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Article

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Dual Action of Hydrotropes at the Water/Oil Interface

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Abstract

Hydrotropes are substances containing small amphiphilic molecules, which increase solubility of nonpolar (hydrophobic) substances in water. Hydrotropes may form dynamic clusters (less or about 1 ns lifetime) with water molecules; such clusters can be viewed as "pre-micelles" or as "micellar-like" structural fluctuations. We present the results of experimental and molecular dynamics (MD) simulation studies of interfacial phenomena and liquid-liquid equilibrium in the mixtures of water and cyclohexane with the addition of a typical nonionic hydrotrope, tertiary butanol. The interfacial tension between the aqueous and oil phases was measured by Wilhelmy plate and spinning drop methods with overlapping conditions in excellent agreement between techniques. The correlation length of the concentration fluctuations, which is proportional to the thickness of the interface near the liquid-liquid critical point, was measured by dynamic light scattering. In addition, we studied the interfacial tension and water-oil interfacial profiles by MD simulations of a model representing this ternary system. Both experimental and simulation studies consistently demonstrate a spectacular crossover between two limits in the behavior of the water-oil interfacial properties upon addition of the hydrotrope: at low concentrations the hydrotrope acts as a surfactant, decreasing the interfacial tension by adsorption of hydrotrope molecules on the interface, while at higher concentrations it acts as a co-solvent with the interfacial tension vanishing in accordance to a scaling power-law upon approach to the liquid-liquid critical point. It is found that the relation between the thickness of the interface and the interfacial tension follows a scaling law in the entire range of interfacial tensions, from a "sharp" interface in the absence of the hydrotrope to a "smooth" interface near the critical point. We also demonstrate the generic nature of the dual behavior of hydrotropes by comparing the studied ternary system with systems containing different hydrocarbons and hydrotropes.

Introduction

Hydrotropes are substances consisting of small amphiphilic molecules. Examples of nonionic hydrotropes are low-molecular-weight alcohols and amines. Hydrotropes may be completely or significantly water-soluble and can increase solubility of hydrophobic substances ("oil") in water, serving as a co-solvents.[1] Like surfactants, small addition of a hydrotrope reduces the interfacial tension between water and oil.[2] Hydrotropes are effectively used as co-surfactants for stabilization of microemulsions.[3] However, unlike surfactants, hydrotropes do not form stable micelles in aqueous solutions because the hydrophobic parts of their molecules are too small.[4-5] Instead, some nonionic hydrotropes (tertiary butanol (TBA) is one of the most characteristic examples) may form dynamic non-covalent molecular clusters in aqueous solutions. Molecular Dynamics (MD) simulations show that these clusters have a size order of 1 nm and lifetime from dozens to hundreds picoseconds, being stabilized by hydrogen bonds between hydrophilic parts of hydrotrope molecules and water (see ref.[6] and a movie in the supporting material, showing the simulation of the formation and dissipation of dynamic micellar-like clusters of TBA in an aqueous solution with 7 mol% TBA). Moreover, hydrotropes may stabilize mesoscopic (100-200 nm) droplets of "oil" preventing or significantly delaying their coalescence.[6-8]

In this work, we present the results of experimental and MD simulation studies of interfacial phenomena and liquid-liquid equilibrium in the mixture of water and cyclohexane (CHX), also referred to as "oil," with the addition of tertiary butanol. TBA is known as "perfect amphiphile" with hydrophobic (hydrocarbon) and hydrophilic (hydroxyl) parts precisely divided by the water and "oil" interface.[9] TBA is completely soluble in both water and