



Application of ϵ - β fishlike phase diagrams on the microemulsion solubilizations of dense nonaqueous phase liquids



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ABSTRACT

The solubilizations of dense nonaqueous phase liquids trichloroethylene (TCE), carbon tetrachloride (CCl₄), 1,2-dichloroethane (DCE) and tetrachloroethene (PCE) in microemulsions containing mixed surfactants 1-dodecyl-3-methylimidazolium bromide (C₁₂mimBr) and sodium lauryl sulfate (SLS), were studied by application of the ϵ - β fishlike phase diagram approach. It was found that the three-phase microemulsions would form at two X_{C₁₂mimBr} ranges of 0.0–0.1 and 0.8–1.0. Compared to the microemulsions containing single surfactant C₁₂mimBr or SLS, the mixed C₁₂mimBr-SLS microemulsions have lower solubility of the alcohol (ϵ_B) and lower mass fraction of the alcohol in the interfacial layer (A^S), but higher solubilization parameter (SP^*) values.

The order of magnitude for the solubilization ability of the chlorohydrocarbons in the C₁₂mimBr-SLS mixed (X_{C₁₂mimBr} = 0.8) microemulsion systems is: TCE > CCl₄ > PCE > DCE. This is consistent with the results of the literature.

As the mass fraction values of oil in oil-water mixture (α) increase, ϵ_B and A^S decrease, while SP^* increases. The effects of both NaCl contents (w) and temperatures (T) on the physicochemical parameters of the microemulsions were also investigated. As the NaCl contents and the temperatures increase, the solubilization ability of the microemulsions increases.

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1. Introduction

Microemulsions are thermodynamically stable colloidal dispersions containing water, oil, surfactant and cosurfactant. They have many unique properties, such as ultra-low interfacial tension, large interfacial area, and super ability to solubilize both aqueous and oil-soluble compounds [1]. The research on microemulsions has attracted a considerable interest in many scientific fields over the last decades. Various microemulsion formulations have been used in chemical flooding to mobilize the remaining oil in the reservoir by reducing the interfacial tension between oil and water (IFT) [2,3]. They have also been widely used in detergency, cosmetics, pharmaceuticals, nanoparticle synthesis, surfactant-enhanced aquifer remediation (SEAR) and other industrial fields [1,4].

Dense nonaqueous phase liquids (DNAPLs), especially chlorinated solvents, pose a threat to groundwater supply. Chlorinated

solvents spread in complex patterns in heterogeneous aquifers. Tetrachloroethene (PCE) and trichloroethylene (TCE) are widely used as industrial solvents and degreasers. Especially, PCE is extremely difficult to remove because of its lower solubility, immiscibility, and relatively slower rates of dissolution.

Considerable attention has been focused on removing these potentially hazardous materials from the environment over the last 20 years [5–14]. The use of zerovalent iron for the remediation of chlorinated solvent contaminated ground waters is one of the effective technologies [8,10,12]. Surfactant-enhanced aquifer remediation (SEAR) [5–7,9,13,14] is another highly effective technology for the removal of DNAPLs from soils and is particularly advantageous for removing DNAPLs from groundwater. The solubilization of chlorinated hydrocarbons by surfactants is helpful to the removal of chlorinated hydrocarbons. Mobilizing residual or pooled NAPL through interfacial tension reduction can also facilitate the removal of the containments.

Baran et al. [6] prepared Winsor type microemulsions containing PCE, aqueous salt solution (with appropriate electrolyte concentration) and anionic surfactants. The surfactants used were a

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combination of sodium dihexyl sulfosuccinate, sulfated Guerbet alcohol ethoxylates and propoxylates. As a short and twin-tailed surfactant, sodium dihexyl sulfosuccinate would both generate classical phase behavior Winsor I \rightarrow III \rightarrow II and function as a cosurfactant for all other surfactant species. The PCE microemulsions of Winsor type were also obtained by using monochain DPDS surfactant phenyloxide monohexadecyl disulfonate (C_{16} MADS), hydrophobic dioctyl sodium sulfosuccinate (Aerosol OT) as the cosurfactant and two organic acids in place of the alcohol. The formation of the C_{16} MADS-AOT middle phase microemulsions significantly increase the solubilization of PCE [7].

Harendra et al. [5] used four types of surfactants to investigate the solubilization of PCE and TCE. The four surfactants used were Sodium lauryl sulfate (SLS), Triton X-100, cetyltrimethylammonium bromide (CTAB) and UH biosurfactant. It was found that Triton X-100 had the highest PCE solubilization, whereas UH biosurfactant had the highest TCE solubilization among the four surfactants studied. In addition, the degradation of PCE both in Triton X-100 and CTAB solutions were also investigated [9].

Mixed cationic and anionic surfactants would exhibit synergistic effects as there are strong attractive interactions between the cationic and anionic ions [15–20]. Upadhyaya et al. used mixtures of a double-tailed anionic surfactant sodium dihexyl sulfosuccinate (SDHS) and an unbalanced-tail (double tailed with tails of different length) cationic surfactant benzethonium chloride (BCI) to form middle-phase microemulsions with four different oils (trichloroethylene, hexane, limonene and hexadecane). They found that mixed anionic-cationic surfactant systems could solubilize more oil than the anionic surfactant alone under optimum middle-phase microemulsion conditions [15]. Chen et al. investigated the aggregation and interfacial behavior of mixtures of anionic (SLS) and cationic (dodecylammonium bromide, DTAB) surfactants in the ionic liquid 1-ethyl-3-methyl imidazolium ethylsulfate ([EMIM][EtSO₄]). Their experiments suggested that there was strong charge screening between anionic and cationic surfactants in ionic liquids [19]. Anionic and cationic surfactants mixture have been widely used in detergents, fabric softening, analytical chemistry, enhanced oil recovery, and pharmaceutical applications [21–23].

The ϵ (the mass fraction of the alcohol in the microemulsion systems)- β (the mass fraction of the surfactant in the microemulsion system) phase diagram method was used to investigate the interfacial composition, solubility and solubilization of the microemulsion systems containing PCE [24], and to examine the effects of various factors on the microemulsion systems [25].

The Winsor type microemulsions have been prepared containing water and chlorinated hydrocarbons of differing polarity (CCl₄, TCE and DCB) [26]. However, these experiments were conducted by scanning electrolyte concentrations under the condition of holding the other variables constant. The optimum salinity, S^* , and the solubilization parameter, σ^* were obtained in this research only in a certain compositions of the microemulsions.

Ionic liquids (ILs) are a class of chemicals with low melting point and low vapor pressure, and have excellent properties such as thermal and chemical stability, high conductivity and extraction behavior. ILs have been widely used in organic synthesis, catalysis and analytical processes. Imidazolium salts are the most studied ionic liquids. The imidazolium-based ILs with long carbon chains can be used as surfactants (SAILs). SAILs have obvious advantages over traditional surfactants [27,28]. The researchers concern the biodegradability problem of ionic liquids. SAILs mainly dissolve in the interfacial layer, less SAILs dissolve in aqueous and oleic phases to cause the pollution problem in Winsor III microemulsions [30]. Therefore, the SAILs molecules in microemulsions may be reprocessed and utilized. Sorption, for example, may play an important role in the removal of the imidazolium-based ILs from wastewater

[29]. It was also reported that the imidazolium-based ILs with the longer alkyl chains were more susceptible to biodegradation than these with the shorter ones [29].

In this paper, cationic 1-dodecyl-3-methylimidazoliumbromide (C_{12} mimBr) and anionic sodium lauryl sulfate (SLS) were used to prepare the Winsor III microemulsions to solubilize the chlorinated solvents PCE, TCE, 1, 2-dichloroethane (DCE) and carbon tetrachloride, respectively with the ϵ - β phase diagram method. The solubility and optimum solubilization of the microemulsions with various compositions would be discussed.

2. Experimental section

2.1. Materials and methods

1-dodecyl-3-methylimidazolium bromide C_{12} mimBr was synthesized and purified according to the literature [31] by our research group. The purity of the product was checked using ¹H NMR spectroscopy. In addition, the curve of surfactant tension with C_{12} mimBr concentrations was also used to examine the purity. There was no minimum point in the curve, indicating no surface-active impurity. Sodium lauryl sulfate (SLS), purchased from Drug Group Chemical Reagent Co., Beijing, China, was of analytical pure and recrystallized with alcohol twice before use.

Tetrachloroethene (PCE), trichloroethylene (TCE), carbon tetrachloride (CCl₄), 1, 2-dichloroethane (DCE), propan-1-ol and NaCl were all purchased from chemical reagent company and its purity levels and sources are listed in Table 1.

An analytical balance (Shanghai, China) and an electrically heated thermostatic bath (Jiangsu, China) were used in this study.

2.2. Methods

The surfactant mixture (C_{12} mimBr and SLS) with fixed molar fraction of C_{12} mimBr to SLS and C_{12} mimBr($X_{C_{12}mimBr}$) were weighed and placed in a series of Teflon-sealed glass tubes. The chlorohydrocarbon (PCE, TCE, CCl₄ or DCE) and aqueous NaCl solution with fixed α values [$\alpha = m_o/(m_o + m_w)$], m_o and m_w are the masses of chlorohydrocarbon and water, respectively] were then added into the glass tubes. Lastly, different amounts of alcohol were mixed with the samples. All samples were weighed at the accuracy of ± 0.0001 g. All samples were placed in a thermostatic water bath for a week to achieve phase equilibrium. Phase equilibrium was determined by visual observations and the volumes of each phase were recorded at the accuracy of ± 0.01 mL.

In $C_{12}mimBr(S_1) + SLS(S_2) + PCE(O) + \text{aqueous NaCl}(W) + \text{propan-1-ol}(A)$ microemulsion systems, ϵ [$= m_A/(m_{S_1} + m_{S_2} + m_A + m_o + m_w)$] is the mass fraction of alcohol in the microemulsion, and β [$= (m_{S_1} + m_{S_2})/(m_{S_1} + m_{S_2} + m_A + m_o + m_w)$] is the mass fraction of surfactants in the microemulsion. An ϵ - β fishlike phase diagram would be plotted using ϵ as the vertical coordinate and β as the horizontal coordinate.

The temperature of the experiments was fixed at (313.2 ± 0.1) K except for the temperature experiments.

2.3. Theoretical considerations

The phase behavior of a microemulsion system at constant temperature and pressure can be represented in a phase tetrahedron, a section through this phase tetrahedron at $\alpha = 0.5$ is a three-phase tie triangle including the microemulsion in the midst line of the Winsor III region (Fig. 1). This section is called a hydrophile-lipophile balanced plane (HLB plane) [30,32]. The composition of the microemulsion in this line obeys the HLB plane equation of

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