Studies on the middle phase microemulsion of alkyl polyglucoside

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The middle phase microemulsions of alkyl polyglucosides (APG) C₈G1.46, C₁₀G1.46, C₁₂G1.46, C₈/₁₀G₁.₃₁ and C₁₂/₁₄G₁.₄₃ have been studied with the alcohol concentration scanning phase diagram. The results show that in the quaternary system of APG/alcohol/alkane/water, the increase in the alcohol concentration causes a series of phase inversion Winsor I (II) → III(III) → H(II). The order of the alcohol width and the minimum alcohol concentration needed to form middle phase microemulsion is: C₈G1.46>C₈/₁₀G₁.₃₁>C₁₀G1.46>C₁₂G1.46>C₁₂/₁₄G₁.₄₃. Along with the increase in APG concentrations, the minimum alcohol concentrations increase, but that for unit APG, the concentrations decrease. The alcohol width increases first and then decreases, but that for per gram of APG decreases monotonously. The longer the alcohol hydrocarbon chain, the smaller both the alcohol width and the minimum alcohol concentration to form middle phase microemulsion, but the larger the solubilizing power. With the increase in NaCl concentrations, the minimum alcohol concentration decreases, but the alcohol width is nearly unchanged. This may be explained by “salting-out” effect. The effect of alkanes is different from that of NaCl concentrations; the minimum alcohol concentration is nearly the same, but the alcohol width increases as the alkane hydrocarbon chain length increases.

In recent years, there is increased emphasis on research on the green surfactants, such as alkyl polyglucosides (APG or CₙGₗ). Alkyl polyglucosides are synthesized from renewable raw materials such as sugars and fatty alcohols and have excellent biodegradability and good surface-active properties. Therefore, they will be one kind of the most prospective surfactants in the 21st century. One potential use for APG is in microemulsion formation. APG-based microemulsion is less sensitive to temperature, which is preferable to polyethylene ether surfactants (CₘEₙ) based microemulsion. It has been applied in cosmetics, detergent and micro-medium for chemical and enzymatic reactions, etc. A lot of work has been done on APG-based microemulsion by theoretical and practical means. Oct-, dec- and dodecane polyglucosides were synthesized by known methods. Their compositions determined by the gas chromatogram method were found to be: C₈G1.₄₆, C₁₀G1.₄₆ and C₁₂G1.₄₆. C₈/₁₀G₁.₃₁ and C₁₂/₁₄G₁.₄₃ were kindly provided by China Research Institute of Daily Chemical Industry and were purified before experiments and their compositions were determined by GC. Water was doubly distilled. Other reagents were of A.R. grades.

Materials and Methods

Oct-, dec- and dodecane polyglucosides were synthesized by known methods. Their compositions determined by the gas chromatogram method were found to be: C₈G1.₄₆, C₁₀G1.₄₆ and C₁₂G1.₄₆. C₈/₁₀G₁.₃₁ and C₁₂/₁₄G₁.₄₃ were kindly provided by China Research Institute of Daily Chemical Industry and were purified before experiments and their compositions were determined by GC. Water was doubly distilled. Other reagents were of A.R. grades.

A GC-9A gas chromatograph (Shimadzu, Japan), an FA1104 electron balance and a 501 super thermostat were used.

APG solutions were prepared by weighing the surfactant into Teflon-sealed glass tubes and diluting to the desired concentration with water. Then, required amount of oil was put into the tubes to get the ratio of water to oil of unity (r_w/o=1) in 10 mL of the total volume of the solution. Samples were prepared by varying alcohol monotonically, keeping APG concentrations at different values. All samples
were allowed to equilibrate at 40±0.1 °C in a water bath for about 10 days. Phase equilibrium was determined by visual observations of a large number of samples. The volumes of the middle phase microemulsions were recorded and the alcohol concentration scanning phase diagrams were plotted.

Results and Discussion

Synthesis and characterization of APG

Alkyl polyglucosides were synthesized from glucoses and corresponding fatty alcohol or mixtures of alcohols by Fischer glycosidation. The products consist of a distribution of species with the different degrees of glycosidation and have many isomerisms, such as stereoisomerism with α- and β-anomers. Their degrees of glycosidation were determined by GC. The GC spectra are shown in Fig. 1, in which the mono-, di-, tri- and tetraglucosides are signed while other polyglucosides are neglected for their contents are very small.

The size of the column used for APG analysis is 0.5 m (length) × 3 mm (inside diameter), and fixing agent 5% Dexsil 300, the rate of raising temperature 8°C min⁻¹ and the temperature range 80-350°C. Nitrogen was used as a carrier gas and held for 5 min at the final temperature. The different signals in Fig. 1A can be described as: the signals 19.658 min and 20.245 min are yielded by α- and β-anomers of monoglucosides, respectively; 24.692 min and 25.412 min belong to diglucosides; 29.790 min belongs to triglucosides and tetroglucosides are observed at 33.633 min. Integrating the intensities of different signals of glucosidation, the average composition is C₈G₁.₄₆ (monoglucoside 68.83%, diglucosides 19.72%, triglucosides 7.56%, tetroglucosides and other polyglucosides 3.89%). Similarly, the compositions of other four kinds of APG are obtained as follows: C₁₀G₁.₄₆ (B) (monoglucoside 70.76%, diglucosides 17.68%, triglucosides 5.95%, tetroglucosides and other polyglucosides 5.61%), C₁₂G₁.₄₆ (C) (monoglucoside 70.71%, diglucosides 17.42%, triglucosides 6.45%, tetroglucosides and other polyglucosides 5.42%), C₈/₁₀G₁.₃₁ (D) (monoglucoside 77.18%, diglucosides 16.61%, triglucosides 4.30%, tetroglucosides and other polyglucosides 1.91%), and C₁₂/₁₄G₁.₄₃ (E) (monoglucoside 71.56%, diglucosides 17.52%, triglucosides 6.77%, tetroglucosides and other polyglucosides 4.15%), respectively.

Scanning phase diagram for different CᵢGᵢ molecules

The alcohol concentration scanning phase diagram for CᵢGᵢ/n-butanol/n-octane/water system is shown in Fig. 1—The GC spectra of C₈G₁.₄₆ (A), C₁₀G₁.₄₆ (B), C₁₂G₁.₄₆ (C), C₈/₁₀G₁.₃₁ (D) and C₁₂/₁₄G₁.₄₃ (E).
Fig. 2. The microemulsion phase inversion Winsor I (2) \(\rightarrow\) III (3) \(\rightarrow\) II (2) occurs as the \(n\)-butanol concentration increases. When the concentration (weight ratio) of \(n\)-butanol is small, an oil-in-water microemulsion in contact with excess oil (2) exists; as \(n\)-butanol concentration increases, the phase inverts into water-in-oil microemulsion in contact with excess water (2) via a middle phase microemulsion in contact with excess oil and water (3). In Winsor I microemulsion region, the curvature of the amphiphilic film is positive (i.e., oil on the concave side of the interfacial layer). As the \(n\)-butanol concentration increases, the amount of \(n\)-butanol dissolved in amphiphilic film increases and the curvature of the closed film decreases. When the curvature of the film opens, the Winsor III (3) microemulsion is formed. With the increase in \(n\)-butanol concentration, the surfactant dissolved in amphiphilic film is enough to convert the curvature of the amphiphilic film to negative (i.e., water on the concave side of the interfacial layer). Thus, Winsor II (2) microemulsion is formed.

The alcohol concentration range from forming to disappearing of the middle phase microemulsion is called alcohol width. The alcohol widths in Fig. 2 are listed in Table 1. Both Fig. 2 and Table 1 show that the order of the minimum alcohol concentrations and alcohol widths is \(C_{8}G_{1.46}>C_{8/10}G_{1.31}>C_{10}G_{1.46}>C_{12}G_{1.46}>C_{12/14}G_{1.43}\). Thus, the longer the APG hydrocarbon chain is, the smaller alcohol needed to form middle phase microemulsion is. The longer the hydrocarbon chains of the APG molecules are, the more lipophilicity of the APG is, and the easier the oil molecules to penetrate the surfactant palisade layer of the micro-droplets is.

**Effect of APG concentration on the phase behavior**

Increase in \(C_{8}G_{1.46}\) concentration for system \(C_{8}G_{1.46}/n\)-butanol/\(n\)-octane/water at 40°C and \(r_{w/o}=1\), the minimum alcohol concentration to form middle phase microemulsion increases, and alcohol widths increase first and then decrease (Fig. 3; Table 2). When \(C_{8}G_{1.46}\) concentration is small, the number of the microemulsion droplets are also small, the curvature of the amphiphilic film changes tremendously from forming to disappearance of the middle phase microemulsion. The larger the \(C_{8}G_{1.46}\) concentration, the larger amount of alcohol to maintain the middle phase microemulsion (when \(C_{8}G_{1.46}\) concentration is smaller than 4.88%). However, when the concentration of \(C_{8}G_{1.46}\) is large, the microemulsion has large solubilizing power and the curvature of the film changes easily from forming to disappearance of the middle phase microemulsion. From this point of view, the alcohol widths will increase at first and then decrease as \(C_{8}G_{1.46}\) concentration increases, and it is indeed so in \(C_{8}G_{1.46}\) concentration range of 2.06%-13.12%. When the alcohol widths are converted to per gram of \(C_{8}G_{1.46}\), the orderliness appears (Table 2). That is, the alcohol widths for per gram of \(C_{8}G_{1.46}\) decrease monotonously along with the increase in \(C_{8}G_{1.46}\) concentrations.

The minimum amount of alcohol needed to form middle phase microemulsion increases (6.44%-14.24%) as the concentration of \(C_{8}G_{1.46}\) increases, however, for per gram of \(C_{8}G_{1.46}\) it decreases (3.13%-1.08%) (Table 2). It is due to the dissolution of alcohol in oil phase. When \(C_{8}G_{1.46}\) concentration is small, the mass ratio of alcohol dissolved in oil phase is large which results in the increase in the amount of alcohol.

<table>
<thead>
<tr>
<th>Range of alcohol concentration (%)</th>
<th>(C_{8}G_{1.46})</th>
<th>(C_{8/10}G_{1.31})</th>
<th>(C_{10}G_{1.46})</th>
<th>(C_{12}G_{1.46})</th>
<th>(C_{12/14}G_{1.43})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol width (%)</td>
<td>10.21</td>
<td>7.54</td>
<td>5.16</td>
<td>2.97</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Table 1 — The alcohol widths for different \(C_{i}G_{j}/n\)-butanol/\(n\)-octane/water systems at 40°C and \(r_{w/o}=1\).
Table 2—The alcohol widths for quaternary system C$_{8}$G$_{1.46}$/n-butanol/n-octane/water

<table>
<thead>
<tr>
<th>Concentrations of C$<em>{8}$G$</em>{1.46}$ (%)</th>
<th>2.06</th>
<th>2.92</th>
<th>4.88</th>
<th>7.00</th>
<th>10.62</th>
<th>13.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol width (%)</td>
<td>6.99</td>
<td>8.03</td>
<td>10.21</td>
<td>9.75</td>
<td>8.68</td>
<td>5.94</td>
</tr>
<tr>
<td>Range of alcohol concentration /g C$<em>{8}$G$</em>{1.46}$</td>
<td>3.13-6.52</td>
<td>2.66-5.41</td>
<td>1.72-3.81</td>
<td>1.28-2.68</td>
<td>1.04-1.86</td>
<td>1.08-1.54</td>
</tr>
<tr>
<td>Alcohol widths /g C$<em>{8}$G$</em>{1.46}$</td>
<td>3.39</td>
<td>2.75</td>
<td>2.09</td>
<td>1.4</td>
<td>0.82</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Effect of different alcohols on the phase behavior

Figure 4 shows the influence of different alcohols on phase diagram for C$_{8}$/10G$_{1.31}$/alcohol/n-octane/water system at 40°C and r$_{w/o}$=1. The alcohol widths obtained from Fig. 4 are: 7.39% (6.10–13.49%, n-butanol), 2.98% (4.27–7.25 %, n-hexanol) and 1.70% (3.28–4.98%, n-octanol), respectively.

Figure 4 shows that the longer the alcohol hydrocarbon chain is, the less both the minimum amount of alcohol to form middle phase microemulsion and the alcohol width are. The longer the alcohol carbon chain is, the larger the lipophilicity property and the larger the ability to change the curvature of the amphiphilic film to form middle phase microemulsion is.

With the increase in the alcohol carbon chain length, the volume of the middle phase microemulsion increases (Fig. 4). That is, the longer the alcohol hydrocarbon chain, the larger the solubilizing power.

Effect of alkane on the phase behavior

The effect of alkanes on the alcohol concentration scanning phase diagram for system C$_{8}$/10G$_{1.31}$/n-butanol/alkane/water at 40°C and r$_{w/o}$=1 is shown in Fig. 6. In Fig. 6, the alcohol widths are 5.12% (8.10–13.22%, n-hexane), 10.21% (8.37–18.58%, n-octane), and 15.01 (8.63–23.64%, n-decane), respectively. It can be seen from Fig. 6 that the minimum amount of alcohol needed to form middle phase microemulsion is 8.76% (4.5%NaCl) and 8.22% (3.42%-7.64%, 6.7%NaCl), respectively.
alcohol needed to form middle phase microemulsion is nearly the same, but evidently different at the end-point of the middle phase microemulsion. The order of the alcohol widths is: \( n \)-decane > \( n \)-octane > \( n \)-hexane. The reason is that the smaller alkane molecules are easier to penetrate the surfactant palisade layer, and the amphiphile layer is easier to convex toward oil. At the beginning of the middle phase microemulsion, the alkane molecules are mainly dissolved in the oil phase and only a small part of alkane molecules penetrate into the interfacial layer. Therefore, the amount of alcohol is nearly the same. With the increase in the amount of alcohol, more and more alkanes solubilize in the palisade layer. Thus, the effect of alkanes on the phase inversion is more important.

**Conclusions**

The increase in alcohol concentration can cause a series of phase inversion Winsor I (2) →III(3) →II(2). Using the APG molecules with longer hydrocarbon chain, it is easier to form the middle phase microemulsion; therefore, less amount of alcohol is needed. The larger the APG concentration is, the larger the solubilizing power is. Alcohol distributes between the interfacial layer and the oil phase, which affects the alcohol width and the solubilizing power of the system. Alcohol with different hydrocarbon chain length has notable influence on the alcohol width, the minimum amount of alcohol to form the middle phase microemulsion and the solubilizing power of the system. NaCl concentration affects the minimum amount of alcohol needed to form middle phase microemulsion markedly, but has less influence on the alcohol width. Alkane affects the alcohol width, but does not affect the minimum amount of alcohol needed to form the middle phase microemulsion.

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**References**