

# Phase Behavior of Alcohol-Free Microemulsion Systems Containing Butyric Acid as a Cosurfactant

Xun-qiang Li, Jin-ling Chai,\* Shu-chuan Shang, Hong-liang Li, Jian-jun Lu, Bao Yang, and Yu-tong Wu

Department of Chemistry, Shandong Normal University, Jinan, Shandong 250014, People's Republic of China

The phase behavior of the alcohol-free microemulsion systems comprising of sodium dodecyl sulfate (SDS) + butyric acid + alkane + NaCl solution has been studied with an  $\epsilon$ - $\beta$  fishlike phase diagram method. The composition of the hydrophile-lipophile balanced (HLB) interfacial layer, the solubility of butyric acid, and the solubilization ability of the system, and so forth, were determined. The effects of the composition of the water phase, such as salts, acids, and alkali, and temperature on the phase behavior were investigated. As the salinity increases, the solubilization ability increases. The cations of the salts have notable influence on the phase diagrams. The influence of acid (HCl) is similar to that of salt (NaCl). However, alkali (NaOH) can remarkably affect the phase diagrams and shift the fish body to an upper position. A comparison of the  $\epsilon$ - $\beta$  phase diagrams is also made between the butyric acid-containing microemulsion systems and the 1-butanol-containing microemulsion systems.

## Introduction

Microemulsions are isotropic and thermodynamically stable systems of surfactant, alcohol, oil, and water. They are widely used in many fields such as enhanced oil recovery, detergency, cosmetics, pharmaceuticals, nanoparticle synthesis, and other chemical engineering industries.<sup>1-4</sup>

In microemulsion formulations short-chain alcohols are often used as a cosurfactant, which can provide the proper hydrophile-lipophile balance at the interfacial layer. Other functions of these alcohols include lowering the viscosity of the system, preventing the formation of rigid structures such as gels, liquid crystals, and precipitates, and reducing interfacial tension. They could also increase the mobility of the hydrocarbon tail, allowing for greater penetration of the oil into the interfacial layer and hence increasing the solubilization of the aqueous and oleic phases.<sup>5-9</sup>

However, the short-chain alcohols are not environmentally friendly because they are volatile and flammable substances. Moreover, the alcohol itself pollutes the groundwater and volatilizes into the atmosphere, causing an added water and air pollution problem. Therefore, nonvolatile alternatives are desirable for the environmental application of microemulsions.<sup>10-14</sup> Furthermore, these nonvolatile alternatives are desirable when airstripping the extracted solutions from the soil remediation processes, further improving system economics, and they may be desirable in consumer products as well.

Fatty acids are environmentally friendly and biodegradable substances and have low volatility. Butyric acid is often used in industrial applications, for example, pharmaceuticals, cosmetics, and food products.<sup>15,16</sup> In this paper, an  $\epsilon$ - $\beta$  fishlike phase diagram was used to study the phase behaviors of both alcohol-containing and alcohol-free microemulsions, which will be beneficial to improving our understanding of these additives.

## Experimental Section

**Materials.** Sodium dodecyl sulfate (SDS with mass fraction purity > 0.990) was purchased from Beijing Chemical Reagent Company, Ltd. and was recrystallized with the alcohol + acetone mixture twice. Butyric acid (with mass fraction purity > 0.99) was purchased from Shuangxi Flavor Reagent Company Ltd., Shanghai, China.

1-Butanol and *n*-hexane (with mass fraction purity > 0.995) were purchased from Sinopharm Chemical Reagent Company, Ltd., China, and are of analytically grade. Both reagents were used without further purification.

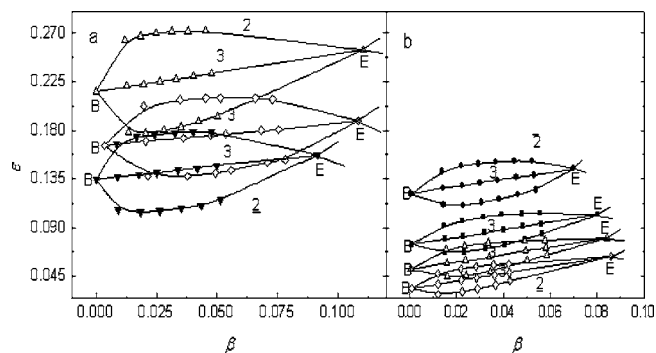
The inorganic salts (NaCl, KCl, CsCl, NaBr, and NaI, with mass fraction purity > 0.99), NaOH (with mass fraction purity > 0.99), and hydrochloric acid are all of analytical grade and were purchased from Sinopharm Chemical Reagent Company, Ltd. Doubly distilled water was used.

An electronic analytical balance (Shanghai, China), a 501 super thermostat (Jiangsu, China), and an 811 ultra centrifuge (Shanghai, China) were used in this experiment.

**Methods.** Samples were prepared by weighing the surfactant in a series of Teflon-sealed glass tubes, and equal masses of oil and water were also weighed in these tubes. Then butyric acid was added into the tubes. Its mass fractions were monotone, changing while the surfactant mass fractions were fixed at different values. The tubes were placed, fully submerged, into a thermostatic water bath at  $(303.15 \pm 0.01)$  K, and left to equilibrate for about 1 week. The samples were observed until the phase equilibrium was approached. The volumes of each phase were recorded.

In a microemulsion system of surfactant (S) + oil (O) + cosurfactant (A) + water (W), the following composition variables are defined as the mass fraction of oil to water plus oil in the system,  $\alpha = m_O/(m_O + m_W)$ ,  $\beta$  the mass ratio of the surfactant in the whole system,  $\beta = m_S/(m_S + m_A + m_O + m_W)$ , and  $\epsilon$  the mass ratio of the alcohol in the whole system,  $\epsilon = m_A/(m_S + m_A + m_O + m_W)$ .

\* Corresponding author. E-mail: jlchai99@163.com. Fax: +86-531-86180743.



**Figure 1.**  $\varepsilon$ - $\beta$  phase diagrams for the quaternary systems SDS + butyric acid (a) or 1-butanol (b) + *n*-hexane + NaCl solution. (a)  $\triangle$ , 0.075 (NaCl);  $\diamond$ , 0.100 (NaCl);  $\blacktriangledown$ , 0.125 (NaCl). (b)  $\bullet$ , 0.025 (NaCl);  $\blacksquare$ , 0.050 (NaCl);  $\triangle$ , 0.075 (NaCl);  $\diamond$ , 0.100 (NaCl). (2, Winsor I; 3, Winsor II; and E, Winsor III microemulsion).

If  $\alpha$ , temperature ( $T$ ), and pressure ( $P$ ) were held constant and  $\beta$  was plotted horizontally and  $\varepsilon$  vertically, a two-dimensional phase diagram  $\varepsilon$ - $\beta$  phase diagram could be obtained.

## Results and Discussion

**$\varepsilon$ - $\beta$  Fishlike Diagrams of the Microemulsion System Containing SDS + Butyric Acid + Oil + NaCl Solution.** The  $\varepsilon$ - $\beta$  phase diagrams for alcohol-free microemulsion systems containing butyric acid as a cosurfactant with different salinities SDS + butyric acid + *n*-hexane + NaCl solution were plotted in Figure 1a. The  $\varepsilon$ - $\beta$  fishlike phase diagrams for alcohol-containing microemulsion systems SDS + 1-butanol + *n*-hexane + NaCl solution were also plotted in Figure 1b for comparison.

It can be seen from Figure 1 that increasing  $\varepsilon$  at constant  $\beta$  causes a series of phase inversions, Winsor I  $\rightarrow$  Winsor III  $\rightarrow$  Winsor II. When  $\varepsilon$  is low, an oil-in-water microemulsion in contact with excess oil exists; as  $\varepsilon$  increases, the phase inverts into a water-in-oil microemulsion in contact with excess water via a middle-phase microemulsion in contact with excess oil and water.

The  $\varepsilon$ - $\beta$  phase diagram in Figure 1b is usually called the fishlike phase diagram according to its shape.<sup>17,18</sup> The “fish head” (point B) is the beginning point of the middle-phase microemulsion, and the “fish tail” (point E) is the intersection between three- and one-phase regions.

The  $\varepsilon$ - $\beta$  fishlike phase diagrams in Figure 1a for butyric acid microemulsion systems have the same shape as the alcohol microemulsion systems, which shows that fatty acid and alcohol play the same role in the formation of microemulsions. That is, butyric acid can act both as a cosurfactant and as a cosolvent in microemulsion systems.<sup>19</sup> Fatty acid can be incorporated into the interfacial layer, changing the curvature of the interfacial layer from positive toward negative values. Besides, part of the

fatty acid is also dissolved in the oil as a cosolvent, promoting a phase inversion of Winsor I  $\rightarrow$  III  $\rightarrow$  II.

At the “fish head”, the middle-phase microemulsion would start to form; so, the coordinates of the “fish head” ( $\beta_B$ ,  $\varepsilon_B$ ) values reflect the solubilities of surfactant ( $\beta_B$ ) and alcohol ( $\varepsilon_B$ ) in the whole system, and the “fish tail” ( $\beta_E$ ,  $\varepsilon_E$ ) shows the solubilization ability of the microemulsion systems.<sup>20</sup>

Some parameters were calculated from Figure 1a,b according to the literature<sup>20</sup> and are listed in Table 1.  $A^S$  is the mass fraction of alcohol in the balanced interfacial layer.  $C_A$  and  $C_S$  are the mass fractions of alcohol and surfactant contained in the interfacial layer in the whole system, respectively.  $R_{mol}$  ( $= n_S/n_A$ ) is the molar ratio of surfactant to alcohol in the balanced interfacial layer.  $SP^*$  is the mass of oil or of water per gram of surfactant in the microemulsion phase at the fish tail.

Table 1 shows that  $\beta_B$  is small and  $\beta_E \approx C_S$ , which means that surfactant SDS is nearly all incorporated into the interfacial layer, and little is solubilized in the aqueous or oleic phase. But,  $\varepsilon_B$  is large, and  $\varepsilon_E \gg C_A$ , which indicates that the alcohol, as mentioned above, has notable solubility in the aqueous or oleic phase apart from their entering into the interfacial layer.

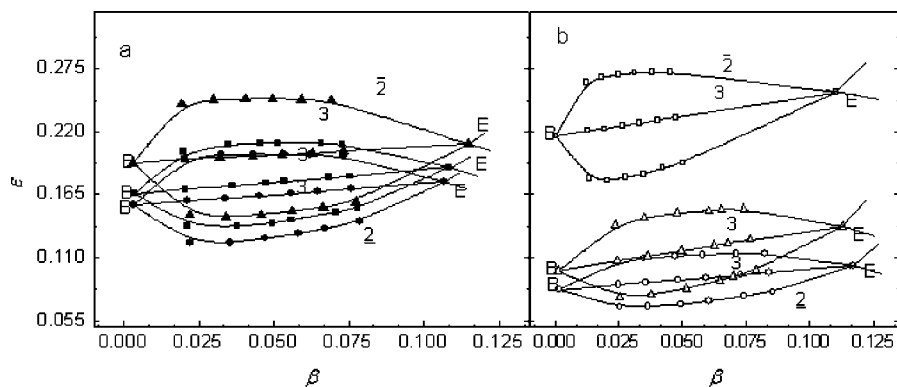
A comparison of the parameters in Table 1 can be made between butyric acid-containing microemulsion systems and 1-butanol-containing microemulsion systems. It can be seen from Table 1 that the solubility ( $\varepsilon_B$ ) of butyric acid is larger than that of 1-butanol. More butyric acid than 1-butanol is needed to solubilize the same quantities of water and oil at the “fish tail” ( $\varepsilon_E$ ), while the difference in the mass ratio of the surfactant ( $\beta_E$ ) is not obvious. In the interfacial layer, the mass fraction of butyric acid ( $A^S$ ) is also larger than that of 1-butanol. The maximum solubilization ability of the system,  $SP^*$ , is smaller for butyric acid microemulsion systems than that for 1-butanol microemulsion systems.

**Effects of Salinity on the  $\varepsilon$ - $\beta$  Fishlike Diagrams.** From Figure 1 and Table 1, it can be seen that salinity has a significant effect on the  $\varepsilon$ - $\beta$  phase diagrams for the quaternary systems SDS + butyric acid + *n*-hexane + NaCl solution and the related physicochemical parameters  $\varepsilon_B$ ,  $\varepsilon_E$ ,  $\beta_E$ ,  $A^S$ , and  $SP^*$ . As the salinity increases, the fishlike phase diagrams move to the lower place; the solubilities of butyric acid ( $\varepsilon_B$ ) decrease, and the mass fraction of butyric acid in the interfacial layer ( $A^S$ ) also decreases. However, the maximum solubilization ability ( $SP^*$ ) increases and tends to be the same as the 1-butanol microemulsion systems.

The decrease in the solubility of butyric acid ( $\varepsilon_B$ ) can be attributed to the salting-out effect of the salts. Besides, since the microemulsion droplets (O/W) are negatively charged, the addition of inorganic salts (such as NaCl) would compress the electrical double layer of the microemulsion droplets, weakening the repulsive forces between the droplets and promoting the phase inversions, so less cosurfactant is needed to change the phase, thus  $\varepsilon_E$  and  $A^S$  decrease.

**Table 1.** Values of  $\beta_B$ ,  $\varepsilon_B$ ,  $\beta_E$ ,  $\varepsilon_E$ ,  $C_S$ ,  $C_A$ ,  $A^S$ ,  $R_{mol}$ , and  $SP^*$  for the Quaternary Systems SDS + Alcohol + *n*-Hexane + NaCl Solution

$w(\text{NaCl})$	$\beta_B$	$\varepsilon_B$	$\beta_E$	$\varepsilon_E$	$C_S$	$C_A$	$A^S$	$R_{mol}$	$SP^*$
SDS + Butyric Acid + <i>n</i> -Hexane + NaCl Solution									
0.075	0.0002 $\pm$ 0.0001	0.216 $\pm$ 0.001	0.111 $\pm$ 0.001	0.254 $\pm$ 0.002	0.111 $\pm$ 0.001	0.079 $\pm$ 0.001	0.41 $\pm$ 0.02	1:2.3	2.88 $\pm$ 0.01
0.100	0.0004 $\pm$ 0.0001	0.166 $\pm$ 0.001	0.108 $\pm$ 0.001	0.189 $\pm$ 0.002	0.150 $\pm$ 0.001	0.048 $\pm$ 0.001	0.35 $\pm$ 0.02	1:1.5	3.26 $\pm$ 0.01
0.125	0.0001 $\pm$ 0.0001	0.134 $\pm$ 0.001	0.091 $\pm$ 0.001	0.157 $\pm$ 0.002	0.019 $\pm$ 0.001	0.041 $\pm$ 0.001	0.30 $\pm$ 0.02	1:1.4	4.12 $\pm$ 0.01
SDS + 1-Butanol + <i>n</i> -Hexane + NaCl Solution									
0.025	0.0007 $\pm$ 0.0001	0.121 $\pm$ 0.001	0.071 $\pm$ 0.001	0.145 $\pm$ 0.002	0.069 $\pm$ 0.001	0.037 $\pm$ 0.001	0.34 $\pm$ 0.02	1:1.4	5.52 $\pm$ 0.01
0.050	0.0008 $\pm$ 0.0001	0.074 $\pm$ 0.001	0.081 $\pm$ 0.001	0.102 $\pm$ 0.002	0.081 $\pm$ 0.001	0.036 $\pm$ 0.001	0.31 $\pm$ 0.02	1:1.0	5.04 $\pm$ 0.01
0.075	0.0005 $\pm$ 0.0001	0.051 $\pm$ 0.001	0.084 $\pm$ 0.001	0.081 $\pm$ 0.002	0.084 $\pm$ 0.001	0.035 $\pm$ 0.001	0.30 $\pm$ 0.02	1:0.8	4.97 $\pm$ 0.01
0.100	0.0009 $\pm$ 0.0001	0.034 $\pm$ 0.001	0.086 $\pm$ 0.001	0.063 $\pm$ 0.002	0.085 $\pm$ 0.001	0.033 $\pm$ 0.001	0.29 $\pm$ 0.02	1:0.6	4.95 $\pm$ 0.01



**Figure 2.** Effects of anions (a) and cations (b) on the  $\varepsilon$ - $\beta$  phase diagrams for systems SDS + butyric acid + *n*-hexane + salt solution with different salinities. (a) Salts ( $1.71 \text{ mol}\cdot\text{L}^{-1}$ ): ●, NaCl; ■, NaBr; ▲, NaI. (b) Salts ( $1.28 \text{ mol}\cdot\text{L}^{-1}$ ): □, NaCl; △, CsCl; ○, KCl.

**Table 2.** Values of  $\beta_B$ ,  $\varepsilon_B$ ,  $\beta_E$ ,  $\varepsilon_E$ ,  $C_S$ ,  $C_A$ ,  $A^S$ , and  $SP^*$  for the Quaternary Systems SDS + Alcohol + Alkane + Salt Solution

salt	$\beta_B$	$\varepsilon_B$	$\beta_E$	$\varepsilon_E$	$C_S$	$C_A$	$A^S$	$SP^*$
SDS + Butyric Acid + <i>n</i> -Hexane + $1.71 \text{ mol}\cdot\text{L}^{-1}$ Salt Solution								
NaCl	$0.004 \pm 0.001$	$0.166 \pm 0.002$	$0.108 \pm 0.001$	$0.189 \pm 0.002$	$0.105 \pm 0.001$	$0.048 \pm 0.001$	$0.314 \pm 0.002$	$3.25 \pm 0.02$
NaBr	$0.003 \pm 0.001$	$0.156 \pm 0.002$	$0.107 \pm 0.001$	$0.176 \pm 0.002$	$0.104 \pm 0.001$	$0.043 \pm 0.001$	$0.293 \pm 0.002$	$3.35 \pm 0.02$
NaI	$0.003 \pm 0.001$	$0.193 \pm 0.002$	$0.115 \pm 0.001$	$0.209 \pm 0.002$	$0.112 \pm 0.001$	$0.047 \pm 0.001$	$0.295 \pm 0.002$	$2.94 \pm 0.02$
SDS + Butyric Acid + <i>n</i> -Hexane + $1.28 \text{ mol}\cdot\text{L}^{-1}$ Salt Solution								
NaCl	$0.0002 \pm 0.0001$	$0.216 \pm 0.002$	$0.111 \pm 0.001$	$0.254 \pm 0.002$	$0.111 \pm 0.001$	$0.079 \pm 0.001$	$0.418 \pm 0.002$	$2.86 \pm 0.02$
CsCl	$0.001 \pm 0.001$	$0.098 \pm 0.002$	$0.113 \pm 0.001$	$0.137 \pm 0.002$	$0.112 \pm 0.001$	$0.056 \pm 0.001$	$0.342 \pm 0.002$	$3.32 \pm 0.02$
KCl	$0.002 \pm 0.001$	$0.082 \pm 0.002$	$0.117 \pm 0.001$	$0.103 \pm 0.002$	$0.116 \pm 0.001$	$0.033 \pm 0.001$	$0.223 \pm 0.002$	$3.33 \pm 0.02$

**Table 3.** Values of  $\beta_B$ ,  $\varepsilon_B$ ,  $\beta_E$ ,  $\varepsilon_E$ ,  $C_S$ ,  $C_A$ ,  $A^S$ , and  $SP^*$  for the Quaternary Systems SDS + Alcohol + Alkane + Aqueous Solution

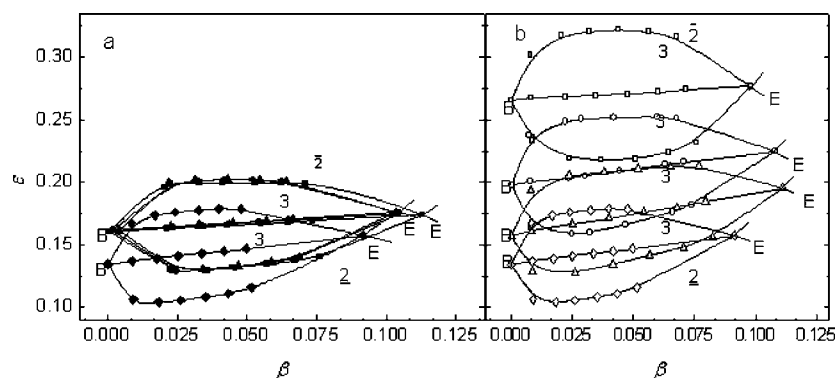
	$\beta_B$	$\varepsilon_B$	$\beta_E$	$\varepsilon_E$	$C_S$	$C_A$	$A^S$	$SP^*$
SDS + Butyric Acid + <i>n</i> -Hexane + (Na,H)Cl Solution								
0.07 (NaCl) + 0.05 (HCl)	$0.0007 \pm 0.0001$	$0.160 \pm 0.001$	$0.113 \pm 0.002$	$0.174 \pm 0.002$	$0.112 \pm 0.001$	$0.037 \pm 0.001$	$0.250 \pm 0.002$	$3.15 \pm 0.02$
0.08 (NaCl) + 0.04 (HCl)	$0.0018 \pm 0.0001$	$0.161 \pm 0.001$	$0.105 \pm 0.002$	$0.175 \pm 0.002$	$0.103 \pm 0.001$	$0.037 \pm 0.001$	$0.262 \pm 0.002$	$3.43 \pm 0.02$
0.10 (NaCl) + 0.02 (HCl)	$0.0041 \pm 0.0001$	$0.162 \pm 0.001$	$0.104 \pm 0.002$	$0.176 \pm 0.002$	$0.100 \pm 0.001$	$0.036 \pm 0.001$	$0.266 \pm 0.002$	$3.46 \pm 0.02$
0.12 (NaCl)	$0.0002 \pm 0.0001$	$0.134 \pm 0.001$	$0.091 \pm 0.002$	$0.157 \pm 0.002$	$0.091 \pm 0.001$	$0.041 \pm 0.001$	$0.308 \pm 0.002$	$4.13 \pm 0.02$
SDS + Butyric Acid + <i>n</i> -Hexane + Na(Cl,OH) Solution								
0.07 (NaCl) + 0.05 (NaOH)	$0.0003 \pm 0.0001$	$0.266 \pm 0.001$	$0.098 \pm 0.002$	$0.277 \pm 0.002$	$0.090 \pm 0.001$	$0.051 \pm 0.001$	$0.341 \pm 0.002$	$3.19 \pm 0.02$
0.08 (NaCl) + 0.04 (NaOH)	$0.0004 \pm 0.0001$	$0.198 \pm 0.001$	$0.108 \pm 0.002$	$0.225 \pm 0.002$	$0.100 \pm 0.001$	$0.061 \pm 0.001$	$0.360 \pm 0.002$	$3.09 \pm 0.02$
0.10 (NaCl) + 0.02 (NaOH)	$0.0003 \pm 0.0001$	$0.157 \pm 0.001$	$0.111 \pm 0.002$	$0.194 \pm 0.002$	$0.111 \pm 0.001$	$0.066 \pm 0.001$	$0.374 \pm 0.002$	$3.13 \pm 0.02$
0.12 (NaCl)	$0.0002 \pm 0.0001$	$0.134 \pm 0.001$	$0.091 \pm 0.002$	$0.157 \pm 0.002$	$0.091 \pm 0.001$	$0.041 \pm 0.001$	$0.308 \pm 0.002$	$4.13 \pm 0.02$

**Effects of Anions and Cations on the  $\varepsilon$ - $\beta$  Fishlike Diagrams.** The effects of the salts with different anions and the same cation (NaCl, NaBr, NaI), and of the salts with the different cations and the same anion (NaCl, CsCl, KCl) on the  $\varepsilon$ - $\beta$  phase diagrams are shown in Figure 2. The parameters were all calculated and are listed in Table 2.

Figure 2 and Table 2 show that the salts with the same cation and different anions have the less influence on the  $\varepsilon$ - $\beta$  phase diagrams than that of the salts with the same anion and different cations.

The microemulsion droplets are negatively charged, and the electrical double layer of the microemulsion is mainly oppressed by cations, so the salts with the same cation and different anions have less influence.

The values of  $\varepsilon_B$ ,  $\varepsilon_E$ , and  $A^S$  in the salts with the same anion and different cations are in the order of NaCl > CsCl > KCl, which may relate to the properties of the cations. According to Puerto and Reed and others,<sup>21,22</sup> the magnitude of the hydrated ion radii is the following:  $\text{Na}^+ > \text{K}^+ > \text{Cs}^+$ .  $\text{Na}^+$  with the maximal hydrated ion radius has the minimal oppression to the



**Figure 3.** Effects of acid (a) and alkali (b) on the  $\varepsilon$ - $\beta$  fishlike diagram for microemulsions SDS + butyric acid + *n*-hexane + aqueous solution with different salinities. (a) ■, 0.07 (NaCl) + 0.05 (HCl); ●, 0.08 (NaCl) + 0.04 (HCl); ▲, 0.10 (NaCl) + 0.02 (HCl); ◆, 0.12 (NaCl). (b) □, 0.07 (NaCl) + 0.05 (NaOH); ○, 0.08 (NaCl) + 0.04 (NaOH); △, 0.10 (NaCl) + 0.02 (NaOH); ◇, 0.12 (NaCl).

**Table 4.** Values of  $\beta_B$ ,  $\epsilon_B$ ,  $\beta_E$ ,  $\epsilon_E$ ,  $C_S$ ,  $C_A$ ,  $A^S$ , and  $SP^*$  for the Microemulsion System SDS + Butyric Acid + *n*-Hexane + NaCl Solution ( $w = 0.10$ )

T/K	$\beta_B$	$\epsilon_B$	$\beta_E$	$\epsilon_E$	$C_S$	$C_A$	$A^S$	$SP^*$
293.15	0.005 ± 0.001	0.156 ± 0.002	0.111 ± 0.002	0.183 ± 0.001	0.107 ± 0.001	0.052 ± 0.001	0.35 ± 0.02	3.12 ± 0.02
303.15	0.004 ± 0.001	0.166 ± 0.002	0.108 ± 0.002	0.187 ± 0.001	0.105 ± 0.001	0.048 ± 0.001	0.35 ± 0.02	3.26 ± 0.02
313.15	0.002 ± 0.001	0.171 ± 0.002	0.094 ± 0.002	0.197 ± 0.001	0.092 ± 0.001	0.051 ± 0.001	0.36 ± 0.02	3.77 ± 0.02
323.15	0.001 ± 0.001	0.167 ± 0.002	0.094 ± 0.002	0.198 ± 0.001	0.093 ± 0.001	0.056 ± 0.001	0.36 ± 0.02	3.77 ± 0.02
333.15	0.003 ± 0.001	0.163 ± 0.002	0.086 ± 0.002	0.191 ± 0.001	0.083 ± 0.001	0.048 ± 0.001	0.36 ± 0.02	4.21 ± 0.02

electrical double layer, and the largest quantity of alcohol is needed to promote the phase inversions.

**Effects of Acid and Alkali on the  $\epsilon$ - $\beta$  Fishlike Diagrams.** The effects of acid (HCl) and alkali (NaOH) on the  $\epsilon$ - $\beta$  fishlike diagrams of system containing SDS + butyric acid + *n*-hexane + NaCl solution are shown in Figure 3, and the related parameters are listed in Table 3.

When the mass ratio of NaCl to HCl was varied, keeping the sum of the mass fractions of NaCl and HCl in the aqueous phase fixed, it was found that the  $\epsilon$ - $\beta$  phase diagrams nearly coincide with each other (Figure 3a). This indicates that  $Na^+$  and  $H^+$  have a close effect on these phase diagrams.

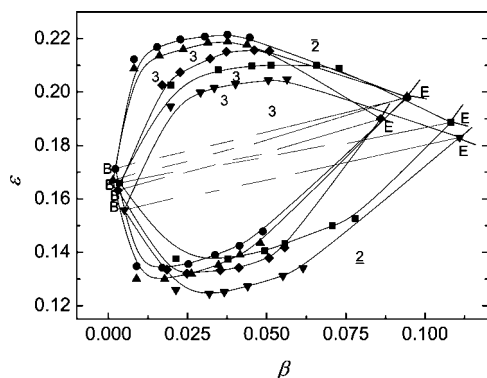
However, if the mass fractions of NaCl and NaOH are fixed, as the mass fraction of NaOH increases, the  $\epsilon$ - $\beta$  phase diagrams move upwardly (Figure 3b). This phenomenon may be explained by the fact that the  $OH^-$  ion may neutralize the cosurfactant butyric acid to form butyrate, decreasing the mass ratio of butyric acid in the system, so more butyric acid is needed as a cosurfactant to balance the interfacial layer; thus, the phase diagrams move upwardly.

**Effect of Temperature on the  $\epsilon$ - $\beta$  Fishlike Diagrams.** Figure 4 shows the effect of temperature on the  $\epsilon$ - $\beta$  fishlike diagram for the microemulsion system SDS + butyric acid + *n*-hexane + 0.10 (NaCl) solution.

As temperature rises from (293.15 to 333.15) K, the phase diagrams in Figure 4 move upwardly a little. The solubility ( $\epsilon_B$ ) of butyric acid listed in Table 4 was a little increased with temperature on the whole, and the composition of the interfacial layer changes ( $A^S$  increases). The maximum solubilization ability of the system,  $SP^*$ , increases with temperature. In short, it was favorable to the solubilization of the system to increase temperatures.

## Conclusions

The  $\epsilon$ - $\beta$  phase diagrams for microemulsion systems containing butyric acid as a cosurfactant, SDS + butyric acid + *n*-hexane + NaCl solution, were studied.



**Figure 4.** Effect of temperature on the  $\epsilon$ - $\beta$  fishlike phase diagrams for the systems SDS + butyric acid + *n*-hexane + NaCl solution ( $w = 0.10$ ).  $\nabla$ , 293.15 K;  $\blacksquare$ , 303.15 K;  $\bullet$ , 313.15 K;  $\blacktriangle$ , 323.15 K;  $\blacklozenge$ , 333.15 K.

Fatty acids can be used as cosurfactant to form microemulsions. Butyric acid can act as both a cosurfactant and a cosolvent in microemulsion systems.

The solubility of butyric acid in microemulsions is larger than that of 1-butanol. In the interfacial layer, the mass fraction of butyric acid is also larger than that of 1-butanol.

As salinities increase, the solubility of butyric acid in aqueous and oleic phases decreases as well as the mass fraction of butyric acid in the interfacial layer, but the maximum solubilization ability ( $SP^*$ ) increases and tends to be the same as the 1-butanol microemulsion systems.

The cations of the salts have notable influence on the  $\epsilon$ - $\beta$  phase diagrams, but the anions of the salts have minimal influence on the phase behavior.

The influence of acid is similar to that of the salt, while  $OH^-$  may neutralize butyric acid, resulting in the phase diagram movement upward.

An increase in temperature from (293.15 to 333.15) K was favorable to the solubilization of the system.

## Literature Cited

- (1) Shinoda, K.; Lindman, B. Organized Surfactant Systems: Microemulsions. *Langmuir* **1987**, *3*, 135–149.
- (2) Friberg, S. E.; Bothorel, P. *Microemulsion: Structures and Dynamics*; CRC Press: Boca Raton, 1987.
- (3) Holmberg, K. Organic and Bioorganic Reactions in Microemulsions. *Adv. Colloid Interface Sci.* **1994**, *51*, 137–174.
- (4) Dungan, S. R.; Solans, C.; Kuneida, H. Industrial Application of Microemulsions; *Surfactant Science Series*; New York, 1997.
- (5) Abdul, A. S.; Gibson, T. L.; Rai, D. N. Selection of Surfactants for the Removal of Petroleum Products from Shallow Sandy Aquifers. *Ground Water* **1990**, *28*, 920–926.
- (6) Jafvert, C. T. Sediment- and Saturated-Soil-Associated Reactions Involving an Anionic Surfactant (dodecylsulfate). 2. Partition of PAH Compounds Among Phases. *Environ. Sci. Technol.* **1991**, *25*, 1039–1045.
- (7) Rouse, J. D.; Sabatini, D. A.; Brown, R. E.; Harwell, J. H. Evaluation of the Ethoxylated Alkylsulfate Surfactants for Use in Subsurface Remediation. *Water Environ. Res.* **1996**, *68*, 162–168.
- (8) Pennell, K. D.; Abriola, L. M.; Weber, W. J., Jr. Surfactant Enhanced Solubilization of Residual Dodecane in Soil Columns. 1. Experimental Investigation. *Environ. Sci. Technol.* **1993**, *27*, 2332–2340.
- (9) Shiau, B. J.; Sabatini, D. A.; Harwell, J. H. Solubilization and Microemulsification of Chlorinated Solvents Using Direct Food Additive (edible) Surfactants. *Ground Water* **1994**, *32*, 561–569.
- (10) Kahlweit, M.; Busse, G.; Faulhaber, B.; Eibl, H. Preparing Nontoxic Microemulsions. *Langmuir* **1995**, *11*, 4185–4187.
- (11) Shiau, B. J.; Sabatini, D. A.; Harwell, J. H. Properties of Food Grade (edible) Surfactants Affecting Subsurface Remediation of Chlorinated Solvents. *Environ. Sci. Technol.* **1995**, *29*, 2929–2935.
- (12) Selle, M. H.; Sjoblom, J.; Skutveit, R. Emulsions Under Elevated Pressure and Temperature Conditions. II. The Model System Water (electrolyte)–Octanoic Acid–Sodium Octanoate–*n*-Heptane at 20 °C. *J. Colloid Interface Sci.* **1991**, *144*, 36–44.
- (13) Sunwoo, C. K.; Wade, W. H. Optimal Surfactant Structures for Cosurfactant-free Microemulsion System I. C16 and C14 Guerbet Alcohol Hydrophobes. *J. Dispersion Sci. Technol.* **1992**, *13*, 491–514.
- (14) Ash, M.; Ash, I. *Handbook of Industrial Surfactants*, 2nd ed.; Synapse Publication: New York, 1997; Vol. 1, pp 1396–1415.
- (15) Ash, M.; Ash, I. *Handbook of Industrial Surfactants*, 2nd ed.; Synapse Publication: New York, 1997; Vol. 2, pp 2403–2420.
- (16) Hellweg, T. Phase Structures of Microemulsions. *J. Colloid Interface Sci.* **2002**, *7*, 50–56.

- (17) Jong-Moon, L.; Kyung-Hee, L. Change in Two-phase Emulsion Morphology in Temperature Amphiphile Concentration or Fish Diagram for Ternary Amphiphile/Oil/Water Systems. *J. Colloid Interface Sci.* **2005**, *290*, 241–249.
- (18) Lohateeraparp, P.; Wilairuengsuwan, P.; Saiwan, C.; Sabatini, D. A.; Harwell, J. H. Study of Alcohol-Free Microemulsion Systems Containing Fatty Acids as Cosurfactants. *J. Surfactants Deterg.* **2003**, *6*, 15–24.
- (19) Yang, X. D.; Li, H. L.; Chai, J. L.; Gao, Y. H.; Chen, J. F.; Lou, A. J. Phase Behavior Studies of Quaternary Systems Containing *N*-lauroyl-*N*-methylglucamide/Alcohol/Alkane/Water. *J. Colloid Interface Sci.* **2008**, *320*, 283–289.
- (20) Puerto, M. C.; Reed, R. L. In Surfactant Selection Using the Three Parameter Diagram, SPE paper 14290, presented at the 60th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Las Vegas, NV, 1985.
- (21) Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Scientific Elsevier: New York, 1981.
- (22) Oh, S. G.; Shah, D. O. Effect of Counterions on the Interfacial Tension and Emulsion Droplet Size in the Oil/Water/Dodecyl Sulfate System. *J. Phys. Chem.* **1993**, *97*, 284–286.

Received for review January 20, 2010. Accepted March 31, 2010. This project was granted financial support from the Natural Science Foundation of Shandong Province of China (Grant ZR2009BM036).

JE100060T