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# Solvent Extraction Equilibria of Acids. V. The Extraction of Hydrobromic, Hydroiodic, and Thiocyanic Acids with Trioctylphosphine Oxide in Hexane

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**Synopsis.** The solvent extraction of hydrohalogenic acids and thiocyanic acid (HX) in 1 mol dm$^{-3}$ electrolyte solutions with trioctylphosphine oxide (E) has been studied at 25 °C. The extraction constant, $K\mathrm{ex}_1 = [\mathrm{HXE}]_{\mathrm{org}}[\mathrm{H}^+]^{-1}[\mathrm{X}^-]^{-1}[\mathrm{E}]_{\mathrm{org}}^{-1}$, for thiocyanic acid was found to be $10^{2.5}$, while $K\mathrm{ex}_2 = [\mathrm{HXE}_2]_{\mathrm{org}}[\mathrm{H}^+]^{-1}[\mathrm{X}^-]^{-1}[\mathrm{E}]_{\mathrm{org}}^{-2}$ for hydrobromic and hydroiodic acids were found to be $10^{0.34}$ and $10^{1.78}$ respectively.

The solvent extraction of such metal ions as halides and thiocyanates has been employed for various purposes. In these systems, an extraction of the hydrohalogenic acids or thiocyanic acid in the aqueous phase should occur when the acidity of the aqueous phase is high. In the present study, the solvent extraction of hydrobromic, hydroiodic, and thiocyanic acids in 1 mol dm$^{-3}$ aqueous electrolyte solutions with trioctylphosphine oxide (TOPO) in hexane has been studied at 25 °C. The extraction constants of these acids were compared with those for other strong inorganic acids under the same conditions.

## Experimental and Statistical

All the experiments were carried out in a thermostatted room at 25 °C. A portion of an aqueous solution and the same volume of an organic solution were placed in a stoppered glass tube, the tube was vigorously agitated for one minute and then centrifuged. The acid in the two phases was titrated with a standard barium hydroxide solution, and the thiocyanate ions, with a standard silver nitrate solution.

In the present study, the acid and TOPO are denoted by HX and E respectively. The subscript "org" denotes a chemical species in the organic phase, while the lack of a subscript denotes one in the aqueous phase. It was assumed that only one species containing X$^-$ was extracted and that the extracted species could be written as HXE$_n$ where $n$ was unity or two. After several trials, these assumptions were confirmed to be reasonable, as will be shown later; thus, the following equations were derived.

The equilibrium under the above assumptions can be written as:[1)]

$$\mathrm{H}^+ + \mathrm{X}^- + n\mathrm{E(org)} \rightleftharpoons \mathrm{HXE}_n\mathrm{(org)}$$

$$K\mathrm{ex}_n = [\mathrm{HXE}_n]_{\mathrm{org}}[\mathrm{H}^+]^{-1}[\mathrm{X}^-]^{-1}[\mathrm{E}]_{\mathrm{org}}^{-n} \quad (1)$$

where $n$ is unity or two.

Since the amount of TOPO in the aqueous phase is probably very small, the following equations can also be written under the above assumptions for the extraction of HX in the presence of Na$^+$, H$^+$, and ClO$_4^-$:[1)]

$$[\mathrm{E}]_{\mathrm{org,initial}} = [\mathrm{E}]_{\mathrm{org}} + 2[\mathrm{HClO_4E_2}]_{\mathrm{org}} + n[\mathrm{HXE}_n]_{\mathrm{org}} \quad (2)$$

$$[\mathrm{H}^+]_{\mathrm{org}} = [\mathrm{HClO_4E_2}]_{\mathrm{org}} + [\mathrm{HXE}_n]_{\mathrm{org}} \quad (3)$$

The concentration of these species containing HX can be determined by titration with silver nitrate and that of the hydrogen-ion by titration with barium hydroxide.

When the aqueous phase contains only the HX acid, the terms of perchloric acid in Eqs. 2 and 3 can be eliminated and the distribution ratio of HX may be defined as:

$$D(\mathrm{HX}) = [\mathrm{HXE}_n]_{\mathrm{org}}[\mathrm{H}^+]^{-1} \quad (4)$$

## Results and Discussion

It was found that the oxidation of iodide to iodine occurred during the two-phase agitation if it was continued for a long time, and the two phases turned pale yellow. This caused an extraction of the HI$_3$E$_n$ species and introduced positive errors. However, when the agitation continued for only one minute, no color appeared in the two phases and still the equilibrium was reached. No trouble of this kind was encountered in the extraction of other acids.

The distribution ratio of thiocyanic acid with 3.0 × 10$^{-2}$ mol dm$^{-3}$ TOPO in hexane from aqueous solutions containing 1.0 × 10$^{-1}$ mol dm$^{-3}$ thiocyanate ions, 9.0 × 10$^{-1}$ mol dm$^{-3}$ perchlorate ions, and hydrogen and sodium ions at various molar ratios was determined as a function of the hydrogen-ion concentration. Under these conditions, the extraction of thiocyanic acid was much better than that of perchloric acid. After several trials, only the solvation number of unity was found to give a reasonable extraction constant; the error of the constant obtained by assuming an extraction of other species such as (HX)$_2$E$_2$ was always larger than that of the constant obtained by assuming the extraction of the

TABLE 1. EXTRACTION DATA OF THIOCYANIC ACID

Aqueous phase initially containing 0.1 mol dm$^{-3}$ of thiocyanate and 0.9 mol dm$^{-3}$ of perchlorate. The organic phase initially contained 3.0 × 10$^{-2}$ mol dm$^{-3}$ TOPO in hexane. The concentration is given by mol dm$^{-3}$.

| $[\mathrm{H}^+]_{\mathrm{initial}}$ | $[\mathrm{H}^+]_{\mathrm{org}}$ | $[\mathrm{SCN}^-]_{\mathrm{org}}$ | $\log K\mathrm{ex}_1$ |
|---|---|---|---|
| 0.24 | 2.34 × 10$^{-2}$ | 2.15 × 10$^{-2}$ | 2.43 |
| 0.20 | 2.21 | 2.03 | 2.37 |
| 0.16 | 2.13 | 1.92 | 2.41 |
| 0.12 | 2.01 | 1.75 | 2.46 |
| 0.10 | 1.85 | 1.62 | 2.41 |
| 0.09 | 1.86 | 1.57 | 2.49 |
| 0.07 | 1.72 | 1.41 | 2.51 |
| 0.06 | 1.61 | 1.31 | 2.50 |
| 0.05 | 1.52 | 1.20 | 2.53 |
| 0.04 | 1.39 | 1.06 | 2.55 |
| 0.03 | 1.17 | 8.97 × 10$^{-3}$ | 2.54 |
| | | Av | 2.47 |

HXE species. Table 1 shows the extraction data and the calculated extraction constants.

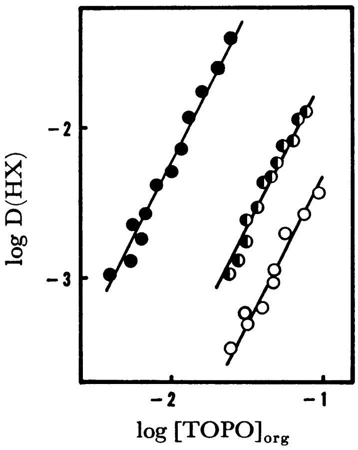

Fig. 1. Distribution ratio of hydrochloric (○) (taken from Ref. 1), hydrobromic (◐), and hydroiodic (●) acid between hexane containing various amounts of TOPO and aqueous 1 mol dm$^{-3}$ of the acid as a function of the free TOPO concentration.

Table 2. Summary of extraction constants at 25°C
Org. phase: hexane containing TOPO (E).
Aq phase: 1 mol dm$^{-3}$ (H, Na) (X, $ClO_4$) for HSCN and 1 mol dm$^{-3}$ HX for others (for $H_2SO_4$, $X^-$ is $HSO_4^-$).

$Kex_n = [HXE_n]_{org}[H^+]^{-1}[X^-]^{-1}[E]_{org}^{-n}$

| HX | log $Kex_1$ | log $Kex_2$ |
|---|---|---|
| HSCN | 2.5 | — |
| HCl[a] | — | −0.31 |
| HBr | — | 0.34 |
| HI | — | 1.78 |
| $HNO_3$[a] | 0.86 | — |
| $HClO_4$[a] | — | 3.20 |
| $H_2SO_4$[a] | — | −0.30 |

a) Data taken from Ref. 1.

The extraction equilibria of hydrobromic and hydroiodic acids were studied when the initial aqueous phase contained 1 mol dm$^{-3}$ of the acid and when the hexane phase contained TOPO at various concentrations. Figure 1 gives the results, together with those of hydrochloric acid, in Ref. 1. From the slope of the plot, the solvation number of these acids was concluded to be two and their extraction constants were determined to be as is listed in Table 2. The solid lines in the figure were drawn on the basis of Eqs. 1 and 4 and the constants in Table 2.

Khopkar and Narayanankutty[2)] reported the value of $Kex_1$ of thiocyanic acid extracted from 1 mol dm$^{-3}$ ammonium thiocyanate solutions at pH 1.6 to 3 with TOPO in xylene to be $10^{2.43}$, which agrees well with the present value. There have also been some reports on the solvent extraction of thiocyanic acid with TOPO.[3,4)]

As may be seen from Table 2, the values of the extraction constant, $Kex_2$, increase in the order of: $HCl < HBr < HI < HClO_4$. This order agrees with the order of the molar volumes of the anion. The extraction constant of $Kex_1$ of thiocyanic acid is much greater than that of nitric acid. Thus, when a metal ion in an acid solution containing thiocyanate ions is extracted with a neutral extractant such as TOPO, the extraction of thiocyanic acid should be taken into account in the analysis of the data, because this thiocyanic acid extraction probably decreases the concentration of thiocyanate ions in the aqueous phase and also that of the free extractant in the organic phase.

## References

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