

Studies on the phase behavior of the system non-ionic surfactant/alcohol/alkane/H₂O

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Abstract

Microemulsions with 1-butanol, 1-pentanol and 1-hexanol as cosurfactants, Triton X-100, -114, -405 or mixtures of non-ionic surfactants as surfactants and, *n*-hexane, *n*-heptane, *n*-octane and *n*-decane as oils were investigated. The effects of polyoxyethylene chain length, chain length of the oil, surfactant to cosurfactant ratio, mixing of surfactants, type of cosurfactant and concentration of salt have been studied. Maximization of solubilization of oil and water was achieved for whole systems at low concentration of surfactants. Optimum surfactant/cosurfactant ratio was determined as 1/0.5. In addition, it was found that surfactant/cosurfactant ratio, type of oil and polyoxyethylene chain length of surfactant had changed the dispersion ratio.

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1. Introduction

The research on microemulsions has made a considerable progress during the last 20 years both from the theoretical and experimental points of view. A microemulsion is a transparent colloidal dispersion of water and hydrocarbon, which forms spontaneously when the components including amphiphile are brought into contact. Though the overwhelming majority of microemulsions are thermodynamically stable, however, the spontaneously formed microemulsions and o/w microemulsions are only kinetically stable and they do separate sometime after preparation [1–9].

Microemulsions can be stabilized by single hydrophobic ionic surfactant of dialkyl type, such as sodium bis(–2-ethyl-hexyl) sulfosuccinate; a single non-ionic surfactant of the polyethylene glycol alkyl ether type or a combination of a hydrophilic surfactant with a hydrophobic amphiphile of medium chain length (the cosurfactant). Systems containing mixtures of ionic surfactant and non-ionic one as cosurfactant have also been investigated [10–13].

The cosurfactants used in the non-ionic systems are mostly medium chain length alcohols, such as pentanol. Other possible compounds less often studied are 2-butanol, 2-methyl-1-butanol and glycol derivatives [14–18].

The microemulsion regions are smaller when alcohols of shorter chain length are used. This is because the longer chain alcohols favor the formation of liquid crystal. On the other hand, the shorter chain alcohols are too soluble in the aqueous phase and they are ineffective as cosurfactants [19–21].

Liquid crystalline structures are found in equilibrium with microemulsion. The role of a cosurfactant is to ensure the existence of the association structures and to destroy the liquid crystalline and/or gel structures. These structures obviate the formation of microemulsion.

One of the aspects in current research on microemulsions concerns the high solubilization of oil and/or water with low content of surfactant. Hexylamine has been reported to be a very effective cosurfactant, giving rise to high solubilization of heptane in water at low concentrations of an ionic surfactant the amine [22]. One of the possible factors attributed by the authors to this desirable property is good solubility of water in the cosurfactant coupled with sparing solubility of the cosurfactant in water. They are also

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aware that the observation would appear to be related to hydrophile–lipophile balance (HLB) of the surfactant system.

In this study, the effects of polyoxyethylene chain length and hydrocarbon chain length of the emulsifier, amount of surfactant, type of oil, mixtures of surfactants, type of cosurfactant, concentration of salt have been studied. Hexane, heptane, octane and decane were used as oil. We also report here the good solubilization of water and hexane in microemulsions by using butanol, pentanol or hexanol as cosurfactants.

2. Experimental

2.1. Materials

The surfactants polyoxyethylene (10) isooctylphenyl ether (Triton X-100), polyoxyethylene (8) isooctylphenyl ether (Triton X-114) and polyoxyethylene (40) isooctylphenyl ether (Triton X-405) were purchased from Aldrich with a stated purity of 99% and were used as received. The alkanols 1-butanol, 1-pentanol, 1-hexanol, and oils *n*-hexane, *n*-heptane, *n*-octane and *n*-decane were obtained from Merck, Darmstadt, FRG. Water was distilled twice.

2.2. Methods

The transparent regions of a microemulsion were determined by titration of water into a mixture of surfactant, cosurfactant and hydrocarbon in a screw capped tube at 25 ± 0.1 °C. For the determination of the phase diagrams, a method similar to that developed by Watt et al. was applied [4]. Upon the addition of a single drop of water the altered weight of the system was recorded and the sample shaken vigorously for approximately 20 s. Owing to the thermodynamic properties of a microemulsion it was assumed the emulsion should form rapidly with no need for the allowance of long equilibration times. Hence a visual observation was made within 60 s of droplet addition. It was determined that

a microemulsion had formed once the mixture had changed from an initial turbid, opaque solution to a translucent bring yellow mix. Subsequent loss of these properties, often to viscous white solutions, was interpreted as the breakdown of the microemulsion.

3. Results and discussion

Non-ionic surfactants Triton X-100, -114 and -405 were used throughout in this study. The completely water-soluble cosurfactants of 1-butanol, 1-pentanol and 1-hexanol were chosen for the study. Figures show huge solubility regions for these structure-forming components. Those normal micellar solutions emanate broadly from the aqueous corner and they continuously converge into the inverse micellar region.

3.1. Effect of surfactant/cosurfactant ratio

The effect of Triton X-100/1-butanol, hexane and water systems to phase diagrams was determined for the three different surfactant/cosurfactant ratios, 1/1, 0.5/1 and 1/0.5, respectively (Table 1). The optimum surfactant/cosurfactant ratio of microemulsion systems was found as 1/0.5. It was observed that the dissolution area of surfactant was low with hexane and water at 0.5/1 and 1/1 surfactant/cosurfactant ratios in the system (Fig. 1). The compositions at the maxima of this system were 15% water, 35.80% hexane and 49.20% Triton X-100/1-butanol. In brief, systems including 1/0.5 surfactant and cosurfactant ratio form a better single-phase region than the systems including other ratios.

3.2. Chain length compatibility and solubilization

Solubilization capacity depends on the nature of both the oil and the surfactant. Significant understanding of the phase behavior of the simple systems of non-ionic surfactants with linear hydrocarbons was achieved [13].

Table 1
Weight ratios of Triton X-100/1-butanol, hexane, water systems

Weight ratios of Triton X-100/1-butanol								
1/1 Weight ratios (%)			1/0.5 Weight ratios (%)			0.5/1 Weight ratios (%)		
Triton X-100/1-butanol	Hexane	Water	Triton X-100/1-butanol	Hexane	Water	Triton X-100/1-butanol	Hexane	Water
43.40	4.80	51.80	17.40	11.70	70.93	68.83	7.65	23.52
42.90	10.72	46.38	30.01	19.99	50.00	63.37	15.84	20.79
36.32	15.56	48.12	41.96	27.97	30.07	58.82	25.21	15.97
26.23	17.49	56.28	49.20	35.80	15.00	48.78	32.52	18.70
23.94	23.94	52.13	47.28	47.28	5.44	37.29	37.29	25.42
26.40	36.60	40.00	39.22	58.82	1.96	32.00	48.00	20.00
32.72	49.08	18.20	34.31	63.73	1.96	30.70	57.02	12.28
28.44	66.35	5.12	29.55	68.97	1.48	27.65	64.52	7.83
18.96	75.64	5.40	24.63	73.89	1.48	22.66	68.00	9.34
–	–	–	19.70	78.82	1.48	18.71	74.91	6.38
–	–	–	9.85	88.67	1.48	9.41	84.71	5.88

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