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A POTENTIOMETRIC AND CALORIMETRIC STUDY OF THE POLYNUCLEAR AND MONONUCLEAR COMPLEXES OF Ni(II) AND Zn(II) WITH 2-MERCAPTOPROPIONIC ACID

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Abstract—The composition and stability constants of the complexes formed between Ni^{2+} and Zn^{2+} and 2-mercaptopropionic acid (thiolactic acid, TLA) were determined by a pH-metrical method at 25°C and in 0·5 M KNO_3. For the system Ni^{2+}/TLA, the complexes BA, BA_2 and B_3A_4 were found. For the system Zn^{2+}/TLA the same complexes as for Ni^{2+} and also the complex B_2A_2 were detected. The enthalpy and entropy changes, accompanying the formation of the complexes were calculated from calorimetric titrations.

INTRODUCTION

ALTHOUGH 2-mercaptopropionic acid (thiolactic acid, TLA) is commercially available no studies of the complexation of this ligand with metal ions could be found in the literature. This is surprising because a similar mercaptocarboxylic acid, thioglycolic acid (TGA) has been intensively studied[1–3]. It was found[4] that this ligand forms with Ni^{2+} a mixture of the polynuclear complexes B_3A_4 and B_4A_6 and the mononuclear complex BA_2. Analogous complexes are detected in the complexation of TGA with Zn^{2+}[3, 5]. the only difference between TGA and TLA is a $-CH_3$ group substituted in α place of the -SH function. When only mononuclear complexes are formed an α-methyl substitution would not strongly influence the stability constants and certainly not the composition of the complexes. When polynuclear complexes are formed the effect of such a substitution cannot be predicted. Therefore we found it interesting to study the complexation of TLA with the metal iohs Ni^{2+} and Zn^{2+} and to compare the results obtained with those found for TGA. In addition and for a better understanding of the driving forces to complexation we also determined the enthalpy and entropy changes accompanying the formation of the complexes.

EXPERIMENTAL

Apparatus

pH-measurements were performed with a digital pH-meter: "Radiometer pHM52", equipped with a G 202 C glass electrode and saturated calomel electrode as reference. The glass electrode was standardized with an NBS standard buffer, 0·01 M borax, which according to Bates[6] gives a pH value of 9·18 at 25°C. All solutions were maintained at that temperature.

Calorimetric measurements were carried out with an "LKB 8700-2 Precision Calorimeter". The reagent was added with an automatical pistion buret: "Tacussel Electroburap", equipped with a preselection unit.

The calculations were performed with a number of FORTRAN IV computer programmes, and executed on a Siemens 4004/150 computer. A complete deck listing and instruction set of the programmes may be obtained by writing to the authors.

Reagents

Stock solutions of 0·2 M nickel and zinc nitrate were prepared and standardized gravimetrically as bis (dimethylglyoximato)-nickel and $ZnNH_4PO_4$ respectively[7]. 2-Mercaptopropionic acid was obtained from Fluka and redistilled just before use. Aqueous solutions of TLA were stable for a long period under condition that they were prepared with oxygen-free water and that they were regularly flushed with pure nitrogen gas[8].

All solutions were made up to an ionic strength of 0·5 with potassium nitrate (Merck p.a.) in order to keep the activity coefficients as constant as possible.

pH-metrical titration procedure

Mixtures of TLA and metal ions were titrated with KOH. The total metal ion concentration was varied from 0·002 M to 0·032 M. The initial concentration of ligand in each titration was equal to five times the total metal ion concentration. After each addition of KOH, an equal volume of a metal ion solution, with concentration twice that in the reaction cell, was added from a second buret. In that way the total metal ion concentration in the titration vessel was kept constant. Air was removed by bubbling a stream of nitrogen gas through the reaction cell.

Calorimetric titration procedure

The composition of the solution, titrated in the calorimeter, is shown in Table 1. As can be seen from this table four calorimetric titrations were carried out for each system.

Table 1.

Number of titration	metalnitrate 0·032 M (ml)	TLA 0·128 M (ml)	0·5 M KNO_3 (ml)
1	0	40	40
2	40	40	0
3	30	30	20
4	20	20	40

To these solutions a 1 M KOH solution was added in 0·25 ml portions. The heat liberated was calculated as described by Wadsö[9]. Before closing the reaction vessel air was removed by a stream of pure nitrogen gas.

RESULTS AND MATHEMATICAL TREATMENT

Symbols

As recommended by the IUPAC commission[10] the symbols used in this work are listed below. They are derived from the symbols used in Sillén's papers[11, 12].

B	total metal ion concentration.
b	free metal ion concentration.
A	total ligand concentration
h_ia	concentration of protonated ligand H_iA.
a	free ligand concn.
pa	$-\log a$.
K_{Hi}	mixed protonation constants of the ligand defined as: $K_{Hi} = \frac{h_ia}{h.h_{i-1}a}$.
N	maximum number of hydrogen ions that the ligand can take up.
h	activity of the hydrogen ion.
C_{base}	concentration of base added.
Z	average number of ligands bound per metal ion.
$\beta_{q,p}$	overall stability constant of a complex B_qA_p defined as $\beta_{q,p} = \frac{(B_qA_p)}{b^q.a^p}$.
$B(A_tB)_n$	representation of a "core + links" series.
t	number of ligands in a link.
n	variable integer: number of links in a "core + links" complex.
Q	total heat liberated by calorimetric titration.
Q_{dil}	heat of dilution of the base added.
ΔH_{H_2O}	enthalpy of formation of H_2O, from H^+ and OH^-.
$\Delta G_{Hi}, \Delta H_{Hi}, \Delta S_{Hi}$	free energy, enthalpy and entropy change of protonation of the ligand H_iA.
$\Delta G_{q,p}, \Delta H_{q,p}, \Delta S_{q,p}$	free energy, enthalpy and entropy change of formation of a complex B_qA_p.

Potentiometric study

The protonation constants K_{Hi} of the carboxylate and mercapto group of thiolactic acid (TLA) were calculated with a method described by Thiers, Van Poucke and Herman[13]. They were found to be respectively 3·535 and 10·078.

From the protonation constants, the measured pH values during titration and the total concentration in the reaction cell, the formation curves $Z(pa)_B$ can be obtained. The formation functions are calculated with a general computer programme ZPAF using Eqns (1) and (2)

$$a = \frac{N.A - C_{base} - (H^+) + (OH^-)}{\sum_{n=1}^{N} N.h^n.a\prod_{i=1}^{n} K_{Hi}}. \qquad (1)$$

$$Z = \frac{A - a\left(1 + \sum_{n=1}^{N} h^n.\prod_{i=1}^{n} K_{Hi}\right)}{B}. \qquad (2)$$

Since the pH never exceeds 9 the term (OH^-) can be neglected. The term (H^+) can be calculated from the activity of hydrogen ions h with a proportional factor[14]. The formation curves calculated in that way for the complex formation between Ni^{2+} and Zn^{2+} and TLA are shown in Figs. 1 and 2. The presence of a "cross-over"

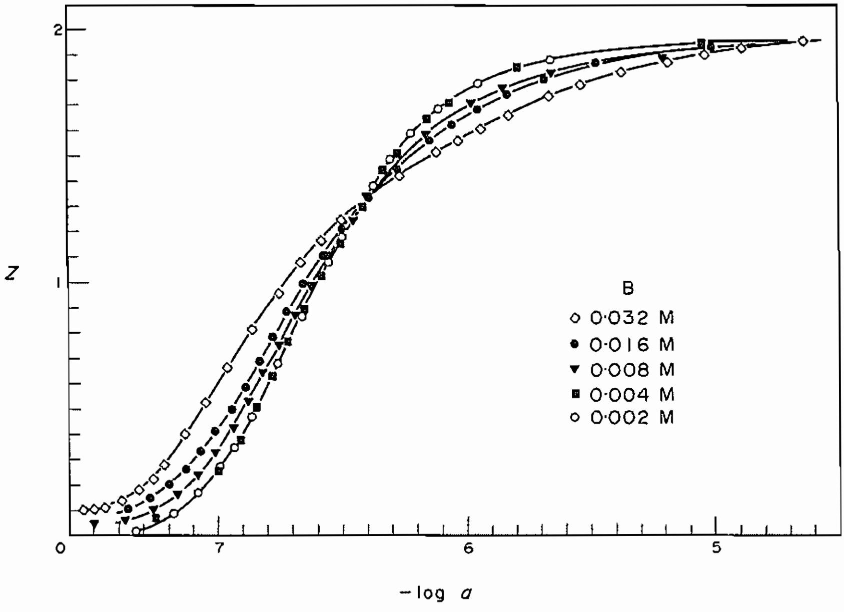

Fig. 1. Formation curves for the Ni^{2+}/TLA system.

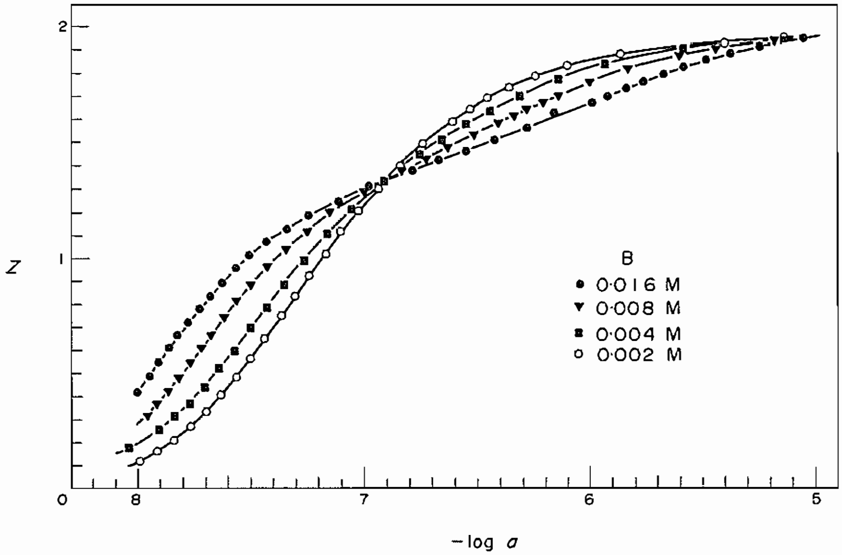

Fig. 2. Formation curves for the Zn^{2+}/TLA system.

point in both cases is a strong indication for a mixture between polynuclear and mononuclear complexes [15, 16]. From the spacing of the curves at the two highest metalion concentrations, according to Eqn (3), a "core + links" system $B(A_2B)_n$ can be derived for the polynuclear complexes.

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

As all the formation curves cross each other at a Z value of 1·3 the two polynuclear species B_2A_2 and B_3A_4 are possible. As the formation curves go to a limit of 2 the mononuclear species BA_2 is certainly present. The complex BA is also possible.

The composition and the stability constants of the complexes cannot be determined with a graphical method. Therefore a computer programme PNUC was written. This programme is based on the following principle: choosing a set of probable present complexes, the formation curves can be calculated from the experimental data a and B and the guessed stability constants $\beta_{q,p}$ with Eqns (4) and (5)

$$Z_{\text{cal}} = \frac{\sum\sum p\beta_{q,p}b^q a^p}{B}, \tag{4}$$

$$B - b = \sum\sum q\beta_{q,p}b^q a^p. \tag{5}$$

The relation between the calculated and experimental Z values is given by the function U.

$$U = \sum (Z_{\text{cal}} - Z_{\text{exp}})^2. \tag{6}$$

The values of the stability constants are searched by minimizing this U function with the "variable metric method" described by Davidon [17]. The minimum value of U, $U_{\min}$, and the standard deviation, given in Eqn (7), are a measure for the agreement between the experimental and the calculated curves.

$$\sigma^2(Z) = U_{\min}/(n_{\text{exp}} - n_{\text{par}}) \tag{7}$$

where n_{exp} is the number of experimental points and n_{par} is the number of complexes.

This calculation is repeated for different sets of possible complexes. That set of complexes really present in solution will give the lowest $U_{\min}$ and $\sigma^2(Z)$ value. During the calculations the $\alpha_{q,p}$ values, given in Eqn (8), are also calculated.

This $\alpha_{q,p}$ value is a measure for the presence of a certain complex.

$$\alpha_{q,p} = \frac{100q\beta_{q,p}b^q a^p}{B}. \tag{8}$$

The results of these calculations performed for the systems Ni^{2+}/TLA and Zn^{2+}/TLA are shown in Tables 2 and 3. As can be seen from Table 2 a lowest $U_{\min}$ and

Table 2. Stability constants of Ni^{2+}/TLA complexes from treatment with PNUC

System	$\log \beta_{q,p}$	max α	present	$U_{\min}$	$\sigma^2(Z)$
BA_2	13·133	99·9	+	0·1767	0·140 10^{-2}
B_3A_4	30·818	65	+		
BA_2	13·138	99·9	+	0·1332	0·107 10^{-2}
B_3A_4	30·747	58	+		
B_2A_2	14·681	9	±		
BA_2	13·144	99·9	+	0·1023	0·083 10^{-2}
B_3A_4	30·691	55	+		
B_2A_2	14·657	9	±		
BA	5·770	7	±		
BA_2	14·144	99·9	+	0·0918	0·074 10^{-2}
B_3A_4	30·709	58	+		
BA	6·052	13	+		

Table 3. Stability constants of Zn^{2+}/TLA complexes from treatment with PNUC

System	$\log \beta_{q,p}$	max α	present	U_{min}	$\sigma^2(Z)$
BA_2	14·295	99·9	+	0·3340	$0{\cdot}309\ 10^{-2}$
B_3A_4	34·916	85	+		
BA_2	14·322	99·9	+	0·0903	$0{\cdot}084\ 10^{-2}$
B_3A_4	34·780	70	+		
B_2A_2	17·291	30	+		
BA_2	14·336	99·9	+	0·0820	$0{\cdot}077\ 10^{-2}$
B_3A_4	34·742	67	+		
B_2A_2	17·157	24	+		
BA	6·849	11	+		
BA_2	14·336	99·9	+	0·1008	$0{\cdot}094\ 10^{-2}$
B_3A_4	34·786	75	+		
BA	7·181	26	+		

$\sigma^2(Z)$ value is found for the set of complexes BA, BA_2 and B_3A_4. The complex B_2A_2 is rejected in this case. For the system Zn^{2+}/TLA the complex formation can best be represented by the four complexes *nl*. BA, BA_2, B_2A_2 and B_3A_4.

Calorimetric study

The enthalpy and entropy change accompanying the protonation of the mercapto- and carboxylate group of TLA were calculated from titration No. 1 indicated in Table 1, with the aid of Eqn (9) and (10)

$$\frac{Q - Q_{dil}}{V} = -(\Delta H_{H_2O} - \Delta H_{Hi})(OH^-) \qquad (9)$$

where (OH^-) means the concentration of base added.

$$\Delta G_{Hi} = -RT \ln K_{Hi} = \Delta H_{Hi} - T\Delta S_{Hi}. \qquad (10)$$

According to Vanderzee and Swanson[18], Hale, Izatt and Christensen[19] and our own experiments, ΔH_{H_2O} was taken to be $-13{\cdot}34$ kcal/mole. The results of this calculations are given in Table 4.

The enthalpy and entropy change accompanying the formation of the complexes were calculated from titrations No. 2, 3 and 4 indicated in Table 1, using Eqn (11)

$$-\frac{Q - Q_{dil}}{V} = \sum_p \sum_q \beta_{q,p} b^q a^p \left[\Delta H_{q,p} + p \sum_{i=1}^{N} (\Delta H_{H_2O} - \Delta H_i)\right] + \sum_{i=0}^{N-1} K_{Hi} \,.\, h^i \,.\, a \left[\sum_{i'=1}^{N-1} (\Delta H_{H_2O} - \Delta H_{i'})\right]. \qquad (11)$$

In Eqns (9) and (11) Q is the total heat liberated. Q_{dil} is the heat produced by the dilution of KOH in a 0·5 M KNO_3 medium. The values a, b and h were calculated from the stability constants $\beta_{q,p}$ and the total concentrations in the reaction cell with a computer programme BDTV. This programme is a FULL FORTRAN IV translation of the series ALGOL'60 procedures written by Arnek[20].

Table 4. Calorimetric results for protonation of TLA

Group	$\log K_{Hi}$	ΔG (kcal/mole)	ΔH (kcal/mole)	ΔS (cal/mole . °K)
–SH	10·08	−13·74	−5·74	+26·84
–COOH	3·54	−4·82	+0·49	+17·84

The $\Delta H_{q,p}$ values were solved from Eqn (11) with the aid of a computer programme THER. The results are given in Tables 5 and 6. In practice only the $\Delta H_{1,2}$ and $\Delta H_{3,4}$ values could be calculated. The concentrations of the complexes BA and B_2A_2 are so low that the heat produced by these complexes is negligible in comparison with the total heat liberated[21].

Table 5. Calorimetric results for Ni^{2+}/TLA

Complex	$\log \beta_{q,p}$	ΔG	ΔH	ΔS
BA	6·052	−8·25	—	—
BA_2	13·144	−17·92	−0·2	+59
B_3A_4	30·709	−41·86	−8	+113

Table 6. Calorimetric results for Zn^{2+}/TLA

Complex	$\log \beta_{q,p}$	ΔG	ΔH	ΔS
BA	6·849	−9·34	—	—
BA_2	14·336	−19·54	−3	+55
B_2A_2	17·157	−23·39	—	—
B_3A_4	34·742	−47·35	−19	+95

DISCUSSION

From Table 2 and 3 it can be seen that the polynuclear B_3A_4 and the mononuclear BA_2 are the predominant complexes formed in both systems. The contribution of the complexes BA and B_2A_2 to these systems can be considered as small. Comparing the results with those obtained for TGA (thioglycolic acid) it is found that with TLA the complex B_4A_6 is not formed. The only difference between TLA and TGA is the α-CH_3 group and the reason of the absence of the complex B_4A_6 must be searched in that direction. According to Leussing[2] the structures of the Ni/TGA complexes are square planar. Assuming the same structure for the Ni/TLA complexes it can be shown that the α-CH_3 group of TLA would give a steric hindrance on the formation of the B_4A_6 complex. We assume that this is the principal reason why between the metal ions Ni^{2+} and Zn^{2+} and TLA the complex B_4A_6 is lacking.

Besides the above mentioned steric hindrance, the α-CH_3 group has some other influence too. It is remarkable that the ΔH_H of protonation of the –SH group of TLA is nearly 1 kcal/mole lower than in the case of TGA (: −6·52 kcal/mol). Wadsö[22] described an analogous effect on the ΔH of protonation of thiols by branching of the alifatic chain. For the following products the respective values are found: CH_3CH_2–SH: −6·42 kcal/mole; $(CH_3)_2CH$SH: −5·38 kcal/mole; $(CH_3)_3C$ SH: −5·3 kcal/mole. An explanation for this phenomena is given by King and King[23] who suggest a solvent orientation effect in the disordered region outside the inner shell of the acid anion.

For the Ni^{2+} complexes the $\Delta H_{q,p}$ values of formation are also lower than those obtained for TGA ($\Delta H_{1,2} = -3$

kcal/mole; $\Delta H_{3,4} = -21$ kcal/mole). As the obtained stability constants are of the same magnitude, the resulting $\Delta S_{q,p}$ values are higher for TLA than for TGA. The obtained $\Delta H_{q,p}$ for Zn^{2+}/TLA and Zn^{2+}/TGA are of the magnitude. More experimental data will be needed for a better understanding of the obtained thermodynamic results.

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