Formation Constants of Sulfato, Acetato and Sulfatoacetato Complexes of Copper(II) at Ionic Strength 1.0

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In the previous papers,[1,2] new polarographic methods were presented for the determination of the formation constants of metal acetato complexes. They were based on the quantitative analysis of the effect of acetate ions on the equilibria of the reaction,

$$\mathrm{M} + \mathrm{L} \rightleftarrows \mathrm{ML}$$

$$\text{or}\quad \mathrm{M} + \mathrm{M'L} \rightleftarrows \mathrm{ML} + \mathrm{M'}$$

where L represents a suitable complex-forming substance such as nitrilotriacetate or ethylenediaminetetraacetate.

The method was extended to the analysis of the effects of acetate ions and co-existing ions Z on the equilibria of the first reaction to determine the formation constants of the complexes with Z ions and those of the mixed ligand complexes with acetate and Z ions.[3,4]

In this study, the method in which the equilibrium of the second reaction is used has been developed and it has been applied to the determination of the formation constants of copper(II) complexes with acetate and/or sulfate ions.

The formation constants of sulfatocopper(II) complexes have been reported by Fronaeus[5,6] and by Näsänen and Lumme[7] and that of sulfatoacetatocuprate(II) by Fronaeus.[5] The values obtained in this study have been compared with those data.

Theoretical

Let us consider the acetate buffer solution which contains two different metal ions, M^{m+} and $\mathrm{M'}^{m'+}$, and ethylenediaminetetraacetate (EDTA) ions and co-existing ions Z. There exist the following equilibria:

$$\mathrm{M}^{m+} + \mathrm{M'Y}^{(m'-4)+} \rightleftarrows \mathrm{MY}^{(m-4)+} + \mathrm{M'}^{m'+} \tag{1}$$

$$\mathrm{MY}^{(m-4)+} + \mathrm{H}^{+} \rightleftarrows \mathrm{MHY}^{(m-3)+} \tag{2}$$

$$\mathrm{M'Y}^{(m'-4)+} + \mathrm{H}^{+} \rightleftarrows \mathrm{M'HY}^{(m'-3)+} \tag{3}$$

$$\mathrm{M}^{m+} + i\,\mathrm{OAc}^{-} + j\,\mathrm{Z}^{z-} \rightleftarrows \mathrm{M(OAc)}_{i}(\mathrm{Z})_{j}{}^{(m-i-zj)+} \tag{4}$$

$$\mathrm{M'}^{m'+} + i'\mathrm{OAc}^{-} + j'\mathrm{Z}^{z-} \rightleftarrows \mathrm{M'(OAc)}_{i'}(\mathrm{Z})_{j'}{}^{(m'-i'-zj')+} \tag{5}$$

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[1] N. Tanaka and K. Kato, This Bulletin, 32, 516 (1959).

[2] N. Tanaka and K. Kato, ibid., 33, 417 (1960).

[3] N. Tanaka and H. Ogino, ibid., 34, 1040 (1961).

[4] N. Tanaka, Y. Saito and H. Ogino, ibid., 36, 794 (1963).

[5] S. Fronaeus, Diss. Lund (1948); *Acta Chem. Scand.*, 4, 72 (1950).

[6] S. Fronaeus, ibid., 5, 859 (1951).

[7] R. Näsänen and P. Lumme, ibid., 5, 13 (1951).

where Y^{4-} means a completely dissociated EDTA anion and Z^{z-}, a co-existing ion such as sulfate. As was mentioned previously,3) the concentrations that can be determined from the polarographic measurement are $[M^{m+}]_{app}$ and $[M'^{m'+}]_{app}$ given by the equations,

$$[M^{m+}]_{app} = \sum_{i=0}^{n}\sum_{j=0}^{p} M(OAc)_i(Z)_j{}^{(m-i-zj)+} \qquad (6)$$

$$[M'^{m'+}]_{app} = \sum_{i'=0}^{n'}\sum_{j'=0}^{p'} M'(OAc)_{i'}(Z)_{j'}{}^{(m'-i'-zj')+} \qquad (7)$$

respectively.

In the present case when the equilibria given by Eqs. 1 to 5 are dealt with, the following equations were obtained by the procedure which is a combination of the procedure for Eq. 14 in Ref. 2 and that for Eq. 13 in Ref. 3 and by replacing β and β' by α_{MHY} and $\alpha_{M'HY}$ respectively.

$$\frac{1}{K^{M}_{M'app}} \sum_{i'=0}^{n'}\sum_{j'=0}^{p'} K_{M'(OAc)_{i'}(Z)_{j'}}[OAc^-]^{i'}[Z^{z-}]^{j'} = \frac{\alpha_{M'HY}}{\alpha_{MHY}K^{M}_{M'}} \sum_{i=0}^{n}\sum_{j=0}^{p} K_{M(OAc)_i(Z)_j}[OAc^-]^{i}[Z^{z-}]^{j} \qquad (8)$$

$$K^{M}_{M'app} = \frac{[M'^{m'+}]_{app}\{[MY^{(m-4)+}]+[MHY^{(m-3)+}]\}}{[M^{m+}]_{app}\{[M'Y^{(m'-4)+}]+[M'HY^{(m'-3)+}]\}} \qquad (9)$$

$$K^{M}_{M'} = \frac{[M'^{m'+}][MY^{(m-4)+}]}{[M^{m+}][M'Y^{(m'-4)+}]} \qquad (10)$$

$$\alpha_{MHY} = 1 + K^{H}_{MHY}[H^+], \quad \alpha_{M'HY} = 1 + K^{H}_{M'HY}[H^+] \qquad (11)$$

where $K_{M(OAc)_i(Z)_j}$ and $K_{M'(OAc)_{i'}(Z)_{j'}}$ represent the overall formation constants of $M(OAc)_i(Z)_j{}^{(m-i-zj)+}$ and $M'(OAc)_{i'}(Z)_{j'}{}^{(m'-i'-zj')+}$, respectively.

Under the condition that $[M]_t + [M']_t > [EDTA]_t$ where subscript t means the total concentration of the species, the concentration of the uncombined EDTA is negligibly small as compared with those of other species in the solution, and consequently $K^{M}_{M'app}$ given by Eq. 9 is obtained by the determination of either $[M^{m+}]_{app}$ or $[M'^{m'+}]_{app}$.

Equation 8 is rewritten as,

$$F_0 = \frac{\alpha_{M'HY}}{\alpha_{MHY}K^{M}_{M'}} \sum_{i=0}^{n}\sum_{j=0}^{p} K_{M(OAc)_i(Z)_j}\,[OAc^-]^{i}[Z^{z-}]^{j} \qquad (8')$$

where the left-hand side of Eq. 8 is replaced by F_0. The values of F_0 are calculated with the known values of $K_{M'(OAc)_{i'}(Z)_{j'}}$ and the $K^{M}_{M'app}$ values which are determined at the given pH, the given ionic strength and various concentrations of acetate and Z^{z-} ions. Equation 8′ is essentially the same as the F_0 function reported previously.3) Therefore, all of $K_{M(OAc)_i(Z)_j}$ can, at least theoretically, be determined by means of the same procedure reported previously.3) On the other hand, when the formation constants of $M(OAc)_i(Z)_j{}^{(m-i-zj)+}$ are known, similar relations are derived, and the values of $K_{M'(OAc)_{i'}(Z)_{j'}}$ can also be determined by the same procedure as for those of $K_{M(OAc)_i(Z)_j}$.

Experimental

Reagents.—Preparations and standardizations of the solutions of copper(II) nitrate, nickel(II) nitrate and ethylenediaminetetraacetate were made in principle by the same procedures as described in the previous paper.2) A solution of sodium sulfate was prepared from the guaranteed grade reagent, and the sulfate concentration was determined by the conventional gravimetric method.8) All other chemicals used were of an analytical reagent grade.

Apparatus and procedure.—A Yanagimoto PB-4 pen-recording polarograph was used for the measurement of the current-voltage curves. All measurements were made in the acetate buffer solutions of pH 4.74±0.02 containing sulfate, copper(II), nickel(II) and EDTA at 25°C and ionic strength 1.0. The ionic strength was adjusted with sodium perchlorate. Total concentrations of copper(II), nickel(II) and EDTA were $1.00_6\times10^{-3}$ M, $9.9_0\times10^{-4}$ M and $1.10_8\times10^{-3}$ M respectively. Gelatin was added as maximum suppressor by 0.01% in concentration.

In the preliminary experiments, the rate of the substitution reaction between copper(II) ions and nickel(II)-EDTA complexes was investigated. The result showed that the equilibrium of the reaction was attained within approximately 80 hours after the initiation of the reaction. Therefore, the reaction mixtures were kept standing at the given temperature for nearly four days after the preparation and, then, subjected to the measurement.

Results and Discussion

The values of $[Cu^{2+}]_{app}$ were obtained at various concentrations of acetate and the given concentrations of sulfate. The left-hand side of Eq. 8 (F_0 in Eq. 8′) was calculated with the $[Cu^{2+}]_{app}$ obtained and the formation constants of sulfatonickel(II), acetatonickel(II), and sulfatoacetatoniccolate(II) complexes which were previously determined.4) The F_0 values thus calculated were plotted against the acetate concentration.

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8) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. 2, John Wiley and Sons, New York (1951), p. 393.

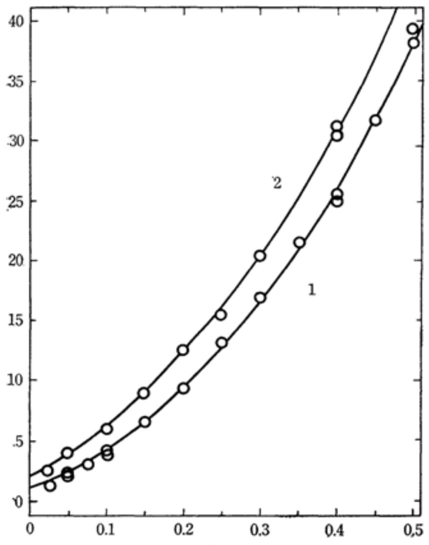

Fig. 1. F_0 (Eq. 8′) as a function of acetate concentration at 25°C.
Concentrations of sulfate are: 0 (1) and 0.193 M (2).
— indicates the calculated, and ○ the experimental value.

Two typical examples of the F_0 plots are shown in Fig. 1. By extrapolating the F_0 plots to the zero acetate concentration, the values for

$$\frac{\alpha_{\mathrm{NiHY}}}{\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}}\left(1+\sum_{j=1}^{p}K_{\mathrm{Cu(SO_4)}_j}[\mathrm{SO_4}^{2-}]^j\right)$$

were determined. The $F_1(\mathrm{OAc})$,

$$F_1(\mathrm{OAc}) \equiv \frac{F_0-\dfrac{\alpha_{\mathrm{NiHY}}}{\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}}\left(1+\sum_{j=1}^{p}K_{\mathrm{Cu(SO_4)}_j}[\mathrm{SO_4}^{2-}]^j\right)}{[\mathrm{OAc}^-]}$$

$$=\frac{\alpha_{\mathrm{NiHY}}}{\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}}\sum_{i=1}^{n}\sum_{j=0}^{p}K_{\mathrm{Cu(OAc)}_i\mathrm{(SO_4)}_j}\times[\mathrm{OAc}^-]^{i-1}[\mathrm{SO_4}^{2-}]^j \qquad (12)$$

was calculated from the F_0 plots and plotted against the acetate concentration, as is given in Fig. 2. Figure 2 shows that the F_1 plots are linear. This fact indicates that n is equal to 2 and that no appreciable amount of the complexes with three acetate or more coordinated is present in the solutions investigated. The same result was also obtained with other concentrations of sulfate.

The F_0 values were also calculated with the $[\mathrm{Cu}^{2+}]_{\mathrm{app}}$ obtained at various concentrations of sulfate and the given concentrations of acetate. They were plotted against the sulfate concentration, which are given in Fig. 3.

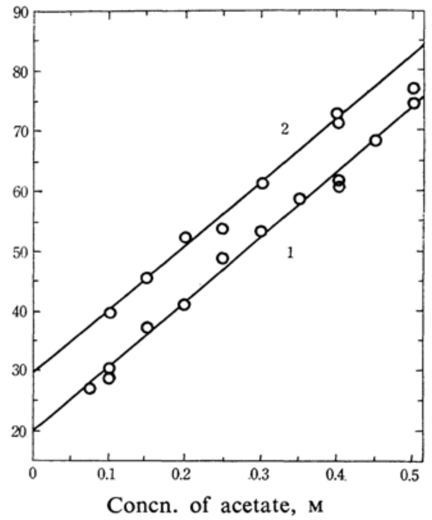

Fig. 2. F_1(Eq. 12) as a function of acetate concentration at 25°C.
Concentrations of sulfate are: 0 (1) and 0.193 M (2).

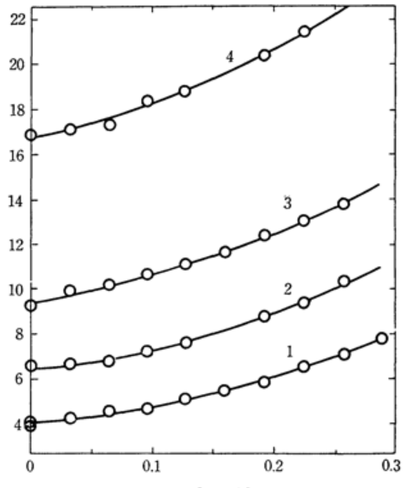

Fig. 3. F_0(Eq. 8′) as a function of sulfate concentration at 25°C.
Concentrations of acetate are: 0.100 M (1), 0.149 M (2), 0.199 M (3) and 0.299 M (4).
— indicates the calculated, and ○ the experimental value.

By extrapolating F_0 plots to the zero sulfate concentration, the values for

$$\frac{\alpha_{\mathrm{NiHY}}}{\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}}\sum_{i=0}^{2}K_{\mathrm{Cu(OAc)}_i}[\mathrm{OAc}^-]^i$$

were obtained. The $F_1(\mathrm{SO_4})$,

$$F_1(\mathrm{SO_4}) \equiv \frac{F_0-\dfrac{\alpha_{\mathrm{NiHY}}}{\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}}\sum_{i=0}^{2}K_{\mathrm{Cu(OAc)}_i}[\mathrm{OAc}^-]^i}{[\mathrm{SO_4}^{2-}]}$$

$$=\frac{\alpha_{\mathrm{NiHY}}}{\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}}\sum_{i=0}^{2}\sum_{j=1}^{p}K_{\mathrm{Cu(OAc)}_i\mathrm{(SO_4)}_j}\times[\mathrm{OAc}^-]^i[\mathrm{SO_4}^{2-}]^{j-1} \qquad (13)$$

was calculated from the F_0 plots and plotted against the sulfate concentration (Fig. 4). The F_1 plots were found to be linear, which indicate that p is equal to 2 and that no appreciable amount of complexes with three sulfates or more coordinated is present in the solutions investigated. These conclusions were confirmed by the direct calculation of n and p of the F_0 function with the aid of an electronic computor NEAC 2230 (the Computing Center, Tohoku University).

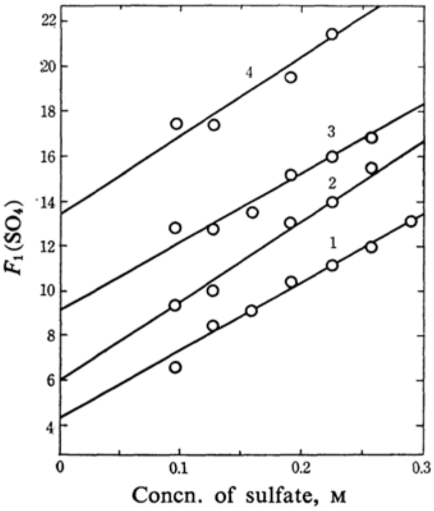

Fig. 4. F_1(Eq. 13) as a function of sulfate concentration at 25°C.
Concentrations of acetate are: 0.100 M (1), 0.149 M (2), 0.199 M (3) and 0.299 M (4).

The result that both n and p are equal to 2 suggests that the complex species, $CuOAc^+$, $Cu(OAc)_2$, $CuSO_4$, $Cu(SO_4)_2^{2-}$, $Cu(OAc)(SO_4)^-$, $Cu(OAc)(SO_4)_2^{3-}$, $Cu(OAc)_2(SO_4)^{2-}$ and $Cu(OAc)_2(SO_4)_2^{4-}$, may exist in the solution. However, it was concluded that $Cu(OAc)_2(SO_4)^{2-}$ and $Cu(OAc)_2(SO_4)_2^{4-}$ are not present in appreciable concentrations : The value of $(\alpha_{\mathrm{NiHY}}/(\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}))K_{\mathrm{Cu(OAc)_2}}$, the coefficient of $[OAc^-]^2$ in the absence of sulfate was found to be identical, within experimental error, with that of $(\alpha_{\mathrm{NiHY}}/(\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}))(K_{\mathrm{Cu(OAc)_2}} + K_{\mathrm{Cu(OAc)_2(SO_4)}}[SO_4^{2-}] + K_{\mathrm{Cu(OAc)_2(SO_4)_2}}[SO_4^{2-}]^2)$, the coefficient of $[OAc^-]^2$ in the presence of sulfate, both the coefficients being obtained by a least square method. An agreement of these values indicates that the terms, $K_{\mathrm{Cu(OAc)_2(SO_4)}}[SO_4^{2-}]$ and $K_{\mathrm{Cu(OAc)_2(SO_4)_2}}[SO_4^{2-}]^2$, are negligible and, consequently, no appreciable amount of $Cu(OAc)_2(SO_4)^{2-}$ and $Cu(OAc)_2(SO_4)_2^{4-}$ is present under the experimental conditions.

The formation constants of other species and the value of $\alpha_{\mathrm{NiHY}}/(\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}})$ were determined by a least square method with the plots of F_0 vs. $[OAc^-]$ and F_0 vs. $[SO_4^{2-}]$.

Determination of the Formation Constants of Acetatocopper(II) Complexes.—The F_0 function obtained in the absence of sulfate is written as

$$F_0 = \frac{\alpha_{\mathrm{NiHY}}}{\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}}}(1 + K_{\mathrm{Cu(OAc)}}[OAc^-] + K_{\mathrm{Cu(OAc)_2}}[OAc^-]^2) \tag{14}$$

Therefore, the formation constants of K_{CuOAc} and $K_{\mathrm{Cu(OAc)_2}}$ and the value of $\alpha_{\mathrm{NiHY}}/(\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}})$ were determined from curve 1 in Fig. 1 by a least square treatment. Using Eq. 14, the uncertainties of the determined values were examined by a graphical treatment.[9,10]

Determination of the Formation Constants of Sulfato and Sulfatoacetatocopper(II) Complexes.—The values of $(K_{\mathrm{CuSO_4}} + K_{\mathrm{Cu(OAc)(SO_4)}}[OAc^-])$ and $(K_{\mathrm{Cu(SO_4)_2}} + K_{\mathrm{Cu(OAc)(SO_4)_2}}[OAc^-])$ were determined by a least square method from the coefficients of $[SO_4^{2-}]$ and $[SO_4^{2-}]^2$ in the plots in Fig. 3, respectively. From the value of $(K_{\mathrm{CuSO_4}} + K_{\mathrm{Cu(OAc)(SO_4)}}[OAc^-])$ obtained for the given concentration of acetate, $K_{\mathrm{CuSO_4}}$ and $K_{\mathrm{Cu(OAc)(SO_4)}}$ were determined by a graphical treatment.[9,10] $K_{\mathrm{Cu(SO_4)_2}}$ and $K_{\mathrm{Cu(OAc)(SO_4)_2}}$ were also determined by the same procedure as in the case of the determination of $K_{\mathrm{CuSO_4}}$ and $K_{\mathrm{Cu(OAc)(SO_4)}}$.

The value of $\alpha_{\mathrm{NiHY}}/(\alpha_{\mathrm{CuHY}}K_{\mathrm{Ni}}^{\mathrm{Cu}})$ was obtained to be 1.0 at pH 4.74, and the formation constants obtained are given in Table I. Using these values, the values of F_0 can be calculated at various concentrations of acetate and/or sulfate. All the solid curves in Figs. 1 and 3 indicate that these calculated values are in satisfactory agreement with the values obtained experimentally.

TABLE I. FORMATION CONSTANTS OF COPPER(II) COMPLEXES AT 25°C AND IONIC STRENGTH 1.0

K_{CuOAc}	$2._0\times10$	$\mathrm{l.\ mol^{-1}}$
$K_{\mathrm{Cu(OAc)_2}}$	$1._1\times10^2$	$\mathrm{l.^2\ mol^{-2}}$
$K_{\mathrm{CuSO_4}}$	<3	$\mathrm{l.\ mol^{-1}}$
$K_{\mathrm{Cu(SO_4)_2}}$	$\sim3\times10$	$\mathrm{l.^2\ mol^{-2}}$
$K_{\mathrm{Cu(OAc)(SO_4)}}$	4×10	$\mathrm{l.^2\ mol^{-2}}$
$K_{\mathrm{Cu(OAc)(SO_4)_2}}$	$\sim7\times10$	$\mathrm{l.^3\ mol^{-3}}$

In the previous study,[2] the formation constants of K_{CuOAc} and $K_{\mathrm{Cu(OAc)_2}}$ at 25°C and ionic strength 0.2 were obtained to be 52 and 93, respectively. The value of K_{CuOAc} at ionic strength 1.0 is considerably smaller than that at ionic strength 0.2, while the value of the $K_{\mathrm{Cu(OAc)_2}}$ is approximately equal to that at ionic strength 0.2. The value of $\alpha_{\mathrm{NiHY}}/\alpha_{\mathrm{CuHY}}$

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[9] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., N. J. (1959), p. 91.

[10] G. Schwarzenbach, A. Willi and R. O. Bach, *Helv. Chim. Acta*, **30**, 1303 (1947).

was calculated with the equilibrium constants, $K^{\mathrm{H}}_{\mathrm{CuHY}}$ and $K^{\mathrm{H}}_{\mathrm{NiHY}}$, given by Schwarzenbach, Gut and Anderegg[11] and was found to be approximately unity for this system at pH 4.74. The $K^{\mathrm{Cu}}_{\mathrm{Ni}}$, the equilibrium constant of the substitution reaction represented by Eq. 1, was obtained to be 1.0 in the present experimental conditions. This value is also smaller than 2.2 which was obtained at 25°C and ionic strength 0.2.[2]

Fronaeus reported the formation constants of copper(II) complexes with acetate and/or sulfate which were determined by the potentiometric method[5] and by the ion-exchange measurements[6] at 20°C and ionic strength 1. The formation constants of sulfatocopper(II) complexes were reported which were obtained by solubility measurements[7] at 20°C and ionic strength 1. These formation constants are given in Table II. It may be seen that the values of $K_{\mathrm{Cu(SO_4)_2}}$ given by Fronaeus and Näsänen are considerably smaller than the value obtained in this study.

TABLE II. THE REPORTED VALUES OF FORMATION CONSTANTS OF COPPER(II) COMPLEXES AT 20°C AND IONIC STRENGTH 1

	Values obtained by Fronaeus [5,6]		Values obtained by Näsänen et al.[7]
K_{CuOAc}	45 [c]		
$K_{\mathrm{Cu(OAc)_2}}$	440 [c]		
$K_{\mathrm{CuSO_4}}$	9 ± 2 [a]	10.6 [b]	≤ 11 [d]
$K_{\mathrm{Cu(SO_4)_2}}$	—	10—17 [b]	~ 3 [d]
$K_{\mathrm{Cu(SO_4)_3}}$	80 [a]	200 [b]	≤ 150 [d]
$K_{\mathrm{Cu(OAc)(SO_4)}}$	190 ± 50 [a]		

a) The e. m. f. method with the quinhydrone electrode.[5]

b) The e. m. f. method with the copper amalgam electrode.[5]

c) The ion exchange method.[6]

d) The solubility method.

Summary

The polarographic method for the determination of the formation constants which is based on the measurement of the effects of acetate and/or other co-existing ions on the equilibrium of the substitution reaction, $\mathrm{M}+\mathrm{M'L} \rightleftarrows \mathrm{ML}+\mathrm{M'}$, has been developed, and applied to the study of the copper(II) complexes with acetate and/or sulfate ions. The formation constants obtained at 25°C and ionic strength 1.0 are: $2._0\times10$ for $K_{\mathrm{Cu(OAc)}}$, $1._1\times10^2$ for $K_{\mathrm{Cu(OAc)_2}}$, < 3 for $K_{\mathrm{CuSO_4}}$, $\sim 3\times10$ for $K_{\mathrm{Cu(SO_4)_2}}$, 4×10 for $K_{\mathrm{Cu(OAc)(SO_4)}}$ and $\sim 7\times10$ for $K_{\mathrm{Cu(OAc)(SO_4)_2}}$.

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[11] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).