

EXTRACTION EQUILIBRIA OF COPPER AND ZINC WITH *N*-8-QUINOLYLSULFONAMIDES

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Key Words: Extraction, Equilibrium, *N*-8-Quinolylsulfonamide, Copper, Zinc

Measurements of the extraction equilibria of copper and zinc with *N*-8-quinolylsulfonamides dissolved in toluene were carried out at 303 K.

It was found that the extractants (HR) exist as monomers and that copper and zinc (M) form a complex of an MR_2 type in toluene diluent with HR.

From the experimental results, it is seen that extraction constants of alkaryl-substituted *N*-8-quinolylsulfonamides are larger than those of alkyl-substituted *N*-8-quinolylsulfonamides.

Introduction

Beginning with the refining of nuclear fuels after World War II, application of the solvent extraction method to hydrometallurgy and waste water treatment has become of interest in recent years. In addition, many extractants of metals have been studied, specially with respect to equilibrium and kinetic behavior of the extraction of diverse metals. However, due to impurities contained in commercial extractants, the mechanism of extraction by such kinds of extractants was difficult to clarify. To solve this problem, the pure extractants, that is, various types of sulfonamide chelating agent, were synthesized in this work.

Sulfonamide chelating agents were first introduced in the 1960's by Billman *et al.*^{1,2)} They obtained insoluble sulfonamide chelate in common organic solvents of six metal ions: Ag^+ , Hg^{2+} , Cu^{2+} , Pb^{2+} , Co^{2+} and Zn^{2+} . In addition, it was reported by Haworth *et al.*⁵⁾ that *N*-8-quinolyl-*p*-toluenesulfonamide is able to form a chloroform-soluble complex with Cu^{2+} which was determined spectrophotometrically. But use of these extractants was not wide at all until LIX34 was developed by Henkel Corp.¹³⁾

Recently, Takagi *et al.*¹²⁾ studied extraction equilibria of Cu^{2+} , Zn^{2+} , Co^{2+} and Cd^{2+} with sulfonamides to conclude that separations of Cu^{2+} and Co^{2+} , and of Co^{2+} and Zn^{2+} are possible and that the metal selectivity of sulfonamide agents is quite different from that of conventional phenolic agents. Moreover, extractions of Zn^{2+} , Pb^{2+} and Cd^{2+} with LIX34 were carried out by Hoh *et al.*,^{6,7,14)} who found the extrac-

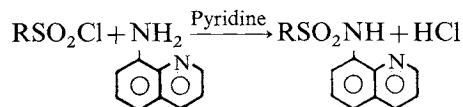
tion optimum pH and the loading capacity of metal ions. Dukov *et al.*³⁾ also studied extraction equilibria of Cu^{2+} and Zn^{2+} with LIX34 (HR) to conclude that the compositions of the extracted complexes are CuR_2 and ZnR_2HR , respectively.

In this work, four *N*-8-quinolylsulfonamides (henceforth SAQ), namely, *N*-8-quinolylbutanesulfonamide, *N*-8-quinolyloctanesulfonamide, *N*-8-quinolyl-*p*-toluenesulfonamide and *N*-8-quinolyl-*p*-dodecylbenzenesulfonamide (henceforth BSAQ, OSAQ, TSAQ and DBSAQ, respectively) were synthesized. Using these four chelating agents, characteristics of extraction equilibria of important divalent transition metals, namely, Cu^{2+} and Zn^{2+} were studied. This work gives the fundamental information to elucidate the extraction mechanism of the metals with the *N*-8-quinolylsulfonamides.

1. Experimental

1.1 Reagents

The four extractants used in this work were synthesized by the following scheme.



Elementary analyses of the products are shown in Table 1.

Toluene of commercial GR grade was used as an organic diluent without further purification. Other inorganic reagents were used, copper nitrate, zinc nitrate, sodium acetate, acetic acid, nitric acid and hydrochloric acid of commercial GR grade.

1.2 Measurement of apparent molecular weight

Apparent molecular weight of SAQ in toluene diluent was measured with a Corona 117 vapor-phase

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Table 1. Elementary analyses of various *N*-8-quinolyl-sulfonamides

		C [%]	H[%]	N [%]
BSAQ	Found	59.76	6.18	10.42
(C ₁₃ H ₁₄ SO ₂ N ₂)	Calcd.	59.08	6.10	10.60
OSAQ	Found	63.52	7.45	8.69
(C ₁₇ H ₂₄ SO ₂ N ₂)	Calcd.	63.72	7.55	8.77
TSAQ	Found	64.41	4.76	9.39
(C ₁₆ H ₁₄ SO ₂ N ₂)	Calcd.	64.41	4.73	9.39
DBSAQ	Found	71.36	8.03	6.16
(C ₂₇ H ₃₆ SO ₂ N ₂)	Calcd.	71.64	8.02	6.19

osmometer, using benzil as a standard material.

1.3 Measurement of extraction equilibrium

The organic solution was prepared by dissolving SAQ in toluene. The aqueous solution was prepared by dissolving copper nitrate or zinc nitrate in de-ionized water. The pH of the aqueous solution was adjusted using 0.1 mol/dm³ sodium acetate-acetic acid buffer solution. At pH value below 2.8, 0.1 mol/dm³ nitric acid was added to the aqueous solution. Thus, the ionic strength of the solution was maintained approximately constant.

Aqueous and organic solutions of equal volumes (20 cm³) were shaken in a flask at constant temperature (303 K) to attain equilibrium. After 48 hours, the two phases were separated. A known volume of the organic phase was stripped by 2 mol/dm³ HCl and diluted in an appropriate ratio. Copper and zinc concentrations in the resulting aqueous samples were determined by a Shimadzu AA646 atomic absorption spectrophotometer. The pH of the aqueous phase after equilibrium was measured with a Hitachi-Horiba F-7SS pH meter.

2. Results and Discussion

2.1 State of aggregation of extractant

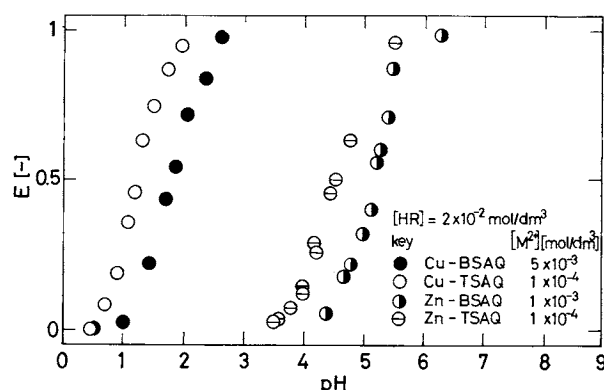
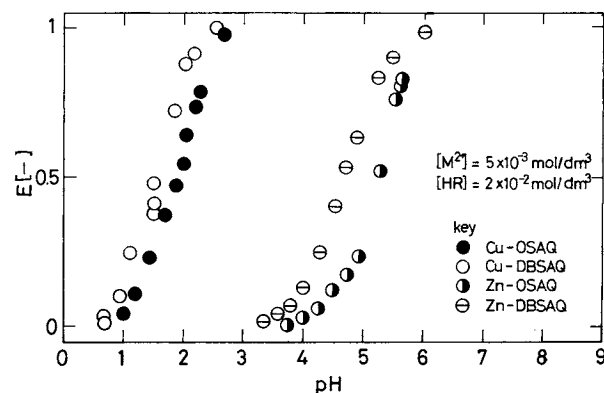
A typical commercial chelating agent, LIX65N, is known to dimerize in non-polar solvents.⁹⁾ With respect to purified LIX34, it was reported that the mean aggregation number is close to one in benzene, carbon tetrachloride and chloroform while marked aggregation occurs in iso-octane.¹¹⁾

Since aggregation state has a considerable influence on the performance of the extraction, it is important to investigate the aggregation state of the extractant in the organic diluents.

Apparent molecular weight of SAQ in toluene by vapor-phase osmometry is shown in Table 2. As is evident from Table 2, the four extractants in toluene are found to be approximately in a monomer state. According to the C-P-K molecular model, it was found that these extractants are difficult to dimerize due to an alkyl or alkaryl group close to the coordination site.

Table 2. Molecular weight from vapor-phase osmometry

	BSAQ	OSAQ	TSAQ	DBSAQ
Found	278.0	339.8	315.5	467.0
Calcd.	264.3	320.5	298.3	452.7

**Fig. 1.** Extraction equilibria of copper and zinc with BSAQ and TSAQ.**Fig. 2.** Extraction equilibria of copper and zinc with OSAQ and DBSAQ.

2.2 Extraction equilibria of copper and zinc

The characteristics of the extraction equilibria of copper and zinc with SAQ in toluene diluent are shown in Figs. 1 and 2. In these figures, *E* represents the extent of the metal extracted, that is, the ratio of the metal concentration in organic phase at equilibrium to the initial one in aqueous phase. It was found that copper and zinc are extracted completely into the organic phase at pH=2.5 and at pH=5.5 for the alkaryl-substituted SAQ and at pH=3 and at pH=6 for the alkyl-substituted SAQ, respectively. This extractability is the same as the result of Takagi *et al.*¹²⁾ obtained from OSAQ in kerosene diluent and TSAQ in benzene diluent.

It is known that copper and zinc ions form complex with acetate anion in the aqueous phase.¹⁰⁾



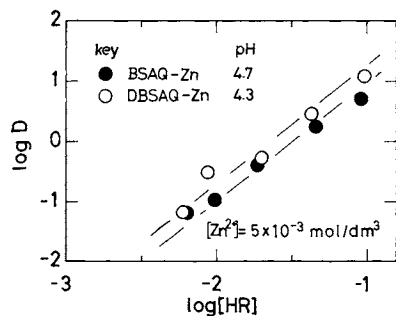


Fig. 3. Determination of x -value for the complexes copper-BSAQ and copper-DBSAQ.

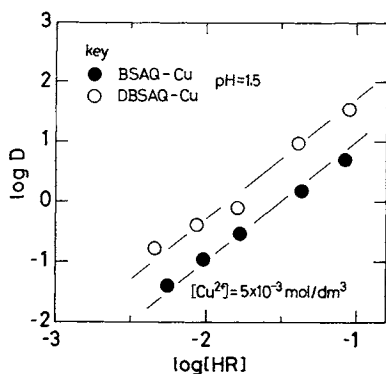


Fig. 4. Determination of x -value for the complexes zinc-BSAQ and zinc-DBSAQ.

$$\beta_i = \frac{[M(OAc)_i]^{(i-2)-}}{[M^{2+}][OAc^-]^i} \quad (2)$$

The following values of β_i ($i=1-4$) are available, for copper ion⁴:

$$\begin{aligned} \beta_1 &= 5.01 \times 10^1 \text{ dm}^3/\text{mol}, \\ \beta_2 &= 5.01 \times 10^2 (\text{dm}^3/\text{mol})^2, \\ \beta_3 &= 1.26 \times 10^3 (\text{dm}^3/\text{mol})^3, \\ \beta_4 &= 7.94 \times 10^2 (\text{dm}^3/\text{mol})^4 \end{aligned}$$

and for zinc ion⁸:

$$\begin{aligned} \beta_1 &= 1.995 \times 10^1 \text{ dm}^3/\text{mol}, \\ \beta_2 &= 1.259 \times 10^2 (\text{dm}^3/\text{mol})^2 \end{aligned}$$

The total concentration of the metallic ion is expressed as follows.

$$\begin{aligned} [M^{2+}]_t &= [M^{2+}]_{aq} + \sum [M(OAc)_i]^{(i-2)-} \\ &= [M^{2+}]_{aq} \{1 + \sum \beta_i [OAc^-]^i\} \end{aligned} \quad (3)$$

Therefore, the concentration of the free metallic ion can be calculated using the following equation.

$$[M^{2+}]_{aq} = \frac{[M^{2+}]_t}{1 + \sum \beta_i [OAc^-]^i} \quad (4)$$

Extraction equilibria of divalent metallic ion (M^{2+}) with SAQ (HR) can be expressed as follows.

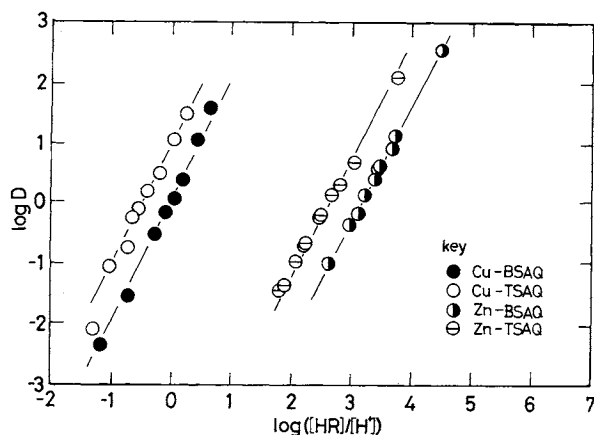
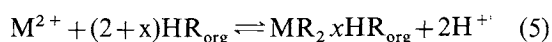


Fig. 5. Determination of K_{ex} for copper and zinc complexed by BSAQ and TSAQ.

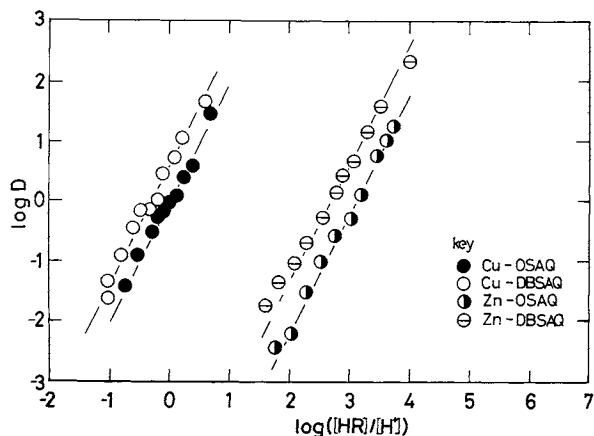


Fig. 6. Determination of K_{ex} for copper and zinc complexed by OSAQ and DBSAQ.

The extraction constant, K_{ex} , is written as follows.

$$K_{ex} = \frac{[MR_2 \cdot xHR]_{org} [H^+]^2}{[M^{2+}] [HR]_{org}^{2+x}} \quad (6)$$

Rearranging Eq. (6), Eq. (7) can be obtained.

$$\log D = (2+X) \log [HR]_{org} + 2 \text{ pH} + \log K_{ex} \quad (7)$$

where

$$D = \frac{[MR_2 \cdot xHR]_{org}}{[M^{2+}]} \quad (8)$$

The experimental results for BSAQ and DBSAQ are arranged according to Eq. (7) and the results are shown in Figs. 3 and 4. Straight lines with a slope of 2 for copper and zinc were obtained. This indicates that $x=0$, metallic ion may be present in the organic phase as MR_2 .

From the above results, Eq. (7) becomes

$$\log D = 2 \log \{[HR]_{org}/[H^+]\} + \log K_{ex} \quad (9)$$

To determine K_{ex} , the experimental results are plotted in Figs. 5 and 6 according to Eq. (9). K_{ex} values obtained from the intersection of the straight

Table 3. Extraction constants

Author	Extractant	Aq. phase	Diluent	Cu		Zn	
				K_{ex}	$[pH_{0.5}]$	K_{ex}	$[pH_{0.5}]$
Sandström <i>et al.</i> ¹¹⁾	LIX34 (p)	—	Chloroform	0.16	—	—	—
Hoh <i>et al.</i> ⁷⁾	LIX34 ^{a)} (up)	NH ₄ OH	Kermac470B	—	—	—	[7.50]
Dukov <i>et al.</i> ³⁾	LIX34 ^{b)} (up)	NaCl-HCl ^{d)}	Kerosene	—	[0.61]	—	[3.95]
This work	Takagi <i>et al.</i> ¹²⁾	—	Kerosene	0.79	[1.75]	1.58×10^{-7}	[5.10]
	OSAQ ^{c)}	—	Benzene	10.0	[1.20]	1.00×10^{-5}	[4.20]
	TSAQ ^{c)}	—	Benzene	10.0	[1.20]	1.00×10^{-5}	[4.20]
	BSAQ	HOAc-NaOAc	Toluene	1.02	[1.82]	4.21×10^{-7}	[5.17]
	OSAQ	HOAc-NaOAc	Toluene	0.92	[1.83]	6.86×10^{-7}	[5.16]
This work	TSAQ	HOAc-NaOAc	Toluene	8.57	[1.23]	5.82×10^{-6}	[4.47]
	DBSAQ	HOAc-NaOAc	Toluene	3.29	[1.58]	4.11×10^{-6}	[4.67]

a) $[HR]_{org} = 10 \text{ wt}\%$. b) $[HR]_{org} = 20 \text{ wt}\%$. c) $[HR]_{org} = 0.02 \text{ mol/dm}^3$.
d) $[Cl^-] = 1.0 \text{ mol/dm}^3$.
*) up: unpurified; p: purified.

line and the ordinate in Figs. 5 and 6 are listed in Table 3.

From Table 3 it can be observed that the K_{ex} value for copper ion is larger than that for zinc ion and that the K_{ex} value of alkaryl-substituted SAQ is larger than that of alkyl-substituted SAQ.

Subsequently, it is possible to separate copper and zinc ions due to the considerable difference between the values for $pH_{0.5}$.

Then, no important difference between K_{ex} values could be appreciated by changing the length of alkyl chain of SAQ.

Comparison of the experimental distribution ratio, D_{obs} , with the calculated one, D_{calc} , by using the extraction constants was carried out and the results are shown in Fig. 7. The calculated results agree with the experimental results.

Comparison of this study with other works^{3,7,11,12)} is shown in Table 3. In general, it is possible to observe a coincidence in the results.

Conclusion

The extraction equilibria of copper and zinc with *N*-8-quinolylsulfonamides in toluene diluent were studied and the following information was obtained:

- 1) *N*-8-quinolylsulfonamide chelating agents exist as monomers.
- 2) The extracted species of the metals with *N*-8-quinolylsulfonamides are MR_2 for copper and zinc. Extraction constants for each extractant were obtained.
- 3) Alkaryl-substituted *N*-8-quinolylsulfonamides are better as the extractant than alkyl-substituted *N*-8-quinolylsulfonamides.

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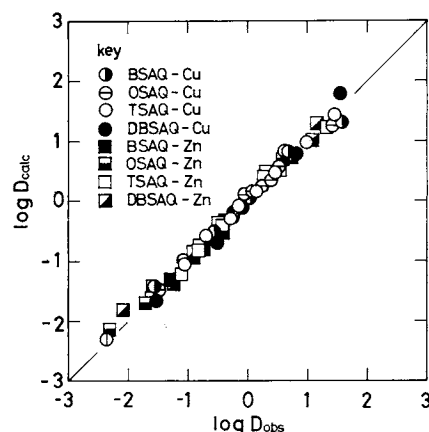


Fig. 7. Comparison of experimental results with calculated results of distribution ratio.

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Nomenclature

D	= distribution ratio of metal	[—]
E	= extent of metal extracted	[—]
i	= number of acetate anions in metal-acetate complex formed	[—]
K_{ex}	= extraction constant	$[(\text{mol/dm}^3)^{-x}]$
x	= number of additional molecules of extractant in extracted species	[—]
$[]$	= concentration	$[\text{mol/dm}^3]$
β_i	= stability constant defined by Eq. (2) ($i=1-4$)	$[(\text{dm}^3/\text{mol})^i]$

<Subscripts>

aq	= aqueous phase
calc	= calculated value
i	= chemical species i
obs	= observed value
org	= organic phase
t	= total

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NUCLEATION AND GROWTH OF NUCLEI FROM ORGANIC VAPORS ON A COLD SURFACE

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Solid condensation of naphthalene vapors onto a cold surface was observed, and the rate of condensation was analyzed by use of an equation that included rates of nucleation and growth of the nuclei. Photographs of the condensation process taken at definite time intervals were analyzed with a digital image processing system to compute the nucleation rates, rates of increase in crystalline areas and the perimeters of the crystals to provide correlations as functions of the supersaturation. The critical point observed in the plots of condensation rates vs. supersaturation was explained as the changes in the nucleation rate and the shapes of the condensates at that point. From the equations developed and the correlations, the volume growth rates of the crystalline particles were found to be proportional to the supersaturation.

Introduction

In fractional sublimation to separate vapor mixtures, the product composition was found to be determined by the relative rates of solid condensation, or rates of desublimation, of the constituents.²⁾ In addition, the rate of solid condensation was found to depend on the supersaturation of the vapor at the condensing surface, flow characteristics and the temperature of the cold surface.^{2,3)} Moreover it was reported that the surface condition itself affects the condensation rates.³⁾ However, owing to the difficulties of observation and measuring the changes in the number of nuclei, further study on the analysis of the solid condensation process remains necessary.

Although the process of solid condensation includes nucleation at the surface and growth of the

nuclei,³⁾ most studies on the fundamentals of solid condensation rates have been concerned with analyses in terms of heat and/or mass transfer rates.^{1,5-7)} As pointed out in the previous study,³⁾ however, the condensates on the surface exist as flakes, not as a continuous layer; hence nucleation at the surface plays an important role in determining the rate of solid condensation.

In the present paper, solid condensation is analyzed as a nucleation process followed by the growth of nuclei to provide quantitative correlations of nucleation and growth rates by the use of a digital image processing technique.

1. Theory

The process of solid condensation from vapors onto a cold surface includes nucleation of crystalline particles and growth of the nuclei. The number of crystalline particles per unit area at contact time θ_c

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