Miscibility of anhydrous cationic surfactant mixtures

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ABSTRACT

Inverse gas chromatography (IGC) has been used for studying the miscibility of anhydrous cationic surfactant mixtures. Dodecyltrimethylammonium bromide (C_{12}TAB), octadecyltrimethylammonium bromide (C_{18}TAB) and their mixtures have been used as stationary phases. In these types of stationary phases, the working temperature was determined by Differential Scanning Calorimetric (DSC) and Inverse Gas Chromatography (IGC) techniques. Values of the interaction parameters between the cationic surfactants obtained at four different compositions of their mixtures and at five temperatures showed that the miscibility depended on the composition and suggested that the interactions became more unfavorable with the increment of C_{18}TAB concentration in the mixtures. The results have been interpreted by comparing the structure of the anhydrous lamellar liquid crystals with that of the lamellar mesophases formed in aqueous solutions. Deviations of the systems from the parameter solubility model have been discussed in terms of the entropy contribution to the Flory-Huggins interaction parameter.

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1. Introduction

There has been a considerable interest in the studies of surfactant mixtures in aqueous solutions during the past decades, from both theoretical and experimental points of view. The majority of these studies are related to dilute micellar solutions, since they provide the necessary information to enhance their performance in several industrial applications [1–3]. By contrast, studies of cationic surfactant mixtures in concentrated solutions are not very common [4,5], and even less those related to anhydrous surfactant mixtures [6].

In ionic anhydrous surfactant systems, the liquid and liquid crystalline structures are based on the simultaneous occurrence of two kinds of interactions: van der Waals' interactions in the hydrocarbon bilayers, and electrostatic ones in the ionic bilayers. In some cases, steric interactions can appear in the hydrocarbon bilayers, and polar interactions as well as hydrogen bonds can be found in the ionic bilayers. A combination of these interactions can appear in mixed amphiphile systems. Study of their thermodynamic properties can lead to a better understanding of their influence in the formation and stability of the mentioned microstructures. Moreover, this understanding will be useful for theoretical and practical uses in the design of new microstructures.

It has been stated in literature that an increase in the chain lengths reduces the miscibility of fatty acids in the solid state [7,8] and in monolayers [9]. It is also known that the melting point of a homologous series of surfactants can follow a different law of dependence on the chain length when the number of carbon atoms is even or odd. Lecuyer and Dervichian [10] found that the crystallization behavior of soap mixtures depends on the difference between the length of the hydrocarbon chains.

Studying phases in the decyltrimethylammonium bromide (C_{10}TAB)/cetyltrimethylammonium bromide (C_{16}TAB) system, Varade et al. [4] observed a synergistic effect. According to these authors, this may be due to the difficulty in the packaging of the hydrocarbon chains of different lengths. In the case of aqueous solution mixtures in the homologous series of alkyltrimethylammonium bromides, positive and negative values of the intra-micellar parameter of interaction between surfactants have been informed [11–14]. Similarly, some authors suggested attractive and repulsive interactions depending on the change in the concentration of surfactants [15–17]. Akisada et al. [18] have analyzed the behavior of mixtures of a homologous series of alkyltrimethylammonium bromides and they concluded that in those systems where the difference in chain lengths is equal or less two carbon atoms, the behavior becomes ideal.

We have previously studied the mixed systems of two twin-tailed cationic surfactants, didodecyldimethylammonium bromide (DC_{12}DAB) and dioctadecyldimethylammonium bromide (DC_{18}DAB) by IGC [6]. The obtained values of the interaction parameter were positive in all the explored concentration and temperature ranges. Thus, they were indicative of high immiscibility, in agreement with the behavior of the same system in aqueous solution [19].

Taking into account all these previous findings, we assumed that these effects can influence the structures of anhydrous liquid crystals. Understanding steric and energetic factors can also be useful in the

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enrichment of the aggregation structure theory. It is then interesting to analyze the behavior of anhydrous surfactant mixtures of the homologous series of alquiltrimethylammonium bromides, in which the hydrocarbon chain length difference is higher than two carbon atoms.

In this work, we inform the results obtained from the study of miscibility of dodecyltrimethylammonium bromide ($C_{12}TAB$) and octadecyltrimethylammonium bromide ($C_{18}TAB$) anhydrous surfactant mixtures by obtaining surfactant–surfactant interaction parameters through IGC. We attempt to analyze the interactions in surfactant mixtures that have a similar polar head to the system previously studied by us [6], but with only one hydrocarbon chain. Our objective was the determination of mutual solubilities of both surfactants and to compare the results with the ones obtained for the same systems in aqueous solutions.

The thermodynamic properties in solutions should be obtained by IGC in temperature zones where the main dissolution process is that of the partition of the probe solute in the stationary phase. In this paper, the working temperature zone has been obtained by DSC and IGC.

IGC is important in analyzing the degree of miscibility in polymers through the different experimentally determined parameters, such as specific retention volume, temperature of glass transition, and parameters of polymer–polymer interaction [20]. An extensive knowledge of the composition-temperature behavior of surfactant-based stationary phases by IGC will be of interest to design new analytical procedures.

2. Materials and methods

2.1. Materials

Dodecyltrimethylammonium bromide ($C_{12}TAB$) and Octadecyltrimethylammonium bromide ($C_{18}TAB$) (Sigma, analytical grade) were used as received. All probe solvents (Merck) were 99% or better.

2.2. Differential scanning calorimetry (DSC)

DSC was performed on a Perkin Elmer DSC 6 calorimeter, between 291 and 473 K, with a scanning rate of $10° min^{-1}$ and using samples of 5–10 mg for pure surfactants and 10–15 mg for materials collected over chromatography support. The instrument was calibrated with indium.

2.3. Inverse gas chromatography (IGC)

Pure $C_{12}TAB$ and $C_{18}TAB$ and their mixtures were used as stationary phases and deposited on Chromosorb W, AW, 60/80, which was employed as a solid support. The packing and conditioning of the column are described in reference [6]. The data employed in the specific retention volume computation were obtained by using a column 100 cm long, 1/4 in. external diameter, and the packing characteristics are included in Supplementary Material (SM). (Table 1 SM).

The working temperature zone has been obtained by IGC with packing columns. The packing columns prepared to study the

Table 1
B (cal.cm^{-3}) interaction parameter in the $C_{12}TAB/C_{18}TAB$ mixtures.

388.1K		393.1K		398.1		403.1K	
ϕ_2	B	ϕ_2	B	ϕ_2	B	ϕ_2	B
0.1543	-8.2 ± 2.7	0.1527	-6.0 ± 2.5	0.1510	-3.7 ± 2.4	0.1492	-1.9 ± 2.3
0.3814	-4.4 ± 1.3	0.3786	-3.8 ± 1.4	0.3755	-2.7 ± 1.3	0.3721	-1.8 ± 1.2
0.6128	-4.4 ± 1.4	0.6100	-3.2 ± 1.3	0.6069	-1.9 ± 1.2	0.6035	-1.1 ± 1.2
0.8803	-4.6 ± 3.2	0.8790	-0.9 ± 2.9	0.8777	1.8 ± 2.7	0.8761	4.3 ± 2.5

retentive behavior of two probe solutes (n-octane and toluene) between 338.1 and 423.1 K and with 10% of stationary phases on Chromosorb W, AW, 60/80, were columns 180 cm long and 1/8 in. external diameter. The retention time measurement for each solute was performed with a Hewlet Packard, HP 6890 series, GC System, equipped with a flame ionization detector (FID). Column temperature was measured in a range between 388.1 and 403.1 K with an Iron–Constantan thermocouple placed in the direct environment of the column. The temperature stability during experiments was of ± 0.2 K. The employed solutes were n-heptane, n-octane, n-nonane, cyclohexane, methylcyclohexane, benzene, toluene, ethyl acetate, dichloromethane, trichloromethane and carbon tetrachloride. The probe solutes were selected trying to cover all possible chemical structures and polarities. Nitrogen was used as carrier gas. Flow rates were measured at the beginning of each experiment with an air-jacketed soap film flowmeter placed at the outlet of the detector. Inlet pressures were measured with a micrometry syringe (through the injector septum) which was connected to an open branch mercury manometer. To ensure that the results were independent of sample size and flow rate and that the measurements were being performed at infinite dilution, the usual checks were made [21].

Solutes were injected with 10 µl Hamilton syringes, as vapor in equilibrium with pure liquid. For all the solutes and for all the range of stationary phase concentrations, the peaks were symmetric. The injector was kept at 423.1 K and the detector at 453.1 K.

Retention times (t_R) were measured with a Chem Station system and the retention specific volumes (V^0_g) were calculated with the following relationship [21]:

$$V_g^0 = j\left(\frac{F_f}{w_L}\right)\left(\frac{273.15}{T_f}\right)(t_R-t_0)(p_0-p_w)/p_0 \tag{1}$$

where j is the James–Martin compressibility correction factor, p_0 represents the outlet column pressure, F_f is the flow rate measured at pressure p_0 and temperature T_f, w_L is the mass of the stationary phase into the column and p_w is the water vapor pressure at T_f; t_0 is the dead time, which was measured by using the methane peak obtained with the FID.

3. Data reductions

The probe solute-surfactant Flory-Huggins interaction parameter, χ_{1i}, can be calculated from the specific retention volumes, V_g^0, by the expression [21,22]:

$$\chi_{1i}^{\infty} = \ln\left(\frac{273.15Rv_i}{V_g^0 p_1^0 V_1}\right) - \left(\frac{p_1^0(B_{11}-V_1)}{RT}\right) - \left(1-\frac{V_1}{V_i}\right). \tag{2}$$

where V_i stands for the specific volume of the surfactant experimentally measured in the laboratory. p_1^0, V_1 and B_{11} are the vapor pressure, the molar volume and the second virial coefficient of the probe solute, respectively. The vapor pressures were computed using the Antoine equations and the coefficients were taken from Riddick, Bunger and Sakano [23]. The solute densities at different temperatures were estimated from Dreisbach's compilation [24]. The second virial coefficient of the solutes was calculated by Tsonopoulos's correlation using critical constants tabulated in Reid et al. [25]. The interaction parameter obtained for probe solutes in $C_{12}TAB$ and $C_{18}TAB$ are included in Table 2 of SM. (Table 2 SM).

When the stationary phase is a surfactant mixture, Eq. (2) allows the determination of the ternary probe solute (1)-surfactant (2)-surfactant (3) interaction parameter, $\chi_{1(23)}$, assuming an additive specific volume