Beeck's results and ours may originate from the fact that Beeck used pure metal films whereas the surfaces of our catalysts are contaminated with promoters and possibly with some residual hydrogen and nitrogen. In Fig. 2 is shown a complete isotherm at 78.5° K. and attention is called to the point that at this temperature the part of curve A corresponding to what is believed to be a first order transition is vertical within limits of experimental accuracy.

It should be noticed that we found a slightly higher value of the heat of adsorption when using the lower temperature interval than at the higher temperature, and we wish to stress the appreciably lower value found for adsorption to the uncondensed phase, which may easily be explained by the transition heat connected with the phase change. The values calculated should be compared with the heat of liquefaction of nitrogen, which is 1336 cal. per mole at -196°. We wish to call attention to the fact that the difference in isosteric heats of adsorption to the phases of higher and lower molecular area is of the same magnitude as the heat of liquefaction of nitrogen. This indicates that the heat of adsorption to the phase of highest molecular area is due to adsorbate–adsorbent forces, solely or at least mainly, whereas adsorbate–adsorbate forces become active in the phase transition range. The value of 1720 cal. determined below the phase transition interval may indicate that a potential of not purely van der Waals nature is active. In this connection the "structural" adsorption described by Cook, Pack and Oblad[10] may be mentioned.

The surface areas of a sample of reduced KM I determined by nitrogen adsorption at 78.5° and by argon adsorption at 89.5° K. were 7.71 m.^{2}/g., and 6.25 m.^{2}/g., respectively. As is evident from the above, we do not attribute this difference to the chemisorption of nitrogen, but to the molecular areas used for nitrogen and argon being not quite correct for representing the true cross-sectional areas of nitrogen and argon in the adsorbed monolayers. This observation is similar to the differences in nitrogen and argon areas for adsorption of these gases on silica gel, as described by Brunauer.[11]

As pointed out by Harkins and Jura[12] the appropriate area of a molecule on a surface—even when physically adsorbed—is somewhat dependent on the properties of the surface.

No measurable chemisorption of CO at liquid oxygen temperature could be established. This failure to observe carbon monoxide chemisorption at -183° is very surprising in view of the results that have been published relative to the chemisorption of CO on the surface of iron synthetic ammonia catalysts. Further it should be mentioned that all nitrogen adsorbed at low temperature is readily given off already at -78°, one more indication that the nitrogen is physically bound.

Acknowledgment.—The authors feel greatly indebted to Mr. Haldor Topsøe for valuable discussions during the work and for permission to publish the results.

---

[10] M. A. Cook, D. H. Pack and A. G. Oblad, *J. Chem. Phys.*, **19**, 367 (1951).

[11] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1945, p. 158.

[12] W. D. Harkins and G. Jura, *J. Chem. Phys.*, **11**, 431 (1943).

HELLERUP, DENMARK RECEIVED MAY 15, 1951

[CONTRIBUTION NO. 1625 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Spectrophotometric Investigation of the Copper(II) Monobromo Complex

BY PAUL S. FARRINGTON[1]

An equilibrium constant for the formation of the monobromo complex of copper(II) in solutions of unit ionic strength has been determined by a spectrophotometric method. At 22 ± 2° the average value for that equilibrium constant was found to be 2.1 ± 0.25. The molar extinction coefficient of $CuBr^+$, ϵ_1, has been determined over the range 260 to 300 millimicrons, and ϵ_1 is reported graphically as a function of wave length.

In the course of the study of the oxidation–reduction equilibrium between cupric copper and bromide made by Farrington, Meier and Swift[2] it became necessary to obtain information concerning the bromide complexes of cupric copper in order to calculate the desired equilibrium constants. For many years it has been known that cupric copper in concentrated bromide solutions (above 3.5 formal HBr) produces a reddish-brown to purple color; however, the only published constant[3] for a bromide complex appeared after the completion of the present investigation. McConnell and Davidson[4] have determined equilibrium constants for both the monochloro and dichloro complexes of cupric copper: the spectrophotometric method which they used is relatively uncomplicated for the determination of a monohalide complex and it was adopted for this investigation. All solutions used for these measurements were adjusted to an ionic strength of unity.

Experimental

Reagents.—A solution of $Cu(ClO_4)_2$ was prepared by dissolving $CuCO_3 \cdot Cu(OH)_2$ in $HClO_4$: the excess $HClO_4$ was very small. A solution of $Na_2S_2O_3$ was prepared and standardized against KIO_3. The $Cu(ClO_4)_2$ solution was then standardized iodometrically and the copper concentration was found to be 1.342 *F*.

A stock solution of NaBr (0.100 *F*) was prepared by dissolving a weighed portion of the reagent grade salt in chloride-free water and diluting to the mark in a volumetric flask. The NaBr had been dried for 1.5 hours at 120°. Solutions 0.0050 *F* and 0.0250 *F* in NaBr were prepared by accurate dilution of the stock solution.

A standard solution of $HClO_4$ (2.673 *F*) was prepared by

---

[1] Merck Graduate Fellow in Analytical Chemistry, 1949-50. Present address: University of California at Los Angeles.

[2] P. S. Farrington, D. J. Meier and E. H. Swift, to be published.

[3] R. Näsänen, *Acta Chem. Scand.*, **4**, 816 (1950).

[4] H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3164 (1950).

diluting 60% acid. Standardization of the acid was accomplished by the iodate method outlined by Swift.[5]

Apparatus.—A Beckman model DU spectrophotometer with hydrogen lamp was used for measurements of optical density. The rectangular right prism quartz cells were of 1.00-cm. path length.

Procedure.—All solutions were prepared by pipetting standard solutions into 50-ml. volumetric flasks and diluting to the marks. Flasks to contain bromide were flushed with CO_2 just before the addition of bromide solution. The $Cu(ClO_4)_2$ concentrations were 0.250 *F*, 0.210 *F*, 0.170 *F*, 0.135 *F* and 0.100 *F*. The NaBr concentration was always 0.005 *F*, and sufficient $HClO_4$ was added in each case to bring the ionic strength to unity. Each blank solution contained the amount of $HClO_4$ used in the corresponding copper complex solution: each copper comparison solution contained the same amount of $Cu(ClO_4)_2$ and $HClO_4$ as the corresponding copper complex solution.

The operation of transferring the copper complex solution to a spectrophotometer cell was performed in a large beaker into which a stream of CO_2 was passed. The cell was then closed with a rubber stopper which had been trimmed to fit the square top of the cell.

The spectrophotometer was balanced with the blank solution at each wave length, then the optical densities of a copper complex solution and the corresponding copper comparison solution were measured. Readings were taken at 5-mμ intervals from 260 to 300 mμ. To check possible drifting of the readings, optical densities of each set of solutions were remeasured at several wave lengths about 15 minutes after the first determination.

Discussion

For solutions of the same ionic strength one is justified in assuming that the activity coefficients of the ions of interest are constant even though the composition of the solutions is varied. Very dilute solutions cannot be used because there would be insufficient complex to give easily measurable absorption. In consideration of these facts a constant ionic strength of unity was chosen for this investigation. In the equilibrium

$$Cu^{++} + Br^- \rightleftarrows CuBr^+$$

let $(CuBr^+) = x$, then $(Cu^{++}) = a - x$ and $(Br^-) = b - x$. For the equilibrium constant, K, one obtains the relation

$$\frac{x}{(a-x)(b-x)} = K$$

If $a \gg b$ and $a \gg x$, as a first approximation

$$\frac{x}{b-x} = Ka$$

or

$$\frac{x}{b} = \frac{Ka}{1+Ka} \qquad (1)$$

By definition

$$D_0 = \epsilon_0 a \text{ and } D_1 = \epsilon_1 x$$

in which D_0 and D_1 are the optical densities of solutions which are a and x formal in Cu^{++} and $CuBr^+$, respectively, and which have a total ionic strength of 1.00. The quantities ϵ_0 and ϵ_1 are the molar extinction coefficients of Cu^{++} and $CuBr^+$, respectively. If D_{01} is the optical density of a solution a formal in copper perchlorate, b formal in sodium bromide and with sufficient perchloric acid to bring the ionic strength to unity, further use of the fact that $a \gg x$ yields the approximation

$$D_{01} = \epsilon_1 x + \epsilon_0 a$$

then

$$D_1 = \epsilon_1 x = D_{01} - D_0$$

Substituting in equation (1)

$$\frac{D_1}{b} = \frac{Ka\epsilon_1}{1+Ka}$$

and

$$\frac{D_{01} - D_1}{b} = \frac{Ka\epsilon_1}{1+Ka}$$

Inversion of this equation yields the relation

$$\frac{b}{D_{01} - D_0} = \left(\frac{1}{K\epsilon_1}\right)\frac{1}{a} + \frac{1}{\epsilon_1} \qquad (2)$$

If $CuBr^+$ is the only complex formed in significant quantity, then a plot of $(b)/(D_{01} - D_0)$ against $1/a$ should be a straight line. When the experimental data were plotted on such a graph, the points were somewhat scattered but no smooth curve other than a straight line could be passed through the points. In equation (2) it can be seen that the equilibrium constant, K, is obtained from the ratio of intercept to slope.

Instead of evaluating K graphically, the method of least squares was used to correlate the data. Although optical densities had been measured at nine wave lengths, the data used for the calculation of K was that which was taken in the region of maximum absorption by $CuBr^+$. After obtaining values of K, a check was made on the change of Cu^{++} concentration by complex formation: the numerical approximations made in deriving equation (2) are within experimental errors.

TABLE I

EQUILIBRIUM CONSTANT FOR THE COPPER(II) MONOBROMO COMPLEX IN SOLUTIONS OF UNIT IONIC STRENGTH

Wave length, mμ	K,[a] liter/mole
275	2.06
280	2.04
285	1.87
290	2.20
295	2.25
Av.	2.08

[a] $K = (CuBr^+)/(Cu^{++})(Br^-)$.

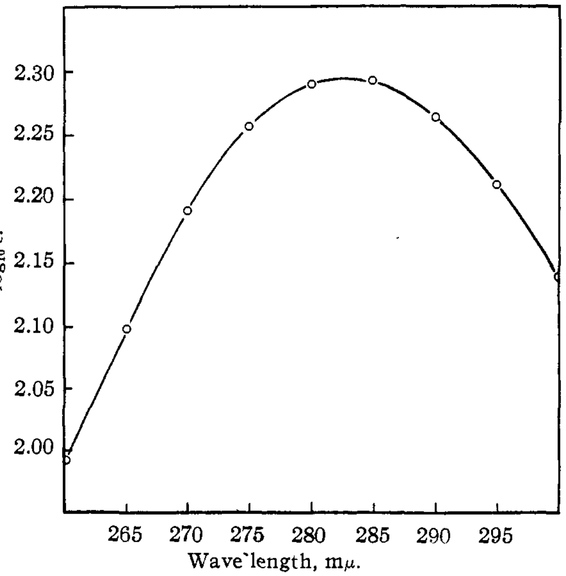

Fig. 1.—Molar extinction coefficient of $CuBr^+$ *vs.* wave length; solutions of unit ionic strength.

---

[5] E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1938, p. 245.

Values of K calculated from data at five wave lengths are presented in Table I. By means of standard formulas the probable error was calculated for each of the five slopes and intercepts. From an average value of the slopes, intercepts, and probable errors in those values, the probable error for the average value of K was found to be 0.249.

For each of the five solutions used in this investigation, the concentration of $CuBr^+$, x, was calculated using the average value of K. From the approximation mentioned above

$$D_1 = D_{01} - D_0$$

then

$$\epsilon_1 = \frac{D_1}{x} = \frac{D_{01} - D_0}{x}$$

Values of the molar extinction coefficient of $CuBr^+$, ϵ_1, were calculated for each of the five solutions, and the average value of ϵ_1 was found for each of the nine wave lengths. Figure 1 shows the curve obtained by plotting $\log_{10} \epsilon_1$ against wave length.

Experimentally, the work of Näsänen[3] differed from this investigation in one major respect: his solutions never contained an excess of cupric copper, and his assumption that higher complexes were negligible is less valid than is the same assumption for the present study. The results of the two investigations agree reasonably well. For solutions of similar ionic strength Näsänen reports an equilibrium constant of 3 to 4 as compared with 2.1 found in this work. In more dilute solutions he found the constant to be about 1.8.

Acknowledgment.—The author wishes to thank Professors N. R. Davidson and E. H. Swift for their helpful advice.

PASADENA, CALIFORNIA RECEIVED AUGUST 27, 1951

[CONTRIBUTION FROM THE FUNDAÇÃO A. E V. MATARAZZO, FACULDADE DE MEDICINA, UNIVERSIDADE DE SÃO PAULO, SÃO PAULO, BRASIL]

Molecular Compounds of Aminoazo Dyes and Bile Acids. II[1]

BY G. CILENTO

The investigation of the coördinating ability of carcinogenic aminoazo dyes for desoxycholic and cholic acids has been extended to *m*'-methyl-*p*-dimethylaminoazobenzene (I), *o*-aminoazotoluene (II) and *p*-diethylaminoazobenzene (III). The choleic acids were prepared and found to be tetracholeic acids. Phase equilibrium diagrams indicate that almost certainly (I) and (III) form an unstable 1:2 molecular compound with cholic acid. Like *p*-dimethylaminoazobenzene, (I) and (III) show quite different spectra in sodium desoxycholate and in sodium cholate solutions. The possible significance of the observed results is recorded.

In previous papers,[2,3] coördination compounds of *p*-aminoazobenzene and *p*-dimethylaminoazobenzene ("butter yellow") with desoxycholic acid were described. It was also reported[3] that none of these azo dyes forms an addition compound with cholesterol, whereas only the methylated azo dye forms a molecular compound, although a very unstable one, with cholic acid. The investigation has been extended to *m*'-methyl-*p*-dimethylaminoazobenzene, *m*,*o*'-dimethyl-*p*-aminoazobenzene ("*o*-aminoazotoluene") and *p*-diethylaminoazobenzene. Of these azo dyes, the first is known to be even more active than *p*-dimethylaminoazobenzene in inducing hepatomas in rats, the next only slightly active for the rat and the last devoid of any activity. Phase equilibrium diagrams of cholesterol and these aminoazo dyes were not investigated since the first systems involving this sterol showed no indication of molecular addition.[3,4]

Choleic Acids.—The choleic acids were prepared by the current procedure. No phase diagrams were worked out.

Like *p*-dimethylaminoazobenzene choleic acid, the choleic acids of the three azo dyes showed an acholic content between that expected for a tetracholeic and a hexacholeic acid. It has been again found that recrystallization from ethyl alcohol raised the percentage of the acholic component. Initially, it was thought that they also[3] may be a mixture of tetracholeic and hexacholeic acids, or that they are perhaps formed in the unusual 1:5 molar ratio. However, another explanation can be advanced, namely, that they are tetracholeic acids contaminated with the solvent, choleic acid. This explanation is supported by the striking rise in melting point following recrystallization observed for some of these choleic acids. It should be noticed that all these choleic acids were analyzed directly for their acholic content, for which reason possible contaminations would not have been masked. On these grounds, a rough estimation for the melting point of pure *m*'-methyl-*p*-dimethylaminoazobenzene- and *o*-aminoazotoluenetetracholeic acids would lead to figures still higher by 2 or 3°. The following sequence would then result: *m*'-methyl-*p*-dimethylaminoazobenzenecholeic acid (m.p. 210°), *p*-dimethylaminoazobenzenecholeic acid (m.p. 207°), *o*-aminoazotoluenecholeic acid (m.p. 200°), *p*-diethylaminoazobenzenecholeic acid (m.p. 194°) and *p*-aminoazobenzenecholeic acid (m.p. 183°). It may be further mentioned that during the preparation of these choleic acids the first two apparently crystallized faster than the others. These facts seem to suggest an increased stability in the choleic acids of carcinogenic aminoazo dyes.

[1] From a paper presented at the 3rd Annual Meeting of the Sociedade Brasileira para o Progresso da Ciência, Belo Horizonte, November, 1951.

[2] G. Cilento, THIS JOURNAL, **72**, 4272 (1950).

[3] G. Cilento, *ibid.*, **73**, 1355 (1951).

[4] A eutectic and very regular curves are depicted in the binary systems of cholesterol with anthracene, 1,2-benzanthracene or 9,10-dimethyl-1,2-benzanthracene (G. Cilento, 2nd Annual Meeting of the Sociedade Brasileira para o Progresso da Ciência, Curitiba, 1950).