Analysis of Interfacial Adsorption Equilibrium and Reaction Rate of Phosphorous Acid with Tri-n-octylamine in Toluene

Analysis of the Interfacial Adsorption Equilibrium and Reaction Rate of Phosphorous Acid with Tri-*n*-octylamine in Toluene

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In order to clarify the extraction mechanism of phosphorous acid with tri-*n*-octylamine from a spent electroless nickel-plating bath, the interfacial adsorption equilibrium of the chemical species relating to the extraction and the interfacial reaction rate of phosphorous acid in the aqueous solution with tri-*n*-octylamine in toluene was investigated at 303K. The interfacial tensions between the aqueous and organic phases, containing various concentrations of phosphorous acid and TOA, were measured and analyzed by the Langmuir and Gibb's adsorption isotherms. The interfacial adsorption constants and the interfacial area occupied by TOA and its complex with phosphorous acid were determined. The initial extraction rate of phosphorous acid with TOA in toluene was measured using a Lewis-type transfer cell. The experimental results were analyzed based on an interfacial reaction model in which the reaction proceeds by successive reactions between TOA and the extraction complexes adsorbed at the interface and the undissociated phosphorous acid in the aqueous solution. The extraction rate in the initial stage of the extraction is interpreted by the rate equation in which the release step of the A'B complex species from the interface is the rate-determining step. The reaction rate constant and the equilibrium constant for the each reaction step were determined.

1. Introduction

Although many studies [1-7] have been reported for the separation and recovery of phosphate as a phosphorus resource from sewage, only a few studies concerning industrial wastewater [8-10] have been reported. Mishima *et al*. [8] have reported the extraction of phosphorous acid with quaternary ammonium salts from a spent plating bath. Shibata *et al*. [9,10] reported on the extraction process for removing phosphoric acid from mixed acid wastewater containing acetic, nitric and phosphoric acid by solvent extraction. The process comprises of two steps; the first is the extraction process for removing acetic and nitric acid from the wastewater using tri-n-octyl phosphate [9], and the second is the extraction process for

removing highly pure phosphoric acid from the raffinate, which contains residual phosphoric acid, using tri-*n*-butyl phosphate [10]. About 130,000 tons of spent electroless nickel-plating bath solutions containing a high concentration (about 20-100 kg/m^3) of phosphorous acid are wasted every year [11]. It has been reported that the mining of accessible phosphate ore will only be possible for about another 50 years [1], therefore, the recovery and recycling of phosphorous resources from spent plating baths could become important in the future.

In order to design a recovery process for phosphorous resources, we investigated the extraction equilibria of hypophosphorous, phosphorous and phosphoric acid with tri-*n*-octylamine in toluene at 303K [12]. The extraction equilibrium of phosphorous acid with tri-*n*-octylamine was expressed by the successive reactions taking place between the undissociated species, A', and the amine, B, to form the mixture of A'$_n$B and (A'B)$_n$ complexes. Also, the overall extraction rate of phosphorous acid with the amine using a vibro-mixer type extractor [13,14] was investigated. The average extraction rate was analyzed by assuming complete mixed flow in the extractor and the average extraction rate constants were determined for each frequency of the vibration plates [15]. Further, a practical process for the recovery of organic, phosphorous and hypophosphorous acids from an actual spent electroless nickel-plating bath by extraction with tri-*n*-octylamine in toluene was developed in a pilot plant which has closed circulation type continuous extraction equipment for the extraction and the back-extraction steps. The practical operation conditions for the pilot plant were also determined [16].

In this study, to facilitate a detailed discussion of the extraction mechanism of phosphorous acid with tri-*n*-octylamine, the interfacial adsorption equilibrium of species relating to the extraction and the initial extraction rate were investigated at 303K. The interfacial adsorption of TOA and the extraction complexes were studied by measurement of the interfacial tension between the organic and aqueous phases in the extraction system. The extraction rate of phosphorous acid from an aqueous sulfuric acid solution with TOA in toluene was measured using a Lewis-type transfer cell. The experimental results of the initial extraction rate were analyzed based on an interfacial reaction model.

2. Experimental

2.1 Materials

Guaranteed grade reagents of tri-*n*-octylamine (hereafter call TOA or B) as the extractant, toluene, phosphorous acid, NaOH, and H$_2$SO$_4$ were purchased from Wako Pure Chemicals Co. and used without further purification. 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 methanol and butanol mixed solution of hydrochloric acid using bromocresol green as the indicator.

2.2 Measurement of interfacial tension using the drop volume method

The interfacial tension between the aqueous solution in the presence or absence of phosphorous acid and the toluene solution in the presence or absence of TOA was measured at 303K by an automatic system based on the principle of the drop volume method. The automatic interfacial tension measurement apparatus (DVS-2000, Yamashita Giken Co.) and the droplet falling unit are shown in **Figs.1** and **2**. The measurement procedure was similar to the reported procedure [17]. Before the interfacial tension measure-
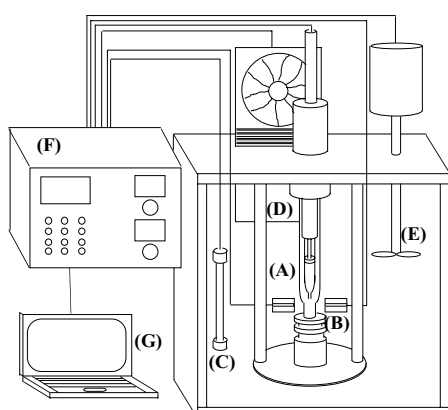
Fig.1 Automatic interfacial tension measurement apparatus
(A): Glass syringe with plunger, (B): Falling droplet detection sensor,
(C): Heater, (D): Electric cooler, (E): Stirrer,
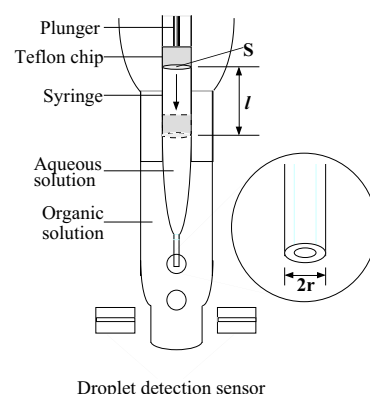(F): Temperature control unit, (G): Computer.

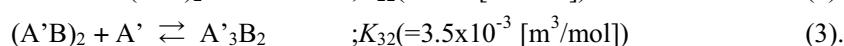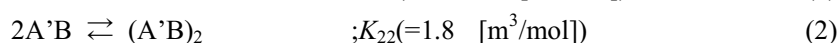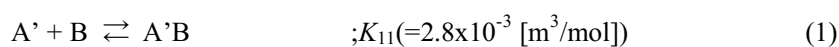**Fig.2 Schematic diagram of the falling droplet unit.**

ments, the aqueous and organic solutions used were equilibrated at 303K. The equilibrated concentrations of phosphorous acid in the aqueous and organic solutions were determined by titration with an aqueous sodium hydroxide solution or a methanol and butanol mixed solution of potassium hydroxide using phenolphthalein as an indicator.

2.3 Measurement of the extraction rate using a Lewis-type transfer cell

The extraction rates of phosphorous acid in the aqueous solutions with TOA in toluene were measured in a Lewis-type transfer cell at 303 K. The apparatus and measurement procedure were similar to that of the methods already reported [18]. The aqueous solution was prepared by dissolving phosphorous acid in distilled water, and adjusting to pH 1.0 by the addition of concentrated sulfuric acid. The concentration of the phosphorous acid in the aqueous solution was determined by capillary electrophoresis (Otsuka electronics Co., CAPI-3200AP) with a commercial buffer solution for organic acid analysis (Otsuka electronics Co., α-ISOB1). The pH values in the aqueous solution were measured using a pH meter (Horiba Co., F-12 pH meter). The concentration of phosphorous acid in the organic solution was calculated from the mass balances of phosphorous acid.

3. Results and discussion

In our previous paper [12], the extraction equilibrium of phosphorous acid with TOA in toluene was measured at 303K. The overall extraction equilibrium was expressed by successive reactions involving the reaction of undissociated acid, A', with the amine, B, forming A'B, $(A'B)_2$ and A'_3B_2 complexes in toluene. The reaction was analyzed using the graphical analysis method [19-21], as shown in the following equations;

$$A' + B \rightleftarrows A'B \qquad ; K_{11}(=2.8 \times 10^{-3} \text{ [m}^3/\text{mol]}) \qquad (1)$$

$$2A'B \rightleftarrows (A'B)_2 \qquad ; K_{22}(=1.8 \text{ [m}^3/\text{mol]}) \qquad (2)$$

$$(A'B)_2 + A' \rightleftarrows A'_3B_2 \qquad ; K_{32}(=3.5 \times 10^{-3} \text{ [m}^3/\text{mol]}) \qquad (3).$$

3.1 The interfacial adsorption equilibrium of TOA and the extracted complexes

The interfacial tensions between the aqueous and the organic solutions were measured. The equilibrated organic solution in the presence or absence of extractant and the aqueous solution in the presence or absence of phosphorous acid were used for the measurements. From the results of the toluene solution containing TOA and the aqueous solution in the absence of phosphorous acid, the interfacial tensions are plotted against the initial TOA concentration, $[B]_0$, in **Fig.3**. The interfacial tension decreases with increasing concentration of TOA in the organic solution. This decrease in the interfacial tension shows the adsorption of TOA on the interface. If TOA (B) is adsorbed on the interface according to the Langmuir adsorption isotherm, the following equation applies;

Fig.3   Relationship between the interfacial tension and $[B]_0$

$$B_{org} + \theta_V \rightleftarrows \theta_B \qquad\qquad ; K_B \qquad\qquad (5)$$
$$K_B = \theta_B/([B]\theta_V) \qquad\qquad (6).$$

where K_B is the adsorption equilibrium constant of TOA, θ is the fraction of the area occupied by the adsorbed species on the interface, respectively.

The relations between θ_B and θ_V is expressed as follows;

$$\theta_B + \theta_V = 1 \qquad\qquad (7).$$

According to the Gibbs' adsorption isotherm, the interfacial tension is related to the equilibrium concentration by the following equation;

$$-d\gamma = RT \Sigma(\theta_i/S_i)d(\ln[i]) \qquad\qquad (8).$$

where γ is interfacial tension, R is gas constant, T is temperature, S is the area occupied per unit mole of the adsorbed species on the interface, and i is the adsorbed species. The following equation was obtained by integrating Eq. (8), and substituting by Eqs. (6) and (7);

$$\gamma_0 - \gamma_B = \frac{RT}{S_B}\ln(1 + K_B[B]) \qquad (9).$$

where γ_0 is the interfacial tension between the organic solution and water. Analyzing the experimental results using Eq. (9), the values of K_B and S_B were determined using the nonlinear least square method as shown in **Table 1**. The solid line in Fig. 3 is the calculated results from Eq. (9) using the values obtained for the constants.

The organic solution containing TOA was equilibrated with the aqueous solution containing
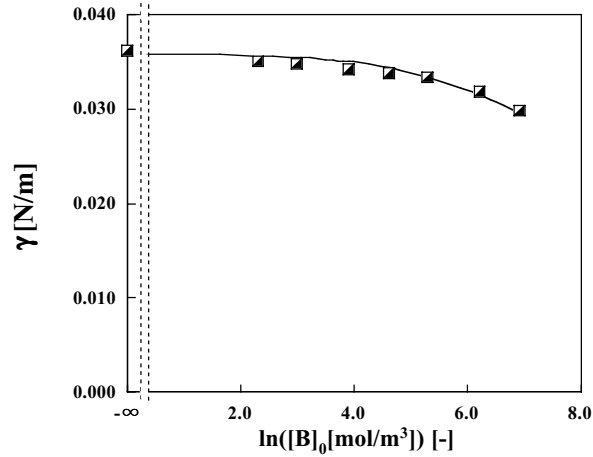
Table 1 Various constants for phosphorous acid extraction

$K_B = 5.1 \times 10^{-3}$ [m^3/mol]

$K_{step2} = 2.1 \times 10^{-7}$ [m^3/mol]

$K_{step3} = 2.8 \times 10^{-4}$ [mol/m^3]

$K_{A'B} = 3.6 \times 10^{3}$ [m^3/mol]

$S_B = 6.7 \times 10^{5}$ [m^2/mol]

$S_{A'B} = 2.1 \times 10^{6}$ [m^2/mol]

$k_0 = 9.3 \times 10^{-1}$ [mol/(m^{2}sec)]

phosphorous acid. The interfacial tensions in this system are plotted against the undissociated phosphorous acid concentration, $[A']_{aq}$ for each $[B]_0$ in **Fig. 4**. The interfacial tension decreases with an increase in $[A']_{aq}$ up to about 50 mol/m^3, and shows a tendency to increase with an increase in $[A']_{aq}$ at over 50mol/m^3. The fraction of the extracted complexes formed in the organic phase at $[B]_0$=50 mol/m^3 calculated using the extraction equilibrium constants [12] and mass
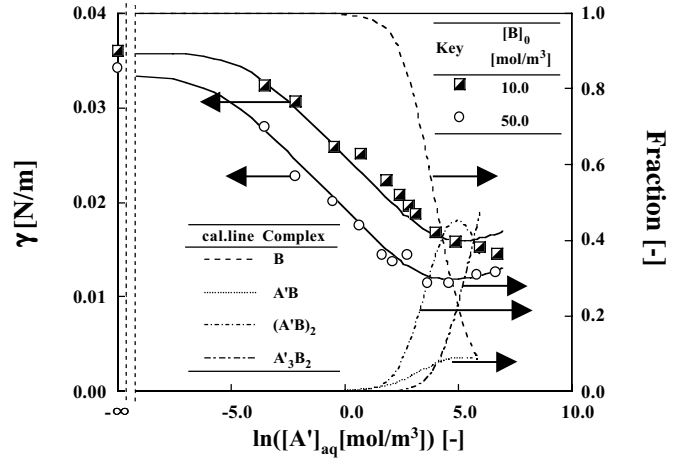

Fig.4   **Relationship between the interfacial tension and $[A']_{aq}$, and the fraction of complexes in the organic phase**

balance are also plotted against $[A']_{aq}$ in Fig.4. The fraction of the B species decreases with an increase in $[A']_{aq}$, and the fractions of the A'B and $(A'B)_2$ species increase with an increase in $[A']_{aq}$ up to about 50mol/m^3 then decrease with a further increase in $[A']_{aq}$, and the A'_3B_2 species increases with an increase in $[A']_{aq}$. The increase the interfacial tension at the high concentration range of $[A']_{aq}$ over 50 mol/m^3 would be caused by a decrease in the concentration of the extracted species adsorbed on the interface. The interfacial adsorption of $(A'B)_2$ and A'_3B_2 would be low. In order to simplify analyses, assuming the interfacial concentrations of the $(A'B)_2$ and A'_3B_2 species are negligibly small, and the B and A'B species are the dominant species on the interface in accordance with the Langmuir adsorption isotherm, the following equations apply;

$$A'B_{org} + \theta_V \rightleftarrows \theta_{A'B} \qquad\qquad ; K_{A'B} \qquad\qquad (10)$$

$$K_{A'B} = \theta_{A'B}/([A'B]\theta_V) \qquad\qquad (11).$$

The relations between θ_B, $\theta_{A'B}$ and θ_V are expressed as follows;

$$\theta_V + \theta_B + \theta_{A'B} = 1 \qquad\qquad (12).$$

The equilibrium concentration of the A'B species can be expressed using the overall extraction constants [1];

$$[A'B] = K_{11}[A'][B] \qquad\qquad (13).$$

The following equation was obtained by substituting Eqs. (11), (12) and (13) into Eq. (8);

$$-d\gamma = \frac{RT}{S_B}\frac{K_B}{1+K_B[B]+K_{A'B}[A'B]}d[B] + \frac{RT}{S_{A'B}}\frac{K_{A'B}}{1+K_B[B]+K_{A'B}[A'B]}d[A'B] \qquad (14).$$

The following equation is derived by the integration of Eq.(14);

$$\gamma_0 - \gamma = \left\{\frac{RT}{S_B}\frac{K_B}{K_B+K_{A'B}K_{11}[A']} + \frac{RT}{S_{A'B}}\left(\frac{K_{A'B}K_{11}[A']}{K_B+K_{A'B}K_{11}[A']}+1\right)\right\}\ln\left(1+K_B[B]+K_{A'B}K_{11}[A'][B]\right)$$

$$-\frac{RT}{S_{A'B}}\ln\left(1+K_B[B]\right) \qquad (15).$$

where $[B] = \dfrac{-\left(1 + K_{11}[A']\right) + \sqrt{(1 + K_{11}[A'])^2 + 8K_{11}^2 K_{22}[A']^2 (1 + K_{32}[A'])[B]_0}}{4K_{11}^2 K_{22}[A']^2 (1 + K_{32}[A'])}$.

The values of $K_{A'B}$ and $S_{A'B}$ were evaluated using the nonlinear least square method as shown in Table1. The solid lines in Fig. 4 are the results calculated by Eq. (15) using the evaluated equilibrium constants. The calculated results agreed well with the experimental results and simulate well the behavior of the interfacial tension at the high [A'] region. The interfacial adsorption equilibrium between the aqueous and organic solutions can be interpreted by the above assumption by the Langmuir and Gibbs' adsorption isotherm.

3.2 Analysis of the extraction rate of phosphorous acid

The extraction rates of phosphorous acid in the Lewis-type transfer cell under the same concentration conditions were independent of the stirring speed and the volume of the organic solution. These results show that the reaction between the extractant and phosphorous acid proceeded at the interface, and that the extraction rates were equal to the interfacial reaction rates. From the experimental results, the phosphorous acid concentration in the organic solution, $[A]_{org}$ were plotted against the reaction time at

constant initial TOA concentration and this is shown in **Fig.5**. $[A]_{org}$ increased with an increase in the reaction time and $[A']_0$. At a constant initial undissociated phosphorous acid concentration, the same dependencies were obtained from these experimental results. Based on these experimental results, the extraction rate of phosphorous acid with TOA is viewed as being dependent on the concentration of phosphorous acid and TOA.
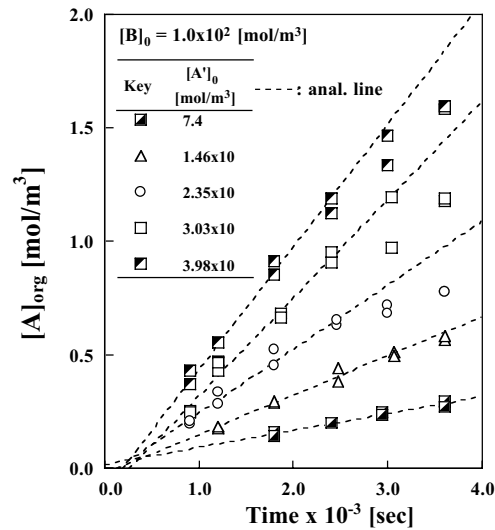

Fig.5   Rate of change of $[A]_{org}$ at various $[A']_0$ for constant $[B]_0$

In the initial extraction stage, the extraction reaction proceeds until A'B complex formation in the organic phase. The interfacial reaction is assumed to consist of the following successive reaction steps;

$$\text{step1} \quad B_{org} + \theta_v \rightleftarrows \theta_B \qquad\qquad ;K_B \qquad\qquad (5)$$
$$\text{step 2} \quad \theta_B + A'_{aq} \rightleftarrows \theta_{A'B} \qquad\qquad ;K_{step2} \qquad\qquad (16)$$
$$\text{step 3} \quad \theta_{A'B} \rightleftarrows A'B_{org} + \theta_v \qquad\qquad ;K_{step3}(=1/K_{A'B}) \qquad\qquad (17).$$

Step 1 is the adsorption of TOA on the interface. Steps 2 is the reaction of the adsorbed species on the interface with A' in the aqueous solution. Steps 3 is desorption of the formed complex into the organic solution from the interface. The effect of the initial TOA concentration,$[B]_0$, on the extraction rate, r_0, for various $[A']_0$ is shown in **Fig.6**. The extraction rate increased with an increase in $[B]_0$, and $[A']_0$. Therefore, step 1 is not the rate-determining step, because the rate equation derived from this assumption has no affect on the concentration of A'. In previous work on the interfacial reaction of organic [22] and inorganic acids

[23] with alkyl amines, the reaction is an instantaneous irreversible reaction and is the rate-determining step. Assuming that step 3 is the rate-determining step, the interfacial reaction rate, r_0, can be derived as follows;

$$r_0 = k_0[\theta_{A'B}] - k_{-0}[A'B]_{org}[\theta_V] \quad (18).$$

where k_0 and k_{-0} are the rate constants for the forward and reverse reactions in Eq. (17), respectively. At the initial stage, the concentration of the A'B species in the organic solution is assumed to be negligibly small, therefore, the rate of the reverse reaction of Eq.(17) can be neglected, and the rate equation is expressed as follows;

$$r_0 = \frac{k_0 K_B K_{step2}[A']_0[B]_0}{1 + K_B[B]_0 + K_B K_{step2}[A']_0[B]_0} \quad (19).$$

From the reciprocal of Eq.(19), the following equation is derived;

$$\frac{1}{r_0} = \frac{1}{k_0 K_B K_{step2}[A']_0} \times \frac{1}{[B]_0} + \frac{1}{k_0} \times \left(\frac{1}{K_{step2}[A']_0} + 1 \right) \quad (20).$$

Fig.6   Effect of $\ln([B]_0)$ on $\ln(r_0)$ for various $[A']_0$

At constant concentrations of the undissociated phosphorous acid in the experimental results, $1/r_0$ was plotted against $1/[B]_0$ in **Fig. 7**. All experimental results are plotted on straight lines that have different slopes for each undissociated phosphorous acid concentration. This shows that the experimental results are represented by Eq. (20). From the values of the slope and the intercept in Fig.7, the values of K_{step2} and k_0 are determined to be 2.1×10^{-7} m^3/mol and 9.3×10^{-1} mol/m^2/sec, respectively. Solid lines in Figs. 6 and 7 are the calculated results from Eq. (19) using the equilibrium and rate constants shown in Table 1. The calculated results agreed well with the experimental results. The initial extraction rate of phosphorous acid in the Lewis-type transfer cell is interpreted by the interfacial reaction model, in which the release step of the A'B complex formed at the interface to the organic phase is the rate-determining step.

Fig.7   Relationship between $(1/r_0)$ and $(1/[B]_0)$

4. Conclusion

The interfacial tensions between the organic and aqueous phases in an extraction system were investigated for various concentrations. The dependency of the interfacial tension on the concentration was analyzed by the Gibb's adsorption isotherm. The interfacial adsorption constants and the interfacial area for TOA and its complexes with phosphorous acid denoted by A'B were determined using a simple interfacial
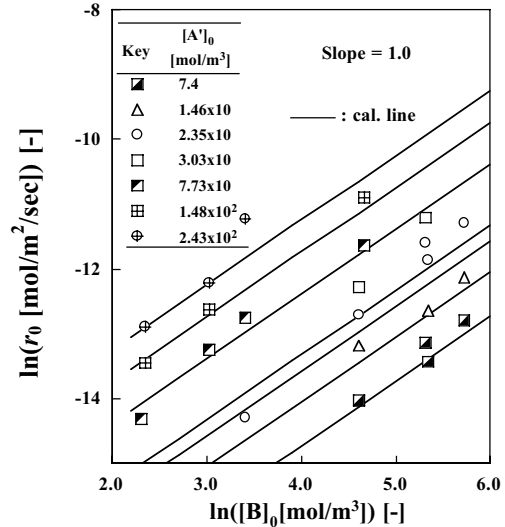
adsorption model. The extraction rate of phosphorous acid with TOA in toluene was investigated using a Lewis-type transfer cell. The experimental results were analyzed based on an interfacial reaction model in which the B species adsorbed on the interface reacts with A' in the aqueous solution to form the complex species A'B. In the extraction of phosphorous acid, the initial rate is controlled by the reaction in which the A'B complex adsorbed on the interface is released into the organic solution. The rate constant for each interfacial reaction and the equilibrium constants were determined based on the proposed interfacial reaction model.

Nomenclature

K_{11}	equilibrium constant of Eq.(1)	[m^3/mol]
K_{22}	equilibrium constant of Eq.(2)	[m^3/mol]
K_{32}	equilibrium constant of Eq.(3)	[m^3/mol]
$K_{A'B}$	adsorption equilibrium constant of A'B	[m^3/mol]
K_B	adsorption equilibrium constant of TOA	[m^3/mol]
K_{step2}	equilibrium constant of Eq.(16)	[m^3/mol]
K_{step3}	equilibrium constant of Eq.(17)	[mol/m^3]
R	gas constant	[Nm/(mol/K)]
S_B	interfacial area occupied by one mole of TOA	[m^2/mol]
$S_{A'B}$	interfacial area occupied by one mole of A'B	[m^2/mol]
T	temperature	[K]
i	adsorbed species	[-]
k_0	forward initial reaction rate constant	[mol/m^2/sec]
k_{-0}	reverse initial reaction rate constant	[mol/m^2/sec)]
$k_{A'}$	overall reaction rate constant observed in a vibro-mixer type extractor	[(m^3/mol)^3/sec]
r_0	initial reaction rate	[mol/m^2/sec]
$r_{A'}$	average extraction rate using a vibro-mixer type extractor	[mol/m^3/sec]
γ	interfacial tension	[N/m]
θ	fraction of active sites at the interface	[-]
τ	residence time of fluids in the reactor	[sec]

<subscripts>

0	initial value	
aq	aqueous solution	
org	organic solution	
v	vacant site	

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