Polarographic Determination of the Formation Constant of Sulfatonickel(II) Complex

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In the previous paper[1], a new method for the determination of the formation constants of metal acetato complexes and its application to acetatonickel(II) complexes were presented. The method is based on the polarographic measurement of the sum of the equilibrium concentrations of hydrated metal ions and metal acetato complexes in the presence of an appropriate auxiliary complex-forming substance. Although similar functions are derived, the method is essentially different from the DeFord and Hume's method[2] that is based on the displacements of the half-wave potential of metal ions in the presence of a complex-forming substance[3].

Because of the increasing interest in the determination of the formation constants of less stable complexes, especially those with two or more different ligands, it seems worth while to generalize the treatment of the method reported in the previous paper[1] and to increase its applicability.

In the present paper, the case where a co-existing ion, Z^{z-}, is added to the system of Ni(II)—auxiliary complex-forming substance—acetate is dealt with. A general procedure for the determination of the formation constants of $Ni(OAc)_i^{(2-i)+}$ and $Ni(Z)_j^{(2-zj)+}$ as well as $Ni(OAc)_i(Z)_j^{(2-i-zj)+}$ is presented, and the formation constants of monosulfatonickel(II) complex, which were determined with sulfate ions used as the co-existing ion, are reported.

Theoretical

Let us consider the acetate buffer solution which contains nickel(II)[4], nitrilotriacetate (NTA)[4] and a co-existing ion. There exist the following equilibria:

$$Ni^{2+} + X^{3-} \rightleftarrows NiX^- \qquad (1)$$

$$NiX^- + H^+ \rightleftarrows NiHX \qquad (2)$$

$$Ni^{2+} + i\,OAc^- + j\,Z^{z-} \rightleftarrows Ni(OAc)_i(Z)_j^{(2-i-zj)+} \qquad (3)$$

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

[2] D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, 73, 5321 (1951).

[3] D. N. Hume, *Anal. Chem.*, 32, 137R (1960).

[4] Nickel(II) and nitrilotriacetate may be replaced by other appropriate metal ions and complex-forming substances, respectively.

where X^{3-} denotes a tervalent NTA anion and Z^{z-}, a co-existing ion, e. g., sulfate.

The total concentration of nickel, $[\mathrm{Ni}]_t$, and that of NTA, $[\mathrm{NTA}]_t$, in the solution are given in terms of the ionic and the molecular species as follows:

$$[\mathrm{Ni}]_t=\sum_{i=0}^{n}\sum_{j=0}^{p}[\mathrm{Ni(OAc)}_i(\mathrm{Z})_j{}^{(2-i-zj)+}] + [\mathrm{NiX}^-]+[\mathrm{NiHX}] \tag{4}$$

$$[\mathrm{NTA}]_t=[\mathrm{NTA}]_f+[\mathrm{NiX}^-]+[\mathrm{NiHX}] \tag{5}$$

where $\sum_{i=0}^{n}\sum_{j=0}^{p}[\mathrm{Ni(OAc)}_i(\mathrm{Z})_j{}^{(2-i-zj)+}]$ represents the sum of the concentrations of hydrated nickel ions and complexes of nickel(II) co-ordinating with acetate and/or Z^{z-} ions, and $[\mathrm{NTA}]_f$, the sum of the concentrations of the uncomplexed NTA.

The polarographic diffusion current of nickel ions obtained in the solution which contains acetate and Z^{z-} ions corresponds to the sum of the diffusion current due to the hydrated nickel ions and of those due to the complexes of nickel(II) co-ordinating with acetate and/or Z^{z-} ions[1]. If the hydrated ion and the complexes have nearly the same diffusion current constants, the sum of their concentrations can be determined from the polarographic diffusion current, if necessary, after correction. Then, we write the equation as,

$$[\mathrm{Ni}^{2+}]_{\mathrm{app}}=\sum_{i=0}^{n}\sum_{j=0}^{p}[\mathrm{Ni(OAc)}_i(\mathrm{Z})_j{}^{(2-i-zj)+}] \tag{6}$$

where $[\mathrm{Ni}^{2+}]_{\mathrm{app}}$ is the concentration that can be determined polarographically. Eq. 4 is rewritten as,

$$[\mathrm{Ni}]_t=[\mathrm{Ni}^{2+}]_{\mathrm{app}}+[\mathrm{NiX}^-]+[\mathrm{NiHX}] \tag{7}$$

The concentrations of NiX^-, Ni^{2+} and X^{3-} are given by

$$[\mathrm{NiX}^-]=\frac{[\mathrm{Ni}]_t-[\mathrm{Ni}^{2+}]_{\mathrm{app}}}{\beta} \tag{8}$$

$$[\mathrm{Ni}^{2+}]=\frac{[\mathrm{Ni}^{2+}]_{\mathrm{app}}}{\sum_{i=0}^{n}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_i(\mathrm{Z})_j}[\mathrm{OAc}^-]^i[\mathrm{Z}^{z-}]^j} \tag{9}$$

$$[X^{3-}]=\frac{[\mathrm{NTA}]_f}{\alpha} \tag{10}$$

where

$$\alpha=1+\frac{[\mathrm{H}^+]}{K_{\mathrm{HX}}}+\frac{[\mathrm{H}^+]^2}{K_{\mathrm{H_2X}}K_{\mathrm{HX}}}+\frac{[\mathrm{H}^+]^3}{K_{\mathrm{H_3X}}K_{\mathrm{H_2X}}K_{\mathrm{HX}}}$$

and

$$\beta=1+K^{\mathrm{H}}_{\mathrm{NiHX}}[\mathrm{H}^+]$$

$K_{\mathrm{H_3X}}$, $K_{\mathrm{H_2X}}$ and K_{HX} represent the first, the second and the third dissociation constant of nitrilotriacetic acid, respectively, $K^{\mathrm{H}}_{\mathrm{NiHX}}$, the equilibrium constant of the reaction given by Eq. 2 and $K_{\mathrm{Ni(OAc)}_i(\mathrm{Z})_j}$, the overall formation constant of $\mathrm{Ni(OAc)}_i(\mathrm{Z})_j{}^{(2-i-zj)+}$. It may be defined that when both i and j are zero, the value of $K_{\mathrm{Ni(OAc)}_i(\mathrm{Z})_j}$ equals unity.

The formation constant of NiX^-, consequently, is given as

$$K_{\mathrm{NiX}}=\frac{[\mathrm{NiX}^-]}{[\mathrm{Ni}^{2+}][X^{3-}]} =\alpha\{[\mathrm{Ni}]_t-[\mathrm{Ni}^{2+}]_{\mathrm{app}}\} \times\frac{\sum_{i=0}^{n}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_i(\mathrm{Z})_j}[\mathrm{OAc}^-]^i[\mathrm{Z}^{z-}]^j}{\beta[\mathrm{Ni}^{2+}]_{\mathrm{app}}[\mathrm{NTA}]_f} \tag{11}$$

Introducing to Eq. 11 the expression for the concentration of uncomplexed NTA given as

$$[\mathrm{NTA}]_f=[\mathrm{Ni}^{2+}]_{\mathrm{app}}-[\mathrm{Ni}]_t+[\mathrm{NTA}]_t \tag{12}$$

the relation

$$\frac{\{[\mathrm{Ni}^{2+}]_{\mathrm{app}}-[\mathrm{Ni}]_t+[\mathrm{NTA}]_t\}[\mathrm{Ni}^{2+}]_{\mathrm{app}}}{[\mathrm{Ni}]_t-[\mathrm{Ni}^{2+}]_{\mathrm{app}}} =\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_i(\mathrm{Z})_j}[\mathrm{OAc}^-]^i[\mathrm{Z}^{z-}]^j \tag{13}$$

is obtained. It may be obvious that both α and β in Eq. 13 are constant in the solution of the given pH and the given ionic strength.

First, the values of $[\mathrm{Ni}^{2+}]_{\mathrm{app}}$ are determined by the polarographic method at the given pH, the given ionic strength and the given concentration of acetate, but at varied concentrations of Z^{z-}, with which the values for the left-hand side of Eq. 13 are calculated. In this case it may be convenient to express Eq. 13 as,

$$F_0=\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i}[\mathrm{OAc}^-]^i +\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i(\mathrm{Z})}[\mathrm{OAc}^-]^i[\mathrm{Z}^{z-}]+\cdots\cdots +\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i(\mathrm{Z})_p}[\mathrm{OAc}^-]^i[\mathrm{Z}^{z-}]^p \tag{13'}$$

where the left-hand side of Eq. 13 is replaced by F_0. Eq. 13′ shows clearly that the plot of F_0 against the concentration of Z^{z-} gives a curves of pth degree with respect to $[Z^{z-}]$. From extrapolation of the F_0 plot to the zero concentration of Z^{z-}, the value of $\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i}[\mathrm{OAc}^-]^i$ is obtained. Then, the function $F_j(\mathrm{Z})$ $(1\leq j\leq p+1)$ is defined as

$$F_j(\mathrm{Z})\equiv$$

$$\frac{F_{j-1}(\mathrm{Z})-\dfrac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_{j-1}}[\mathrm{OAc}^-]^i}{[\mathrm{Z}^{z-}]}$$

$$=\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_j}[\mathrm{OAc}^-]^i$$

$$+\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_{j+1}}[\mathrm{OAc}^-]^i[\mathrm{Z}^{z-}]$$

$$+\cdots\cdots \tag{14}$$

$F_j(\mathrm{Z})$ is plotted against the concentration of Z^{z-} and the value of $\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n}K_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_j}[\mathrm{OAc}^-]^i$ is determined by extrapolating the $F_j(\mathrm{Z})$ plot to zero concentration of Z^{z-}. Repeating the procedure until the relation,

$$F_{p+1}(\mathrm{Z})=0$$

is obtained, the value of p can be determined.

Secondly, the values of $[\mathrm{Ni}^{2+}]_{\mathrm{app}}$ are determined by the polarographic method at the given pH, the given ionic strength and the given concentration of Z^{z-}, but at varied concentrations of acetate. The left-hand side of Eq. 13 is calculated and plotted against the concentration of acetate. Eq. 13 is also written as a function of the concentration of acetate:

$$F_0=\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(Z)}_j}[\mathrm{Z}^{z-}]^j$$

$$+\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)(Z)}_j}[\mathrm{Z}^{z-}]^j[\mathrm{OAc}^-]+\cdots\cdots$$

$$+\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_n\mathrm{(Z)}_j}[\mathrm{Z}^{z-}]^j[\mathrm{OAc}^-]^n \tag{13''}$$

From extrapolation of the F_0 plot to zero acetate concentration, the value of $\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(Z)}_j}[\mathrm{Z}^{z-}]^j$ is obtained.

The function $F_i(\mathrm{OAc})$ $(1\leq i\leq n+1)$ is also defined as,

$$F_i(\mathrm{OAc})\equiv$$

$$\frac{F_{i-1}(\mathrm{OAc})-\dfrac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_{i-1}\mathrm{(Z)}_j}[\mathrm{Z}^{z-}]^j}{[\mathrm{OAc}^-]}$$

$$=\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_j}[\mathrm{Z}^{z-}]^j$$

$$+\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_{i+1}\mathrm{(Z)}_j}[\mathrm{Z}^{z-}]^j[\mathrm{OAc}^-]+\cdots\cdots \tag{15}$$

$F_i(\mathrm{OAc})$ is plotted against the concentration of acetate and the value of $\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{j=0}^{p}K_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_j}[\mathrm{Z}^{z-}]^j$ is detremined. If the procedure concerning the $F_i(\mathrm{OAc})$ plot is repeated at $p+1$ different concentrations of Z^{z-}, $(n+1)(p+1)$ pieces of equations with $(n+1)(p+1)$ unknown quantities, which are $K_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_j}$ $(0\leq i\leq n,\ 0\leq j\leq p$ except $i=j=0)$ and $\frac{\alpha}{\beta K_{\mathrm{NiX}}}$, are yielded. Solving these equations, all of $\mathrm{K}_{\mathrm{Ni(OAc)}_i\mathrm{(Z)}_j}$ can, at least theoretically, be determined.

Experimental

Reagents.—A standard solution of nickel nitrate was prepared by dissolving an appropriate amount of pure nickel metal in nitric acid. The concentration of nickel was determined by the conventional gravimetric method with dimethylglyoxime[5]. A solution of disodium nitrilotriacetate was prepared from the commercial nitrilotriacetic acid (DOTITE NTA), and standardized against the standard solution of nickel(II) nitrate by amperometric titration with a similar procedure for ethylenediaminetetraacetate[6,7]. A solution of potassium sulfate was prepared from the guaranteed grade reagent. The sulfate concentration was determined by the conventional gravimetric method[8]. All other chemicals used were of analytical reagent grade.

Apparatus and Procedure.—A Yanagimoto PB-4 pen-recording polarograph was used for the measurement of the current-voltage curves. The dropping mercury electrode used had an m value of 2.13 mg./sec. and a drop time t_d of 4.07 sec., being measured in an air-free 0.2 M potassium nitrate solution containing 2×10^{-6} M polyoxyethylene lauryl ether (LEO) at 25°C and at -0.5 V vs. SCE. The sum of the diffusion currents of hydrated nickel ions, acetatonickel(II), sulfatonickel(II) and, if any, acetatosulfatoniccolate(II) complexes were determined in the acetate buffer of pH 3.66±0.02 containing sulfate, nickel(II) and a slight excess of NTA at 15, 25 and 35°C. The concentration of acetate in the buffer was varied from 0.025 to 0.100 M at the constant concentration of sulfate of 0.03 M, while that of sulfate was varied from 0.01 to 0.05 M at the constant concentration of acetate of 0.05 M. The ionic strength of the solution was adjusted to be 0.2 with potassium nitrate. LEO was added as a maximum suppressor by 1×10^{-6} M (at 15°C) or 2×10^{-6} M (at 25 and 35°C) in concentration. The pH of the solution was measured

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[5] F. P. Treadwell and W. T. Hall, "Analytical Chemistry", Vol. 2, John Wiley & Sons, Inc., New York (1951), p. 193.

[6] N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), **6**, 86 (1957).

[7] N. Tanaka, I. T. Oiwa and M. Kodama, *Anal. Chem.*, **28**, 1555 (1956).

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

accurately, after the polarographic measurement, with a Hitachi Model EHP-1 pH meter with a glass electrode.

Results and Discussion

The polarograms were recorded with the solution of pH 3.66 containing 1.00×10^{-3} M nickel nitrate, 1.09×10^{-3} M NTA and various concentrations of acetate and sulfate, unless otherwise stated. Nickel(II) gave an irreversible wave with the half-wave potential of about -1.05 V vs. SCE in the acetate-sulfate-nitrate media. This wave is considered to be due to the reductions of hydrated nickel(II) ions, acetatonickel(II), sulfatonickel(II) and, if any, acetatosulfatoniccolate(II) complexes. The limiting current of the wave was found to be proportional to the concentration of the electroactive species and also to the square root of the effective height of mercury column on the dropping mercury electrode. This clearly showed that the limiting current is diffusion-controlled.

The apparent diffusion current constants of nickel(II) were determined from the measurements of the diffusion current at various acetate and sulfate concentrations. The values of $[\mathrm{Ni}^{2+}]_{\mathrm{app}}$ of Eq. 6 were calculated, with the aid of those apparent diffusion current constants, from the limiting currents obtained with the reaction mixtures.

Presence of Sulfato Complexes.—The polarograms were recorded with the solutions containing 0.0500 M actate and various concentrations of sulfate at various temperatures. With the values of $[\mathrm{Ni}^{2+}]_{\mathrm{app}}$ obtained, the left-hand side of Eq. 13, F_0, was calculated and plotted against the sulfate concentration. The results are shown in Fig. 1, where it is clearly seen that the plots of F_0 vs. $[\mathrm{SO}_4{}^{2-}]$ give straight lines. This fact indicates that p is equal to 1 and no appreciable amount of complexes with two sulfates or more co-ordinated is present in the solution under the experimental conditions. From the plots in Fig. 1, the values of

$\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n} K_{\mathrm{Ni(OAc)}_i}[\mathrm{OAc}^-]^i$ and

$\frac{\alpha}{\beta K_{\mathrm{NiX}}}\sum_{i=0}^{n} K_{\mathrm{Ni(OAc)}_i(\mathrm{SO}_4)}[\mathrm{OAc}^-]^i$ in Eq. 13′ were determined, the former being given by the intercept at $[\mathrm{SO}_4{}^{2-}]=0$ and the latter, by the slope.

Absence of Acetatosulfato Complexes.—The polarograms were recorded with the solutions containing 0.0297 M sulfate and various concentrations of acetate at 25°C, and the values of $[\mathrm{Ni}^{2+}]_{\mathrm{app}}$ were determined. The left-hand side of Eq. 13, F_0, was calculated and plotted against the acetate concentration. (A in Fig. 2). A linear relation between F_0 and the concentration of acetate clearly indicates that n is equal to 1 and no appreciable amount of complexes with two acetates or more co-ordinated is present in the solution under the experimental condition. The fact that n and p are equal to 1, respectively, suggests that NiOAc^+, NiSO_4 and $\mathrm{Ni(OAc)(SO_4)}^-$ may exist in the solution under the experimental condition.

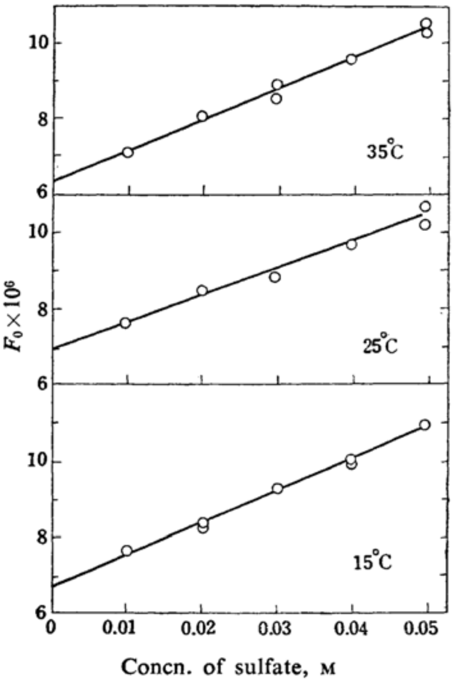

Fig. 1. Relation between the values of left-hand side of Eq. 13, F_0, and the concentration of sulfate at various temperatures. Acetate concentration is 0.0500 M.

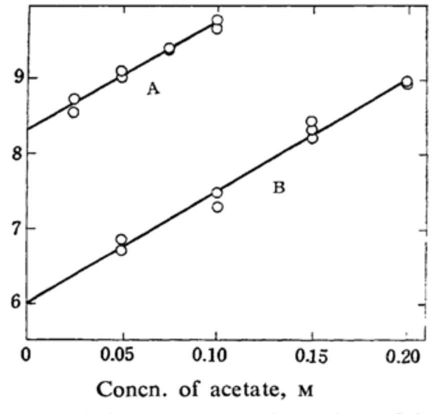

Fig. 2. Relations between the value of left-hand side of Eq. 13, F_0, and the concentration of acetate at 25°C, obtained in the presence of 0.0297 M sulfate (A) and in the absence of sulfate (B).

TABLE II. THE REPORTED VALUES OF FORMATION CONSTANTS OF SULFATONICKEL(II) COMPLEX

Investigator	Method	Temp., °C	Ionic strength	$K_{\mathrm{NiSO_4}}$	Ref.
Money et al.	e. m. f.	25	0	250	9
			0.2	22*	
Brown et al.	freezing point	0	0	114~244	10
			0.2	8~16*	
Kenttämaa	freezing point	0	0	220	11
			0.2	15*	

* These are the formation constants which were calculated by the present authors with the values reported in the literature referred to.

From the following experiment, however, it is concluded that $\mathrm{Ni(OAc)(SO_4)^-}$ is not present in an appreciable concentration: The polarograms were obtained with the solutions containing 1.00×10^{-3} M nickel nitrate, 1.10×10^{-3} M NTA and various concentrations of acetate but none of sulfate at 25°C and pH 3.68. The values of F_0 were calculated with the observed $[\mathrm{Ni^{2+}}]_{\mathrm{app}}$'s and plotted against the acetate concentration with a linear relation as shown by B in Fig. 2. The value of $\frac{\alpha}{\beta K_{\mathrm{NiX}}}K_{\mathrm{NiOAc}}$ which was determined from the slope of plot B in Fig. 2 is 1.48×10^{-5}, while that of $\frac{\alpha}{\beta K_{\mathrm{NiX}}}(K_{\mathrm{NiOAc}}+K_{\mathrm{Ni(OAc)(SO_4)}}[\mathrm{SO_4^{2-}}])$ obtained from the slope of plot A in Fig. 2 is 1.41×10^{-5}. The agreement of these two values indicates that the term of $K_{\mathrm{Ni(OAc)(SO_4)}}[\mathrm{SO_4^{2-}}]$ is negligible and, therefore, no appreciable amount of $\mathrm{Ni(OAc)(SO_4)^-}$ is present under the experimental condition.

The Determination of the Formation Constant of Sulfatonickel(II) Complex.—It has been known that nickel(II) forms only a monoacetato complex in the solution containing acetate up to 0.2 M in concentration at ionic strength 0.2 at temperature ranging from 15 to 35°C[1]. From this and the fact that $\mathrm{Ni(OAc)(SO_4)^-}$ is considered not to be present under the experimental condition, Eq. 13′ is simplified as,

$$F_0=\frac{\alpha}{\beta K_{\mathrm{NiX}}}+\frac{\alpha}{\beta K_{\mathrm{NiX}}}K_{\mathrm{NiOAc}}[\mathrm{OAc^-}]+\frac{\alpha}{\beta K_{\mathrm{NiX}}}K_{\mathrm{NiSO_4}}[\mathrm{SO_4^{2-}}]$$

The formation constant of acetatonickel(II) complex has been given as 2.6 and 2.4 at 15 and 35°C, respectively[1]. The value at 25°C was determined to be 2.5 from plot B in Fig. 2, and this value was in satisfactory agreement with that obtained previously[1]. With the aid of these values, the formation constants of sulfatonickel(II) complex at various temperatures were obtained from the intercepts and the slopes in Fig. 1. These are given in Table I.

TABLE I. FORMATION CONSTANTS OF SULFATONICKEL(II) COMPLEX AT VARIOUS TEMPERATURES

Temp., °C	$K_{\mathrm{NiSO_4}}$
15	14.3±0.4*
25	11.6±0.9*
35	14.6±0.7*

* The accuracy of $K_{\mathrm{NiSO_4}}$ was calculated with the standard deviations of the intercepts and the slopes of the F_0 plots.

The formation constants of the sulfatonickel(II) complex which have been reported by other researchers are given in Table II. The original values in their papers were corrected for ionic strength and also listed in Table II. In this calculation, the activity coefficients of nickel(II) and sulfate ions were estimated to be 0.33 and 0.27, respectively[12], at 25°C and ionic strength 0.2. At 0°C and ionic strength 0.2, they were estimated to be 0.29 and 0.23, respectively[12]. It is probably seen that the formation constants of monosulfatonickel(II) complex obtained in this study are in an essential agreement with those given in Table II.

Besides, Table I clearly indicates that the formation constants of monosulfatonickel(II) complex, $K_{\mathrm{NiSO_4}}$, are almost independent of temperature at 15 to 35°C. The same tendency has been found for the formation constants of monoacetatonickel(II) complex reported previously[1].

Summary

A method for the determination of the formation constants of less stable metal complexes has been developed. The method is based on the polarographic measurement of the sum of the equilibrium concentrations of

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[9] R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

[10] P. G. Brown and J. E. Prue, *Proc. Roy. Soc.*, **A**, **232**, 320 (1955).

[11] J. Kenttämaa, *Suomen Kemistilehti*, **29B**, 59 (1956).

[12] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

hydrated metal ions and the complexes coordinating with acetate and/or co-existing ions in the presence of an appropriate auxiliary complex-forming substance. Essential advantages of the method are those of the method that was previously reported and applied to the formation constants of acetatonickel(II) complex.

The procedure developed is applied to the study of the nickel(II) complexes present in the acetate buffer solution containing nitrilotriacetate as an auxiliary complex-forming substance and sulfate as co-existing ions. The results obtained reveal that, under the experimental condition, the monoacetatonickel(II) ions $NiOAc^+$ and the monosulfatonickel(II) $NiSO_4$ are present in the solution but not the acetatosulfatoniccolate(II) $Ni(OAc)(SO_4)^-$. The formation constants of monosulfato complex, K_{NiSO_4}, at ionic strength 0.2 are calculated to be 14.3 ± 0.4 at 15°C, 11.6 ± 0.9 at 25°C and 14.6 ± 0.7 at 35°C.

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