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# The Determination of Formation Constants by Measurements of Molar-volume Changes

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**Synopsis.** Density measurements were made with a solution containing equivalent amounts of diethylenetriamine and the copper(II) ion, and with solutions of different concentrations of potassium hydroxide. The measurements were also made with systems in which the above-mentioned solutions were mixed. The molar-volume changes due to the complex formation were calculated from the density.[1] The results were used for the calculation of the formation constant of the monohydroxo-diethylenetriamine-copper(II) ion.

When ions of opposite charges combine in aqueous solutions, the molar-volume change can be expected to increase as the electroconstriction is weakened.[2] This phenomenon has been established in various acid-base systems.[1,3,4] When a copper(II) ion is coordinated with dienthylenetriamine (abbreviated as dien) at a ratio of 1: 1, the copper(II) ion tends to assume a square-planar structure, with a water molecule at one of its four coordination sites.[5] With the increase in the pH of this solution, the coordinated water molecule easily dissociates a proton and the electric charge of the Cu-dien$(OH_2)^{2+}$ complex changes from +2 to +1. Therefore, the addition of hydroxide ions to a solution containing the 1: 1 complex of Cu(II) and dien is ex pected to bring about an increase in the molar-volume change of Cu(II). In this study, the molar-volume change of Cu(II) mentioned above was determined at various concentrations of hydroxide ions. The results indicated the presence of a correlation between the formation of the complex and the molar-volume change. Consequently, the formation constant of this hydroxo complex was determined on the basis of the molar-volume change, and a comparison was made with the results obtained by the potentiometric titration method.[5].

## Experimental

The copper nitrate solution was standardized gravimetrically by using 8-quinolinol. The diethylenetriamine was distilled twice and diluted with decarbonated water. Its solution was standardized by potentiometric titration using nitric acid of a known concentration. The potassium hydroxide was standardized by the method used in the case of dien. The density measurement was made by means of a pycnometer (14 $cm^3$ in volume) in a constant-temperature bath maintained at 25.0±0.01 °C.

The initial compositions of the solutions before mixing were as follows:

Solution 1: 0.050 M Cu(II), 0.050 M dien, and the pH controlled at 4.7 by using nitric acid.

Solution 2: Potassium hydroxide in ten different concentrations ranging from 0 to 0.2 M.

## Results and Discussion

Martell and his co-workers[4] indicate, on the basis of there potentiometric study, that, in solutions containing equivalent amounts of Cu(II) and dien, the three nitrogen atoms of dien are all coordinated with a copper(II) ion above pH 4 and that the possibility of the formation of a dimer and a dihydroxo complex is small. They also concluded that a normal complex, Cu-dien$(OH_2)^{2+}$, was completely formed in the pH range from 4 to 8. Therefore, the following equilibrium has been established above pH 8:

$$\text{Cu-dien}(OH_2)^{2+} = \text{Cu-dien}(OH)^{+} + H^{+} \qquad (1)$$

The molar-volume changes of Cu(II) due to the mixing of Solution 1 and Solution 2 are shown in Fig.1 as a function of the pH of the mixed solution. In Solution 1 (pH 4.7 before mixing), Cu-dien$(OH_2)^{2+}$ complex ions are completely formed. In Fig. 1, the molar-volume change remains constant at −1.4 ($cm^3$ $mol^{-1}$) in the pH range from 4.7 to 7.2. This agrees with the finding obtained by the potentiometric titration, that the Cu-dien$(OH_2)^{2+}$ complex is completely formed in the solution of pH 4—8. The gradual increase in the molar-volume change in the pH range from 7.9 to 10 corresponds to the shift of the equilibrium (1) to the right, resulting in the increase in the Cu-dien$(OH)^{+}$ complex. At pH>12, the molar-volume change reaches a limiting value +17.1 ($cm^3$ $mol^{-1}$); this suggests that Cu-dien$(OH)^{+}$ complexes are completely formed in this pH range.

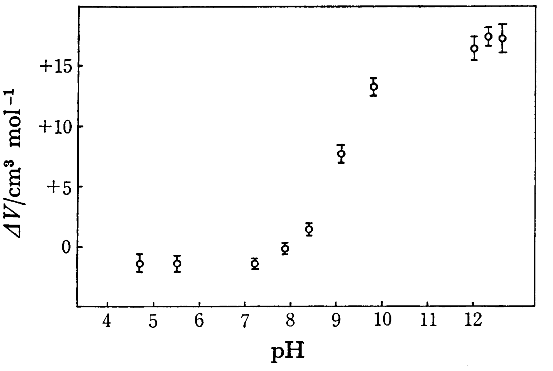

Fig. 1. Molar volume changes of Cu(II) due to the mixing of Solution 1 and Solution 2.

The molar-volume change of −1.4 ($cm^3$ $mol^{-1}$) at pH 4.7—7.2 is denoted by the symbol $V$(Cu-dien$(OH_2)$). Similarly, the molar-volume change of +17.1 ($cm^3$ $mol^{-1}$) at pH>12 is denoted by the symbol $V$(Cu-dien(OH)). By analogy with the equation commonly used in spectrophotometric studies,[5] the equilibrium concentrations of Cu-dien$(OH_2)^{2+}$ and Cu-dien$(OH)^+$, denoted by $C_1$ and $C_2$ respectively, can be expected to be given by Eq. (2) in terms of the molar-volume change, $\varDelta V$, at pH 8—11.

$$\frac{C_2}{C_1} = \frac{V(\text{Cu-dien}(\text{OH}_2)) - \varDelta V}{\varDelta V - V(\text{Cu-dien}(\text{OH}))} \tag{2}$$

Equation (2) can be used for the determination of the formation constant of Cu-dien$(OH)^+$, as can be expected from:

$$K_{\text{Cu-dien(OH)}} = \frac{C_2 \cdot [\text{H}^+]}{C_1} \tag{3}$$

The hydrogen-ion concentration $[H^+]$ was obtained by converting the reading of the pH meter using the hydrogen-ion activity coefficients by means of the Debye-Hückel equation. In order to eliminate the effects of other ions no foreign electrolytes such as $KNO_3$ was used in the present study. As a consequence, the ionic strength after mixing varies in the range from 0.15 to 0.2. By means of Eqs. (2) and (3), the formation constants of Cu-dien$(OH)^+$ were calculated to be:

$$\text{p}K_{\text{Cu-dien(OH)}} = 9.0 \text{ at pH } 9.1$$

$$\text{p}K_{\text{Cu-dien(OH)}} = 9.1 \text{ at pH } 9.8$$

The formation constants thus obtained from the molar-volume change data agree well with those of Martell and his co-workers ($pK=9.0$), determined by potentiometric titration.[4]

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