Studies on the phase behaviour and solubilization of \( p \)-octyl polyethylene glycol phenyl ether/oil/1-pentanol/water microemulsion systems

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Phase behaviour and solubilization ability of the microemulsion systems consisting of the nonionic surfactant \( p \)-octyl polyethylene glycol phenyl ether/oil/1-pentanol/brine have been studied using \( \varepsilon-\beta \) fishlike phase diagrams. From these phase diagrams, solubility of the alcohol, composition of the interfacial layer, and solubilization ability of the microemulsion systems have been studied. The effects of different oils, salinities and temperature on the phase behaviour and solubilization ability have been investigated. The solubilization ability increases with decrease in the length of the alkanes. With decrease in salinity or temperature, the solubilization ability and the solubility of the alcohol increase.

**Keywords**: Phase behaviour, Solubilization, Microemulsions, Surfactants

Microemulsions containing ionic as well as non-ionic surfactants are well studied.\(^1\)-\(^3\) The structures, dynamics, and transport properties of microemulsions have been well reported\(^4\)-\(^6\) because of the numerous scientific and technological applications of microemulsion systems, starting from tertiary oil recovery to nanoparticle synthesis. Due to their amphoteric nature, surfactants can form monolayers between oil and water, and the curvature of the monolayers plays a key role in determining the microstructure of the microemulsion systems.\(^7\) The curvature of the interfacial layer depends on the nature of the surfactant and the composition, the composition of the oil and aqueous phases, additives and temperature.

The function of cosurfactants in microemulsion formations is to decrease the interactions between surfactant molecules, and thus decrease the oil/water interface energy.\(^8\),\(^9\) Since the longer chain alcohols favor the formation of liquid crystal, and the shorter chain alcohols are too soluble in the aqueous phase, they are ineffective as cosurfactants.\(^10\)-\(^12\) The cosurfactants used in the nonionic microemulsion systems are mostly medium chain length alcohols, such as 1-pentanol. Other possible compounds, less often used as cosurfactants, are 2-butanol, 2-methyl-1-butanol and glycol derivatives.\(^13\)-\(^17\)

The effects of oils and salinity on the phase behaviour of microemulsions have also been investigated by many researchers. Fanun et al.\(^18\) found that the solubilization ability of drugs in microemulsions depends on the kind of oils used. Liu et al.\(^19\) found significant salt effects on the microemulsion phase transition behaviour. Ajith et al.\(^20\) studied the microstructure and macroscopic phase changes of the pseudoternary system, alkane/Brij 35/ propanol/water, in the presence of different amounts of sodium chloride at different temperatures. They found that the increase in temperature and the presence of NaCl cause drastic changes on the pseudoternary phase diagram. Deen et al.\(^21\) studied the phase behaviour of a non-ionic microemulsion consisting of pentaethyleneglycol dodecyl ether. They found that the efficiency of the surfactant and the monomeric solubility in oil depend on the alkyl chain length of the oil. The efficiency and solubility decrease with increasing alkyl chain length of 1-chloroalkane.

Kunieda\(^22\) first showed that the phase boundaries of a ternary microemulsion system at equal volume fractions of water and oil resemble the shape of a “fish” or “whale”, and established the HLB equation to calculate quantitatively the physical-chemical parameters of the system. Our research group has investigated the phase behaviour of some microemulsion systems using the \( \varepsilon-\beta \) fishlike phase diagram method.\(^23\),\(^24\),\(^25\)

Nonionic surfactants are considered superior to ionic surfactants in some aspects. Nonionic surfactants are typically more hydrophobic than ionic surfactants. They are less sensitive to high electrolyte concentrations or multivalent cations. The nonionic surfactant, \( p \)-octyl polyethylene glycol phenyl ether (OP) consists of oxyethylene groups as polar head and octylphenyl as hydrophobic region. OP-based microemulsions have been used in many fields such as synthesis of nonionic reactive emulsifier
(OP acrylate), the cleanout industry and so on.26-28 Phase behaviour and the properties of OP-based microemulsions are less studied.

Herein, the ε-β fishlike phase diagrams for p-octyl polyethylene glycol phenyl ether (OP)/1-pentanol/oil/water systems have been constructed. From the phase diagrams, the physical-chemical parameters relating the phase diagrams have been obtained. The present study will be beneficial for better use of nonionic surfactant-based microemulsion systems.

**Experimental**

P-Octyl polyethylene glycol phenyl ether (OP) was of CP grade and was purchased from Shanghai Chemical Reagent Company, China. All other reagents were AR grade and were used without further purification. Doubly distilled water was used throughout. FA1104 electronic analytical balance (Shanghai, China) and DF-101S constant temperature magnetic mixer (Jiangsu, China) were used in this study.

The microemulsion samples were prepared by weighing different quantities of OP into a series of teflon-sealed glass tubes, and then brine, oil and alcohol were added into the tubes. The alcohol content was increased monotonically while the mass of surfactant, alcohol, oil and water, respectively, the symbols, α, β and ε were defined as

\[ \alpha = m_s/(m_w + m_a), \quad \beta = m_s/(m_s + m_w) \]

The short length alkanes (n-decane, n-octane and n-hexane), cyclohexane and tetrachloroethylene were used as oil phase. The ε-β fishlike phase diagrams for OP/1-pentanol/oil/brine (5% NaCl) quaternary systems at 40°C and α = 0.5 are plotted in Fig. 1.

Figure 1 shows the inversion of microemulsion phases of three basic types: Type I (Winsor I) corresponding to O/W microemulsion and excess water (2), type II (Winsor II) corresponding to W/O and excess oil (2), and type III (Winsor III) corresponding to middle-phase microemulsion and excess water and oil (3).

When the ε values are small, the phase is Winsor I type. As ε values increase, a phase inversion Winsor I (2) →III(3)→ II (2) occurs.

![Fig. 1 –The fishlike phase diagrams of OP/1-pentanol/oil/brine (5% NaCl) microemulsion systems at 40 °C and α = 0.5. (Oil: (▼) n-decane; (★) n-octane; (▲) n-hexane; (■) cyclohexane; (●) tetrachloroethylene. (2) Winsor I; (2) Winsor II; (3) Winsor III. (Point B): “fish head”; (point E) “fish tail”).](image)

<table>
<thead>
<tr>
<th>Alkane</th>
<th>( V_m^{a} )</th>
<th>( \beta_B )</th>
<th>( \varepsilon_B )</th>
<th>( \beta_i )</th>
<th>( \varepsilon_i )</th>
<th>( A^T )</th>
<th>( R_{mol} )</th>
<th>( \beta_E )</th>
<th>( \varepsilon_E )</th>
<th>SP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>130.7</td>
<td>0.002</td>
<td>0.086</td>
<td>0.298</td>
<td>0.059</td>
<td>0.165</td>
<td>1:1.45</td>
<td>0.299</td>
<td>0.115</td>
<td>0.98</td>
</tr>
<tr>
<td>n-Octane</td>
<td>162.5</td>
<td>0.008</td>
<td>0.087</td>
<td>0.377</td>
<td>0.076</td>
<td>0.168</td>
<td>1:1.47</td>
<td>0.381</td>
<td>0.124</td>
<td>0.65</td>
</tr>
<tr>
<td>n-Decane</td>
<td>194.9</td>
<td>0.004</td>
<td>0.088</td>
<td>0.43</td>
<td>0.102</td>
<td>0.200</td>
<td>1:1.74</td>
<td>0.432</td>
<td>0.149</td>
<td>0.48</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>108.002</td>
<td>0.041</td>
<td>0.329</td>
<td>0.055</td>
<td>0.146</td>
<td>1:1.22</td>
<td>0.331</td>
<td>0.081</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>102.2</td>
<td>0.004</td>
<td>0.006</td>
<td>0.364</td>
<td>0.023</td>
<td>0.059</td>
<td>1:0.46</td>
<td>0.367</td>
<td>0.027</td>
<td>0.83</td>
</tr>
</tbody>
</table>

*Note: Molecular volume of oil (ml/mol)
In order to investigate the solubilization ability and the solubility of the surfactant and cosurfactant in microemulsion systems, the parameters of the fishlike phase diagrams in Fig. 1 were obtained according to literature. The “fish head” (βB, εB) and the “fish tail” (βE, εE), A5 (the mass fraction of alcohol in the balanced interfacial layer), εi, βi (the mass fractions of alcohol and surfactant contained in the interfacial layer in the whole system, respectively), and Rmol (=nS/nA, the molar ratio of surfactant to alcohol in the balanced interfacial layer) are listed in Table 1.

The βB values in Table 1 are very small, which shows that a small amount of surfactant is solubilized in the aqueous or oil phase. In fact, maximum surfactant is solubilized in the interfacial layer. The large εB values indicate that the alcohol is not only solubilized in the interfacial layer, but also solubilized in the aqueous or oil phase.

From βi and εi values in Table 1, A5 can be calculated (Eq. 1).

\[ A^5 = \frac{\varepsilon_i}{\varepsilon_i + \beta_i} \]  

The A5 and Rmol values are in the same order of n-decane > n-octane > n-hexane > cyclohexane > tetrachloroethylene, i.e., as the molecular volume Vm (Table 1) of the oil increases, A5 and Rmol increase. This phenomenon can be explained in terms of the penetrating ability of the oil to the surfactant palisade layer. It is easier for the smaller oil molecules to penetrate the surfactant palisade layer. The amphiphile layer tends to be convex towards oil, which favors change of the curvature of the amphiphile layer. Therefore, less cosurfactant is needed to balance the hydrophilic-lipophilic property of the amphiphile layer. This is especially so for the tetrachloroethylene microemulsion system which has the smallest A5 and Rmol values.

Substantial amounts of oil and water can be solubilized in microemulsion phase. Solubilization ability (SP) is defined as the mass of oil or of water per gram of surfactant in the microemulsion phase. At the fish tail, equal mass of oil and water was solubilized in the middle phase of the microemulsions, and the solubilization ability of the microemulsion systems reached the maximum value. At this optimum composition, SP is referred to as optimum solubilization parameter, SP*, and can be calculated using the coordinates of the fish tail (εE, βE) (Eq. 2).

\[ SP^* = \frac{1 - \beta_E - \varepsilon_E}{2\beta_E} \]  

The values of SP* are listed in Table 1. SP* reflects the optimum solubilization ability of the system. Solubilization ability notably depends on the nature of the oils. According to SP* values, the solubilization ability is in the order: n-decane < n-octane < tetrachloroethylene < cyclohexane < n-hexane.

The above order indicates that the solubilization ability increases with decrease in the length of the alkanes. The solubilized amount of the oil largely depends on its ability to penetrate the palisade of the interfacial layer. It is easy for the smaller oil molecules to penetrate the surfactant palisade layer. As a result, the surfactant monolayer tends to be convex towards oil, and therefore the solubilization ability increases.

The effect of salinity on the ε-β fishlike phase diagrams of OP/1-pentanol/n-octane /brine microemulsion systems is shown in Fig. 2. The parameters of the ε-β fishlike phase diagram in Fig. 2 were calculated and are listed in Table 2.

It can be seen from Fig. 2 and Table 2 that the solubility of the alcohol (εB) decreases with the increase in salinity. The decrease in εB values causes
the fishlike phase diagrams to shift downwards. This can be explained as the salting-out effect, resulting in the separation of the alcohol from the bulk phases.\textsuperscript{32,33}

The salt effect may also decrease the adsorption efficiency of the alcohol and surfactant at the interfacial layer. As a result, the mass fractions of alcohol and surfactant contained in the interfacial layer in the whole system (\(\epsilon_i\) and \(\beta_i\)) increase. As \(\beta_E\) values significantly increase, the solubilization ability (SP\(^*\)) would decrease greatly. In contrast, the molar ratio of alcohol to surfactant in the balanced interfacial layer (\(R_{mol}\)) only changes to a small extent.

The effect of temperature on the \(\epsilon-\beta\) fishlike phase diagrams of OP/1-pentanol/n-octane/5\% NaCl microemulsion systems at 40 °C and \(\alpha = 0.5\) is shown in Fig. 3 and the related physical-chemical parameters are listed in Table 3.

As temperature increases, the \(\epsilon-\beta\) fishlike phase diagrams shift to the lower position in Fig. 3. In addition, the solubility of the alcohol (\(\epsilon_B\)) decreases, the mass fraction of alcohol in the balanced interfacial layer (\(A^S\)) increases to a small extent, and the solubilization ability of the system (SP\(^*\)) notably decreases. The increase in temperature would weaken the hydrogen bond, resulting in decrease in the solubility of the alcohol (\(\epsilon_B\)).

The hydrophilicity of OP decreases with increasing temperature. This would result in an increase in the interfacial area of the head group of OP molecules and therefore the adsorption ability of the surfactant decreases. As such, more OP and cosurfactant in the interfacial layer are needed to solubilize the same quantities of oil and water, causing the solubilization ability of the system (SP\(^*\)) to decrease.

In the present study, the \(\epsilon-\beta\) fishlike phase diagrams for the microemulsion systems containing \(p\)-octyl polyethylene glycol phenyl ether (OP)/1-pentanol/oil/brine show that surfactant OP is mainly solubilized in the interfacial layer, while the alcohol is solubilized both in the interfacial layer and in the aqueous or oil phase.

In the balanced interfacial layer, the mass fraction of alcohol, \(A^S\), in the surfactant and alcohol mixture increases with the increase in the molecular volume, \(V_m\), of the oil molecules. The solubilization ability, SP\(^*\), increases with the decrease in the length of the alkanes. With the increases in salinities, the solubility of the alcohol and the solubilization ability decreases.

### Table 2 – Values of \(\beta_B, \epsilon_B, \beta_i, \epsilon_i, A^S, R_{mol}, \beta_E, \epsilon_E\) and SP\(^*\) of the microemulsion systems OP/1-pentanol/oil/brine

<table>
<thead>
<tr>
<th>System</th>
<th>(\beta_B)</th>
<th>(\epsilon_B)</th>
<th>(\beta_i)</th>
<th>(\epsilon_i)</th>
<th>(A^S)</th>
<th>(R_{mol})</th>
<th>(\beta_E)</th>
<th>(\epsilon_E)</th>
<th>SP(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.018</td>
<td>0.148</td>
<td>0.268</td>
<td>0.060</td>
<td>0.182</td>
<td>1:1.64</td>
<td>0.274</td>
<td>0.154</td>
<td>1.04</td>
</tr>
<tr>
<td>5 % NaCl</td>
<td>0.008</td>
<td>0.087</td>
<td>0.377</td>
<td>0.076</td>
<td>0.168</td>
<td>1:1.48</td>
<td>0.381</td>
<td>0.124</td>
<td>0.65</td>
</tr>
<tr>
<td>7.5 % NaCl</td>
<td>0.005</td>
<td>0.056</td>
<td>0.44</td>
<td>0.089</td>
<td>0.174</td>
<td>1:1.48</td>
<td>0.443</td>
<td>0.119</td>
<td>0.49</td>
</tr>
<tr>
<td>10 % NaCl</td>
<td>0.007</td>
<td>0.040</td>
<td>0.452</td>
<td>0.098</td>
<td>0.178</td>
<td>1:1.59</td>
<td>0.455</td>
<td>0.116</td>
<td>0.47</td>
</tr>
</tbody>
</table>

### Table 3 — The values of \(\beta_B, \epsilon_B, \beta_E, \epsilon_E, A^S, R_{mol}, \beta_E, \epsilon_E\) and SP\(^*\) of the systems OP/1-pentanol/oil/brine (5 \% NaCl)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(\beta_B)</th>
<th>(\epsilon_B)</th>
<th>(\beta_i)</th>
<th>(\epsilon_i)</th>
<th>(A^S)</th>
<th>(R_{mol})</th>
<th>(\beta_E)</th>
<th>(\epsilon_E)</th>
<th>SP(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.016</td>
<td>0.138</td>
<td>0.275</td>
<td>0.052</td>
<td>0.159</td>
<td>1:1.13</td>
<td>0.286</td>
<td>0.145</td>
<td>0.99</td>
</tr>
<tr>
<td>40</td>
<td>0.008</td>
<td>0.087</td>
<td>0.377</td>
<td>0.076</td>
<td>0.168</td>
<td>1:1.21</td>
<td>0.381</td>
<td>0.124</td>
<td>0.65</td>
</tr>
<tr>
<td>50</td>
<td>0.009</td>
<td>0.049</td>
<td>0.455</td>
<td>0.096</td>
<td>0.182</td>
<td>1:1.26</td>
<td>0.459</td>
<td>0.118</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Fig. 3 – Effect of temperature on the \(\epsilon-\beta\) fishlike phase diagrams of OP/1-pentanol/n-octane/brine (5 \% NaCl) microemulsion systems and \(\alpha = 0.5\). [■] 30°C; [▲] 40°C; [★] 50°C. (1) Winsor I; (2) Winsor II; (3) Winsor III. Point B: “fish head”; Point E: “fish tail”.
As temperature increases, the solubility of the alcohol and the solubilization ability of the system notably decrease.

Acknowledgement
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References