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Journal of Colloid and Interface Science 295 (2006) 230–242
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Percolation phenomenon in mixed reverse micelles: The effect of additives

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Received 15 April 2005; accepted 29 July 2005
Available online 24 August 2005

Abstract

The conductivity of AOT/IPM/water reverse micellar systems as a function of temperature, has been found to be non-percolating at three different concentrations (100, 175 and 250 mM), while the addition of nonionic surfactants [polyoxyethylene(10) cetyl ether (Brij-56) and polyoxyethylene(20) cetyl ether (Brij-58)] to these systems exhibits temperature-induced percolation in conductance in non-percolating AOT/isopropyl myristate (IPM)/water system at constant compositions (i.e., at fixed total surfactant concentration, ω and X_{nonionic}). The influence of total surfactant concentration (micellar concentration) on the temperature-induced percolation behaviors of these systems has been investigated. The effect of Brij-58 is more pronounced than that of Brij-56 in inducing percolation. The threshold percolation temperature, T_p has been determined for these systems in presence of additives of different molecular structures, physical parameters and/or interfacial properties. The additives have shown both assisting and resisting effects on the percolation threshold. The additives, bile salt (sodium cholate), urea, formamide, cholesteryl acetate, cholesteryl benzoate, toluene, a triblock copolymer [$(EO)_{13}(PO)_{30}(EO)_{13}$, Pluronic, PL64], polybutadiene, sucrose esters (sucrose dodecanoates, L-1695 and sucrose monostearate S-1670), formamide distinctively fall in the former category, whereas sodium chloride, cholesteryl palmitate, crown ether, ethylene glycol constitute the latter for both systems. Sucrose dodecanoates (L-595) had almost marginal effect on the process. The observed behavior of these additives on the percolation phenomenon has been explained in terms of critical packing parameter and/or other factors, which influence the texture of the interface and solution properties of the mixed reverse micellar systems. The activation energy, E_p for the percolation process has been evaluated. E_p values for the AOT/Brij-56 systems have been found to be lower than those of AOT/Brij-58 systems. The concentration of additives influence the parameters T_p and E_p for both systems. A preliminary report for the first time on the percolation phenomenon in mixed reverse micelles in presence of additives has been suggested on the basis of these parameters (T_p and E_p).

Keywords: Mixed reverse micelles; Threshold percolation temperature; Activation energy; Additive effects; AOT; Isopropyl myristate

1. Introduction

Reverse micelles (RMs) are generally described as nanometer-sized water droplets dispersed in an apolar solvent with the aid of a surfactant monolayer, forming a thermodynamically stable and optically transparent solution. The entrapped water is heterogeneous in nature and its properties gradually change as a function of ω (= $[H_2O]/[\text{surfactant}]$), and depends on the distance from the polar head layer. Sometimes they contain solubilized water in excess of certain amount and known as w/o microemulsions [1–5]. RMs or w/o microemulsions find applications starting from tertiary oil recovery to nanoparticle synthesis [1,6–10]. Reverse micelles possess highly dynamic structures whose components rearrange themselves over time and space through interactions or collisions, coalescing and redispersing. The structure and properties of reverse micellar systems have been investigated extensively by numerous methods [2,3,6–10]. Of these, the measurement of conductivity is a useful technique in obtaining information on micellar interactions [6,11,12].

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2005.07.072

The phenomenon of electrical percolation is characterized by sudden increase in electrical conductivity when either the temperature or the volume fraction of the dispersed phase reaches a certain threshold value. The nature and the basic understanding of the percolation process have been investigated by a number of research workers [13–17]. The enhanced conductance has been considered to take place by the formation of infinite clusters/association of dispersed water droplets (stabilized by the amphiphiles) in the oil continuous medium. The easy flow of charges (ions) takes place by "hopping" [18–21] from droplet to droplet or are transferred by way of "fusion, mass transfer and mass exchange" [22–25]. As a consequence of the ion transfer, the conductance can be enhanced by 100 to 1000 folds. The composition of the system and other environmental conditions such as the presence of additives controls the percolation threshold values [26–30].

AOT can form reverse micelles under wide range of conditions (such as, water content, temperature, solvent, electrolyte type and concentrations) without the need of cosurfactant [31]. Over the past decade a number of studies have been carried out on the effects of various kinds of additives on the electrical conductivity and other properties of water/AOT/hydrocarbon oils reverse micelles by several researchers [25,27,32–43]. The percolation phenomenon has been shown to occur earlier (assistance) or be delayed (retardation) in presence of additives; however, many of them remained totally ineffective. The "transient-fusion-mass transfer-fission" model has been found to be more applicable over the "hopping" model in most of the cases to explain the percolation phenomenon. Of these studies, the work of Moulik et al. [25,27,32–36], Garcia-Rio et al. [38–40] are noteworthy. Above reports concern mainly the percolation of conductance in water/AOT/hydrocarbon w/o microemulsions. Investigations on the microstructures and properties of reverse micelles formed with mixed surfactants (i.e., addition of a second surfactant to water/single surfactant/oil system) has seldom been carried out to understand the basic mechanism of the phenomenon taking place inside them. However, reports available on the latter aspect are due to Alexandradis et al. [28], Nazario et al. [44], Eicke et al. [45,46], Li et al. [47,48], Liu et al. [49,50], Bumajdad et al. [51].

In our previous studies, the solubilization behavior of water in anionic (AOT) or cationic didodecyldimethylammonium bromide (DDAB)/nonionic surfactants (of different chemical structures and physicochemical properties) mixed reverse micellar systems stabilized in isopropyl myristate, isobutyl benzene and cyclohexane at different temperatures has been reported [12,52]. In a subsequent study [6], the effects of water content (ω), micelle concentrations, content of nonionic surfactant of different types (Brijs, Spans, Tweens) on the temperature-induced percolation of conductance of AOT-nonionics and DDAB-nonionics [polyoxyethylene(10) cetyl ether (Brij-56) and polyoxyethylene(20) cetyl ether (Brij-58) only] mixed reverse micelles in a nontoxic oil IPM, which is widely used in biologically resembling sytems, pharmaceutical and drug delivery [53] have been reported.

In continuation of our previous studies, the present study is aimed to measure the electrical conductivity of the water/AOT/Brij-56 or Brij-58/IPM reverse micellar systems in presence of additives of various types with different structures and physical parameters and/or interfacial properties, as they can alter the texture of the interface. Besides, some of the additives are frequently used in the study of mass transfer processes. No study on the effect of additives on the percolation of conductance in mixed reverse micellar systems has yet been reported. The activation energy for percolation of conductance of these systems can be interesting and instructive to interpret the percolation phenomenon. Hence, the activation energy has been estimated in presence of additives.

2. Experimental

2.1. Materials and methods

The following surfactants were used without further purification, Sodium bis-(2-ethylhexyl) sulfosuccinate (AOT, 99%) was purchased from Sigma, USA. Polyoxyethylene (10) cetyl ether (Brij-56), polyoxyethylene(20) cetyl ether (Brij-58) are products of Fluka (Switzerland). Toluene (Tl), benzyl alcohol (BA), formamide (FA), ethylene glycol (EG), urea, NaCl are of AR and extrapure grade of SRL, India. Isopropyl myristate (IPM) is a product of Fluka (Switzerland). Two types of sucrose dodecanoates, (L-1695 and HLB, 16.0; L-595 and HLB, 5.0) and sucrose monostearate (S-1670, HLB, 15.0) were gifted by Mitsubishi Chemical Corporation, Yokohama, Japan. L-1695 (sucrose monolaurate) is the mixture of 83.6% sucrose monododecanoate, 15.2% didodecanoate and 1.2% tridodecanoate. L-595 (sucrose dilaurate) is the lipophilic sucrose multi-dodecanoate and the contents of monoester, diester and triester are 30.0, 39.3 and 30.4%, respectively [54,55]. A polymeric surfactant [a triblock copolymer $(EO)_{13}(PO)_{30}(EO)_{13}$, Pluronic L64, MW = 2900], polybutadiene (PBD), dicyclohexano-18-crown-6 (crown ether, CE) are products of Fluka, Switzerland. Cholesterol (Ch) and its derivatives (cholesteryl acetate, CA, palmitate, CP and benzoate, CB) and sodium cholate (NaC) are products of Sigma, USA. The chemical structures of the surfactants and some of the additives are represented in Scheme 1. Double distilled water was used with conductance less than 3 $\mu S\,cm^{-1}$.

2.2. Construction of phase diagram

To construct the phase diagram in a Gibbs triangle, calculated amount of surfactant(s) and oil were taken in sealed test tubes and equilibrated at 30 °C in a thermostatic water bath accurate to ±0.1 °C. Then water was added into it in small increment with the help of a micro-syringe, shaken