

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

By

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This study is intended to determine the species formed in the heterogeneous equilibrium between aqueous hydrochloric acid and tributyl phosphate and to clarify the mechanism of extraction. In addition to the conventional distribution measurement of hydrochloric acid and water, physico-chemical measurements of volume-change, density and viscosity were carried out with the equilibrated organic phases. Infra-red absorption spectra were also measured. It was found that the major extracting species is $[\text{TBP}\cdot\text{H}_2\text{O}]$ at the equilibrated acid concentration in aqueous phase below 2.0 M. Above 2.0 M, two other species were found to exist as a result of solute-solvent interactions in the system studied; the one formed at lower acid concentration has the general formula $[(\text{TBP})_2\cdot\text{H}_3\text{O}^+\cdot(y+1)\text{H}_2\text{O}\cdots\text{Cl}^-]$ (y was determined as 3.5) and the another formed at higher acid concentration has the formula $[\text{TBP}\cdot\text{H}_3\text{O}^+\cdot 2\text{H}_2\text{O}\cdots\text{Cl}^-]$. With Redlich-Kister equations on the equilibrium distribution in two components system, the activities and activity coefficients of two species $[\text{TBP}\cdot\text{H}_2\text{O}]$ and $[(\text{TBP})_2\cdot\text{H}_3\text{O}^+\cdot 4.5(\text{H}_2\text{O})\cdots\text{Cl}^-]$ and the equilibrium constant of the two species in organic phase at lower acid concentration were determined.

1. Introduction

Liquid-liquid solvent extraction, born as a separating method in analytical chemistry, has developed as one of the most important processes in extraction metallurgy. Of the solvent extractions in metallurgical processes, metal nitrate-nitric acid-tri-n-butyl phosphate (TBP) system is most widely used and has been studied thoroughly by many investigators¹⁾⁻⁴⁾. Metal chloride-hydrochloric acid-TBP system, equally important in the extraction of metals such as transition metals of lower valencies, is expected in extensive applications in the near future, and has been less explored than the nitrate system⁵⁾⁶⁾.

To clarify the extraction of metal chloride by this system, it seems necessary to start from the basic system water-hydrochloric acid-TBP, as the first step. Kertes⁷⁾ studied this basic system and found by physico-chemical

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measurements that the species extracted from aqueous phase at lower acidity is $[(\text{TBP})_2 \cdot \text{HCl} \cdot (\text{H}_2\text{O})_6]$, and that $[\text{TBP} \cdot \text{HCl} \cdot (\text{H}_2\text{O})_3]$ is extracted at higher acidity.

The water-hydrochloric acid-TBP system is studied in this paper intending to determine the species formed by the interactions between aqueous and organic phases. Several physico-chemical measurements are used.

The study is also intended to determine the chemical equilibrium in a part of the system, based upon the extracting species and their interactions with electrolyte. Redlich-Kister equations on the activity coefficients of the species are applied to calculate their activities.

2. Experimental

2.1 Materials

Commercial TBP is supposed to be contaminated with MBP (Mono-butyl phosphate) and DBP (Di-butyl phosphate), and it was purified by the following procedures³. It was stirred several times with an equal volume of 4% aqueous NaOH solution containing 4% KMnO_4 until a faint pink color remained in the organic phase. The resulting organic phase was washed three times with an equal volume of water. With this, acidic impurities such as MBP and DBP were hydrolysed into water-soluble sodium salts and washed out into the aqueous phase. The organic phase thus obtained was distilled in a flask to remove water and volatile impurities of lower boiling points. The portion distilled at about 160°C under 15 to 20 mmHg was collected. Distilled TBP was dehydrated with anhydrous magnesium sulphate and was kept in a dark brown bottle. "Analytical Reagent" grade hydrochloric acid and deionized water were used throughout this study.

2.2 Experimental Procedures

5 ml of the purified TBP was carefully added to 10 ml-graduated (0.1 ml-scale) glass centrifuge tube containing 5 ml of aqueous hydrochloric acid of various concentrations. Both phases were equilibrated by shaking the stopped tube for 30 minutes in a water bath kept at $25 \pm 0.1^\circ\text{C}$. The tube was then centrifuged at 3,000 rpm for 10 minutes to separate phases. After centrifugation, the swelling of the organic phase was measured with cathetometer. Water concentration in the organic phase was determined with Karl Fisher Reagent. Acid concentration in the aqueous phase was titrated against a standard sodium hydroxide solution with phenolphthalein as an indicator. Density and viscosity of the organic phase were measured with pycnometer and

Ostwald type viscosimeter, respectively. The organic phase was put in a TII-TlBr cell and its infra-red spectrum in the range of 900 cm^{-1} to 4000 cm^{-1} were taken with Model No. DS-301 Nippon Bunko Infra-Red Spectrophotometer.

2.3 Results

2.3.1. Hydrochloric acid concentration in organic phase

The molarity concentration of hydrochloric acid in organic phase $M_{\text{HCl}}^{\text{O}}$ was calculated from the measured molarity acid concentration in the equilibrated aqueous phase $M_{\text{HCl}}^{\text{A}}$. It is found from Fig. 1 that hydrochloric acid is scarcely extracted into the organic phase below $2.0 M_{\text{HCl}}^{\text{A}}$ and that the $M_{\text{HCl}}^{\text{O}}$ increases above $2.0 M_{\text{HCl}}^{\text{A}}$.

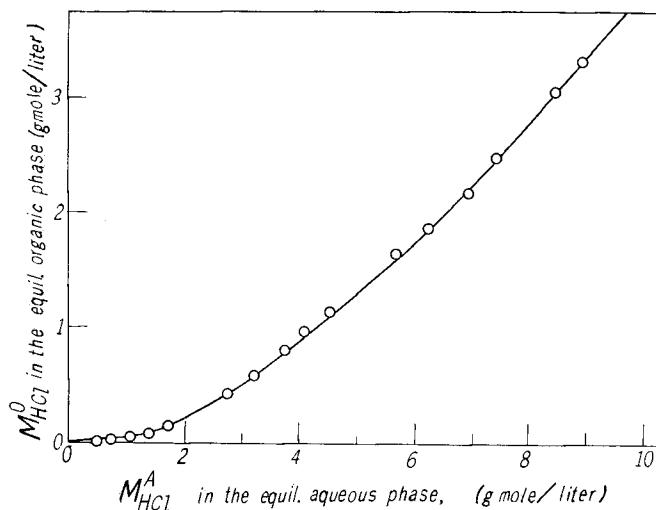


Fig. 1. HCl molarity in the equilibrated organic phase versus its molarity in the equilibrated aqueous phase.

2.3.2 Density of organic phase

Fig. 2 shows the relationship between the density of the organic phase and the ratio of hydrochloric acid molarity concentration to TBP molarity concentration in the organic phase, $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$. It is seen from the figure that the density remains at about 0.980 in the region below $2.0 M_{\text{HCl}}^{\text{A}}$ (where $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}} \approx 0$), and it increases with the rise of $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$. Two curve breaks were found at about 0.5 and 1.0 of $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$.

2.3.3 Volume ratio of organic phase to aqueous phase

In Fig. 3, the ratio of organic phase volume V_{O} to that of aqueous phase V_{A} , $V_{\text{O}}/V_{\text{A}}$, is plotted against $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$. The $V_{\text{O}}/V_{\text{A}}$ remains almost con-

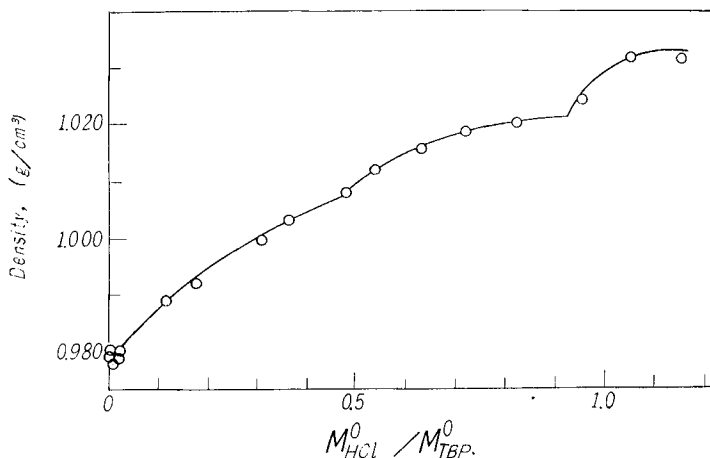


Fig. 2. Density of the equilibrated organic phase versus the ratio M_{HCl}^0 / M_{TBP}^0 .

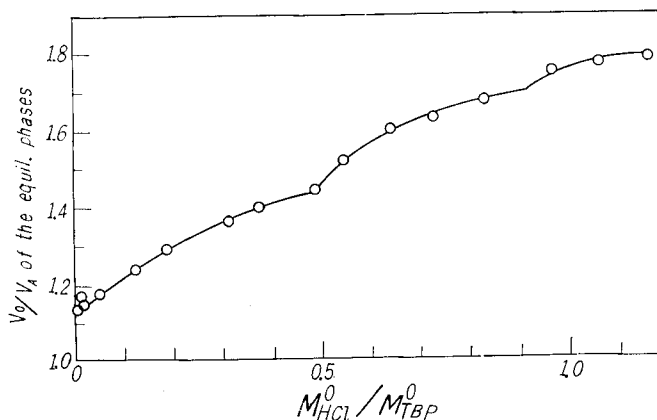


Fig. 3. The ratio V_O / V_A of the equilibrated phases versus the ratio M_{HCl}^0 / M_{TBP}^0 .

stant in the region of M_{HCl}^A below 2.0 and it increases with the M_{HCl}^O / M_{TBP}^O . Two breaks are observed clearly; the first lies at 0.5 and the second at 1.0 of M_{HCl}^O / M_{TBP}^O .

2.3.4 Viscosity of organic phase

The viscosity of organic phase was plotted against M_{HCl}^O / M_{TBP}^O in Fig. 4. It is constant below 2.0 M_{HCl}^A and then it increases with the M_{HCl}^O / M_{TBP}^O , giving two breaks. The first one lies at 0.5 of M_{HCl}^O / M_{TBP}^O and the second is at 1.0 of M_{HCl}^O / M_{TBP}^O .

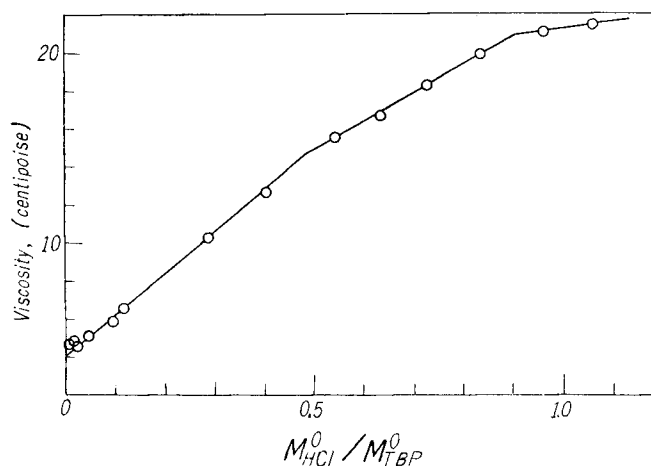


Fig. 4. Viscosity of the equilibrated organic phase versus the ratio M_{HCl}^O / M_{TBP}^O .

2.3.5 Water content in organic phase

Water content in the equilibrated organic phase in form of molarity concentration ratio $M_{H_2O}^O / M_{TBP}^O$ was plotted against M_{HCl}^O / M_{TBP}^O in Fig. 5. $M_{H_2O}^O / M_{TBP}^O$ is kept at about 1 in the region below 2.0 M_{HCl}^O / M_{TBP}^O ($M_{HCl}^O / M_{TBP}^O \neq 0$). And, in the region of 0 to 0.5 of M_{HCl}^O / M_{TBP}^O , a straight line relationship is observed whose slope is calculated as 3.5. This indicates that each two hydrochloric acid molecules accompany seven water molecules while being transported from aqueous phase to organic phase. In the region of 0.5 to 0.7 of M_{HCl}^O / M_{TBP}^O , straight line was not obtained but a convexed curve seems to represent the relationship. In the region of 0.7 to 1.0, another straight line relationship whose slope is 0.2 is most fitted. Above 1.0 of M_{HCl}^O / M_{TBP}^O , water content in the organic phase has little change and its mean value is about three. This shows that one TBP molecule combines with three water molecules in this region of acidity.

2.3.6 Infra-Red absorption spectra of organic phase

Fig. 6 illustrates the infra-red absorption spectra of TBP used in this study, (I), of the equilibrated organic phase obtained from equal volumes of water-TBP, (II), 4.24M HCl-TBP, (III), 5.87M HCl-TBP, (IV), 8.37M HCl-TBP, (V), and 11.30M HCl-TBP, (VI). ν and δ in the figure indicate the stretching vibration and deformation vibration, respectively.

According to Nukada⁹⁾, the absorptions at 2960 cm^{-1} in the infrared spectrum of TBP (I) are attributed to CH stretching vibration of n-butyl group, and those at 1470 cm^{-1} and 1388 cm^{-1} are to CH_3 and CH_2 deformation vibration of

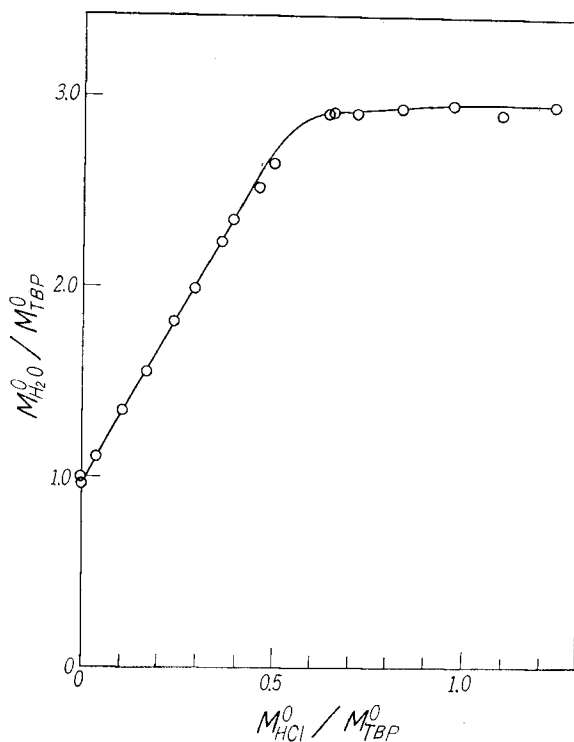


Fig. 5. The ratio $M_{H_2O}^0 / M_{TBP}^0$ versus the ratio M_{HCl}^0 / M_{TBP}^0 .

n-butyl group, respectively. The absorption at 1284 cm^{-1} indicates the stretching vibration of P=O group, and three absorptions at 1058 cm^{-1} , 1020 cm^{-1} and 990 cm^{-1} are based on P-O-C group. The causes of other absorptions are not obvious at this stage, but the absorptions at 3560 cm^{-1} and 1640 cm^{-1} seem to be based on stretching vibration and deformation vibration of O-H group, respectively. Thus, based upon the infra-red absorption spectrum of TBP used in this study, water could not be removed completely during the purification of TBP.

In the spectrum (II), the absorption due to P=O group is shifted from 1284 cm^{-1} in TBP (I) to 1264 cm^{-1} . And, on the other hand, the three absorptions between 1058 cm^{-1} and 990 cm^{-1} coincide with those in TBP (I). It is thought, therefore, that this 20 cm^{-1} shift of P=O group comes from a weak hydrogen-bond between P=O group and H_2O and that the water molecule does not form hydrogen-bond with P-O-C group in TBP⁸⁾.

In the spectra of (III), (IV), (V) and (VI), the absorption based on P=O group is shifted from 1282 cm^{-1} in TBP (I) to 1235 cm^{-1} in (VI) as hydrochloric acid concentration rises in the equilibrated organic phase. With increasing

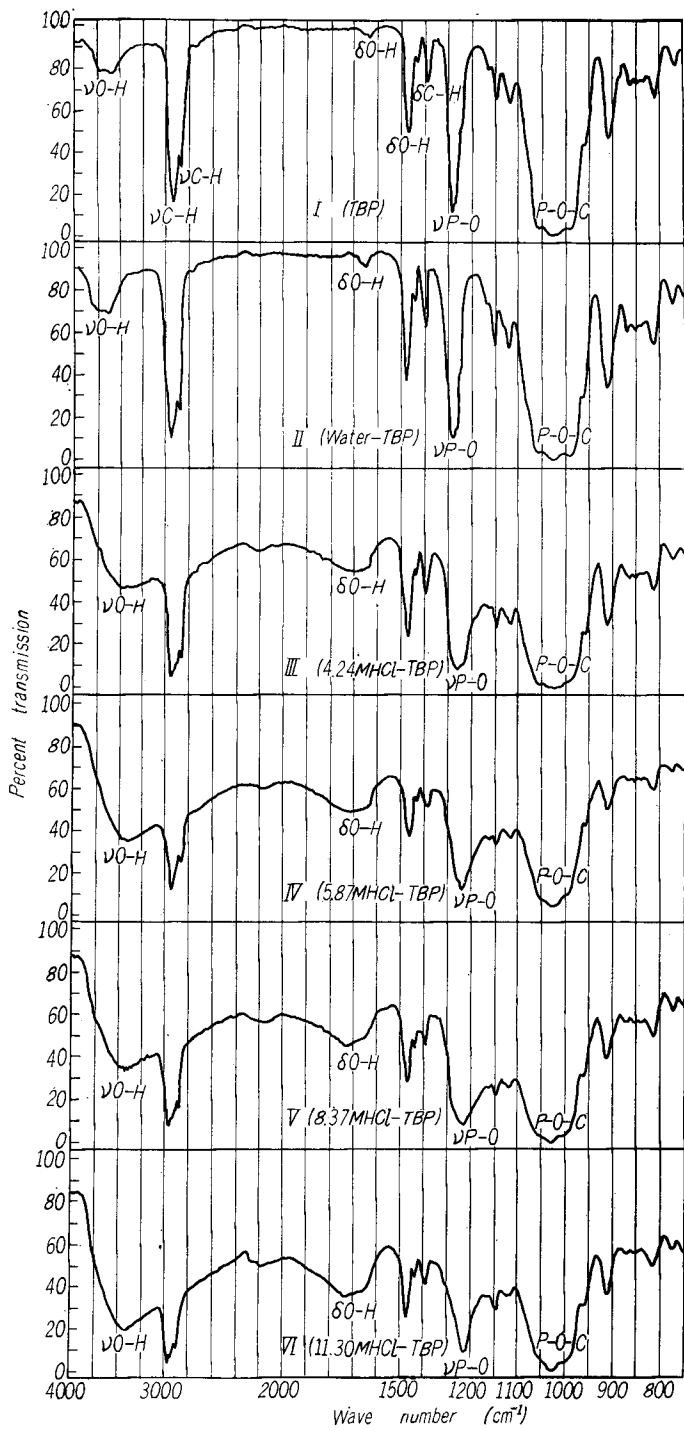


Fig. 6. Infra-red absorption spectra of organic phase extracted.

hydrochloric acid concentration in the organic phase, the absorption due to stretching vibration of O-H group is shifted from 3560 cm^{-1} in (I) to 3340 cm^{-1} in (VI) and that of deformation vibration of O-H group from 1640 cm^{-1} (I) to 1725 cm^{-1} (VI).

Fig. 7 summarizes the shifts of absorption of P=O group and of O-H group due to stretching vibrations. It is seen from the figure that both absorptions of P=O and O-H groups are widely shifted and that the slopes of both lines seem to change at about 0.5 of $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$. This also may indicate the different species in the organic phase in both regions of hydrochloric acid concentration.

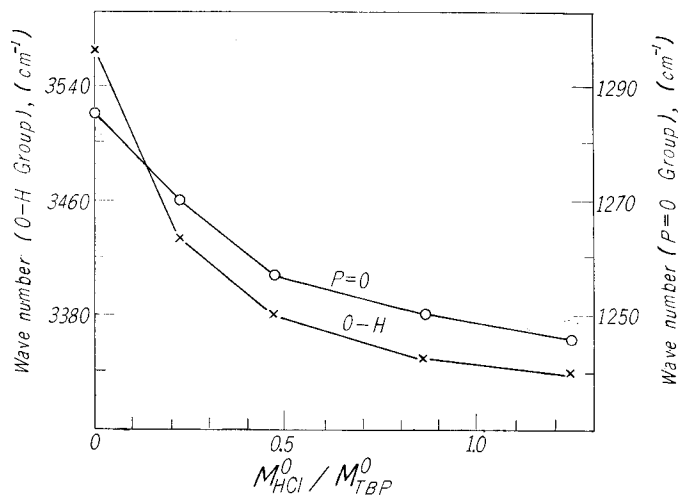


Fig. 7. Wave number of P=O Group and O-H Group versus the ratio $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$.

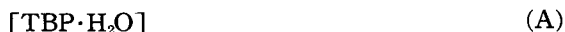
3. Discussion

3.1 On the Extracting Species

From the measurements mentioned above with equilibrated organic phase in the system of TBP-HCl-H₂O, three curve breaks were observed at 2.0 of $M_{\text{HCl}}^{\text{A}}$, 0.5 of $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ (which corresponds to $5.2 M_{\text{HCl}}^{\text{A}}$) and 1.0 of $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ ($\approx 8.0 M_{\text{HCl}}^{\text{A}}$). These curve breaks are thought to be due to different interactions between aqueous hydrochloric acid and TBP, and different species in the equilibrated organic phases are expected in these regions of $M_{\text{HCl}}^{\text{A}}$.

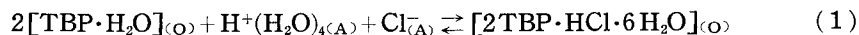
In the lower acidity region of the equilibrated aqueous hydrochloric acid ($M_{\text{HCl}}^{\text{A}} \leq 2.0$), the main interaction between organic and aqueous phases is the extraction of H₂O into organic phase and HCl is scarcely transported into

organic phase. Physico-chemical properties of the equilibrated organic phase do not change in this region. Molarity concentration ratio, $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ is almost zero and $M_{\text{H}_2\text{O}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ was found at about 1 (Fig. 5). Thus, the major species stable in the equilibrated organic phase in this acidity region is thought to have a composition :

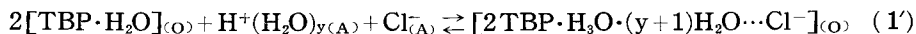


In higher acidity region of hydrochloric acid concentrations, H_2O and HCl have interactions with TBP and both compounds are extracted into the organic phase. As mentioned above, two curve breaks were found and the regions 2.0 to 5.2 $M_{\text{HCl}}^{\text{A}}$ and 5.2 to 8.0 $M_{\text{HCl}}^{\text{A}}$ are better discussed separately.

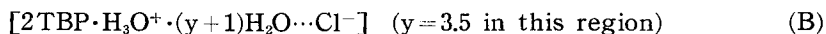
It was demonstrated in 2.3.5 that the slope of $M_{\text{H}_2\text{O}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ has a value of 3.5 between 2.0 and 5.2 $M_{\text{HCl}}^{\text{A}}$ and that two hydrochloric acid molecules transported into the organic phase accompanies seven water molecules. In the region of 2.0 to 5.2 $M_{\text{HCl}}^{\text{A}}$, $[\text{TBP}\cdot\text{H}_2\text{O}]$ is stable with another species B ; $[\text{TBP}\cdot\text{H}_2\text{O}]$ is predominant at 2.0 $M_{\text{HCl}}^{\text{A}}$ and the species B is predominant at 5.2 $M_{\text{HCl}}^{\text{A}}$. Since the ratio of $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ is 0.5 at 5.2 $M_{\text{HCl}}^{\text{A}}$, it is thought that two molecules of TBP combine with one molecule of HCl in this species B. Beckey⁹⁾ found, by means of mass spectrometer with field emission source, that singly charged hydrated hydronium ion H_3O , H_5O_2 , H_7O_3 , and H_9O_4 exist in aqueous solution and that H_9O_4 is a considerably more important species in the absence of the field. On the assumption that the hydrated hydronium ion in aqueous phase has a composition H_9O_4 in this region, the extraction of hydrochloric acid into organic phase is shown by the equation,



According the equation, the expected slope of $M_{\text{H}_2\text{O}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ against $M_{\text{HCl}}^{\text{O}}/M_{\text{TBP}}^{\text{O}}$ (Fig. 5) should be 4 instead of the measured value 3.5. Thus H_7O_3 , besides H_9O_4 , is also expected to be present in the aqueous phase. Therefore, the extraction of hydrochloric acid into organic phase is generally described by the following equation,



The composition of species B is, therefore, thought to be expressed by,



H_2O molecules within the species are said to act as a bridge between the TBP molecules and the hydronium ion protons⁹⁾, in higher TBP concentration. Thus, a possible structure for the extracting species B in this region is illustrated as follows:

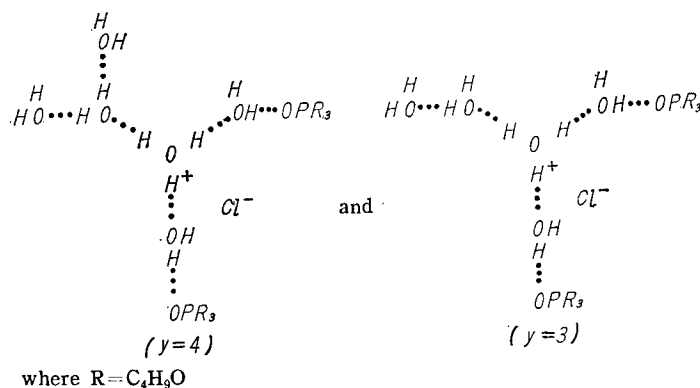
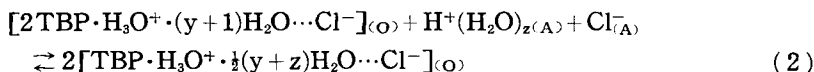


Fig. 8. A possible structure of species B.

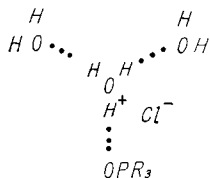
In the acidity region of 5.2 to 8.0 M_{HCl}^A , three extracting species A, B and C coexist and species A disappears and species C becomes predominant with rising the hydrochloric acid concentration. Species C is most predominant at 8.0 M_{HCl}^A which corresponds to $M_{HCl}^O/M_{TBP}^O = 1$; one molecule of TBP combines with one molecule of HCl in this species. Kertes⁷⁾ showed that the hydration of hydronium ion decreases at higher hydrochloric acid concentration and that the dehydrated form is also expected in this region. Thus, the extraction of aqueous hydrochloric acid in this region is generally shown by,



In Fig. 5, it was shown that $M_{H_2O}^O/M_{TBP}^O$ is almost 3 at 8.0 M_{HCl}^A and that the slope of $M_{H_2O}^O/M_{TBP}^O$ against M_{HCl}^O/M_{TBP}^O is calculated as 0.2 in the upper part of this acidity region which means that five molecules of hydrochloric acid accompany one molecule of water while being transported into the organic phase. Thus, the values of $\frac{1}{2}(y+z)$ and z can be assumed to be 2 and 0.2, respectively. From this, y becomes 3.8 instead of 3.5 in species B. From the above discussions on species B, it is understandable that the y value can vary between 3 and 4. The composition of the third species C is shown as,



And its possible structure is illustrated as:



where $R = C_4H_9O$

Fig. 9. A possible structure of species C.

3.2 On the Activities of Extracting Species in Lower Acidity Region

It was demonstrated in the preceding section that the species $[\text{TBP}\cdot\text{H}_2\text{O}]$ and $[2\text{TBP}\cdot\text{H}_3\text{O}^+\cdot 4.5\text{H}_2\text{O}\cdots\text{Cl}^-]$ coexist in the organic phase equilibrated with aqueous hydrochloric acid phase of 2.0 to 5.2 $M_{\text{HCl}}^{\text{A}}$. The activities and activity coefficients of these extracting species are discussed in this section.

E. Glueckauf¹⁰⁾, W. Baldwin¹¹⁾, W. McManamey¹²⁾ and G. Arcand¹³⁾ studied the distribution of electrolyte between aqueous and organic phase with Glueckauf's procedure. In this method of calculation, the distribution of electrolyte is assumed to be shown by following expressions:

$$\text{Electrolyte}_{(\text{A})} + n\text{H}_2\text{O}_{(\text{A})} = \text{Electrolyte}_{(\text{O})} \quad (3)$$

$$\log \gamma^{\text{O electrolyte}} = \beta m^{\text{O electrolyte}} \quad (4)$$

where

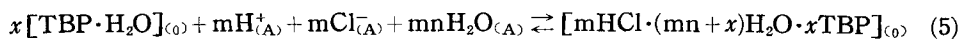
$\gamma^{\text{O electrolyte}}$: activity coefficient of the electrolyte in organic phase

$m^{\text{O electrolyte}}$: molality of electrolyte in organic phase

β : constant

This method does not take care of the extracting species containing electrolyte and also boldly assumes that the activity coefficient of electrolyte in organic phase is proportional to its molality concentration.

In place of this method, it seems necessary for discussing equilibrium in the system to take care of the extracting species and their interactions with electrolyte. In the region of 2.0 to 5.2 $M_{\text{HCl}}^{\text{A}}$, the interaction equation (1') between extracting species and electrolyte is generalized as follows:



For the equilibrium, we have

$$K' = \frac{(a_{\text{H}^+})_{\text{A}}^m (a_{\text{Cl}^-})_{\text{A}}^m (a_{\text{w}})_{\text{A}}^{mn} (\text{TBP}\cdot\text{H}_2\text{O})_{\text{O}}^x}{(m\text{HCl}\cdot(mn+x)\text{H}_2\text{O}\cdot x\text{TBP})_{\text{O}}} \quad (6)$$

where

- K' : equilibrium constant
 $(a_{\text{H}^+})_{\text{A}}$: activity of H^+ in aqueous phase
 $(a_{\text{Cl}^-})_{\text{A}}$: activity of Cl^- in aqueous phase
 $(a_{\text{w}})_{\text{A}}$: activity of water in aqueous phase
 $(\text{TBP}\cdot\text{H}_2\text{O})_{\text{O}}$: activity of $[\text{TBP}\cdot\text{H}_2\text{O}]$ in organic phase
 $(m\text{HCl}\cdot(mn+x)\text{TBP})_{\text{O}}$: activity of $[m\text{HCl}\cdot(mn+x)\text{H}_2\text{O}\cdot x\text{TBP}]$ in organic phase

Of these activities,

$$(a_{\text{H}^+})_{\text{A}} = \gamma_{\pm} m_{\text{HCl}}^{\text{A}} \alpha = \gamma_{\pm\text{HCl}} m_{\text{HCl}}^{\text{A}} \quad (7)$$

where

- $\gamma_{i\pm}$: mean activity coefficient of hydrochloric acid ion
 $m_{\text{HCl}}^{\text{A}}$: molality of hydrochloric acid in aqueous phase
 α : degree of dissociation
 $\gamma_{\pm\text{HCl}}$: mean activity coefficient of hydrochloric acid ;
 $(\gamma_{\pm\text{HCl}} = \gamma_{i\pm}\alpha)$

Similarly,

$$(a_{\text{Cl}^-})_{\text{A}} = \gamma_{i\pm} m_{\text{HCl}}^{\text{A}} \alpha = \gamma_{\pm\text{HCl}} m_{\text{HCl}}^{\text{A}} \quad (8)$$

Concerning the mole fraction of two extracting species, $[\text{TBP}\cdot\text{H}_2\text{O}]$ and $[\text{mHCl}\cdot(\text{mn}+x)\text{H}_2\text{O}\cdot x\text{TBP}]$,

$$x_{\text{A}} = \frac{\frac{1000}{\text{M}} - \frac{x}{m} m_{\text{HCl}}^0}{\frac{1000}{\text{M}} + m_{\text{HCl}}^0 - \frac{x}{m} m_{\text{HCl}}^0 + m_{\text{fw}}^0} \quad (9)$$

$$x_{\text{B}} = \frac{m_{\text{HCl}}^0}{\frac{1000}{\text{M}} + m_{\text{HCl}}^0 - \frac{x}{m} m_{\text{HCl}}^0 + m_{\text{fw}}^0} \quad (10)$$

where

- x_{A} : mole fraction of $[\text{TBP}\cdot\text{H}_2\text{O}]$
 x_{B} : mole fraction of $[\text{mHCl}\cdot(\text{mn}+x)\text{H}_2\text{O}\cdot x\text{TBP}]$
 M : molecular weight of $[\text{TBP}\cdot\text{H}_2\text{O}]$
 m_{HCl}^0 : molality of hydrochloric acid in organic phase
 m_{fw}^0 : molality of free water in organic phase

With these equations (9) and (10), activities of the extracting species are expressed as,

$$(\text{TBP}\cdot\text{H}_2\text{O})_0 = \gamma_{\text{A}} x_{\text{A}} \quad (11)$$

$$(\text{mHCl}\cdot(\text{mn}+x)\text{H}_2\text{O}\cdot x\text{TBP}) = \gamma_{\text{B}} x_{\text{B}} \quad (12)$$

where

- γ_{A} : activity coefficient of $[\text{TBP}\cdot\text{H}_2\text{O}]$
 γ_{B} : activity coefficient of $[\text{mHCl}\cdot(\text{mn}+x)\text{H}_2\text{O}\cdot x\text{TBP}]$

Substituting equations (7), (8), (11) and (12) in equation (6),

$$K' = \frac{(m_{\text{HCl}}^{\text{A}})^{2m} \gamma_{\text{HCl}}^2 a_{\text{w}}^{\text{mn}} (\gamma_{\text{A}} x_{\text{A}})^x}{\gamma_{\text{B}} \gamma_{\text{B}}} \quad (13)$$

With equation (1') in the preceding section, $m=1$, $n=3.5$ and $x=2$, and equation (13) becomes,

$$K' = \frac{(m_{\text{HCl}}^{\text{A}})^2 \gamma_{\text{HCl}}^2 a_{\text{w}}^{3.5} (\gamma_{\text{A}} x_{\text{A}})^2}{\gamma_{\text{B}} x_{\text{B}}} \quad (14)$$

or

$$\frac{\gamma_A^2}{\gamma_B} = \frac{K' x_B}{(m_{\text{HCl}}^A)^2 \gamma_{\pm\text{HCl}}^2 a_w^{3.5} x_A^2} \quad (14')$$

With equations (9) and (10),

$$\frac{\gamma_A^2}{\gamma_B} = \frac{K' \left(\frac{m_{\text{HCl}}^0}{\frac{1000}{M} + m_{\text{HCl}}^0 - \frac{x}{m} m_{\text{HCl}}^0 + m_{\text{fw}}^0} \right)}{(m_{\text{HCl}}^A)^2 \gamma_{\pm\text{HCl}}^2 a_w^{3.5} \left(\frac{\frac{1000}{M} - \frac{x}{m} m_{\text{HCl}}^0}{\frac{1000}{M} + m_{\text{HCl}}^0 - \frac{x}{m} m_{\text{HCl}}^0 + m_{\text{fw}}^0} \right)}$$

substituting $M=284.34$ and $m_{\text{fw}}^0=0$,

$$\frac{\gamma_A^2}{\gamma_B} = \frac{K' \left(\frac{m_{\text{HCl}}^0}{3.517 - m_{\text{HCl}}^0} \right)}{(m_{\text{HCl}}^A)^2 \gamma_{\pm\text{HCl}}^2 a_w^{3.5} \left(\frac{3.517 - 2m_{\text{HCl}}^0}{3.517 - m_{\text{HCl}}^0} \right)^2} \quad (15)$$

Logarithmic expression of equation (15) is

$$\begin{aligned} \log \frac{\gamma_A^2}{\gamma_B} &= \log K' + \log \left(\frac{m_{\text{HCl}}^0}{3.517 - m_{\text{HCl}}^0} \right) - 2 \log m_{\text{HCl}}^A \\ &\quad - 2 \log \gamma_{\pm\text{HCl}} - 3.5 \log a_w - 2 \log \left(\frac{3.517 - 2m_{\text{HCl}}^0}{3.517 - m_{\text{HCl}}^0} \right) \end{aligned} \quad (16)$$

On the other hand, the activity coefficients γ_A and γ_B are shown by Redlich-Kister equations with three-constants and found-suffix type¹⁴⁾, as,

$$\log \gamma_A = x_B^2 [B - C + D + (4C - 8D)x_A + 12Dx_A^2] \quad (17)$$

$$\log \gamma_B = x_A^2 [B + C + D - (4C + 8D)x_B + 12Dx_B^2] \quad (18)$$

With these equations (17) and (18), $\log(\gamma_A^2/\gamma_B)$ is,

$$\begin{aligned} \log \frac{\gamma_A^2}{\gamma_B} &= B(x_B^2 + x_B - x_A) + C\{(4x_A - 1)x_B^2 + (6x_B x_A - 1)\} \\ &\quad + D\{(12x_A^2 - 8x_A + 1)x_B^2 + (x_B - x_A)(x_A^2 - 6x_A x_B + x_B^2)\} \end{aligned} \quad (19)$$

Therefore, resulting equation from equation (16) and (19) has a form of,

$$\begin{aligned} &\log K - B(x_B^2 + x_B - x_A) - C\{(4x_A - 1)x_B^2 + (6x_B x_A - 1)\} \\ &\quad + D\{(12x_A^2 - 8x_A + 1)x_B^2 + (x_B - x_A)(x_A^2 - 6x_A x_B + x_B^2)\} \\ &= \log \left(\frac{m_{\text{HCl}}^0}{3.517 - m_{\text{HCl}}^0} \right) - 2 \log m_{\text{HCl}}^A - 2 \log \gamma_{\pm\text{HCl}} - 3.5 \log a_w \\ &\quad - 2 \log \left(\frac{3.517 - 2m_{\text{HCl}}^0}{3.517 - m_{\text{HCl}}^0} \right) \end{aligned} \quad (20)$$

In this equation, x_A and x_B calculated from equations (9) and (10), respectively. $\gamma_{\pm\text{HCl}}$ are given by R. Robinson¹⁵⁾ and H. Harned¹⁶⁾ and a_w are obtained

from H. Kuivila's paper¹⁷). With a set of these values for measured hydrochloric acid concentrations, $m_{\text{HCl}}^{\text{O}}$ and $m_{\text{HCl}}^{\text{A}}$, equation (20) has a general form of,

$$A + b_i B + c_i C + d_i D = e_i \quad (21)$$

where b_i , c_i , d_i , and e_i represent the given variables of hydrochloric acid concentration measured and A, B, C and D are unknown constants to be obtained.

With seven sets of data in the range of 2.0 to 5.2 $M_{\text{HCl}}^{\text{A}}$, A, B, C and D are determined by least square method. From these, we have

$$K' = 10.78 \quad (22)$$

$$\log \gamma_A = x_B^2(0.3993 - 0.0748x_A - 0.3854x_A^2) \quad (23)$$

$$\log \gamma_B = x_A^2(0.4904 - 0.4392x_B + 0.3854x_B^2) \quad (24)$$

With equations (23) and (24), the activities and activity coefficients of species A and B are plotted against mole fraction of species B in Figs. 10 and 11, respectively.

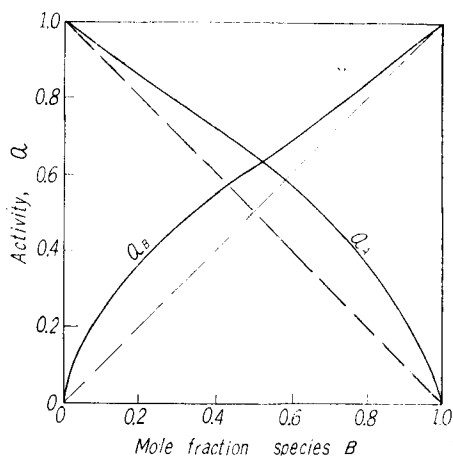


Fig. 10. Activities of species A and B versus mole fraction of species B.

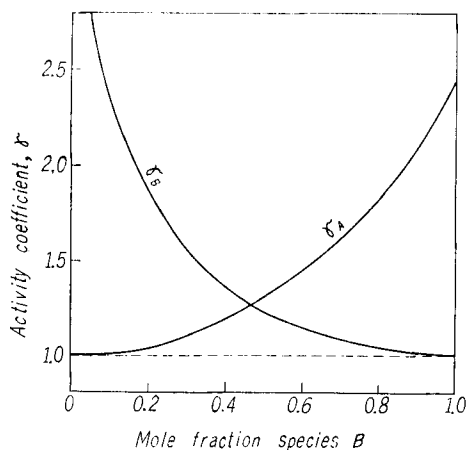


Fig. 11. Activity coefficients of species A and B versus mole fraction of species B.

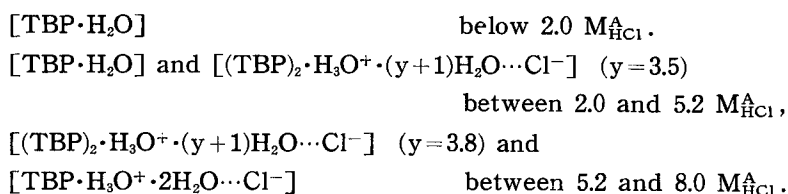
The activities of both species are found to have positive departures from ideality. And accordingly, the activity coefficients of both species have values more than unity.

4. Summary

The equilibrated organic phase in the system of HCl-H₂O-TBP was studied by means of the measurements of distribution of hydrochloric acid and water,

volume swelling, density, viscosity and infra-red absorption spectra.

It was found that there are three curve breaks in the figures of physico-chemical data against the hydrochloric acid concentration in equilibrated aqueous phase. These critical M_{HCl}^A are 2.0, 5.2 and 8.0. And the major extracting species are determined as



A possible structure of $[(\text{TBP})_2\cdot\text{H}_3\text{O}^+\cdot(y+1)\text{H}_2\text{O}\cdots\text{Cl}^-]$ and $[\text{TBP}\cdot\text{H}_3\text{O}^+\cdot 2\text{H}_2\text{O}\cdots\text{Cl}^-]$ are illustrated in Figs. 8 and 9, respectively.

Keeping these extracting species in mind, the equilibrium in the acidity region 2.0 to 5.2 M_{HCl}^A was studied. From chemical equilibrium between the above-mentioned species and Relich-Kister equations concerning the activity coefficients of two components, the equilibrium constant and the activity coefficients of the species were calculated with least square method.

The activities of both species were found to have positive departure from ideality and their activity coefficients are more than unity in this acidity region.

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