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Extraction of Lead(II) in Aqueous Halide-Perchlorate Solutions with Trioctylphosphine Oxide in Hexane

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Synopsis. The stability and the extractability with trioctylphosphine oxide(L) in hexane of lead(II) halide complexes in 1 mol dm^{-3} Na(ClO$_4$) were studied. The complexes were stable and more extractable in the following order of the ligands: Cl$^-$<Br$^-$<I$^-$. The maximum numbers of the ligand (n) in the complexes PbX_n^{2-n} were 2(Cl$^-$), 3 (Br$^-$), and 4 (I$^-$). The chemical forms of the extracted species with L were in all cases $Pb(ClO_4)_2L_2$, $PbX(ClO_4)L_3$, and PbX_2L_2.

The solvent extractions of lead(II) in aqueous 1 mol dm^{-3} Na(X, ClO$_4$) ionic media (where X$^-$ is Cl$^-$, Br$^-$, or I$^-$) with 2-thenoyltrifluoroacetone (TTA) in carbon tetrachloride and with trioctylphosphine oxide (TOPO) in hexane have been measured at 25 °C and the stability constants of the PbX_n^{2-n} species as well as their extraction constants with the latter extractant were calculated.

Experimental and Statistical

Experiments were made in the same way as described previously[1] except that sodium halides were used instead of sodium thiocyanate. The initial aqueous concentration of lead(II) was always 1×10^{-4} mol dm^{-3}. The distribution ratio of lead(II) is defined by:

$$D = [\mathrm{Pb(II)}]_{\mathrm{org}}/[\mathrm{Pb(II)}] \tag{1}$$

$$= K_{\mathrm{TTA,0}}[\mathrm{H}^+]^{-2}[\mathrm{Htta}]_{\mathrm{org}}{}^2/ (1+\beta_1[\mathrm{X}^-]+\beta_2[\mathrm{X}^-]^2+\cdots+\beta_n[\mathrm{X}^-]^n) \tag{2}$$

$$D[\mathrm{H}^+]^2[\mathrm{Htta}]\mathrm{org}^{-2}/K_{\mathrm{TTA,0}} = D/D_0 = 1/(1+\sum\beta_i[\mathrm{X}^-]^i), \tag{3}$$

where D_0 is the distribution ratio in the absence of halide ions. The stability constants may be calculated from the decrease in the distribution ratio as a function of the ligand concentration.

The distribution ratio in the extraction with TOPO(L) from these solutions could be represented by:

$$D = \sum[\mathrm{PbX}_n(\mathrm{ClO_4})_{2-n}\mathrm{L}_m]_{\mathrm{org}}/[\mathrm{Pb}^{2+}](1+\sum\beta_i[\mathrm{X}^-]^i) = \sum K_{\mathrm{ex}\,n,m}[\mathrm{X}^-]^n[\mathrm{ClO_4}^-]^{2-n}[\mathrm{L}]_{\mathrm{org}}{}^m/ (1+\sum\beta_i[\mathrm{X}^-]^i), \tag{4}$$

where $n=0$ to 2, $m=4-n$, and the extraction constants are defined by:

$$K_{\mathrm{ex}\,n,m} = \frac{[\mathrm{PbX}_n(\mathrm{ClO_4})_{2-n}\mathrm{L}_m]_{\mathrm{org}}}{[\mathrm{Pb}^{2+}][\mathrm{X}^-]^n[\mathrm{ClO_4}^-]^{2-n}[\mathrm{L}]_{\mathrm{org}}{}^m}. \tag{5}$$

The free TOPO concentration at equilibrium, $[\mathrm{L}]_{\mathrm{org}}$, can be related to its initial concentration, $[\mathrm{L}]_{\mathrm{org,I}}$, as:

$$[\mathrm{L}]_{\mathrm{org,I}} = [\mathrm{L}]_{\mathrm{org}} + \sum m[\mathrm{PbX}_n(\mathrm{ClO_4})_{2-n}\mathrm{L}_m]_{\mathrm{org}} + 3[\mathrm{NaClO_4L_3}]_{\mathrm{org}} = [\mathrm{L}]_{\mathrm{org}} + \sum mK_{\mathrm{ex}\,n,m}[\mathrm{X}^-]^n[\mathrm{ClO_4}^-]^{2-n}[\mathrm{L}]^m_{\mathrm{org}} + 3K_{\mathrm{ex\,Na}}[\mathrm{ClO_4}^-][\mathrm{L}]_{\mathrm{org}}{}^3. \tag{6}$$

The extraction constants of lead perchlorate, $K_{\mathrm{ex}\,0,4}$, and sodium perchlorate, $K_{\mathrm{ex\,Na}}$ with TOPO in hexane have been reported to be $10^{6.92}$,[1] and $10^{1.01}$,[2] respectively. By using a least squares program including a successive approximation procedure of the free TOPO concentration on the basis of Eqs. 4 and 6, the stability constants and the extraction constants were calculated.

Results and Discussion

In the lead(II) extraction with TTA from aqueous solutions above 0.04 mol dm^{-3} of iodide, the recovery of the metal was not quantitative and dark-red precipitations were found on the interface. Thus the chelate extraction from the iodide solutions was made only in the concentration range lower than this. The extraction of lead(II) from the 1 mol dm^{-3} Na(X, ClO$_4$) solutions with TOPO in hexane as a function of the ligand concentration in the aqueous phase is shown in Figs. 1 and 2. Precipitations of iodide were not observed in the case of TOPO extraction, but loss of the metal from the two phases was found when TOPO concentration was 2×10^{-3} mol dm^{-3} and the iodide concentration was 0.1 to 0.2 mol dm^{-3}. For this reason, those data were not included in the data analysis.

In the chloride and bromide systems, a set of stability constants which could explain both the TTA and TOPO extraction data were obtained; these are listed in Table 1. In the iodide system, the TTA extraction could be carried out only in the lower ligand concentration range and thus only β_1 could be obtained. On the other hand, the TOPO extraction could cover the whole concentration range and the values β_1, β_2, β_3, and β_4

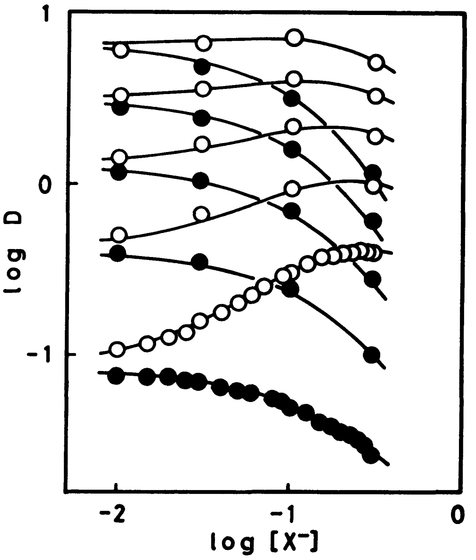

Fig. 1. Extraction of Pb(II) in 1 mol dm^{-3} Na(X, ClO$_4$) with TOPO in hexane, where X$^-$=Cl$^-$ (●) and Br$^-$ (○). The initial concentration of TOPO in the organic phase was 0.03, 0.025, 0.02, 0.015, and 0.01 mol dm^{-3} from the top to bottom, respectively. The solid curves were calculated by Eqs. 4 and 6 using the constants in Table 1.

Table 1. Summary of the stability and extraction constants of lead(II) halide complexes

X^-	log β_1	log β_2	log β_3	log β_4	log $K_{ex1,3}$	log $K_{ex2,2}$
Cl^-	0.83 ± 0.20	1.3	nil	nil	5.52 ± 0.21	3.5
Br^-	0.93 ± 0.21	1.6 ± 0.3	2.0	nil	6.52 ± 0.15	5.57 ± 0.11
I^-	1.29 ± 0.15	1.8	3.0	3.9	8.0	8.35 ± 0.11

The possible error is 3σ. When the possible error is not given, it is larger than 0.3. The $K_{ex\ n,m}$ (Eq. 5) were calculated by means of Eq. 4, using the above stability constants and the value of $K_{ex\ 0,4} = 10^{6.92}$.

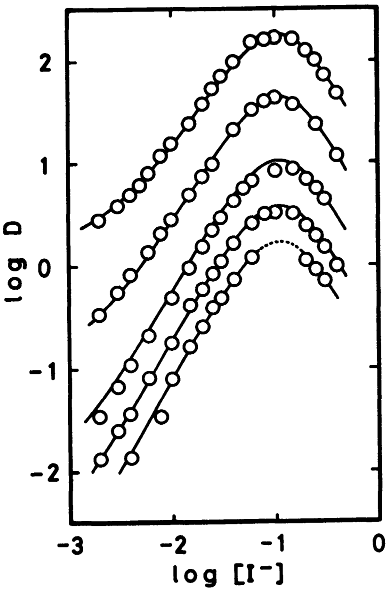

Fig. 2. Extraction of Pb(II) in 1 mol dm^{-3} Na(I, ClO_4) solutions with TOPO in hexane. The initial concentration of TOPO in the organic phase was 0.02, 0.01, 0.005, 0.003, and 0.002 mol dm^{-3} from the top to bottom, respectively. The solid curves were calculated by Eqs. 4 and 6 using the constants in Table 1.

were obtained. However, the possible errors of these constants are not small. The extraction constants with TOPO of the lead(II) species listed in Table 1 were also computed from these data.

The stability constants of lead(II) halide complexes in the present paper agreed well with the literature values obtained under the identical conditions by means of polarography.[3,4] The first complexes, PbX^+, are more stable than the thiocyanate complex ($\beta_1 = 10^{0.49}$).[1] The sum of the number of the ligand and TOPO molecules in the extracted species was always four, although that of the thiocyanate complexes was four or five.[1] Similar numbers were reported in the extraction of zinc(II) from perchlorate–halide[5] and –thiocyanate[6] systems. This suggests that the ligand ions and TOPO molecules are coordinated with the metal ion in the halides but some of the ligand ions are electrostatically attracted in the extracted thiocyanate species.

The extraction of lead(II) under the same concentration of TOPO and a certain given ligand ions was in the order of $I^- > SCN^- > Br^- > Cl^-$, while the stabilities of the lead complexes in the aqueous phase was $I^- > Br^- > Cl^- > SCN^-$. In the case of zinc(II),[5] the order of the stability in the aqueous solution was $SCN^- > Cl^- > Br^- > I^-$ and that of the extraction was $SCN^- > I^- > Br^- > Cl^-$. The orders found with zinc(II) were explained in the previous paper in terms of the size and the stability of the halide and thiocyanate complexes. The extractability of the unchanged complexes with TOPO is represented by:

$$MX_2 + 2L(org) \rightleftarrows MX_2L_2(org)$$

$$K^*_{ex\ 2,2} = [MX_2L_2]_{org}[MX_2]^{-1}[L]_{org}{}^{-2} = K_{ex\ 2,2}/\beta_2. \quad (7)$$

The following values of $K^*_{ex2.2}$ were obtained from the results in Table 1: $10^{2.2}$, $10^{4.0}$, and $10^{6.6}$ for $PbCl_2$, $PbBr_2$, and PbI_2, respectively. Dihalogenozinc(II) complexes are too unstable to be measured, but it should be reasonable to assume that the β_2 values are smaller than unity. Thus from Eq. 7, the $K^*_{ex2.2}$ values for dihalogenozinc(II) complexes should be larger than the $K_{ex2.2}$ values, ($10^{3.64}$($ZnCl_2$), $10^{4.51}$($ZnBr_2$), and $10^{6.12}$(ZnI_2)).[5] From the range of these $K^*_{ex2.2}$ values, the dihalogenolead(II) complexes are assumed to be less extractable with TOPO than the corresponding zinc(II) complexes, although they are thermodynamically more stable than the corresponding zinc(II) complexes.

The extractability of uncharged complexes with solvating extractants such as TOPO is affected by both of the partition coefficient of the unchanged complexes and by their tendency to solvate in the organic phase,[7] but since the values $[PbX_2]_{org}/[PbX_2]$ for hexane containing no TOPO were too small to be determined, no conclusion about this problem could be reached in this study.

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