Studies on the System Perchloric Acid-Water-Tri-n-Butyl Phosphate

By

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It is intended in this study on the system $HClO_4$-H_2O-TBP to determine the species formed in the equilibrated organic phase and to clarify the extraction equilibrium in a part of the system. On the same line as the previous papers$^{6),7)}$ published in this Memoir, physico-chemical measurements of volume swelling, density, viscosity and electrical conductivity were carried out on the organic phase in addition to the distribution measurements of perchloric acid and water between organic and aqueous phases. The extracting species determined are summarized in Table 1. The species at lower acidity regions are supposed to be almost completely ionized. Dehydration of the organic phase occurs at higher acidity regions. The activities and activity coefficients of the two species $[TBP\cdot H_2O]$ and $[(TBP)_{20}H_3O^+(H_2O)_{23}]+[ClO_4^-]$ stable at the lowest acidity region were determined with Redlich-Kister equations.

1. Introduction

In the field of inorganic liquid-liquid solvent extraction, the systems composed of strong acid-water-basic organic compound are thought to be basic ones in regards to their industrial applications. These systems are also of physico-chemical interest from the viewpoint that the extraction involves competition among the anion, the water and the basic organic extractant for the proton.$^{1),2),3)}$

Among strong acid-water-TBP systems, the system of perchloric acid-water-TBP chosen in this study has not been so widely studied because of very little complex formation between perchlorate ion and metal ion in either phase of the liquid-liquid extraction system. However, this system is reported to have different properties from other systems; such as a remarkable ionization of acid in the organic phase at lower acid concentrations$^{4),5)}$ and dehydration of the organic phase at higher acid concentrations.$^{1),4)}$

On the system of perchloric acid-water-diluted TBP (0.5 to 4% TBP in benzene), Hesford and McKay$^{5)}$ suggested that the principal species extracted at higher acidities is $[TBP\cdot HClO_4]$ and, at lower acidities, $[2TBP\cdot HClO_4]$ is a probable

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constituent. Kertes4) studied on the system of perchloric acid-water-TBP and suggested that there are four main species involved; [$4TBP \cdot HClO_4 \cdot 8H_2O$] at low acid concentrations, [$2TBP \cdot HClO_4 \cdot 5H_2O$] at medium acid concentrations, [$4TBP \cdot 3HClO_4 \cdot 10H_2O$] at medium to high acid concentrations and [$TBP \cdot HClO_4 \cdot 2.5 H_2O$] at very high acid concentrations.

In this paper, the perchloric acid-water-TBP system is studied with several physico-chemical methods to determine the species formed by interactions between the aqueous and organic phases. The study is also intended to estimate the chemical equilibrium in a part of the system, based on the species determined and on their interactions with acid and water. Redlich-Kister equations on the activity coefficients of the species are used to calculate their activities.

2. Experimental

2.1 Material and Experimental Procedures

TBP used throughout this study was prepared according the procedure described in the previous paper.6) "Analytical Reagent" grade perchloric acid and deionized water were used.

In addition to the conventional distribution measurement of perchloric acid and water, measurements of volume swelling, density, viscosity and electrical conductivity were carried out with the equilibrated organic phase.6)

2.2 Results

2.2.1 Acid concentration in organic phase

The molarity concentration of perchloric acid in organic phase, $M^{O}_{HClO_4}$ shown in Fig. 1, was calculated from the measured molarity acid concentration in the equilibrated aqueous phase, $M^{A}_{HClO_4}$, compensating for the swelling of organic phase. From the equilibrium distribution curve shown in Fig. 1, it is seen that the extraction of acid into the organic phase increases abruptly at lower $M^{A}_{HClO_4}$. This becomes more evident in Fig. 2 which illustrates the relationship between the distribution coefficient α defined as $M^{O}_{HClO_4}/M^{A}_{HClO_4}$ and the $M^{O}_{HClO_4}/M^{O}_{TBP}$. α shows a sharp peak below 0.1 of $M^{O}_{HClO_4}/M^{O}_{TBP}$.

2.2.2 Water content in the organic phase

The water content in the organic phase in the form of molarity concentration ratio $M^{O}_{H_2O}/M^{O}_{TBP}$ was plotted in Fig. 3 against $M^{O}_{HClO_4}/M^{O}_{TBP}$. The slopes of straight lines in each region of $M^{O}_{HClO_4}/M^{O}_{TBP}$ were determined. They are 4 between 0 and 0.05, 2 between 0.05 and 0.25, 1 between 0.25 and 0.5, -1.2 between 0.5 and 0.75 and -0.4 above 0.75 of $M^{O}_{HClO_4}/M^{O}_{TBP}$, respectively. This indicates that dehydration occurs in the organic phase of higher acid concentrations

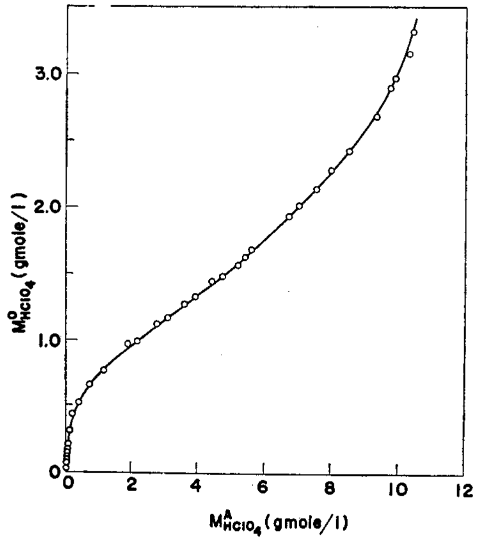

Fig. 1. Equilibrium Distribution of $HClO_4$.

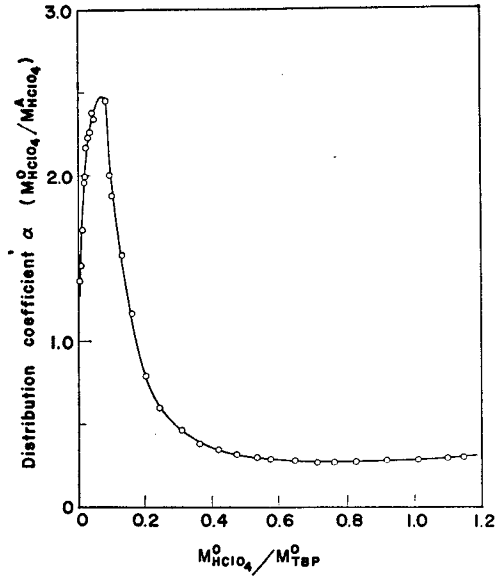

Fig. 2. Equilibrium Distribution Coefficient of $HClO_4$.

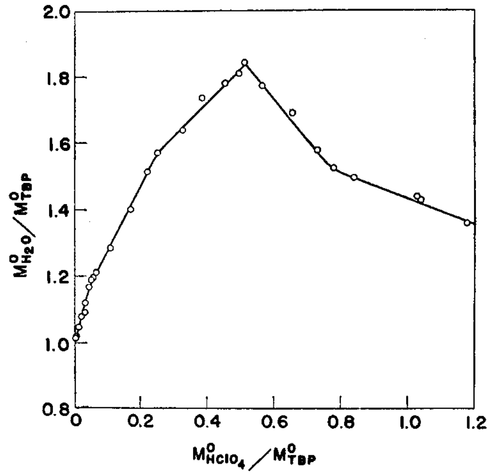

Fig. 3. Water Concentration in the Equilibrated Organic Phase.

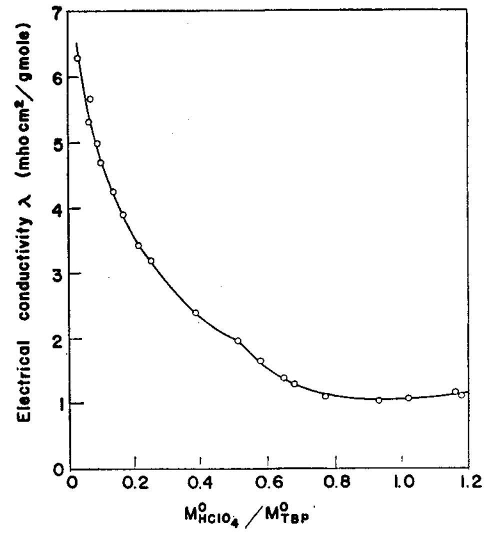

Fig. 4. Electrical Conductivity of the Equilibrated Organic Phase.

(above 0.5 of $M^0_{HClO_4}/M^0_{TBP}$).

2.2.3 Electrical conductivity of organic phase

Fig. 4 illustrates the relationship between the equivalent conductivity of organic phase, λ, and $M^0_{HClO_4}/M^0_{TBP}$. It is seen from this figure that λ decreases with acid concentration from its maximal value at very low $M^0_{HClO_4}/M^0_{TBP}$ to its minimal value at about 0.75 of $M^0_{HClO_4}/M^0_{TBP}$. A curve break is observed at about 0.5 of $M^0_{HClO_4}/M^0_{TBP}$.

2.2.4 Volume ratio of organic phase to aqueous phase

The ratio of organic phase volume V_O to aqueous phase volume V_A is plotted in Fig. 5 against $M^0_{HClO_4}/M^0_{TBP}$. It is observed in this figure that the V_O/V_A increases with $M^0_{HClO_4}/M^0_{TBP}$ and that three curve breaks were found at 0.05, 0.25 and 0.75 of $M^0_{HClO_4}/M^0_{TBP}$.

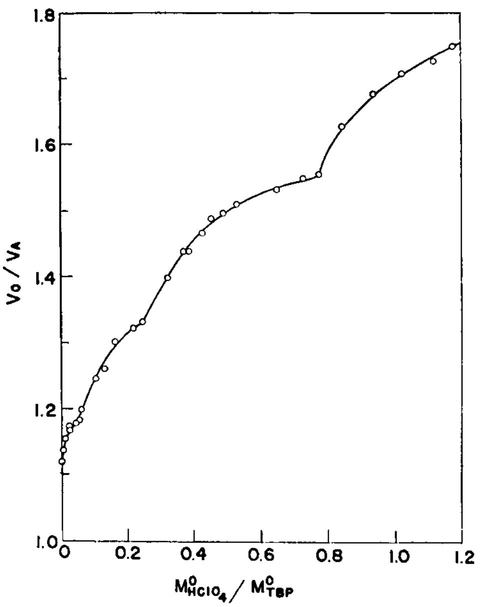

Fig. 5. Volume Ratio of the Equilibrated Phases.

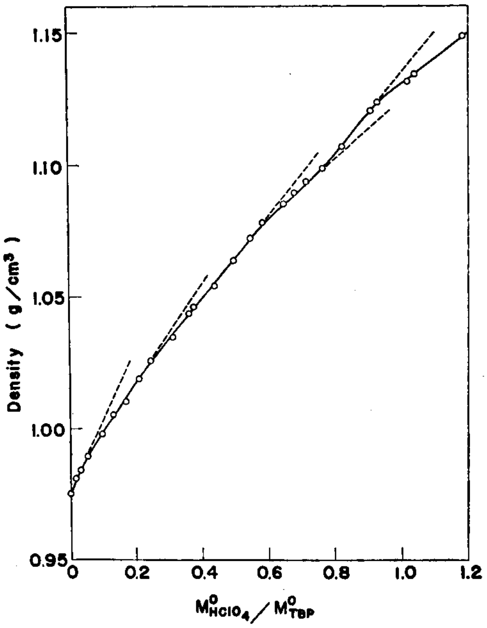

Fig. 6. Density of the Equilibrated Organic Phase.

2.2.5 Density of organic phase

Fig. 6 shows the plot of density of organic phase against $M^0_{HClO_4}/M^0_{TBP}$. The density increases with $M^0_{HClO_4}/M^0_{TBP}$ and five curve breaks are observed at about 0.05, 0.25, 0.5, 0.75 and 1.0 of $M^0_{HClO_4}/M^0_{TBP}$, respectively.

2.2.6 Viscosity of organic phase

Fig. 7 illustrates the viscosity of the organic phase against $M^0_{HClO_4}/M^0_{TBP}$. It is seen in this figure that three curve breaks were found at about 0.25, 0.75 and 1.0 of $M^0_{HClO_4}/M^0_{TBP}$.

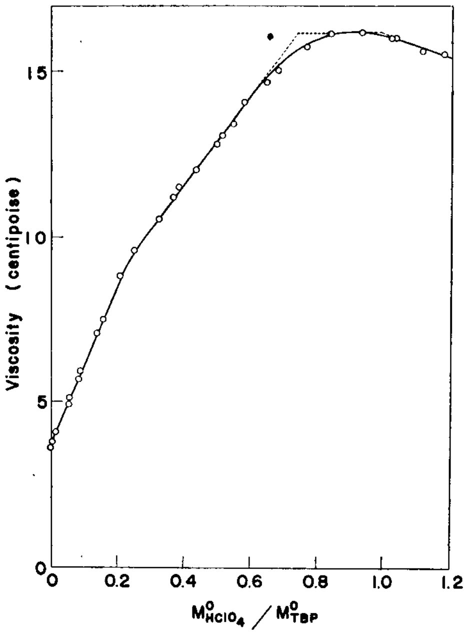

Fig. 7. Viscosity of the Equilibrated Organic Phase.

3. Discussion

From the experimental data above mentioned, it becomes clear that this system has the following two different properties from the systems of HCl-H_2O-TBP[6] and H_2SO_4-H_2O-TBP[7]; high equivalent conductivity of the organic phase at lower acid concentrations (Fig. 4) and the dehydration of organic phase above 0.5 of $M^0_{HClO_4}/M^0_{TBP}$ (Fig. 3). Keeping these in mind, the extracting species and their equilibrium are discussed.

3.1 Dissociation of Extracting Species

Assuming that Walden's rule for infinite dilution can be extended for electrolyte of finite dilution, α_0 in the following equation (1) indicates the approximate degree of ionization of ion-pair in the electrolyte.[8]

$$\alpha_0 = \mu\eta/\mu_0\eta_0 \qquad (1)$$

where μ is the molar conductivity and η is the viscosity in centipoise. Subscript "o" denotes infinite dilution.

With numerical constant of 29 given by Hesford and McKay[5] for $\mu_0\eta_0$ of this system, Walden's degree of ionization α_0 can be calculated from the measured conductivity and viscosity. It is plotted against $M^{o}_{HClO_4}/M^{o}_{TBP}$ in Fig. 8. It is seen from this figure that the extracting species at very low acid concentration in the organic phase dissociates partly and its degree of ionization increases with the acid concentration. After reaching its maximal value at about 0.25 of $M^{o}_{HClO_4}/M^{o}_{TBP}$, it decreases. This indicates that the extracting species at these low acid concentrations are almost completely ionized.

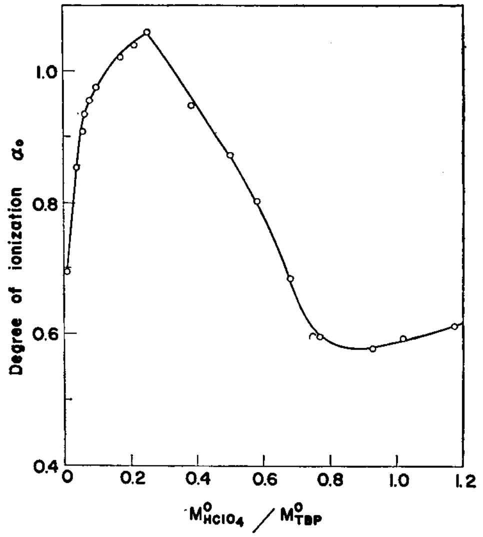

Fig. 8. Walden's Degree of Ionization.

3.2 Determination of Extracting Species

From the physico-chemical measurements with the equilibrated organic phase mentioned in **2.**, five curve breaks were observed at 0.05, 0.25, 0.5, 0.75 and 1.0 of $M^{o}_{HClO_4}/M^{o}_{TBP}$ which correspond to 0.08, 1.3, 4.7, 7.8 and 9.7 of $M^{A}_{HClO_4}$, respectively. These curve breaks are supposed to be due to different interactions between the aqueous and organic phases. And the extracting species in each region of $M^{o}_{HClO_4}/M^{o}_{TBP}$ are better discussed separately, since different species are expected in the organic phases of different acidities.

It is known[6,7] that

$$[TBP \cdot H_2O] \qquad \text{(A)}$$

is a stable extracting species in H_2O-TBP system. It is seen in Fig. 3 that $M^{o}_{H_2O}/M^{o}_{TBP} \fallingdotseq 1$ at $M^{o}_{HClO_4}/M^{o}_{TBP}=0$.

In the lower acidity region of the equilibrated aqueous phase ($M^{A}_{\mathrm{HClO_4}} \leq 0.08$), H_2O and $HClO_4$ have interactions with TBP and both are extracted. The extraction of $HClO_4$ increases very rapidly and the distribution coefficient of acid between aqueous and organic phases shows a sharp peak, as illustrated in Fig. 2. H_2O is also extracted into the organic phase; Fig. 3 demonstrates that the slope of $M^{O}_{\mathrm{H_2O}}/M^{O}_{\mathrm{TBP}}$ against $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$ is 4 and that the ratio of $M^{O}_{\mathrm{H_2O}}/M^{O}_{\mathrm{TBP}}$ is 1.2 at 0.05 of $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$. Walden's degree of ionization α_0 increases in this region; the extracting species is supposed to be ionized completely. In this region of 0 to 0.05 $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$, $[\mathrm{TBP \cdot H_2O}]$ and the another species (B) are thought to be stable components; $[\mathrm{TBP \cdot H_2O}]$ is predominant at 0 of $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$ and the species (B) is predominant at 0.05 of $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$. With this pseudo-binary system in mind, the composition of species (B) is determined with $M^{O}_{\mathrm{H_2O}}/M^{O}_{\mathrm{TBP}} = 1.2$ at $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}} = 0.05$. It is ionized and can be expressed by,

$$[(\mathrm{TBP})_{20}\mathrm{H_3O^+}(\mathrm{H_2O})_{23}] + [\mathrm{ClO_4^-}] \tag{B}$$

And the extracting equation in this acidity region is expressed by,

$$\begin{aligned} &20[\mathrm{TBP \cdot H_2O}]_{(O)} + \mathrm{H^+}(\mathrm{H_2O})_{4(A)} + \mathrm{ClO^-_{4(A)}} \\ &\quad \rightleftarrows [(\mathrm{TBP})_{20}\mathrm{H_3O^+}(\mathrm{H_2O})_{23}]_{(O)} + [\mathrm{ClO_4^-}]_{(O)}\,. \end{aligned} \tag{2}$$

The slope of $M^{O}_{\mathrm{H_2O}}/M^{O}_{\mathrm{TBP}}$ against $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$ indicates the number of water molecules accompanied by a molecule of acid in its transportation into the organic phase. The number is four which is shown by the number of water molecules transfered per $HClO_4$ which appeared on the left side of equation (2).

In the acidity region of 0.08 to 1.3 $M^{A}_{\mathrm{HClO_4}}$, it is presumed that the species (A) disappears and that the species (B) coexists with another species (C); species (B) is predominant at 0.05 of $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$ and species (C) is predominant at 0.25 of $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$. With the experimental results mentioned in **2.** that $M^{O}_{\mathrm{H_2O}}/M^{O}_{\mathrm{TBP}} = 1.6$ at $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}} = 0.25$, that Walden's degree of ionization is almost 1 in this region and that the slope of $M^{O}_{\mathrm{H_2O}}/M^{O}_{\mathrm{TBP}}$ against $M^{O}_{\mathrm{HClO_4}}/M^{O}_{\mathrm{TBP}}$ is 2, the composition of species (C) and the extracting equation are determined as,

$$[(\mathrm{TBP})_{4}\mathrm{H_3O^+}(\mathrm{H_2O})_{27/5}] + [\mathrm{ClO_4^-}] \tag{C}$$

and

$$\begin{aligned} &\tfrac{1}{5}[(\mathrm{TBP})_{20}\mathrm{H_3O^+}(\mathrm{H_2O})_{23}]_{(O)} + \tfrac{1}{5}[\mathrm{ClO_4^-}]_{(O)} \\ &\quad + \tfrac{4}{5}\mathrm{H^+}(\mathrm{H_2O})_{2(A)} + \tfrac{4}{5}\mathrm{ClO^-_{4(A)}} \\ &\quad \rightleftarrows [(\mathrm{TBP})_{4}\mathrm{H_3O^+}(\mathrm{H_2O})_{27/5}]_{(O)} + [\mathrm{ClO_4^-}]_{(O)}\,. \end{aligned} \tag{3}$$

Similarly, in the acidity region of 1.3 to 4.7 $M^{A}_{\mathrm{HClO_4}}$, the species (C) coexists with species (D) which becomes predominant at 0.5 of $M^{O}_{HClO_4}/M^{O}_{TBP}$. $M^{O}_{H_2O}/M^{O}_{TBP}=1.85$ at $M^{O}_{HClO_4}/M^{O}_{TBP}=0.5$. Walden's degree of ionization decreases from 1 to about 0.85 in this region. The slope of $M^{O}_{H_2O}/M^{O}_{TBP}$ against $M^{O}_{HClO_4}/M^{O}_{TBP}$ is 1. From these results, the composition of species (D) and the extracting equation are expressed by,

$$\left.\begin{array}{l}[(TBP)_2H_3O^+(H_2O)_{27/10}]+[ClO_4^-]\\ [(TBP)_2H_3O^+(H_2O)_{27/10}\cdots ClO_4^-]\end{array}\right\} \tag{D}$$

and

$$\begin{array}{l}\frac{1}{2}[(TBP)_4H_3O^+(H_2O)_{27/5}]_{(O)}+\frac{1}{2}[ClO_4^-]_{(O)}+\frac{1}{2}H^+(H_2O)_{(A)}+\frac{1}{2}ClO^-_{4(A)}\\ \rightleftarrows\left\{\begin{array}{l}[(TBP)_2H_3O^+(H_2O)_{27/10}]_{(O)}+[ClO_4^-]_{(O)}\\ [(TBP)_2H_3O^+(H_2O)_{27/10}\cdots ClO_4^-]_{(O)}\end{array}\right\}.\end{array} \tag{4}$$

Dehydration occurs in the higher acidity regions. In the acidity region of 4.7 to 7.8 $M^{A}_{HClO_4}$, this species (D) equilibrates with species (E) which is predominant at 0.75 of $M^{O}_{HClO_4}/M^{O}_{TBP}$. $M^{O}_{H_2O}/M^{O}_{TBP}=1.55$ at $M^{O}_{HClO_4}/M^{O}_{TBP}=0.75$. Walden's degree of ionization continues decreasing. The slope of $M^{O}_{H_2O}/M^{O}_{TBP}$ against $M^{O}_{HClO_4}/M^{O}_{TBP}$ is -1.2 which indicates the dehydration of organic phase. The composition of species (E) and the extracting equation are;

$$\left.\begin{array}{l}[(TBP)_{4/3}H_3O^+(H_2O)_{16/15}]+[ClO_4^-]\\ [(TBP)_{4/3}H_3O^+(H_2O)_{16/15}\cdots ClO_4^-]\end{array}\right\} \tag{E}$$

and

$$\begin{array}{l}\left\{\begin{array}{l}\frac{2}{3}[(TBP)_2H_3O^+(H_2O)_{27/10}]_{(O)}+\frac{2}{3}[ClO_4^-]_{(O)}\\ \frac{2}{3}[(TBP)_2H_3O^+(H_2O)_{27/10}\cdots ClO_4^-]_{(O)}\end{array}\right\}+\frac{1}{3}H^+_{(A)}+\frac{1}{3}ClO^-_{4(A)}\\ \rightleftarrows\left\{\begin{array}{l}[(TBP)_{4/3}H_3O^+(H_2O)_{16/15}]_{(O)}+[ClO_4^-]_{(O)}\\ [(TBP)_{4/3}H_3O^+(H_2O)_{16/15}\cdots ClO_4^-]_{(O)}\end{array}\right\}+\frac{6}{15}H_2O_{(A)}.\end{array} \tag{5}$$

In the highest acidity region studied where $M^{A}_{HClO_4}$ is 7.8 to 9.7, the organic phase continues to dehydrate. In this acidity region, the species (E) coexists with species (F); the latter becomes predominant towards 1.0 of $M^{O}_{HClO_4}/M^{O}_{TBP}$. $M^{O}_{H_2O}/M^{O}_{TBP}=1.55$ at $M^{O}_{HClO_4}/M^{O}_{TBP}=1.0$. Walden's degree of ionization remains constant at about 0.6. The slope of $M^{O}_{H_2O}/M^{O}_{TBP}$ against $M^{O}_{HClO_4}/M^{O}_{TBP}$ is -0.4 which indicates again the dehydration. The composition of species (F) and the extracting equation are expressed by;

$$\left.\begin{array}{l}[(TBP)H_3O^+(H_2O)_{9/20}]+[ClO_4^-]\\ [(TBP)H_3O^+(H_2O)_{9/20}\cdots ClO_4^-]\end{array}\right\} \tag{F}$$

and

$$\left\{\begin{array}{l}\frac{3}{4}[(\mathrm{TBP})_{4/3}\mathrm{H_3O^+}(\mathrm{H_2O})_{16/15}]_{(\mathrm{O})}+\frac{3}{4}[\mathrm{ClO_4^-}]_{(\mathrm{O})}\\ \frac{3}{4}[(\mathrm{TBP})_{4/3}\mathrm{H_3O^+}(\mathrm{H_2O})_{16/15}\cdots\mathrm{ClO_4^-}]_{(\mathrm{O})}\end{array}\right\}+\frac{1}{4}\mathrm{H^+_{(A)}}+\frac{1}{4}\mathrm{ClO^-_{4(A)}}$$

$$\rightleftarrows\left\{\begin{array}{l}[(\mathrm{TBP})\mathrm{H_3O^+}(\mathrm{H_2O})_{9/20}]_{(\mathrm{O})}+[\mathrm{ClO_4^-}]_{(\mathrm{O})}\\ [(\mathrm{TBP})\mathrm{H_3O^+}(\mathrm{H_2O})_{9/20}\cdots\mathrm{ClO_4^-}]_{(\mathrm{O})}\end{array}\right\}+\frac{1}{10}\mathrm{H_2O_{(A)}}\,. \qquad (6)$$

The extracting species (A) to (F) found in this study are summarized in Table 1 and they are compared with those determined by Kertes.[4]

Table 1. Extracting Species.

Acidity where the species is predominant ($M^{O}_{HClO_4}/M^{O}_{TBP}$)	Species (this work)	Species (Kertes[4])
0	$[\mathrm{TBP\cdot H_2O}]$	$[\mathrm{TBP\cdot H_2O}]$
0.05	$[(\mathrm{TBP})_{20}\mathrm{H_3O^+}(\mathrm{H_2O})_{23}]+[\mathrm{ClO_4^-}]$	
0.25	$[(\mathrm{TBP})_4\mathrm{H_3O^+}(\mathrm{H_2O})_{27/5}]+[\mathrm{ClO_4^-}]$	$[(\mathrm{TBP})_4\cdot\mathrm{HClO_4}\cdot(\mathrm{H_2O})_8]$
0.5	$\{[(\mathrm{TBP})_2\mathrm{H_3O^+}(\mathrm{H_2O})_{27/10}]+[\mathrm{ClO_4^-}]$ $[(\mathrm{TBP})_2\mathrm{H_3O^+}(\mathrm{H_2O})_{27/10}\cdots\mathrm{ClO_4^-}]$	$[(\mathrm{TBP})_2\cdot\mathrm{HClO_4}\cdot(\mathrm{H_2O})_5]$
0.75	$\{[(\mathrm{TBP})_{4/3}\mathrm{H_3O^+}(\mathrm{H_2O})_{16/15}]+[\mathrm{ClO_4^-}]$ $[(\mathrm{TBP})_{4/3}\mathrm{H_3O^+}(\mathrm{H_2O})_{16/15}\cdots\mathrm{ClO_4^-}]$	$[(\mathrm{TBP})_4\cdot(\mathrm{HClO_4})_3\cdot(\mathrm{H_2O})_{10}]$
1.0	$\{[(\mathrm{TBP})\mathrm{H_3O^+}(\mathrm{H_2O})_{9/20}]+[\mathrm{ClO_4^-}]$ $[(\mathrm{TBP})\mathrm{H_3O^+}(\mathrm{H_2O})_{9/20}\cdots\mathrm{ClO_4^-}]$	$[\mathrm{TBP\cdot HClO_4\cdot(H_2O)_{2.5}}]$

Except for the lower acidity region of less than 0.25 $M^{O}_{HClO_4}/M^{O}_{TBP}$ where the species $[(\mathrm{TBP})_{20}\mathrm{H_3O^+}(\mathrm{H_2O})_{23}]+[\mathrm{ClO_4^-}]$ was found in this work, the composition of the species determined in these two works coincide well, though their water content is a little bit biased each other.

3.3 Activities of Extracting Species in the Lowest Acidity Region

It was mentioned in the preceding section that the species $[\mathrm{TBP\cdot H_2O}]$ equilibrates with the ionized species $[(\mathrm{TBP})_{20}\mathrm{H_3O^+}(\mathrm{H_2O})_{23}]+[\mathrm{ClO_4^-}]$ in the acidity region of below 0.05 $M^{O}_{HClO_4}/M^{O}_{TBP}$. The activities and activity coefficients of these species are intended to be estimated in this section.

The interaction equation between the species and electrolyte is generalized as follows;

$$x[\mathrm{TBP\cdot H_2O}]_{(\mathrm{O})}+\mathrm{H^+_{(A)}}+\mathrm{ClO^-_{4(A)}}+y\mathrm{H_2O_{(A)}}$$

$$\rightleftarrows[x\mathrm{TBP\cdot H_3O^+}(x+y-1)\mathrm{H_2O}]_{(\mathrm{O})}+[\mathrm{ClO_4^-}]_{(\mathrm{O})}\,. \qquad (7)$$

And its equilibrium constant K is,

$$K=\frac{(x\mathrm{TBP\cdot H_3O^+}(x+y-1)\mathrm{H_2O})_{\mathrm{O}}(a_{\mathrm{ClO_4^-}})_{\mathrm{O}}}{(\mathrm{TBP\cdot H_2O})^{x}_{\mathrm{O}}(a_{\mathrm{H^+}})_{\mathrm{A}}(a_{\mathrm{ClO_4^-}})_{\mathrm{A}}(a_{\mathrm{H_2O}})^{y}_{\mathrm{A}}} \qquad (8)$$

where

$(\mathrm{TBP \cdot H_2O})_{\mathrm{O}}$: activity of [TBP·H$_2$O] in organic phase
$(a_{\mathrm{H^+}})_{\mathrm{A}}$: activity of [H$^+$] in aqueous phase
$(a_{\mathrm{ClO_4^-}})_{\mathrm{A}}$: activity of [ClO$_4^-$] in aqueous phase
$(a_{\mathrm{H_2O}})_{\mathrm{A}}$: activity of water in aqueous phase
$(x\mathrm{TBP \cdot H_3O^+}(x+y-1)\mathrm{H_2O})_{\mathrm{O}}$
: activity of [xTBP·H$_3$O$^+$(x+y−1)H$_2$O] in organic phase
$(a_{\mathrm{ClO_4^-}})_{\mathrm{O}}$: activity of [ClO$_4^-$] in organic phase.

Of these activities in mole fraction scale, the product $(a_{\mathrm{H^+}})_{\mathrm{A}}(a_{\mathrm{ClO_4^-}})_{\mathrm{A}}$ is written as,

$$(a_{\mathrm{H^+}})_{\mathrm{A}}(a_{\mathrm{ClO_4^-}})_{\mathrm{A}} = (a_{\pm\mathrm{HClO_4}})^2_{\mathrm{A}} = \left(\frac{M_{\mathrm{W}}}{1000}\right)^2 (\gamma_{\pm\mathrm{HClO_4}})^2 (m^{\mathrm{A}}_{\mathrm{HClO_4}})^2 \tag{9}$$

where

$(a_{\pm\mathrm{HClO_4}})_{\mathrm{A}}$: mean activity of perchloric acid in aqueous phase
$m^{\mathrm{A}}_{\mathrm{HClO_4}}$: molality of perchloric acid in aqueous phase
$\gamma_{\pm\mathrm{HClO_4}}$: mean activity coefficient of perchloric acid
M_{W} : molecular weight of water.

Concerning the activities of [TBP·H$_2$O] and ionized species [xTBP·H$_3$O$^+$(x+y−1)·H$_2$O]+[ClO$_4^-$] in organic phase,

$$(\mathrm{TBP \cdot H_2O})_{\mathrm{O}} = f_{\mathrm{A}} N_{\mathrm{A}} \tag{10}$$

$$(x\mathrm{TBP \cdot H_3O^+}(x+y-1)\mathrm{H_2O})_{\mathrm{O}} = f_{\mathrm{B^+}} N_{\mathrm{B^+}} \tag{11}$$

and

$$(a_{\mathrm{ClO_4^-}})_{\mathrm{O}} = f_{\mathrm{B^-}} N_{\mathrm{B^-}} \tag{12}$$

where subscripts A and B denote the species, and
f : activity coefficient of the species
N: mole fraction.

Substituting equations (9) to (12) into equation (8),

$$\begin{aligned} K &= \frac{(f_{\mathrm{B^+}} N_{\mathrm{B^+}})(f_{\mathrm{B^-}} N_{\mathrm{B^-}})}{(f^x_{\mathrm{A}} N^x_{\mathrm{A}})\left(\frac{M_{\mathrm{W}}}{1000}\right)^2 (\gamma_{\pm\mathrm{HClO_4}})^2 (m^{\mathrm{A}}_{\mathrm{HClO_4}})^2 (a_{\mathrm{H_2O}})^y_{\mathrm{A}}} \\ &= \frac{f^2_{\mathrm{B}} N^2_{\mathrm{B}}}{(f^x_{\mathrm{A}} N^x_{\mathrm{A}})\left(\frac{M_{\mathrm{W}}}{1000}\right)^2 (\gamma_{\pm\mathrm{HClO_4}})^2 (m^{\mathrm{A}}_{\mathrm{HClO_4}})^2 (a_{\mathrm{H_2O}})^y_{\mathrm{A}}} \,. \end{aligned} \tag{13}$$

In this equation (13), we use the mean activity coefficient f_{B} of the species B defined by,

$$f_{\mathrm{B}} = \sqrt{f_{\mathrm{B^+}} f_{\mathrm{B^-}}} \tag{14}$$

and its mole fraction $N_{B^+}=N_{B^-}=N_B$. By comparing equation (7) with equation (2), we have $x=20$ and $y=4$, and equation (13) becomes,

$$K=\frac{f_B^2 N_B^2}{f_A^{20} N_A^{20}\left(\frac{M_W}{1000}\right)^2 (\gamma_{\pm HClO_4})^2 (m^A_{HClO_4})^2 (a_{H_2O})^4_A} \tag{15}$$

or

$$\frac{f_A^{20}}{f_B^2}=\frac{N_B^2}{N_A^{20}\left(\frac{M_W}{1000}\right)^2 (\gamma_{\pm HClO_4})^2 (m^A_{HClO_4})^2 (a_{H_2O})^4_A K} \tag{16}$$

and it is intended with this equation (16) to estimate the activity coefficients f_A and f_B and the equilibrium constant K.

Before applying Redlich-Kister equations[9] with three-constants and four-suffix type, some investigations are to be made on the mole fractions N_A and N_B, the mean activity coefficient of aqueous perchloric acid $\gamma_{\pm HClO_4}$ and the activity of water.

The mole fractions of the extracting species are generally given by,

$$N_A=\frac{\frac{1000}{M}-x m^O_{HClO_4}}{\frac{1000}{M}+m^O_{HClO_4}-x m^O_{HClO_4}+m^O_{fw}} \tag{17}$$

and

$$N_B=\frac{m^O_{HClO_4}}{\frac{1000}{M}+m^O_{HClO_4}-x m^O_{HClO_4}+m^O_{fw}}. \tag{18}$$

where

M : molecular weight of $[TBP\cdot H_2O]$
$m^O_{HClO_4}$: molality of perchloric acid in organic phase
m^O_{fw} : molality of free water in organic phase.

The activity coefficients of aqueous perchloric acid are given by Robinson[10] in the molality range of 0.1 to 6.0. The necessary activity coefficients were read from a $\gamma - m$ diagram prepared with these data, since the acidity in this region is below 0.08. In this acidity region, the activity of water may be assumed to be unity. Substituting $M=284.34$, $x=20$ and $m^O_{fw}=0$ into equations (17) and (18),

$$N_A=\frac{3.517-20m^O_{HClO_4}}{3.517-19m^O_{HClO_4}} \tag{19}$$

$$N_B=\frac{m^O_{HClO_4}}{3.517-19m^O_{HClO_4}}. \tag{20}$$

And finally, equation (16) has a form of,

$$\frac{f_{\mathrm{A}}^{20}}{f_{\mathrm{B}}^{2}} = \frac{\left(\dfrac{m_{\mathrm{HClO_4}}^{\mathrm{O}}}{3.517-19\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}\right)^2}{\left(\dfrac{3.517-20\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}{3.517-19\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}\right)^{20}\left(\dfrac{M_{\mathrm{W}}}{1000}\right)^2(\gamma_{\pm\mathrm{HClO_2}})^2(m_{\mathrm{HClO_4}}^{\mathrm{A}})^2K}\,. \tag{21}$$

Logarithmic expression of this equation (21) is

$$\log\frac{f_{\mathrm{A}}^{20}}{f_{\mathrm{B}}^{2}} = -\log K+2\log\left(\frac{m_{\mathrm{HClO_4}}^{\mathrm{O}}}{3.517-19\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}\right)-20\log\left(\frac{3.517-20\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}{3.517-19\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}\right)$$
$$-2\log\left(\frac{M_{\mathrm{W}}}{1000}\right)-2\log\gamma_{\pm\mathrm{HClO_4}}-2\log m_{\mathrm{HClO_4}}^{\mathrm{A}}\,. \tag{22}$$

On the other hand, the activity coefficients are shown by Redlich-Kister equations as,

$$\log f_{\mathrm{A}} = N_{\mathrm{B}}^2[B-C+D+(4C-8D)N_{\mathrm{A}}+12DN_{\mathrm{A}}^2] \tag{23}$$
$$\log f_{\mathrm{B}} = N_{\mathrm{A}}^2[B+C+D-(4C+8D)N_{\mathrm{B}}+12DN_{\mathrm{B}}^2]\,. \tag{24}$$

With these equations (23) and (24), $\log(f_{\mathrm{A}}^{20}/f_{\mathrm{B}}^{2})$ is,

$$\log\frac{f_{\mathrm{A}}^{20}}{f_{\mathrm{B}}^{2}} = B(20N_{\mathrm{B}}^2-2N_{\mathrm{A}}^2)$$
$$+C\{20N_{\mathrm{B}}^2(4N_{\mathrm{A}}-1)+2N_{\mathrm{A}}^2(4N_{\mathrm{B}}-1)\}$$
$$+D\{20N_{\mathrm{B}}^2(12N_{\mathrm{A}}^2-8N_{\mathrm{A}}+1)-2N_{\mathrm{A}}^2(12N_{\mathrm{B}}^2-8N_{\mathrm{B}}+1)\}\,. \tag{25}$$

And the resulting equation from equations (22) and (25) has a form of

$$\log K+2\log\left(\frac{M_{\mathrm{W}}}{1000}\right)+B(20N_{\mathrm{B}}^2-2N_{\mathrm{A}}^2)$$
$$+C\{20N_{\mathrm{B}}^2(4N_{\mathrm{A}}-1)+2N_{\mathrm{A}}^2(4N_{\mathrm{B}}-1)\}$$
$$+D\{20N_{\mathrm{B}}^2(12N_{\mathrm{A}}^2-8N_{\mathrm{A}}+1)-2N_{\mathrm{A}}^2(12N_{\mathrm{B}}^2-8N_{\mathrm{B}}+1)\}$$
$$= 2\log\left(\frac{m_{\mathrm{HClO_4}}^{\mathrm{O}}}{3.517-19\,m_{\mathrm{HCl_4O}}^{\mathrm{O}}}\right)-20\log\left(\frac{3.517-20\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}{3.517-19\,m_{\mathrm{HClO_4}}^{\mathrm{O}}}\right)$$
$$-2\log\gamma_{\pm\mathrm{HClO_4}}-2\log m_{\mathrm{HClO_4}}^{\mathrm{A}}\,. \tag{26}$$

N_{A} and N_{B} in this equation are given by equations (19) and (20), respectively. $\gamma_{\pm\mathrm{HClO_4}}$ are given by Robinson. Thus, equation (26) demonstrates the relationship between unknown constants $\log K+2\log(M_{\mathrm{W}}/1000)$, B, C and D and measured variables of $m_{\mathrm{HClO_4}}^{\mathrm{O}}$ and $m_{\mathrm{HClO_4}}^{\mathrm{A}}$. In other words, a generalized form of equation (26) is expressed as,

$$A+Bb_i+Cc_i+Dd_i = e_i \tag{27}$$

where b_i, c_i, d_i and e_i represent the given variables of perchloric acid concentration measured and A, B, C and D are the unknown constants to be determined. With twelve sets of data in the range of 0 to 0.08 $M^{A}_{HClO_4}$, A, B, C and D were determined by the least square method. Thus we have,

$$K = 2.2722 \times 10^6 \tag{28}$$

$$\log f_A = N_B^2(1.4688-3.0126N_A+4.6707N_A^2) \tag{29}$$

$$\log f_B = N_A^2(1.5193-3.2149N_B+4.6707N_B^2)\,. \tag{30}$$

With equations (29) and (30), the activities and the activity coefficients of species A and B were calculated and they were demonstrated in Figs. 9 and 10, respectively.

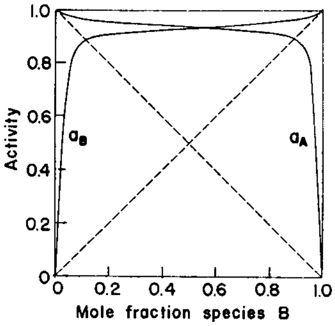

Fig. 9. Activities of Species A and B.

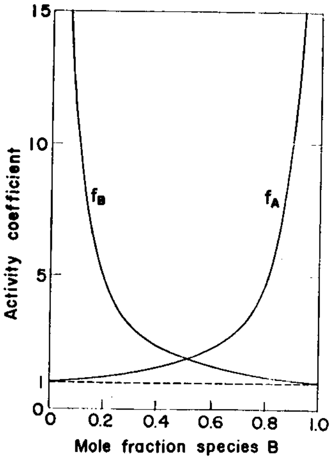

Fig. 10. Activity Coefficients of Species A and B.

It is seen in these figures that the activities of both species have positive departures from ideality and accordingly, that their activity coefficients have values higher than unity.

Summary

The system perchloric acid-water-TBP was studied in order to clarify its equilibrium relationships. Distribution of perchloric acid and water between organic and aqueous phases was determined. Physico-chemical properties of the organic phase, such as its volume swelling, density, viscosity and electrical conductivity were also measured.

Five breaks were observed on the curves of physico-chemical data against the perchloric acid concentrations. These critical $M^{A}_{HClO_4}$ are 0.08, 1.3, 4.7, 7.8 and

9.7. On the assumption that each acidity region thus divided is composed of two extracting species, the composition of major extracting species and their extracting equations were determined. They are summarized and compared with those suggested by Kertes (Table 1). At lower acidity region of below 0.08 $M^{A}_{HClO_4}$, a new extracting species

$$[(TBP)_{20}H_3O^+(H_2O)_{23}]+[ClO_4^-]$$

was suggested to exist. From the measurements of equivalent conductivity of the organic phase, the extracting species at lower acid concentrations are supposed to be almost completely ionized. Dehydration of the organic phase occurs at higher acidity regions.

Keeping these extracting species in mind, the equilibrium between the species and electrolyte was studied in the acidity region of 0 to 0.08 $M^{A}_{HClO_4}$. With the chemical equilibrium of the species A, B and electrolyte and with Redlich-Kister equations concerning the activity coefficients of the two species, the equilibrium constant, the activities and the activity coefficients of the species were estimated with least square method. The activities of both species were found to have positive departures from ideality and their activity coefficients are more than unity.

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