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Studies on the Solvent Extraction of Metal Perchlorates. I. Partition of Sodium(I) between Aqueous Perchlorate, Thiocyanate, and Iodide Solution and Hexane Containing Trioctylphosphine Oxide

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Synopsis. Extraction equilibria of sodium (I) in aqueous 1 mol dm^{-3} sodium salt-hexane containing trioctylphosphine oxide systems were measured at 25 °C. The extracted species was always trisolvate, the extraction being improved in the order $NaClO_4 > NaSCN > NaI > NaNO_3$. This is explained in terms of the hydrofobic and hydrophilic tendencies of the anions.

The solvent extraction behavior of metal perchlorates with solvating type extractants differs somewhat from that of other salts in which the interactions between the metal ion and the anions are to some extent coordinative. We have measured the distribution ratio of sodium(I) between aqueous perchlorate solutions and hexane containing trioctylphosphine oxide (TOPO). In the present paper, the results are compared with those in other systems containing other kinds of anion.

Experimental

All the reagents were of reagent grade. A weighed amount of TOPO, supplied by Dojindo Laboratories, Kumamoto, was dissolved in hexane and washed with 0.1 mol dm^{-3} sodium hydroxide, the supernatant portion of organic phase being washed with water. Sodium perchlorate was recrystallized three times from water. The sodium salts were dissolved in water and the concentration was measured by gravimetry.

The distribution measurements were carried out in a room thermostated at 25±0.3 °C. A 5—7 cm^3 portion of a 1 mol dm^{-3} sodium salt solution and the same volume of a TOPO–hexane solution were placed in stoppered glass tube, agitated mechanically and centrifuged. A portion of the organic phase was transferred into another tube and the sodium (I) was back-extracted into 0.01 or 1 mol dm^{-3} nitric acid. The sodium content was measured by flame photometry.

Results and Discussion

The extraction of sodium(I) as ion-pairs with an anion, X^-, with TOPO can be expressed by

$$\mathrm{Na^+ + X^- + \mathit{n}TOPO(org) \rightleftharpoons Na(TOPO)_{\mathit{n}}{}^+X^-(org)}, \tag{1}$$

where "org" denotes chemical species in the organic phase. When the organic phase is an essentially nonpolar solvent, the dissociation of the extracted ion-pairs can be neglected. Since the solvation number was always three, we obtain the equation

$$D = [\mathrm{Na(I)}]_{\mathrm{org}}/[\mathrm{Na(I)}] = [\mathrm{Na(TOPO)_3{}^+X^-}]_{\mathrm{org}}/[\mathrm{Na^+}] = K_{\mathrm{ex3}}[\mathrm{X^-}][\mathrm{TOPO}]^3_{\mathrm{org}}, \tag{2}$$

where K_{ex3} is the extraction constant defined by

$$K_{\mathrm{ex3}} = [\mathrm{Na(TOPO)_3{}^+X^-}]_{\mathrm{org}}/[\mathrm{Na^+}][\mathrm{X^-}][\mathrm{TOPO}]^3_{\mathrm{org}}. \tag{3}$$

Since perchloric acid[1] as well as thiocyanic and hydroiodic acid[2] are well extracted with TOPO, we get

$$[\mathrm{TOPO}]_{\mathrm{total}} = [\mathrm{TOPO}]_{\mathrm{org}} + m[\mathrm{HX(TOPO)}_m]_{\mathrm{org}} + 3[\mathrm{Na(TOPO)_3{}^+X^-}]_{\mathrm{org}} \tag{4}$$

$$= [\mathrm{TOPO}]_{\mathrm{org}} + mK_{\mathrm{h}}[\mathrm{H^+}][\mathrm{X^-}][\mathrm{TOPO}]^m_{\mathrm{org}} + 3K_{\mathrm{ex3}}[\mathrm{Na^+}][\mathrm{X^-}][\mathrm{TOPO}]^3_{\mathrm{org}} \tag{5}$$

where K_{h} is given by

$$K_{\mathrm{h}} = [\mathrm{HX(TOPO)}_m]_{\mathrm{org}}/[\mathrm{H^+}][\mathrm{X^-}][\mathrm{TOPO}]^m_{\mathrm{org}}. \tag{6}$$

When the extraction of the acid is negligible, we have

$$[\mathrm{TOPO}]_{\mathrm{org}} = [\mathrm{TOPO}]_{\mathrm{total}} - 3K_{\mathrm{ex3}}[\mathrm{Na^+}][\mathrm{X^-}][\mathrm{TOPO}]^3_{\mathrm{org}}. \tag{7}$$

Equation 5 indicates that the "free" TOPO concentration decreases with an increase in acidity and consequently a decrease in metal extraction. This was experimentally confirmed. For example, when the total TOPO concentration was 0.1 mol dm^{-3} and the aqueous phase was a perchlorate medium, the log D was −2.3 if the aqueous phase was neutral. However, it turned out to be −2.6 and −3.4 when the acid concentration in the initial aqueous phase was 0.01 and 0.03 mol dm^{-3}, respectively.

The free TOPO concentration and extraction constants were calculated by a successive approximation procedure by means of Eqs. 2 and 7 using a least squares computer program. A good fit of the calculated values and experimental data was obtained only when an extraction of trisolvates, $\mathrm{Na(TOPO)_3{}^+X^-}$, was assumed. The constants obtained are:

$NaClO_4$: $\log K_{\mathrm{ex3}} = 1.01 \pm 0.14$
NaSCN : $\log K_{\mathrm{ex3}} = 0.38 \pm 0.11$
NaI : $\log K_{\mathrm{ex3}} = -0.46 \pm 0.14$

where the limit of the error is 3σ. Figure 1 shows the dependence of the distribution ratio on the calculated free TOPO concentration. The solid lines were calculated by introducing these values into Eq. 2.

Attempts were made to analyze the acid dependence of the perchlorate extraction by means of Eqs. 2 and 5 using the K_{h} value of perchloric acid,[1] $10^{3.15}$. However, the results were lower than the calculated ones when the TOPO and/or acid concentration was high. This may be due to changes in the activity coefficients of the chemical species in the organic phase. When both the acid and TOPO concentrations were high (*e.g.* initial TOPO and acid concentrations 0.1 mol dm^{-3}), a second organic phase appeared.

Experiments were carried out with sodium nitrate, bromide, and chloride. The extractions were very poor. After careful purification of TOPO by the procedure

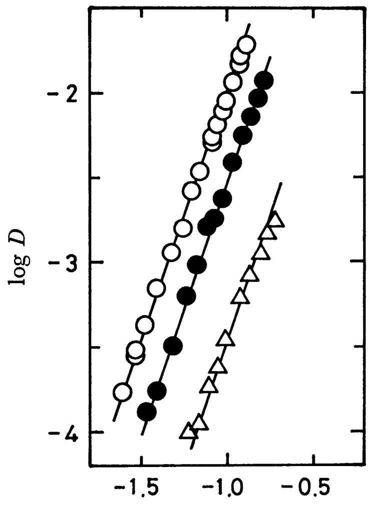

Fig. 1. The distribution of sodium perchlorate (○), thiocyanate (●), and iodide (△) as a function of the calculated free TOPO concentration in hexane. The aqueous phase was 1.0 mol dm^{-3} solution of each salt.

described, the distribution ratio was, in all cases, lower than 10^{-4} with 0.1 mol dm^{-3} TOPO.

The interactions between sodium ion and the anion in the ion-pairs might mainly be electrostatic and thus the effect of the anion on the solvation of the metal ion should be slight. This may be the reason why only the solvation number of 3 was found among the three sodium salts in the present study, differing from the findings previously reported: the solvation number of perchlorates of cobalt(II),$^{3)}$ nickel(II),$^{4)}$ and zinc(II)$^{5)}$ with TOPO is larger than that of their thiocyanates. It is also different from the TOPO extraction of mineral acids into hexane. The solvation number of TOPO of thiocyanic and nitric acid was unity while that of perchloric and hydrohalogenic acid was two. This can be explained on the assumption that the interactions between the proton and the anion of the acid is not purely electrostatic in this nonpolar solvent.

The distribution ratio of sodium(I) under identical conditions is higher in the order, perchlorate>thiocyanate>iodide>nitrate. In all cases, the nature of the cations in the ion-pairs, $Na(TOPO)_3{}^+X^-$, should be similar and the extraction is mainly affected by the extractability of the anion. The large size and small tendency of hydration of perchlorate ion are favorable for its extraction. Thiocyanate ion is also large, and not as hydrophilic as to interfere with its extraction. The two anions differ from nitrate ion: although nitrate ion is large, its hydrophilic nature should make its extraction much poorer. The order observed among the halides may also be explained from this standpoint.

It should be noted that the extraction of sodium perchlorate from 1 mol dm^{-3} sodium perchlorate solution is not very poor when the TOPO concentration is high. Even at high pH where the extraction of perchloric acid is negligible, the sodium perchlorate extraction somewhat decreases the TOPO concentration. For example, when the initial TOPO concentration in hexane is 0.1 and 0.2 mol dm^{-3}, the extraction of sodium perchlorate from its 1 mol dm^{-3} solution decreases the free TOPO concentration to 0.083 and 0.13 mol dm^{-3}, *viz.*, the free TOPO concentration decreases to 83 and 65% under these conditions. However, when the TOPO concentration is lower than 0.018 mol dm^{-3}, the decrease is calculated to be less than 1%. The same is true in the thiocyanate and iodide extraction systems though the effect is smaller than in the perchlorate system.

Several reports have appeared on the solvent extraction of sodium(I).$^{6)}$ However, only a few deal with that of sodium salts;$^{7-9)}$ no quantitative analysis seems to have been made on their extraction equilibria. However, since sodium perchlorate solutions are often employed as the ionic media of solvent extraction of metal ions with solvating type extractants in nonpolar solvents, this type measurement is indispensable for a precise analysis of metal extraction equilibria in such systems.

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