a Beckman Photoelectric Spectrophotometer, Model DU, with a cell length of one centimeter.

Data.—Seven solutions, all 0.001 *M* with respect to cupric acetate and ranging from zero to 0.006 *M* with respect to dodecylamine, were made up in a solvent comprising 90% of trichloromethane and 10% of ethanol by volume. The absorption spectra of these solutions were determined through the range 500–850 mμ. Figure 1 presents the curves obtained. A second series of measurements, similar to the first but with trichloromethane alone as the solvent, was made on mixtures of dodecylamine and cupric acetate from 2:1 to 6:1 and on a solution of pure bis-dodecylamino-cupric acetate in trichloromethane at the same concentration. (Solution of cupric acetate alone and in the 1:1 mixture cannot be effected in this solvent at this concentration.) The data are presented in Fig. 2.

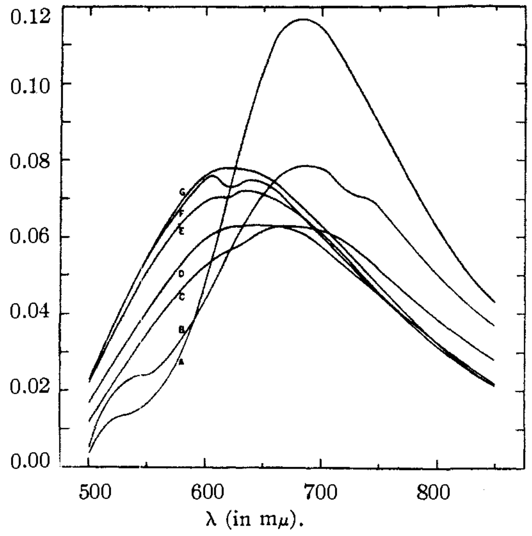

Fig. 1.—Spectra of dodecylamine-cupric acetate mixtures in 90% chloroform–10% ethanol. All solutions are 0.001 *M* with respect to copper: A, 0:1; B, 1:1; C, 2:1; D, 3:1; E, 4:1; F, 5:1; G, 6:1 (amine to copper).

Equimolar solutions (0.001 *M*) of cupric acetate and of dodecylamine, in the trichloromethane–ethanol solvent, were mixed in a series of ratios, the final volume being the same in every case. The spectra of these mixtures were determined at eight wave lengths from 550 to 900 mμ. However, the construction of γ curves at any of these wave lengths gave inconclusive results. Even the 2:1 complex, which is known to exist, could not be demonstrated by this means.

When a dilute trichloromethane solution of bis-dodecylamino-cupric acetate is shaken with water the compound is split, the copper salt passing into the aqueous layer and the amine remaining in the trichloromethane. Inasmuch as water alone has no effect on the compound at room temperature, it is obvious that dissociation occurs in trichloromethane solution. This dissociation can be used to explain the appearance of the curves in Figs. 1 and 2, and also the failure of the Method of Continuous Variations to yield conclusive results. The shift toward the shorter wave lengths with the addition of amine indicates a suppression of dissociation. In the presence of dissociation the procedures of Vosburgh and Cooper are inapplicable, since it is a primary requirement that the compound formed be stable in the absence of a significant excess of either component.

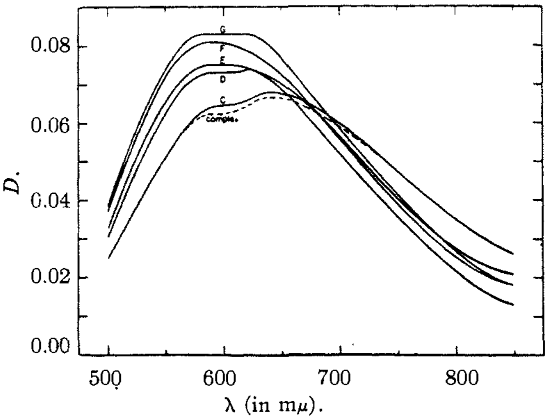

Fig. 2.—Spectra of dodecylamine–cupric acetate mixtures and of bisododecylamino-cupric acetate in chloroform. All solutions are 0.001 *M* with respect to copper: C, 2:1; D, 3:1; E, 4:1; F, 5:1; G, 6:1 (amine to copper).

The existence of dissociation should be demonstrable by the synthesis of an absorption curve from that for cupric acetate and that for undissociated complex. From some data not recorded here it has been ascertained that cupric acetate in trichloromethane has an absorption spectrum similar to that in the 90–10% mixture, with its maximum at the same wave length, 680 mμ. The exact height of such a curve could not be ascertained, since the

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[2] M. H. Thornton is a member of the Department of Agricultural Chemistry, Purdue University Agricultural Experiment Station, Lafayette, Indiana.

[3] Broome, Ralston and Thornton, THIS JOURNAL, **68**, 67 (1946).

[4] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

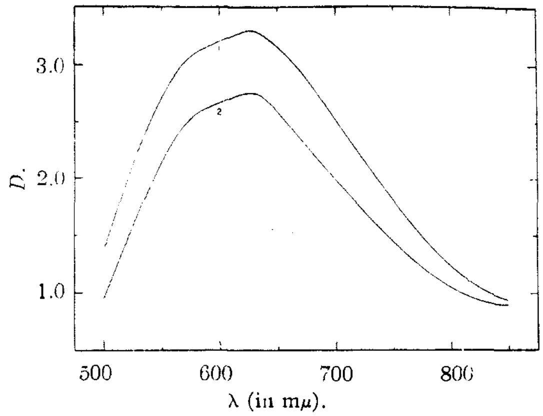

Fig. 3.—Calculated "10%-dissociation" spectrum and spectrum of 0.04 *M* bisdodecylammino-cupric acetate in chloroform. Explanation in text.

solution used was too dilute to be analyzed quantitatively. However, it is reasonable to assume that the curve in trichloromethane is very near to that in the mixed solvent. Since it has been found that the absorption spectrum of a solution containing amine and cupric acetate in the molar ratio of 10:1 is little different from that obtained from the 6:1 mixture, the latter may be assumed to represent the curve for undissociated complex. Thus a combination of the absorption curve for cupric acetate (curve A, Fig. 1) and that for the 6:1 mixture (curve G, Fig. 2), in suitable proportion, should yield a curve similar to that for the complex itself. Curve 1 of Fig. 3 is such a synthetic curve, constructed by the addition of 10% of curve A, Fig. 1, to 90% of curve G, Fig. 2. It thus represents a "10%-dissociation" curve. For purposes of comparison, the values were multiplied by a factor of 40. Curve 2 of Fig. 3 represents the spectrum of a 0.04 *M* solution of bisdodecylammino-cupric acetate in trichloromethane. The two curves are nearly identical, except that the second is lower. This indicates a departure from Beer's law, which is further evidenced by data depicted in Fig. 4, where curve 1 represents forty times the spectrum of a 0.001 *M* solution of cupric acetate containing 0.006 mole of dodecylamine per liter, and curve 2 represents the spectrum of a 0.04 molar solution of cupric acetate containing 0.24 mole of dodecylamine per liter. Both solutions were made up in trichloromethane.

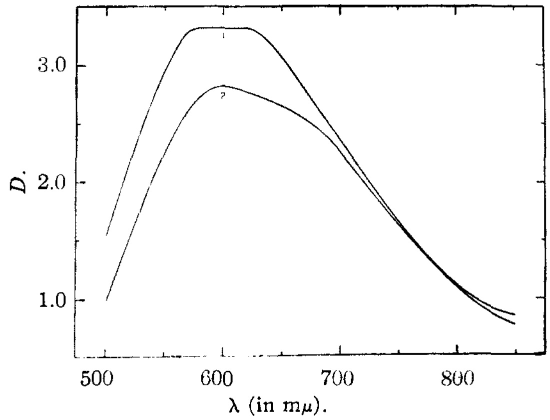

Fig. 4.—Spectra of 6:1 mixtures of dodecylamine and cupric acetate in chloroform. Curve 1, 0.001 *M* in respect to copper (times 40); curve 2, 0.04 *M* in respect to copper.

In Fig. 5 are presented absorption data at several wave lengths throughout the range from 500 to 850 mμ for varying concentrations of bisdodecylamino-cupric acetate. These data indicate that Beer's law is not obeyed except at wave lengths in the neighborhood of 600 mμ. This behavior is to be expected since a dissociable complex cannot obey Beer's law except in the special case in which it exhibits the same absorption characteristics as its products. Reference to Fig. 1 shows that this condition is obtained approximately in the region of 600 mμ.

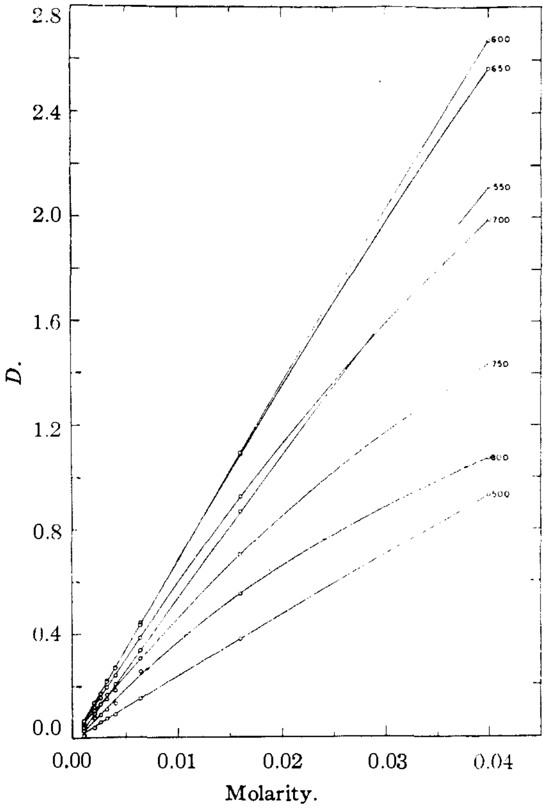

Fig. 5.—Densities of bisdodecylamino-cupric acetate solutions in chloroform at various wave lengths.

Discussion

One of the conditions set up by Vosburgh and Cooper[4] is that the complex formed shall be sufficiently stable so that no significant excess of either component is required as a stabilizing agent. It is evident that this condition is not fulfilled by the dodecylamine–cupric acetate system. Hence it is impossible to evaluate the results by the Method of Continuous Variations, and it is not to be expected that meaningful γ curves could be constructed. It cannot definitely be stated that ratios of amine to copper other than 2:1 do not exist. However, the present study has presented no evidence for the existence of such ratios in solution.

The evidence for the dissociation of bis-dodecylamino-cupric acetate in solution is threefold. First, there is the complete decomposition of the complex in trichloromethane solution when shaken with water. Second, there is the observed shift of maximum absorption toward the shorter wave lengths with increasing amine concentration. Since this shift is gradual and is unaccompanied by any sudden change in shape, it argues against the formation of higher ratios. The third line of evidence is furnished by the synthesis of a curve assuming dissociation which is almost identical with an experimental curve. The maxima of the curves are at the same wave length, 630 mμ, while there is a secondary maximum in each case at 580 mμ. The difference in height can be explained as a departure from Beer's law, which is attested by the data of Figs. 4 and 5.

In the construction of the "dissociation" curve, two assumptions were made. The first is that cupric acetate in trichloromethane exhibits the same spectrum as in trichloromethane–ethanol. The shape and position of the curves have been experimentally proved identical, and a slight difference in height would not alter the conclusion of dissociation, but would require only that a different percentage of dissociation be assumed. The second assumption, that the 6:1 curve represents the spectrum of the undissociated complex, is justified by the fact that curves obtained from solutions containing higher ratios of amine to copper are little different from the 6:1 curve. It is not contended that exactly 10% dissociation of this complex in trichloromethane exists at a 0.04 M concentration, but the actual percentage dissociation is in that neighborhood. It may quickly be demonstrated that calculated dissociations of 5 and 15% do not give curves which resemble the experimental curve very closely. At the higher dissociation, the secondary maximum disappears, while at the lower, this maximum exceeds the true maximum.

Summary

1. A spectrophotometric study of bisdodecylamino-cupric acetate has disclosed its dissociation in trichloromethane solution. At room temperature, a 0.04 M solution in trichloromethane is approximately 10% dissociated into dodecylamine and cupric acetate.

2. Due to its dissociation, this compound does not obey Beer's law except in a special instance.

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The Solubilities of Hexyl- and Dodecylammonium Chloride in Various Dilutions of Aqueous Ethanol

BY A. W. RALSTON AND C. W. HOERR

It has been observed by several investigators[1-4] that the solubility of colloidal electrolytes in water is unusual in that, beyond a certain critical concentration, the solubility increases enormously within a small temperature interval. For example, the solubility of dodecylammonium chloride in water increases from 0.4% by weight to 26.5% within the temperature range 28.0 to 30.0°. This solubility increase occurs at a concentration coincident with marked changes in the electrical behavior of the system, namely, an abrupt decrease in the equivalent conductance of the solutions and a sudden increase in the transference numbers of the colloidal ions. In view of this behavior, it would appear that micelle formation is accompanied by a marked change in the solubilities of the paraffin chain salts.

The solubilities of a number of the primary alkylammonium chlorides in 95% ethanol have recently been reported.[5,6] These salts present a quite normal behavior in this solvent in that their solubilities increase uniformly with increased temperatures. The comparison of this regular behavior in alcohol with the abnormal behavior of these salts in pure water suggested the investigation of both the electrical properties and the solubility characteristics of the alkylammonium chlorides in various mixtures of ethanol and water. Such studies should demonstrate the influence of the solvent upon micelle formation and may contribute to the better understanding of this phenomenon.

We have, therefore, determined the solubility of a typical colloidal electrolyte, dodecylammonium chloride, in various dilutions of aqueous ethanol, and have compared its behavior with that of a lower homolog, hexylammonium chloride. This latter salt can be assumed to function as an ordinary uni-univalent electrolyte.[7,8] The electrical properties of these salts in aqueous ethanol will be the subject of a subsequent report.

Experimental

Hexyl- and dodecylammonium chlorides were prepared from the corresponding primary amines, which had been previously purified by vacuum distillation in a Stedman-packed column. The salts were obtained by treating a benzene solution of the amine with concentrated hydrochloric acid and subsequent removal of the water by azeotropic distillation. The amine salts were recrystallized three times from benzene and analyzed for alkylammonium

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[1] Tartar and Wright, THIS JOURNAL, **61**, 539 (1939).

[2] Tartar and Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).

[3] Ralston, Hoffman, Hoerr and Selby, THIS JOURNAL, **63**, 1598 (1941).

[4] Hoerr and Ralston, *ibid.*, **64**, 2824 (1942).

[5] Harwood, Ralston and Selby, *ibid.*, **63**, 1916 (1941).

[6] Sedgwick, Hoerr and Ralston, *J. Org. Chem.*, **10**, 498 (1945).

[7] Ralston and Hoerr, THIS JOURNAL, **64**, 772 (1942).

[8] Paquette, Lingafelter and Tartar, *ibid.*, **65**, 686 (1943); Scott and Tartar, *ibid.*, **65**, 692 (1943).