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Studies on the phase behavior of the microemulsions formed by sodium dodecyl sulfonate, sodium dodecyl sulfate and sodium dodecyl benzene sulfonate with a novel fishlike phase diagram

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Abstract

The middle-phase behavior for the quaternary system of sodium dodecyl sulfonate (AS) (sodium dodecyl sulfate, SDS; sodium dodecyl benzene sulfonate, SDBS)/alcohol/oil/water has been studied with a novel ε–β fishlike phase diagram at 40 °C. The composition of the hydrophile–lipophile balanced interfacial layer was determined. The coordinates of the start point B and the end point E of the middle-phase microemulsion, and the solubilities of sodium dodecyl sulfonate, sodium dodecyl sulfate, sodium dodecyl benzene sulfonate and alcohol in the oil phase were calculated. The solubilization power of the middle-phase microemulsion was investigated. The effects of different alcohols, oils and inorganic salts on both the phase behavior and the composition of the interfacial layer were also investigated. The shorter the carbon chain lengths of the oils and the longer the carbon chain lengths of the alcohols, the higher the solubilization of the microemulsions. The inorganic salt (NaCl) facilitates the microemulsion inversion Winsor I → III → II.

Keywords: Sodium dodecyl sulfonate; Sodium dodecyl sulfate; Sodium dodecyl benzene sulfonate; Microemulsion; Fishlike phase diagram

1. Introduction

Microemulsions are isotropic, transparent or translucent, thermodynamically stable dispersions of surfactant, alcohol, oil and water, and have been used in various fields, such as enhanced oil recovery (EOR), pharmaceutics, nanoparticle synthesis, liquid–liquid extraction, cosmetic, detergency and other chemical engineerings, due to their very low interfacial tension, nanometer-sized droplets, good solubilization power, etc. [1–4].

Both Winsor type [5–9] and δ–γ fishlike phase diagrams [10–16] are mostly used to study the phase behavior of the microemulsion. From Winsor phase diagram, the effects of some factors (such as salt concentration and temperature) on the phase inversion of the microemulsion can be observed directly. However, the composition of the balanced interfacial layer and the solubilization power of the microemulsion cannot be obtained. The δ–γ fishlike phase diagram overcomes the disadvantages of the Winsor phase diagram, and the composition of the middle-phase microemulsion, and the solubilization power can be calculated. Nevertheless, since the midst line of the middle-phase region in δ–γ fishlike phase diagram is a steep curve, and the HLB plane equation contains a reciprocal term ($1/\gamma$), it is difficult to draw out the midst line and calculate the composition of the interfacial layer accurately, especially when the γ values are very small. Therefore, a novel ε–β fishlike phase diagram was used in this paper, which overcomes the disadvantages of both Winsor and δ–γ fishlike phase diagrams. From the ε–β fishlike phase diagram, the phase inversion and the solubilization power of the microemulsion can be observed, and the related physicochemical parameters of the system can be calculated precisely.

Common anionic surfactants often appear in microemulsion formulations [17–21] and are used as microemulsion detergency. The phase inversion of Winsor I to Winsor III may deliver robust detergency under home laundry conditions, so research on the phase inversion and the solubilization power of the middle-phase microemulsion is of great importance. In this paper, the middle-phase behavior and the solubilization power

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of the microemulsion formed by sodium dodecyl sulfonate (AS), sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) were studied. The study will be of great significance both in the further understanding of the middle-phase microemulison and the practical use of the surfactants.

2. Experimental

2.1. Materials and apparatus

AS, SDS, SDBS, *n*-octane, *n*-hexane, *n*-decane, *n*-dodecane, *n*-butanol, etc. were all of A.R. grade. Water was doubly distilled.

An FA 1104 electron balance, a 501 super thermostat and an 811 ultra centrifuge were used in this experiment.

2.2. Methods

The samples were prepared by weighting the surfactant and the alcohol into Teflon-sealed glass tubes and diluting with water to certain concentrations. Equal oil was weighted into the glass tubes, and then all samples were allowed to equilibrate at $(40 \pm 0.1)\,^{\circ}$C in a water bath for about 1 week. Phase equilibrium was determined by visual observations; the volumes of each phase were recorded.

For a quaternary system of surfactant (S, g)/oil (O, g)/alcohol (A, g)/water (W, g), the following symbols were defined, α represents the mass fraction of oil in water plus oil, $\alpha = O/(W+O)$, β the mass ratio of surfactant in the whole system, $\beta = S/(W+O+S+A)$, and ε, the mass fraction of alcohol in the whole system, $\varepsilon = A/(W+O+S+A)$. If α, temperature (T) and pressure (P) were held constant, β was plotted horizontally and ε plotted vertically, a two dimensional phase diagram—ε–β phase diagram could be obtained.

3. Results and discussion

3.1. The ε–β fishlike phase diagram

The ε–β fishlike phase diagram for the quaternary system AS (SDS, SDBS)/*n*-butanol/*n*-octane/5% NaCl aqueous solution at 40 °C and $\alpha = 0.5$ is shown in Fig. 1.

It can be seen from Fig. 1 that increasing ε at constant β causes a series of phase inversions from oil-in-water (O/W) microemulsion in contact with excess oil (Winsor I or $\underline{2}$) to water-in-oil (W/O) microemulsion in contact with excess water (Winsor II or $\bar{2}$) via middle-phase microemulsion in contact with excess oil and water (Winsor III or 3). The middle-phase microemulsion forms at point B ("fish head", β_B, ε_B), and disappears at point E ("fish tail", β_E, ε_E). At point E, equal amount of oil and water are solubilized into a single-phase microemulsion.

Fig. 1 shows that the head of the ε–β fishlike phase diagram is downward. It may be the result of the solubility of alcohol in oil. In the process of forming middle-phase microemulsion, part amount of alcohol is oriented into the interfacial layer, and the other part dissolves in oil. The fraction of the alcohol dissolved in oil in the whole system increases as β decreases [12,22].

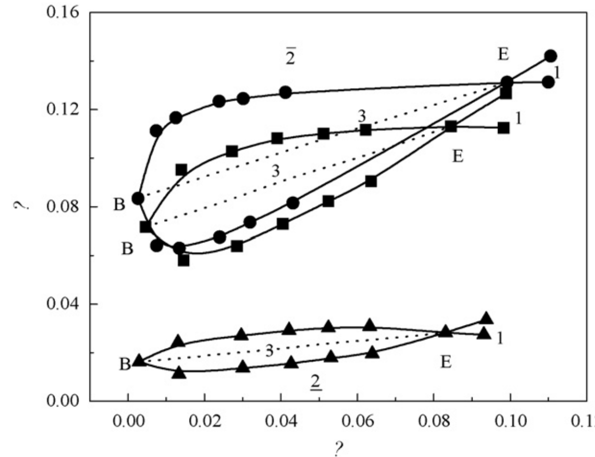

Fig. 1. ε–β fishlike phase diagram for the quaternary system AS (SDS, SDBS)/*n*-butanol/*n*-octane/5.0% NaCl aqueous solution for AS (●), SDS (■) and SDBS (▲). B–E line is the midst line of the middle-phase region.

3.2. Calculation of A^S by HLB plane equation

It is known that the whole phase behavior of a quaternary system at constant temperature and pressure can be represented in a phase tetrahedron, a section through such a phase tetrahedron at $\alpha = 0.5$ is a particular three-phase tie triangle including the microemulsion in the midst of the Winsor III region. This section is called a hydrophile–lipophile balanced plane (HLB plane), and its location is characterized by the locus of $\bar{\varepsilon}$, the mid-point of ε in the three-phase region for given values of α and β (Fig. 1).

The hydrophile–lipophile property of the mixed interfacial layer in the quaternary system is just balanced in the midst line of the middle-phase region (the broken line in Fig. 1). The ε–β HLB plane equation can be deduced based on the Kunieda's δ–γ HLB plane equation. For a quaternary system, the composition of the microemulsion in the midst line of the middle-phase region obeys [11]

$$\bar{\delta} = A^{S} + F\alpha\left(\frac{1}{\gamma} - 1\right) \tag{1}$$

In Eq. (1), $\bar{\delta}$ and γ are defined as follows

$$\bar{\delta} = \frac{A}{S+A} = \frac{\bar{\varepsilon}}{\beta + \bar{\varepsilon}} \tag{2}$$

$$\gamma = \frac{S+A}{W+O+S+A} = \beta + \bar{\varepsilon} \tag{3}$$

Combination of Eqs. (1)–(3), the ε–β HLB plane equation was then obtained as Eq. (4)

$$\bar{\varepsilon} = \frac{A^{S} - F\alpha}{1 - A^{S} + F\alpha}\beta + \frac{F\alpha}{1 - A^{S} + F\alpha}; \quad F = \frac{A^{O}S^{S} - S^{O}A^{S}}{1 - S^{S} - A^{O}} \tag{4}$$

where S^{O} and A^{O} are the solubilities of surfactant monomer and alcohol in oil, respectively, and S^{S}, A^{S}, the mass fractions of surfactant and alcohol in the hydrophile–lipophile layer, which is composed of surfactant and alcohol. If the slope and intercept