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

By

Ryota MITAMURA,* Sanji NISHIMURA* and Yoshio KONDO*

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It is intended in this study on the system H_2SO_4-H_2O-TBP to determine the species formed in the equilibrated organic phase and to clarify the extracting mechanism of aqueous sulphuric acid into organic phase. As in the previous report[1] published in this Memoir, physico-chemical measurements of volume-swelling, density, viscosity and electrical conductivity were carried out with the equlibrated organic phase in addition to the conventional distribution measurement of sulphuric acid and water. It was found that the extracting species is $[TBP \cdot H_2O]$ at the equilibrated acid concentration in aqueos phase below 2.0 M and that three other species were found to exist above 2.0 M; the one formed at lower acid concentration has the general formula $[(TBP)_3 \cdot H_3O^+(x+2)H_2O \cdots HSO_4^-]$, (x was determined as 2.5), the one formed at medium acid concentration is $\left[TBP \cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O \cdots HSO_4^-\right]$ (y was determined as 0.25), and the one formed at higher acid concentration is $\left[TBP \cdot 2\left\{H_3O^+\left(\frac{x+5y-3}{6}\right)H_2O \cdots HSO_4^-\right\}\right]$. They dissociate partly. The activities and activity coefficients of the two species $[TBP \cdot H_2O]$ and $[(TBP)_3 \cdot H_3O^+ 4.5H_2O \cdots HSO_4^-]$ stable at lower acid concentration and the equilibrium constant between them were determined with Redlich-Kister equations.

1. Introduction

For the study on liquid-liquid solvent extraction, systems involving water-strong acid-basic organic compound are regarded as its basic system and are also of physico-chemical interest from the viewpoint that the extraction involves competition for proton among acid anion, water and basic organic compound.[2),3),4)] Water-sulphuric acid-TBP system chosen in this study is one of these basic systems. Metal sulphate-sulphuric acid-TBP system as well as metal chloride-hydrochloric acid-TBP system are expected in extensive applications in near future, though they have been less investigated than the nitrate system.

On this system of water-sulphuric acid-TBP, Giganov[5)] found that the species extracted from aqueous phase at lower acidity is $[TBP \cdot H_2SO_4 \cdot (H_2O)_2]$,

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and that [TBP·H_2SO_4·H_2O] is the extracting species at higher acidity. And on the system of water-sulphuric acid-diluted TBP (1 to 5% TBP in kerosene), Brauer and Högfeldt[6] indicated that the extraction from aqueous to organic phase can be explained by,

$$TBP_{(O)} + 2H^+(H_2O)_{4(A)} + SO^{=}_{(A)} \rightleftarrows TBP\cdot(H_2O)_8\cdot H_2SO_{4(O)}.$$

In this paper, the water-sulphuric acid-TBP system is studied with several physico-chemical methods to determine the species formed by interactions between aqueous and organic phases. The study is also intended to determine the chemical equilibrium in a part of the system, based on 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 and Experimental Procedures

Purified TBP used in this study was prepared according to the procedure described in the previous paper.[1] "Analytical Reagent" grade sulphuric acid and deionized water were used throughout the study.

Measurements of volume-swelling, density and viscosity were carried out with the equilibrated organic phase in addition to the conventional distribution measurement of sulphuric acid and water.[1] Electrical conductivity of organic phase was also measured.

2.2 Results

2.2.1 Sulphuric acid concentration in organic phase

The molarity concentration of sulphuric acid in organic phase, $M^O_{H_2SO_4}$, was calculated from the measured molarity acid concentration in equilibrated aqueous phase, $M^A_{H_2SO_4}$. It is seen in Fig. 1 that sulphuric acid is scarcely extracted into organic phase below 2.0 $M^A_{H_2SO_4}$ and that the $M^O_{H_2SO_4}$ increases above 2.0 $M^A_{H_2SO_4}$.

2.2.2 Density of organic phase

Fig. 2 shows the relationship between the density of equilibrated organic phase and the ratio of sulphuric acid molarity concentration to TBP molarity concentration in the organic phase, $M^O_{H_2SO_4}/M^O_{TBP}$. It is seen from the figure that the density remains at about 0.980 in the region below 2.0 $M^A_{H_2SO_4}$ (where $M^O_{H_2SO_4}/M^O_{TBP}=0$) and it increases with the rise of $M^O_{H_2SO_4}/M^O_{TBP}$.

Three curve breaks were observed at about 1/3, 1 and 2 of $M^O_{H_2SO_4}/M^O_{TBP}$.

2.2.3 Volume ratio of organic phase to aqueous phase

In Fig. 3, the ratio of organic phase volume V_O to aqueous phase volume

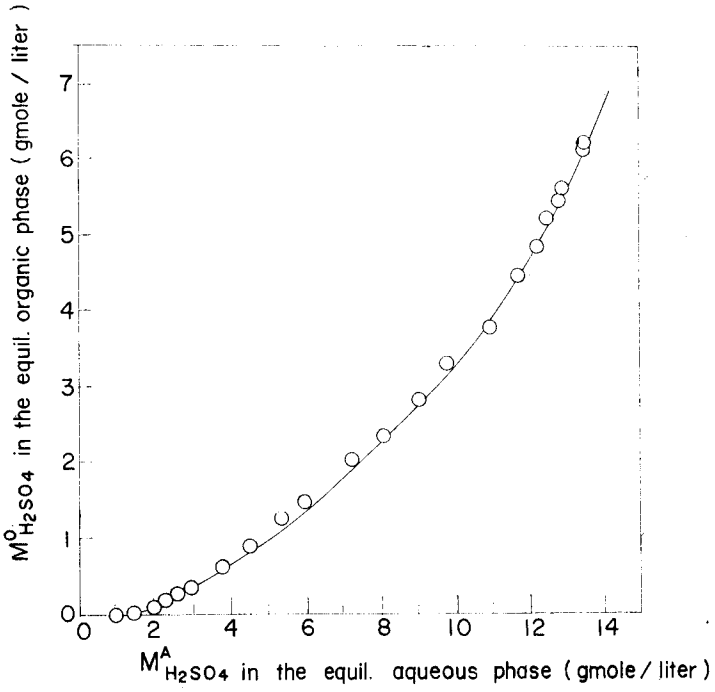

Fig. 1 H_2SO_4 molarity in the equilibrated organic phase versus its molarity in the equilibrated aqueous phase

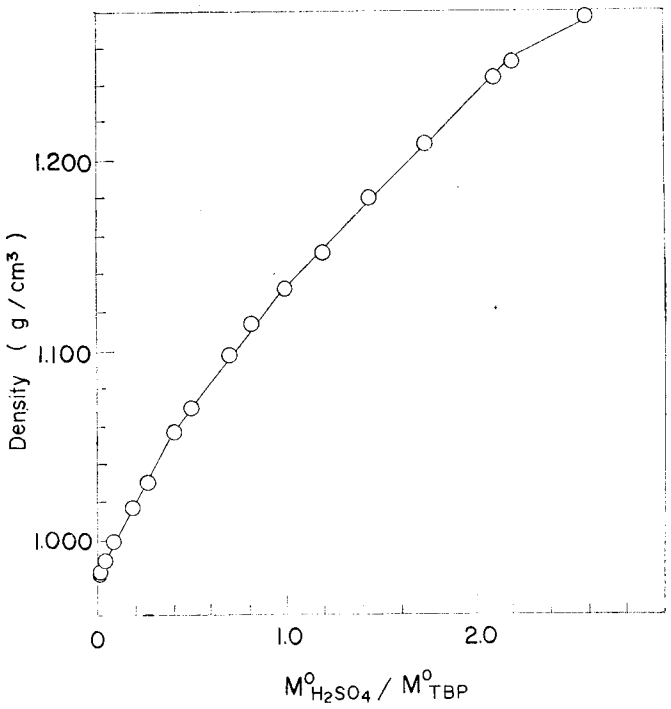

Fig. 2 Density of the equilibrated organic phase

V_A is plotted against $M^O_{H_2SO_4}/M^O_{TBP}$. The V_0/V_A remains constant in the region of $M^A_{H_2SO_4}$ below 2.0 and it increases with the $M^O_{H_2SO_4}/M^O_{TBP}$. Two breaks are observed; the one lies at 1.0 and the other is at 2.0 of $M^O_{H_2SO_4}/M^O_{TBP}$. Aqueous phase disappears above 4.5 of $M^O_{H_2SO_4}/M^O_{TBP}$.

2.2.4 Viscosity of organic phase

Fig. 4 illustrates the viscosity of organic phase against $M^O_{H_2SO_4}/M^O_{TBP}$. It remains constant below 2.0 $M^A_{H_2SO_4}$ and increases to its maximal value at about 2.0 of $M^O_{H_2SO_4}/M^O_{TBP}$.

2.2.5 Electrical conductivity of organic phase

The equivalent conductivity of organic phase, λ, was plotted against $M^O_{H_2SO_4}/M^O_{TBP}$ in Fig. 5. It takes its maximal value at 1/3 of $M^O_{H_2SO_4}/M^O_{TBP}$ and minimal value at 1 of $M^O_{H_2SO_4}/M^O_{TBP}$.

2.2.6 Water content in organic phase

Water content in the equilibrated organic phase was plotted in Fig. 6 in the form of molarity concentration ratio $M^O_{H_2O}/M^O_{TBP}$ against $M^O_{H_2SO_4}/M^O_{TBP}$. $M^O_{H_2O}/M^O_{TBP}$ remains at about 1 below 2.0 $M^A_{H_2SO_4}$ ($M^O_{H_2SO_4}/M^O_{TBP} \fallingdotseq 0$), and in the region of 0 to 1/3 of $M^O_{H_2SO_4}/M^O_{TBP}$, a straight line relationship whose slope is calculated as 2.5 is observed. This indicates that each two sulphuric acid

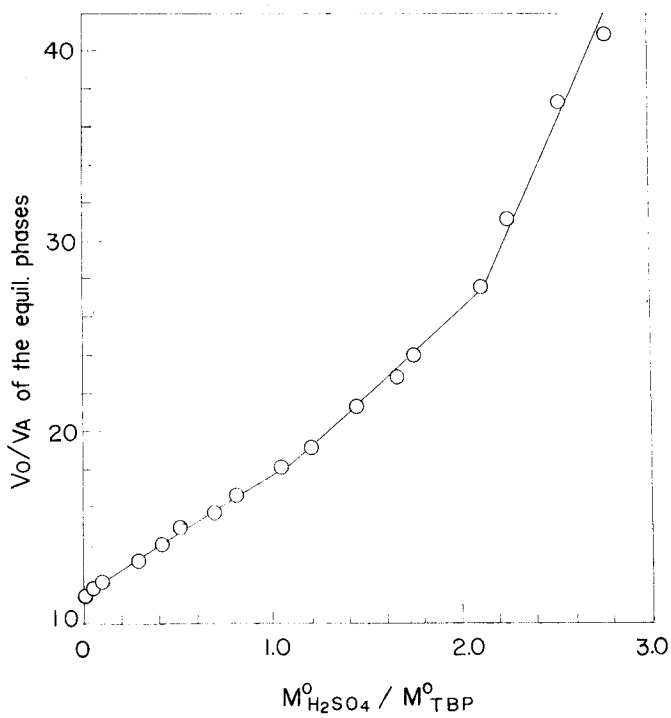

Fig. 3 The ratio V_O/V_A of the equilibrated phases

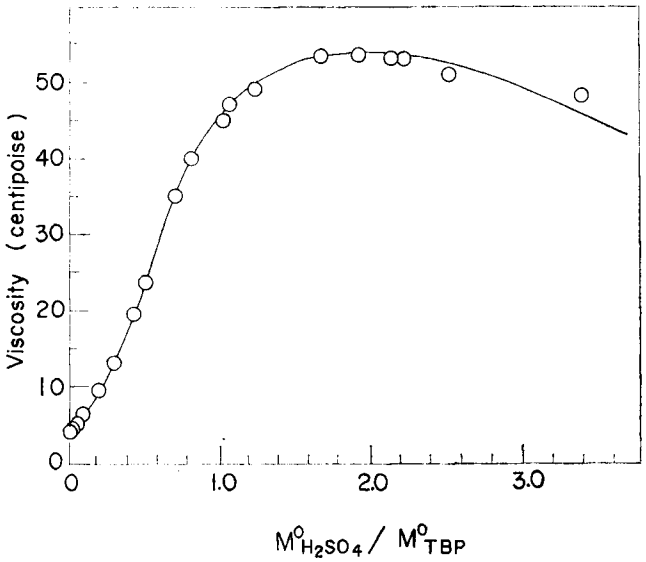

Fig. 4 Viscosity of the equilibrated organic phase

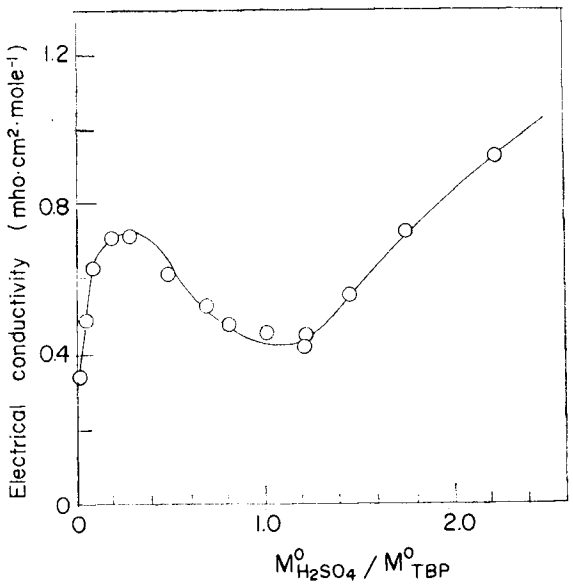

Fig. 5 Electrical conductivity of the equilibrated organic phase

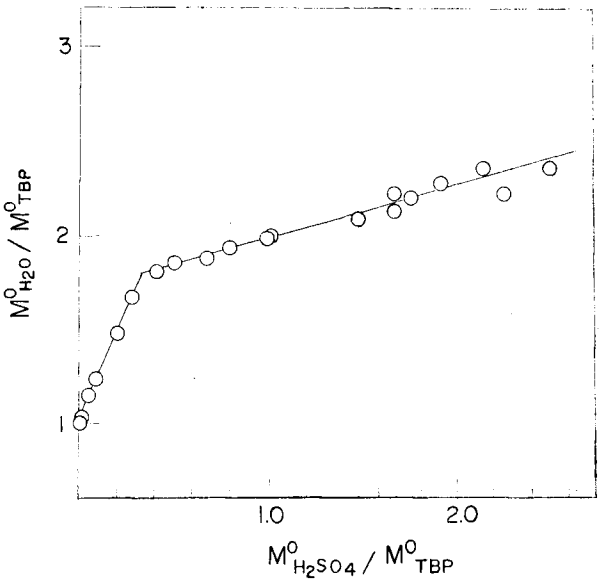

Fig. 6 Water content of the equilibrated organic phase

molecules accompany five water molecules while being transported from aqueous phase to organic phase. In the region above 1/3 of $M^o_{H_2SO_4}/M^o_{TBP}$, another straight line relationship whose slope is 0.25 is most fitted. In this region, therefore, each four sulphuric acid molecules carry one water molecule when it is transported from aqueous to organic phase.

3. Discussion

3.1 Dissociation of Extracting Species in Organic Phase

From the results on conductivity measurents with organic phase (Fig. 5), the extracting species are thought to dissociate partly. If Walden's rule in infinite dilution,

$$\mu_0\eta_0 = \text{const.}$$

where μ is the molar conductivity,

η is the viscosity in centipoise and the suffix "o" denotes infinite dilution,

can be extended for electrolyte in finite dilution, α in the following equation (1), indicates the approximate degree of dissociation of ion-pair in the electrolyte.[7]

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

With this equation, the approximate degree of dissociation can be calculated from the measured μ and η, when the constant $\mu_0 \eta_0$ is given. The numerical constant $\mu_0\eta_0$ is suggested by Hesford and Mckay[8] to be 30 in mineral acid-TBP system.

The second dissociation of H_2SO_4 is rather weak and is suppressed by the hydrogen ion from its strong first dissociation, so that H_2SO_4 behaves actually as an 1:1-electrolyte consisting of H^+ and HSO_4^-. With this assumption, the equivalent conductivity measured in this study is equal to its molar conductivity, because we are presumably dealing with its single stage ionization.[8]

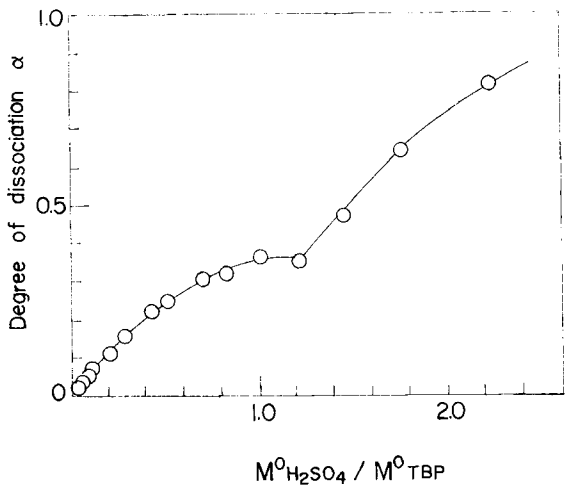

Fig. 7 Degree of dissociation of extracting species in organic phase

Fig. 7 shows the approximate degree of dissociation, α, thus calculated from the measured conductivity and viscosity. With general formula of $(TBP)_m \cdot H_2SO_4 \cdot (H_2O)_n$ for the extracting species in organic phase, it is seen from Fig. 7 that the extracting species at lower acid concentration in organic phase does not dissociate and has the ion-paired form, $(TBP)_mH^+(H_2O)_n \ldots HSO_4^-$, and it dissociates into $(TBP)_mH^+(H_2O)_n$ and HSO_4^- with increase of acid concentration.

3.2 Determination of Extracting Species

In the measurements mentioned above with the equilibrated organic phase, four curve breaks were observed at 2.0 $M^A_{H_2SO_4}$, ($M^O_{H_2SO_4}/M^O_{TBP} \fallingdotseq 0$) and at 1/3, 1 and 2 of $M^O_{H_2SO_4}/M^O_{TBP}$ which correspond to 4.7, 9.1 and 12.2 $M^A_{H_2SO_4}$, respectively. These curve breaks are supposed to be due to different interactions between aqueous sulphuric acid and TBP, and different species in the equilibrated organic phases are expected in each region of $M^A_{H_2SO_4}$.

In the lower acidity region of the equilibrated aqueous sulphuric acid ($M^A_{H_2SO_4} \leq 2.0$), the main interaction between organic and aqueous phases is the extraction of H_2O into organic phase and H_2SO_4 is scarcely extracted. Physicochemical properties of the equilibrated organic phase do not change in this region. Molarity concentration ratio, $M^O_{H_2SO_4}/M^O_{TBP}$ is almost zero and $M^O_{H_2O}/M^O_{TBP}$ was found at about 1 (Fig. 6). Thus, the major species stable in organic phase in this acidity region, is thought to have the following composition,

$$[TBP \cdot H_2O]. \qquad (A)$$

In higher sulphuric acid concentration region, H_2O and H_2SO_4 have interactions with TBP and both are extracted into organic phase. As mentioned above, three curve breaks were found and the regions 2.0 to 4.7 $M^A_{H_2SO_4}$, 4.7 to 9.1 $M^A_{H_2SO_4}$ and 9.1 to 12.2 $M^A_{H_2SO_4}$ are better discussed separately.

In the acidity region of 2.0 to 4.7 $M^A_{H_2SO_4}$, $[TBP \cdot H_2O]$ is stable with another species B; $[TBP \cdot H_2O]$ is predominant at 2.0 $M^A_{H_2SO_4}$ and species B is predominant at 4.7 $M^A_{H_2SO_4}$. Since the ratio of $M^O_{H_2SO_4}/M^O_{TBP}$ is 1/3 at 4.7 $M^A_{H_2SO_4}$, it is thought that three molecules of TBP combine with one molecule of H_2SO_4 in this species B. It was demonstrated in **3.1** that most part of the extracting species in this region exist in ion-paired form. And on the assumption that one molecule of H_2SO_4 accompanies x molecules of H_2O when it is transported into organic phase, the extraction of sulphuric acid into organic phase is generally described by the following equation,

$$3[TBP \cdot H_2O]_{(O)} + H^+(H_2O)_{x(A)} + HSO_4^-{}_{(A)} \rightleftharpoons [(TBP)_3 \cdot H_3O^+(x+2)H_2O \cdots HSO_4^-]_{(O)}. \qquad \cdots\cdots (2)$$

In Fig. 6, it was shown that the slope of $M^O_{H_2O}/M^O_{TBP}$ against $M^O_{H_2SO_4}/M^O_{TBP}$ is 2.5 in this acidity region. This indicates that two molecules of H_2SO_4 carry five molecules of H_2O in their transportation into organic phase. Thus, the values of x can be determined as 2.5 and the composition of species B is thought to be expressed by,

$$[(TBP)_3 \cdot H_3O^+(x+2)H_2O \cdots HSO_4^-]. \qquad (x=2.5 \text{ in this region}) \qquad (B)$$

In the acidity region of 4.7 to 9.1 $M^A_{H_2SO_4}$, species B coexists with another species C; species B disappears and species C becomes predominant with increasing sulphuric acid concentration. Species C is most predominant at 9.1 $M^A_{H_2SO_4}$ which corresponds to $M^O_{H_2SO_4}/M^O_{TBP}=1$; one molecule of TBP combines with one molecule of H_2SO_4 in this species. It was shown in 3.1 that the degree of dissociation increases in this region. Some of the species are dissociated and some are ion-paired. Assuming that one molecule of H_2SO_4 accompanies y molecules of H_2O while being transported into organic phase,

general extraction equation in this acidity region is expressed by,

$$[(TBP)_3\cdot H_3O^+(x+2)H_2O\cdots HSO_4^-]_{(O)}+2H^+(H_2O)_{y(A)}+2HSO_{4(A)}^- \rightleftharpoons \begin{cases} 3\left[TBP\cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O\cdots HSO_4^-\right]_{(O)} \\ 3\left[TBP\cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O\right]_{(O)}+3HSO_{4(O)}^-. \end{cases} \quad \cdots\cdots\cdots\cdots(3)$$

It was found in Fig. 6 that a straight line relationship between $M^O_{H_2O}/M^O_{TBP}$ and $M^O_{H_2SO_4}/M^O_{TBP}$ is observed and its slope is 0.25 in this region. This means each four sulphuric acid molecules accompany one water molecule in its transportation into organic phase. Thus, y in Equation (3) is equal to 0.25 and the composition of species C is shown by the following expression,

$$\left[TBP\cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O\cdots HSO_4^-\right]. \quad (x=2.5,\ y=0.25 \text{ in this region}) \qquad (C)$$

In the actidity region of 9.1 to 12.2 $M^A_{H_2SO_4}$, another new species D becomes predominant with rising sulphuric acid concentration. It is most predominant at 12.2 $M^A_{H_2SO_4}$ which corresponds to $M^O_{H_2SO_4}/M^O_{TBP}=2$; one molecule of TBP combines with two molecules of H_2SO_4 in this species. It is seen in Fig. 7 that the dissociation of extracting species increases in this acidity region. From the slope of 0.25 with $M^O_{H_2O}/M^O_{TBP}$ against $M^O_{H_2SO_4}/M^O_{TBP}$ shown in Fig. 6, four H_2SO_4 molecules accompany one H_2O molecule while being transported into organic phase. With these keeping in mind, the general extraction equation in this acidity region can be shown as follows,

$$\left.\begin{matrix}\left[TBP\cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O\cdots HSO_4^-\right]_{(O)} \\ \left[TBP\cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O\right]_{(O)}+HSO_{4(O)}^-\end{matrix}\right\}+H^+(H_2O)_{y(A)}+HSO_{4(A)}^- \rightleftharpoons \begin{cases}\left[TBP\cdot 2\left\{H_3O^+\left(\frac{x+5y-3}{6}\right)H_2O\cdots HSO_4^-\right\}\right]_{(O)} \\ \left[TBP\cdot 2\left\{H_3O^+\left(\frac{x+5y-3}{6}\right)H_2O\right\}\right]_{(O)}+2HSO_{4(O)}^-.\end{cases} \quad \cdots\cdots\cdots\cdots(4)$$

And the composition of species D is determined as,

$$\left[TBP\cdot 2\left\{H_3O^+\left(\frac{x+5y-3}{6}\right)H_2O\cdots HSO_4^-\right\}\right]. \quad (x=2.5,\ y=0.25 \text{ in this region}) \quad (D)$$

3.3 Activities of Extracting Species in Lower Acidity Region

It was demonstrated in the preceding section that the species $[TBP\cdot H_2O]$ equilibrates with $[3TBP\cdot H_3O^+4.5H_2O\cdots HSO_4^-]$ in organic phase in the acidity region of 2.0 to 4.7 $M^A_{H_2SO_4}$. The activities and activity coefficients of these extracting species are discussed in this section. The interaction equation

between extracting species and electrolyte in this acidity region is generalized as follows:

$$x[\mathrm{TBP}\cdot\mathrm{H_2O}]_{(O)} + m\mathrm{H}^+_{(A)} + m\mathrm{HSO_4^-}_{(A)} + mn\mathrm{H_2O}_{(A)} \rightleftarrows [m\mathrm{H_2SO_4}\cdot(mn+x)\mathrm{H_2O}\cdot x\mathrm{TBP}]_{(O)} \quad \cdots\cdots(5)$$

For the equilibrium, we have

$$K = \frac{(m\mathrm{H_2SO_4}\cdot(mn+x)\mathrm{H_2O}\cdot x\mathrm{TBP})_O}{(a_{\mathrm{H}^+})_A^n(a_{\mathrm{HSO_4^-}})_A^m(a_w)_A^{mn}(\mathrm{TBP}\cdot\mathrm{H_2O})_O^x} \quad \cdots\cdots(6)$$

where

K	:	equilibrium constant
$(a_{\mathrm{H}^+})_A$	:	activity of H^+ in aqueous phase
$(a_{\mathrm{HSO_4^-}})_A$	:	activity of HSO_4^- in aqueous phase
$(a_w)_A$	:	activity of water in aqueous phase
$(\mathrm{TBP}\cdot\mathrm{H_2O})_O$	:	activity of $[\mathrm{TBP}\cdot\mathrm{H_2O}]$ in organic phase
$(m\mathrm{H_2SO_4}\cdot(mn+x)\mathrm{H_2O}\cdot x\mathrm{TBP})_O$	:	activity of $[m\mathrm{H_2SO_4}\cdot(mn+x)\mathrm{H_2O}\cdot x\mathrm{TBP}]$ in organic phase

Of these activities,

$$(a_{\mathrm{H}^+})_A = \gamma_{i\pm} m^A_{\mathrm{H_2SO_4}}\alpha = \gamma_{\pm\mathrm{H_2SO_4}} m^A_{\mathrm{H_2SO_4}} \quad \cdots\cdots(7)$$

where

$\gamma_{i\pm}$	:	mean activity coefficient of sulphuric acid ion
$m^A_{\mathrm{H_2SO_4}}$	:	molality of sulphuric acid in aqueous phase
α	:	degree of dissociation
$\gamma_{\pm\mathrm{H_2SO_4}}$	:	mean activity coefficient of sulphuric acid,

$$(\gamma_{\pm\mathrm{H_2SO_4}} = \gamma_{i\pm}\alpha)$$

and similarly,

$$(a_{\mathrm{HSO_4^-}})_A = \gamma_{i\pm} m^A_{\mathrm{H_2SO_4}}\alpha = \gamma_{\pm\mathrm{H_2SO_4}} m^A_{\mathrm{H_2SO_4}} \quad \cdots\cdots(8)$$

Concerning the mole fraction of $[\mathrm{TBP}\cdot\mathrm{H_2O}]$ and $[m\mathrm{H_2SO_4}\cdot(mn+x)\mathrm{H_2O}\cdot x\mathrm{TBP}]$,

$$x_A = \frac{\dfrac{1000}{M} - \dfrac{x}{m} m^O_{\mathrm{H_2SO_4}}}{\dfrac{1000}{M} + m^O_{\mathrm{H_2SO_4}} - \dfrac{x}{m} m^O_{\mathrm{H_2SO_4}} + m^O_{f_w}} \quad \cdots\cdots(9)$$

$$x_B = \frac{m^O_{\mathrm{H_2SO_4}}}{\dfrac{1000}{M} + m^O_{\mathrm{H_2SO_4}} - \dfrac{x}{m} m^O_{\mathrm{H_2SO_4}} + m^O_{f_w}} \quad \cdots\cdots(10)$$

where

x_A	:	mole fraction of $[\mathrm{TBP}\cdot\mathrm{H_2O}]$
x_B	:	mole fraction of $[m\mathrm{H_2SO_4}\cdot(mn+x)\mathrm{H_2O}\cdot x\mathrm{TBP}]$

M : molecular weight of [TBP·H_2O]

$m^{O}_{H_2SO_4}$: molality of sulphuric acid in organic phase

$m^{O}_{f_w}$: molality of free water in organic phase

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

$$(\mathrm{TBP}\cdot\mathrm{H_2O})_O = \gamma_A x_A \qquad \cdots\cdots(11)$$

$$(m\mathrm{H_2SO_4}\cdot(mn+x)\mathrm{H_2O}\cdot x\mathrm{TBP}) = \gamma_B x_B \qquad \cdots\cdots(12)$$

where

γ_A : activity coefficient of [TBP·H_2O]

γ_B : activity coefficient of [$m H_2SO_4\cdot(mn+x)H_2O\cdot x$TBP]

Substituting equations (7), (8), (11) and (12) into equation (6), we have

$$K = \frac{\gamma_B x_B}{(m^{A}_{H_2SO_4})^{2m}(\gamma_{\pm H_2SO_4})^{2m} a_w^{mn}(\gamma_A x_A)^x} \qquad \cdots\cdots(13)$$

From discussion in the preceding section, $m=1$, $n=2.5$ and $x=3$, and equation (13) becomes,

$$K = \frac{\gamma_B x_B}{(m^{A}_{H_2SO_4})^{2}(\gamma_{\pm H_2SO_4})^{2} a_w^{2.5}(\gamma_A x_A)^3} \qquad \cdots\cdots(14)$$

or

$$\frac{\gamma_A^3}{\gamma_B} = \frac{x_B}{(m^{A}_{H_2SO_4})^{2}(\gamma_{\pm H_2SO_4})^{2} a_w^{2.5} x_A^3 K} \qquad \cdots\cdots(14')$$

With equation (9) and (10),

$$\frac{\gamma_A^3}{\gamma_B} = \frac{\left(\dfrac{m^{O}_{H_2SO_4}}{\dfrac{1000}{M} + m^{O}_{H_2SO_4} - \dfrac{x}{m} m^{O}_{H_2SO_4} + m^{O}_{f_w}}\right)}{(m^{A}_{H_2SO_4})^{2}(\gamma_{\pm H_2SO_4})^{2} a_w^{2.5}\left(\dfrac{\dfrac{1000}{M} - \dfrac{x}{m} m^{O}_{H_2SO_4}}{\dfrac{1000}{M} + m^{O}_{H_2SO_4} - \dfrac{x}{m} m^{O}_{H_2SO_4} + m^{O}_{f_w}}\right)^3 K}$$

Substituting $M=284.34$ and $m^{O}_{f_w}=0$,

$$\frac{\gamma_A^3}{\gamma_B} = \frac{\left(\dfrac{m^{O}_{H_2SO_4}}{3.517 - 2m^{O}_{H_2SO_4}}\right)}{(m^{A}_{H_2SO_4})^{2}(\gamma_{\pm H_2SO_4})^{2} a_w^{2.5}\left(\dfrac{3.517 - 3m^{O}_{H_2SO_4}}{3.517 - 2m^{O}_{H_2SO_4}}\right)^3 K} \qquad \cdots\cdots(15)$$

Logarithmic expression of equation (15) is

$$\log\frac{\gamma_A^3}{\gamma_B} = -\log K + \log\left(\frac{m^{O}_{H_2SO_4}}{3.517 - 2m^{O}_{H_2SO_4}}\right) - 2\log m^{A}_{H_2SO_4}$$
$$-2\log\gamma_{\pm H_2SO_4} - 2.5\log a_w - 3\log\left(\frac{3.517 - 3m^{O}_{H_2SO_4}}{3.517 - 2m^{O}_{H_2SO_4}}\right) \qquad \cdots\cdots(16)$$

On the other hand, the activity coefficients γ_A and γ_B are shown by Redlich-Kister equations with three-constants and four-suffix type[9] as,

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

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

With these equations (17) and (18), $\log(\gamma_A^3/\gamma_B)$ is,

$$\log \frac{\gamma_A^3}{\gamma_B} = B(3x_B^2-x_A^2)+C\{2x_Ax_B(3+4x_B)-2x_B^2-1\} + D\{(3x_B^2-x_A^2)+8x_Ax_B(3x_Ax_B-4x_B+1)\} \quad \cdots\cdots(19)$$

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

$$\begin{aligned}\log K &+ B(3x_B^2-x_A^2)+C\{2x_Ax_B(3+4x_B)-2x_B^2-1\} \\ &+ D\{(3x_B^2-x_A^2)+8x_Ax_B(3x_Ax_B-4x_B+1)\} \\ &= \log\left(\frac{m^O_{H_2SO_4}}{3.517-2m^O_{H_2SO_4}}\right)-2\log m^A_{H_2SO_4}-2\log \gamma_{\pm H_2SO_4} \\ &-2.5\log a_w-3\log\left(\frac{3.517-3m^O_{H_2SO_4}}{3.517-2m^O_{H_2SO_4}}\right) \quad \cdots\cdots(20)\end{aligned}$$

x_A and x_B in this equation are obtained with equations (9) and (10), respectively. $\gamma_{\pm H_2SO_4}$ and a_w are given by R. Robinson.[10] With a set of these values for measured sulphuric acid concentration, $m^O_{H_2SO_4}$ and $m^A_{H_2SO_4}$, equation (20) has a general form of

$$A+b_iB+c_iC+d_iD = e_i \quad \cdots\cdots(21)$$

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

With seven sets of data in the range of 2.0 to 4.7 $M^A_{H_2SO_4}$, A, B, C and D are determined by least square method.

From these, we have

$$K = 0.2191 \quad \cdots\cdots(22)$$

$$\log \gamma_A = x_B^2(1.1643-2.0268x_A+2.0748x_A^2) \quad \cdots\cdots(23)$$

$$\log \gamma_B = x_A^2(0.8425-0.7396x_B+2.0748x_B^2) \quad \cdots\cdots(24)$$

With equations (23) and (24), the activities and activity coefficients of species A and B are plotted against mole fraction of species B in Fig. 8 and 9, respectively.

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.

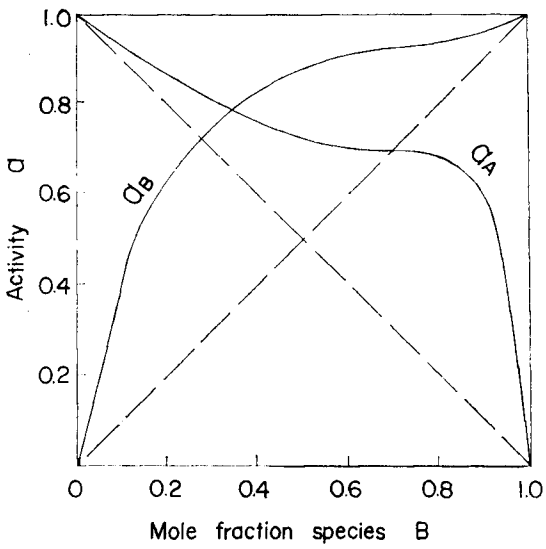

Fig. 8 Activities of species A and B

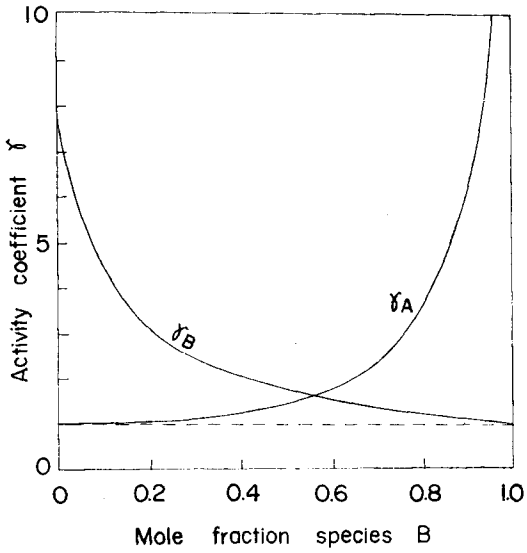

Fig. 9 Activity coefficients of species A and B

4. Summary

The equilibrated organic phase in the system H_2SO_4-H_2O-TBP was studied by means of measurements of distribution of sulphuric acid and water, volume swelling, density, viscosity and electrical conductivity.

Four curve breaks were found on the physico-chemical data against the sulphuric acid concentration in equilibrated phase. These critical $M^A_{H_2SO_4}$ are 2.0, 4.7, 9.1 and 12.2. And the major extracting species are determined as

$[TBP \cdot H_2O]$ below 2.0 $M^A_{H_2SO_4}$

$[TBP \cdot H_2O]$ and $[(TBP)_3 \cdot H_3O^+(x+2)H_2O \cdots HSO_4^-]$ $(x=2.5)$

between 2.0 and 4.7 $M^A_{H_2SO_4}$,

$[(TBP)_3 \cdot H_3O^+(x+2)H_2O \cdots HSO_4^-]$ and

$\left[TBP \cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O \cdots HSO_4^-\right]$ $(x=2.5,\ y=0.25)$

between 4.7 and 9.1 $M^A_{H_2SO_4}$ and

$\left[TBP \cdot H_3O^+\left(\frac{x+2y}{3}\right)H_2O \cdots HSO_4^-\right]$ and

$\left[TBP \cdot 2\left\{H_3O^+\left(\frac{x+5y-3}{6}\right)H_2O \cdots HSO_4^-\right\}\right]$ $(x=2.5,\ y=0.25)$

between 9.1 and 12.2 $M^A_{H_2SO_4}$.

From the measurement of equivalent conductivity of organic phase, these extracting species are supposed to dissociate to some extent; the species stable at lower acidity has ion-paired form and, with increasing acid concentration, the stable species tends to dissociate.

Keeping these extracting species in mind, the equilibrium in the acidity region of 2.0 to 4.7 $M^A_{H_2SO_4}$ was studied. From chemical equilibrium between above-mentioned species A and B and with Redlich-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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