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A POTENTIOMETRIC AND CALORIMETRIC STUDY OF THE POLYNUCLEAR AND MONONUCLEAR COMPLEXES OF NICKEL(II) WITH THIOGLYCOLIC ACID

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Thioglycolic acid forms very stable complexes with many metal ions. The replacement in complexiметry of potassium cyanide by thioglycolic acid as a masking agent has been thoroughly discussed by Přibil and Vesely[1]. However, it would be very interesting to know which types of complexes are formed and why these complexes are so stable. In this study, particular attention is paid to the nickel(II) complexes. In the first papers devoted to this subject, the system was considered as mononuclear. Stability constants were calculated from one formation curve only[2]. Later Leussing *et al.*[3] showed that polynuclear complexes are formed as well as mononuclear complexes; they claimed that a good description of the system was obtained by considering the complexes B_4A_6 and BA_2, B being the metal ion and A the ligand. Perrin and Sayce[4] repeated the experiments of Leussing, and treated the experimental data with a GAUSS computer programme. They found, in addition to the above-mentioned complexes, the complexes B_3A_4, B_2A_2 and BA_3, and also some evidence for the complex BA. Below pH 5.5, the complex B_3A_4 predominates; in neutral medium, B_4A_6 is the main compound, and in basic medium the complex formation is mononuclear with BA_2 as the most important species. In this study, an attempt was made to determine the enthalpy and entropy changes accompanying the complex formation from calorimetric experiments.

Therefore it was necessary to study the system again and to search for those regions where one complex largely predominates or where several complexes are simultaneously present in almost equal amounts, since only under these conditions can significant enthalpy changes be obtained. Furthermore, it was necessary to have sufficiently high concentration of the complexes, otherwise the heat liberated was too small for precise measurements.

EXPERIMENTAL

Apparatus

pH measurements were performed with a Radiometer pHM4 pH-meter, equipped with a G202c glass electrode and a saturated calomel electrode as reference. The glass electrode was standardized against a 0.01 *M* borax buffer solution as described by Bates[5]. All solutions were maintained at 25 ± 0.1°C.

Calorimetric measurements were carried out with an LKB 8700-2 Precision Calorimeter.

Reagents

Thioglycolic acid (Fluka) was redistilled before use. Aqueous solutions were prepared with oxygen-free water and regularly flushed with pure nitrogen gas. Under these conditions, the solutions were stable for a long period[6]. A stock solution of 0.2 *M* nickel nitrate was prepared and standardized gravimetrically as bis(dimethylglyoximato)nickel[7]. In order to keep the activity coefficients as constant as possible, all solutions were made up to an ionic strength of 0.5 with potassium nitrate (Merck *p.a.*). Before use, all solutions were abundantly flushed with pure nitrogen gas.

Procedure for pH titration

A mixture of metal ion and thioglycolic acid was titrated with potassium hydroxide. Four titrations were performed with total metal ion concentrations of respectively 0.032 *M*, 0.008 *M*, 0.002 *M* and 0.0005 *M* and an initial concentration of total ligand equal to five times the concentration of the metal ion. The total metal ion concentration was kept constant by adding, after each addition of potassium hydroxide, an equal volume of metal ion solution with concentration twice that of the total metal ion in the cell. During titration, the solution was protected from air by vigorously bubbling a stream of nitrogen gas through it.

Procedure for calorimetric titration

Four thermometric titrations were performed. In each titration, the total volume pipetted into the reaction vessel was 80 ml; the mixtures were composed as shown in Table I. To these solutions a 1 *M* potassium hydroxide solution was added in 0.25-ml portions. After each addition the heat capacity of the solution was determined by quantitative electrical heating. From this and from the change in temperature during the addition, the heat effect in calories was obtained as described by Wadso[8]. Before closing the reaction vessel, air was removed by a stream of pure nitrogen.

TABLE I

COMPOSITION OF TITRATED MIXTURES

Titration number	*Vol. 0.032 M $Ni(NO_3)_2$ (ml)*	*Vol. 0.128 M ligand (ml)*	*Vol. 0.5 M KNO_3 (ml)*
1	0	30	50
2	40	40	0
3	30	30	20
4	20	20	40

RESULTS AND MATHEMATICAL TREATMENT

The symbols used here are the same as in the papers of Sillén[9,10,11] and are listed below:

B total concentration of Ni^{2+}

b concentration of free Ni^{2+}

A total ligand concentration
h_2a concentration of $SH–CH_2–COOH$
ha concentration of $SH–CH_2–COO^-$
a concentration of $^-S–CH_2–COO^-$
$pa = -\log a$
h activity of hydrogen ion
c_{base} concentration of base added
Z average number of ligands bound per Ni^{2+} ion
t number of ligands in a link
n variable integer: number of links in a core+links complex
$\bar{n}$ average number of links in a core+links complex
K_{Hi} mixed protonation constants of the ligand, defined as $K_{Hi} = h_i a/h \cdot h_{i-1} a$
β_{pq} overall stability constant for a B_qA_p complex, defined as $\beta_{pq} = (B_qA_p)/b^q \cdot a^p$
$\log F = \log B/b$
$u = a^t b$
β_i overall stability constant for a complex $B(A_tB)_i$
$g = \sum_{i=1}^{n} \beta_i u^i$
$y = Z/t$
$x = t \log a + \log B$
N maximum number of hydrogen ions that the ligand can take up

Potentiometric study

The formation function $Z(a)$ was calculated from eqns. (1) and (2) by means of a general computer programme[12]. The results were printed, plotted and punched on cards for further use.

$$a = \frac{NA - c_{base} - [H^+] + [OH^-]}{\sum_{n=1}^{N} nh^n a \prod_{i=1}^{n} K_{Hi}} \quad (1)$$

$$Z = \left[A - a\left(1 + \sum_{n=1}^{N} h^n \prod_{i=1}^{n} K_{Hi}\right)\right]/B \quad (2)$$

In the pH range investigated (3–9), the terms $[H^+]$ and $[OH^-]$ can be neglected. As can be seen, the protonation constants K_{Hi} for the carboxyl and mercapto groups are needed to start the calculation of the formation function. These constants were obtained as described by Thiers *et al.*[13] and found to be, respectively, 3.548 and 10.048.

The formation curves $Z(pa)_B$ obtained by these calculations are shown in Fig. 1. As can be seen, a set of parallel curves was found for Z values lower than 1.3. Since a was small over the range investigated, we can assume that b is not negligible in comparison with B. According to Sillén[9,10,11], systems which give such curves in these conditions are polynuclear and form a so-called "core+links" system of general formula $B(A_tB)_n$. The value of t can be determined from the spacing of the curves with the aid of eqn. (3):

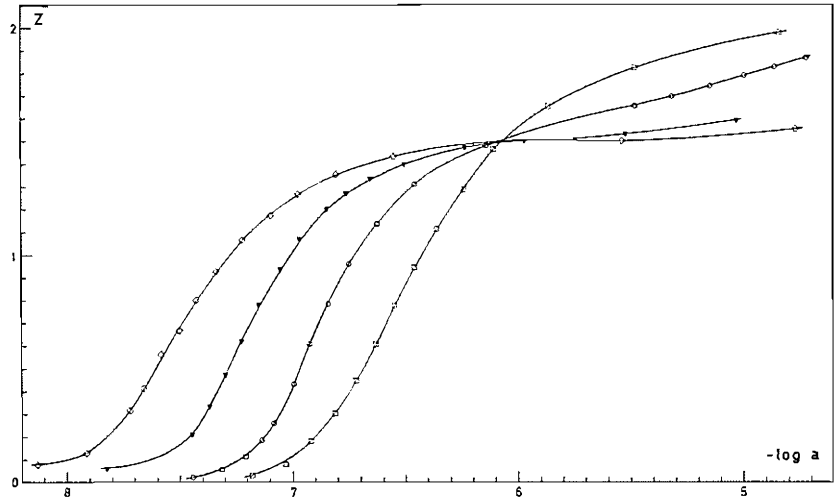

Fig. 1. The formation curves of the system nickel(II)– and thioglycolic acid. B: (◇) 0.032 M, (▼) 0.008 M, (○) 0.002 M, (□) 0.0005 M.

$$t = -\left(\frac{\partial \log B}{\partial \log a}\right)_Z \tag{3}$$

A plot of log B versus log a at a given Z below 1.3 gives a straight line of slope $t=2$. The complexes present can therefore be represented by the general formula $B(A_2B)_n$. It can be observed (Fig. 1) that for larger values of B, the curve $Z(pa)_B$ tends to a value of $Z=1.5$, which indicates that a very stable complex is formed. As can be seen from eqn. (4), for $Z \leqslant 1.5$, the highest possible value of n is 3:

$$Z = \frac{p}{q} = \frac{2n}{n+1} = 1.5 \tag{4}$$

Accordingly, three polynuclear species can be formed, namely B_2A_2, B_3A_4 and B_4A_6. This was confirmed by calculating the function $y(x)$, which is shown in Fig. 2. As y and x are both functions of the same variable u, all $y(x)$ curves must coincide. For y values below 0.6, this criterion was satisfied but for higher values deviations were observed. These deviations are due to the conversion of polynuclear to mononuclear species. During the titration the colour of the solution suddenly changed from brown to pink. As Z_{max} is 2 (Fig. 1), mononuclear species BA and BA_2 could be formed. To summarize, it can be stated that below $Z=1.5$ polynuclear species were formed, which were converted to mononuclear in the range $Z=1.5$–2.0.

In order to determine the stability constants of the polynuclear species, $\bar{n}$ can be calculated from eqn. (5):

$$\bar{n} = \frac{y}{1-y-F^{-1}} \tag{5}$$

F was found by calculating the following integral

$$\log F = 0.434y + \int_{-\infty}^{x} y\,dx \tag{6}$$

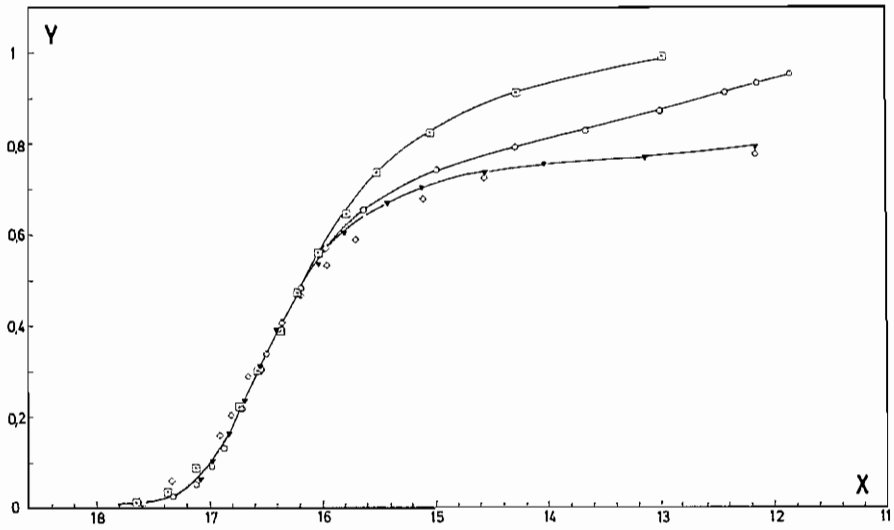

Fig. 2. The y,x curve of the system nickel(II)- and thioglycolic acid. *B*: As for Fig. 1.

TABLE II

CALCULATION OF $\bar{n}$

y	$\bar{n}$	y	$\bar{n}$
0.015	2.004	0.605	2.870
0.07	2.112	0.645	2.901
0.095	2.037	0.685	2.923
0.175	2.176	0.705	2.966
0.285	2.475	0.720	3.008
0.385	2.572	0.730	3.027
0.485	2.854	0.750	3.088
0.555	2.889		

Integration was started at a finite value of x, and the residual integral could be neglected. The results are given in Table II. $\bar{n}$ varies between 2 and 3, indicating that the complex B_2A_2 will not be formed.

The functions g and u were calculated. The successive extrapolation method of Fronaeus[14] and Leden[15] is used to obtain the stability constants.

The function $f_1 = g/u = \beta_1 + \beta_2 u + \beta_3 u^2$ was extrapolated for $u = 0$ in order to obtain a value for β_1. Another function $f_2 = (f_1 - \beta_1)/u$ was calculated and again extrapolated for $u = 0$. This extrapolation procedure was repeated until the function $f_n = (f_{n-1} - \beta_{n-1})/u$ was constant. This was found for $n = 3$, as expected. The results are given in Table III. The complex B_2A_2 was found not to be present.

For the calculation of the stability constants of the mononuclear species, the following points should be noted. As polynuclear species were assumed to predominate in the Z area $0 \rightarrow 1.5$, the stability constant of the mononuclear BA could not be determined. The stability constant of the mononuclear BA_2 could be

TABLE III

STABILITY CONSTANTS OF COMPLEXES

Log	*Extrapolation procedure*	*After modification*	*PNUC*	*Leussing et al.*[3]
$\beta_{3,4}$	32.079	32.699	32.219	33.845
$\beta_{4,6}$	49.643	49.301	49.157	49.845
$\beta_{1,2}$	12.809	12.666	12.759	13.040

determined from the data of the Z area 1.5→2, where a mixture of B_4A_6 and BA_2 was considered; the presence of B_3A_4 in that region could be neglected.

The following equations can be written:

$$B = b + \beta_{1,2} ba^2 + 4\beta_{4,6} b^4 a^6 \tag{7}$$

$$BZ = 2\beta_{1\ 2} ba^2 + 6\beta_{4\ 6} b^4 a^6 \tag{8}$$

Since data for $Z(a)_B$ are known, the two unknown factors are $\beta_{1,2}$ and b. Elimination of b from eqns. (7) and (8) yields:

$$a^8(2-Z)\beta_{1,2}^4 + 2a^6(4Z-9)\beta_{1,2}^3 + 18a^4(3-Z)\beta_{1,2}^2 + 54a^2\beta_{1,2} + 27Z - 2\beta_{4,6} a^6 B^3 (3-2Z)^4 = 0 \tag{9}$$

This fourth-power equation in $\beta_{1,2}$ can be solved by the method of Newton, to give $\log \beta_{1,2} = 12.809$.

The formation curves were recalculated and plotted from eqns. (10) and (11) with the aid of an IBM 360/30 computer

$$Z = \frac{2\beta_{1,2} ba^2 + 4\beta_{3,4} b^3 a^4 + 6\beta_{4,6} b^4 a^6}{b + \beta_{1,2} ba^2 + 3\beta_{3,4} b^3 a^4 + 4\beta_{4,6} b^4 a^6} \tag{10}$$

$$B = b + \beta_{1,2} ba^2 + 3\beta_{3,4} b^3 a^4 + 4\beta_{4,6} b^4 a^6 \tag{11}$$

It was found that the stability constants needed to be modified. The final results are given in Table III.

Later, the data of this experiment were treated by means of a PNUC computer programme, with a least-squares procedure. The square error sum U is given by

$$U = (Z_{exp} - Z_{calc})^2 \tag{12}$$

Z_{calc} was calculated with estimated values for β_{qp} from eqns. (10) and (11). The function U was minimized by the variable metric method, described by Davidon[16]. The standard deviation $s(Z)$ was calculated from:

$$s(Z) = [U_{min}/(n_{exp} - n_{par})]^{\frac{1}{2}} \tag{13}$$

where U_{min} is the value for U at the minimum, n_{exp} the number of experimental points and n_{par} the number of parameters. The values of β_{qp} corresponding with U_{min} are the "best" parameters. These results are also given in Table III.

Other possible species present in solution are the complexes BA and B_2A_2. Perrin and Sayce[4] even found evidence for the presence of BA_3. Each of these three complexes was added to the system and the minimum U_{min} was again calculated. As no better minimum was found, these three species were rejected.

Calorimetric study

From titration 1 (Table I), the heats and entropies of protonation for the carboxylate and the mercaptan group were calculated with the aid of eqns. (14) and (15):

$$Q - Q_{dil} = -(\Delta H_{H_2O} - \Delta H_{Hi})[OH^-] \quad (14)$$

$$\Delta G_{Hi} = -RT \ln K_{Hi} = \Delta H_{Hi} - T\Delta S_{Hi} \quad (15)$$

ΔH_{H_2O} was taken to be -13.34 kcal mole^{-1}, as established by Vanderzee and Swanson[17], Hale *et al.*[18] and the present experiments. The results are given in Table IV.

TABLE IV

HEAT AND ENTROPY OF COMPLEX FORMATION

	log K_{ni}/*log* β	ΔG (*kcal mole*$^{-1}$)	ΔH (*kcal mole*$^{-1}$)	ΔS (*cal mole* K^{-1})
–COOH	3.548	−4.84	+0.11	+16.6
–SH	10.084	−13.75	−6.52	+24.3
BA_2	12.759	−17.39	−3	+48
B_3A_4	32.219	−43.91	−21	+75
B_4A_6	49.157	−67.00	−31	+118

The heats and entropies of formation of the complexes were calculated from titrations 2,3 and 4 with the aid of the equation:

$$\begin{aligned}&\Delta H_{1.2}(-\beta_{1.2}ba^2) + \Delta H_{3.4}(-\beta_{3.4}b^3a^4) + \Delta H_{4.6}(-\beta_{4.6}b^4a^6)\\ &\quad + (\Delta H_{H1} + \Delta H_{H2})(a + 2\beta_{1.2}ba^2 + 4\beta_{3.4}b^3a^4 + 6\beta_{4.6}b^4a^6)\\ &\quad + \Delta H_{H1}haK_{H2} - Q + Q_{dil} = 0\end{aligned} \quad (16)$$

The values for b, a and h were calculated from the stability constants and the total concentrations in the titration cell with the aid of the computer program BDTV[19]. The final values of $\Delta H_{1.2}$, $\Delta H_{3.4}$ and $\Delta H_{4.6}$ were obtained with the aid of a computer program THER. The results are given in Table IV.

DISCUSSION

As can be seen from Table II the nickel(II)–thioglycolic acid system can be represented by the formation of three complexes: BA_2, B_4A_6 and B_3A_4. The contribution of B_3A_4 to the system can be considered as small. These results are in good agreement with the work of Leussing *et al.*[3]. In contrast to the results of Perrin and Sayce[4], no evidence for the existence of the species BA, B_2A_2 or BA_3 was found.

From the formation function at different temperatures, Leussing *et al.* derived the enthalpy of formation of the complexes BA_2 and B_4A_6 and found -3.5 kcal mole^{-1} and -31 kcal mole^{-1}, respectively. The present calorimetric results (Table IV) confirm these values, and in addition a value for $\Delta H_{3.4}$ was deter-

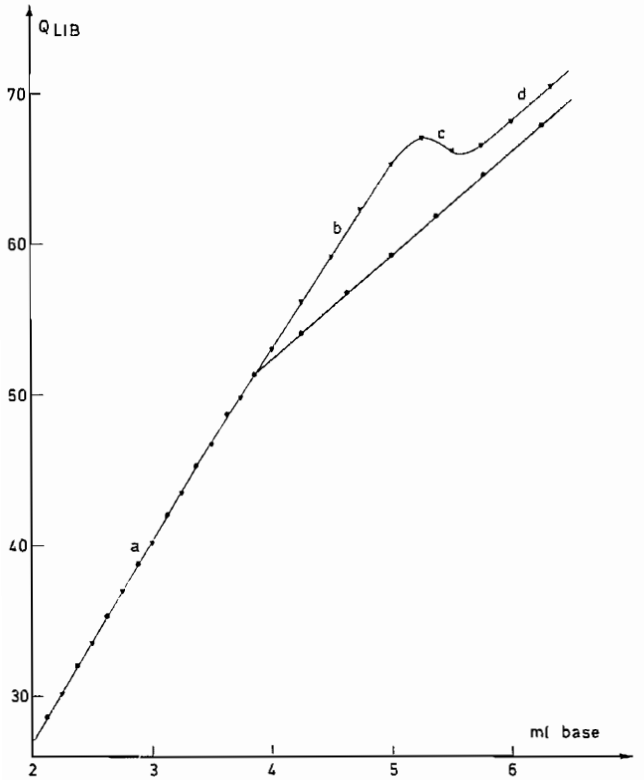

Fig. 3. Calorimetric curves for thioglycolic acid and for a mixture of nickel(II) and thioglycolic acid with potassium hydroxide. (●) Titration 1, (▼) titration 3.

mined as -21 kcal mole^{-1}. It is obvious that more heat is liberated per nickel ion when polynuclear complexes are formed than for mononuclear species. This is illustrated in Fig. 3, where two plots of the heat liberated during a titration *versus* the amount of added base are given. The first plot is related to titration 1 (Table I); two straight lines are obtained for the neutralization of the carboxylic and the mercaptan group, respectively.

The data obtained from titration 3 are shown in the second plot; the curve obtained can roughly be divided in four parts: (a) the carboxylic group is neutralized but no complexes are formed; (b) mainly polynuclear complexes are formed; (c) the polynuclear complexes are converted to mononuclear ones, the reaction being endothermic; (d) all metal ions are bound as BA_2, the heat liberated being due to the neutralization of the mercaptan group.

If it is accepted that the structures of the complexes proposed by Leussing *et al.*[3] are correct and that there are 6 double (Ni–S) and 4 (Ni–O) bonds for the B_4A_6 complex, 4 double (Ni–S) and 4 (Ni–O) bonds for the B_3A_4 complex, and 2 single (Ni–S) and 2(Ni–O) bonds for the BA_2 complex, then it can be calculated that a double (Ni–S) bond gives a contribution to the enthalpy of formation of about -5 kcal mole^{-1}. The heat liberated at the formation of a B_4A_6 complex will almost entirely be caused by the formation of six double (Ni–S) bonds.

As would be expected, the effect on enthalpy of a bonding carboxylate group is very small. It can also be shown that a single (Ni–S) bond gives an enthalpy effect less than one third of the effect of a double (Ni–S) bond. The stability of the mononuclear BA_2 is mainly caused by the entropy term; indeed, per nickel ion, the entropy contribution to the free energy is considerably higher than in the case of the B_3A_4 or B_4A_6 complex. The high entropy term could be caused by the chelating ability of the carboxylate group. This would explain why for analogous ligands such as 2-mercaptoethanol and 3-mercapto-1,2-propanediol, which lack a chelating group at the end of the aliphatic chain, the polynuclear chain formation is continued[20], polymeric complexes are formed, and no mononuclear species is found.

The fact that thioglycolic acid forms strong complexes can be ascribed to two different causes: in the first place the polynuclear complexes are very stable, which is mainly due to the favourable enthalpy change accompanying the linking of two metal ions by one sulphur atom; in the second place, when mononuclear complexes are formed, the stability is enhanced by chelate formation.

SUMMARY

The complex formation between nickel(II) and thioglycolic acid was studied by a potentiometric method at 25°C and in 0.5 *M* KNO_3. In solution two polynuclear complexes, B_3A_4 and B_4A_6, and one mononuclear complex, BA_2, were detected, and the following stability constants were determined: $\log \beta_{3,4} = 32.219$; $\log \beta_{4,6} = 49.157$; $\log \beta_{1,2} = 12.759$. The enthalpies of formation of the double (Ni–S–Ni) and single (Ni–S) bond were determined by calorimetric titration, and were found to be -5 kcal mol^{-1} and -1.5 kcal mol^{-1}, respectively. It was shown that the stability of the polynuclear complexes is due to the enthalpy term, whereas the stability of the mononuclear complexes can be ascribed principally to the entropy term.

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