[CONTRIBUTION FROM THE UNIVERSITY OF KENTUCKY]

Spectrophotometric Study of Cobalt(II) in Strongly Alkaline Solutions

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The system consisting of cobalt(II) in strongly alkaline solutions has been investigated spectrophotometrically over the range of 400 to 700 mμ. The absorbing species has been shown to obey Beer's law over the range of 3 through 12 *M* potassium hydroxide. A method has been presented the results of which indicate that the blue complex is a trihydroxy-cobalt(II) ion. The method is based upon the absorbancy of alkaline solutions saturated with cobalt(II) as a function of the hydroxyl ion activities.

Although the reaction involving the dissolution of cobalt(II) in strongly alkaline solutions producing a deep blue color has been utilized for the qualitative detection of cobalt,[2] the spectrophotometric properties of this colored complex have not been investigated. In addition, the only studies concerning the structure of this blue complex have involved electrometric and solubility measurements. Grube and Feucht[3] through investigations of the anodic dissolution of cobalt in 8 *M* potassium hydroxide proposed the following equation for the reaction

$$Co^{++} + 3OH^- \rightleftarrows HCoO_2^- + H_2O$$

Gayer and Garrett[4] by determining the solubility of cobaltous hydroxide in dilute sodium hydroxide solutions showed that the principal ionic reaction which determined the solubility was that for the formation of the acid anionic salt radical, or the trihydroxy complex, *i.e.*

$$Co(OH)_2 + OH^- \rightleftarrows HCoO_2^- + H_2O, \text{ or } Co(OH)_3^-$$

The present investigation was undertaken in order to determine the spectrophotometric properties of the absorbing species of cobalt(II) present in strongly alkaline solutions, and to obtain data which might be used for the determination of the structure of the blue complex ion.

Apparatus and Reagents.—Transmittancy data were obtained with a Beckman DU spectrophotometer using matched 1.00-cm. corex cells. Spectral band widths of the order of 5 mμ were used.

The cobaltous nitrate hexahydrate was C.P. reagent quality. U.S.P. potassium hydroxide was used. The strongly alkaline solutions containing cobalt were prepared by adding several drops of saturated cobaltous nitrate solution to the alkali hydroxide solution with vigorous stirring. After the predetermined amount of dissolution of the cobaltous hydroxide had been attained, the mixture was filtered through a fine fritted-glass funnel. Aliquots of the filtrate were removed for analysis, and the remainder was used for the spectrophotometric measurements. After acidification with sulfuric acid, the cobalt concentrations were determined, by the nitroso-R-salt spectrophotometric method of Young, Pinkney and Dick.[5]

Experimental

Spectral Characteristics.—The spectrophotometric curves of per cent. transmittancy as a function of wave length for a series of seven different concentrations of cobalt in 12 *M* potassium hydroxide solutions were determined over the range 400 to 700 mμ. These curves are presented in Fig. 1. They exhibit absorption maxima at wave lengths of 535, 585 and 625 mμ. The conformity to Beer's law of these solutions at the absorption peaks of 535 and 585 mμ is demonstrated in Fig. 2. Assuming that the intercept constant is negligible and within experimental error, (it being about 2% of the value for A when C equals 100 mg./liter), molar absorption coefficients of 137 and 216 were obtained at 535 and 585 mμ, respectively.

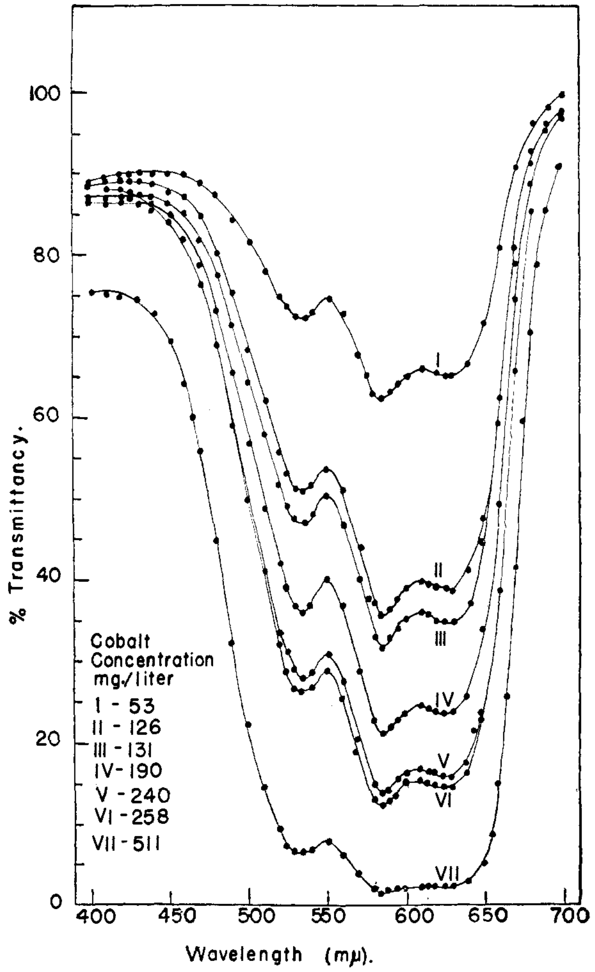

Fig. 1.—Per cent. transmittancy as a function of wave length for cobalt(II) in 12 *M* potassium hydroxide; 1.00 cm. cells, 30°.

The spectral curves for saturated solutions of cobalt in 3 through 12 *M* potassium hydroxide exhibit the same types of curves as did the various concentrations of cobalt in twelve molar potassium hydroxide. The obedience to Beer's law for this series of solutions, where each point represents a different hydroxyl ion concentration in the 3–12 *M* range, may be seen in Fig. 3. Again, assuming that the intercept constant is negligible, molar absorption coefficients of 134 and 216 were obtained for 535 and 585 mμ, respectively.

From these data one may conclude that either the com-

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[2] Saul Gordon and J. M. Schreyer, *Anal. Chem.*, **23**, 381 (1951).

[3] George Grube and O. Feucht, *Z. Elektrochem.*, **28**, 568 (1922).

[4] K. H. Gayer and A. B. Garrett, THIS JOURNAL, **72**, 3921 (1950).

[5] R. S. Young, E. T. Pinkney and R. Dick, *Ind. Eng. Chem., Anal. Ed.*, **18**, 474 (1946).

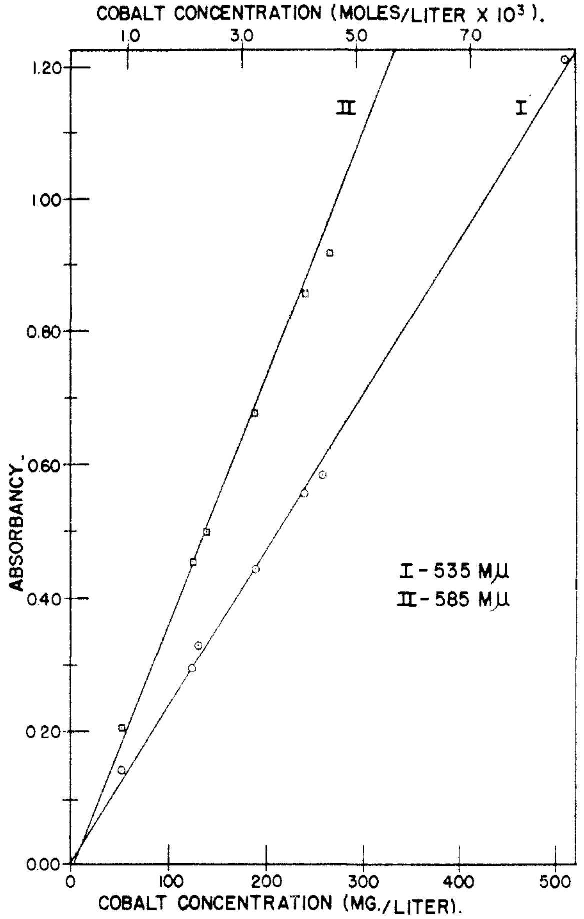

Fig. 2.—Absorbancy as a function of cobalt(II) concentration in 12 M potassium hydroxide; 1.00 cm. cells; 0.020 mm., slit width, 30°.

plex contains only one cobalt atom per ion species or is negligibly dissociated.

The Number of Coördinated Hydroxyl Ions.—It was not feasible to apply the method of continuous variations[6a,b] to the determination of the number of complexing hydroxyl ions because of the limited solubility of the cobalt in alkaline solutions. The molar ratio[7] method was deemed inapplicable because the ratio of the cobalt concentration to the hydroxyl ion concentration on a molar basis had a maximum value of about 1×10^{-3}. The slope ratio method[7] was not used because varying the hydroxyl ion concentration from 3 through 12 M was without effect upon the absorption coefficient of the complex ion, as shown in Fig. 3. It became apparent that a solution of the problem lay in the effect of the hydroxyl ion concentration on the solubility of the cobalt(II). The following method was developed by which the solubility could be related to the observed absorbancy.

It was assumed that the two equilibria which represent the system, consisting of alkaline solution saturated with respect to cobalt at 25°, are those for the precipitation of cobaltous hydroxide and the formation of the hydroxy complex ion of cobalt. The former may be represented as

$$Co(H_2O)_6^{++} + 2OH^- \rightleftarrows Co(OH)_2(H_2O)_4 \downarrow + 2H_2O \qquad (1)$$

with the solubility product constant

$$K_{sp} = [Co(H_2O)_6^{++}][OH^-]^2 \qquad (2)$$

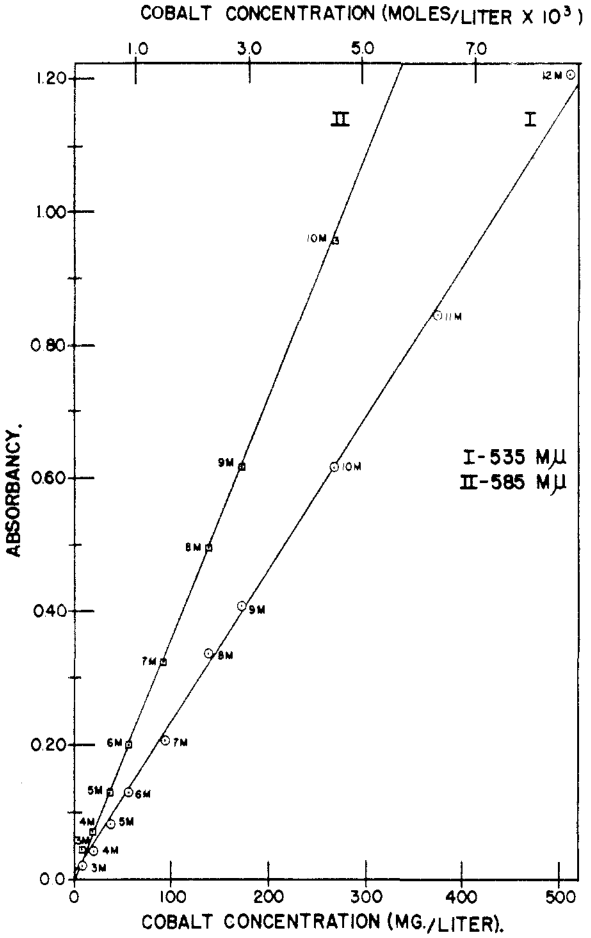

Fig. 3.—Absorbancy as a function of saturated cobalt(II) concentration in 3–12 M potassium hydroxide solutions; 1.00 cm. cells; 0.020 mm., slit width; 30°.

and the latter assuming one cobalt(II) atom per complex as

$$Co(H_2O)_6^{++} + nOH^- \rightleftarrows Co(OH)_n(H_2O)_{6-n}^{2-n} + nH_2O \qquad (3)$$

with the instability constant

$$K_i = \frac{[Co(H_2O)_6^{++}][OH^-]^n}{[Co(OH)_n(H_2O)_{6-n}^{2-n}]} \qquad (4)$$

Since the equilibrium concentration of (saturated) cobaltous ion is the same for both the cobaltous hydroxide and the complex ion, we can solve equation (2) for the cobaltous ion concentration and substitute it for the concentration in equation (4) obtaining

$$K_i = \frac{[K_{sp}][OH^-]^n}{[OH^-]^2[Co(OH)_n(H_2O)_{6-n}^{2-n}]}$$

which upon rearrangement becomes

$$[Co(OH)_n(H_2O)_{6-n}^{2-n}] = \frac{[OH^-]^{n-2}K_{sp}}{K_i}$$

Substituting A/ab for the complex ion concentration, which is essentially equal to the analytical concentration of the cobalt in solution, and taking logarithms of both sides of the equation, we have

$$\log (A/ab) = (n - 2) \log [OH^-] + \log K_{sp}/K_i)$$

or

$$\log A = (n - 2) \log [OH^-] + \log (K_{sp}(ab)/K_i)$$

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(6) (a) P. Job, *Ann. chim.*, [10] 9, 113 (1928); (b) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, 63, 437 (1941).

(7) E. A. Harvey, Jr., and D. L. Manning, *ibid.*, 72, 4488 (1950).

Assuming that the ratio of the values of the solubility product and instability constants for the cobaltous hydroxide and hydroxy–cobalt complex ion, respectively, remain constant over the range of hydroxyl ion concentration involved, we may plot the logarithm of the absorbancy *versus* the logarithm of the hydroxyl ion activity. Hydroxyl ion activities[8] are used instead of molar concentrations because of the high concentrations used. We should obtain a straight line whose slope is $(n - 2)$, where n is the number of hydroxyl ions complexing the cobaltous ion to form the light-absorbing ion species in strongly alkaline solutions.

The data for the determination of $(n - 2)$ are presented in Fig. 4. The straight lines for the values at the two absorption peaks of 535 and 585 mμ were drawn from the equations determined by the method of least squares for the concentration range of 5 to 5 M. The corresponding slopes, which are both equal to 1.24, yield a value of 3.24 for n, the number of hydroxyl ions in the coördination sphere of the hydroxy-cobalt(II) complex ion. Above 5 M hydroxyl ion concentration the straight line veers off and forms another straight line which was similarly treated by the method of least squares. The values for their slopes were found to be 0.784 and 0.774, at 535 and 585 mμ, respectively. These values for $(n - 2)$ resulted in n being equal to 2.78 and 2.77, respectively. Again, they are approximately equal to a hydroxyl ion coördination value of three for the complex. Considering the ionic strengths and activities of these strongly alkaline solutions and their consequent departures from ideality, the experimentally determined value is indicative of the existence of the trihydroxy-cobalt(II) complex ion in the alkali hydroxide solutions.

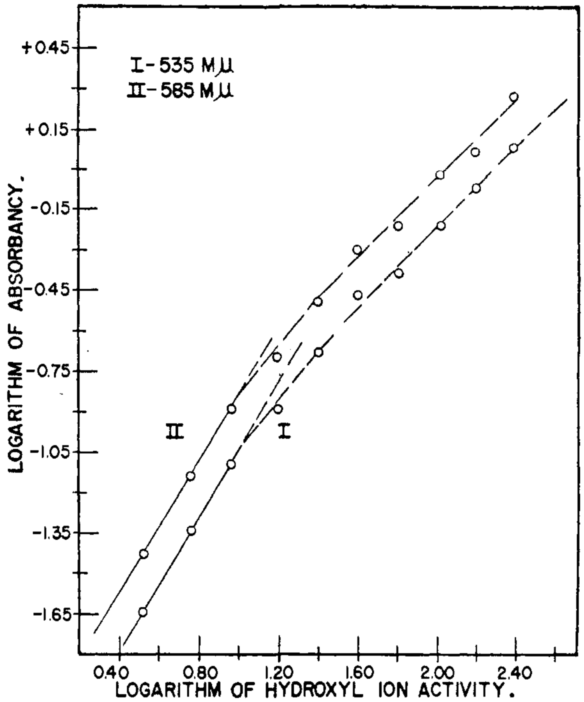

Fig. 4.—Logarithm of absorbancy as a function of hydroxyl ion activity in potassium hydroxide solutions saturated with cobalt(II); 1.00 cm. cells; 0.020 mm., slit width; 25°.

The reaction for the formation of this complex ion may be represented by the equation

$$Co(H_2O)_6^{++} + 3OH^- \rightleftarrows Co(OH)_3(H_2O)_3^- + 3H_2O$$

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[8] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

NOTES

Chlorination of Benzenesulfonyl Derivatives of Aromatic Amines

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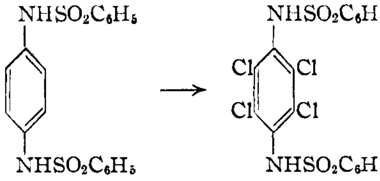
Chlorination of *p*-phenylenedibenzenesulfonamide (I) in nitrobenzene by means of chlorine resulted in the formation of a mixture of dichloro derivatives. The tetrachloro derivative (II), which was desired, has been prepared previously by the rather tedious route of successive oxidations and additions of hydrogen chloride to *p*-phenylenedibenzenesulfonamide.[2] By use of the solvent, dimethylformamide, the synthesis of the tetrachloro derivative (II) was readily achieved in a one step chlorination. This solvent is itself chlorinated with an exothermic reaction, but by keeping the reaction mixture below 60° through regulation of the flow of chlorine, the tetrachloro compound resulted in good yield. The amount of chlorine used was a critical factor and was determined empirically. Too large an excess of chlorine failed to give the compound desired.



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In a similar manner, several other polychlorinated

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[1] An abstract of a portion of a thesis submitted by Mr. B. H. Braun to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements of the Degree of Doctor of Philosophy.

[2] R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952).