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Nonaqueous Liquid-Liquid Extraction of Manganese from Ethylene Glycol Solution with Trioctylphosphine Oxide

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The nonaqueous liquid-liquid extraction of manganese was investigated between the nonpolar solvents (cyclohexane or toluene) containing tri-*n*-octylphosphine oxide and ethylene glycol containing hydrogen chloride.

Manganese was extracted in the two different hydrogen chloride concentration regions in the ethylene glycol phase. One of the manganese extractions was found at the higher hydrogen chloride concentration (above about 10^{-2}M), and the extracted form was $MnCl_2 \cdot 2TOPO$. Another was caused at the lower hydrogen chloride concentration (below about 10^{-3}M) and the extracted species was presumed to be manganese (deprotonated ethylene glycol)$_2 \cdot n$TOPO complex.

KEY WORDS: Nonaqueous extraction/ Manganese/ Ethylene glycol/

INTRODUCTION

In order to gain the information on the chemical equilibria of metal ions in the nonaqueous solvents, we have started to study the liquid-liquid extraction of metals in nonaqueous systems. For example, the nonaqueous extractions of zinc and cadmium from ethylene glycol solutions of chloride and bromide by tri-*n*-octylphosphine oxide were investigated.1,2) The formation constants of zinc chloride and perchlorate in ethylene glycol, propylene glycol, and methanol-water were reported.3,4)

In this paper, nonaqueous extraction of manganese by tri-*n*-octylphosphine oxide (TOPO) from ethylene glycol solution of hydrogen chloride was investigated.

EXPERIMENTAL

Apparatus and Reagents

Radioactivity countings were carried out with a Metro NaI(Tl) well-type scintillation counter, Model PbW-6 connected with a Metro single channel pulse height analyzer, Model SS-1061H.

Reagent grade ethylene glycol was dried with anhydrous sodium sulfate for several days and distilled under reduced pressure (25 mmHg) over anhydrous sodium sulfate.

The radioisotope, manganese-54 was supplied by the New England Nuclear,

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Boston, Mass., U.S.A., as chloride in hydrochloric acid solution. The tracer was dried on a hot plate and dissolved in the purified ethylene glycol.

Hydrochloric acid in ethylene glycol was prepared by passing dry hydrogen chloride gas through the solvent and then standardized by titrating it with standard aqueous alkali after mixing with water.

A manganese stock solution was prepared by dissolving its dry chloride with ethylene glycol.

Tri-*n*-octylphosphine oxide(TOPO) was purchased from the Dojindo Co., Ltd., Research Laboratories.

All other reagents were GR grade materials and were used without further purification.

Procedure

Ten milliliters of an ethylene glycol solution containing a radioactive tracer, a carrier, and various amounts of hydrogen chloride were placed in a 30 ml glass-stoppered centrifuge tube. Ten milliliters of toluene containing TOPO were added. Two phases in the tube were shaken for 30 min at about 25° and centrifuged until they got clear. Two milliliters of each phase were pipetted out into test tubes, and γ-activities were measured with a NaI(Tl) scintillation counter.

RESULTS AND DISCUSSION

Extraction of Manganese Chloride

Figure 1 presents the distribution of manganese in a few nonpolar solvents with

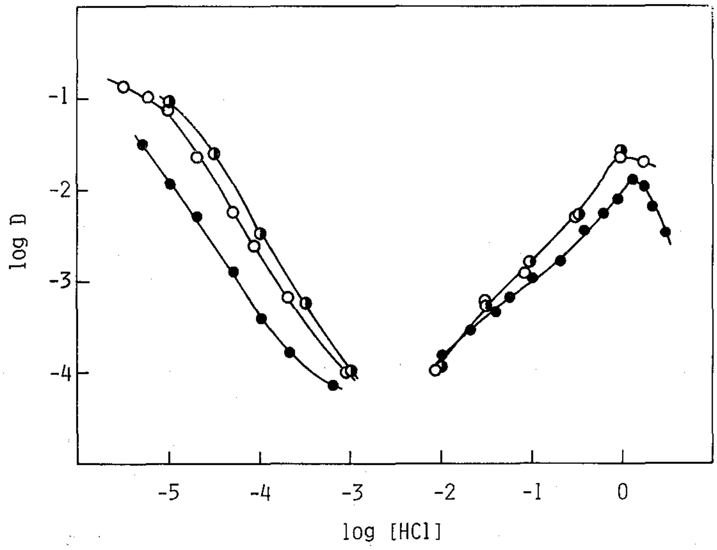

Fig. 1. The distribution ratio of manganese as a function of hydrogen chloride concentration.

TOPO: 0.1 M, ●: toluene, ○: cyclohexane, ◑: decaline

0.1 M TOPO as a function of hydrogen chloride concentration in the ethylene glycol phase. As seen in the figure, manganese was extracted at two different hydrogen chloride concentration regions. One type of extraction was found at the hydrogen chloride concentration above about 10^{-2}M, and the other was found at the hydrogen chloride concentration below about 10^{-3}M. The former extraction was at first investigated. The distribution ratio of manganese rised with the increase of hydrogen chloride concentration in nonpolar solvents such as cyclohexane, toluene, and decaline, and so the extracted species can be imagined to be manganese chloride complexes.

The distribution ratio of manganese may be written as

$$D=\frac{[MnCl_2\cdot k\mathrm{TOPO}]+[HMnCl_3\cdot l\mathrm{TOPO}]+[H_2MnCl_4\cdot m\mathrm{TOPO}]}{[Mn^{2+}]_e+[MnCl^+]_e+[MnCl_2]_e+[MnCl_3^-]_e+[MnCl_4^{2-}]_e}$$

The subscript *e* refers to the ethylene glycol phase.

The extraction curve of manganese with 0.1 M TOPO in toluene at different concentrations of lithium chloride in the presence of a constant concentration of hydrogen chloride (1.0×10^{-2}M) in ethylene glycol is shown in Fig. 2. The curve of log D *vs.* chloride concentration in the lithium chloride system is almost the same to the curve in the hydrogen chloride system below 0.8 M of the chloride concentration. Rapid decrease of the manganese distribution at more than 1.8 M of hydrogen chloride may be caused by the fact that such anion complexes as $MnCl_3^-$ and $MnCl_4^{2-}$ are formed in the ethylene glycol phase and free TOPO concentration in the toluene phase decreases as the extraction of hydrogen chloride. The steep rise of log D above 0.5 M

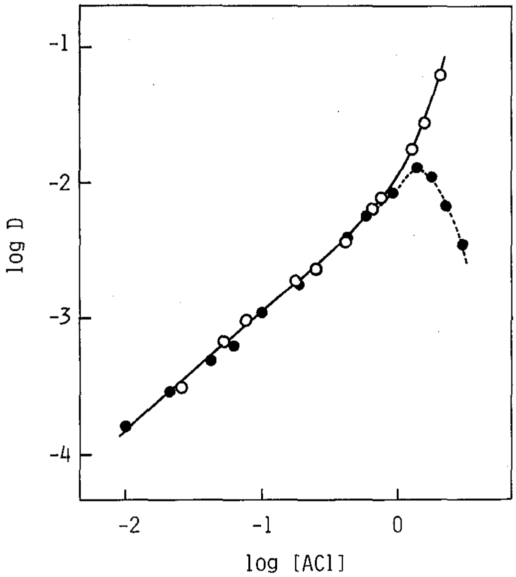

Fig. 2. The distribution ratio of manganese as a function of chloride concentration.

TOPO: 0.1 M in toluene, ●: A=H, ○: A=Li.

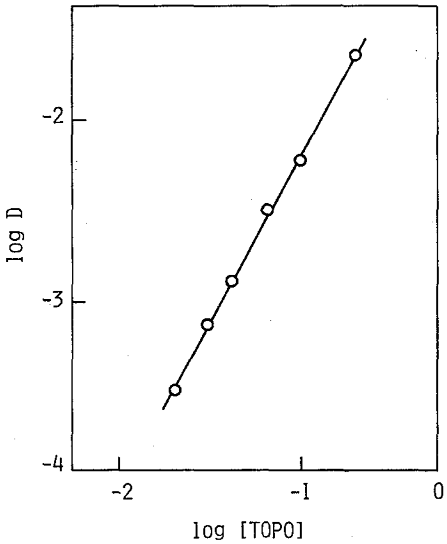

Fig. 3. The distribution ratio of manganese as a function of TOPO concentration in toluene.

HCl: 0.85 N.

of lithium chloride can be explained in terms of the salting out. These suggest that the extracted species are not such acid complexes as $HMnCl_3 \cdot l TOPO$ and $H_2MnCl_4 \cdot m TOPO$, but $MnCl_2 \cdot k TOPO$. Figure 3 shows the change in the distribution ratio of manganese as a function of the concentration of TOPO. The number of molecules of TOPO directly associated with the extracted manganese species may be deduced from the results in Fig. 3. In the constant concentrations of manganese, chloride, and H^+, the slope of the plot log D against log[TOPO] gives the number of the ligand. Therefore the extracted species is $MnCl_2 \cdot 2TOPO$ as the slope is about 2.

Figure 4 shows the effect of the concentration of manganese on the distribution ratio, D, in the range from 5×10^{-2} to 7×10^{-6}M of [Mn]. The value D at given values of the hydrogen chloride concentration is found to be independent of the metal concentration, and this indicates that manganese complexes in both the ethylene glycol and the toluene phase are mononuclear.

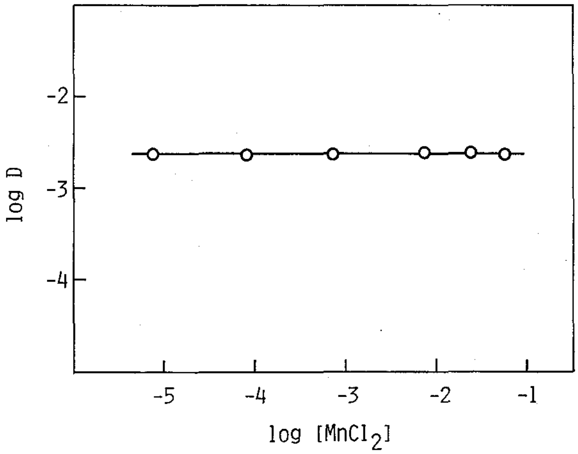

Fig. 4. The distribution ratio of manganese as a function of metal concentration. TOPO: 0.1 M in toluene, HCl: 1.0×10^{-3}N, LiCl: 2.6×10^{-1}M.

Extraction of Manganese at the Lower Hydrogen Chloride Concentration

As seen in the Fig. 1, manganese distribution ratio increases with decreasing the hydrogen chloride concentration below 10^{-3}M. The same behaviour have been found on the zinc extraction with TOPO.[3] Figure 5 shows the distribution ratio of manganese as a function of TOPO concentration. The distribution ratio of manganese is unchanged in the range of 10^{-1}M to 10^{-3}M of TOPO concentration. The total activities in two phases are diminished under 5×10^{-4}M of TOPO concentration. This deficiency may be explained in terms of the adsorption of manganese to the glass and the interface of two layers.

Though the species of manganese (deprotonated ethylene glycol)$_2 \cdot n$TOPO is expected to be extracted in the cyclohexane or toluene phase, there needs a more detailed investigation to make the extraction mechanism clear.

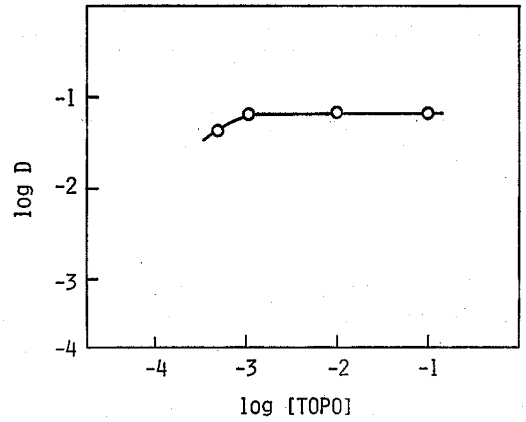

Fig. 5. The distribution ratio of manganese as a function of TOPO concentration in cyclohexane.
HCl: 1.0×10^{-5}N.

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