INTERFACIAL ADSORPTION EQUILIBRIUM OF VERSATIC ACID

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Precise and detailed information about the interfacial adsorption equilibrium is nearly indispensable for the analysis of extraction kinetics of metals by extractants of high interfacial activity, because it is considered that the complex-forming reactions take place at the interface between two immiscible liquids in these extraction systems⁸⁾.

Accordingly, there have been some publications^{1,3)} on the interfacial adsorption equilibrium of several kinds of hydroxyoximes such as LIX 65N, LIX 63 and SME 529. Several authors^{2,9,11,12)} also tried to find some correlations between the interfacial adsorption properties and the extraction rate for these extractants. Though many works^{4,9,10)} have been carried out on the interfacial properties of fatty acids from the standpoint of surface science, the reports on those of commercial carboxylic acids such as Versatic acid (Shell Chemical Co., Ltd.) and naphthenic acid have apparently not been published to date.

In the previous papers, the authors reported the aqueous solubility of Versatic 10⁵⁾, a newly developed Versatic acid, and also reported the adsorption equilibrium of acetic acid at the interface between water and organic diluents such as *n*-hexane, cyclohexane and benzene⁶⁾.

In the present paper, the interfacial adsorption equilibrium of Versatic 10 between aqueous ammonium nitrate-ammonia mixture and *n*-hexane solution is reported.

1. Experimental

Interfacial tension was measured by drop-weight method at 30°C after a *n*-hexane solution of Versatic 10 of known concentration (C_{B0}) reached equilibrium with aqueous ammonium nitrate-ammonia mixture, the ionic strength of which was kept constant.

The pH of the aqueous phase was varied with the change of amount of ammonia added and was measured by pH-meter. The concentration of Versatic 10 in the organic phase after equilibration ($C_{Borg.}$) was calculated from C_{B0} and pH⁵⁾.

In Fig. 1, the experimental results are shown as the relationship between interfacial tension and $C_{Borg.}$ for

various values of pH.

2. Discussion

From the results of the previous paper⁵⁾, the aqueous solubility of Versatic 10 is expressed as follows.

where

$$K_1 = C_{HR}^2 / C_{H_2R_2} = 9.6 \times 10^{-7} \text{ mol/l} \quad (3)$$

$$K_2 = C_H + C_{R-} / C_{HR} = 1.1 \times 10^{-6} \text{ mol/l} \quad (4)$$

It was assumed in this study that only HR and R^- , the monomeric species of Versatic 10 and its anionic species, respectively, can be adsorbed at the interface while H_2R_2 , dimeric species of Versatic 10, which is predominant in the organic phase, cannot be adsorbed. Based on Langmuir's monolayer adsorption model, adsorption of these species is expressed as follows.

where

$$K_{Ai} = \theta_i / S_i (1 - \theta) \cdot C_i \quad (i = HR, R^-) \quad (7)$$

$$\theta = \theta_{HR} + \theta_{R-} \quad (8)$$

According to Gibbs' adsorption isotherm, the relation between interfacial tension and the concentration of adsorbed species is expressed for an ideal solution as follows.

$$-d\gamma = \sum_i \Gamma_i d\mu_i = RT \cdot \sum_i (\theta_i / S_i) \cdot d(\ln C_i) \quad (9)$$

The numbers in parentheses denote pH after equilibration.

Fig. 1 Variation of interfacial tension by $C_{Borg.}$ and pH

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Fig. 2 Variation of fractional coverage of each component by pH

If it is assumed that S_i , the interfacial area occupied by the i -th adsorbed species, is nearly equal to each other for each adsorbed species, i. e.

$$S_{HR} \approx S_{R^-} = S \quad (10)$$

Equation (9) is reduced to Eq. (11) by integration using Eqs. (4), (7) and (8).

$$\gamma = \gamma_0 - \frac{RT}{S} \cdot \ln \{ 1 + (K_{AHR} + K_{AR} - K_2 / C_{H^+}) \cdot S \cdot C_{HR} \} \quad (11)$$

Since it is considered that Versatic 10 exists as the dimeric species in such nonpolar diluent as n -hexane, C_{HR} is expressed by Eq. (12).

$$C_{HR} = (K_1 C_{H_2R_2})^{1/2} \approx (K_1 C_{Borg.} / 2)^{1/2} \quad (12)$$

Therefore, Eq. (11) is rewritten as follows.

$$\gamma = \gamma_0 - (RT/S) \times \ln \{ 1 + (K_{AHR} + K_{AR} - K_2 / C_{H^+}) \cdot S \cdot (K_1 C_{Borg.} / 2)^{1/2} \} \quad (13)$$

The optimum values of K_{AHR} , K_{R^-} and S which give the least standard deviation between experimental and calculated values expected from Eq. (13) were evaluated by Marquardt's nonlinear least square method⁷⁾ as follows. $K_{AHR} = 2.8 \times 10^{-5} \text{ l/cm}^2$, $K_{AR} = 4.2 \times 10^{-6} \text{ l/cm}^2$, $S = 4.1 \times 10^9 \text{ cm}^2/\text{mol}$.

The solid lines in Fig. 1 are the calculated results based on Eq. (13) using these values and the average pH values. The maximum deviations between the experimental and the calculated results are about $\pm 20\%$ though some plotted points, especially those the average pH of which is 8.60, apparently deviate much more from the theoretical lines since they were calculated using average pH. It is concluded that the interfacial tension can be expressed well by Eq. (13).

Figure 2 shows the variations of θ_{HR} and θ_{R^-} with pH calculated from Eqs. (7) and (8). The variation with $C_{Borg.}$ is negligibly small in the concentration range of $C_{Borg.} = 0.1\text{--}1.0 \text{ mol/l}$. From Fig. 2, it is evident that in the region of $\text{pH} < 6$, HR is predominant at the interface and θ_{R^-} is in inverse proportion to C_{H^+} while in

the region of $\text{pH} > 7.5$, R^- is predominant and θ_{HR} is proportional to C_{H^+} as expressed in this figure.

Nomenclature

C_B	= total concentration of Versatic 10 in the organic phase	[mol/l]
C_i	= concentration of i -th component ($i = H^+, HR, H_2R_2, R^-$)	[mol/l]
HR	= species of monomeric form of Versatic 10	
H_2R_2	= species of dimeric form of Versatic 10	
K_1	= partition constant of Versatic 10 into the aqueous phase defined by Eq. (3)	[mol/l]
K_2	= dissociation constant of Versatic 10 in the aqueous phase	[mol/l]
K_{Ai}	= interfacial adsorption equilibrium constant of i -th species ($i = HR, R^-$)	[l/cm ²]
R	= gas constant	[dyne·cm/deg·mol]
R^-	= anionic species of Versatic 10	
S	= average interfacial area occupied by adsorbed species	[cm ² /mol]
S_i	= interfacial area occupied by i -th adsorbed species ($i = HR, R^-$)	[cm ² /mol]
T	= temperature	[K]
Γ_i	= moles of i -th adsorbed component per unit area	[mol/cm ²]
γ	= interfacial tension	[dyne/cm]
γ_0	= interfacial tension of diluent	[dyne/cm]
θ	= total fractional coverage of interface	[—]
θ_i	= fractional coverage of interface by i -th adsorbed species	[—]
μ_i	= chemical potential of i -th component	[dyne·cm/mol]

<Subscript>

aq.	= aqueous phase
ad.	= adsorbed
org.	= organic phase
0	= initial

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