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Solvent Extraction of Hydrochloric and Perchloric Acids from Diethylene Glycol Solution with TOPO in Decaline

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A study has been made of the extraction of hydrochloric and perchloric acids from diethylene glycol solution with TOPO in decaline. The extracted species for hydrochloric acid system was mainly $\text{HCl}(\text{TOPO})_2$ over 0.06 M of TOPO, where extraction constants, $K_{\text{ex},1}$ and $K_{\text{ex},2}$ were 0.27 and 13, respectively. The extracted species for perchloric acid system was $\text{HClO}_4(\text{TOPO})_3$ below 0.09 M of HClO_4 and changed in turn to $\text{HClO}_4\cdot\text{TOPO}$ as the HClO_4 concentration increased.

KEY WORDS: Solvent Extraction/ Diethylene Glycol/ Hydrochloric Acid/
Perchloric Acid/ TOPO/

INTRODUCTION

Solvent extraction equilibria of such monobasic acids (HX) as hydrochloric acid and perchloric acid with tri-*n*-octylphosphine oxide (TOPO) from aqueous solution have been investigated by Diamond¹⁻³ et al. and Sekine et al.⁴⁻⁶. The extracted species was $\text{H}^+(\text{TOPO})_2 \cdot \text{X}^-$ at the low concentration range of TOPO and the acid. As the acid concentration increases, the species changed into $\text{H}^+(\text{TOPO}) \cdot \text{ClO}_4^-$ for the HClO_4^- extraction and into $\text{H}^+(\text{TOPO}) \text{HX}_2^-$ via $\text{H}^+(\text{TOPO}) \cdot \text{X}^-$ for $\text{HX}(\text{X}=\text{Cl}, \text{Br}, \text{I})$.

In our previous papers the solvent extractions of metals from a nonaqueous solution such as ethylene and propylene glycols into an immiscible nonpolar organic solvent have been investigated, in which the formation constants of zinc chloride and perchlorate in ethylene glycol^{7,8}, propylene glycol⁹ and aqueous methanol¹⁰ were determined from the extraction curves. Diethylene glycol has a dielectric constant, 31.7, which is almost identical to that of propylene glycol (32.0) and lower than that of ethylene glycol (37.7). This polar solvent is immiscible with a nonpolar solvent such as decaline. The object of the present study is to study the extraction of hydrochloric and perchloric acids in diethylene glycol with TOPO in decaline, comparing it with the extraction from the aqueous solution and the other nonaqueous solutions.

EXPERIMENTAL

Reagents. Reagent grade diethylene glycol (DEG) was dried for several days with Molecular Sieves 3 A which was treated for 3 h at 270°C *in vacuo* and was distilled under reduced pressure. The glycol solution of hydrochloric acid was prepared by passing dry

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hydrogen chloride gas into the glycol and then standardized by titrating it with standard aqueous alkali after mixing with pure water.

The aqueous glycol solution of perchloric acid was made up by dilution of reagent grade 70% perchloric acid. Water contents of the solution was calculated from the weight of the acid and the amount of the perchloric acid which was determined by acid-base titration. The extraction of perchloric acid was performed from the diethylene glycol solution containing 2 wt% of water. Sodium chloride, lithium chloride and lithium perchlorate solutions of the glycol were prepared by dissolving their reagent grade materials dried at 100°C under reduced pressure.

Tri-*n*-octylphosphine oxide (TOPO) was purchased from the Dojindo Research Laboratories. All other reagents were GR grade materials and were used without further purification.

Procedure. All procedures were carried out at 20°C in the almost same manner to those described previously⁷⁻¹⁰. Two phases of 10 ml decaline solution of TOPO and 10 ml diethylene glycol containing a definite amount of mineral acid were placed in a 30 ml glass-stoppered vessel, shaken for 1 h in a room regulated at 25°C and centrifuged. The mineral acid extracted into the nonpolar organic phase was back-extracted into an aqueous phase and the amount of the mineral acid in both aqueous phases was determined by the acid-base titration.

RESULTS AND DISCUSSION

Figures 1 and 2 show the distribution coefficients, $\log D_{\text{HCl}}$ and $\log D_{\text{HClO}_4}$, as a function of the acid concentration of the acids in diethylene glycol at three different TOPO concentrations,

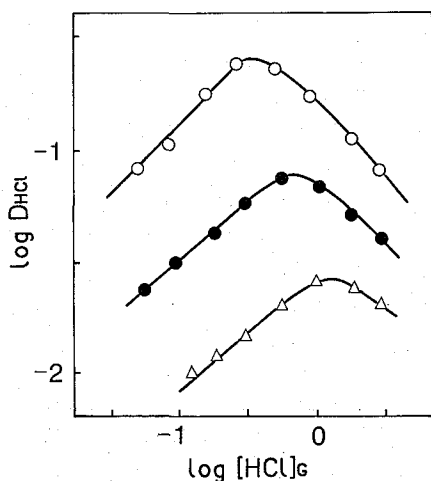


Fig. 1. Extraction of hydrochloric acid in diethylene glycol with TOPO in decaline. TOPO; ○ 0.2 M, ● 0.1 M, △ 0.05 M in decaline.

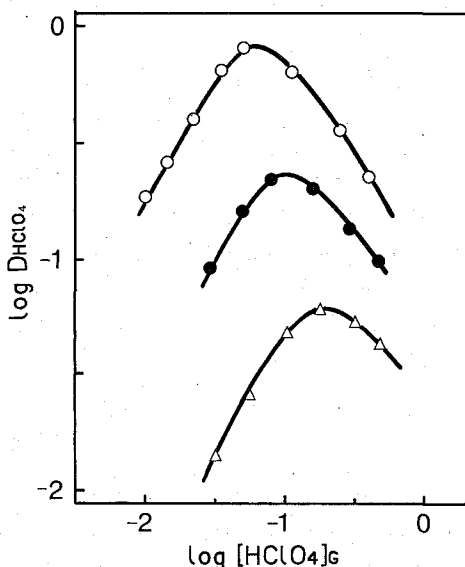
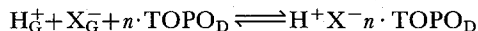


Fig. 2. Extraction of perchloric acid in diethylene glycol with TOPO in decaline. TOPO; ○ 0.2 M, ● 0.1 M, △ 0.05 M in decaline.

when decaline is used as a nonpolar organic solvent. Both the values of $\log D_{\text{HCl}}$ and $\log D_{\text{HClO}_4}$ increase initially by the slope of about 1, reaching a maximum, and decrease by the slope of about -1 ; the maximum is shifted to the higher concentration as the TOPO concentration in decaline decreases in each extraction system. When the dissociation of the acid in the decaline phase can be neglected, the extraction equilibrium can be written as;



$$K_{\text{ex},n} = \frac{\Sigma [\text{H}^+ \text{X}^- n \cdot \text{TOPO}]_D}{[\text{H}^+]_G [\text{X}^-]_G [\text{TOPO}]_D} \quad (1)$$

where $K_{\text{ex},n}$ denotes the extraction constant, subscripts G and D stand for glycol and decaline phases, and X^- represents Cl^- or ClO_4^- . Then the acid concentration in decaline can be expressed as;

$$\log [\text{HX}]_D = \log ([\text{H}^+]_G \cdot [\text{A}^-]_G) + n \log [\text{TOPO}]_D + \log K_{\text{ex},n} \quad (2)$$

$$\log \frac{[\text{HX}]_D}{[\text{H}^+]_G [\text{X}^-]_G} = n \log [\text{TOPO}]_D + \log K_{\text{ex},n} \quad (3)$$

The $\log [\text{HX}]_D$ vs. $\log [\text{H}^+]_G [\text{X}^-]_G$ plots shown in Figs. 3 and 4 can be obtained from the data in Figs. 1 and 2; the $\log [\text{HX}]_D$ values increase initially linearly with a slope of about 1 and approach to a definite value at high values of $\log [\text{H}^+]_G [\text{X}^-]_G$.

Figures 5 and 6 show the change in the left-hand side of Eq. 3, $\log [\text{HX}]_D / [\text{H}^+]_G [\text{X}^-]_G$, as a function of $\log [\text{TOPO}]_D$; the number of TOPO associated with the extracted acid species can be deduced from the slope of the plots. In the extraction of hydrochloric acid, the slope is approximately 2 below 0.45 N of total hydrochloric acid, but decreases gradually over this concentration. Similarly the slope for the HClO_4 extraction is 2.8 in the range less than 0.09 N of the acid, and decreases with the increase of the acid.

The slope of the curve at 0.45 N of hydrochloric acid in Fig. 5 is equal to 2.0 in the range over 0.06 M of TOPO, which indicates that the extracted species is $\text{HCl}(\text{TOPO})_2$. In the

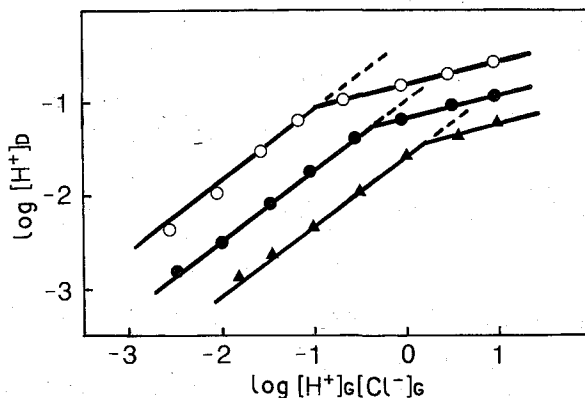


Fig. 3. The plots of $\log [\text{H}^+]_D$ vs. $\log [\text{H}^+]_G [\text{Cl}^-]_G$ in diethylene glycol-decaline system. TOPO; \circ 0.2 M, \bullet 0.1 M, \blacktriangle 0.05 M in decaline.

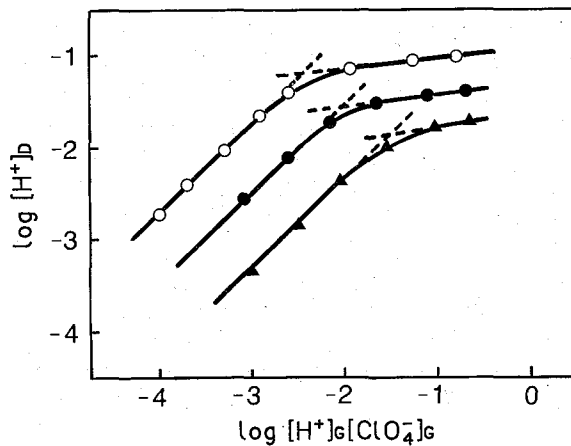


Fig. 4. The plots of $\log[H^+]_D$ vs. $\log[H^+]_G[ClO_4^-]_G$ in diethylene glycol-decaline system. TOPO; \circ 0.2 M, \bullet 0.1 M, \blacktriangle 0.05 M in decaline.

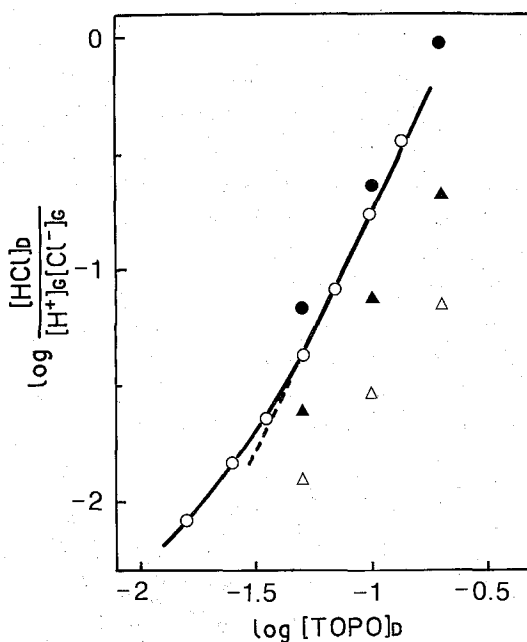


Fig. 5. The plots of $\log \frac{[HCl]_D}{[H^+]_G [Cl^-]_G}$ vs. $\log [TOPO]_D$ in diethylene glycol-decaline system. HCl; Δ 1.9 M, \blacktriangle 1.0 M, \circ 0.45 M, \bullet 0.19 M in diethylene glycol.

other hand this slope decreases as the TOPO concentration in decaline decreases. This means that the extracted species are present as a mixture of $HCl \cdot TOPO$ and $HCl \cdot (TOPO)_2$ in the range below 0.06 M TOPO. Therefore the following equation can be set up for the two extracted species.

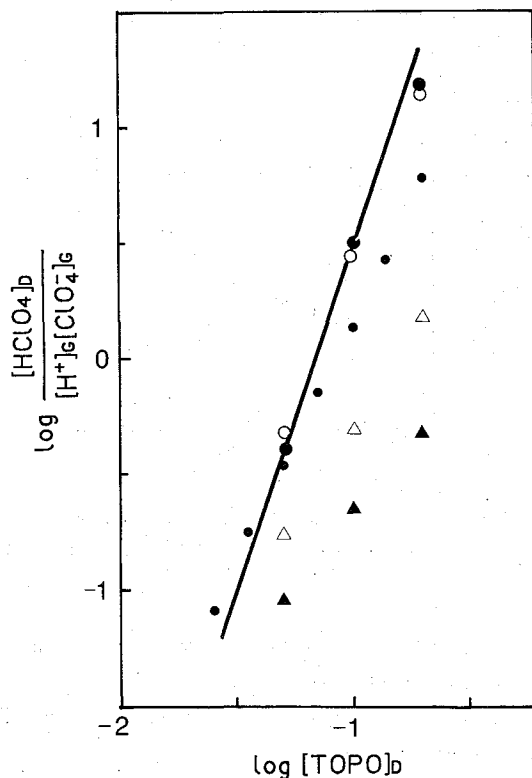


Fig. 6. The plots of $\log \frac{[\text{HClO}_4]_D}{[\text{H}^+]_G [\text{ClO}_4^-]_G}$ vs. $\log [\text{TOPO}]_D$. HClO_4 ; \blacktriangle 0.49 M, \triangle 0.32 M, \bullet 0.18 M, \circ 0.090 M, \bullet 0.032 M in diethylene glycol.

$$\log \frac{[\text{HCl}]_D}{[\text{H}^+]_G [\text{Cl}^-]_G [\text{TOPO}]_D} = \log (K_{\text{ex},1} + K_{\text{ex},2} [\text{TOPO}]_D) \quad (4)$$

where $[\text{HCl}]_D = [\text{HCl} \cdot \text{TOPO}]_D + [\text{HCl} \cdot (\text{TOPO})_2]_D$

$$K_{\text{ex},1} = \frac{[\text{HCl} \cdot \text{TOPO}]_D}{[\text{H}^+]_G [\text{Cl}^-]_G [\text{TOPO}]_D}$$

$$K_{\text{ex},2} = \frac{[\text{HCl} \cdot (\text{TOPO})_2]_D}{[\text{H}^+]_G [\text{Cl}^-]_G [\text{TOPO}]_D^2}$$

Figure 7 shows the plot of the left-hand side of Eq. 4 against $\log [\text{TOPO}]_D$. The extraction constants, $K_{\text{ex},1}$ and $K_{\text{ex},2}$, calculated by curve fitting method^{11,12} from these plots are 0.27 and 13, respectively. The solid curve in Fig. 7 is obtained by substituting these value for $K_{\text{ex},1}$ and $K_{\text{ex},2}$ in Eq. 4.

The main conclusion to be drawn from these results is as follows. The extracted species in the HCl-TOPO extraction system are considered to be $[\text{HCl} \cdot \text{TOPO}]$ and $[\text{HCl} \cdot (\text{TOPO})_2]$ in the lower concentration range of hydrochloric acid less than 0.45 M, and move to $[\text{HCl} \cdot (\text{TOPO})_2]$ as TOPO increases more than 0.06 M of TOPO. At the higher concentration of hydrochloric acid, $[\text{H}^+ (\text{TOPO}) \cdot (\text{HCl}_2)^-]$ may be extracted because the acid can be extracted beyond the TOPO concentration. In the extraction of perchloric acid, the species

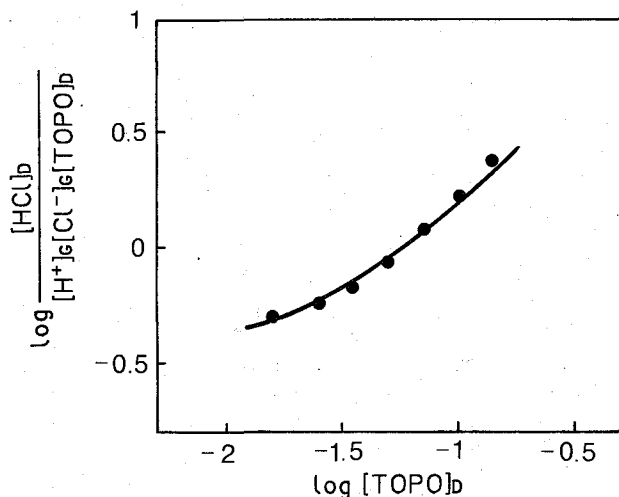


Fig. 7. Extraction of hydrochloric acid from diethylene glycol. The solid line is obtained by the equation, $\log \frac{[\text{HCl}]_D}{[\text{H}^+]_C [\text{Cl}^-]_C [\text{TOPO}]_D} = \log (0.27 + 13 \times [\text{TOPO}]_D)$.

extracted is $\text{HClO}_4 \cdot (\text{TOPO})_3$ in the lower concentration of perchloric acid ($< 0.09 \text{ M}$), and changes to $\text{HClO}_4 \cdot \text{TOPO}$ via $\text{HClO}_4 \cdot (\text{TOPO})_2$ as the perchloric acid concentration increases. However, the concentration of the acid extracted never exceeds that of TOPO in decaline different from the HCl extraction.

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