

# EFFECT OF HYDROPHOBICITY ON DISTRIBUTION AND INTERFACIAL ADSORPTION EQUILIBRIA OF *N*-8-QUINOLYLSULFONAMIDE

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Using five kinds of alkylbenzene-substituted *N*-8-quinolylsulfonamide having different alkyl-chain lengths, the effect of hydrophobicity on distribution and interfacial adsorption equilibria was examined.

It was found that the equilibrium constants of distribution and interfacial adsorption of the extractants between organic and aqueous solutions were remarkably affected by the hydrophobicity of the extractant, but the acid dissociation constant and the interfacial area occupied by unit mole of the extractant were not affected.

## Introduction

Commercial extractants for metal recovery from leaching solution usually possess both hydrophilic and hydrophobic properties. The polar head groups of the extractants are necessary to interact with the metallic ions in the aqueous solution and to give the metal complexes which are soluble in the organic solution. The hydrophobic property of the extractants is required to maximize the solubility of the metal complexes in the organic solution and also to minimize the solubility of the extractants in the aqueous solution. Such compounds clearly exhibit interfacial activity; that is, the interfacial concentration exceeds the bulk concentration of the extractants in the organic solution due to adsorption at the oil-water interface.

Data concerning these properties of the extractants are very important to elucidate the kinetics and mechanism of metal extraction or to screen potential metal extractants, as reviewed and discussed previously.<sup>1-4,5,7,8,13,14</sup> Recently, Szymanowski *et al.* attempted to obtain experimentally the relationship between the rate constants of copper extraction with homologues of hydroxyoxime which have different alkyl-chain lengths, and the values of hydrophilic-lipophilic balance (HLB) which provide a measure of interfacial activity.<sup>11,12</sup> The correlation was helpful in the screening of potential metal extractants or in the qualitative interpretation of the extraction mechanism, but not always satisfactory in predicting quantitatively the rate constants of copper extraction

by HLB values.

In the present work, using homologues of *N*-8-quinolylsulfonamide which have different alkyl-chain lengths, the effect of hydrophobicity on distribution and interfacial adsorption equilibria was experimentally examined to obtain more definite information on the extraction mechanism.

## 1. Experimental

### 1.1 Reagents

Five kinds of alkylbenzene-substituted *N*-8-quinolylsulfonamide shown in **Fig. 1** (henceforth  $nC_{18}phSAQ$ ,  $nC_{12}phSAQ$ ,  $C_{12}phSAQ$ ,  $nC_6phSAQ$  and  $C_1phSAQ$ , or abbreviated as HR) were synthesized and purified by recrystallization in methanol for  $nC_{18}phSAQ$ ,  $nC_{12}phSAQ$  and  $C_1phSAQ$ , and by chromatography over a silica-gel column with benzene for  $C_{12}phSAQ$  and  $nC_6phSAQ$ , which have low melting points as mentioned later.<sup>9,14,16</sup> The copper complex ( $CuR_2$ ) was prepared and purified by the same method described in a previous paper.<sup>15</sup> The organic solution was prepared by dissolving HR or  $CuR_2$  in toluene. As the aqueous solution, 100 mol/m<sup>3</sup> acetic acid-sodium acetate buffer solution was used to adjust pH. In the range of low pH (pH < 2.8), 100 mol/m<sup>3</sup> nitric acid was added and in the range of high pH (pH > 7.8), 100 mol/m<sup>3</sup> sodium hydroxide solution was added to the aqueous solution.

### 1.2 Distribution equilibrium of the extractants

The distribution equilibrium of each extractant between the organic and aqueous solutions was measured at 303 K, by the same method reported previously.<sup>14</sup> The concentration of the extractant in toluene was determined with a spectrophotometer.

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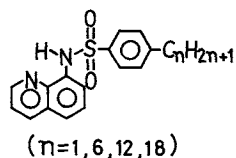


Fig. 1. Structure of extractant (*N*-8-quinolylsulfonamide).

The extinction coefficient of each extractant at 309 nm is  $4.37 \times 10^2$  m<sup>2</sup>/mol for nC<sub>18</sub>phSAQ,  $4.31 \times 10^2$  m<sup>2</sup>/mol for nC<sub>12</sub>phSAQ,  $4.27 \times 10^2$  m<sup>2</sup>/mol for nC<sub>6</sub>phSAQ and  $4.28 \times 10^2$  m<sup>2</sup>/mol for C<sub>1</sub>phSAQ.

The solubilities of HR and CuR<sub>2</sub> in toluene at 303 K were also determined with a spectrophotometer.

### 1.3 Interfacial tension

Interfacial tension between the organic and aqueous solutions was measured at 303 K by the pendant drop method to examine the interfacial adsorption equilibria of the extractants and the copper complexes. Using nC<sub>18</sub>phSAQ, the interfacial tension was also measured at 288 K and 318 K.

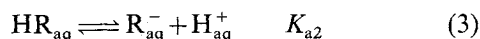
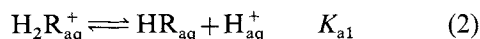
## 2. Results and Discussion

### 2.1 Solubilities of extractants and copper complexes

The solubilities of the extractants and the copper complexes in toluene at 303 K are shown in Table 1, along with the melting point of each species. It is suggested that there is an optimum alkyl-chain length of the extractant to maximize the solubility of extractants or of the copper complexes. From a comparison between the copper complexes prepared by nC<sub>12</sub>phSAQ and C<sub>12</sub>phSAQ, it is found that the solubility of the copper complex in toluene increases with branching of the alkyl chain.\*<sup>1)</sup>

### 2.2 Distribution equilibrium of the extractants

As shown in the previous paper,<sup>14)</sup> the extractants are distributed between the organic and aqueous solutions, accompanied with dissociation in the range of high pH, or with protonation in the range of low pH, as follows:



where  $K_D$ ,  $K_{a1}$  and  $K_{a2}$  are the equilibrium constants and subscripts org and aq denote the organic and aqueous phases, respectively.

From these equations, the following equations for the apparent distribution constant,  $D_{\text{HR}}$ , are obtained.

$$D_{\text{HR}} = K_D + (K_D/K_{a1}) \cdot a_{\text{H}} \quad (\text{low pH}) \quad (4)$$

\*<sup>1)</sup> C<sub>12</sub>phSAQ, the active component of commercial extractant LIX 34, was prepared by using dodecylbenzene involving several kinds of isomers of branching alkyl group,<sup>14)</sup> while nC<sub>12</sub>phSAQ was prepared by using *n*-dodecylbenzene.

Table 1. Solubilities of extractant and copper complex in toluene

	Extractant mp [K]	$C_{\text{HRS}}$ [mol/m <sup>3</sup> ]	Copper complex mp [K]	$C_{\text{CuR}_2\text{S}}$ [mol/m <sup>3</sup> ]
nC <sub>18</sub> phSAQ	329.0–329.4	$7.10 \times 10^2$	413.7–414.7	2.41
nC <sub>12</sub> phSAQ	324.2–325.2	$1.11 \times 10^3$	415.7–416.7	$4.58 \times 10^1$
nC <sub>6</sub> phSAQ	314.7–315.7	$2.09 \times 10^3$	511.7–512.2	$1.45 \times 10^1$
C <sub>1</sub> phSAQ	430.2–430.8	$8.18 \times 10^1$	>573.2	$8.96 \times 10^{-1}$
C <sub>12</sub> phSAQ <sup>14)</sup>	317.2–319.2	$7.20 \times 10^2$	413.2–414.2	$1.30 \times 10^2$

$$D_{\text{HR}} = K_D + (K_D \cdot K_{a2})/a_{\text{H}} \quad (\text{high pH}) \quad (5)$$

where  $a_{\text{H}}$  is the activity of hydrogen ion, and  $D_{\text{HR}}$  is defined as follows:

$$D_{\text{HR}} = \frac{[\text{HR}]_{\text{aq}}}{C_{\text{HR}}} \quad (6)$$

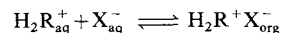
where  $[\text{HR}]_{\text{aq}}$  is the summation of concentrations of  $\text{HR}_{\text{aq}}$  and  $\text{H}_2\text{R}_{\text{aq}}^+$  or  $\text{R}_{\text{aq}}^-$ , and  $C_{\text{HR}}$  is the concentration of  $\text{HR}_{\text{org}}$ .<sup>\*2)</sup>

As shown in Fig. 2, the experimental results of  $D_{\text{HR}}$  for each extractant were correlated with Eqs. (4) or (5) to obtain the equilibrium constants shown in Table 2. The value of  $K_D$  falls extremely with increasing alkyl-chain length for the extractants which contain fewer than 12 carbon atoms in the alkyl group, but the values of  $K_{a1}$  and  $K_{a2}$  are not affected by alkyl-chain length or branching of alkyl-chain, as the equilibrium constant of metal extraction,  $K_{\text{ex}}$ , mentioned in the previous paper was so.<sup>16)</sup>

Figure 3 shows the relation between the number of carbon atoms in the alkyl chain ( $n$ ) and the logarithm of the distribution equilibrium constant ( $-\log K_D$ ) along with other studies on the distribution equilibrium constant of oxime-type extractants.<sup>8,10)</sup> From Fig. 3, it is found that for extractants having fewer than 6 carbon atoms in the alkyl chain the  $K_D$  value decreases significantly with increasing alkyl-chain length, and for extractants having more than 6 carbon atoms in the alkyl chain, the value decreases gradually with increasing alkyl chain length, that is,  $-\log K_D = 4.62 + 0.06n$ .

The  $K_{a2}$  values of *E*-2-hydroxy-5-nonylaceto-phenone oxime (HNAPO), the active component of the commercial extractant SME 529 measured by Miyake *et al.*,<sup>8)</sup> and that of *E*-2-hydroxy-5-nonylbenzophenone oxime (HNBPO), the active compo-

\*<sup>2)</sup> As shown in the previous paper,<sup>16)</sup> these extractants in toluene were in the monomeric state. In the range of low pH, an ion pair complex  $\text{H}_2\text{R}^+ \text{X}^-$  is formed as follows:



where  $\text{X}_{\text{aq}}^-$  is an anion of acid. But the concentration of  $\text{H}_2\text{R}^+ \text{X}_{\text{org}}^-$  is negligibly small compared with the concentration of  $\text{HR}_{\text{org}}$ , as shown in the previous paper.<sup>14,15)</sup>

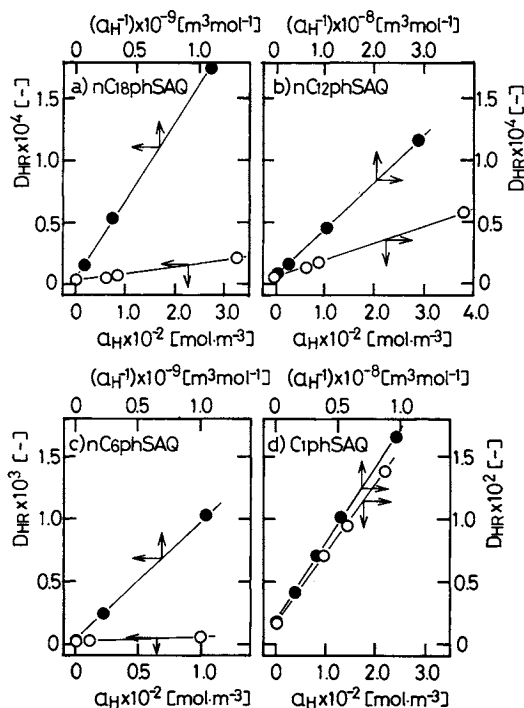


Fig. 2. Distribution equilibrium of extractant. a)  $nC_{18}$ -phSAQ; b)  $nC_{12}$ phSAQ; c)  $nC_6$ phSAQ; d)  $C_1$ phSAQ.

Table 2. Distribution equilibrium constant and acid dissociation constant of each extractant

Extractant	$K_D$ [—]	$K_{a1}$ [mol/m <sup>3</sup> ] ( $pK_{a1}$ )	$K_{a2}$ [mol/m <sup>3</sup> ] ( $pK_{a2}$ )
$nC_{18}$ phSAQ	$(2.08 \pm 0.34) \times 10^{-6}$	$32.5 \pm 0.44$ (1.49)	$(6.73 \pm 1.95) \times 10^{-8}$ (10.17)
$nC_{12}$ phSAQ	$(4.48 \pm 0.02) \times 10^{-6}$	$33.2 \pm 0.22$ (1.48)	$(8.50 \pm 0.04) \times 10^{-8}$ (10.07)
$nC_6$ phSAQ	$(1.08 \pm 0.08) \times 10^{-5}$	$32.9 \pm 0.03$ (1.48)	$(9.43 \pm 1.47) \times 10^{-8}$ (10.06)
$C_1$ phSAQ	$(1.75 \pm 0.03) \times 10^{-3}$	$32.3 \pm 0.97$ (1.49)	$(8.78 \pm 0.13) \times 10^{-8}$ (10.06)
$C_{12}$ phSAQ <sup>14)</sup>	$(2.15 \pm 0.24) \times 10^{-6}$	$32.3 \pm 2.78$ (1.48)	$(8.49 \pm 1.74) \times 10^{-8}$ (10.07)

ment of the commercial extractant LIX 65N measured by Komasaawa *et al.*<sup>6)</sup> are as follows:

$$\text{HNAPO} : K_{a2} = 2.0 \times 10^{-8} \text{ mol/m}^3 (pK_{a2} = 10.70)$$

$$\text{HNBPO} : K_{a2} = 3.0 \times 10^{-6} \text{ mol/m}^3 (pK_{a2} = 8.52)$$

The present results and the above results suggest that the commercial chelating extractants have an acid dissociation constant as low as  $10^{-5.5} - 10^{-8}$ , which corresponds to the acid dissociation constant of phenol.

### 2.3 Interfacial tension

Interfacial tension between the organic and aqueous solutions is reduced by the addition of extractants to the organic solution, due to the adsorption of HR at the interface, as shown in Figs. 4 and 5a. The relationship between the interfacial tension,  $\gamma$ ,

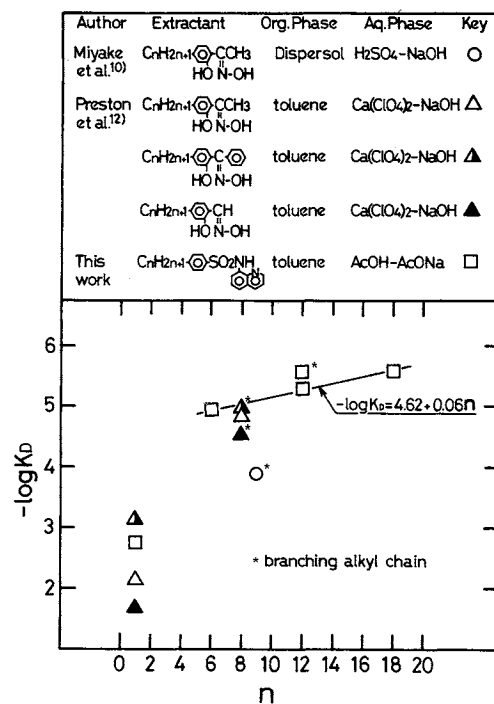
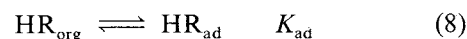


Fig. 3. Relation between number of carbon atoms in alkyl chain ( $n$ ) and logarithm of distribution equilibrium constant ( $-\log K_D$ ).

and the concentration of  $HR_{org}$ ,  $C_{HR}$ , is derived from the Gibbs equation for adsorption, assuming a Langmuir adsorption isotherm to express the relation between the amount of HR adsorbed and  $C_{HR}$ , as follows:

$$\gamma = \gamma_0 - (\mathcal{R}T/S_{HR}) \ln(1 + K_{ad}C_{HR}) \quad (7)$$

where  $\gamma_0$  is the interfacial tension between toluene and the aqueous solution,  $S_{HR}$  is the interfacial area occupied by one mole of  $HR_{org}$ , and  $K_{ad}$  is the adsorption equilibrium constant, defined as follows:



where the subscript ad denotes the adsorption state at the interface.

From the experimental results shown in Figs. 4 and 5a, and Eq. (7), the values of  $K_{ad}$  and  $S_{HR}$  for each extractant were obtained by nonlinear regression, as shown in Table 3.<sup>\*)</sup> The experimental result of  $C_1$ phSAQ suggests that  $C_1$ phSAQ is not adsorbed at the interface. The values of  $K_{ad}$  increase with increasing alkyl-chain length and with branching alkyl chain, but the values of  $S_{HR}$  are not affected by hydropho-

<sup>\*)</sup> Interfacial tension of  $C_{12}$ phSAQ was measured by the drop-weight method, as reported in the previous paper.<sup>14)</sup> In this study, it was confirmed that the experimental results obtained by the pendant drop and the drop-weight methods agreed very well with each other; for example,  $\gamma = 3.12 \times 10^{-2} \text{ N/m}$  for the pendant drop method and  $\gamma = 3.13 \times 10^{-2} \text{ N/m}$  for the drop-weight method, in the case of  $C_{HR} = 100 \text{ mol/m}^3$ , for  $C_{12}$ phSAQ.

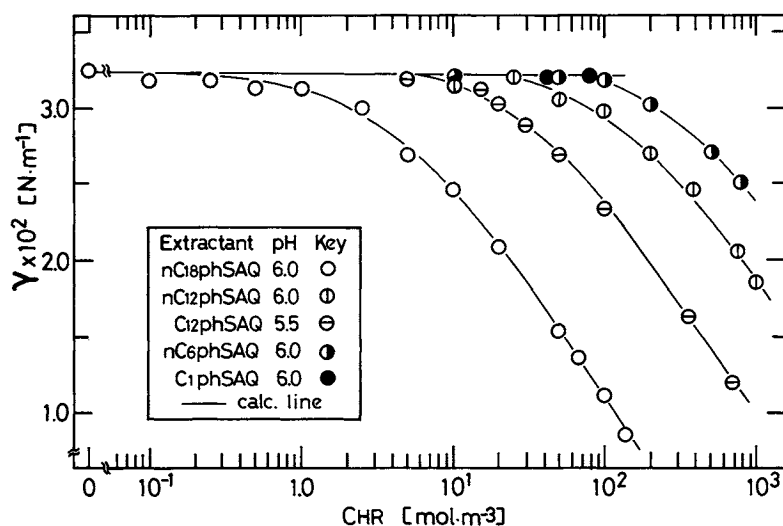


Fig. 4. Interfacial tension of extractant.

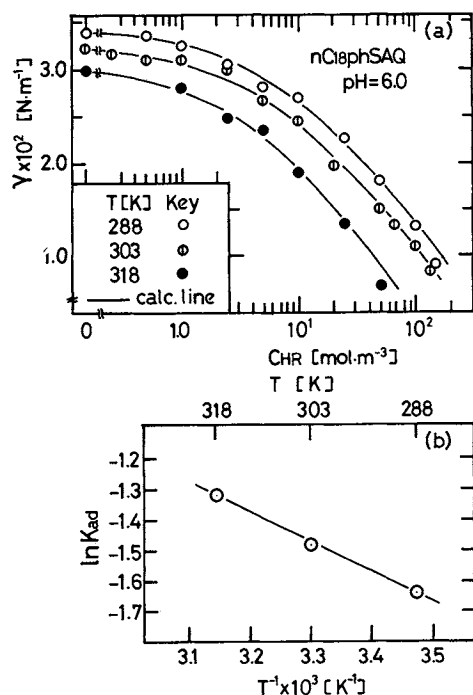


Fig. 5. Effect of temperature on interfacial adsorption equilibrium of  $nC_{18}phSAQ$ . a) interfacial tension of  $nC_{18}phSAQ$ ; b) relationship between  $\ln K_{ad}$  and  $1/T$ .

bicity of the extractant. The values of  $S_{HR}$  correspond to the size of the sulfonamidoquinoline group as described in the previous paper.<sup>14)</sup>

The  $K_{ad}$  and  $S_{HR}$  values of HNAPO measured by Miyake *et al.*<sup>8)</sup> and the  $S_{HR}$  value of HNBPO measured by Komasaawa *et al.*<sup>6)</sup> are as follows:

$$\begin{aligned} \text{HNAPO: } K_{ad} &= 0.77 \text{ m}^3/\text{mol}, \\ S_{HR} &= 3.03 \times 10^5 \text{ m}^2/\text{mol} \\ & (= 51 \text{ \AA}^2/\text{molecule}) \end{aligned}$$

$$\begin{aligned} \text{HNBPO: } S_{HR} &= 5.71 \times 10^5 \text{ m}^2/\text{mol} \\ & (= 95 \text{ \AA}^2/\text{molecule}) \end{aligned}$$

It is found that the  $K_{ad}$  value of HNAPO is about three times larger than that of  $nC_{18}phSAQ$ , and the  $S_{HR}$  value of HNAPO is nearly equal to that of these *N*-8-quinolylsulfonamides, but the  $S_{HR}$  value of HNBPO is twice that of the others. The results reflect the different characteristics and structure of the extractants' coordinating group.

The interfacial tension in the case of  $nC_{18}phSAQ$  falls with increasing temperature, as shown in Fig. 5a, but the values of  $K_{ad}$  increase slightly with temperature as shown in Table 3. From the relationship between  $\ln K_{ad}$  and  $1/T$ , shown in Fig. 5b, the enthalpy change of the interfacial adsorption,  $\Delta H_{ad}$ , was obtained; that is,  $\Delta H_{ad} = 8.4 \pm 5.0 \text{ kJ/mol}$ .

Furthermore, though the interfacial tension of the copper complex prepared by each extractant was also measured, it was confirmed that the interfacial tension was not lowered by the addition of the copper complex; that is, the copper complex was not adsorbed at the interface as mentioned in the previous paper.<sup>14)</sup>

## Conclusion

Using five kinds of alkylbenzene-substituted *N*-8-quinolylsulfonamide which have different alkyl chain lengths, the effect of hydrophobicity on distribution and interfacial adsorption equilibria was examined. The following results were obtained.

(1) The distribution constants of the extractants were reduced extremely with increasing alkyl-chain length for the extractants containing fewer than 12 carbon atoms in the alkyl group, but the acid dissociation constants were not affected by the hydrophobicity.

(2) The adsorption equilibrium constants of the extractants increased with increasing hydrophobicity, but the interfacial area occupied by unit mole of the extractants was not affected by the hydrophobicity.

**Table 3.** Adsorption equilibrium constant and interfacial area occupied by unit mol of each extractant

Extractant	$T$ [K]	$K_{ad}$ [m <sup>3</sup> /mol]	$S_{HR}$ [m <sup>2</sup> /mol] (Å <sup>2</sup> /molecule)
nC <sub>18</sub> PhSAQ	288.2	$(1.92 \pm 0.33) \times 10^{-1}$	$(3.46 \pm 0.22) \times 10^5$ (57 ± 3)
nC <sub>18</sub> PhSAQ	303.2	$(2.25 \pm 0.24) \times 10^{-1}$	$(3.68 \pm 0.13) \times 10^5$ (61 ± 2)
nC <sub>18</sub> PhSAQ	318.2	$(2.66 \pm 0.31) \times 10^{-1}$	$(3.32 \pm 0.19) \times 10^5$ (55 ± 3)
nC <sub>12</sub> PhSAQ	303.2	$(4.10 \pm 0.85) \times 10^{-3}$	$(2.97 \pm 0.36) \times 10^5$ (49 ± 6)
nC <sub>6</sub> PhSAQ	303.2	$(1.58 \pm 0.38) \times 10^{-3}$	$(2.88 \pm 0.44) \times 10^5$ (48 ± 7)
C <sub>12</sub> PhSAQ <sup>(14)</sup>	303.2	$(1.98 \pm 0.29) \times 10^{-2}$	$(3.18 \pm 0.23) \times 10^5$ (53 ± 4)

#### Nomenclature

$a_H$	= activity of hydrogen ion	[mol/m <sup>3</sup> ]
$C_{HR}$	= concentration of HR in organic phase	[mol/m <sup>3</sup> ]
$C_{HRS}$	= saturated concentration of HR in organic phase	[mol/m <sup>3</sup> ]
$D_{HR}$	= apparent distribution constant	[—]
$\Delta H_{ad}$	= enthalpy change of interfacial adsorption	[kJ/mol]
$K_{ad}$	= adsorption equilibrium constant	[m <sup>3</sup> /mol]
$K_{ai}$	= acid dissociation constant ( $i=1, 2$ )	[mol/m <sup>3</sup> ]
$K_D$	= distribution equilibrium constant	[—]
$R$	= gas constant	[Nm/(molK)]
$S_{HR}$	= interfacial area occupied by one mole of HR	[m <sup>2</sup> /mol]
$T$	= temperature	[K]
$[HR]_{aq}$	= summation of concentration of HR <sub>aq</sub> and H <sub>2</sub> R <sup>+</sup> or R <sup>-</sup>	[mol/m <sup>3</sup> ]
$\gamma$	= interfacial tension	[N/m]

#### <Subscripts>

ad	= adsorption state at the interface
aq	= aqueous solution
0	= initial state
org	= organic solution

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