Middle-phase microemulsions of green surfactant alkyl polyglucosides

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Abstract The microemulsion behavior in the quaternary system alkyl polyglucoside ($C_8G_{1.46}$, $C_{10}G_{1.54}$)/1-butanol/cyclohexane/water has been studied at 40℃ with the alcohol concentration scanning and the fishlike phase diagram methods. Increasing d at a constant ã causes a phase inversion from an oil-in-water microemulsion in contact with excess oil (Winsor I or $\underline{2}$) to a water-in-oil microemulsion in contact with excess water (Winsor II or $\overline{2}$) via a middle-phase microemulsion in contact with excess oil and water (Winsor III or 3). By using the simple mass balance equation and the HLB plane equation, the mass fraction of 1-butanol in the interfacial layer, S_2^s, the monomeric solubilities of APG and 1-butanol, S_1 and S_2, in the oil phase, and the mass fractions of APG and 1-butanol in the interfacial layer (C_1 and C_2) have been calculated, respectively. The effects of different alcohols, aqueous media and oils on the phase behavior and the composition of the interfacial layer are also investigated. It is found that the alcohols with longer hydrocarbon chain, oil molecules with smaller molecular volume and the addition of inorganic salt can increase the solubilization of the microemulsions .

Keywords: alkyl polyglucoside, microemulsion, HLB plane, phase diagram, solubilization.

Microemulsions are important organized molecular assembles in surfactant solutions and are used in various fields such as tertiary oil recovery, pharmaceutics, cosmetics, nanoparticle synthesis and chemical engineering. The more commonly used nonionic surfactants to produce microemulsions are the ethylene oxide-based compounds (C_iE_j). In recent years alkyl polyglucosides have been received considerable attention in producing microemulsions[1—7]. Alkyl polyglucosides (APG), which are widely used as surfactants in commercial products, represent a complex mixture of C_iG_j homologues, where i is the number of carbon atoms in the hydrocarbon chain and j the number of glucose units in the hydrophilic head group. These surfactants are synthesized from renewable raw materials such as sugars and fatty alcohols, and have excellent biodegradability and good surface-active properties[1—8]. Compared with C_iE_j, APG microemulsions are less influenced by temperature on both the phase behavior and properties[7]. So research on the APG microemulsion systems is of great significance. In the previous papers[9—13], we have investigated the formation and properties of middle phase microemulsion of different systems using concentration scanning method. A cut through the multidimensional phase diagram varying the *d* and *g* at fixed *a* is called fishlike phase diagram, because the three-phase body and its contiguous V-shaped region of one-phase microemulsion can be said to form the body and tail of a fish. In this paper we have studied the fishlike phase diagram to investigate the ternary phase behavior of the system of alkyl polyglucoside ($C_8G_{1.46}$, $C_{10}G_{1.54}$)/1-butanol/cyclohexane/water. The detailed microstructure of the balanced interfacial layer in the middle-phase region of alkyl polyglucoside microemulsion systems has been studied using the simple mass balance equation and the HLB plane equation, which will lead to better utilization of alkyl polyglucoside microemulsion in some industrial applications.

1 Experimental

1.1 Materials and apparatus

Two kinds of alkyl polyglucosides were synthesized from the corresponding long-chain alcohols by our research group, and their compositions were determined by the chromatograms to be $C_8G_{1.46}$ and $C_{10}G_{1.54}$. The other materials used in this study are all A.R. grade and used without further purification. Water was doubly distilled.

GC-9A gas chromatograph (Shimadzu, Japan), FA1104 electron balance, 501 super thermostat, and ultra centrifuge were used in this experiment.

1.2 Methods

Phase equilibrium was determined by visual observations 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 ± 0.1)℃ in a water bath for one or two weeks. Then the volumes of the middle-phase microemulsions were recorded and the fishlike phase diagrams were plotted. Experiment shows that temperature has little influence on the phase behavior.

2 Results and discussion

2.1 Synthesis and product composition of alkyl polyglucoside

Octyl- and decyl-polyglucosides are synthesized[14—16] from glucose and alcohols using the one-step method in the presence of acid catalyst. The gas chromatographs were used to determine the degrees of glycosidation. The GC spectra are shown in fig. 1.

The size of the column used for the determination of GC is 0.5 m (length) × 3 mm (inside diameter), the fixing agent 5% Dexsil 300, the rate of raising temperature $8℃\cdot min^{-1}$, and the temperature range 80—350℃.

Alkyl polyglucosides consist of a distribution of species with different degrees of glycosidation and have many isomerisms such as stereoisomerism with α- and β-anomers. The different

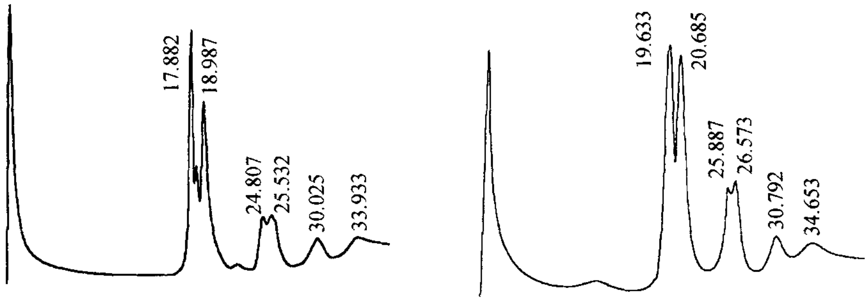

Fig. 1. GC spectra of octyl polyglucoside (left) and decyl polyglucoside (right).

signals in fig. 1 can be assigned in this way: The two signals of 17.882 and 18.987 (left), 19.633 and 20.685 min (right) are yielded by α- and β-anomers of octyl- and decyl-monoglucosides, respectively. 24.807 and 25.532 (left), 25.887 and 26.573 min (right) are yielded by α- and β-anomers of octyl- and decyl-diglucosides, respectively. octyl- and decyl-triglucosides are found at 30.025 (left) and 30.792 min (right). octyl- and decyl-tetraglucosides can be found at 33.933 (left) and 34.653 min (right). Integrating the intensities of different signals allows calculation of the degrees of glycosidation of alkyl polyglucosides. The calculated results of the average compositions of octyl- and decyl-polyglucosides are $C_8G_{1.46}$ (monoglucoside 70.00%, diglucoside19.00%, triglucoside 6.00%, tetraglucoside or more 5.00%) and $C_{10}G_{1.54}$ (monoglucoside 68.80%, diglucoside17.20%, triglucoside 5.50%, tetraglucoside or more 8.50%), respectively.

2.2 Alcohol concentration scanning phase diagram

The alcohol concentration scanning phase diagram for the quaternary system alkyl polyglucoside ($C_8G_{1.46}$ or $C_{10}G_{1.54}$)/1-butanol/cyclohexane/water is shown in fig. 2. It can be seen from fig. 2 that when the concentration (weight ratio) of 1-butanol is lower than 6.64% ($C_8G_{1.46}$) or 3.44% ($C_{10}G_{1.54}$), an oil-in-water microemulsion in contact with excess oil ($\underline{2}$) exists. When the alcohol concentration is higher than 11.47% ($C_8G_{1.46}$) or 5.77% ($C_{10}G_{1.54}$), the phase inverts to a water-in-oil microemulsion in contact with excess water ($\overline{2}$) via a middle-phase microemulsion in contact with excess oil and water (3). Compared the widths of alcohol of the middle-phase microemulsion for $C_8G_{1.46}$ and $C_{10}G_{1.54}$, the former is from 6.64% to 11.47%, and the latter is from 3.44% to 5.77%. To obtain

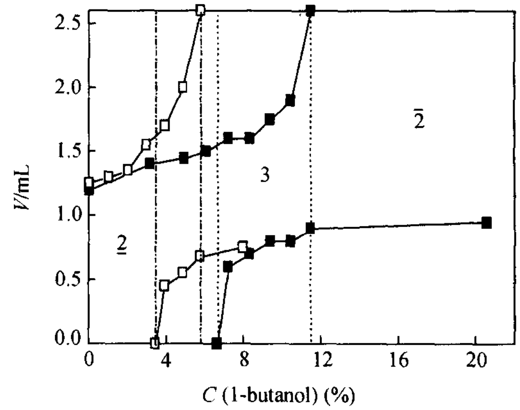

Fig. 2. Alcohol concentration scanning phase diagram for system alkyl polyglucoside/1-butanol/cyclohexane/water at 40℃. $\alpha = 0.5$. [APG]=7%; ■, $C_8G_{1.46}$; □, $C_{10}G_{1.54}$.

more information and parameters about the middle-phase microemulsion, the fishlike phase diagrams are studied as follows.

2.3 Fishlike phase diagrams and the calculation of related parameters

According to Kahlweit and his coworkers[17] for a quaternary system of water(A)-oil (B)-alcohol(C)-surfactant (D), the following composition variables are most suitable for our purposes and defined as the mass ratio of oil to water plus oil in the system, $a = B/(A+B)$, the mass fraction of the surfactant and cosurfactant in the system, $g = (C+D)/(A+B+C+D)$, and the mass fraction of alcohol in the surfactant and alcohol mixture, $d = D/(C+D)$. Making a two-dimensional phase diagram for a quaternary mixture requires that three of the variables T, P, a, g and d be held constant. If $T((40\pm0.1)℃)$ and a (0.50) are constants (with pressure P constant at ambient), the $\tilde{a}$ is plotted horizontally and the d is plotted vertically, a two-dimensional phase diagram (d-$\tilde{a}$) can be obtained. The phase diagram for alkyl polyglucoside ($C_8G_{1.46}$ or $C_{10}G_{1.54}$)/1-butanol/cyclohexane/water system as functions of the composition variables $\tilde{a}$ and d, at a = 0.50 and 40℃, is shown in fig. 3.

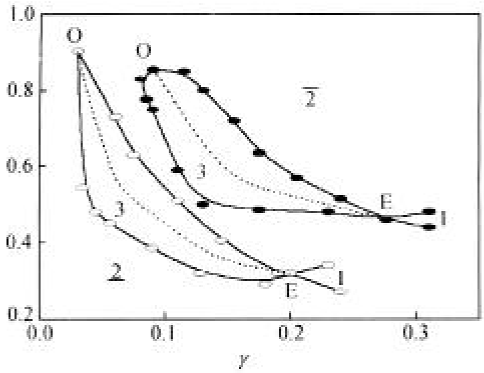

Fig. 3. Fishlike phase diagram of the quaternary system alkyl polyglucoside ($C_8G_{1.46}$ or $C_{10}G_{1.54}$)/1-butanol/cyclohexane/water system at 40℃ as functions of γ and δ. $\alpha = 0.5$; ●, $C_8G_{1.46}$, ○, $C_{10}G_{1.54}$.

It can be seen from fig. 3 that an oil-in-water microemulsion coexists with excess oil phase ($\underline{2}$) at a low d. With increasing d, surfactant aggregates separate from water, and a three-phase body consisting of excess water, surfactant (microemulsion), and excess oil phases appears. With further increase in d, surfactant mainly dissolves in oil and a water-in-oil microemulsion coexists with excess water phase. The phase inversion is caused mainly by the dissolve of alkanol in the interfacial layer, and thereby, its properties and the curvature of the amphiphile layer are changed 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). The $\tilde{a}$-d graph in fig. 3 is usually called fishlike phase diagram[18].

The middle-phase region in fig. 3 is shifted to the higher d at the lower $\tilde{a}$, which shows that much higher proportions of 1-butanol are necessary to reach three-phase coexistence, at lower $\tilde{a}$ than that at higher ã, which is a direct consequence of the competition, between the incorporation of 1-butanol molecules into the interfacial layer and its solubility in the bulk oil phase. When alcohol is added to the system, part of the alcohol is dissolved in the oil and 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 layer. The fraction of alcohol extracted into the oil phase increases with decreasing $\tilde{a}$. In order to compensate for this dissolved alcohol, a higher fraction of alcohol is needed to obtain a balanced interfacial layer. In addition, 1-butanol partitions into the oil and causes the oil to become effectively more polar, which will also promote a phase inversion of $\underline{2}$ -3- $\bar{2}$.

Alkyl polyglucoside changes from hydrophilic to lipophilic via a middle-phase region, and its hydrophile-lipophile property in a given system is just balanced in the midst of the middle-phase region[10,12]. Since the whole phase behavior of the present four-component system can be expressed by a composition tetrahedron at constant temperature and pressure, the particular three-phase tie triangle including the microemulsion in the midst of the middle-phase region should be a plane in it. This plane is called hydrophile-lipophile balanced plane (HLB plane)[11] and defined by the condition of equal mass fractions of oil and water solubilized in the surfactant phase. The midst of the middle-phase region (fig. 3) can be characterized by the locus of $\bar{d}$, the mid-point value of d in the middle-phase region for given values of a and $\tilde{a}$. The HLB plane equation can be expressed as follows[18]:

$$\begin{aligned} \bar{d} &= S_2^{\mathrm{s}} + Aa(1/\bar{g} - 1), \\ A &= \frac{S_2 S_1^{\mathrm{s}} - S_1 S_2^{\mathrm{s}}}{1 - S_1 - S_2}, \end{aligned} \tag{1}$$

where S_1 and S_2 are monomeric solubilities of APG and 1-butanol in oil, respectively, and S_1^{s} and S_2^{s} denote the mass fractions of surfactant and 1-butanol in the interfacial layer which is composed of surfactant and 1-butanol. A plot of $\bar{d}$ vs. $1/\bar{g} - 1$ is shown in fig. 4, showing that a plot of $\bar{d}$ vs. $1/\bar{g} - 1$ is indeed a straight line. With this relation, S_2^{s} represents the intercept of eq. (1), extrapolation of the experimental values of $\bar{d}$, yields S_2^{s} to be 0.317 ($C_8G_{1.46}$) and 0.238 ($C_{10}G_{1.54}$).

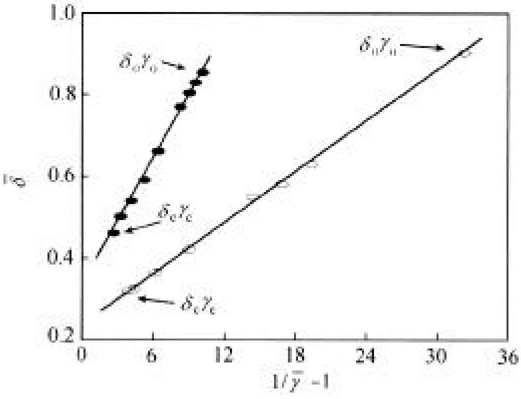

Fig. 4. Plot of $\bar{\delta}$ vs. $1/\bar{\gamma}-1$ for the $\bar{\delta}$, $\bar{\gamma}$-values in the middle of the three-phase body. $\alpha = 0.5$. ●, $C_8G_{1.46}$; ○, $C_{10}G_{1.54}$.

The middle-phase region is terminated (i) at high d and low $\tilde{a}$, where the microemulsion phase disappears ("head", $\tilde{a}_0$, d_0) and (ii) at low d and high $\tilde{a}$, where equal amount of water and oil are solubilized in a one-phase microemulsion ("tail", $\tilde{a}_e$, d_e). The compositions of these two points cannot be determined directly with acceptable accuracy, as the volumes of the middle phase become zero at the "head" ($\tilde{a}_0$, d_0) and that of the two excess phases become zero at the "tail" ($\tilde{a}_e$, d_e).

The volume fraction f of the middle

phase at the mid-point $\bar{d}$ is measured for a series of $\tilde{a}$ values and plotted as a function of $\bar{g}$ (fig. 5). Extrapolation of this linear function to $f = 0$ and to $f = 1$ yields $\tilde{a}_0 = 0.09$ ($C_8G_{1.46}$), 0.03 ($C_{10}G_{1.54}$) and $\tilde{a}_e = 0.276$ ($C_8G_{1.46}$), 0.200 ($C_{10}G_{1.54}$). The values of d at these two points (d_0 and d_e) can be obtained by applying the HLB plane equation (eq. (1)). Substituting the values of $\tilde{a}_0$ into eq. (1), the values of d_0 are obtained to be 0.855 ($C_8G_{1.46}$) and 0.902 ($C_{10}G_{1.54}$), and that of d_e are also obtained in the same way to be 0.460 ($C_8G_{1.46}$) and 0.320 ($C_{10}G_{1.54}$).

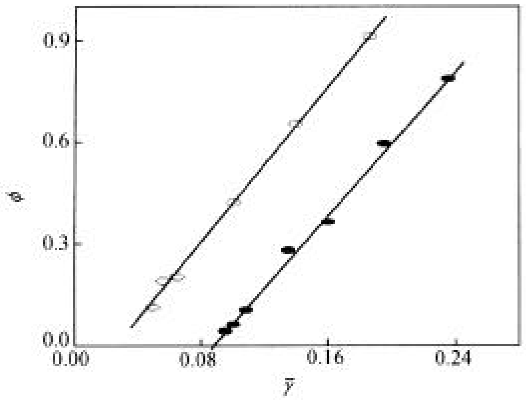

Fig. 5. Volume fractions, ϕ, of the middle-phase at the mid-point of the middle-phase region as a function of $\bar{\gamma}$. $\alpha = 0.5$; ●, $C_8G_{1.46}$; ○, $C_{10}G_{1.54}$.

With the approximation that the solubilities of surfactant and alcohol in the water phase are neglected, and the excess oil phase is saturated with surfactant and alcohol, S_1 and S_2 can be obtained from the composition of point O[19]:

$$S_1 = \frac{(1-d_0)g_0}{a(1-g_0)+g_0}, \qquad S_2 = \frac{d_0 g_0}{a(1-g_0)+g_0}. \tag{2}$$

From eq. (2), S_1 and S_2 are obtained to be 0.0130 and 0.077 ($C_8G_{1.46}$), and 0.0029 and 0.027 ($C_{10}G_{1.54}$), respectively.

Since surfactant molecules at water-oil interface inside a microemulsion phase are related to the solubilization, it is necessary to calculate the composition of the interfacial layer at the HLB plane. If excess water phase is pure water and the composition of excess oil phase is the same as that in the micro-oil domain of microemulsion, the mass fractions of APG and 1-butanol in the interfacial layer (C_1 and C_2) can be calculated by using the simple mass balance equation. For a surfactant and a cosurfactant system, the following relations hold[20]

$$C_1 = (1-d_e)g_e - \frac{aS_1(1-g_e)}{1-S_1-S_2}, \qquad C_2 = d_e g_e - \frac{aS_2(1-g_e)}{1-S_1-S_2}, \tag{3}$$

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 ($\tilde{a}_e$, d_e) in fig. 3. Inserting S_1 and S_2 values into eq. (3) and using the values of d_e and $\tilde{a}_e$, C_1 and C_2 are obtained to be 0.139 and 0.066 ($C_8G_{1.46}$), and 0.134 and 0.042 ($C_{10}G_{1.54}$), respectively. The ratio of 1-butanol to APG molecules in the balanced interfacial layer can be calculated from the values of C_1 and C_2 to be about 1∶2.3 ($C_8G_{1.46}$) and 1∶1.6 ($C_{10}G_{1.54}$).

Eqs. (2) and (3) can be used to calculate the relative proportions of surfactant and alcohol in the interfacial layer not only for point E, but also for any other points along the trajectory $\bar{d}$, $\bar{g}$ of the mid-points of the three-phase region, if one uses the appropriate values of $\bar{d}$, $\bar{g}$ instead of d_e, $\tilde{a}_e$ in eq. (3). The result shows that the proportions of surfactant and alcohol in the interfacial layer remain constant through the entire three-phase region. This result is consistent with the expectation that along this trajectory, the mean curvature H of the interfacial layer should be zero, and a certain ratio of 1-butanol to APG in the interfacial layer exists.

In order to conform the former results (S_2^s), we can calculate the S_2^s in another way. From the values of C_1 and C_2, the mass fractions of surfactant and 1-butanol in the interfacial layer, $S_2^s = C_2/(C_1 + C_2)$, can be calculated. The values of $C_2/(C_1 + C_2)$ are 0.322 ($C_8G_{1.46}$) and 0.239 ($C_{10}G_{1.54}$). It can be seen that S_2^s values obtained from eq. (1) are in agreement with the $C_2/(C_1 + C_2)$ values calculated from eq. (3). This result implies that both the methods are adequate for calculation of the composition of the interfacial film at the HLB plane .

The fact that the effective $\tilde{a}_e$ value $\tilde{a}_{eff}$ (= $C_1 + C_2$) is lower than $\tilde{a}_e$, can be attributed to the solubility of APG and 1-butanol in the oil domains of the microemulsion.

Point *E* in fig. 3 indicates the intersection between three-phase and single-phase regions, and $\tilde{a}_e$ reveals the minimum concentration of APG for getting a single microemulsion system while the ratio of water to oil equals 1[20]. The smaller the $\tilde{a}_e$ value, the larger the solubilization of the system. The solubilization of the microemulsion $C_{10}G_{1.54} > C_8G_{1.46}$. That is, the longer the hydrocarbon chain of APG molecules, the larger the solubilization. $C_{10}G_{1.54}$ molecules are less hydrophilic and less alcohol is needed to balance the hydrophile-lipophile property of the surfactant in a given water-oil system.

2.4 Effect of alcohol on the phase behavior

The *d*-*ã* phase diagram for $C_8G_{1.46}$/different alcohols/cyclohexane/water systems is plotted in fig. 6. The values of $\tilde{a}_e$, d_e, S_1, S_2, C_1, C_2 and S_2^s for these systems calculated from eqs. (1)–(3) are listed in table 1.

From table 1 we see that the solubilization ($\tilde{a}_e$) of the microemulsion with different alcohols increases and the ratio of 1-butanol to APG molecules in the balanced interfacial layer decreases as the alcohol chain length increases. As we have discussed above, alcohol acts as both cosurfactant and cosolvent in microemulsions. As a cosurfactant, alcohol molecules arrange themselves in the layer with the OH group oriented toward the aqueous domain and in this way, the amphiphilic mixture may be conceived as such a double-tailed surfactant as AOT. There are two predominant effects of the alcohol in the interfacial layer: one is to change the hydrophilicity of the amphiphilic mixture, the other is to increase the solubilizing capacity of the amphiphilic

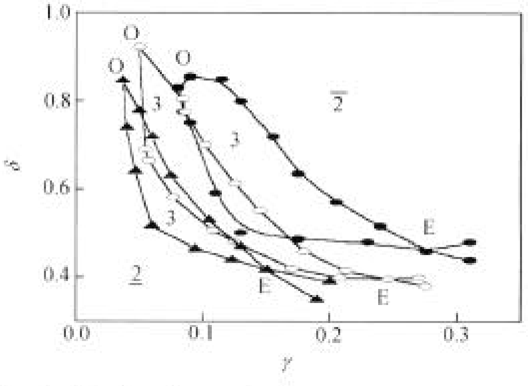

Fig. 6. δ-γ phase diagram for the quaternary system *n*-octyl polyglucoside $C_8G_{1.46}$/different alcohols/cyclohexane/water. $\alpha = 0.5$; ●, 1-butanol; ○, 1-hexanol; ▲, 1-octanol.

mixture. The longer the alcohol chain length, the larger the bending elastic modulus of the mixed layer[19], the larger the solubilization. Therefore, the ratio of 1-butanol to APG molecules in the balanced interfacial film decreases.

Table 1 Values of $\tilde{a}_e$, d_e, S_1, S_2, C_1, C_2 and S_2^S for the quaternary systems *n*-octyl polyglucoside $C_8G_{1.46}$ /different alcohols/cyclohexane/H_2O

Alcohol	$\tilde{a}_e$	d_e	S_1	S_2	C_1	C_2	$C_2/(C_1+C_2)$ a)	S_2^S b)	R_{mol} c)
1-Butanol	0.276	0.460	0.013	0.077	0.139	0.066	0.322	0.317	1∶2.3
1-Hexanol	0.246	0.395	0.0039	0.046	0.146	0.060	0.291	0.293	1∶1.4
1-Octanol	0.150	0.417	0.0057	0.031	0.082	0.035	0.299	0.298	1∶1.2

a) Obtained from eq. (3); b) obtained from eq. (1); c) the ratio of 1-butanol to APG molecules in the balanced interfacial layer.

2.5 Effect of aqueous medium on the phase behavior

The *d*-$\tilde{a}$ phase diagram for *n*-octyl polyglucoside $C_8G_{1.46}$ /1-butanol/cyclohexane/different aqueous media systems is plotted in fig. 7. The parameters for these systems calculated from eqs. (1)—(3) are listed in table 2. From table 2, we see that the aqueous medium influences the solubilization ($\tilde{a}_e$) of the microemulsion and the ratio of 1-butanol to APG molecules in the balanced interfacial layer R_{mol} significantly. The possible explanation is that the interfacial layer is slightly negatively charged[21] and forms the electric double layer, and the addition of NaCl may suppress the electric double layer and reduce the repulsion force between the microemulsion droplets, which increase the ability for microemulsion to solubilize water and oils. In HCl medium, H_3O^+ ions may enter the interfacial layer, and cause the interfacial layer slightly positively charged. The repulsion force between the microemulsion droplets increases, and the solubilization ($\tilde{a}_e$) of the microemulsion decreases. In 5% NaOH medium, middle-phase microemulsion cannot form. This is most likely related to the deprotonation of the glucose molecule. In a strong alkaline solution, it would be expected that a fraction of APG is deprotonated and those molecules therefore act as an anionic surfactant. This deprotonation favors the hydration of the hydrophilic headgroup, which makes it difficult to form middle-phase microemulsion.

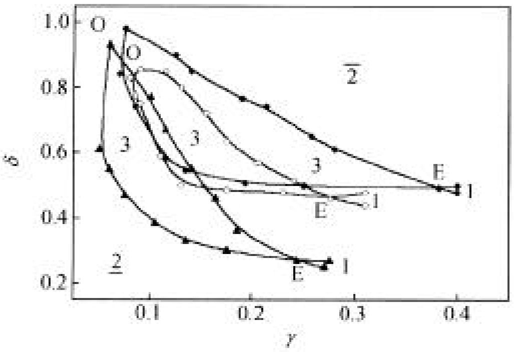

Fig. 7. δ-γ phase diagram for the quaternary system *n*-octyl polyglucoside $C_8G_{1.46}$ /1-butanol/cyclohexane/different aqueous media. $\alpha = 0.5$; ●, 5% HCl; ○, H_2O; ▲, 8% NaCl.

Table 2 Values of $\tilde{a}_e$, d_e, S_1, S_2, C_1, C_2 and S_2^S for the quaternary systems *n*-octyl polyglucoside $C_8G_{1.46}$ /1-butanol/cyclohexane/different aqueous media

Aqueous medium	$\tilde{a}_e$	d_e	S_1	S_2	C_1	C_2	$C_2/(C_1+C_2)$ a)	S_2^S b)	R_{mol} c)
NaCl (8%)	0.243	0.269	0.004	0.056	0.174	0.020	0.103	0.105	1:0.6
H_2O	0.276	0.460	0.013	0.077	0.139	0.066	0.322	0.317	1:2.3
HCl (5%)	0.382	0.492	0.000	0.073	0.194	0.139	0.417	0.411	1:3.5

a), b) and c) are the same as that in table 1.

2.6 Effect of oils on the phase behavior

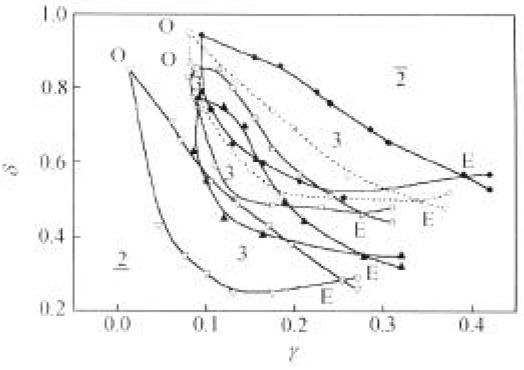

Fig. 8. δ-γ phase diagram for the quaternary system *n*-octyl polyglucoside $C_8G_{1.46}$/1-butanol/different oils/water. $\alpha = 0.5$; ●, octane; ○, hexane; □, cyclohexane; ▲, toluene; ▽, CCl_4.

It can be seen from fig. 8 and table 3 that oil has a notable influence on the phase behavior and the related parameters. The solubilization ($\tilde{a}_e$) of the microemulsion in various oils decreases in the following order: CCl_4 > toluene ~ cyclohexane > hexane > octane (table 3). That is, as the molecular volume V_m (see table 3) of oil increases, the solubilization decreases except CCl_4. 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) is needed to balance the hydrophile-lipophile property of the amphiphile layer[20]. As for the exception of CCl_4, it is mainly due to the smaller solubilities of APG and 1-butanol in CCl_4.

Table 3 Values of $\tilde{a}_e$, d_e, S_1, S_2, C_1, C_2 and S_2^S for the quaternary systems *n*-octyl polyglucoside $C_8G_{1.46}$/1-butanol/different oils/H_2O

Oil	V_m a)	$\tilde{a}_e$	d_e	S_1	S_2	C_1	C_2	$C_2/(C_1+C_2)$ b)	S_2^S c)	R_{mol} d)
Toluene	106.3	0.277	0.345	0.021	0.070	0.165	0.040	0.195	0.203	1∶1.2
Cyclohexane	108	0.276	0.460	0.013	0.077	0.139	0.066	0.322	0.317	1∶2.3
CCl_4	122.4	0.253	0.284	0.000	0.013	0.181	0.062	0.255	0.256	1∶1.6
Hexane	130.7	0.347	0.492	0.004	0.076	0.174	0.117	0.402	0.402	1∶3.2
Octane	162.5	0.391	0.568	0.005	0.089	0.165	0.162	0.495	0.495	1∶4.7

a) Molecular volume of oil ($mL \cdot mol^{-1}$); b), c) and d) are the same as a), b) and c) in table 1 respectively.

3 Conclusions

The alcohol concentration scanning phase diagram for the quaternary system alkyl polyglucoside ($C_8G_{1.46}$ or $C_{10}G_{1.54}$)/1-butanol/cyclohexane/water was studied, and the result shows that the widths of alcohol for the middle-phase microemulsion of $C_8G_{1.46}$ and $C_{10}G_{1.54}$ is from 6.64% to 11.47%, and from 3.44% to 5.77%, respectively.

The fishlike phase diagram for alkyl polyglucoside ($C_8G_{1.46}$ or $C_{10}G_{1.54}$)/1-butanol/cyclohexane/water system has been plotted at 40℃ in terms of the variables $\tilde{a}$ and d. 1-Butanol in these microemulsion systems acts as both a cosurfactant and a cosolvent. The distorted shape of the middle-phase region 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" ($\tilde{a}_0$, d_0) and "tail" ($\tilde{a}_e$, d_e) points of the phase diagram are obtained by applying the HLB plane equation. $\tilde{a}_e$ reveals the minimum concentration of APG for getting a single microemulsion system while the ratio of water to oil is equal to 1. The solubilization of the microemulsions $C_{10}G_{1.54}$ is larger than that of $C_8G_{1.46}$. The shorter the hydrocarbon chain length of the APG molecules, the larger the solubilization.

In addition, the effects of oil, aqueous medium and alcohol on the phase behavior are also investigated. The result shows that they have a notable influence on the middle-phase region, and the composition of the amphiphile layer (C_1, C_2 and S_2^s). It is found that the alcohols with longer hydrocarbon chain, oil molecules with smaller molecular volume and the addition of inorganic salt can increase the solubilization of the microemulsions.

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