Effects of Hydrophobic Groups in Surfactants and Alkanes on the Phase Equilibrium Rate of Middle Phase Microemulsion

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The effects of alkyl chain lengths in sodium alkyl sulfates (SCN) and n-alkanes (ACN) on the phase equilibrium rate of middle-phase microemulsion have been investigated. The phase equilibrating rate at optimum salinity, at which middle-phase microemulsion forms, increased with decreasing SCN, or with increasing ACN. This may be attributed to the fact that phase equilibrating rate is closely related to removal rate of excess solubilized water and/or oil in the middle phase, that is, the removal rate increases with a decrease in the magnitude of individual strengths of hydrophilic and hydrophobic interactions at oil/water interface.

1. Introduction

It is now recognized that the application of the microemulsion systems is of industrial and practical importance for enhanced oil recovery¹⁻⁵ and for preparation of ultramicroparticles⁶⁻⁸. A multiphase microemulsion in an anionic surfactant/oil/co-surfactant/brine system shows a Winsor-type phase transition as a function of salinity, concentration of co-surfactant, temperature etc.⁴⁻⁵. In particular, a middle-phase microemulsion in Winsor III-type indicates the highest mutual solubilization power of oil and water⁹, and the lowest interfacial tension between them⁹,¹⁰. That is to say, the function of microemulsions can be greatly enhanced in the middle phase.

As a microemulsion phase of the Winsor-type exists in equilibrium with excess oil and/or water phase, the partition of each component (especially the surfactant) in each phase is of great importance for the elucidation of microemulsion formation.

In this paper, we report the effects of alkyl chain lengths of anionic surfactants and n-alkanes on phase equilibrating rate at optimum salinity, for the formation of middle-phase microemulsion, by measurements of time-course of the partition of surfactant in middle phase.

2. Experimental

2.1 Materials

Sodium alkyl sulfates (CₙH₂ₙ₊₁OSO₃Na; n=8, 10, and 12), as anionic surfactants, were supplied by Nihon Surfactant Industries Co. The sulfates (n=8 and 10) were recrystallized from n-propanol and the sulfate (n=12) was recrystallized from ethanol. These sulfates were then extracted with diethyl ether in a Soxhlet extractor, and dried in a vacuum oven. The purity was ascertained by surface tension measurements and DSC measurements.

n-Alkanes (CₘH₂ₘ₊₂; m=10, 12, and 14) as an oil, n-hexanol as a co-surfactant, sodium chloride for brine, ethyl violet (cationic dye) and benzene for the extraction-spectrophotometric determination, were reagent grade and were used without further purification.

Water used in this experiment was twice distilled and was de-ionized by an ion-exchange instrument (NANO pure D-1791 of Barnstead Co.).

2.2 Methods

2.2.1 Preparation of Microemulsion

Sodium alkyl sulfate (2.0 wt%), n-alkane (47.0 wt%), n-hexanol (4.0 wt%), and brine (47.0 wt%) of varying salinities were placed in a measuring cylinder (tube) and sealed. The tubes were shaken and allowed to attain equilibrium over a period of 10 days at 35±0.1°C. At this time, the microemulsion phase volumes were recorded, and recordings were repeated until no further changes in volume were observed. This was done to verify equilibrium conditions. An optimal middle-phase microemulsion formation was observed at the intermediate salinity between two critical salinities where Winsor I=Winsor III and Winsor...
III-Winsor II phase transitions occur\textsuperscript{4,5}.

2.2.2 Determination of Anionic Surfactants

The determination of anionic surfactant (sodium alkyl sulfate) contents in each phase of the multiphase microemulsion system was carried out by the same method (extraction-spectrophotometric method) described previously\textsuperscript{12-15}. These experiments were carried out at 35\textdegree{}C.

2.2.3 Phase Equilibrium Rate

The phase equilibrium rate (PER) was calculated on the basis of the following equation:

\[
\text{PER} (%) = \left[1 - \frac{V_t - V_e}{V_0 - V_e}\right] \times 100 \quad (1)
\]

where \(V_t\) is the volume of the middle phase at a given time \(t\); \(V_e\), the volume of the middle phase at which equilibrium had been established; \(V_0\), the initial volume of the system. When the PER becomes 100\% and/or constant, the system attains an equilibrium.

3. Results and Discussion

Figure 1 shows the effect of SCN on the time dependence of the phase equilibrium rate (PER) in the multiphase microemulsion system at optimum salinity. The PER increases with the passage of time in every system, that is, phase volume of the middle phase decreases with the elapse of time and is constant as the phase equilibrium is reached. The phase equilibrating rate increases with decreasing SCN.

Figure 2 depicts the effect of ACN on the time dependence of the PER in the multiphase microemulsion at optimum salinity. As can be seen in Fig. 2, the phase equilibrating rate increases with an increase in ACN.

Now, we consider why increasing of SCN and/or decreasing of ACN resulted in decreasing of PER. The process of multiphase microemulsion formation is considered as follows: amphoteric substance molecules (surfactant and cosurfactant) adsorb on the interface of water and oil; and then, the microemulsion phases, solubilizing both water and oil over its limit of solubilizing power, form temporarily, owing to some external energy such as stirring; subsequently, the excess solubilized both water and oil in the middle phase would be gradually removed to the excess phases (upper and lower) until equilibrium is established, because of the solubilization parameter, which is restricted by its system. This process corresponds to the time-course of PER as shown in Figs. 1 and 2, that is, phase volume of the middle phase decreases with elapse of time. The removal process is rate-determining step in the phase separation process, which is influenced by strengths of hydrophilic and hydrophobic interactions at the oil/water interface.

In the previous paper\textsuperscript{4,5}, we have described that just as the individual strengths of hydrophilic and hydrophobic interactions at oil/water interface would increase when SCN increases and/or ACN decreases, the amount of the mutual solubilization between oil and water (the solubilization parameter) can be increased.

Consequently, the system having strong interactions at oil/water interface, or in other words, the system having strong molecular interactions between amphoteric substance and oil (or water), will find it difficult to remove excess oil and water to the excess phases; and as a result, the
phase equilibrating rate would require more time. This is the reason why PER decreases with increasing SCN and/or decreasing ACN.

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References

要 旨
ミドル相マイクロエマルションの相平衡速度に及ぼす界面活性剤の硫水基並びにアルカンの影響

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ミドル相マイクロエマルションの相平衡速度に及ぼす硫酸アルキル塩並びにアルカンの炭化水素鎖長の影響を検討した。
ミドル相マイクロエマルションの最終生成塩濃度における相平衡速度とは、硫酸アルキル塩の炭化水素鎖長（SCN）の減少、あるいはアルカンの炭化水素鎖長（ACN）の増加に伴い増加した。これは、相平衡到達速度がミドル相中に過剰に可溶化されている水または油の放出速度と密接に関係しており、その放出速度が油/水界面における親水性相互作用と親油性相互作用の強度の減少に伴い増加するために起こるものと考えられる。

Keywords
Middle phase microemulsion, Sodium alkyl sulfate, Phase equilibrium rate, Spectrophotometry, Hydrophilic interaction, Hydrophobic interaction