The Formation Constants of Metal Acetate Complexes. I. Polarographic Determination of the Formation Constants of Acetatonickel(II) Complexes

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In the course of our studies on the inorganic reactions involving metal complexes[1,2], the necessity for the use of the formation constants of various acetato complexes has been realized. Although many of those constants have been reported[3], they were not determined under the conditions which satisfy our present requirements. They were obtained by various researchers by various methods under various conditions.

In order to determine the formation constants of various acetato complexes under the given conditions, a systematic study has been carried out. The careful considerations of various methods which can be applied to the determination of the formation constants led to the conclusion that none of the methods is satisfactory for the present purpose. The potentiometric methods, which are considered to have the widest applicability, generally include uncertainties due to the estimation of the liquid junction potential and that of the activity coefficients of the ions present. The solubility studies have only a limited applicability. The polarographic method which was applied by Hume and his co-workers[4,5] to their study on the acetatolead(II) complexes is available only when the electrode processes are reversible at the dropping mercury electrode.

In the present paper, the principle of a new method for the determination of the

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[1] N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).

[2] Unpublished

[3] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants. Part I. Organic Ligands", The Chemical Society, London (1957), p. 3.

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

[5] E. A. Burns and D. N. Hume, ibid., **78**, 3958 (1956).

formation constants and the application of the method to acetatonickel(II) complexes are presented. The method is similar to that proposed by Schwarzenbach and his co-workers[6-8], but applicable without data of the dissociation and the formation constants concerning the auxiliary complex-forming substance, which Schwarzenbach's method requires.

Theoretical

Let us consider the acetate buffer solution which contains nickel(II) and nitrilotriacetate (NTA) ions[9]. There exist the following equilibria:

$$Ni^{2+} + n\,OAc^- \rightleftarrows Ni(OAc)_n^{(2-n)+} \tag{1}$$

$$Ni^{2+} + X^{3-} \rightleftarrows NiX^- \tag{2}$$

$$NiX^- + H^+ \rightleftarrows NiHX \tag{3}$$

where X^{3-} denotes a tervalent NTA anion. The total concentration of nickel, $\sum[Ni]$, and that of NTA, $\sum[NTA]$, in the solution are given in terms of the ionic and molecular species as follows:

$$\sum[Ni] = [Ni^{2+}] + \sum_1^n [Ni(OAc)_n^{(2-n)+}] + [NiX^-] + [NiHX] \tag{4}$$

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

where $[Ni^{2+}]$ represents the concentration of hydrated nickel ions and $[NTA]_f$, the sum of the concentrations of uncomplexed NTA. In the polarographic measurement it is impossible to measure separately either the concentration of hydrated nickel ions or that of acetatonickel(II) complexes in an acetate medium. On the contrary, the polarographic diffusion current of nickel corresponds to the sum of the diffusion current due to the hydrated nickel ions and that due to the acetatonickel(II) complexes. If the hydrated nickel ion and the acetatonickel(II) 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,

$$[Ni^{2+}]_{app.} = [Ni^{2+}] + \sum_1^n [Ni(OAc)_n^{(2-n)+}] \tag{6}$$

where $[Ni^{2+}]_{app.}$ is the concentration that can be determined from the polarographic diffusion current. Eq. 4 is rewritten as,

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

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

$$[NiX^-] = (\sum[Ni] - [Ni^{2+}]_{app.})/\beta \tag{8}$$

$$[Ni^{2+}] = [Ni^{2+}]_{app.}/(1 + \sum_1^n K_{Ni(OAc)_n}[OAc^-]^n) \tag{9}$$

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

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

and $\beta = 1 + K_{NiHX}^{H}[H^+]$

where K_{H_3X}, K_{H_2X} and K_{HX} represent the first, the second and the third dissociation constant of nitrilotriacetic acid, respectively, and $K_{Ni(OAc)_n}$ and K_{NiHX}^{H} represent the overall formation constant of $Ni(OAc)_n^{(2-n)+}$ and the equilibrium constant of the reaction given by Eq. 3, respectively. The formation constant of NiX^-, consequently, is given as

$$K_{NiX} = \frac{[NiX^-]}{[Ni^{2+}][X^{3-}]} = \frac{\alpha\{\sum[Ni] - [Ni^{2+}]_{app.}\}\{1 + \sum_1^n K_{Ni(OAc)_n}[OAc^-]^n\}}{\beta[Ni^{2+}]_{app.}[NTA]^f} \tag{11}$$

From Eqs. 5 and 7, the concentration of uncomplexed NTA is given as,

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

Introducing Eq. 12 into Eq. 11, the relation

$$\frac{\{[Ni^{2+}]_{app.} - \sum[Ni] + \sum[NTA]\}[Ni^{2+}]_{app.}}{\sum[Ni] - [Ni^{2+}]_{app.}} = \frac{\alpha}{\beta K_{NiX}} + \frac{\alpha}{\beta K_{NiX}}\sum_1^n K_{Ni(OAc)_n}[OAc^-]^n \tag{13}$$

is obtained.

When the values of K_{H_3X}, K_{H_2X}, K_{HX}, K_{NiX} and K_{NiHX}^{H} are known, the formation constants of acetatonickel(II) complexes can be determined with Eq. 13 from the measurements of $[Ni^{2+}]_{app.}$ at n different concentrations of acetate. However, the equilibrium constant K_{NiHX}^{H} has not been reported and the other constants K_{H_3X},

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[6] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1492 (1951).

[7] G. Schwarzenbach and E. Freitag, ibid., **34**, 1503 (1951).

[8] H. Ackermann and G. Schwarzenbach, ibid., **32**, 1543 (1949).

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

$K_{\mathrm{H_2X}}$, K_{HX} and K_{NiX} have been determined[6,10,11] in conditions not convenient for our study.

An alternative and better procedure for determining the formation constants of acetatonickel(II) complexes was developed. It is obvious that both α and β in Eq. 13 are constant in the solution of the given pH and the given ionic strength. The values of $[\mathrm{Ni}^{2+}]_{\mathrm{app.}}$ are determined by the polarographic method at the given pH and ionic strength, but at varied concentrations of acetate. The left-hand side of Eq. 13 is calculated and plotted against the concentration of acetate. If the left-hand side of Eq. 13 is denoted with F_0, it is expressed as,

$$F_0=\frac{\alpha}{\beta K_{\mathrm{NiX}}}+\frac{\alpha}{\beta K_{\mathrm{NiX}}}K_{\mathrm{NiOAc}}[\mathrm{OAc}^-]+\frac{\alpha}{\beta K_{\mathrm{NiX}}}K_{\mathrm{Ni(OAc)_2}}[\mathrm{OAc}^-]^2+\cdots\cdots \quad (13')$$

From extrapolation of the plot to zero acetate concentration, $\alpha/\beta K_{\mathrm{NiX}}$ is obtained. Then we obtain,

$$F_1=\frac{F_0-\dfrac{\alpha}{\beta K_{\mathrm{NiX}}}}{\dfrac{\alpha}{\beta K_{\mathrm{NiX}}}[\mathrm{OAc}^-]}=K_{\mathrm{NiOAc}}+K_{\mathrm{Ni(OAc)_2}}[\mathrm{OAc}^-]+\cdots\cdots \quad (14)$$

$$F_2=\frac{F_1-K_{\mathrm{NiOAc}}}{[\mathrm{OAc}^-]}=K_{\mathrm{Ni(OAc)_2}}+K_{\mathrm{Ni(OAc)_3}}[\mathrm{OAc}^-]+\cdots\cdots \quad (15)$$

F_1 is plotted against $[\mathrm{OAc}^-]$ and the K_{NiOAc} is determined by extrapolating the plot to zero acetate concentration. The further treatment leads to the determinations of $K_{\mathrm{Ni(OAc)}_n}$, if higher acetato complexes are present in the solution.

Experimental

Reagents. — The solution of disodium nitrilotriacetate was prepared from the commercial nitrilotriacetic acid (DOTITE NTA), and standardized against the standard solution of copper(II) nitrate by amperometric titration with the same procedure for ethylenediaminetetraacetate[12 13]. The standard solution of nickel nitrate was prepared by dissolving a known amount of pure nickel metal in reagent-grade nitric acid. Commercial guaranteed reagents were used for buffers and supporting electrolytes without further purification.

Apparatus and Procedure. — A Shimadzu RP-2 pen-recording polarograph was used for the measurement of the current-voltage curves. The dropping mercury electrode used had an m value of 1.27 mg./sec. and a drop time t of 3.69 sec. in an air-free 0.1 M potassium chloride solution at 25°C with open circuit.

The sum of the diffusion currents of hydrated nickel ions and acetatonickel(II) complexes were determined in the acetate buffer of pH 3.83±0.01 containing nickel(II) and a slight excess of NTA at 15, 25 and 35°C. The concentration of acetate in the acetate buffer was varied from 0.05 M to 0.20 M. The ionic strength of the solution was adjusted to be 0.2 with potassium nitrate, unless otherwise stated. Polyoxyethylene lauryl ether (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 accurately, after the polarographic measurement, with a Hitachi Model EHP-1 pH meter with a glass electrode.

In the preliminary experiment, it was observed that the formation of nickel-NTA complexes nearly completed within 30 minutes under the experimental condition. Therefore, all reaction mixtures were kept in a thermostat for 3 hours to reach the completely equilibrated condition before being subjected to the polarographic measurement.

Results

The polarograms were recorded with the solutions of the same pH containing 1.00×10^{-3} M nickel nitrate, 1.12×10^{-3} M

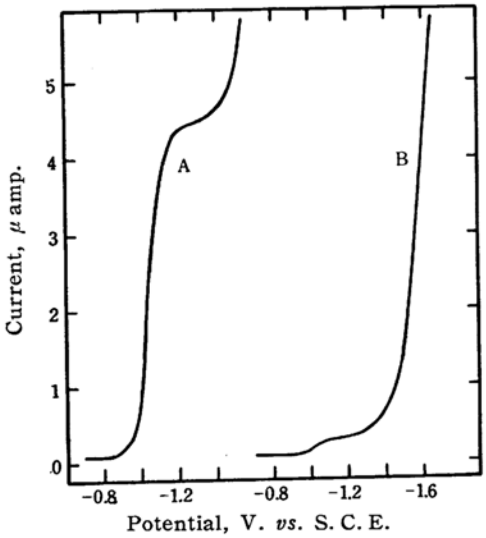

Fig. 1. Polarograms of 1.00×10^{-3} M nickel (II) obtained in the acetate-nitrate media of pH 3.83 at 25°C in the absence (curve A) and in the presence of 1.12 $\times10^{-3}$ M NTA (curve B). The residual current is not corrected.

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[10] G. Schwarzenbach, H. Ackermann and H. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).

[11] V. L. Hughes and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1319 (1956).

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

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

NTA and various concentrations of acetate. Fig. 1 shows the polarograms obtained in the absence and the presence of a slight excess of NTA. Nickel(II) gives an irreversible wave with the half-wave potential of about −1.05 volts *vs.* S. C. E. in the acetate-nitrate media. (Curve A in Fig. 1). This wave is due to the reductions of the hydrated nickel(II) ions and the acetatonickel(II) complexes. The presence of a slight excess of NTA decreases to a great extent the height of the nickel wave, but does not obliterate the wave completely. A small wave which was followed by the depolarization of the supporting electrolyte is clearly seen in Fig. 1 (Curve B). The limiting current of the wave was found to be proportional 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 and is proportional to the concentration of the electroactive species.

The apparent diffusion current constants were determined from the measurement of the diffusion current of nickel(II) at various acetate concentrations at the given ionic strength. In Fig. 2, typical examples of those measurements are given. The values of $[Ni^{2+}]_{app.}$ of Eq. 6 were calculated with the aid of those diffusion current constants from the limiting currents obtained with reaction mixtures. The results are given in Table I, which indicate that $[Ni^{2+}]_{app.}$ increases with increasing concentration of acetate.

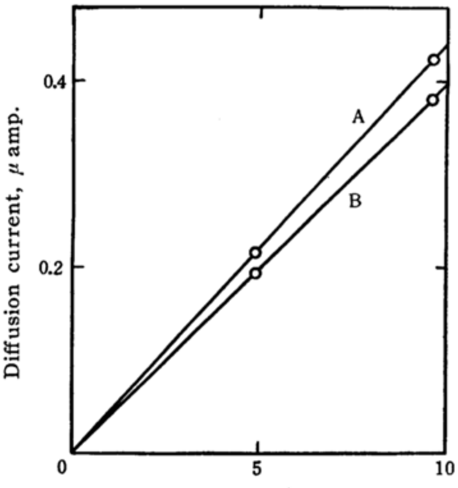

Fig. 2. Relation between diffusion current and concentration of nickel nitrate in acetate buffer solutions of pH 3.83 at 25°C. Acetate concentrations are: A, 0.05 M; B, 0.20 M.

The left-hand side of Eq. 13 was calculated with the values of $[Ni^{2+}]_{app.}$ given in Table I, and was plotted against the acetate concentration. The results are shown in Fig. 3, where it is clearly seen that there is a linear relation between the values of the left-hand side of Eq. 13 and the concentration of acetate. This indicates conclusively that only one type of acetato complex, $NiOAc^+$, exists in the solution under the experimental condition. From the plots in Fig. 3, the values of

TABLE I. $[Ni^{2+}]_{app.}$ OBTAINED EXPERIMENTALLY AT VARIOUS TEMPERATURES

Concn. of acetate, M	$[Ni^{2+}]_{app.}\times10^5$, M		
	15°C	25°C	35°C
0.05	3.77	3.86	3.87
	3.80	3.77	3.89
0.10	4.06	4.11	4.23
	4.12	4.19	4.30
			4.30
0.15	4.46	4.42	4.63
	4.33	4.50	4.54
			4.63
0.20	4.78	4.76	4.87
	4.66	4.88	4.83
			4.87

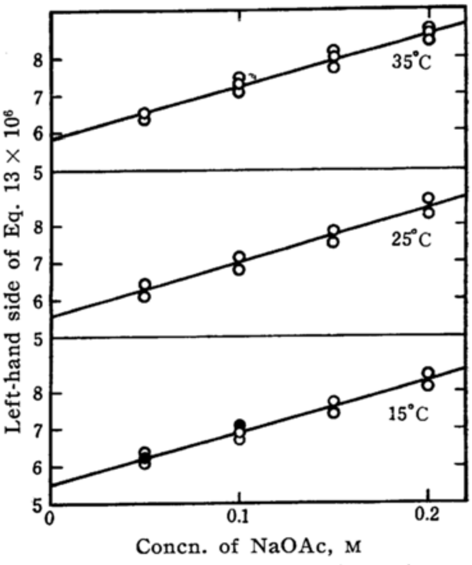

Fig. 3. Relation between the value of left-hand side of Eq. 13 and the concentration of acetate at various temperatures. ○ indicates the values obtained in nitrate media, and ● in perchlorate media.

$\alpha/\beta K_{\mathrm{NiX}}$ and $\alpha K_{\mathrm{NiOAc}}/\beta K_{\mathrm{NiX}}$ in Eq. 13′ were determined, the former being given by the intersept at $[\mathrm{OAc}^-]=0$ and the latter, by the slope. The experimental results obtained at 25°C were also treated by the least square method, with the result that the probable errors of $\alpha/\beta K_{\mathrm{NiX}}$ and $\alpha K_{\mathrm{NiOAc}}/\beta K_{\mathrm{NiX}}$ were ±1.5% and ±4.1%, respectively. The formation constants of the monoacetatonickel(II) complex at 15°, 25° and 35°C were obtained by dividing the values of $\alpha K_{\mathrm{NiOAc}}/\beta K_{\mathrm{NiX}}$ by those of $\alpha/\beta K_{\mathrm{NiX}}$. These are given in Table II.

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

Temp., °C	K_{NiOAc}
15	2.6
25	2.6
35	2.4

Discussions

The formation constants of monoacetatonickel(II) complex, K_{NiOAc}, are found to be almost independent of temperature in the range from 15° to 35°C. Jena, Aditya and Prasad[14] studied the acetatonickel(II) complex by the e.m.f. method and reported the thermodynamic formation constant of the monoacetatonickel(II) complex to be 13.5 at 30°C. The formation constant at ionic strength 0.2 was calculated from this value to be 4.5, when the activity coefficient of acetate ions was assumed to be equal to that of monoacetatonickel(II) ions and the activity coefficient of nickel ions was estimated to be 0.33[15]. The resulting value of 4.5 seemed to be in good agreement with the formation constant obtained in this study. Both values were determined by completely different methods and the value obtained by the e.m.f. method involves the uncertainty due to the estimation of the activity coefficient. Fronaeus[16] studied the formation of the complex by means of the ion-exchanger and also by means of the measurement with a quinhydrone electrode and obtained the formation constants of 4.7 and 5.5, respectively, at ionic strength 1.0 (sodium perchlorate) at 20°C. They also seem to support the value obtained in this study.

The experimental solution contained a certain quantity of potassium nitrate, which was added to adjust the ionic strength of the solution. It is expected that the nitrate ion has such a small tendency to form a complex with the nickel(II) ion that it seems unnecessary to consider the effect of the nitrate ion in the present calculation. The confirmation of this was attained in the comparison of the experimental results observed in nitrate and perchlorate media. The perchlorate has been known to have the least complex-forming ability. If an appreciable amount of nitrato complex is formed in the nitrate media, the values of the left-hand side of Eq. 13 obtained at the same concentration of acetate are expected to be larger in the nitrate media than in the perchlorate media. The measurement of $[\mathrm{Ni}^{2+}]_{\mathrm{app.}}$ was carried out in the solution of which the ionic strength was adjusted with sodium perchlorate instead of potassium nitrate. The value of $[\mathrm{Ni}^{2+}]_{\mathrm{app.}}$ agreed completely with that obtained in the solution containing nitrate. From this fact it may be concluded that the nitrate ions show least complex-forming tendency and, consequently, the use of nitrate ions requires no correction on the present calculation.

In conclusion it should be noted here that the method for the determination of the formation constant given in this paper may be applicable to the study of other metal complexes of relatively small formation constants. The method is more rigorous than the e. m. f. method, because the latter method requires the estimations of the liquid junction potential and the activity coefficient. The determination of the sum of the concentration of hydrated nickel ions and that of acetatonickel(II) complexes may be carried out by other methods.

Summary

A new method for the determination of the formation constants of metal acetate complexes has been developed. The method is based on the polarographic measurement of the sum of the equilibrium concentrations of hydrated metal ions and metal acetate complexes in the presence of an appropriate auxiliary complex-forming substance. One of the advantages of the method is that no estimation is required in the course of the calculation. The other is that no information of the dissociation and formation constants is

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[14] P. K. Jena, S. Aditya and B. Prasad, *J. Indian Chem. Soc.*, **30**, 735 (1953).

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

[16] S. Fronaeus, *Acta Chem. Scand.*, **6**, 1200 (1952).

required concerning the auxiliary complex-forming substance.

The method is applied to the study of acetatonickel(II) complexes using nitrilotriacetate as an auxiliary ccmplex-forming substance. The results reveal that only monoacetatonickel(II) ions, $NiOAc^+$, exist in the solution containing acetate up to 0.2 M in concentration. The formation constants K_{NiOAc} at ionic strength 0.2 are calculated to be 2.6 at 15°C, 2.6 at 25°C and 2.4 at 35°C.

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