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A Solvent-Extraction Study of Zinc(II) Complexes with Several Divalent Anions of Carboxylic and Inorganic Acids

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Synopsis. Stability constants of zinc(II) mono- and biscomplexes with C_2 to C_6 dicarboxylic acids and with sulfate, thiosulfate and selenate ions determined at 25 °C by solvent extraction are described. The stability order of the dicarboxylate complexes decreases in an order of $C_2 > C_3 > C_4 \simeq C_5 \simeq C_6$ whereas that of the inorganic acids are nearly similar.

In previous papers of the present authors, the stability constants of zinc(II) with thiocyanate,[1] halide,[2] and monocarboxylate[3] ions in sodium perchlorate media at 25 °C have been determined. In the present paper, a further determination of the stability constants of zinc(II) complexes with several divalent anions has been made in 1 M sodium perchlorate media at 25 °C, using a chelate extraction method with β-isopropyltropolone (IPT).

Experimental

All the experiments were done in a thermostated room at 25±0.3 °C in a way similar to that described in the previous papers.[1-4] Ghe initial concentration of the zinc(II) in the aqueous phase was 1×10^{-6} M. Ghe aqueous phase in some experiments was buffered with acetate (the initial aqueous concentration was 0.01 M). It was confirmed that at this concentration the buffer has no effect on the extraction of zinc(II). Ghe dissociation constants of certain dicarboxylic acids were determined by the method described by Speakman.[5]

Results and Discussion

The statistical treatment of the experimental data was the same as in the previous papers.[1-3]

$$\beta_n = [\mathrm{ZnL}_n{}^{2-2n}][\mathrm{Zn}^{2+}]^{-1}[\mathrm{L}^{2-}]^{-n} \qquad (1)$$

The extraction of zinc(II) with IPT (HA) is generally written as:[6]

$$\mathrm{Zn}^{2+} + 2\mathrm{HA(org)} \rightleftharpoons \mathrm{ZnA_2(org)} + 2\mathrm{H}^+ \qquad (2)$$

$$\mathrm{ZnA_2(org)} + \mathrm{HA(org)} \rightleftharpoons \mathrm{ZnA_2HA(org)} \qquad (3)$$

$$\begin{aligned} D_0 &= ([\mathrm{ZnA_2}]_{\mathrm{org}}+[\mathrm{ZnA_2HA}]_{\mathrm{org}})/[\mathrm{Zn}^{2+}] \\ &= K_{\mathrm{ex0}}[\mathrm{HA}]^2_{\mathrm{org}}[\mathrm{H}^+]^{-2}(1+K_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}}) \qquad (4) \end{aligned}$$

where K_{ex0} and K_{org} are the equilibrium constants for the reactions in Eqs. (2) and (3) respectively. When the concentration, $[\mathrm{HA}]_{\mathrm{org}}$, is kept constant in a series of experiments, Eq. (4) can be rewritten as:

$$D_0[\mathrm{H}^+]^2 = K_0 \qquad (5)$$

where $K_0 = K_{\mathrm{ex0}}[\mathrm{HA}]^2_{\mathrm{org}}(1+K_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}})$. It was confirmed that the value of K_0 is constant, at least when $D_0 < 10$ (K_0 is $10^{-11.76}$, $10^{-10.44}$, or $10^{-8.39}$ when $[\mathrm{HA}]_{\mathrm{org}}$ is 5.0×10^{-3} M, 2.0×10^{-2} M, or 1.0×10^{-1} M respectively). The distribution ratio when zinc(II) forms complexes with the L^{2-} is written as follows if the $[\mathrm{HA}]_{\mathrm{org}}$ value is also kept the same:

$$\begin{aligned} D = {} & ([\mathrm{ZnA_2}]_{\mathrm{org}}+[\mathrm{ZnA_2HA}]_{\mathrm{org}})/([\mathrm{Zn}^{2+}] \\ & +[\mathrm{ZnL}]+[\mathrm{ZnL_2}{}^{2-}]+\cdots) \qquad (6) \end{aligned}$$

and from Eqs. (1), (5), and (6):

$$D[\mathrm{H}^+]^2K_0^{-1} = (1+\beta_1[\mathrm{L}^{2-}]+\beta_2[\mathrm{L}^{2-}]^2+\cdots)^{-1} \qquad (7)$$

It was confirmed that the distribution ratio at a certain ligand concentration is proportional to $[\mathrm{H}^+]^{-2}$ with all the ligands studied; thus, it was concluded that Eq. (7) can be used for the analysis of the experimental data.

Figures 1 and 2 show the decrease in the zinc(II) extraction as a function of the ligand-anion concentration in the aqueous phase. The ranges of the hydrogen-ion concentration in the aqueous phase were $10^{-6.1}$—$10^{-6.8}$ M (divalent carboxylate), $10^{-3.6}$—$10^{-3.7}$ M (sulfate), and $10^{-4.5}$—$10^{-5.2}$ M (selenate and thiosulfate), and the association of the ligand anion with protons in these hydrogen-ion concentration ranges was corrected by using the acid dissociation constants in Table 1 and in Ref. 8. Since the relative concentration of the HL^--type anion is rather low (the protonated species of oxalate and the inorganic ligand anions were negligible whereas the contributions of the HL^- and $\mathrm{H_2L}$ species were 7 and 0.2% respectively at the maximum for the other divalent carboxylate ligands), and since the stability constants of the complexes containing the HL^--form ligand may be much smaller than those for the ZnL and $\mathrm{ZnL_2}{}^{2-}$ complexes, as has been reported by, for example, Ostacoli and his co-workers,[9] the formation of such species as ZnHL^+ could be excluded from consideration. On these assumptions, the data in the figures were analyzed graphically and the stability constants listed in Tables 1(a) and 1(b) were obtained. The solid curves in the

Table 1. Stability constants

(a) Carboxylate complexes[a]

Ligands	pK_{a1}	pK_{a2}	$\log\beta_1$	$\log\beta_2$
Oxalate	—	3.54[b]	3.42	6.16
Malonate	2.68	5.15	2.47	3.80
Succinate	3.97	5.13	1.48	2.00
Glutarate	4.18	4.94	1.25	1.74
Adipate	4.29	4.97	1.23	1.78

(b) Sulfate, thiosulfate and selenate complexes[c]

Ligands	$\log\beta_1$	$\log\beta_2$
Sulfate	0.69	1.48
Thiosulfate	0.62	2.28
Selenate	0.73	1.38

a) The organic phase was chloroform containing 2×10^{-2}M IPT (oxalate) or containing 5×10^{-3}M IPT (the others). b) Ref. 7. c) The organic phase was chloroform containing 1×10^{-1}M IPT.

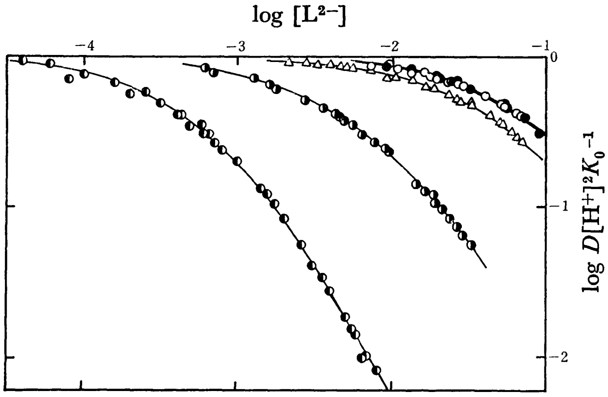

Fig. 1. Decrease in the IPT extraction of Zn(II) as a function of the ligand concentration. Org. phase: $CHCl_3$ containing 2×10^{-2}M IPT for oxalate and 5×10^{-3}M IPT for others. Aq. phase: 1M Na(½L^{2-}, ClO_4^-) where L^{2-} is oxalate (◐), malonate (◑), succinate (△), glutarate (○), and adipate (●). The solid curves were drawn by using the following equation in which K_0 is defined by Eq. (5) and the values are given in the text; $\log D[H^+]^2K_0^{-1}=-\log(1+\beta_1[L^{2-}]+\beta_2[L^{2-}]^2)$.

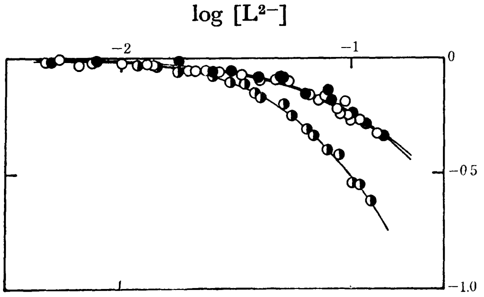

Fig. 2. Decrease in the IPT extraction of Zn(II) as a function of the ligand concentration. Org. phase: $CHCl_3$ containing 1×10^{-1}M IPT. Aq. phase: 1M Na(½L^{2-}, ClO_4^-) where L^{2-} is sulfate (●), thiosulfate (◑), and selenate (○). The solid curves were drawn by using the following equation in which K_0 is defined by Eq. (5) and the values are given in the text; $\log D[H^+]^2K_0^{-1}=-\log(1+\beta_1[L^{2-}]+\beta_2[L^{2-}]^2)$.

figures were drawn by introducing these constants into Eq. (7).

There have been several literature values of the stability constants of zinc(II) complexes with these dicarboxylate ions,[9–15] but these stability constants were determined at lower ionic concentrations; furthermore, only a few data are available on the ZnL_2^{2-}-type.

Schwarzenbach and his co-workers[16–19] pointed out that the stability is the greatest with complexes having a five-membered chelate ring, it is less with those having a six-membered ring, and it reaches almost a constant value even when the member of the CH_2 group increases more. Such a tendency was also found with zinc(II) complexes with these divalent carboxylate ligands.[11–13]

This tendency may also be observed in the present results (Table 1(a)). It is remarkable that the same tendency can also be found among the second complexes, as may also be seen in Table 1(a). The β_2 values for the zinc(II) complexes with oxalate and malonate previously reported also show such a decrease with the increase in the member of the ring.[13] The tendency for the stabilities of the complexes with succinate, glutarate, and adipate to be similar to each other has been explained by previous workers[11,16–19] on the assumption that more members than seven is too large a number to form a stable chelate ring with the metal ion. The present results also seem to support this concept.

There have been some literature values of the stability constants of zinc(II) complexes with sulfate,[20] thiosulfate,[21,22] and selenate[23] ions. However, since the ionic concentrations in the literature (0 to 0.05 M) are different from that in the present study, a comparison of the values under different conditions is difficult.

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