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Extraction of Lead(II) in Aqueous Thiocyanate-Perchlorate Solutions wtih Trioctylphosphine Oxide in Hexane and with 4-Methyl-2-pentanone

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Synopsis. The stability of lead(II) thiocyanate complexes and the extraction behavior of lead(II) in 1 mol dm^{-3} Na(SCN, ClO$_4$) were studied. By an extraction method with thenoyltrifluoroacetone, $\log\beta_1 = 0.49$ was obtained for PbSCN$^+$. The extraction was poor with 4-methyl-2-pentanone but effective with trioctylphosphine oxide in hexane. Not only Pb(SCN)$_2$ but also Pb(SCN)(ClO$_4$) and Pb(ClO$_4$)$_2$ were extracted into both of the solvents.

The complex formation equilibria of lead(II) in aqueous 1 mol dm^{-3} Na(SCN,ClO$_4$) solutions were determined by an extraction method with thenoyltrifluoroacetone (TTA). The extraction equilibria of this metal ion from these ionic media into 4-methyl-2-pentanone (MIBK) and hexane containing trioctylphosphine oxide (TOPO) were studied as follows.

Experimental and Statistical

All of the reagents used were of a reagent grade. Sodium perchlorate was recrystallized from water. The solutions of sodium thiocyanate and sodium perchlorate were standardized by gravimetry. The extractants, TTA and TOPO, were obtained from Dojindo Laboratories in Kumamoto. TOPO and MIBK were purified as described previously.[1,2] A carbon tetrachloride solution containing 0.1 mol dm^{-3} TTA, hexane solutions containing TOPO at various concentrations and MIBK were used as the organic solutions.

All of the experiments were carried out in a thermostated room at 25 °C in a manner essentially similar to that described previously[3] except that the initial metal concentration was 1×10^{-4} mol dm^{-3} and that the metal concentration in the two phases was determined by an atomic absorption method.

In the present paper, the chemical species in the organic phase are denoted by the subscript "org," while the lack of any subscript denotes those in the aqueous phase. The distribution ratio is defined as $D = [\mathrm{Pb(II)}]_{\mathrm{org}}/[\mathrm{Pb(II)}]$. The total concentration of lead(II) in aqueous solution containing thiocyanate ions can be described as:

$$[\mathrm{Pb(II)}] = [\mathrm{Pb}^{2+}](1 + \textstyle\sum\beta_i[\mathrm{SCN}^-]^i), \tag{1}$$

where β_i is the stability constant of the "i-th" complex.

The TTA extraction can be written as:

$$\mathrm{Pb}^{2+} + 2\mathrm{Htta}_{(\mathrm{org})} \rightleftarrows \mathrm{Pb(tta)}_{2(\mathrm{org})} + 2\mathrm{H}^+$$

$$K_{\mathrm{TTA,0}} = D_0[\mathrm{H}^+]^2[\mathrm{Htta}]_{\mathrm{org}}^{-2}, \tag{2}$$

where D_0 is the distribution ratio in the absence of thiocyanate ions. If the concentration of TTA in the organic phase and of the hydrogen-ion in the aqueous phase are kept constant, the following equation can be obtained:

$$D/D_0 = 1/(1+\textstyle\sum\beta_i[\mathrm{SCN}^-]^i). \tag{3}$$

The MIBK extraction can be treated as follows. Since it was found that only the PbSCN$^+$ species was the complex in the aqueous phase and that $[\mathrm{Pb(II)}]_{\mathrm{org}} = [\mathrm{Pb(ClO_4)_2}]_{\mathrm{org}} + [\mathrm{Pb(SCN)(ClO_4)}]_{\mathrm{org}} + [\mathrm{Pb(SCN)_2}]_{\mathrm{org}}$, the distribution ratio is written as:

$$D = (K_{\mathrm{MIBK,0}}[\mathrm{ClO_4}^-]^2 + K_{\mathrm{MIBK,1}}[\mathrm{SCN}^-][\mathrm{ClO_4}^-] + K_{\mathrm{MIBK,2}}[\mathrm{SCN}^-]^2)/(1+\beta_1[\mathrm{SCN}^-]), \tag{4}$$

where

$$K_{\mathrm{MIBK},n} = [\mathrm{Pb(SCN)}_n(\mathrm{ClO_4})_{2-n}]_{\mathrm{org}}/([\mathrm{Pb}^{2+}][\mathrm{SCN}^-]^n[\mathrm{ClO_4}^-]^{2-n}). \tag{5}$$

The TOPO(L) extraction was as follows.

$$[\mathrm{Pb(II)}]_{\mathrm{org}} = [\mathrm{Pb(ClO_4)_2L_4}]_{\mathrm{org}} + [\mathrm{Pb(SCN)(ClO_4)L_4}]_{\mathrm{org}} + [\mathrm{Pb(SCN)(ClO_4)L_3}]_{\mathrm{org}} + [\mathrm{Pb(SCN)_2L_3}]_{\mathrm{org}}$$

$$D = (K_{\mathrm{ex0,4}}[\mathrm{ClO_4}^-]^2[\mathrm{L}]_{\mathrm{org}}^4 + K_{\mathrm{ex1,4}}[\mathrm{SCN}^-][\mathrm{ClO_4}^-][\mathrm{L}]_{\mathrm{org}}^4 + K_{\mathrm{ex1,3}}[\mathrm{SCN}^-][\mathrm{ClO_4}^-][\mathrm{L}]_{\mathrm{org}}^3 + K_{\mathrm{ex2,3}}[\mathrm{SCN}^-]^2[\mathrm{L}]_{\mathrm{org}}^3)/(1+\beta_1[\mathrm{SCN}^-]) \tag{6}$$

where

$$K_{\mathrm{ex}n,m} = \frac{[\mathrm{Pb(SCN)}_n(\mathrm{ClO_4})_{2-n}\mathrm{L}_m]_{\mathrm{org}}}{[\mathrm{Pb}^{2+}][\mathrm{SCN}^-]^n[\mathrm{ClO_4}^-]^{2-n}[\mathrm{L}]_{\mathrm{org}}^m} \tag{7}$$

The data were treated by a least squares program in order to find the values of the constant which give the best fit.

Results and Discussion

From the extraction of lead(II) with TTA, the value of $K_{\mathrm{TTA,0}}$ in Eq. 2 was obtained to be $10^{-10.60}$. This was valid up to $-\log[\mathrm{H}^+]$ 4.0. Figure 1 shows the decrease in the TTA extraction as a function of the thiocyanate concentration in the aqueous phase. By the least squares treatment, the data were found to be explained by assuming only the PbSCN$^+$ species. The value of β_1 determined was $10^{0.49}$.

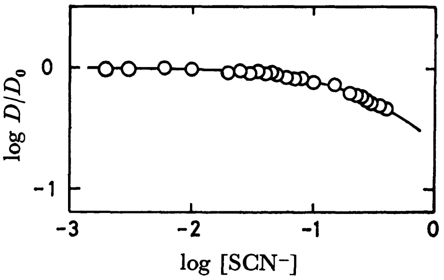

Fig. 1. Decrease in the lead (II) extraction with TTA *vs.* the aqueous thiocyanate concentration. Org. phase; CCl$_4$ containing 0.1 mol dm^{-3} TTA. Aq. phase; 1 mol dm^{-3} Na (SCN, ClO$_4$). The solid curve gives; $\log D/D_0 = -\log(1+10^{0.49}[\mathrm{SCN}^-])$.

The results of the extraction of lead(II) into MIBK are shown by Fig. 2. The extraction constants obtained by the least squares calculation on the basis of Eq. 4 using $\beta_1 = 10^{0.49}$ are listed in Table 1. The curve is calculated from these constants and Eq. 4.

Figure 2 also shows the extraction curves of lead(II) with TOPO in hexane. The value of $K_{\mathrm{ex0,4}}$ was obtained separately from the extraction data from 1 mol dm^{-3} sodium perchlorate solutions as $10^{6.92}$. Using the above β_1 and $K_{\mathrm{ex0,4}}$ values, the values of the extraction constants

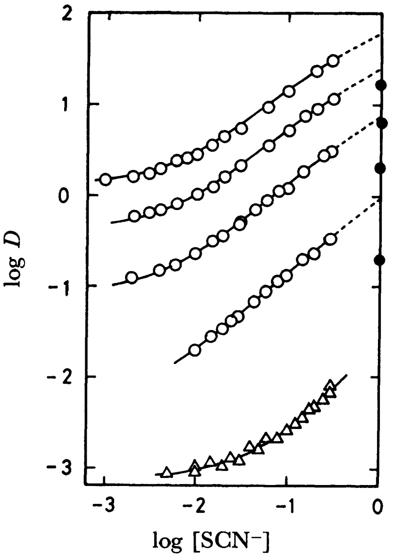

Fig. 2. Extraction curves of lead (II) with 4-methyl-2-pentanone (△) and triocylphosphine oxide in hexane (○) from 1 mol dm^{-3} Na (SCN, ClO$_4$) solutions. The concentration of TOPO in the organic phase is 0.02, 0.015, 0.01, and 0.005 mol dm^{-3} from top to bottom. The solid curves are calculated ones by means of Eqs. 4 and 6 using the constants in Table 1. The closed circles at 1 mol dm^{-3} thiocyanate indicate the values obtained experimentally (see text).

TABLE 1. SUMMARY OF THE EQUILIBRIUM CONSTANTS[a),b)]

MIBK		TOPO in hexane	
$\log K_{\mathrm{MIBK},0}$	-3.11	$\log K_{\mathrm{ex},0,4}$	6.92
$\log K_{\mathrm{MIBK},1}$	-1.68	$\log K_{\mathrm{ex},1,4}$	8.81
$\log K_{\mathrm{MIBK},2}$	-1.03	$\log K_{\mathrm{ex},1,3}$	6.96
		$\log K_{\mathrm{ex},2,3}$	7.48

a) Stability constant of aqueous complex, $\log \beta_1 = 0.49$.
b) Extraction constant of Pb(ClO$_4$)$_2$, Pb(SCN)(ClO$_4$)$_2$, and Pb(SCN)$_2$ species; *cf.* Eqs. 5 and 7.

were determined by means of Eq. 6 also by the least squares method. The best-fit constants are shown in Table 1.

The stability constants of lead(II) thiocyanate have been reported as $\log \beta_1 = 0.20$ and $\log \beta_2 = 0.90$ in 1 mol dm^{-3} Na(SCN,ClO$_4$)[4] and $\log \beta_1 = 0.54$, $\log \beta_2 = 0.88$, $\log \beta_3 \simeq -1$, and $\log \beta_4 = 0.85$ in 2 mol dm^{-3} Na(SCN, ClO$_4$)[5] solutions at 25 °C by polarography. The present β_1 is similar to these literature values, though no higher complexes were found in the present study. The value of β_1 of this metal ion is lower than that for several bivalent transition metals,[6-8] cadmium,[6] mercury(II),[2] and zinc(II).[3]

The MIBK extraction of lead(II) from thiocyanate solutions is poorer than zinc(II),[3] cobalt(II),[7] and mercury(II)[2] but better than nickel(II).[8] The MIBK extraction of lead(II) from 1 mol dm^{-3} Na(SCN,ClO$_4$) was calculated to be mainly due to Pb(ClO$_4$)$_2$ and Pb(SCN)(ClO$_4$) species; the contribution of the Pb(SCN)$_2$ species is rather small up to 0.3 mol dm^{-3} thiocyanate.

It was calculated that under the conditions in Fig. 2, the Pb(SCN)$_2$(TOPO)$_3$ species is not dominant in the organic phase even at 0.3 mol dm^{-3} thiocyanate. This is due to the instability of the metal thiocyanate and also the high extractability of the lead(II) perchlorate and the mixed thiocyanate. The extraction from sodium thiocyanate solutions containing no perchlorate was poorer than the calculated values, as indicated in Fig. 2. This is due to changes in the activity coefficients of chemical species by the replacement of the anion in the aqueous phase.

The extraction constant of the mixed thiocyanate, $K_{\mathrm{ex1,3}}$, is not very much different from that of the dithiocyanate, $K_{\mathrm{ex2,3}}$, in Table 1. This evidence, that the extraction of Pb(SCN)$_2$ is rather similar to Pb(SCN)(ClO$_4$), seems to indicate that the interactions of the second thiocyanate ion with the metal ion are not so strong in the Pb(SCN)$_2$ species. This instability of the dithiocyanate complex should be the reason for its high solvation number, three; it seems to be rather common that if the di-complex of a bivalent metal ion is stable it tends to be extracted as a disolvate.[2,9]

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