

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.^{1-4,5,7,8,13,14} 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.^{11,12} 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.^{9,14,16} The copper complex (CuR_2) was prepared and purified by the same method described in a previous paper.¹⁵ The organic solution was prepared by dissolving HR or CuR_2 in toluene. As the aqueous solution, 100 mol/m³ acetic acid-sodium acetate buffer solution was used to adjust pH. In the range of low pH (pH < 2.8), 100 mol/m³ nitric acid was added and in the range of high pH (pH > 7.8), 100 mol/m³ 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.¹⁴ The concentration of the extractant in toluene was determined with a spectrophotometer.

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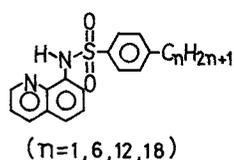


Fig. 1. Structure of extractant (*N*-8-quinolylsulfonamide).

The extinction coefficient of each extractant at 309 nm is 4.37×10^2 m²/mol for nC₁₈phSAQ, 4.31×10^2 m²/mol for nC₁₂phSAQ, 4.27×10^2 m²/mol for nC₆phSAQ and 4.28×10^2 m²/mol for C₁phSAQ.

The solubilities of HR and CuR₂ 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 nC₁₈phSAQ, the interfacial tension was also measured at 288 K and 318 K.

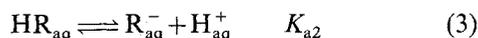
2. Results and Discussion

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 nC₁₂phSAQ and C₁₂phSAQ, it is found that the solubility of the copper complex in toluene increases with branching of the alkyl chain.*¹⁾

2.2 Distribution equilibrium of the extractants

As shown in the previous paper,¹⁴⁾ 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_{HR} , are obtained.

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

*¹⁾ C₁₂phSAQ, the active component of commercial extractant LIX 34, was prepared by using dodecylbenzene involving several kinds of isomers of branching alkyl group,¹⁴⁾ while nC₁₂phSAQ was prepared by using *n*-dodecylbenzene.

Table 1. Solubilities of extractant and copper complex in toluene

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

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

where α_{H} is the activity of hydrogen ion, and D_{HR} is defined as follows:

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

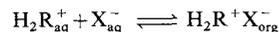
where $[\text{HR}]_{\text{aq}}$ is the summation of concentrations of HR_{aq} and $\text{H}_2\text{R}_{\text{aq}}^+$ or R_{aq}^- , and C_{HR} is the concentration of HR_{org} .^{*2)}

As shown in Fig. 2, the experimental results of D_{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_{ex} , mentioned in the previous paper was so.¹⁶⁾

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.^{8,10)} 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.*,⁸⁾ and that of *E*-2-hydroxy-5-nonylbenzophenone oxime (HNBPO), the active compo-

*²⁾ As shown in the previous paper,¹⁶⁾ 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 X_{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 HR_{org} , as shown in the previous paper.^{14,15)}

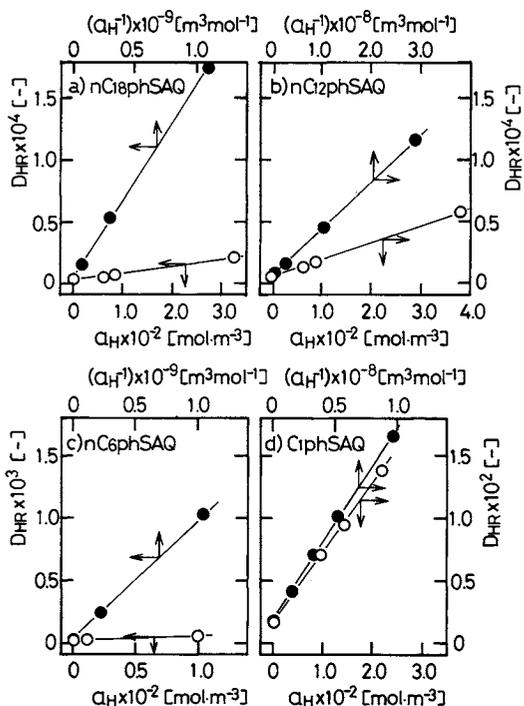


Fig. 2. Distribution equilibrium of extractant. a) nC_{18} -phSAQ; b) nC_{12} -phSAQ; c) nC_6 -phSAQ; d) C_1 -phSAQ.

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

Extractant	K_D [—]	K_{a1} [mol/m ³] (pK_{a1})	K_{a2} [mol/m ³] (pK_{a2})
nC_{18} -phSAQ	$(2.08 \pm 0.34) \times 10^{-6}$	32.5 ± 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 ± 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 ± 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 ± 0.97 (1.49)	$(8.78 \pm 0.13) \times 10^{-8}$ (10.06)
C_{12} -phSAQ ¹⁴⁾	$(2.15 \pm 0.24) \times 10^{-6}$	32.3 ± 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.*⁶⁾ 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, γ ,

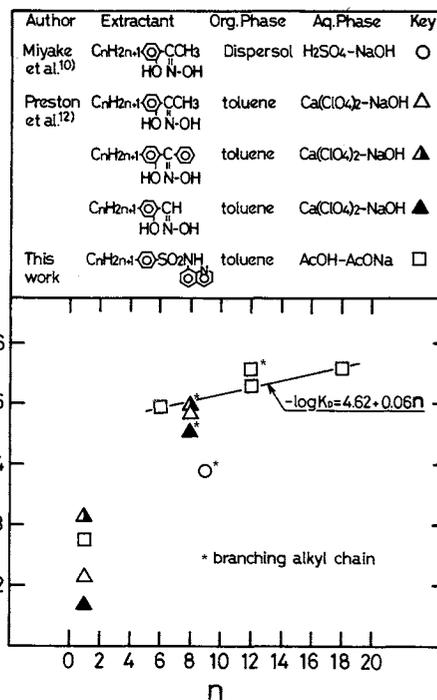
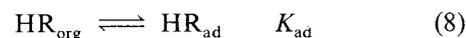


Fig. 3. Relation between number of carbon atoms in alkyl chain (n) and logarithm of distribution equilibrium constant ($-\log K_D$).

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 γ_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.^{*)} 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-

*) Interfacial tension of C_{12} -phSAQ was measured by the drop-weight method, as reported in the previous paper.¹⁴⁾ 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, $\gamma = 3.12 \times 10^{-2}$ N/m for the pendant drop method and $\gamma = 3.13 \times 10^{-2}$ N/m for the drop-weight method, in the case of $C_{HR} = 100$ mol/m³, for C_{12} -phSAQ.

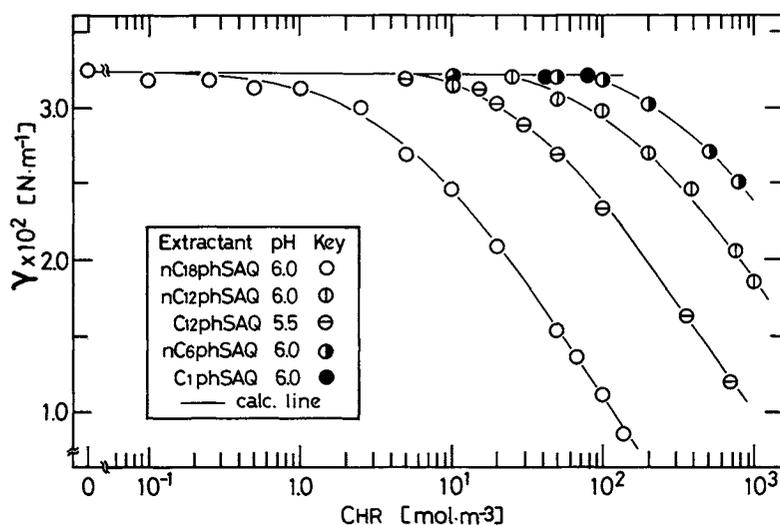


Fig. 4. Interfacial tension of extractant.

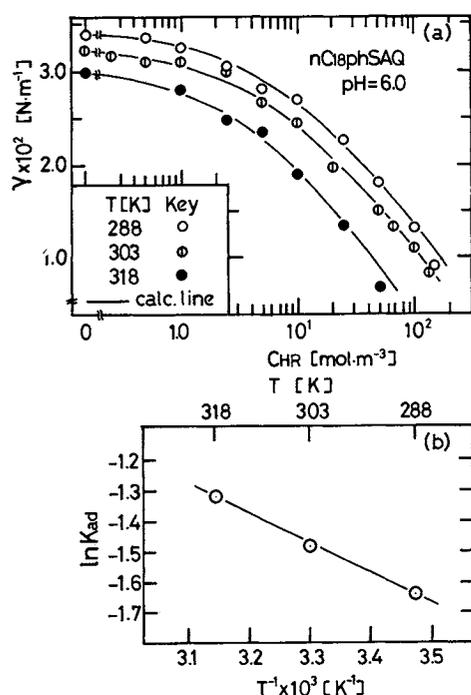


Fig. 5. Effect of temperature on interfacial adsorption equilibrium of nC₁₈phSAQ. a) interfacial tension of nC₁₈phSAQ; b) relationship between ln K_{ad} and $1/T$.

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

The K_{ad} and S_{HR} values of HNAPO measured by Miyake *et al.*⁸⁾ and the S_{HR} value of HNBPO measured by Komasaawa *et al.*⁶⁾ 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 nC₁₈phSAQ, 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 nC₁₈phSAQ 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, ΔH_{ad} , was obtained; that is, $\Delta H_{ad} = 8.4 \pm 5.0$ 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.¹⁴⁾

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

Nomenclature

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

<Subscripts>

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

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