Available online at www.sciencedirect.com

Journal of Colloid and Interface Science 287 (2005) 273–287

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Preferential solubilization of dodecanol from dodecanol–limonene binary oil mixture in sodium dihexyl sulfosuccinate microemulsions: Effect on optimum salinity and oil solubilization capacity

Erika Szekeres [a], Edgar Acosta [a], David A. Sabatini [b,*], Jeffrey H. Harwell [a,c]

[a] *School of Chemical Engineering and Materials Science, Sarkeys Energy Center, University of Oklahoma, 100 East Boyd, Room T-334, Norman, OK 73019, USA*
[b] *Department of Civil Engineering and Environmental Science, Carson Engineering Center, University of Oklahoma, 202 West Boyd, Room 334, Norman, OK 73019, USA*
[c] *College of Engineering, Carson Engineering Center, University of Oklahoma, 202 West Boyd, Room 107, Norman, OK 73019, USA*

Received 4 May 2004; accepted 25 January 2005

Abstract

Solubilization of dodecanol–limonene binary oil mixtures has been studied in saturated Winsor type I and III sodium dihexyl sulfosuccinate microemulsions. The systems showed different oil solubilization behavior below and above dodecanol volume fraction 0.2. Below 0.2 dodecanol volume fraction regular Winsor type microemulsions formed. The oil solubilization was characterized in this concentration range by the optimum salinity and the maximum characteristic length. Dodecanol showed Langmuirian-type surface excess adsorption at the vicinity of the surfactant layer. Variation of the optimum salinity and middle phase characteristic length with increasing dodecanol concentration could be linked to changes in the dodecanol surface excess. These relationships were used to develop new mathematical models for the optimum salinity and characteristic length as a function of oil phase composition. Both models yield excellent agreement with the data. Above dodecanol volume fraction 0.2 regular Winsor type III microemulsions are not formed. Therefore our new models are not applicable in this concentration range.

Keywords: Microemulsion; Phase behavior; Anionic surfactant; Polar and nonpolar oil mixture; Solubilization; Curvature; Bending rigidity; Optimum salinity; Characteristic length; Synergism

1. Introduction

Solubilization of polar and nonpolar oil mixtures in microemulsions can be encountered in surfactant-enhanced aquifer remediation (SEAR) processes for various reasons. Oil contaminants at a remediation site are likely oil mixtures of both polar and nonpolar (e.g., hydrocarbons, aromatics, chlorocarbons, ketones, etc.) components [1–4]. Polar oil (e.g., dodecanol) may also be introduced intentionally into a surfactant solution as an additive in order to increase solubilization of hydrophobic oil contaminants [5–8]. Solubilization of single-component oils and oil mixtures containing similar oil components has been well studied [9–13]. In contrast, oil mixtures with polar and nonpolar components have received much less attention. In the present study, we investigate the solubilization of binary mixtures of polar and nonpolar oils in microemulsions formed using an anionic surfactant.

To assess the remediation performance of SEAR, it is necessary to know how much oil is solubilized in the microemulsion [4,9–12]. However, comparing two microemulsions is difficult, because solubilization depends on a number of factors [13], including the type/concentration of oil, surfactant, additives (electrolyte, alcohol), and temperature.

---

[*] Corresponding author. Fax: +1(405)325-4217.
E-mail address: sabatini@ou.edu (D.A. Sabatini).

0021-9797/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2005.01.092

Salager suggested [14] comparing the solubilization ability of different microemulsions at a common reference point. For this purpose, a convenient reference point is the optimum formulation. At the optimum formulation equal volumes of oil and water are solubilized, the solubilization parameter is at a maximum, and the interfacial tension between the oil/microemulsion and water/microemulsion phases reaches a minimum. Therefore two items of information are needed to characterize microemulsions: (a) the set of independent formulation variables (e.g., composition and temperature) that is necessary to produce the optimum formulation, and (b) the solubilization capacity of the surfactant at the optimum formulation [15,16].

In this study, NaCl additive is used to fine-tune the surfactant formulation to reach optimum. The concentration of NaCl at which the optimum formulation is achieved is called the optimum salinity [16]. The characteristic length [17] at the optimum formulation gives information about the solubilization ability of the surfactant. The characteristic length is essentially equal to the average radius of the oil droplets in direct (o/w droplet type or Winsor type I) microemulsions and the average half thickness of the oil (or water) domain that can be correlated to the surfactant layer in bicontinuous (Winsor type III) microemulsions at the optimum formulation.

Both optimum salinity and optimum characteristic length depend on the type of oil to be solubilized, if all other conditions are kept constant. To decide whether a surfactant could efficiently solubilize a specific oil mixture, knowledge is necessary of these two parameters as a function of the oil phase composition. Our objective in this research is to study and model the dependence of the optimum salinity and characteristic length at optimum oil phase composition with polar/nonpolar oil mixtures.

2. Model development

2.1. Background

In order to find the optimum formulation experimentally for an oil/ionic surfactant pair at a fixed temperature, detailed phase behavior studies are carried out [9,18–20]. Optimum salinity for a single-component oil can be calculated using the surfactant affinity difference (SAD) concept, introduced by Salager et al. [14–16]. For anionic surfactants SAD is given as

$$\begin{aligned}\frac{\mathrm{SAD}}{RT} &= \mu_{\mathrm{s}}^{*,\mathrm{o}} - \mu_{\mathrm{s}}^{*,\mathrm{w}} \\ &= \ln S - K \cdot \mathrm{EACN} - f(A) + \sigma - a_T \Delta T, \qquad (1)\end{aligned}$$

where R is the gas constant, T is the absolute temperature, $\mu_{\mathrm{s}}^{*,\mathrm{o}}$ and $\mu_{\mathrm{s}}^{*,\mathrm{w}}$ are the standard chemical potentials of the surfactant in the oil and in the water, respectively, S is the salinity, K is a constant depending on the type of the surfactant, EACN is the equivalent alkane carbon number of the oil, $f(A)$ is a function which depends on the alcohol, σ is a constant which depends on the surfactant, and a_T is the coefficient of the temperature effect on the SAD. At the optimum formulation $\mathrm{SAD} = 0$, and the optimum salinity is given as

$$\ln S^* = K \cdot \mathrm{EACN} + f(A) - \sigma + a_T \Delta T. \qquad (2)$$

Baran et al. [21] proposed an optimum salinity model for oil mixtures using the pseudocomponent assumption for the oil. When the pseudocomponent assumption [13,22,23] is valid, the oil behaves in a collective way. The composition of the solubilized oil is equal to the initial oil phase composition. If there is excess oil phase in equilibrium with the microemulsion, the solubilized oil composition and the excess oil phase composition are equal. The $\mathrm{EACN}_{\mathrm{mix}}$ of the oil mixture is computed by applying a linear mixing rule,

$$\mathrm{EACN}_{\mathrm{mix}} = \sum_i x_i \cdot \mathrm{EACN}_i, \qquad (3)$$

where $\mathrm{EACN}_{\mathrm{mix}}$ and EACN_i are the equivalent alkane carbon numbers of the mixture and component i, respectively, and x_i is the mole fraction of component i in the oil mixture. Combining Eqs. (2) and (3) yields the expression for the optimum salinity of the oil mixture

$$\ln S_{\mathrm{mix}}^* = \sum_i x_i \cdot \ln S_i^*, \qquad (4)$$

where S_i^* is the optimum salinity of the single component oil i.

One finds however, that the solubilized oil composition deviates from the initial oil composition when the polarity and/or molecular volume of the oil components are different [24,25]. For these mixtures, the pseudocomponent assumption is not valid, and it is not clear how the mixture optimum salinity should be computed. The experimentally determined optimum salinity has also been found to deviate from the one predicted by Eq. (4).

To our knowledge, a mathematical model to predict the middle phase characteristic length of oil mixtures as a function of oil composition has not been proposed. However, instead of the characteristic length, the optimum solubilization parameter has been used to describe the oil solubilization ability of the surfactant in the SEAR related literature. For example, an optimum solubilization parameter model for oil mixtures has been developed and used in UTCHEM [26]. UTCHEM is a multiphase, multicomponent flow simulator developed at the University of Texas at Austin. The solubilization parameter is defined as the solubilized oil volume per unit volume of surfactant [11–16]. Similarly to the characteristic length it provides information about the solubilization ability of the surfactant. It is a linear function of the mixture EACN [26],

$$\beta(S) = s(S) \cdot \mathrm{EACN}_{\mathrm{mix}} + h(S), \qquad (5)$$

where $\beta(S)$ is the solubilization parameter at salinity S and $s(S)$ and $h(S)$ are salinity-dependent empirical parameters,