Polarographic Determination of the Formation Constants of Sulfato, Acetato and Sulfatoacetato Complexes of Nickel(II) at Ionic Strength 1.0

By Nobuyuki TANAKA, Yu SAITO and Hiroshi OGINO

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In the previous study[1], a method for the polarographic determination of the formation constants of weak complexes, $Ni(OAc)_i \cdot (Z)_j^{(2-i-zj)+}$ $(0 \leq i \leq n,\ 0 \leq j \leq p)$, was developed and applied to the nickel(II) complexes in sulfate-acetate media. The results indicated that mixed ligand complexes were not present in appreciable concentrations at ionic strength 0.2.

Because of the increasing interest in the determination of the formation constants of weak complexes with two or more different ligands, it seems worthwhile to apply the method under the conditions favorable for the formation of mixed ligand complexes. In the present paper, the formation of complexes of nickel(II) with sulfate and/or acetate is demonstrated in a solution containing higher concentrations of these anions, and the formation constants of these complexes determined at 25°C and ionic strength 1.0 are presented.

Experimental

The method employed in this study was in principle the same as in the previous paper[1]. However, the ionic strength of the solution was adjusted to 1.0 with sodium perchlorate, and sodium sulfate was used instead of potassium sulfate.

Results and Discussion

The polarograms were recorded with the acetate buffer solutions of pH 3.72 containing 9.90×10^{-4} M nickel nitrate, 1.06×10^{-3} M NTA, and various concentrations of sulfate and acetate. The limiting current of nickel(II) was found to be diffusion-controlled.

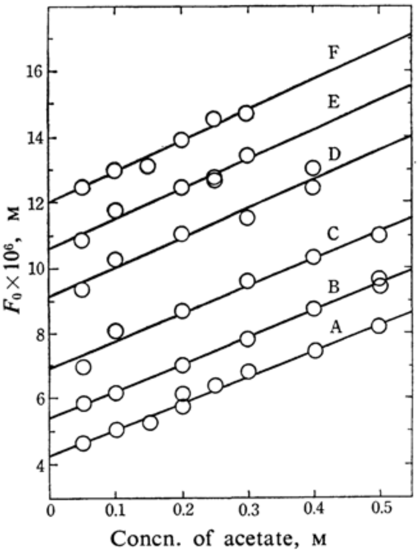

Fig. 1. F_0 as a function of acetate concentration at 25°C. Concentrations of sulfate are: 0 (A), 0.05 M (B), 0.10 M (C), 0.15 M (D), 0.175 M (E) and 0.20 M (F).

The values of $[Ni^{2+}]_{app}$, which is the sum of the concentrations of hydrated nickel ions and nickel(II) complexes with sulfate and/or acetate, were obtained at various concentrations of acetate and the given concentration of sulfate. The F_0 values were calculated according to the left-hand side of Eq. 13 of the previous paper[1] and were plotted against the acetate concentration (Fig. 1). The straight plots clearly indicate that n is equal to 1 and that no appreciable amount of complexes with two acetates or more coordinated is present in the solution investigated. Consequently, the F_0 function is written as follows:

$$F_0=\frac{\alpha}{\beta K_{NiX}} \times\sum_{i=0}^{1}\sum_{j=0}^{p} K_{Ni(OAc)_i(SO_4)_j}\,[OAc^-]^i[SO_4^{2-}]^j \qquad (1)$$

Next, F_0 was calculated with $[Ni^{2+}]_{app}$ obtained at various concentrations of sulfate and the given concentration of acetate and plotted against the sulfate concentration. A typical example of these F_0 plots is shown in Fig. 2. By extrapolating the F_0 plot as given in Fig. 2 to the zero sulfate concentration, the value of

$$\frac{\alpha}{\beta K_{NiX}}\quad(1+K_{NiOAc}[OAc^{-1}])$$

was obtained. The F_1 function

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[1] N. Tanaka and H. Ogino, This Bulletin, 34, 1040 (1961).

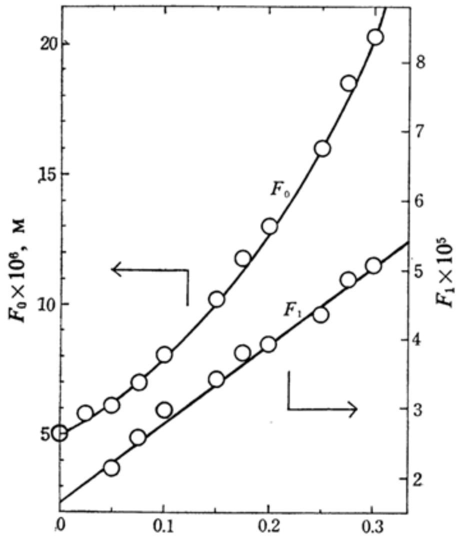

Fig. 2. F_0 (Eq. 1) and F_1 (Eq. 2) as a function of sulfate concentration at 25°C. Acetate concentration is 0.1 M.

$$F_1 \equiv \frac{F_0-\dfrac{\alpha}{\beta K_{\mathrm{NiX}}}(1+K_{\mathrm{NiOAc}}[\mathrm{OAc}^-])}{[\mathrm{SO_4}^{2-}]}$$

$$=\frac{\alpha}{\beta K_{\mathrm{NiX}}}$$

$$\times\sum_{i=0}^{1}\sum_{j=1}^{p}K_{\mathrm{Ni(OAc)}_i\mathrm{(SO_4)}_j}\ [\mathrm{OAc}^-]^i[\mathrm{SO_4}^{2-}]^{j-1} \tag{2}$$

was calculated from the F_0 plot and plotted against the sulfate concentration, as seen in Fig. 2, where the F_1 plot shows as a straight line. This indicates that p is equal to 2 and that no appreciable amount of complexes with three sulfates or more coordinated is present in the solution investigated. The same result was also obtained with other concentrations of acetate.

The fact that n and p are equal to 1 and 2 respectively suggests that complex species of NiOAc^+, $\mathrm{Ni(SO_4)}$, $\mathrm{Ni(OAc)(SO_4)}^-$, $\mathrm{Ni(SO_4)_2}^{2-}$, and $\mathrm{Ni(OAc)(SO_4)_2}^{3-}$ may exist in the solution. Therefore, Eq. 1 is written as

$$F_0=\frac{\alpha}{\beta K_{\mathrm{NiX}}}\{1+K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]+K_{\mathrm{NiSO_4}}[\mathrm{SO_4}^{2-}]$$

$$+K_{\mathrm{Ni(OAc)(SO_4)}}[\mathrm{OAc}^-][\mathrm{SO_4}^{2-}]+K_{\mathrm{Ni(SO_4)_2}}[\mathrm{SO_4}^{2-}]^2$$

$$+K_{\mathrm{Ni(OAc)(SO_4)_2}}[\mathrm{OAc}^-][\mathrm{SO_4}^{2-}]^2\} \tag{3}$$

The formation constants and the value of $\alpha/(\beta K_{\mathrm{NiX}})$ were determined from the plots in Fig. 1 by a graphical treatment similar to that reported previously[1]. The value for $\alpha/(\beta K_{\mathrm{NiX}})$ was obtained to be $4.2_8\times10^{-6}$ mol. l.$^{-1}$ at pH 3.72, and the formation constants obtained are given in Table I. The uncertainties of the determined values were examined by a graphical method[2,3].

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

K_{NiOAc}	1.9	l. mol^{-1}
$K_{\mathrm{NiSO_4}}$	$3._7$	l. mol^{-1}
$K_{\mathrm{Ni(SO_4)_2}}$	$2._6\times10$	l.^{2} mol^{-2}
$K_{\mathrm{Ni(OAc)(SO_4)}}$	1	l.^{2} mol^{-2}
$K_{\mathrm{Ni(OAc)(SO_4)_2}}$	$\sim$3	l.^{3} mol^{-3}

Using the $\alpha/(\beta\ K_{\mathrm{NiX}})$ thus obtained and the formation constants given in Table I, the values of F_0 can be calculated at various concentrations of sulfate and acetate. Two sets of F_0 values were calculated as a function of sulfate concentration at two different concentrations of acetate. The solid curves in Fig. 3 indicate these calculated values, which are in satisfactory agreement with the F_0 values obtained experimentally at various sulfate concentrations.

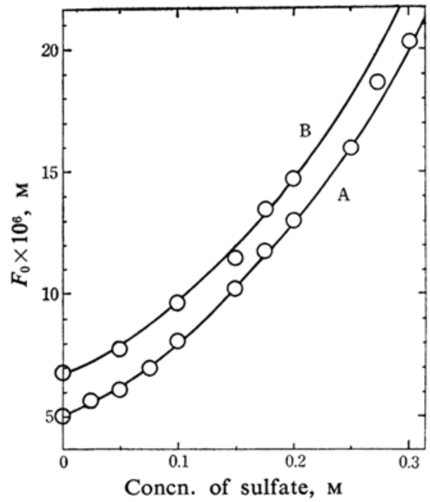

Fig. 3. Calculated and experimental values of F_0 at various concentrations of sulfate in the presence of 0.1 M (A) and 0.3 M (B) of acetate at 25°C: — indicates the calculated, and ○ the experimental value.

The formation constants of K_{NiOAc} and $K_{\mathrm{NiSO_4}}$ at 25°C and ionic strength 0.2 have been given as 2.5 and 11.6 respectively[1]. The formation constants given in Table I are apparently smaller than these values; especially, $K_{\mathrm{NiSO_4}}$ at ionic strength 1.0 is considerably smaller than that at ionic strength 0.2.

In the previous study, at ionic strength 0.2, complex species, $\mathrm{Ni(SO_4)_2}^{2-}$, $\mathrm{Ni(OAc)(SO_4)}^-$ and $\mathrm{Ni(OAc)(SO_4)_2}^{3-}$, were not found to exist

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

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

in appreciable concentrations, whereas in the present study, at ionic strength 1.0, the existence of these complexes is confirmed. It should be noted that the existence of these complex species was confirmed not because of the increase in ionic strength but because of the increase in the concentrations of sulfate and acetate ions. This obviously suggests that the increase in ligand concentration is one of the most important conditions in the study of weak complexes with two or more different ligands.

Summary

The formation of nickel(II) complexes with sulfate and/or acetate has been studied at 25°C and ionic strength 1.0 by the polarographic method reported previously1). The results obtained reveal that complex species, $NiOAc^+$, $NiSO_4$, $Ni(SO_4)_2{}^{2-}$, $Ni(OAc)(SO_4)^-$ and $Ni(OAc)(SO_4)_2{}^{3-}$, are present in the solution. The formation constants determined are: $K_{NiOAc} = 1.9$, $K_{NiSO_4} = 3._7$, $K_{Ni(SO_4)_2} = 2._6 \times 10$, $K_{Ni(OAc)(SO_4)} = 1$ and $K_{Ni(OAc)(SO_4)_2} = \sim 3$ at 25°C and ionic strength 1.0.

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Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai