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Polynuclear Complex Formation Between Zinc(II) and 2-Mercaptoethanol and 3-Mercapto-1,2-Propanediol

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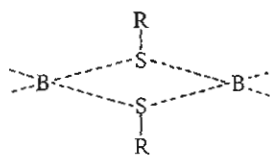
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Polynuclear complex formation between zinc(II) and 2-mercaptoethanol (MEL) and 3-mercapto-1,2-propanediol (MPD) was studied by a pH-metrical method at 25°C and in 0.5 M KNO₃.

According to Sillén's theory the complex formation can be represented by a «core+links» system $B(A_3B)_n$ where B means the metal ion and A the ligand. The maximum value of n was found to be five. So only the following complexes are present: B_2A_3 , B_3A_6 , B_4A_9 , B_5A_{12} , B_6A_{15} . The stability constant of each of these complexes was determined using the extrapolation method of Fronaeus and Leden. The stability constants were tested and refined by comparing theoretical curves with the experimental data.

Introduction

Much work is done about the study of complex formation between metal ions and mercaptide containing ligands. Nearly all complexes found are polynuclear. Leussing and Co.^{1,2,3} studied the complexes of the thioglycolate ion, the 2,3-dimercapto-1-propanol ion and 1,2-ethanedithiol ion. They found that the polynuclear character of these species could easily be described using as a basis the multiply coordinated sulfur structure, already proposed by Jicha and Busch,⁴ the sulfur ion forming a bridge between two metal ions as is shown below



Most mercaptide ligands contain other chelating groups or two or more mercaptide groups as in the investigations of Leussing.^{1,2,3} Complex formation with such ligands is influenced by these groups and does not give a picture of the possibility of the sulfur ion to link two metal ions. Therefore in these study ligands are used where only one mercaptide ion is present. However, the alkyl mercaptides are rather

insoluble in water. So, in order to obtain more soluble ligands, hydroxyderivates were purchased. At relatively low pH there is no danger that the hydroxyl group should participate in the complex formation.

In this work the result of a pH metrical study of the zinc(II) complexes of 2-mercaptoethanol and 3-mercapto-1,2-propanediol is dealt with. As polynuclear complex formation was expected the measurements were interpreted in terms of the theory exposed by Sillén^{5,6,7,8} and coworkers.

Experimental Section

Reagents. Both mercaptans (Fluka) were redistilled before use. Aqueous solutions of the mercaptans were prepared with oxygen-free water and regularly flushed with pure nitrogen gas. Only freshly prepared solutions were used for the measurements. A stock solution of zinc nitrate (Baker) 0.2 M was made and standardized⁹ gravimetrically as $ZnNH_4PO_4$. In order to keep the activity coefficients as constant as possible all solutions were prepared in 0.5 M KNO₃. Before use all solutions were abundantly flushed with pure nitrogen gas.

Titration Procedure. A mixture of metal ion and ligand solution was titrated with KOH under a nitrogen atmosphere.

Six titrations were performed. The total metal ion concentration was respectively: 0.016 M, 0.008 M, 0.004 M, 0.002 M, 0.001 M, and 0.0005 M. The initial total concentrations of the ligand were 0.08 M, 0.04 M, 0.02 M, 0.01 M, 0.005, and 0.0025 M. After each addition of KOH an equal volume of a metal ion solution, with concentration two times the total metal ion concentration in the titration cell, was added, in order to keep the total metal ion concentration constant. The pH was measured with a Radiometer pHM4, using a glass electrode type C, and a saturated calomel electrode as reference. The glass electrode was standardized against a 0.01 M borax buffer according to Bates.¹⁰ All measurements were carried out at 25°C.

(5) L.G. Sillén, *Acta Chem. Scand.*, 8, 299 (1954).

(6) L.G. Sillén, *Acta Chem. Scand.*, 8, 318 (1954).

(7) H. Kakihana and L.G. Sillén, *Acta Chem. Scand.*, 10, 985 (1956).

(8) G. Biedermann and L.G. Sillén, *Acta Chem. Scand.*, 10, 1011 (1956).

(9) A.I. Vogel, «A Textbook of Quantitative Inorganic Analysis», Longmans, Green and Co. Ltd, London.

(10) R.G. Bates: «Determination of pH», p. 76, John Wiley and Sons Inc., New York.

(1) D.L. Leussing, R.E. Laramy, and Gene S. Alberts, *J. Am. Chem. Soc.*, 82, 4826 (1960).

(2) D.L. Leussing, *J. Am. Chem. Soc.*, 81, 4240 (1959).

(3) D.L. Leussing and G.S. Alberts, *J. Am. Chem. Soc.*, 82, 4458 (1960).

(4) D.C. Jicha and D.H. Busch, 135th National Meeting of the Am. Chem. Soc., Boston, Mass., April, 1959.

Results and mathematical treatment

The symbols used here are the same as in the papers of Sillén^{5,6,7,8} and are listed below

B	total concentration of Zn^{2+}
b	concentration of free Zn^{2+}
A	total ligand concentration
ha	concentration of protonated ligand
a	concentration of free ligand
h	activity of the hydrogen ion
C_{base}	concentration of base added
Z	average number of ligands bound per Zn^{2+}
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_a	mixed acidity constant of ligand; defined as $K_a = \frac{h \cdot a}{ha}$
K_{pq}	defined as $K_{pq} = \frac{(B_q A_p)}{b^q \cdot a^p}$
K_i	an abbreviation for $K_{i+1,1,i}$

$$\log F = \log \frac{B}{b}$$

$$u = a^t b$$

$$g = \sum_{i=1}^n K_i u^i$$

$$y = \frac{Z}{t}$$

$$x = t \log a + \log B$$

The formation function $Z(a)$ was calculated from equations (1) and (2)

$$Z = \frac{A - (A - C_{base}) \frac{h + K_a}{h}}{B} \quad (1)$$

$$a = (A - C_{base}) \frac{K_a}{h} \quad (2)$$

These equations are valid, since the complex formation takes place in a pH range from 4 to 8, where both the hydroxyl ion and the hydrogen ion concentrations may be neglected. In order to calculate the formation function the acidity constants are needed as can be seen from equation (1) and (2). These acidity constants were obtained using a method described by Thiers, Van Poucke, and Herman.¹¹ The acidity constants of MEL and MPD are found to be respectively $3.23 \cdot 10^{-10}$ and $3.77 \cdot 10^{-10}$.

The formation curves obtained in this way are shown in Figure 1 and Figure 2. As can be seen from these figures a family of parallel formation curves is found in each case. Since a is small until the flat part of the formation curve is reached it can be assumed that b is not negligible in comparison with

B. According to Sillén^{5,6,7,8} systems which give such curves in these conditions, are polynuclear and form a so-called «core+links» system of general formula $B(A_3B)_n$. The value of t may be found from the spacing of the curves with the aid of equation (3)

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

In both cases t was found to be three.

So, the complexes can be represented by the general formula $B(A_3B)_n$, where n is the number of links A_3B and B is the core. If this is true, then all the curves $y(x)$ must coincide.

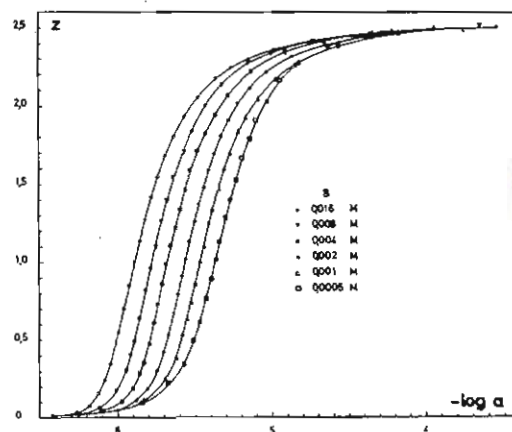


Figure 1. The formation curves of the system zinc(II) and 2-mercaptoethanol.

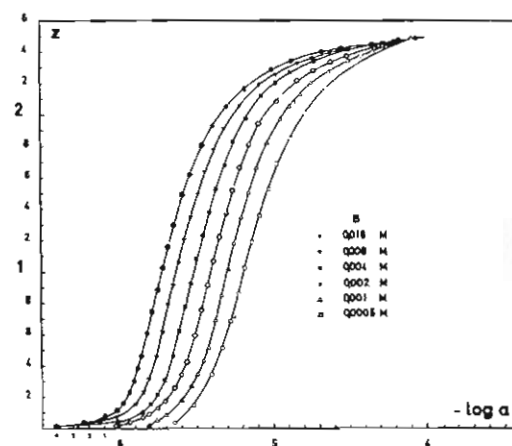


Figure 2. The formation curves of the system zinc(II) and 3-mercapto-1,2-propanediol.

Indeed, y and x are functions of the same variable u . As can be seen from Figures 3 and 4, the curves $y(x)$ satisfy this criterion over the whole range investigated. As y tends to a maximum of 0.833, and assuming that at the maximum value for y one complex predominates, one can calculate⁶ from formula (4) that the number of links tends to a maximum value of five.

$$y_{max} = \frac{n \max}{1 + n \max} \quad (4)$$

(11) G.F. Thiers, L.C. Van Poucke, M.A. Herman, *J. Inorg. Nucl. Chem.*, 30, 1543 (1968).

The possible complexes in solution are $B(A_3B)$, $B(A_3B)_2$, $B(A_3B)_3$, $B(A_3B)_4$, $B(A_3B)_5$.

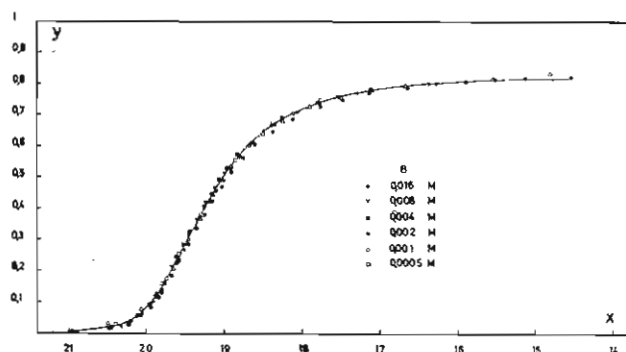


Figure 3. The y,x curve of the system zinc(II) and 2-mercaptoethanol.

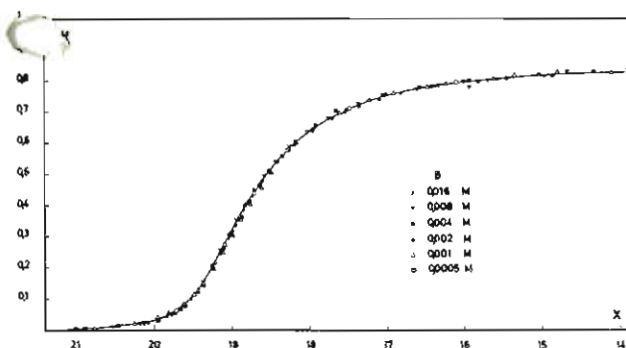


Figure 4. The y,x curve of the system zinc(II) and 3-mercapto-1,2-propanediol.

Further evidence for this is given by calculating⁷ \bar{n} from equation (5)

$$\bar{n} = \frac{y}{1-y-F^{-1}} \quad (5)$$

F was found by calculating⁷ the following integral

$$\log F = 0.434 y + \int_{-\infty}^x y dx \quad (6)$$

Integration was started from $x=21$ and $x=21.34$ respectively for MEL and MPD. Since the values of y corresponding with these values of x are very small the residual integrals $\int_{-\infty}^x y dx$ can be neglected. The results are given in Table I. \bar{n} varies between one and five as proposed before.

Another interesting function⁷ g is given by equation (7)

$$g = F(1-y) - 1 \quad (7)$$

g is function of u alone and $\log u$ can be calculated⁷ from equation (8)

$$\log u = x - \log F \quad (8)$$

Since g and u are known the stability constants K_i can be calculated with one of the usual methods. Regarding the great number of complexes present a

Table I.

MEL		MPD	
y	\bar{n}	y	\bar{n}
0.2	1.204	0.05	1.091
0.04	1.427	0.11	1.317
0.11	1.712	0.225	1.679
0.190	1.944	0.32	1.929
0.285	2.128	0.41	2.121
0.420	2.309	0.515	2.281
0.505	2.529	0.615	2.502
0.600	2.767	0.695	2.839
0.695	3.069	0.745	3.238
0.725	3.175	0.765	3.469
0.754	3.350	0.784	3.751
0.765	3.541	0.798	4.005
0.780	3.731	0.810	4.288
0.800	4.073	0.820	4.564
0.810	4.295	0.83	4.884

graphical procedure seems the most suitable method. So, the successive extrapolation method of Fronaeus¹² and Leden¹³ is used to obtain the stability constants. The function $f_1 = g/u = K_1 + K_2u + K_3u^2 + K_4u^3 + K_5u^4$ was extrapolated for $u=0$ in order to obtain a value for K_1 .

With this value another function $f_2 = \frac{g/u - K_1}{u}$ was calculated and again extrapolated for $u=0$. This extrapolation procedure was repeated until the function $f_n = \frac{f_{n-1} - K_{n-1}}{u}$ was constant. In practice this was found for $n=5$ as could be expected.

The results are tested by comparing the experimental $y(x)$ curve with a theoretical $y(x)$ curve calculated from equation (9) and (10).

$$y = \frac{K_{1,3}u + 2K_{3,6}u^2 + 3K_{4,9}u^3 + 4K_{5,12}u^4 + 5K_{6,15}u^5}{1 + 2K_{2,3}u + 3K_{3,6}u^2 + 4K_{4,9}u^3 + 5K_{5,12}u^4 + 6K_{6,15}u^5} \quad (9)$$

$$10^x = u + 2K_{2,3}u + 3K_{3,6}u^2 + 4K_{4,9}u^3 + 5K_{5,12}u^4 + 6K_{6,15}u^5 \quad (10)$$

Since the first incorrect values of g will influence the values of the stability constants, those were slightly modified until a good fit between experimental and theoretical curves was obtained. In practice, it was only necessary to modify the first two stability constants. From Figures 3 and 4 it is seen that the theoretical curves agree well and over the whole range with the experimental points. The modified stability constants are given in Table II.

Table II.

	MEL	MPD
pK_s	9.49	9.43
$\log K_{2,3}$	18.32	18.00
$\log K_{3,6}$	38.52	37.85
$\log K_{4,9}$	57.80	56.75
$\log K_{5,12}$	77.20	74.75
$\log K_{6,15}$	95.92	93.84

(12) S. Fronaeus, *Diss. Lund.* (1948).

(13) I. Leden, *Diss. Lund.* (1943).

Discussion

As seen above MEL and MPD form 5 complexes with zinc(II) with the following formulas: $B_2A_3^+$; B_3A_6 ; $B_4A_9^{1-}$; $B_5A_{12}^{2-}$; $B_6A_{15}^{3-}$. Each of these complexes could be derived from the first member $B_2A_3^+$ by adding a certain amount of links BA_3^- , the latter being not present as such in aqueous solution.

As only one complexing group is present it must be accepted that some of these groups are bound to two different zinc ions. Basing on the normal tetrahedral surrounding of Zn^{II} two possible structures can be proposed for $B_6A_{15}^{3-}$: a chain structure with alternatively one and three mercaptide bridges and a ring

structure with alternatively one and two mercaptide bridges.

It can be shown that none of these structure can take up another link without changing the symmetry of the complex. So, the «core+links» system ends at a maximum value of five. The lower complexes could be represented by cutting of links from $B_6A_{15}^{3-}$, water filling the free coordination places.¹

As mentioned before no difference in the reaction mechanism is found between the complexes of MEL and MPD. Although the acidity constants are nearly the same the last complexes are slightly less stable as can be seen from Table II. Steric hindrance can be a possible reason for this difference.