



EXTRACTION EQUILIBRIA OF HYPOPHOSPHOROUS, PHOSPHOROUS AND PHOSPHORIC ACIDS BY TOLUENE SOLUTION OF TRI-n-OCTYLAMINE

Takashi SANA², Koichiro SHIOMORI¹, and Yoshinobu KAWANO^{1*}

¹ Department of Applied Chemistry, Miyazaki Univ., Miyazaki 889-2192, Japan
e-mail: ykawano@cc.miyazaki-u.ac.jp

² Yoshitama Surface Finishing Co., LTD, Nobeoka 882-0024, Japan

ABSTRACT

The extraction equilibria of hypophosphorous, phosphorous and phosphoric acids with tri-n-octylamine as an extractant in toluene were measured at 303K. Under these conditions, undissociated acid (A') reacts with the amine (B) to form various complexes in toluene. The complexes formed and equilibrium constants were estimated by a graphical analysis method. The complexes formed in these systems were found to be A_nB type species for hypophosphorous acid, A_nB_m type species for phosphorous acid, (A'B)_n type species for phosphoric acid, respectively. The experimental results could be explained by reaction models and equilibrium constants for each acid.

Keywords: Hypophosphorous acid; Phosphorous acid; Phosphoric acid; Tri-n-octylamine; Extraction equilibrium

INTRODUCTION

Solvent extraction gives the advantage of selective separation in the recycling of useful materials [1,2]. The nonelectrolytic nickel-plating wastewater consists of nickel, some organic acids, hypophosphorous acid, phosphorous acid, and phosphoric acid. In order to design a new wastewater treatment equipment of nonelectrolytic nickel-plating, it is necessary to clarify the extraction equilibrium and kinetics for each component contained in wastewater. For that fundamental knowledge, the extraction equilibrium and kinetic for nickel with 5-dodecylsalicylaldoxime [3,4] as well as

* Corresponding author

equilibria and kinetics for some organic acids with tri-n-octylamine [5,6] were examined. However the extraction equilibria and kinetics for hypophosphorous acid, phosphorous acid, and phosphoric acid appearing in the wastewater have not been thoroughly discussed [7]. In the optimum design of the wastewater treatment equipment, the extraction equilibria and kinetics for hypophosphorous acid, phosphorous acid and phosphoric acid with the extractant (TOA) must be clarified.

In this paper, the extraction equilibria of hypophosphorous acid, phosphorous acid and phosphoric acid in the aqueous solution with tri-n-octylamine in toluene were investigated. The experimental results for the reaction of undissociated acids in the aqueous solution and amine in an organic solution were analyzed using the graphical analysis method [8,9,10]. The species formed and the formation equilibrium constants were determined.

EXPERIMENTAL

Tri-n-octylamine ((C₈H₁₇)₃N - TOA) was used as an extractant without purification. Toluene, hypophosphorous, phosphorous, and phosphoric acid were special grade chemicals (Wako Pure Chemical Industries, Ltd.). The organic solution was prepared by dissolving TOA in toluene. The initial concentration of TOA in the organic solution was measured by titration with a butanol and methanol mixed solution of hydrochloric acid. Equal volumes (3.00×10⁻²dm³) of the aqueous and organic solutions were placed in a vial immersed in a 303 K water bath and mechanically shaken for 15 hrs to attain equilibrium. The both solutions were allowed to settle for 2 hrs after the equilibration, and were separated completely into the respective solutions. Total acid concentrations in the aqueous solution were determined by titration with a aqueous sodium hydroxide solution. Total acid concentrations in the organic solution were determined by titration with a butanol and methanol mixed solution of potassium hydroxide. The perfect neutralization point for phosphoric acid is difficult to determine because it shows an indistinct end point for the third neutralization. Therefore, phosphoric acid concentration was determined by 1/2 times of the titration volume from the second neutralization point using phenolphthalein as an indicator. The equilibrium pH values of aqueous solution were measured using a pH-meter (Horiba Co. F-12 pH-meter).

RESULTS AND DISCUSSION

Aqueous solution containing hypophosphorous, phosphorous and phosphoric acids was equilibrated with toluene. The concentrations of these acids in toluene could not be detected by the titration. The distributions of these acids into toluene were assumed to be negligible.

The extraction equilibria of hypophosphorous, phosphorous and phosphoric acids with toluene of TOA were investigated. The equilibrium concentration of hypophosphorous acid in toluene, $C_{A,org}$, is plotted against

the equilibrium concentration of hypophosphorous acid in the aqueous solution, $C_{A, \text{aq}}$, in Fig. 1. $C_{A, \text{org}}$ increased with increasing $C_{A, \text{aq}}$. Solid lines refer to the fit found from the reaction model, and the equilibrium constants are shown. For phosphorous and phosphoric acids, dependencies of $C_{A, \text{aq}}$ on $C_{A, \text{org}}$ had the same profile as for hypophosphorous acid.

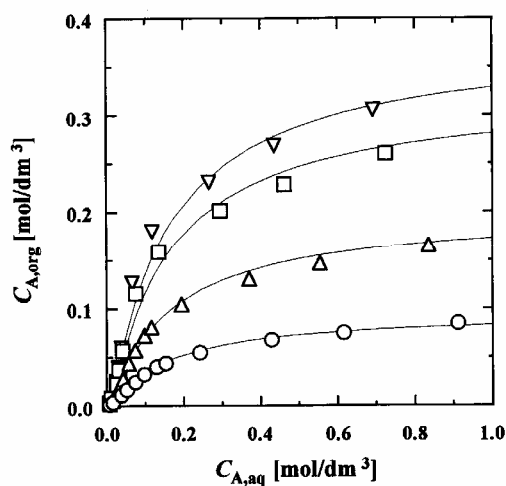


Fig. 1. Effect of the equilibrium hypophosphorous acid concentration in the organic solution on the total equilibrium hypophosphorous acid concentration in the aqueous solution at various concentration of TOA. The initial TOA concentrations are; (O) $4.76 \times 10^{-2} \text{ mol/dm}^3$, (Δ) $9.89 \times 10^{-2} \text{ mol/dm}^3$, (\square) $1.61 \times 10^{-1} \text{ mol/dm}^3$, (∇) $1.89 \times 10^{-1} \text{ mol/dm}^3$, respectively.

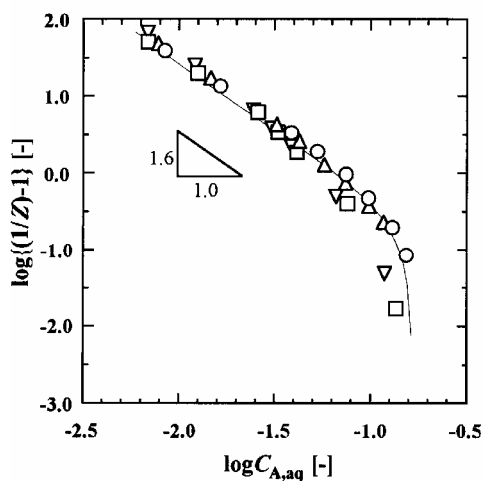


Fig. 2 The correlation between $\log\{(1/Z)-1\}$ and $\log C_{A, \text{aq}}$ for hypophosphorous acid. The initial TOA concentrations are; (O) $4.76 \times 10^{-2} \text{ mol/dm}^3$, (Δ) $9.89 \times 10^{-2} \text{ mol/dm}^3$, (\square) $1.61 \times 10^{-1} \text{ mol/dm}^3$, (∇) $1.89 \times 10^{-1} \text{ mol/dm}^3$, respectively.

In Fig. 2, $\log\{(1/Z)-1\}$ is plotted against $\log C_{A, \text{aq}}$ for hypophosphorous acid, where Z defined as $C_{A, \text{org}}/C_{B, 0}$ was the extraction ratio of the acid by amine. The plot of $\log\{(1/Z)-1\}$ approached a straight line with a slope of 1.6 independent of $C_{B, 0}$ as $C_{A, \text{aq}}$ decreased, but shifted below the straight line as $C_{A, \text{aq}}$ increased. The experimental results of these equilibria systems were analyzed by the graph fitting method (Appendix) described in the previous paper [8,9,10]

In the aqueous solution, the acid, H_nA , was assumed to dissociate into some ions and a proton by the following steps:



where, $n=1$ for hypophosphorous acid, $n=2$ for phosphorous acid and $n=3$ for phosphoric acid. The total acid concentration in the aqueous solution was represented as the sum of dissociated and undissociated species.

$$[H_nA]_0 = [H_nA] + [H_{n-1}A^-] + \dots\dots\dots + [A^{n-}] \quad (4)$$

Considering Eq.(4), the concentration of undissociated acid was as follows:

$$[H_nA] = \frac{[H_nA]_0}{\left(1 + \sum_{n=1}^N [H^+]^{-n} \prod_{i=1}^n K_{ai}\right)} \quad (5)$$

The fraction of undissociated acid was calculated from the proton concentration and the dissociation constants [11] of the acids using Eq.(5). $C_{A, \text{org}}$ is plotted against pH values in Fig. 3. $C_{A, \text{org}}$ decreased with increasing pH. In Fig. 3, the fraction of dissociated and undissociated hypophosphorous acid is also shown against the pH as the broken line. The fraction of undissociated acid, A' , decreased with increasing pH, and the fraction of dissociated acid, A^- , increased with increasing pH. The curve profiles of $C_{A, \text{org}}$ against pH were the same as that of the undissociated acid. The concentrations of undissociated species of phosphorous and phosphoric acids in the aqueous solution, $C_{A', \text{aq}}$, were also evaluated, and are shown plotted against $C_{A, \text{org}}$ in Figs. 4 and 5. The undissociated species of each acid also decreased with increasing pH. The behavior of the fraction of undissociated acids species against the pH had the same profiles as the experimental results. As it results from the experimental data, the undissociated acid is the only species which can interact with TOA.

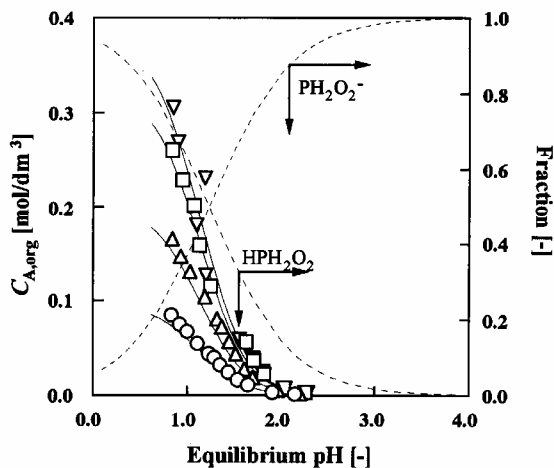


Fig.3. Effect of the fraction of dissociated and undissociated hypophosphorous acid species and the equilibrium hypophosphorous acid concentration in the organic solution on the equilibrium pH.

The initial TOA concentrations are; (○) 4.76×10^{-2} mol/dm³, (Δ) 9.89×10^{-2} mol/dm³, (□) 1.61×10^{-1} mol/dm³, (▽) 1.89×10^{-1} mol/dm³, respectively.

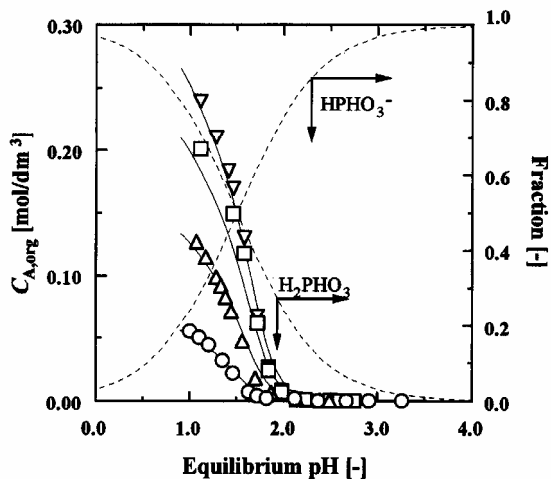


Fig.4. Effect of the fraction of dissociated and undissociated phosphorous acid species and the equilibrium phosphorous acid concentration in the organic solution on the equilibrium pH.

The initial TOA concentrations are; (○) 4.43×10^{-2} mol/dm³, (Δ) 1.04×10^{-1} mol/dm³, (□) 1.63×10^{-1} mol/dm³, (▽) 2.06×10^{-1} mol/dm³, respectively.

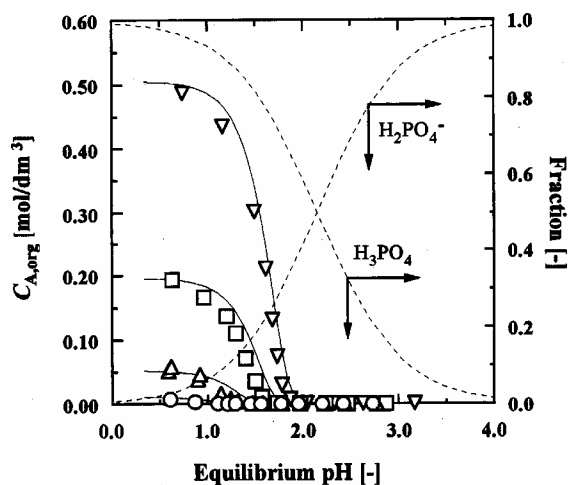


Fig.5. Effect of the fraction of dissociated and undissociated phosphoric acid species and the equilibrium phosphoric acid concentration in the organic solution on the equilibrium pH.

The initial TOA concentrations are; (○) 1.13×10^{-2} mol/dm³, (Δ) 5.19×10^{-2} mol/dm³, (□) 1.96×10^{-1} mol/dm³, (▽) 5.06×10^{-1} mol/dm³, respectively.

The extraction of hypophosphorous acid with TOA

Z is plotted against $C_{A',aq}$ in Fig. 6. Z increased with increasing $C_{A',aq}$ independent of $C_{B,0}$, and approached 2.0. The curve profile in Fig. 6 suggested the formation of A'_nB types species ($n=1$ and 2).

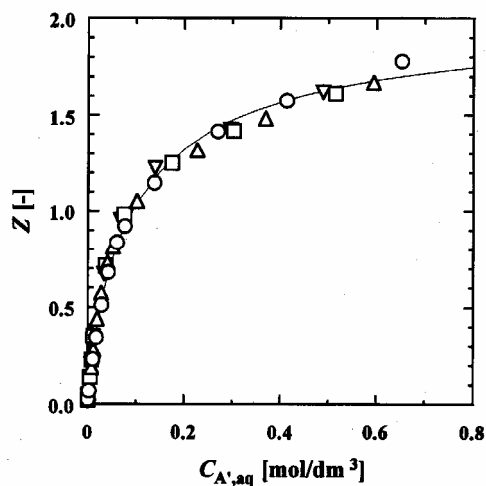


Fig.6. Relationship between Z and the equilibrium undissociated hypophosphorous acid concentration in the aqueous solution at various concentration of TOA.

The initial TOA concentrations are; (○) 4.76×10^{-2} mol/dm³, (Δ) 9.89×10^{-2} mol/dm³, (□) 1.61×10^{-1} mol/dm³, (▽) 1.89×10^{-1} mol/dm³, respectively.

In Fig. 7, $\log\{(1/Z)-1\}$ is plotted against $\log C_{A',aq}$. The value of $\log\{(1/Z)-1\}$ increased with decreasing $C_{A',aq}$, and its plot approached the straight line with a slope of 1.0, but shifted below the straight line as $C_{A',aq}$ increased. From the experimental results in Figs. 6 and 7, only A'_nB ($n=1$ and 2) species were assumed to be formed by the following consecutive reaction:



The mass balance equation for the amine is given as follows:

$$C_{B,0} = C_B + K_{11}C_A C_B + K_{11}K_{21}C_A^2 C_B \quad (8)$$

The mass balance equation for the acid in the organic solution is given as follows:

$$C_{A,org} = K_{11}C_A C_B + 2K_{11}K_{21}C_A^2 C_B \quad (9)$$

Considering the mass balances of the amine and acid, Z can be written as follows:

$$Z = (K_{11}C_A + 2K_{11}K_{21}C_A^2) / (1.0 + K_{11}C_A + K_{11}K_{21}C_A^2) \quad (10)$$

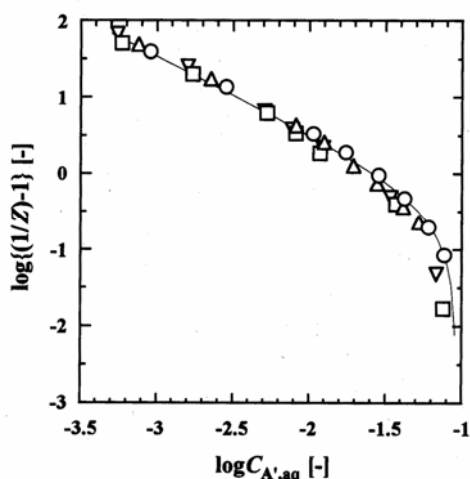


Fig. 7. The correlation between $\log\{(1/Z)-1\}$ and $\log C_{A',aq}$ for hypophosphorous acid. The initial TOA concentrations are; (O) 4.76×10^{-2} mol/dm³, (Δ) 9.89×10^{-2} mol/dm³, (\square) 1.61×10^{-1} mol/dm³, (∇) 1.89×10^{-1} mol/dm³, respectively.

Using the extended value of $C_{A',aq}$ at $\log\{(1/Z)-1\}=0$ on a straight line in Fig. 7, the value of K_{11} was evaluated. Using the value of $C_{A',aq}$ at $Z=1.0$ on the curve experimentally obtained in Fig. 6, the value of K_{21} was evaluated. The values of K_{11} and K_{21} are shown in Table 1. The solid lines in Figs. 1, 2 and 6, and 7 refer to the fit found from the reaction model with the value of K_{11} and K_{21} . The solid lines well corresponded with the experimental results. The extraction equilibrium of hypophosphorous acid with TOA in toluene

was interpreted by the reaction model in which two species of A'_nB ($n=1$ and 2) are formed in the organic solution.

The extraction of phosphorous acid with TOA

Z is plotted against $C_{A',aq}$ in Fig. 8. Z increased with increasing $C_{A',aq}$, and depended on $C_{B,0}$. Z exceeded 1.0. The curve profiles showed the formation of A'_nB type ($n>1$) and other type species.

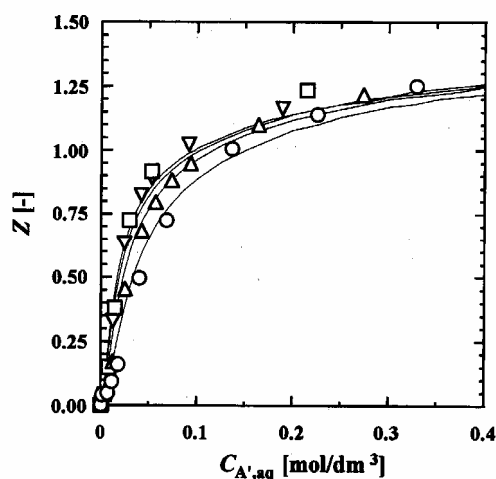


Fig.8. Relationship between Z and the equilibrium undissociated phosphorous acid concentration in the aqueous solution at various concentration of TOA. The initial TOA concentrations are; (O) 4.43×10^{-2} mol/dm³, (Δ) 1.04×10^{-1} mol/dm³, (\square) 1.63×10^{-1} mol/dm³, (∇) 2.06×10^{-1} mol/dm³, respectively.

In Fig. 9, $\log\{(1/Z)-1\}$ is plotted against $\log C_{A',aq}$. In the low $C_{A',aq}$ region, $\log\{(1/Z)-1\}$ was independent of $C_{B,0}$. In the high $C_{A',aq}$ region, $\log\{(1/Z)-1\}$ depended on $C_{B,0}$. The curve profiles suggested the formation of a mixture of A'_nB and $(A'B)_n$ type species as shown in the previous paper [5,8,9,10].

In order to facilitate the calculation, three types of $A'B$, $(A'B)_2$ and A'_3B_2 species were assumed to be formed by the following consecutive reactions:



The mass balance for the amine is shown as the following equation:

$$C_{B,0} = C_B + K_{11}C_A C_B + 2K_{11}^2 K_{21} C_A^2 C_B^2 + 2K_{11}^2 K_{22} K_{32} C_A^3 C_B^2 \quad (14)$$

The mass balance for the acid in the organic solution is shown as the following equation:

$$C_{A,org} = K_{11}C_A C_B + 2K_{11}^2 K_{21} C_A^2 C_B^2 + 3K_{11}^2 K_{22} K_{32} C_A^3 C_B^2 \quad (15)$$

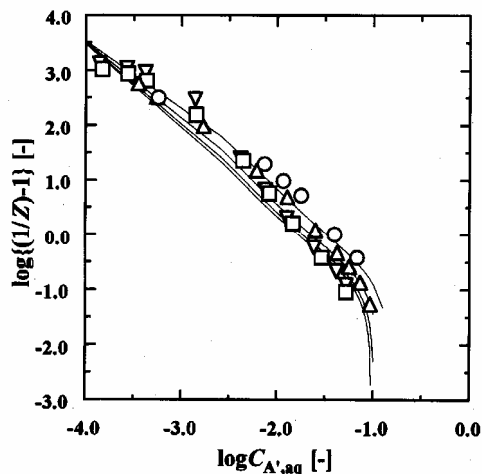


Fig.9. The correlation between $\log\{(1/Z)-1\}$ and $\log C_{A',aq}$ for phosphorous acid. The initial TOA concentrations are; (O) 4.43×10^{-2} mol/dm³, (Δ) 1.04×10^{-1} mol/dm³, (\square) 1.63×10^{-1} mol/dm³, (∇) 2.06×10^{-1} mol/dm³, respectively.

Using the extended value of $C_{A',aq}$ at $\log\{(1/Z)-1\}=0$ on the straight line in Fig. 9, the value of K_{11} was evaluated. Using the experimental results in Figs. 8 and 9, K_{22} and K_{32} were determined by the nonlinear least square estimation method as shown in Table 1. The solid lines in Figs. 4, 8 and 9 refer to the fit found from the reaction model with the values of K_{11} , K_{22} and K_{32} . The extraction equilibrium of phosphorous acid was interpreted by the reaction model in which three species of A'_nB_m ($n=1,2,3$ and $m=1,2$; $n \geq m$) are formed in the organic solution.

The extraction of phosphoric acid with TOA

Z is plotted against $C_{A',aq}$ in Fig. 10. Z increased with increasing $C_{A',aq}$ depending on $C_{B,0}$. Z was less than 1.0. One mole of the amine should react with one mole of the acid.

In Fig. 11, $\log\{(1/Z)-1\}$ is plotted against $\log C_{A',aq}$. The values of $\log\{(1/Z)-1\}$ were shown to depend on $C_{B,0}$. In the low $C_{A',aq}$ region, $\log\{(1/Z)-1\}$ approached the straight line having a slope of 1.0. In the high $C_{A',aq}$ region, $\log\{(1/Z)-1\}$ shifted below the straight line and approached the straight line depending on $C_{B,0}$. From the experimental results of Figs. 10 and 11, $(A'B)_n$ species were estimated to be formed in the organic solution. The experimental results were analyzed by assuming the consecutive reaction model in $n=1,2,3$ and 4 as follows:





The mass balance of the amine was written as the following equation:

$$C_{B,0} = C_B + K_{11}C_A'C_B + 2K_{11}^2K_{22}C_A'^2C_B^2 + 3K_{11}^2K_{22}K_{33}C_A'^3C_B^3 + 4K_{11}^2K_{22}K_{33}K_{44}C_A'^4C_B^4 \quad (20)$$

The mass balance for the acid is written as the following equation:

$$C_{A',org} = K_{11}C_A'C_B + 2K_{11}^2K_{22}C_A'^2C_B^2 + 3K_{11}^2K_{22}K_{33}C_A'^3C_B^3 + 4K_{11}^2K_{22}K_{33}C_A'^4C_B^4 \quad (21)$$

Using an extended value of $C_{A,aq}$ at $\log\{(1/Z)-1\}=0$ on the straight line obtained in Fig.11, K_{11} was evaluated.

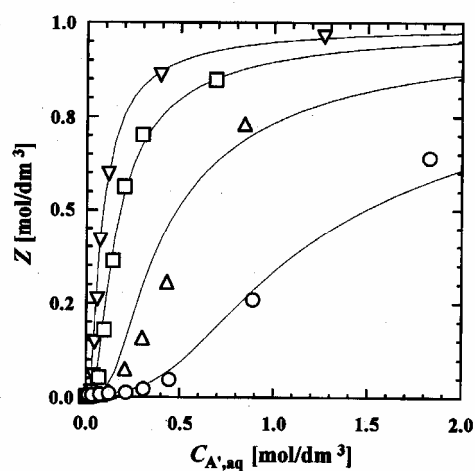


Fig.10. Relationship between Z and the equilibrium undissociated phosphoric acid concentration in the aqueous solution at various concentration of TOA. The initial TOA concentrations are; (O) 1.13×10^{-2} mol/dm³, (Δ) 5.19×10^{-2} mol/dm³, (\square) 1.96×10^{-1} mol/dm³, (∇) 5.06×10^{-1} mol/dm³, respectively.

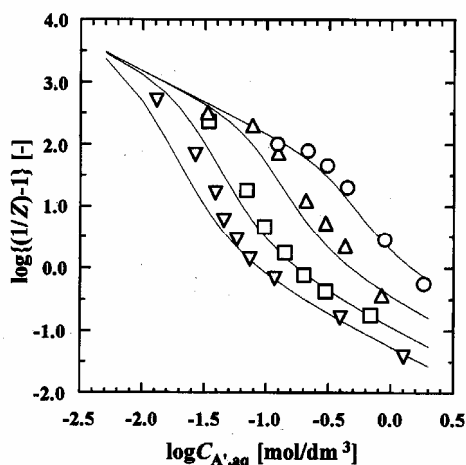


Fig.11. The correlation between $\log\{(1/Z)-1\}$ and $\log C_{A',aq}$ for phosphoric acid. The initial TOA concentrations are; (O) 1.13×10^{-2} mol/dm³, (Δ) 5.19×10^{-2} mol/dm³, (\square) 1.96×10^{-1} mol/dm³, (∇) 5.06×10^{-1} mol/dm³, respectively.

Using the experimental results in Figs. 10 and 11, K_{22} , K_{33} and K_{44} were determined by the nonlinear least square estimation method as shown in Table 1.

Tab. 1. Complex types between TOA-toluene solutions and hypophosphorous, phosphorous and phosphoric acid system and formation equilibrium constants

Acid	Complex type	K_{11} [dm ³ /mol]	K_{nm} [dm ³ /mol]
Hypophosphorous acid	A'nB n=1,2	30	4.0(K_{21})
Phosphorous acid	A'nBm $\begin{matrix} n=1,2,3 \\ m=1,2 \end{matrix}$ $n \geq m$	2.8	$1.8 \times 10^3(K_{22})$ $3.5(K_{32})$
Phosphoric acid	(A'B) _n n=1,2,3,4	6.6×10^{-2}	$5.0 \times 10(K_{22})$ $8.5 \times 10^2(K_{33})$ $2.7 \times 10^3(K_{44})$

A' : the undissociated acid B: TOA

The solid lines in Figs. 10 and 11 refer to the fit found from the reaction model with the values of K_{11} , K_{22} , K_{33} and K_{44} . The extraction equilibrium of phosphoric acid by TOA in toluene was interpreted by the reaction model in

which four species of $(A'B)_n$ ($n=1, 2, 3$ and 4) are formed in the organic solution.

CONCLUSION

The extraction equilibria of hypophosphorous, phosphorous and phosphoric acids (written as A) with TOA (written as B) in toluene were investigated at 303K. The experimental results were interpreted and analyzed by the assumptions of some reaction models using the graph fitting method. The three acids react as the undissociated acid, A' in the aqueous solution with B in the organic solution. For the reaction of the three acids with TOA, other species except A'B were cleared to form each other. For hypophosphorous acid, A'B and A'_nB ($n=2$) type species were formed. For phosphorous acid, A'B and A'_nB_m ($n=2,3$ and $m=2 : n \geq m$) type species were formed. For phosphoric acid, A'B and $(A'B)_n$ ($n=2,3,4$) type species were formed. In each case, formation constants for these species were estimated by the graph fitting method. The calculated results for each reaction models proposed corresponded well with each experimental value.

Appendix [8,9,10]

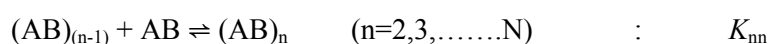
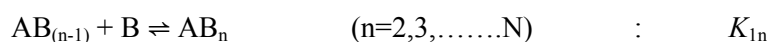
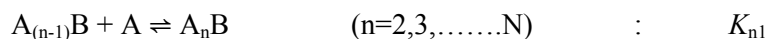
The acid, A, reacts with the amine, B, to form species AB in the organic solution by following reaction.



The equilibrium constant is written as follows;

$$K_{11} = C_{AB}/C_A C_B$$

The species AB would react successively with A or B or itself to form A_nB , AB_n or $(AB)_n$ ($n=2,3,\dots,N$) in the organic phase by the following reactions;



At the equilibrium for the system, total concentrations of A and B in the organic solution were represented as follows;

$$C_{A,org} = K_{11}C_A \times g_1(K_{ij}, C_A, C_B)$$

$$C_{B,0} = C_B + g_2(K_{ij}, C_A, C_B)$$

where, $g_1(K_{ij}, C_A, C_B)$ and $g_2(K_{ij}, C_A, C_B)$ are the functions of equilibrium constants, K_{ij} and concentrations of A in the aqueous solution and B in the organic solution, depending on the type of the species formed.

Using the above relations, $\{(1/Z)-1\}$ was written as follows;

$$(1/Z)-1 = \{1/(K_{11}C_A)\} \times f(K_{ij}, C_A, C_B)$$

where, $f(K_{ij}, C_A, C_B)$ is the function of K_{ij} , C_A and C_B , depending on the species formed. The value of $\{(1/Z)-1\}$ is rearranged as follows;

$$\log\{(1/Z)-1\} = -\log(K_{11}C_{A,aq}) + \log f(K_{ij}, C_A, C_B)$$

In the case where AB species were formed alone in the system, the function of $f(K_{ij}, C_A, C_B)$ is 1.0. The curves plotting of $\log\{(1/Z)-1\}$ against $\log(C_A)$ is a straight line independent of $C_{B,0}$. In the case where AB and other species are formed in the system, the function f differed from 1.0. The curve plotting of $\log\{(1/Z)-1\}$ against $\log(C_A)$ differed from the straight line shown above. The curves for the species except A_nB and $(AB)_n$ approach to the straight line of AB in low C_A . The typical curves are shown in Fig. A.

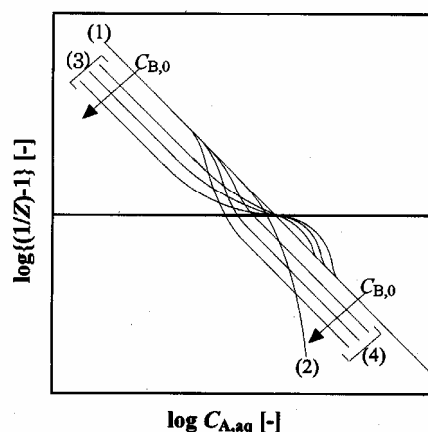


Fig. A.

The type of species formed except AB and the equilibrium constants are estimated by the divergence from the straight line (1).

The formation of A_nB type specie shows a curve independent on $C_{B,0}$ as the line (2).

The formation of AB_n type specie shows the curves dependent on $C_{B,0}$ as the lines (3).

The formation of $(AB)_n$ type specie shows the curves dependent on $C_{B,0}$ as the lines (4).

List of symbols and abbreviations

C	concentration	$[\text{mol}/\text{dm}^3]$
K	equilibrium constant for the reaction	$[-]$
Z	extraction ratio ($C_{A,\text{org}}/C_{B,0}$)	$[-]$
n	aggregation number of species	$[-]$

Subscripts

A	acid
A^-	dissociated acid
A'	undissociated acid
org	organic solution
aq	aqueous solution
B	amine
0	initial

REFERENCES

- [1] M. Tanaka, M. Kobayashi, M.A.S. Alghamdi, K. Tatsumi, *Shigen to Sozai*, 2001, 117, 507-511.
- [2] M. Niinae, A. Itoh, K. Kenchu, *Shigen to Sozai*, 1998, 114, 63-68.
- [3] T. Sana, K. Shiomori, Y. Kawano, K. Nagayoshi, *Solv. Extr. Res. Devel., Jpn*, 2000, 7, 206-211.
- [4] T. Sana, R. Fujii, K. Shiomori, Y. Kawano, K. Nagayoshi, *Ars Sepatatoria Acta*, 2002, 1, 35-44.
- [5] T. Sana, K. Nagayoshi, K. Shiomori, Y. Baba, Y. Kawano, *Kagaku Kogaku Ronbunshu*, 1997, 23, 243-250.
- [6] Y. Kawano, K. Kusano, *J. Chem. Eng., Japan*, 1983, 16, 519-521.
- [7] K. Mishima, M. Nagatani, Y. Arai, *Solvent Extraction*, 1990, 117-182.
- [8] Y. Kawano, K. Kusano, in: *Novel Graphical Method to Estimate Chemical Species Produced in Successive Equilibria*, S. A. Newman (Ed.), ANNARBOR SCIENCE, Michigan, USA, 1982, p. 487-508.
- [9] Y. Kawano, K. Kusano, F. Nakashio, *Kagaku Kogaku Ronnunshu*, 1983, 9, 473-475.
- [10] Y. Kawano, Y. Yoshida, T. Matsui, K. Kondo, F. Nakashio, *Kagaku Kogaku Ronbunshu*, 1990, 16, 280-285.
- [11] The Society of Japan: *Kagakubinran Basic vol.*, 4th ed., 2, pp317, Maruzen Co., LTD, Japan 1993.