Chinese Chemical Letters Vol. 15, No. 3, pp 361-364, 2004 361
http://www.imm.ac.cn/journal/ccl.html

Studies on Phase Behavior of Alkyl Polyglucoside Based on Microemulsions with Modified Fishlike Phase Diagram

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Abstract: The three-phase behavior in the quaternary system of an alkyl ($C_{8/10}$- or $C_{12/14}$-) polyglucoside / 1-butanol / *n*-octane / water has been studied at 40 ℃ with the modified fishlike phase diagram, which is presented by us for the first time. The mass fraction of 1-butanol in the hydrophile-lipophile balanced interfacial layer, A^S, the coordinates of the start point B and the end point E of the phase diagram, and the solubilities of alkyl polyglucoside and 1-butanol in *n*-octane phase were calculated. The solubilization of the microemulsion was also discussed.

Keywords: Alkyl polyglucoside, microemulsion, phase diagram, solubilization.

Alkyl polyglucosides (APG) are green nonionic surfactants which have been received attention in recent years[1-3]. One potential use for APG is in microemulsion formulations[4]. Compared with the ethylene oxide-based compounds (C_iE_j), the more commonly used nonionic surfactants to produce microemulsions, APG-based micro-emulsions are less influenced by temperature and have many advantages[5]. Therefore, the research on APG-based microemulsions is of great importance.

Surfactant systems, which form microemulsions containing equal amounts of oil and water, are called balanced. Of particular interest are the microstructure[6,7] of the balanced interfacial film and the solubilizing power for these systems. The fishlike phase diagram is often used to calculate the composition of the film and evaluate the solubilizing power[8-10]. Since the midst line of the middle-phase region in this kind of phase diagram is a steep curve, and its HLB plane equation contains a reciprocal term ($1/\gamma$), therefore it is difficult to draw out the midst line precisely and calculate the composition of the film accurately, when the γ values are very small. In addition, the abscissas of the start point B (γ_B) and the end point E (γ_E) of the phase diagram represent the mass fractions of the total amounts of APG and 1-butanol, lacking clear physical meanings.

In the present paper, a modified fishlike phase diagram is presented for the first time and it has advantages over the fishlike phase diagram in visual observations of the phase changes and the solubilization of the microemulsion, and calculating the related physical

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parameters.

Experimental

The commercial alkyl polyglucosides with mixed-chain $C_{8/10}G_{1.31}$ and $C_{12/14}G_{1.43}$ used in this work were kindly provided by Research Institute of Daily Chemical Industry, China, which are supplied as 50 wt% solutions in water with high pH value to avoid microbial attack. Their compositions were determined by chromatograms to be $C_{8/10}G_{1.31}$ (monoglucoside 77.18%, diglucoside 16.61%, triglucoside 4.30%, tetraglucoside 1.91%) and $C_{12/14}G_{1.43}$ (monoglucoside 71.56%, diglucoside 17.52%, triglucoside 6.77%, tetraglucoside 4.15%), respectively.

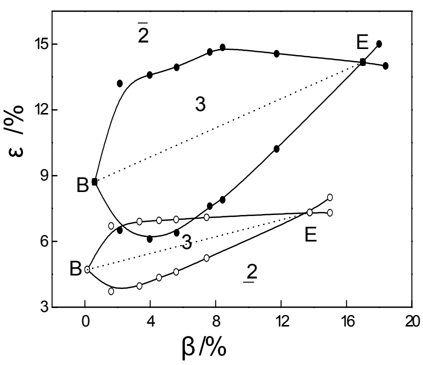
Samples are prepared where 1-butanol varies monotonically, while the APG concentrations are fixed at different values. A water- to- octane weight ratio of unity is preferred. All samples are allowed to equilibrate at (40±0.1)℃ in a water bath for one or two weeks. Phase equilibrium was determined by visual observations of a large number of samples. At last the volumes of the middle-phase microemulsions were recorded and the modified fishlike phase diagrams were plotted.

The methodology used here is established by ourselves. For a quaternary system of water(W)-oil(O)-alcohol(A)-surfactant(S), the following composition variables are most suitable for our purposes and are defined as the mass ratio of oil to water plus oil in the system, α = O/(W+O); the mass fraction of the surfactant in the system, β= S/(W+O+A+S); and the mass fraction of alcohol in the system, ε= D/(W+O+A+S). If α was held constant (0.50), the β is plotted horizontally and the ε is plotted vertically, a two-dimensional phase diagram (β～ε) can be obtained.

Results and Discussion

The phase diagram for water/APG/1-butanol/*n*-octane system is shown in **Figure 1**.

Figure 1 The modified fishlike phase diagram of the quaternary system $C_{8/10}G_{1.31}$ or $C_{12/14}G_{1.43}$ / 1-butanol / *n*-octane / water system at 40 ℃ and α =0.5



●- $C_{8/10}G_{1.31}$; ○- $C_{12/14}G_{1.43}$

It can be seen that increasing β at constant ε causes a series of phase inversions

Winsor I→III→II. It is known that the whole phase behavior of a quaternary system at constant temperature and pressure can be done in a phase tetrahedron, a section through such a phase tetrahedron at $\alpha=0.5$ is a particular three-phase tie triangle including the microemulsion in the midst of the Winsor III region (**Figure 1**). This section is called a hydrophile-lipophile balanced plane (HLB plane)[8].

The hydrophile-lipophile property of the mixed amphiphilic film in the quaternary system is just balanced in the midst line of the middle-phase region (see the broken line in **Figure 1**). The composition of the microemulsion in the midst line of the Winsor III region obeys the HLB plane equation

$$\varepsilon = \frac{A^S - F\alpha}{1 - A^S + F\alpha}\beta + \frac{F\alpha}{1 - A^S + F\alpha} \qquad F = \frac{A^o S^s - S^o A^s}{1 - S^o - A^o} \tag{1}$$

Where S^o and A^o are solubilities of APG monomers and 1-butanol in oil, and S^S, A^S denote the mass fractions of APG and 1-butanol in the interfacial film which is composed of surfactant and 1-butanol, respectively. A plot of ε *vs.* β is a straight line (the broken line in **Figure 1**). If the slope and intercept of Eq. (1) are K and I, respectively, then A^S can be obtained by

$$A^S = \frac{K + I}{1 + K} \tag{2}$$

The experimental values of A^S can be obtained from Eq. (2) and shown in **Table 1.**

Table 1 Physical parameters of β_B, ε_B, β_E, ε_E, S^o, A^o, and A^S for the quaternary systems alkyl polyglucoside / 1- butanol / *n*-octane /H_2O

APG	β_B	$\varepsilon_{,B}$	β_E	$\varepsilon_{,E}$	S^O	A^O	A^S
$C_{8/10}G_{1.31}$	0.0059	0.0871	0.170	0.142	0.011	0.159	0.296
$C_{12/14}G_{1.43}$	0.0015	0.0471	0.138	0.0732	0.003	0.090	0.200

The volume fraction ϕ of the middle phase at the midst line (**Figure 1**) was measured for a series of β values and plotted as a function of β (the Fig. was omitted). Extrapolation of this linear function to $\phi=0$ and $\phi=1$ yields the abscissas of the start point B (β_B) and the end point E (β_E). The ordinates of these two points (ε_B and ε_E) can be obtained by using the HLB plane equation (Eq. 1). The values are listed in **Table 1**. From β_B and ε_B values, the solubilities of APG and 1-butanol in *n*-octane can be obtained (See **Table** 1), respectively. β_E and ε_E reveal the minimum concentration of APG and 1-butanol, respectively, for getting a single microemulsion system while the ratio of water to oil is equal 1.

Acknowledgment

This project is supported by the National Natural Science Foundation of China (No:20243005).

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Received 12 February, 2003