Available online at www.sciencedirect.com
SCIENCE @ DIRECT®
Journal of Colloid and Interface Science 285 (2005) 351–359
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

Investigation of interaction parameters in mixed micelle using pulsed field gradient NMR spectroscopy

H. Gharibi [a,b,*], S. Javadian [c], B. Sohrabi [a], R. Behjatmanesh [a]

[a] *Tarbiat Modarres University, Department of Chemistry, P.O. Box 14155-4838 Tehran, Iran*
[b] *Iranian Information and Documentation Center (IRANDOC), P.O. Box 13185-1371, Tehran, Iran*
[c] *Institute for Advanced Studies in Basic Sciences, Department of Chemistry, P.O. Box 4595-159, Zanjan, Iran*

Received 11 June 2004; accepted 8 November 2004

Available online 12 January 2005

Abstract

Pulsed field gradient NMR spectroscopy was used to determine the partitioning of surfactant between monomeric and micellar forms in a mixed CTAB (hexadecyltetramethylammonium bromide) and Triton X-100 [p-(1,1,3-tetramethylbutyl)polyoxyethylene] system. In addition, potentiometric and surface tension measurements were used to determine the free concentration of ionic surfactant and the critical micelle concentration (CMC) of mixtures of n-alkyltrimethylammonium bromide (C_nTAB, $n = 12, 14, 16, 18$) and Triton X-100. Regular solution theory cannot describe the behavior of the activity coefficient and the excess Gibbs free energy of mixtures of ionic and nonionic surfactants. To overcome these shortcomings, we developed a new model that combines Van Laar expressions and the theory of nonrandom mixing in mixed micelles. The Van Laar expressions contain an additional parameter, ρ, which reflects differences in the size of the components of the mixture. Nonrandom mixing theory was introduced to describe nonrandom mixing in mixed micelles. This effect was modeled by a packing parameter, P^*. The proposed model provided a good description of the behavior of binary surfactant mixtures. The results indicated that head group size and packing constraints are important contributors to nonideal surfactant behavior. In addition, the results showed that as the chain length of the C_nTAB molecule in C_nTAB/Triton X-100 mixtures was increased, the head group size parameter remained constant, but the interaction and packing parameters increased. Increase of the temperature caused an increase in the interaction parameter β and a decrease in the packing parameter (P^*).

© 2004 Elsevier Inc. All rights reserved.

Keywords: Surfactant; Mixed micelles; Triton X-100; Alkyltrimethylammonium bromide; Regular solution theory; Packing parameter; Head group size; PFG-NMR; Ion-selective electrode; Surface tension

1. Introduction

Commercial surfactant solutions typically contain mixtures of surfactants because it is cheaper to produce surfactant mixtures than isomerically pure surfactants. An additional impetus for using surfactant mixtures is that in many applications, mixtures of dissimilar surfactants exhibit properties superior to those of the individual constituent surfactants due to synergistic interactions between the surfactant molecules [1,2]. The widespread use of surfactant mixtures in industry has stimulated interest in these systems, and in recent years many papers have been published on the solution properties of mixed surfactant systems.

The pseudo-phase separation (PPS) model is the most widely used model for studying surfactant mixtures [3]. In the PPS model, the micelles are treated as a separate, infinite phase in equilibrium with the monomer phase. If micelle formation is ideal, the critical micelle concentration (CMC) of the mixture can be determined from the CMC values of pure samples of the surfactants in the mixture [4]. Nonideal micelle formation is most commonly modeled using regular solution theory (RST) [5]. RST has proved successful in accounting for the nonideal behavior of a number of

---

[*] Corresponding author.
E-mail address: gharibi@irandoc.ac.ir (H. Gharibi).

0021-9797/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2004.11.024

binary surfactant systems. Thermodynamic treatments have been developed to calculate micelle properties such as micellar composition [6–8]. Molecular thermodynamics allows the calculation of the total free energy of micellization and the prediction of a broad spectrum of solution properties [9]. From these results, an interaction energy parameter, β, was introduced into RST. Two simpler working models of molecular thermodynamics have also been proposed, which consider only the electrostatic contribution to the free energy of micellization [10,11]. Another model uses a modified form of RST that includes a variable interaction energy parameter β' [12,13]. The performance of these models has been examined by comparison with experimental results and there is good agreement between them [14].

The measurement of surfactant self-diffusion coefficients using pulsed field gradient nuclear magnetic resonance (PFG-NMR) spectroscopy is another promising technique for analyzing mixed-micelle composition [15–18]. The use of NMR pulsed gradient spin-echo diffusion methods to study mixed surfactant systems offers various advantages over the more commonly used method of measuring CMCs. From NMR data, the partitioning between micellar and monomeric forms of each individual surfactant can be extracted through analysis of self-diffusion coefficients. This method allows direct calculation of the activity coefficients for each component present in a solution, which is more accurate and convenient than the indirect approach of fitting CMCs for a series of solutions. Moreover, because the NMR approach gives the micelle composition directly, it can be used to probe the mixed micelle composition at concentrations near the CMC, where the micelle composition differs significantly from the solution composition. ^{1}H NMR spectroscopy and ^{1}H NMR relaxation have been used to study the structure and dynamics of mixed micelles of CTAB and Triton X-100 [19].

Hall and Gharibi in various works developed the ion-selective electrode (ISE) technique to determine the characteristics of a binary mixture of n-alkyltrimethylammonium bromide (C_nTAB) and Triton X-100 [13,20,21]. Ruiz and Aguiar used a fluorescent probe technique to study the surfactant pair CTAB/Triton X-100 [22]. In the present study, CTAB/Triton X-100 binary surfactant systems were studied over a wide range of concentrations and compositions using PFG-NMR spectroscopy. Finally, the interaction of C_nTAB and Triton X-100 at various temperatures was investigated.

2. Experimental

2.1. Materials

C_nTAB ($n = 14$, 16, 18) and Triton X-100 were obtained from Aldrich and Merck Co., respectively. Dodecyltrimethylammonium bromide, DOTAB (Aldrich), was purified by repeated recrystallization from acetone and diethyl ether [23]. D_2O (99.95% purity) was obtained from Fluka Co.

2.2. Methods

The CMC of each mixed surfactant system was determined from surface tension measurements using a Kruss tensiometer. The results were accurate within ± 0.1 mN m^{-1}.

A cationic-surfactant-selective electrode and a bromide-ion-selective electrode (Corning electrode) were used to measure the concentrations of monomeric cationic surfactant and counterion. The cationic-surfactant-selective electrode was fabricated as described previously [24–27]. The experimental errors in the potentiometry measurements were ± 0.2 mV.

For each solution, the surfactant ion (C_nTA$^+$) and counterion (Br$^-$) activities were determined using the following two cells:

Surfactant electrode | test solution |
reference electrode (calomel) Cell (1)

and

Bromide ion electrode | test solution |
reference electrode (calomel) Cell (2).

All experiments were performed at 30 °C, except for C_{16}TAB and C_{14}TAB, which were investigated at various temperatures.

PFG-NMR experiments were carried out on a Bruker 500 MHz NMR spectrometer. All NMR measurements were performed at 25 °C. The gradient strength was calibrated using 0.05% H_2O in D_2O as a reference on the assumption that $D_s = 1.85 \times 10^{-9}$ at 25 °C, since D_s is introduced as a diffusion coefficient of H_2O [28]. The basic sequence was used with a pulsed field duration, δ, of 5 ms and a time interval, Δ, between the two gradient pulses of 200 ms. The echo attenuation (A) was recorded as a function of gradient amplitude (g). The signal intensity was found to obey the Stejskal–Tanner relation [29,30],

$$A = A_0 \exp\bigl(-\gamma^2\delta^2 g^2 D(\Delta - \delta/3)\bigr), \qquad (1)$$

where γ is the proton magnetogyric ratio, g is the field gradient strength, D is the self-diffusion coefficient of the surfactant, and A_0 is a fitting parameter. In the case of CTAB and Triton X-100, the N-methyl proton peak and the oxyethylene proton were selected, respectively, and the surfactant self-diffusion coefficient was obtained from the decrease in the peak height with increasing pulse gradient duration. Self-diffusion coefficients were calculated using the Core program (the normalized global error squared sum is 0.1). The value of A_0 was also calculated by the ILT method for confidence in the attenuation data. These two methods give the same results [31,32].

Download English Version:

https://daneshyari.com/en/article/10378108

Download Persian Version:

https://daneshyari.com/article/10378108

Daneshyari.com