Studies on the System Nitric Acid—Water—Tri-n-butyl Phosphate

By

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It is intended in this study to determine the composition of species formed in the equilibrated organic phase and to clarify the extraction mechanism in the system of HNO_3-H_2O-TBP. Similarly as the previous papers on the systems of mineral acid-H_2O-TBP, [14)~16)] physico-chemical measurements of volume swelling, density, viscosity and electrical conductivity were carried out on the equilibrated organic phase, in addition to the conventional distribution measurement of HNO_3 and water between organic and aqueous phases.

It was found that the major extracted species are $(TBP)_2 \cdot HNO_3 \cdot H_2O$ and $(TBP)_2 \cdot H_2O \cdot H_3O^+ \cdots NO_3^-$ in the medium acidity region and $TBP \cdot HNO_3$ and $TBP \cdot HNO_3 \cdot H_3O^+ \cdots NO_3^-$ in the higher acidity region.

Apparent degree of dissociation in the organic phase is below 0.05 over the whole range of nitric acid concentration studied, and the extracted species are almost undissociated or ion-paired.

1. Introduction

In the field of liquid-liquid solvent extraction in hydrometallurgical processes, the system composed of nitric acid-metal nitrate-water-tri-n-butyl phosphate (TBP) has most widely been used.[1)~3)] Especially, along with the developments in the field of nuclear energy utilization, it is expected that the solvent extraction technique will widely be applied in this field in the near future.

The system of nitric acid-water-TBP is basic in the industrial solvent extraction and has been studied by many workers,[4)~10)] though its extracted species and the equilibrium have not been thoroughly clarified. In the studies on the system of strong acid-water-basic organic solvent, on the other hand, it is of physico-chemical interest that the extraction involves competition for proton among acid anion, water and basic organic compound.[11)~13)] Moreover, this system is known to have some different properties from other systems such as the dehydration of organic phase which occurs with the increase of acid concentration in aqueous phase.

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This paper is concerned with the system of nitric acid-water-undiluted TBP with an intention to determine the composition of extracted species and to clarify the extracting mechanism.

2. Experimental

2.1 Materials and Experimental Procedures

TBP used in this study was prepared according to the procedure described in the previous paper[14]. "Analytical Reagent" grade nitric acid and deionized water were used.

In addition to the conventional distribution measurement of nitric acid and water between aqueous and organic phases, physico-chemical measurements of volume swelling, density, viscosity and electrical conductivity were carried out on the equilibrated organic phase.[14]~[16]

2.2 Experimental Results

2.2.1 Equilibrium Distribution Coefficient of HNO_3

Fig. 1 shows a plot of the equilibrium distribution coefficient of HNO_3, $\alpha = M^O_{HNO_3}/M^A_{HNO_3}$, against the molarity concentration ratio of HNO_3 to TBP in the organic phase, $M^O_{HNO_3}/M^O_{TBP}$. $M^O_{HNO_3}$ was calculated from the measured concentration in the equilibrated aqueous phase, $M^A_{HNO_3}$, compensating for the volume swelling of the organic phase.

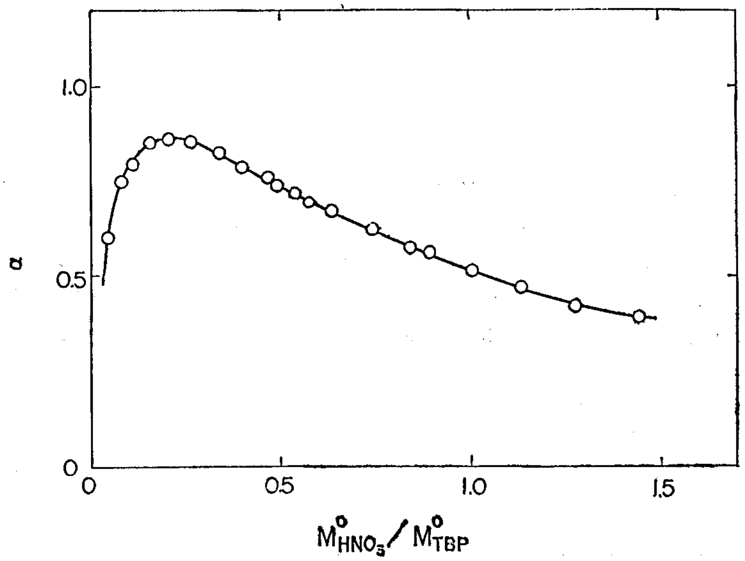


Fig. 1. Distribution Coefficient

It is seen from this figure that the value of α increases abruptly with increase of $M^O_{HNO_3}/M^O_{TBP}$ in the lower acidity region and it decreases after reaching the maximal value at $M^O_{HNO_3}/M^O_{TBP}=0.2$.

2.2.2 Water Concentration in Organic Phase

Fig. 2 illustrates a plot of water concentration in the organic phase, $M^O_{H_2O}$, in the form of $M^O_{H_2O}/M^O_{TBP}$ against $M^O_{HNO_3}/M^O_{TBP}$. It is seen in this figure that $M^O_{H_2O}/M^O_{TBP}$ decreases gradually as $M^O_{HNO_3}/M^O_{TBP}$ increases. This is the dehydration of organic phase which increases with the extraction of HNO_3 into organic phase.

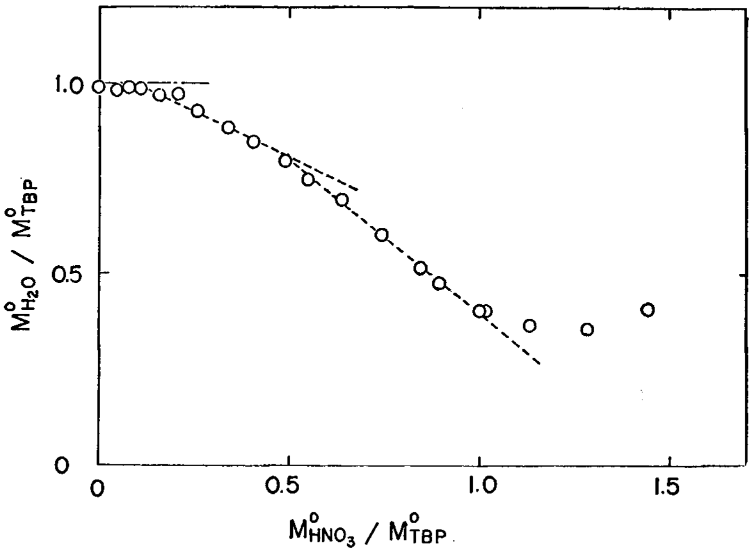


Fig. 2. Water Concentration

However, $M^O_{H_2O}/M^O_{TBP}$ seems to increase slightly beyond the minimal point located at $M^O_{HNO_3}/M^O_{TBP}=1.0$. By further examination of this figure, two curve breaks are observed at $M^O_{HNO_3}/M^O_{TBP}=0.1$ and 0.5 in addition to the minimal point. The slopes of straight line in each region of 0.1 to 0.5 and 0.5 to 1.0 $M^O_{HNO_3}/M^O_{TBP}$ were determined as -0.5 and -0.8, respectively. The slope is 0 between 0 and 0.1 $M^O_{HNO_3}/M^O_{TBP}$.

2.2.3 Volume Ratio of Organic Phase to Aqueous Phase

Fig. 3 shows a plot of the volume ratio of organic phase to aqueous phase, V_O/V_A, against $M^O_{HNO_3}/M^O_{TBP}$. V_O/V_A increases with increasing HNO_3 concentration in organic phase and two curve breaks are observed at about 0.5 and 1.0 $M^O_{HNO_3}/M^O_{TBP}$.

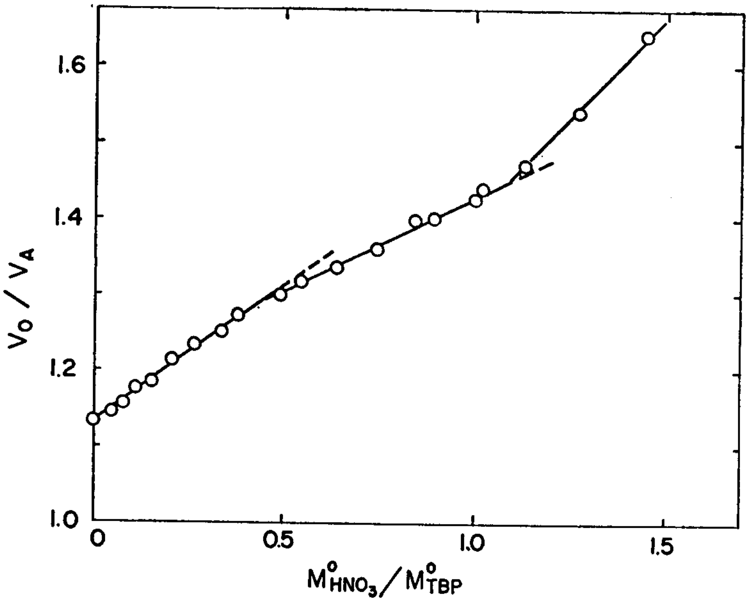


Fig. 3. Volume Ratio

2.2.4 Density

Fig. 4 demonstrates the relationship between the density of organic phase and $M^o_{HNO_3}/M^o_{TBP}$. In this figure, it is seen that the density also increases with HNO_3 concentration in the organic phase, and three curve breaks are observed at about 0.1, 0.5 and 1.0 $M^o_{HNO_3}/M^o_{TBP}$. The plot shows good linearity in each region.

2.2.5 Viscosity

The plot of viscosity of organic phase against $M^o_{HNO_3}/M^o_{TBP}$ is illustrated in Fig. 5. The viscosity increases with $M^o_{HNO_3}$ in its lower region. It reaches maximum at $M^o_{HNO_3}/M^o_{TBP}=0.5$ and then decreases with $M^o_{HNO_3}$.

2.2.6 Specific Conductivity

Fig. 6 shows the relationship between the specific conductivity of organic phase and $M^o_{HNO_3}/M^o_{TBP}$. The specific conductivity increases as HNO_3 concentration increases and it is found to be constant between 0.5 and 1.0 of $M^o_{HNO_3}/M^o_{TBP}$. Thus, two curve breaks can be mentioned at about 0.5 and 1.0 $M^o_{HNO_3}/M^o_{TBP}$, respectively.

Table 1 summarizes the experimental results mentioned and demonstrates the values of $M^o_{HNO_3}/M^o_{TBP}$ where some curve breaks are observed in the physico-chemical properties of the organic phase.

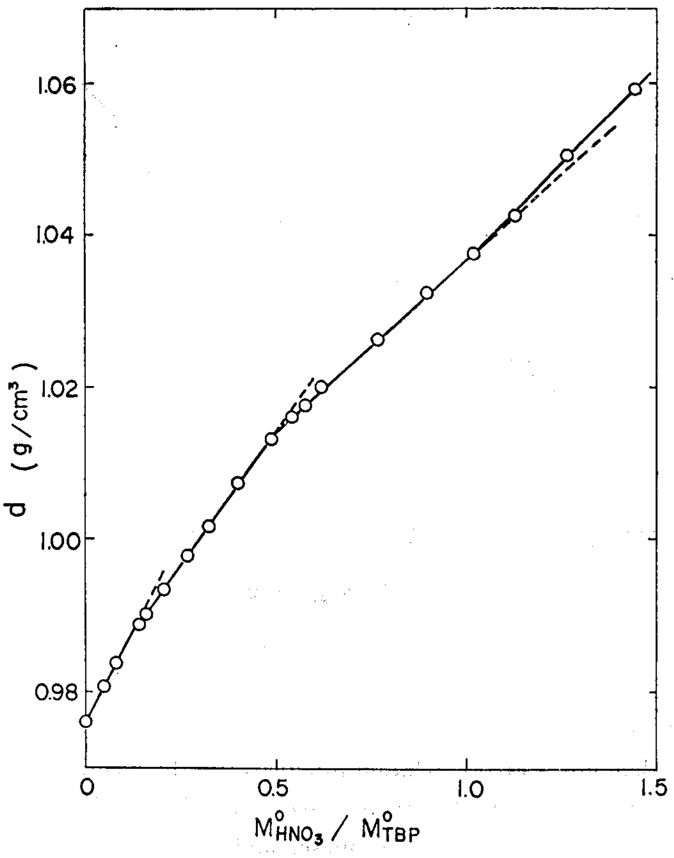


Fig. 4. Density

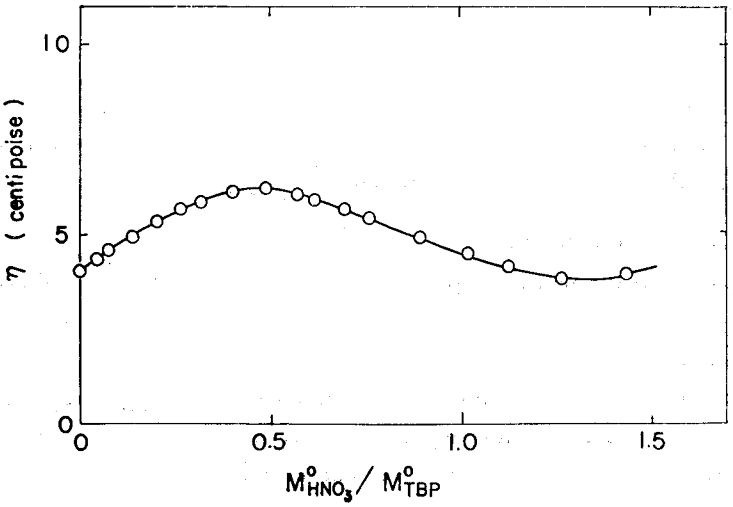


Fig. 5. Viscosity

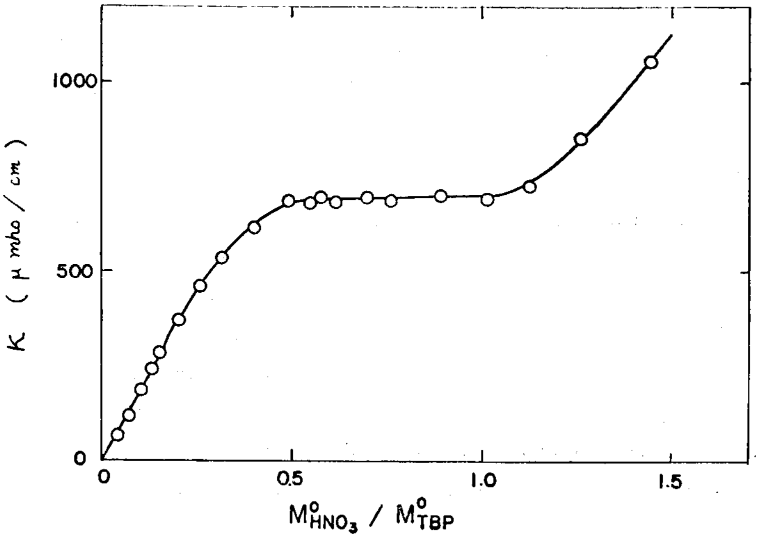


Fig. 6. Specific Conductivity

Table 1. Curve Breaks in the Physico-chemical Properties of the Organic Phase.

Physico-chemical property		Position of curve breaks ($M^{O}_{HNO_3}/M^{O}_{TBP}$)		
volume ratio	(V_O/V_A)		0.5	1.0
density	(α)	0.1	0.5	1.0
viscosity	(η)		0.5	
specific conductivity	(κ)		0.5	1.0

3. Discussion

From the experimental results illustrated above, the equilibrated extracted species and the extracting equation are discussed.

3.1 Apparent Degree of Dissociation in Organic Phase

Assuming that Walden's rule for infinite dilution can be extended for the electrolyte of finite dilution, α' in the following equation (1) indicates the apparent degree of dissociation of ion-pair in the electrolyte.[17]

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

where μ is the molar conductivity and η is the viscosity in centipoise. Subscript "0" indicates infinite dilution. Biddle[9] suggested the numerical constant of 60 for $\mu_0\eta_0$ in this system.

α' is plotted against $M^{O}_{HNO_3}/M^{O}_{TBP}$ in Fig. 7. It is seen in this figure that the value of α' is below 0.05 over the whole range of HNO_3 concentration measured and that the extracted species are hardly dissociated. This result is in line with those of Biddle[9] and is quite different from the results observed in the systems containing other mineral acid.[9],[14]~[16],[18]

3.2 Determination of Extracted Species

It is reported on this system[4],[7] that $TBP \cdot HNO_3$ and its hydrated form, such as $TBP \cdot HNO_3 \cdot H_2O$, are the stable extracted species in addition to $TBP \cdot H_2O$. The molar ratio of TBP to HNO_3 in the two species is unity and they are thought to be stable at $M^O_{HNO_3}/M^O_{TBP}=1$ in Fig. 2. From Table 1, however, it is supposed that the curve breaks of the physico-chemical properties at 0.1 and 0.5 $M^O_{HNO_3}/M^O_{TBP}$ also suggest some changes in the extraction mechanism.

Among these properties, viscosity demonstrated in Fig. 5 is considered. Viscosity of a binary solution without any interactions between the components is to satisfy the following Kendall's equation.[19]

$$\log \phi = x \log \phi_1 + (1-x) \log \phi_2 \qquad (2)$$

where ϕ is fluidity or a reciprocal expression of viscosity. On the assumption that the equilibrated organic phase between 0 and 1.0 of $M^O_{HNO_3}/M^O_{TBP}$ is composed of two extracted species, one predominant at $M^O_{HNO_3}/M^O_{TBP}=0$ and the other at $M^O_{HNO_3}/M^O_{TBP}=1.0$, the maximal viscosity at $M^O_{HNO_3}/M^O_{TBP}=0.5$ shown in Fig. 5 cannot be explained by the Kendall's equation. The presence of maximum in the viscosity at $M^O_{HNO_3}/M^O_{TBP}=0.5$ may suggest some interaction between the two extracted species. Other physico-chemical properties summarized in Table 1 have their curve breaks at $M^O_{HNO_3}/M^O_{TBP}=0.5$ and this suggests the formation of some extracted species stable at $M^O_{HNO_3}/M^O_{TBP}=0.5$. Keeping these results in mind, the extracted species in this system are pursued.

Concerning the system of H_2O-TBP, it is seen in Fig. 2 that $M^O_{H_2O}/M^O_{TBP}$ is about unity at $M^O_{HNO_3}/M^O_{TBP}=0$, and the composition of the extracted species is,

$$TBP \cdot H_2O \qquad (A)$$

The extracting equation is expressed by,

$$TBP_{(O)} + H_2O_{(A)} = TBP \cdot H_2O_{(O)} \qquad (3)$$

Many infrared spectra and proton magnetic resonance studies[20]~[24] indicate that the hydrogen bonding is formed between the PO group of TBP and the proton of water and that most of the water is monodentate. Therefore, water in this species may be present in the form of

$$R_3P \rightarrow O \cdots H\text{-}O\text{-}H$$

In the region of lower nitric acid concentration of 0 to 0.1 $M^{O}_{HNO_3}/M^{O}_{TBP}$, water concentration is not changed. This indicates the formation of hydrated species containing HNO_3, such as $TBP \cdot HNO_3 \cdot H_2O$ which is suggested by Biddle[9] and Damiani.[7] Though some workers[5],[6] insist on the non-existence of other hydrated species than $TBP \cdot H_2O$, they seem not to be able to interpret the experimental result that the sum of the number of moles of HNO_3 and H_2O is beyond that of TBP. And it is a reasonable presumption that another hydrated species is present in this acidity region, though its fraction is rather small.

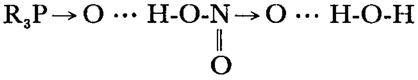
Before the investigations on this hydrated species, it is thought better to clarify some features of hydrogen bonding in the extracted species. Fletcher[10] mentioned that the phosphoryl-oxygen atom in TBP molecule is coordinated directly to hydrogen and yields the following three kinds of hydrogen bonding.

(1) Bonding to one of the hydrogen atoms of a water molecule: this bonding is found in $TBP \cdot H_2O$.

(2) Bonding to the hydrogen atom of an undissociated acid: this is well illustrated in $TBP \cdot HNO_2$ where fairly strong PO→H bonding is observed.

(3) Bonding to the hydronium ion, H_3O^+: Diamond[25] revealed that TBP molecule can readily participate in the trisolvation of this ion in mineral acid-H_2O-TBP systems.

From these features of hydrogen bonding, the hydrated extracted species is supposed to have the form of,



$$R_3P \rightarrow O \cdots H\text{-}O\text{-}\underset{\overset{\|}{O}}{N} \rightarrow O \cdots H\text{-}O\text{-}H \qquad (A')$$

In the acidity region of 0.1 to 0.5 $M^{O}_{HNO_3}/M^{O}_{TBP}$, dehydration of the organic phase occurs. Slope of the regression line of $M^{O}_{H_2O}/M^{O}_{TBP}$ upon $M^{O}_{HNO_3}/M^{O}_{TBP}$ in this region was found at -0.5 from Fig. 2. This indicates that one molecule of H_2O is expelled from the organic phase when two molecules of HNO_3 are extracted.

It is assumed that the predominant extracted species is $TBP \cdot H_2O$ at 0.1 $M^{O}_{HNO_3}/M^{O}_{TBP}$ and that this species coexists in this region with another extracted species (B) which becomes predominant at 0.5 $M^{O}_{HNO_3}/M^{O}_{TBP}$. From this assumption together with the experimental results, the composition of this extracted species is described as,

$$(TBP)_2 \cdot HNO_3 \cdot (H_2O)_x \qquad (B)$$

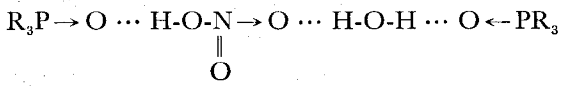
where x is estimated at about 1.6 from Fig. 2, because $M^{O}_{H_2O}/M^{O}_{TBP}=0.8$ at 0.5 $M^{O}_{HNO_3}/M^{O}_{TBP}$.

The extracting equation is written as,

$$2\,[\mathrm{TBP}\cdot\mathrm{H_2O}]_{(O)}+\mathrm{HNO}_{3(A)} \rightleftarrows [(\mathrm{TBP})_2\cdot\mathrm{HNO_3}\cdot(\mathrm{H_2O})_{1.5}]_{(O)}+\frac{1}{2}\mathrm{H_2O}_{(A)} \qquad (4)$$

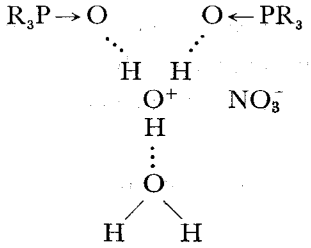
In this equation, x is assumed at 1.5 which is very close to 1.6.

From the descriptions on the hydrogen bonding mentioned above, the following structure of an extracted species is presumed,



$$\mathrm{R_3P\rightarrow O\cdots H\text{-}O\text{-}\underset{\underset{\displaystyle O}{\|}}{N}\rightarrow O\cdots H\text{-}O\text{-}H\cdots O\leftarrow PR_3} \qquad (B_1)$$

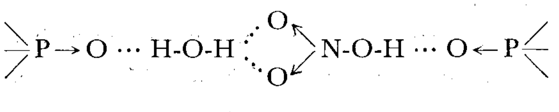
Moreover, this species of $(\mathrm{TBP})_2\cdot\mathrm{HNO_3}\cdot\mathrm{H_2O}$ is assumed to coexist with another species of $(\mathrm{TBP})_2\cdot\mathrm{HNO_3}\cdot(\mathrm{H_2O})_2$. This presumption may give an interpretation of the experimental results of electrical conductivity of organic phase; the species $(\mathrm{TBP})_2\cdot\mathrm{HNO_3}\cdot(\mathrm{H_2O})_2$ is able to be ionized and to contribute to the electrical conductivity. The structure of this species is assumed[10] to be,



(B_2)

It goes without saying that the species (B_2) is hardly ionized in the organic phase and is almost in the form of ion-pair; the apparent degree of dissociation shown in Fig. 7 is below 0.05.

Tuck[5] reported that the viscosity of the equilibrated organic phase in this system becomes maximal at 1.5 M $\mathrm{HNO_3}$ and suggested that this is due to a strong interaction between $\mathrm{TBP}\cdot\mathrm{H_2O}$ and $\mathrm{TBP}\cdot\mathrm{HNO_3}$ in their transition state whose type is presumed as,



which is similar to the species (B_1). It is the authors' thought from the experimental results that the extracted species (B_1) and (B_2) is predominant at 0.5 $M^O_{HNO_3}/M^O_{TBP}$.

Similar procedure is applied for determining the composition of the species (C) which is predominant at 1.0 $M^O_{HNO_3}/M^O_{TBP}$. In the acidity region of 0.5 to 1.0 $M^O_{HNO_3}/M^O_{TBP}$, the slope of regression line of $M^O_{HNO_3}/M^O_{TBP}$ on $M^O_{HNO_3}/M^O_{TBP}$ was determined at about -0.8 from Fig. 2.

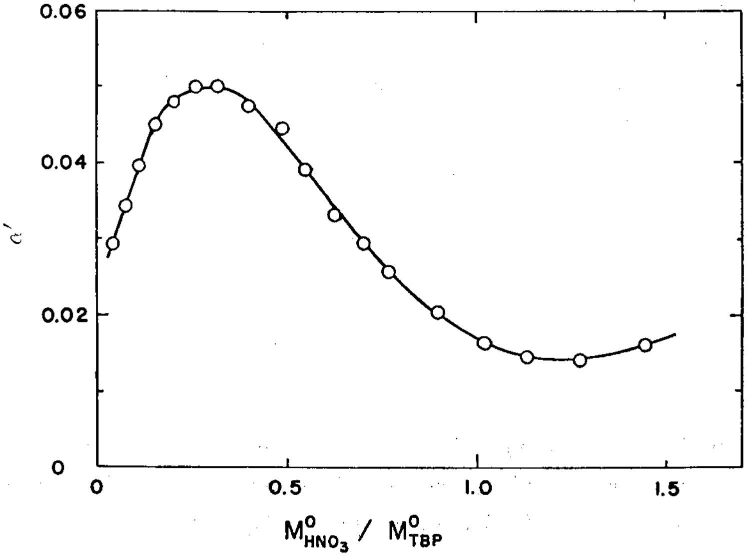


Fig. 7. Degree of Dissociation

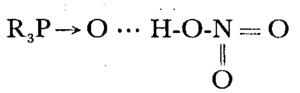
Assuming that the slope is -1.0 instead of -0.8 in this region, the composition of the species (C) and its extracting equation become,

$$\mathrm{TBP \cdot HNO_3 \cdot (H_2O)}_x \qquad \text{(C)}$$

where x is 0.25, and

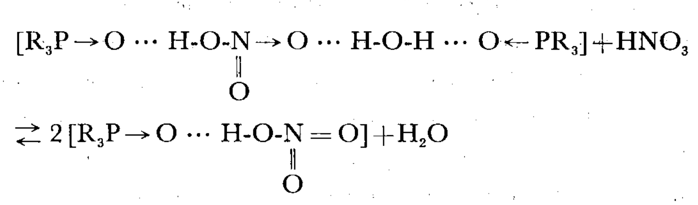
$$[(\mathrm{TBP})_2 \cdot \mathrm{HNO_3} \cdot (\mathrm{H_2O})_{1.5}]_{(O)} + \mathrm{HNO_{3(A)}} \rightleftarrows 2\,[\mathrm{TBP} \cdot \mathrm{HNO_3} \cdot (\mathrm{H_2O})_{0.25}]_{(O)} + \mathrm{H_2O_{(A)}} \qquad (5)$$

This composition of extracted species (C) is interpreted as that in which two extracted species coexist in the organic phase. One of them is of anhydrous form whose presumable structure is,



$$\mathrm{R_3P \rightarrow O \cdots H\text{-}O\text{-}\underset{\underset{\displaystyle O}{\|}}{N} = O} \qquad (\mathrm{C_1})$$

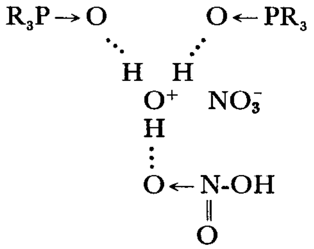
This species is formed by the dehydration of species (B_1) as,



$$[\mathrm{R_3P \rightarrow O \cdots H\text{-}O\text{-}\underset{\underset{\displaystyle O}{\|}}{N} \rightarrow O \cdots H\text{-}O\text{-}H \cdots O \leftarrow PR_3}] + \mathrm{HNO_3} \rightleftarrows 2\,[\mathrm{R_3P \rightarrow O \cdots H\text{-}O\text{-}\underset{\underset{\displaystyle O}{\|}}{N} = O}] + \mathrm{H_2O} \qquad (6)$$

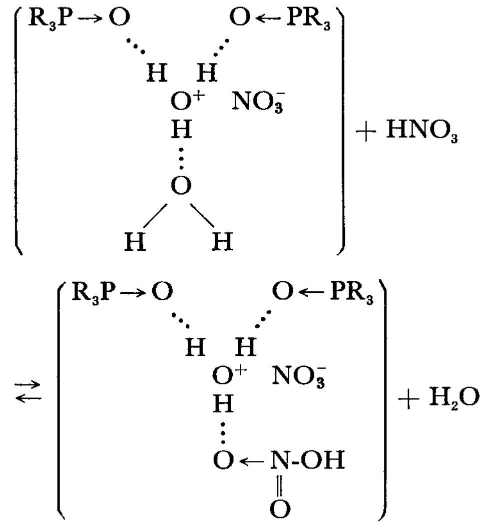
And the presence of this anhydrous species, $\mathrm{TBP \cdot HNO_3}$, has been ascertained by many workers.4)~7),9)

The existence of H_2O in the species (C) leads to a presumption that another extracted species is also present in this acidity region. This species is of ionic character and its structure is presumed as,



(C_2)

Along with the increasing HNO_3 concentration in the organic phase, it is supposed that the weak bonding between H_3O^+ and H_2O in the species (B_2) is broken and HNO_3 replaces H_2O and the species (C_2) is formed by the following reaction.



The presence of this ionic species (C_2) may contribute to the electrical conductivity of organic phase though its degree of dissociation is rather low.

It was mentioned above that the species (B_1) and (B_2) are predominant at $M^O_{HNO_3}/M^O_{TBP}=0.5$. And their concentration is thought to be equimolar from the composition of (B). When these two species (B_1) and (B_2) are changed into the species (C_1) and (C_2), respectively, the overall extracting equation and the overall composition of the extracted species are well represented by the equation (5) and (C), respectively.

Moreover, it is seen from Fig. 2 that $M^{O}_{H_2O}/M^{O}_{TBP}$ is 0.35 at 1.0 $M^{O}_{HNO_3}/M^{O}_{TBP}$ instead of an assumed value of 0.25 and that the minimal water concentration and the curve breaks of physico-chemical properties do not exactly correspond to 1.0 $M^{O}_{HNO_3}/M^{O}_{TBP}$. These results may suggest that some other extracted species, such as $HNO_3 \cdot H_2O$[4], is also being extracted into the organic phase in this acidity region.

4. Summary

The system of nitric acid-water-TBP was studied in order to determine the extracted species in the organic phase and to clarify the extraction mechanism. Distribution of nitric acid and water between organic and aqueous phases was measured. Physico-chemical properties of the equilibrated organic phase, such as volume swelling, density, viscosity and electrical conductivity were also measured.

Three breaks were found on the curves of physico-chemical properties at 0.1, 0.5 and 1.0 of $M^{O}_{HNO_3}/M^{O}_{TBP}$. Based on these experimental results obtained, interactions among water, nitric acid and TBP were discussed and the composition of extracted species and their extracting equation was determined. The major extracted species are,

$$\begin{array}{ll}
TBP \cdot H_2O & \text{at } M^{O}_{HNO_3}/M^{O}_{TBP} = 0 \\
\left.\begin{array}{l} (TBP)_2 \cdot HNO_3 \cdot (H_2O) \text{ and} \\ (TBP)_2 \cdot H_2O \cdot H_3O^+ \cdots NO_3^- \end{array}\right\} & \text{at } M^{O}_{HNO_3}/M^{O}_{TBP} = 0.5 \\
\left.\begin{array}{l} TBP \cdot HNO_3 \text{ and} \\ (TBP)_2 \cdot HNO_3 \cdot H_3O^+ \cdots NO_3^- \end{array}\right\} & \text{at } M^{O}_{HNO_3}/M^{O}_{TBP} = 1.0
\end{array}$$

Presumed structures of these species are also suggested.

Apparent degree of dissociation of the equilibrated organic phase calculated by Walden's equation is below 0.05 and the extracted species are supposed to be hardly ionized.

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