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Dynamics of percolation and energetics of clustering of water/AOT/isooctane microemulsions in the presence of propylene glycol and its oligomers

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Abstract

The temperature-induced percolation of water/AOT/isooctane microemulsion systems has been studied at different concentrations of AOT in the presence of varying concentrations of mono-, di-, and tri-propylene glycols employing conductometric technique. Volume-induced percolation of these microemulsion systems as a function of temperature has also been studied using the same method. The volume-induced percolation data has been analyzed to find the threshold percolation volume fraction. The performance of the scaling equation for volume-induced percolation was tested. The results from temperature-induced percolations have been analyzed to quantify the threshold percolation temperature, performance of the scaling equation, the activation energy for the percolation process, and the thermodynamic parameters of clustering of the dispersed nanodroplets. A simple structural model has been applied in the calculation of the various parameters, i.e. aggregation number (n), core radius (r_n), surface number density of the surfactant molecules at the interface (α_s), and the number of droplets per unit volume. The structural parameters were rationalized in terms of the percolation temperatures for the microemulsion systems under investigation.

Keywords: Microemulsion; Percolation; Conductometry; Aggregation; Surfactant

1. Introduction

Microemulsions are thermodynamically stable, transparent, and isotropic dispersions of water-in-oil or oil-in-water achieved by the proper selection of surfactant and cosurfactant, and their combined addition at appropriate concentrations. The dispersed component can be oil and the continuous phase water or an aqueous solution, in which case the system is described as an oil-in-water (o/w) microemulsion, or the oil and water can exchange roles, in which case the systems are termed water-in-oil (w/o) microemulsions. The water/oil systems described in the present study can be considered as swollen reverse micelles, having a distinct water pool in the core. Among the studies on structural transitions of microemulsions, the intriguing phenomenon of electrical percolation has received special significance in the literature [1–8]. The percolation of conductance in w/o microemulsions can be induced by either a change in the volume fraction of water (ϕ) or the temperature (θ) [9–11]. At constant temperature, after a threshold volume fraction of water, conductance can be enhanced 100–1000 times. At a constant mole fraction of water and amphiphile, a multi-fold increase in conductance is also observed above a threshold temperature. The enhanced conductance has been attributed to the formation of "infinite clusters" of the dispersed particles in the oil continuous medium (w/o). The easy flow of charges takes place either by "hopping" [12–14] or by way of a "transient fusion and mass exchange" [15–18] mechanism.

Moderately low concentrations of additive are known to affect the percolation threshold [19–23]. It has been found that the introduction of additives that make the surfactant membrane more rigid hinder electrical percolation [24], whereas additives that increase membrane flexibility advance it [6,25]. These results and those relating electrical percolation to mass exchange among droplets suggest that the phenomenon is not associated with the formation of two continuum structures, but rather that discrete droplets prevail [17,26–29].

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Recently, the percolation and water solubilization of mixed nonionic-AOT microemulsion systems has been studied by Paul and Mitra [30–32]. Also, Yang et al. [33] recently studied the percolation behavior of AOT reverse micelles in the presence of bile salts in terms of percolation temperature and the diffusion coefficients for the reverse micelles under the influence of these additives.

In the present study, the effect of mono-, di-, and tri-propylene glycols on both the temperature and volume-induced percolation of water/AOT/isooctane microemulsions has been investigated employing a conductometric method. Propylene glycol contains two hydroxyl groups and is expected to function as a short-chained alcohol, lowering the percolation temperature. The additives di- and tri-propylene glycol possess, in addition to two hydroxyl groups, ethylene oxide moieties, which are known to lower the rigidity of the interface of the microemulsion droplet. It is therefore expected that both di- and tri-propylene glycol will result in a further decrease in the percolation temperature.

In the temperature-induced percolation study, the threshold percolation temperature, scaling equation parameters, and energy of activation for the physiochemical process have been calculated. Thermodynamics of clustering for various AOT concentrations as well as various additive concentrations have also been determined. In the volume-induced percolation study, threshold volume-fraction, scaling equation parameters, and structural parameters have been evaluated for the microemulsion systems.

2. Materials

AOT (sodium bis(2-ethylhexyl)sulfosuccinate), propylene glycol (PG), di-propylene glycol (di-PG), tri-propylene glycol (tri-PG), and isooctane (2,2,4-trimethylpentane) were purchased from Sigma–Aldrich, USA and used as received. Aqueous solutions were prepared using triply-deionized water.

3. Methods

Conductivity measurements (with 0.5% accuracy) were made on a CDM conductometer using a temperature compensated cell with a constant of 0.978 cm^{-1} and a measuring frequency of 1 kHz. The solution temperature was controlled with a Haake F3 digital thermostated water bath at a temperature accuracy of ±0.1 °C.

3.1. Temperature-induced percolation

Microemulsions were prepared at the same composition ($\omega = [\mathrm{H_2O}]/[\mathrm{AOT}] = 25$) for all solutions. Conductivity measurements were taken as a function of temperature for the water/AOT/isooctane systems at AOT concentrations of 0.25, 0.375, and 0.5 M. The conductance of the microemulsion sample at a fixed composition was measured with increasing temperature until a rapid rise in the conductance was observed. The conductance measurement was made after careful equilibration of the system at each temperature. Similar sets of measurements were taken on samples of different compositions.

3.2. Volume-induced percolation

A constant AOT concentration of 0.5 M was kept throughout the volume-induced percolation study. The conductance measurements were taken upon addition of water or aqueous solution of glycol to this system. The threshold volume fraction of water (ϕ_v) was obtained by analyzing the data by means of the Sigmoidal–Boltzmann equation [34].

4. Results and discussion

4.1. Percolation courses and threshold temperature

The percolation courses of water/AOT/isooctane at varying concentration of the additive tri-propylene glycol and constant [AOT] are shown in Fig. 1. The percolation temperature (θ_t) was found to decrease with increasing concentration of additive. Fig. 2 demonstrates a decrease in θ_t as a function of AOT concentration at a constant concentration of glycol additive. Fig. 3 illustrates that the percolation temperature in the

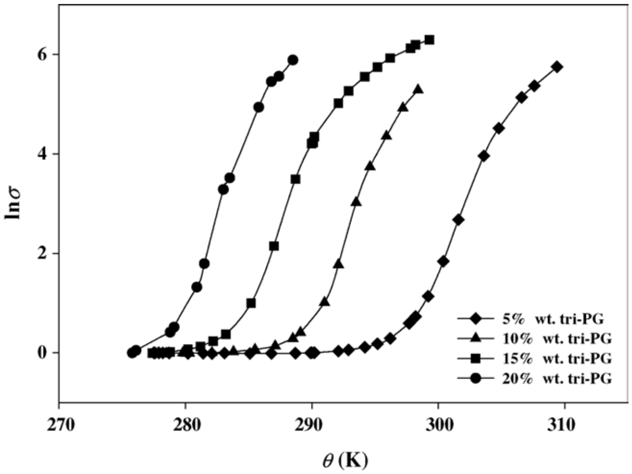

Fig. 1. Percolation courses of water/AOT/isooctane microemulsions varying percentage of tri-propylene glycol additive (0.375 M AOT).

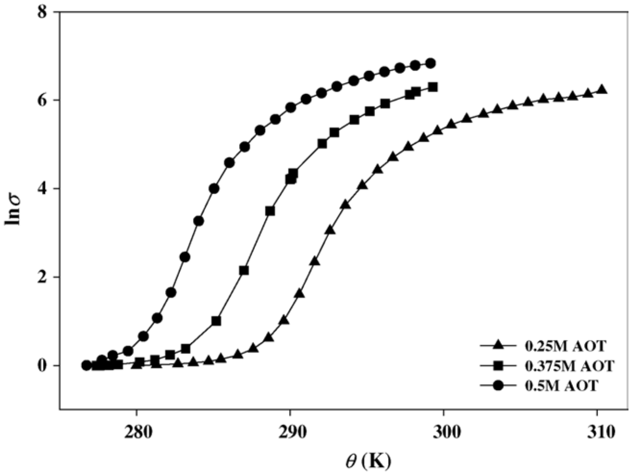

Fig. 2. Percolation courses of water/AOT/isooctane microemulsions with 15% tri-propylene glycol additive varying the concentration of AOT.