Table 3. Constants for Antoine equation and AAD*

Compounds	Constants for Antoine equation**			AAD [%]
	A	B	C	
Naphthalene	22.8929	4025.35	−102.243	1.1
Acenaphthene	22.9288	5183.86	−80.153	1.0
Fluorene	17.0935	2815.52	−153.984	1.1
Phenanthrene	20.3950	3931.20	−139.743	1.0
Dibenzofuran	22.1098	4707.68	−92.332	1.8

* Absolute average deviation.
** Temperature range of these constants is given Tables 1 and 2.

These data were correlated by using the Antoine equation. The Antoine equation is as follows:

$$\ln P = A - B/(T + C) \qquad (2)$$

where P is in pascals and T is in degrees Kelvin. The constants A, B and C were determined from nonlinear least square fitting to experimental data. The determined values of A, B and C and absolute average deviation (AAD) for five compounds are summarized in **Table 3**. It was found that these experimental vapor pressures could be well correlated with the Antoine equation within the temperature ranges measured in this work.

Nomenclature

A, B, C	= constant in the Antoine equation	[—]
M	= molar mass	[—]
P	= saturated vapor pressure	[Pa]
R	= gas constant	$[\mathrm{J \cdot K^{-1} \cdot mol^{-1}}]$
T	= temperature	[K]
ρ	= apparent vapor density	$[\mathrm{g \cdot m^{-3}}]$

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INTERFACIAL ADSORPTION EQUILIBRIA OF AQUEOUS MERCURY SOLUTION AND XYLENE SOLUTION OF DICYCLOHEXYL-24-CROWN-8

Takeshi KATAOKA, Tadaaki NISHIKI and Masao YAMAUCHI

Department of Chemical Engineering, University of Osaka Prefecture, Sakai 591

The crown ether has been used as a carrier of liquid membrane[1] because it selectively forms complexes with cations. The authors previously studied the liquid-liquid extraction equilibria of mercury by dicyclohexyl-24-crown-8 (C-24)[2] to obtain fundamental information for applying liquid membranes to the separation and concentration of mercury.

In this work, interfacial tensions between several aqueous solutions and xylene solutions of C-24 in equilibrium state were measured to investigate the interfacial adsorption equilibria of C-24 and the extracted mercury complex, $HgCl_2 \cdot C\text{-}24$.[2] The adsorption equilibrium phenomena could be approximately interpreted by the model based on Langmuir's adsorption and Gibbs' adsorption isotherm.

1. Experimental

C-24 was obtained from Nippon Soda Co., Ltd. It was a purified product and was used without further purification. An organic solution was prepared by dissolving a weighed amount of C-24 in xylene. Distilled water, $1 \, \mathrm{kmol/m^3}$ NaCl solution and $0.1 \, \mathrm{kmol/m^3}$ $HgCl_2$ solution were used as an aqueous phase.

Known volumes of aqueous and organic phases were equilibrated in an Erlenmeyer flask by shaking the two phases in an air bath maintained at 298 K. The interfacial tension between the two equilibrated solutions was measured by a drop-weight method at 298 K.

2. Results

The effect of C-24 concentration C_B on the in-

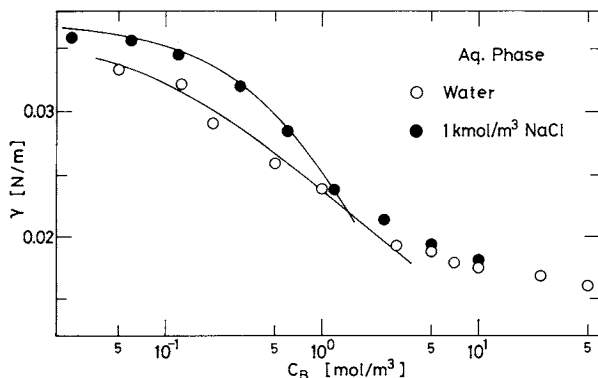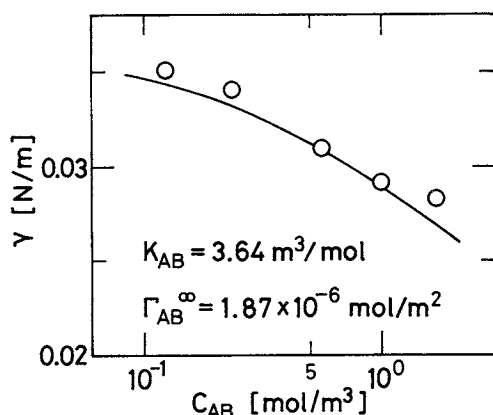**Fig. 1.** Relation between interfacial tension and C-24 concentration.

Fig. 2. Relation between interfacial tension and $HgCl_2 \cdot$C-24 concentration.

terfacial tension γ between the distilled water and xylene solution of C-24 is shown in **Fig. 1**. The value of γ decreases with increasing C_B and C-24 is therefore found to be interfacially active. In the region of C_B more than $10 \, mol/m^3$, it is expected that C-24 is adsorbed at the interface in a saturated state because the variation of γ value with C_B is small.

The result for $1 \, kmol/m^3$ NaCl solution is also shown in Fig. 1. It represents a similar tendency to that of distilled water.

Figure 2 shows the relation between γ and the complex ($HgCl_2 \cdot$C-24) concentration C_{AB}. The result was obtained under the condition in which all C-24 in the organic phase formed complexes by contacting the aqueous solution of $0.1 \, kmol/m^3$ $HgCl_2$.[2] The complex ($HgCl_2 \cdot$C-24) is also interfacially active, but the activity is weaker than that of C-24.

3. Adsorption Equilibrium Model

The relation between interfacial tension and the amount of chemical species adsorbed at the interface is expressed by Gibbs' adsorption equation. For the ideal solution it is written as follows:

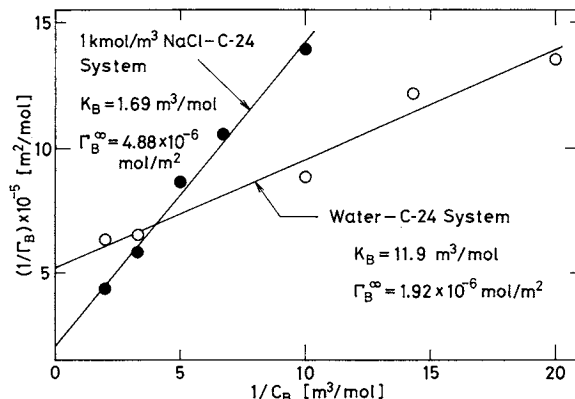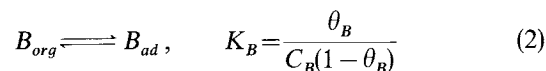$$-d\gamma = RT \sum_i \Gamma_i d\ln C_i, \qquad i = B, AB \qquad (1)$$

Fig. 3. Plot of $1/\Gamma_B$ vs. $1/C_B$.

When the aqueous phase dose not contain mercury, only the following equilibrium holds because no complex exists in the organic phase.

$$B_{org} \rightleftharpoons B_{ad}, \qquad K_B = \frac{\theta_B}{C_B(1 - \theta_B)} \qquad (2)$$

From Eq. (2), Γ_B is given by

$$\Gamma_B = \Gamma_B^\infty (K_B C_B / 1 + K_B C_B) \qquad (3)$$

Substituting Eq. (3) into Eq. (1) and integrating the resultant equation, the following relation is obtained.

$$\gamma = \gamma_0 - RT\Gamma_B^\infty \ln(1 + K_B C_B) \qquad (4)$$

Equations (1) and (3) are respectively transformed as follows:

$$\frac{1}{\Gamma_B} = 1 \Big/ \left(-\frac{1}{RT} \frac{d\gamma}{d\ln C_B} \right) \qquad (5)$$

$$1/\Gamma_B = (1/\Gamma_B^\infty K_B)(1/C_B) + (1/\Gamma_B^\infty) \qquad (6)$$

The value of $1/\Gamma_B$ was calculated from both Eq. (5) and the plot of γ vs. $\ln C_B$ presented in Fig. 1 and is plotted against $1/C_B$ in **Fig. 3**. The results satisfy the relation of Eq. (6). The values of Γ_B^∞ and K_B, which could be obtained from an intercept and slope of the straight line, are represented in the figure. The interfacial tensions calculated from Eq. (4) by using the values of Γ_B^∞ and K_B obtained are shown by solid lines in Fig. 1. The calculated results are in satisfactory agreement with the observed values in the region of low concentration of C-24.

When all C-24 in the organic phase exists in a state of complex, the following equilibrium relation holds.

$$(AB)_{org} \rightleftharpoons (AB)_{ad}, \qquad K_{AB} = \frac{\theta_{AB}}{C_{AB}(1 - \theta_{AB})} \qquad (7)$$
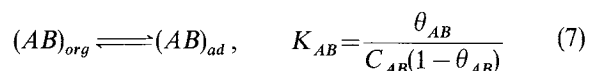
The relation of interfacial tension and AB concentration is derived in the same manner as Eq. (4).

$$\gamma = \gamma_0 - RT\Gamma_{AB}^\infty \ln(1 + K_{AB} C_{AB}) \qquad (8)$$

The γ values calculated from Eq. (8) by using the

values of Γ_{AB}^{∞} and K_{AB} obtained from a plot similar to Fig. 3 are represented by a solid line in Fig. 2. The calculated result approximately agrees with the observed values.

The interfacial areas occupied by one molecule of C-24 in water–C-24 system and of $HgCl_2 \cdot$ C-24, which were calculated from the values of Γ_B^{∞} and Γ_{AB}^{∞}, are 87 and 89 A²/molecule, respectively. These values nearly correspond to the size of the crown ether ring of C-24 obtained from the molecular model. However, the value for C-24 in 1 kmol/m³ NaCl–C-24 system was calculated as 34 A²/molecule, and the adsorbed state of C-24 in this case is not clear.

Nomenclature

C_i	= concentration of species i in organic phase	[mol/m³]
K_i	= adsorption equilibrium constant of species i	[m³/mol]
R	= gas constant	[N·m/(mol·K)]
T	= temperature	[K]
Γ_i	= interfacial excess concentration of adsorbed species i	[mol/m²]
Γ_i^{∞}	= saturated interfacial concentration of adsorbed species i	[mol/m²]
γ	= interfacial tension	[N/m]
γ_0	= interfacial tension between water and xylene	[N/m]
θ_i	= fraction of adsorbed species i	[—]

⟨Subscripts⟩

AB	= complex, $HgCl_2 \cdot$ C-24	
ad	= adsorption state at interface	
B	= C-24	
i	= species i ($i = B$, AB)	
org	= organic phase	

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THEORETICAL ANALYSIS OF A NEW SEPARATION PROCESS UTILIZING EXTRACTION AND ENZYME REACTIONS

Haruo Ishikawa, Hirokazu Nishida and Haruo Hikita

Department of Chemical Engineering, University of Osaka Prefecture, Sakai 591

Introduction

Extraction is one of the important unit operations which utilize effectively the partitioning of components between two immiscible solvents or the difference of the partition coefficients between components. Therefore, a number of investigations on extraction have been carried out, and extensive efforts still continue for developing effective extraction processes and extractors. Recently some remarkable techniques have been introduced in this field. One of them is a liquid membrane technique first developed by Li.[3] A number of liquid membrane processes have been demonstrated over the past ten years, and some of them are said to be near commercialization.

Introduction of enzymatic reactions has also brought promising effects. Removal of phenol in waste water[4] and separation of optical isomers[5,7] are typical separation processes in which enzyme reactions have been successfully combined with extraction or liquid membrane technique. However, the enzymes in most of these processes easily become deactivated, because they are simply confined in the aqueous phase.

The purpose of this work is to develop a new and effective extraction process to achieve both the separation and enrichment of valuable substances. The process consists of simultaneous conversion of objective components by enzymatic reaction and extraction of resulting products by solvents. For an idealized extractor, the performance has been analyzed numerically by using the matrix method.