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Physicochemical investigations of microemulsification of eucalyptus oil and water using mixed surfactants (AOT + Brij-35) and butanol

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Abstract

Microemulsification of a vegetable oil (eucalyptus) with single and mixed surfactants (AOT and Brij-35), cosurfactant of different lipophilicities (isomers of butanol), and water were studied at different surfactant and cosurfactant mixing ratios. The phase diagrams of the quaternary systems were constructed using unfolded and folded tetrahedron, wherein the phase characteristics of different ternary systems can be underlined. The microemulsion zone was found to be dependent upon the mixing ratios of surfactant and cosurfactant; the largest microemulsion zone was formed with 1:1 (w/w) S:CS. The effects of temperature and additives (NaCl, urea, glucose, and bile salts of different concentrations) on the phase behavior were examined. The mixed microemulsion system showed temperature insensitivity, whereas the Brij-35 (single) stabilized system exhibited a smaller microemulsion zone at elevated temperature. NaCl and glucose increased the microemulsion zone up to a certain concentration, beyond which the microemulsion zones were decreased. These additives decreased the microemulsion zones as temperature was increased. The effect of urea on microemulsion zone was found to be insignificant even at the concentration 3.0 mol dm^{-3}. Little effect on microemulsion zone was shown by NaC (sodium cholate) at 0.25 and 0.5 mol dm^{-3} at different temperatures. The conductance of the single (AOT) and mixed microemulsion system (AOT + Brij-35) depends upon the water content and mixing ratios of the surfactants, and a steep rise in conductance was observed at equal weight percentages of oil and water. Viscosities for both single (AOT) and mixed (AOT + Brij-35) surfactant systems passed through maxima at equal oil and water regions showing structural transition. The viscosities for microemulsion systems increased with increasing Brij-35 content in the AOT + Brij-35 blend. Conductances and viscosities of different monophasic compositions in the absence and presence of additives (NaCl and NaC) were measured at different temperatures. The activation energy of conduction ($\Delta E^*_{\mathrm{cond}}$) and the activation enthalpy for viscous flow ($\Delta H^*_{\mathrm{vis}}$) were evaluated. It was found that both $\Delta E^*_{\mathrm{cond}}$ and $\Delta H^*_{\mathrm{vis}}$ were a function of the nature of the dispersion medium. Considering the phase separation point of maximum solubility, the free energy of dissolution of water or oil (ΔG^0_{s}) at the microdispersed state in amphiphile medium was estimated and found to be a function of surfactant composition.

Keywords: Eucalyptus oil; AOT; Brij-35; Microemulsion; Phase behavior; Additives; Viscosity; Conductivity; Thermodynamics

1. Introduction

Microemulsions are thermodynamically stable, isotropic dispersions of otherwise immiscible oil and water stabilized by surfactants [1]. Owing to their diphilic nature, surfactants distribute their head and tail parts to the corresponding polar and nonpolar solvents forming a monolayer film between them. This decreases the interfacial tension to an ultralow value, which results in the solubilization of the otherwise immiscible components. Generally, a second surfactant, called cosurfactant, is added into the microemulsion system with reference to various applications in pharmacy and drug delivery and, therefore, its role is well documented [2–8]: (i) prevent formation of rigid structures such as gels, liquid crystals, precipitates, etc.; (ii) lower the viscosity of

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the system; (iii) reduce interfacial tension; (iv) increase the fluidity of the interface and thereby increasing the entropy of the system; (v) increase the mobility of the hydrocarbon tail and allow greater penetration of the oil into this region; and (vi) influence the solubility properties of the aqueous and oleic phases due to its partitioning between the phases. Several attempts to substitute traditional cosurfactants with other components [9–14], for example, nonionic surfactants, alkanoic acids, alkanediols, amines, aldehydes, ketones, butyl lactate, and oleic acid, have been carried out from the viewpoint of suitable applications of microemulsions. The roles of cosolvents and additives in the preparation of microemulsions are also reported [15–17]. The structural characteristics of microemulsions and their dynamics and transport behaviors with basic understanding of their formation, state of aggregation, internal composition, and stability with reference to their probable uses have been reviewed in detail by Moulik and Paul [18]. Structural studies of microemulsions stabilized by AOT have been reported by Eastoe et al. [19].

As a consequence of many potential advantages of microemulsions (for example, their clarity, high stability and interfacial area, ease of preparation) interest has rapidly grown in the use of microemulsions starting from tertiary oil recovery to nanoparticle synthesis. A comprehensive account of the phase equilibria characterization, structure, uses, and applications of the microemulsions has been reported by Paul and Moulik [20], Sjoblom et al. [21], De and Maitra [22], Solans and Garcia-Celma [23], Solans and Kunieda [24], Mittal and Kunieda [25], and Mittal and Shah [26]. Recently, microemulsions have been employed as liquid membranes [18,25] to study transport behavior of both polar and nonpolar species across them, which have importance in biology for understanding the fundamentals of membrane transport and offers the prospect as a method of separation. In light of the above, several authors have contributed a good number of publications on the formation of microemulsions using biocompatible and nontoxic ingredients (both surfactant and oils) for applications in pharmaceutics and drug delivery, cosmetics, food, agrochemical, and micellar enzymology [27–38]. Of these, the systematic investigations made by Moulik et al. on the formulation and development of these systems as mentioned above are note worthy. Moulik et al. [12,27–30] came up with a series of studies on the formulation and development of multicomponent systems containing biologically occurring components (with biocompatibility and nontoxicity) and their stability, physicochemical properties. The active ingredients used in these systems were Tween-20, Tween-60, Brij-30, Brij-52, Brij-92, and sodium oleate as surfactants; ethanol, isopropyl alcohol, and cinnamic alcohol as cosurfactants; and eucalyptus, coconut, ricebran, clove, isopropyl myristate, and saffola as oils. These systems were found to be fairly stable at 37 °C. The physicochemical properties, viz., viscosity, conductance, compressibility, and specific volumes, of these systems have been reported. In recent studies [29,30], hydrodynamic diameter, diffusion coefficient, and polydispersity of dispersed droplets of different compositions have been determined from dynamic light scattering (DLS) experiments. In addition, the energetic parameters (free energy, enthalpy, and entropy) have been evaluated from calorimetric measurements to aid the understanding of the formation and stability of these systems. An analysis comprising all these data has been rationalized and presented. The activity of enzyme (alkaline phosphatase) [31] and kinetics of alkali fading of crystal violet [28b] in biological microemulsion media containing vegetable oil (clove and ricebran) and cinnamic alcohol [31] have been presented, and a striking difference in the enzymatic process as well as spectral behavior in microheterogeneous media with both hydrocarbon and vegetable oil has been observed.

A vast literature as cited above concerns mainly the use of single ionic or nonionic surfactants to prepare microemulsions using biocompatible and nontoxic ingredients. Such studies, specially microemulsification of plant/vegetable oils using mixed surfactants, have seldom been carried out, though these oils have several uses in pharmaceutical and industrial preparations [39]. In previous studies [40,41], physicochemical investigations on the microemulsification of oils of different types (plant/vegetable, ester of myristic acid, and hydrocarbon) and water using mixed surfactants of different charges with other characteristics and cosurfactants (alkanols and butyl lactate) in the presence and absence of additives have been reported. The phase behaviors of these systems have been represented by Gibbs triangle and fish-tail diagrams and have compared the efficiency of different surfactants (single and mixed) with respect to the area of monophasic region formed. The structural features of these systems have been investigated using conductivity and viscosity measurements.

The present investigation was taken up to microemulsify eucalyptus oil and water by mixed surfactants [AOT, sodium bis-2(ethylhexyl) sulfosuccinate] and nonionic surfactant [Brij-35, polyoxyethylene(23) lauryl ether] and 1-butanol as cosurfactant at different mixing ratios (w/w) of the surfactants as well as at different ratios (w/w) of surfactant and cosurfactant. The phase behaviors of the pseudoternary mixed systems were examined to understand the mutual solubility and topological nature of the multicomponent mixtures using Gibbs triangle and tetrahedral (both unfolded and folded) representations. The effect of mixing ratio of the surfactants, ratio of surfactant–cosurfactant (S:CS), sodium chloride, urea, glucose, sodium cholate at different concentrations, and temperature on the phase behavior of the microemulsion systems are presented. It is expected that the results of present study will be useful in pharmaceutical and related applications. Therefore, information on the phase behavior and stability of the studied microemulsion systems in the presence of additives of biological relevance and importance would be worthwhile. We herein present the