Phase Behaviour of Microemulsion Systems Containing Tween-80 and Brij-35 as Surfactant

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ABSTRACT
Influence of Tween-80 and Brij-35 on the phase behaviour of system containing eucalyptus oil and water was investigated by means of phase diagram. Ethanol was used as co-surfactant. The surfactant/co-surfactant mixing ratios were 1:1, 2:1 and 3:1. The extension of the microemulsion domain was very dependent upon the nature of the surfactant and on the surfactant/co-surfactant mixing ratios.

KEY WORDS – microemulsion, Tween-80, Brij-35, phase diagram
INTRODUCTION

Microemulsions are thermodynamically stable, clear fluids of low viscosity and may form a number of different structures, e.g., oil-in-water (o/w) or water-in-oil (w/o) droplets, and bicontinuous structures, over a wide range of compositions dependent on the properties of the oil and the surfactant. Usually, the interfacial tension of microemulsions is ultralow (~10^{-2} mN/m), and the size of droplets in microemulsions is less than 100 nm, smaller than the wavelength of light, which is the reason for their transparency.\(^1\)

Many approaches have been used to explore the mechanisms of microemulsion formation and stability. Early theories considered interfacial aspects of microemulsions and did not distinguish between thermodynamically stable systems and very fine kinetically stable emulsions. For microemulsions to form spontaneously, the free energy involved when the interfacial area is increased, \(\Delta G (\Delta G = \gamma \Delta A, \text{where } \Delta A \text{ is the increase in interfacial area}) \) must be negative. An essential requirement is that the interfacial tension between the oil and water phases \(\gamma\) is reduced to a very low value by the interfacial film, giving a small but positive free-energy value. The dispersion of the droplets in the continuous phase increases the entropy of the system. Microemulsions form because the negative free energy changes due to the entropy of the dispersion of droplets in the continuous phase overcomes the positive product of the small interfacial tension and the large interfacial area \(A\). The curvature of the oil–water interface in microemulsions varies from highly curved towards oil (o/w) or water (w/o) to zero mean curvature in bicontinuous structures.\(^2\)

The aim of the present study was to investigate the influence of oil phase, surfactant and surfactant – co-surfactant ratio on the phase characteristic of the prepared microemulsion by pseudo ternary phase diagram.

MATERIALS AND METHODS

Material

Tween-80 (Polyethylene glycol sorbitan monolaurate) and Brij-35 (Polyoxyl 23 lauryl ether) were purchased from S.D. Fine chemicals Ltd., Mumbai and Loba chem. Pvt. Ltd. Mumbai respectively. Eucalyptus oil, were from Ases chemical works, Jodhpur. Ethanol was purchased from Fisher scientific, Mumbai.

Method

Construction of pseudo-ternary phase diagrams:

In order to find out the concentration range of components for the existence range of microemulsions, pseudo-ternary phase diagrams were constructed by titration method. For this purpose a series of mixtures of oil (eucalyptus oil) and surfactants (Tween-80 and Brij-35) with other adjuvant co-surfactant (ethanol) were titrated with distilled water at room temperature. Tween-80 and Brij-35 were premixed with ethanol separately to obtain the surfactant mixture (\(S_{\text{mix}}\)). The proportion of surfactant was varied keeping the concentration of co-surfactant fixed, the resulting surfactant co-surfactant mixtures in the following ratios were obtained 1:1, 2:1 and 3:1 respectively. For each phase diagram at specific surfactant/co-surfactant ratio, the ratio of oil/\(S_{\text{mix}}\) were varied as 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1. The mixture of oil, surfactant and co-surfactant at certain
component ratios were titrated with distilled water drop wise, under moderate magnetic stirring until a uniform phase was obtained. After being equilibrated, the mixtures were assessed visually and determined as being microemulsions. Gels were claimed for those clear and highly viscous mixtures that did not show a change in the meniscus after tilted to an angle of 90˚. No attempts were made to identify in detail other regions of the phase diagram which have been described only in terms of their visual appearance.

RESULT AND DISCUSSION

The aim of the construction of pseudo-ternary phase diagrams was to find out the existence range of microemulsions for the selected oily mixture of eucalyptus with Brij-35 and Tween-80 in presence of different ratios of surfactant : co-surfactant viz 1:1, 2:1 and 3:1. The main factor determining the range of formation of microemulsion zone is the physicochemical properties of the oil phase, aqueous phase and surfactant with some essential conditions required for microemulsion formation. These include the existence of a very low surface tension at the oil–water interface, the presence of highly fluid interfacial film of surfactant and the penetration and association of oil molecules with the interfacial surfactant film.3 Surfactant–oil miscibility can thus give initial indication on the possibility of microemulsion formation with this system.

Eucalyptus oil / Tween-80 / Ethanol/ Water system:

Phase behaviour investigations of this system demonstrated the suitable approach to determine the water phase, oil phase, surfactant and co-surfactant concentration for which transparent, one phase, low viscous system form. The effect of three different surfactant co-surfactant ratios 1:1, 2:1 and 3:1 was determined in this system of eucalyptus oil/Tween-80/ethanol/water [Fig.1. (a), (b), (c)]. The transparent microemulsion region is presented in phase diagram. At very low oil concentration a maximum of 32.43 % of water was solubilized in the tween-80 eucalyptus oil blend with surfactant co-surfactant ratio of 1:1.

The amount of incorporated water was reduced progressively with increasing oil concentrations. Significant difference was observed in three phase diagram of microemulsion with different surfactant to co-surfactant ratios, as Tween-80: ethanol ratio increases microemulsion region shrank. The explanation for the differences in the phase diagrams might be ascribed to the decrease of hydrophilicity of the surfactant mixture as ethanol is polar solvent with the tendency to highly incorporate into water, and the relatively lower ethanol content in the microemulsion system decreased the hydrophilicity of the mix-surfactant, so the area of microemulsion was small. In brief, system at surfactant co-surfactant ratio of 1:1 formed a large single phase region then systems at other surfactant co-surfactant ratio. It was reported that at the optimum surfactant co-surfactant ratio the co-surfactant was insert into the cavities between the surfactant molecules exactly, and the formed microemulsion had a maximum solubilization capacity4. Thus the effectiveness of alcohols as co-surfactants also depends on the extent of their distribution in the interface.

For a single surfactant to form a microemulsion its lipophilic chains should be short or at least
containing a fluidizing group such as double bonds. This explains the ability of Tween-80 to form microemulsion with eucalyptus oil as it contains double bond in its lipophilic chain in addition to its complete miscibility with the oil. Introduction of co-surfactants provides further reduction in the surface tension and fluidizes the interfacial surfactant film which can expand the area of existence of microemulsion system.

Eucalyptus oil / Brij-35 / Ethanol / Water system:

The effect of three different surfactant co-surfactant ratios 1:1, 2:1 and 3:1 was determined in this system of eucalyptus oil/Brij-35/ethanol/water [Fig. 2. (a), (b), (c)]. The transparent microemulsion region is presented in phase diagram. At very low oil concentration a maximum of 29.08 % of water was solubilised in the Brij-35 eucalyptus oil blend with surfactant co-surfactant ratio of 1:1, on the other hand only 15.97% and 6.54% of water was solubilised at lower oil concentration in Brij-35 eucalyptus oil blend with surfactant co-surfactant ratio of 2:1 and 3:1 respectively.

The amount of incorporated water was reduced progressively with increasing oil concentrations. At Brij-35: ethanol ratio of 3:1 the extent of the microemulsion domain was drastically reduced. Thus the diagrams correspond to limited ranges of variation of the surfactant/co-surfactant ratio.

Comparison of Figs 1 and 2 shows the effect of substitution of the Tween-80 by Brij-35.

The microemulsion regions of the two systems with surfactant/co-surfactant ratios of 1:1 differed only in that the Tween-80 systems extended over a wider surfactant region. A greater difference was observed for Tween-80 and Brij-35 systems containing surfactant/co-surfactant ratios of 2:1 and 3:1. Microemulsions prepared with Brij-35 had lower eucalyptus oil content and were formed over a narrower range of total surfactant: co-surfactant concentration.

Fig. 1: Pseudo-ternary phase diagrams of microemulsions composed of oil (eucalyptus Oil), surfactant (tween-80), co-surfactant (ethanol) and water. (a) 1:1 ratio of tween-80 to ethanol, (b) 2:1 ratio of tween-80 to ethanol, (c) 2:1 ratio of tween-80 to ethanol
Fig. 2: Pseudo-ternary phase diagram of microemulsions composed of oil (eucalyptus oil), Surfactant (Brij- 35), co-surfactant (ethanol) and water. (a) 1:1 ratios of Brij- 35 to ethanol, (b) 2:1 ratios of Brij- 35 to ethanol, (c) 3:1 ratios of Brij- 35 to ethanol
REFERENCES


