

Studies on Middle-Phase Microemulsions of Green Surfactant *n*-Dodecyl Polyglucoside C₁₂G_{1.46}

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The three-phase behavior in the quaternary system of *n*-dodecyl polyglucoside C₁₂G_{1.46}/1-butanol/cyclohexane/water has been studied at 40 °C in terms of the variables γ and δ . Increasing δ at constant γ causes a phase inversion from an oil-in-water microemulsion in contact with excess oil (winsor I or $\bar{2}$) to a water-in-oil microemulsion in contact with excess water (winsor II or $\bar{2}$) via a middle-phase microemulsion in contact with excess oil and water (winsor III or 3). By taking into account the different solubilities of alkyl polyglucoside and 1-butanol in the oil phase, the composition of the hydrophile-lipophile balanced interfacial film in the middle of the three-phase body can be calculated. The effects of different oils and aqueous media on the phase behavior and on the composition of the interfacial film and the efficiency for alkyl polyglucoside to make equal weights of water and oil to a single phase were investigated. It was found that the oil molecules with small molecular volumes can improve the solubilizing efficiency of the surfactant to form single-phase microemulsion. In inorganic salt (NaCl) and acid (HCl) solutions, less 1-butanol is needed than that in alkali (NaOH) solution to form middle-phase microemulsion.

Keywords alkyl polyglucoside, microemulsion, phase diagram, interfacial film

Introduction

There is at present great interest in developing chemicals that are made from renewable raw materials. This is certainly true also for the case of surfactants. Alkyl polyglucosides (APG) are an interesting class of green nonionic surfactants that have received considerable attention in recent years.^{1,2} These surfactants are synthesized from renewable raw materials such as sugars and fatty alcohols, and have excellent biodegradability and good surface-active properties. One potential use for APG is in microemulsion formulations.³ Microemulsions are thermodynamically stable, isotropic mixtures of water, oil, alcohol and surfactant, and are used in various fields such as tertiary oil recovery, pharmaceuticals, cosmetics, nanoparticle synthesis and chemical engineering. The more commonly used nonionic surfactants so far to produce

microemulsions are the ethylene oxide-based compounds (C_iE_j). In microemulsion systems containing C_iE_j surfactants, a partial dehydration of the oxyethylene chain of C_iE_j molecules may be caused and phase inversion may be promoted by raising temperature, this sensitivity to temperature can be a disadvantage in certain fields of application. It has been found that temperature has only a weak influence on the phase behavior and other properties of microemulsion systems containing alkyl polyglucoside.⁴ This insensitivity of APG microemulsion systems was invariable with the change of temperature resulting from the strength of the hydrogen bonds between the hydroxy groups of the glucose moiety and water molecules, which prevents any significant dehydration of the head group in the relevant temperature range. So APG microemulsion systems can replace C_iE_j³ in many applications of microemulsion systems.

Surfactant systems, which form microemulsions containing equal amount of oil and water, are termed balanced. Of particular interest are such surfactant systems that achieve this with low amount of surfactants. The microstructure of these systems is typically bicontinuous and consists of a monolayer of surfactant of near-zero mean curvature separating oil domains from water domains. In the present paper, the detailed microstructure of the balanced interfacial film in the middle of the three-phase region of C₁₂G_{1.46} microemulsion systems has been studied.

Experimental

Materials

n-Dodecyl polyglucoside was synthesized by our research group, and its composition was determined by GC to be C₁₂G_{1.46} (monoglucoside 70.71%, diglucoside 17.42%, triglucoside 6.45% and tetraglucoside or more 5.42%). The other materials used in this study are all of A. R. grade and

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are used without further purification. Water was doubly distilled.

Methods

Phase equilibrium was determined by visual inspections of a large number of samples with different overall compositions. The samples were prepared by weight in Teflon-sealed glass tubes and allowed to equilibrate at 40 °C in a water bath for one or two weeks.

The phase behavior in a cut through the multidimensional phase diagram defined by a constant temperature, pressure and water-to-oil ratio was studied. The methodology used here was introduced by Kahweit and coworkers⁵ for a quaternary system of water (A)-oil (B)-surfactant (C)-alcohol (D). 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, $\alpha = m(B)/[m(A) + m(B)]$, the mass fraction of the surfactant and cosurfactant in the system, $\gamma = [m(C) + m(D)]/[m(A) + m(B) + m(C) + m(D)]$, and the mass fraction of alcohol in the surfactant and alcohol mixture, $\delta = m(D)/[m(C) + m(D)]$. Making a two-dimensional phase diagram for a quaternary mixture requires that three of the variables T , p , α , γ and δ be held constant. If T (40 °C) and α (0.50) are held constant (with pressure p constant at ambient), the γ is plotted horizontally and the δ is plotted vertically, a two-dimensional phase diagram ($\delta \sim \gamma$) can thus be obtained.

Results and discussion

Phase diagram

The phase diagram for C₁₂G_{1.46}/1-butanol/cyclohexane/water system as functions of the composition variables γ and δ , at $\alpha = 0.50$ and 40 °C, is shown in Fig. 1.

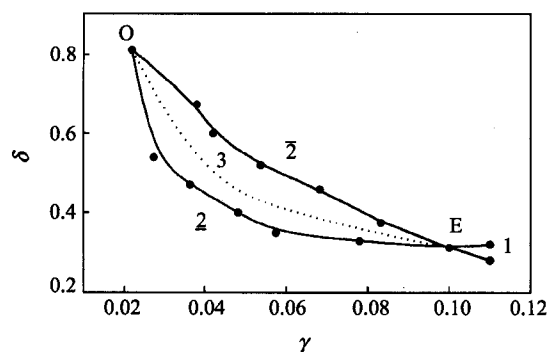


Fig. 1 Phase diagram of the quaternary C₁₂G_{1.46}/1-butanol/cyclohexane/water system at 40 °C and $\alpha = 0.5$ as functions of γ and δ . 2, Winsor I region, 3, Winsor III region, 2-bar, Winsor II region, 1, single-phase region; O, start point, E, end point of the three-phase region.

It can be seen from Fig. 1 that increasing δ at constant γ causes a phase inversion from an oil-in-water microemul-

sion in contact with excess oil (2) to a water-in-oil microemulsion in contact with excess water (2-bar) via a middle-phase microemulsion in contact with excess oil and water (3). The $\gamma \sim \delta$ graph in Fig. 1 is usually called *fishlike* phase diagram.

An alcohol can act both as a cosurfactant and as a cosolvent in microemulsion systems.⁶ As a cosurfactant, 1-butanol is incorporated into the interfacial film, changing the curvature of the amphiphile film from positive values (*i. e.*, oil on the concave side of the interfacial film) toward negative values (*i. e.*, water on the concave side of the film). Accordingly, 1-butanol is expected to cause a transition from oil-in-water droplet microemulsion (2) to water-in-oil droplet microemulsion (2-bar). As a hydrophobic cosolvent, 1-butanol partitions predominantly into the oil and causes the oil to become effectively more polar. As a consequence the surfactant C₁₂G_{1.46} will also partition more and more into the oil phase where it can support a water-in-oil droplet microemulsion. So 1-butanol as a hydrophobic cosolvent will also promote a phase inversion of 2-3-2-bar.

The distorted shape of the three-phase body in Fig. 1 shows that much higher proportions of alcohol are necessary to reach three-phase coexistence, at low γ than at high γ , which is a direct consequence of the competition, between the incorporation of 1-butanol molecules into the interfacial film and its solubility in the bulk oil phase.⁷ When an alcohol is added to the system, part of it is dissolved in the oil and is not available as cosurfactant. This preferential extraction of 1-butanol from the amphiphile mixture (surfactant and alcohol) leads to a decreasing lipophilicity of the interfacial film. The fraction of alcohol that is extracted into the oil phase increases with decreasing γ . In order to compensate for this dissolved alcohol, a higher fraction of alcohol is needed to obtain a balanced interfacial film.

Region of three-phase body

With increasing γ , three-coexisting-phase forms at point O ("head", γ_o, δ_o), and terminates at point E where equal amount of water and oil are solubilized in a single-phase microemulsion ("tail", γ_e, δ_e). The compositions of these two points cannot be determined directly with acceptable accuracy, as the volumes of the middle phase becomes zero at the "head" (γ_o, δ_o) and the volumes of the two excess phases become zero at the "tail" (γ_e, δ_e). The volume fraction ϕ of the middle phase at the mid-point $\bar{\delta}$ was measured for a series of γ values and plotted as a function of γ (Fig. 2). Extrapolation of this linear function to $\phi = 0$ and to $\phi = 1$ yields $\gamma_o = 0.022$ and $\gamma_e = 0.100$, as shown in Table 1. The values of δ at these two points were obtained by applying the equation of the HLB plane [Eq. (1)]. A nonionic surfactant changes from hydrophilic to lipophilic via a three-phase region, the hydrophile-lipophile property of the surfactant in a given system is just balanced in the midst of the three-phase region. The hydrophile-lipophile balanced plane (HLB plane)⁸ is defined by the condition of equal mass fractions of

oil and water in the surfactant phase.

The whole phase behavior of the present four-component system can be expressed by a composition tetrahedron at constant temperature and pressure.⁸ The location of the three-phase region in the α - δ - γ composition space can be characterized by the locus of $\bar{\delta}$, the mid-point value of δ in the three-phase region for given values of α and γ . The locus of $\bar{\delta}$ is just an intersection of the HLB plane at the given α , and $\bar{\delta}$ is given by⁸

$$\bar{\delta} = S_2^S + A\alpha(1/\gamma - 1); \quad A = \frac{S_2 S_1^S - S_1 S_2^S}{1 - S_1 - S_2} \quad (1)$$

where S_1 and S_2 are monomeric solubilities of $C_{12}G_{1.46}$ and 1-butanol in oil, respectively, and S_1^S , S_2^S denote respectively the mass fractions of surfactant and 1-butanol in the interfacial film which is composed of surfactant and 1-butanol. A plot of $\bar{\delta}$ vs. $(1/\gamma - 1)$ shown in Fig. 3 is indeed a straight line, then we obtain $\delta_0 = 0.811$ and $\delta_e = 0.312$. The experiment values of γ_e , δ_e and S_2^S are shown in Table 1.

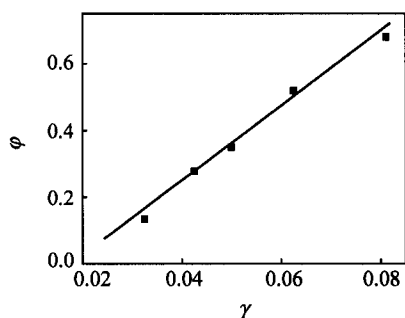


Fig. 2 Volume fractions, φ , of the middle-phase at the mid-point of the three-phase body as a function of γ at $\alpha = 0.5$.

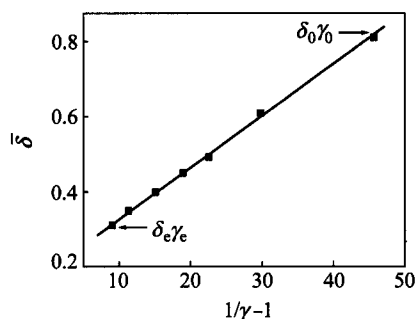


Fig. 3 Plot of $\bar{\delta}$ vs. $1/\gamma - 1$ for the $\bar{\delta}$, γ -values in the middle of the three-phase body.

Point E in Fig. 1 indicates the intersection between three-phase and single-phase regions, and it reveals the minimum concentration of APG for getting a single microemulsion system while the ratio of water to oil is equal to 1.⁷ The γ_e value of $C_{12}G_{1.46}$ is small, so the solubilizing power of $C_{12}G_{1.46}$ is fairly large.

Composition of the amphiphile film at the HLB plane

The mass fractions of APG and 1-butanol in the interfacial film can be calculated by using the simple mass balance equation.⁷ For a surfactant and a cosurfactant system, the following relations hold

$$C_1 = (1 - \delta_e)\gamma_e - \frac{\alpha S_1(1 - \gamma_e)}{1 - S_1 - S_2}$$

$$C_2 = \delta_e\gamma_e - \frac{\alpha S_2(1 - \gamma_e)}{1 - S_1 - S_2} \quad (2)$$

where C_1 and C_2 are the mass fractions of APG and 1-butanol in the water-oil interface region of the point E. (γ_e , δ_e) in Fig. 1. In Eq. (2) the solubilities of surfactant and alcohol in the water phase are neglected. Since these solubilities are very small, this approximation can not influence C_1 and C_2 values significantly.⁶ S_1 and S_2 can be obtained from the composition of point O.⁸

$$S_1 = \frac{(1 - \delta_0)\gamma_0}{\alpha(1 - \gamma_0) + \gamma_0} \quad S_2 = \frac{\delta_0\gamma_0}{\alpha(1 - \gamma_0) + \gamma_0} \quad (3)$$

where γ_0 , δ_0 are the composition of the system at point O. From Eq. (3) one obtains $S_1 = 0.008$ and $S_2 = 0.035$ (Table 1), substituting these values into Eq. (2) and using the values of δ_e and γ_e , $C_1 = 0.0650$ and $C_2 = 0.0148$ are obtained and shown in Table 1. The effective γ_e value $\gamma_{\text{eff}} = C_1 + C_2 = 0.080$. The fact that γ_{eff} is lower than $\gamma_e(0.100)$ can be attributed to the solubility of APG and 1-butanol in the oil domains of the microemulsion. From the values of C_1 and C_2 , the mass fractions of surfactant and 1-butanol in the interfacial film, $S_1^S = C_1/(C_1 + C_2)$, and $S_2^S = C_2/(C_1 + C_2)$, can be calculated. At point E we obtain $S_1^S = 0.815$ and $S_2^S = 0.185$. Eqs. (2) and (3) can be used to calculate the relative proportions of surfactant and alcohol in the interfacial film not only for point E, but also for any other point

Table 1 Values of γ_e , δ_e , S_1 , S_2 , C_1 , C_2 and S_2^S for the quaternary systems n -dodecyl polyglucoside $C_{12}G_{1.46}$ /1-butanol/different oils/ H_2O

| Oil | V_m^a | γ_e | δ_e | S_1^b | S_2^b | C_1^c | C_2^c | $C_2/(C_1 + C_2)^c$ | $S_2^S^d$ |
|-------------|---------|------------|------------|---------|---------|---------|---------|---------------------|-----------|
| Toluene | 106.3 | 0.101 | 0.235 | 0.004 | 0.013 | 0.0753 | 0.0180 | 0.193 | 0.193 |
| Cyclohexane | 108 | 0.100 | 0.312 | 0.008 | 0.035 | 0.0650 | 0.0148 | 0.185 | 0.186 |
| Hexane | 130.7 | 0.163 | 0.328 | 0.001 | 0.069 | 0.109 | 0.0224 | 0.170 | 0.170 |
| Octane | 162.5 | 0.204 | 0.326 | 0.007 | 0.093 | 0.134 | 0.0256 | 0.160 | 0.159 |

^a Molecular volume of oil ($\text{mL} \cdot \text{mol}^{-1}$); ^b obtained by Eq. (3); ^c obtained by Eq. (2); ^d obtained by Eq. (1).

along the trajectory $\bar{\delta}$, γ of the mid-points of the three-phase region, if one uses the appropriate values of $\bar{\delta}$, γ instead of δ_e , γ_e in Eq. (2). The result shows that the proportions of surfactant and alcohol in the interfacial film remain constant through the entire three-phase region. This result is consistent with expectation that along this trajectory, the mean curvature H of the interfacial film should be zero, and a certain ratio of 1-butanol to APG in the interfacial film exists.

S_2^S represents the intercept of Eq. (1). Extrapolation of the experimental values of $\bar{\delta}$, yields $S_2^S = 0.186$ in agreement with the above calculation. This agreement of the two S_2^S values implies that two methods are adequate for calculation of S_2^S .

Effects of oil and aqueous medium on the phase behavior

The $\delta \sim \gamma$ phase diagrams for $C_{12}G_{1.46}$ /1-butanol/oil/water system in various oils and various aqueous media are plotted in Figs. 4 and 5. The values of γ_e , δ_e , S_1 , S_2 , C_1 , C_2 and S_2^S for these systems calculated from Eqs. (1)–(3) are listed in Tables 1 and 2, respectively. It can be seen from Figs. 4 and 5 and Tables 1 and 2 that oil and aqueous medium have notable influence on the region of three-phase body and on the composition of the amphiphile film at the HLB plane (C_1 , C_2 and S_2^S) and the solubilizing power (γ_e).

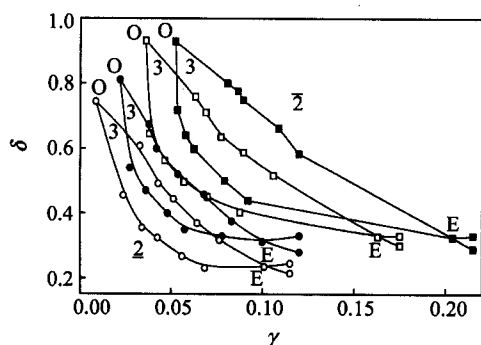


Fig. 4 $\delta \sim \gamma$ Phase diagram for the quaternary system *n*-dodecyl polyglucoside $C_{12}G_{1.46}$ /1-butanol/different oils/water at $\alpha = 0.5$. ■, Octane; □, hexane; ●, cyclohexane; ○, toluene.

The solubilizing power of the microemulsion in various oils decreases in the following order: toluene \sim cyclohexane

$>$ hexane $>$ octane (Table 1). That is, as the molecular volume V_m (Table 1) of oil increases, the solubilizing power decreases. This phenomenon can be explained in terms of the penetrating ability of oil to the surfactant palisade layer. Since the smaller oil tends to penetrate the surfactant palisade layer, the amphiphile layer tends to be convex toward oil, which favors the change of the curvature of the amphiphile layer, so less surfactant mixture (surfactant and cosurfactant, especially surfactant) is needed to balance the hydrophilic-lipophile property of the amphiphile layer.⁷ Therefore note that the ratio of surfactant and cosurfactant [S_2^S or $C_2/(C_1 + C_2)$] decreases a little in these microemulsion systems.

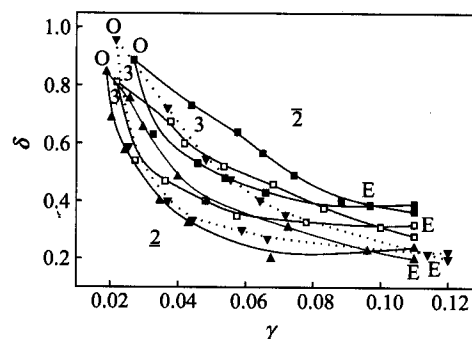


Fig. 5 $\delta \sim \gamma$ Phase diagram for the quaternary system *n*-dodecyl polyglucoside $C_{12}G_{1.46}$ /1-butanol/cyclohexane/different aqueous media at $\alpha = 0.5$. ■, 0.2 mol/L NaOH; □, H_2O ; ▲, 0.2 mol/L NaCl; ▼, 0.2 mol/L HCl.

From Table 2 we see that aqueous medium with acid or base property influences the ratio of surfactant and cosurfactant [S_2^S or $C_2/(C_1 + C_2)$] in the water-oil interface region, and the mass fraction of alcohol in the surfactant and alcohol mixture, δ_e , significantly. In 0.2 mol/L NaCl and HCl solutions, “salting out” effect exists and favors the phase inversion, so less cosurfactant is needed to form middle-phase microemulsion. In 0.2 mol/L NaOH solution, δ_e and S_2^S values are larger than that in any other three water media. This is most likely related to the deprotonation of the glucose molecule. In strong alkaline solution it would be expected that a fraction of APG is deprotonated and these molecules therefore act as an anionic surfactant.⁹ This deprotonation favors the hydration of the hydrophilic headgroup, which makes the amount of alcohol needed to form middle-phase microemulsion increases.

Table 2 Values of γ_e , δ_e , S_1 , S_2 , C_1 , C_2 and S_2^S for the quaternary systems *n*-dodecyl polyglucoside $C_{12}G_{1.46}$ /1-butanol/cyclohexane/different aqueous media

| Aqueous medium | γ_e | δ_e | S_1^a | S_2^a | C_1^b | C_2^b | $C_2/(C_1 + C_2)^b$ | $S_2^S^c$ |
|------------------|------------|------------|---------|---------|---------|---------|---------------------|-----------|
| HCl (0.2 mol/L) | 0.114 | 0.218 | 0.002 | 0.041 | 0.0883 | 0.0060 | 0.064 | 0.065 |
| NaCl (0.2 mol/L) | 0.096 | 0.227 | 0.006 | 0.031 | 0.0716 | 0.0071 | 0.090 | 0.105 |
| H_2O | 0.100 | 0.312 | 0.008 | 0.035 | 0.0650 | 0.0148 | 0.185 | 0.186 |
| NaOH (0.2 mol/L) | 0.097 | 0.386 | 0.006 | 0.046 | 0.0567 | 0.0152 | 0.211 | 0.212 |

^a Obtained by Eq. (3); ^b obtained by Eq. (2); ^c obtained by Eq. (1).

Conclusions

The phase diagram for $C_{12}G_{1.46}$ /1-butanol/cyclohexane/water system as functions of the composition variables γ and δ , at $\alpha = 0.50$ and $40\text{ }^\circ\text{C}$, has been plotted. 1-Butanol in this microemulsion system can act both as a cosurfactant and as a cosolvent. The distorted shape of the three-phase body is believed to be a direct consequence of the competition, between the incorporation of 1-butanol molecules into the interfacial film and its solubility in the bulk oil phase.

The coordinates at the "head" (γ_0 , δ_0) and "tail" (γ_e , δ_e) points of the phase diagram were obtained by applying the equation of the HLB plane. The γ_e values of $C_{12}G_{1.46}$ is small, so the solubilizing power of $C_{12}G_{1.46}$ is fairly large. The mass fraction of 1-butanol in the interfacial film in the $C_{12}G_{1.46}$ /1-butanol/cyclohexane/water system, S_2^S , was calculated to be 0.186.

In addition, the effects of oil and aqueous medium on the phase behavior were also investigated, which shows that oil and aqueous medium have notable influence on the region of three-phase body and on the composition of the amphiphile film (C_1 , C_2 and S_2^S) and the solubilizing power (γ_e). It was found that the oil molecules with small molecular volumes

can improve the solubilizing efficiency of the surfactant to form single-phase microemulsion. In inorganic salt (NaCl) and acid (HCl) solutions, less 1-butanol is needed than that in alkali (NaOH) solution to form middle-phase microemulsion.

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