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Comparative study of the physicochemical properties of aqueous solutions of the hydrocarbon and fluorocarbon surfactants and their ternary mixtures

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ABSTRACT

Speed of sound and density of aqueous solutions of hydrocarbon p-(1,1,3,3-tetramethylbutyl) phenoxypoly(ethyleneglycols) (Triton X-100 (TX100), Triton X-165 (TX165)) and fluorocarbon (Zonyl FSN-100 (FSN100), Zonyl FSO-100 (FSO100)) surfactants as well as their ternary mixtures were measured at 293 K. Taking into account these values and the literature data of the surface tension and viscosity of the studied systems, the values of the isentropic compressibility, apparent specific adiabatic compressibility, hydration number, apparent specific volume and Jones Dole's *A* and *B*-coefficients were determined. For the systems containing FSO100 also the values of dB/dT were determined on the basis of the values of viscosity measured at different temperatures. Next, the calculated thermodynamic properties have been discussed in the term of intermolecular interactions between the components of the mixtures.

1. Introduction

Perfluorocarbons, the surfactants where all the hydrogen atoms in the hydrophobic moiety have been replaced by fluorine, have been much less studied than the corresponding hydrogenated surfactants, despite their technical interest resulting from their potential applicability. Fluorine is the most electronegative of all elements, and its dense electron cloud has very low polarizability [1,2]. The fluorine–carbon bond is very strong, but intermolecular interactions of fluorocarbons are weak. This results in an exceptional combination of properties of fluorocarbons, such as thermal, chemical, and biological inertness, and low solubility for water as well as polar and nonpolar organic solvents, high density, fluidity, compressibility, and high dielectric constants [3,4]. These unique properties of perfluorocarbon materials are exploited in various technical applications such as fire extinguishing media, electroplating bath, water proofing sprays, and lubricants [3,5]. Due to the surface characteristics that result from a perfluoroalkyl chain, there is also growing interest in partially fluorinated amphiphiles for cosmetic, pharmaceutical, and medical applications [6,7]. So, these properties confer special characteristics on the amphiphiles compared with the corresponding hydrogenated ones.

The extensive use of surfactants in a wide range of household, technological and commercial applications usually involves mixtures of surfactants. In such formulations different types of surfactants are blended to optimize different aspects of performance, and to produce greater flexibility in processing and formulation. Hence understanding the nature of surfactant mixing in solution and at interfaces is of paramount importance. Although there have been many studies on micelles and the surface behaviour of surfactant mixtures [8,9], most of them focus on the interaction parameters of mixed micelles of hydrocarbon surfactants calculated from the surface tension measurements by using the Rubingh's equations [10–12]. On the other hand, the speed of sound is an important property in the study of physics and chemistry, as speed of sound when used along with other properties, allows the derivation of a wide range of thermophysical properties including isentropic and isothermal compressibilities, isobaric thermal expansion coefficient, thermal pressure coefficient, the Joule–Thomson coefficient, isobaric and isochoric heat capacities, ratio of isobaric and isochoric heat capacities, and the reduced bulk modulus. All of these derivative properties are connected, with speed of sound directly or indirectly, by thermodynamic relationships and are essential for the accurate design and optimization of several industrial processes.

In the earlier studies dealing with the ternary mixtures of nonionic hydrocarbon, p-(1,1,3,3-tetramethylbutyl) phenoxypoly(ethylene glycols), Triton X-100 (TX100) and Triton X-165 (TX165), and the

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nonionic fluorocarbon surfactants, Zonyl FSN-100 (FSN100) and Zonyl FSO-100 (FSO100) [13,14] the values of the speed of sound, u, of these mixtures were not measured but were calculated on the basis of the Auerbach's relation which correlates the values of the surface tension of the solution with its density [15]. As follows from these calculations at the studied concentration (10^{-8}–5×10^{-4} M) the relation between the speed of sound and isentropic compressibility versus the concentration of added FSN100 and FSO100 was reversible to the typical plots found in the literature [16,17]. It was suggested that the theoretically calculated values of u are wrong or that with the concentration of added FSN100 and FSO100 their pre-micelles and/or micelles become packed to a smaller degree [14]. From this point of view, it was interesting to measure the values of the speed of sound of the mentioned ternary mixtures of surfactants, based on them calculate some volumetric properties of their micellar solutions and compare them to the properties of the aqueous solutions of single surfactants. For the calculations the values of surface tension, density and viscosity of the studied surfactants and their mixtures at 293 K were taken from the literature [13,14,16–18]. Additionally the viscosity measurements of the aqueous solutions of the systems including fluorocarbon surfactant, FSO100, were performed at 298, 303, 308, 313 and 318 K.

2. Experimental

2.1. Materials

p-(1,1,3,3-tetramethylbutyl) phenoxypoly(ethyleneglycols), Triton X-100 (TX100) ($C_{14}H_{21}$ $(CH_2CH_2O)_x$ OH, $x = 10$) (Fluka), Triton X-165 (TX165) ($C_{14}H_{21}$ $(CH_2CH_2O)_x$ OH, $x = 16$) (Fluka) and the fluorocarbon surfactants: Zonyl FSN-100 (FSN100) (DuPont) and Zonyl FSO-100 (FSO100) (DuPont) were used for preparation of aqueous solutions of their different ternary mixtures in the concentration range from 10^{-8} to 2×10^{-3} M using doubly distilled and deionized water obtained from a Destamat Bi18E distiller. Zonyl FSN-100 (FSN100) and Zonyl FSO-100 (FSO100) are ethoxylated nonionic fluorosurfactants, having an average 14 (from 1 to 26) and 10 (from 1 to 16) oxyethylene units and, 6 (from 1 to 9) and 5 (from 1 to7) CF_2 groups, respectively.

The following ternary mixtures of surfactants were studied:

M_1 – TX100 + TX165 (α TX100 = 0.8, γ_{LV} = 60 mN/m) + FSN100 ($C = 10^{-8}$–2×10^{-3} M),
M_2 – TX100 + TX165 (α TX100 = 0.8, γ_{LV} = 50 mN/m) + FSN100 ($C = 10^{-8}$–2×10^{-3} M),
M_3 – TX100 + TX165 (α TX100 = 0.8, γ_{LV} = 60 mN/m) + FSO100 ($C = 10^{-8}$–2×10^{-3} M),
M_4 – TX100 + TX165 (α TX100 = 0.8, γ_{LV} = 50 mN/m) + FSO100 ($C = 10^{-8}$–2×10^{-3} M).

Thus, for example, the mixture M_1 was prepared by adding FSN100 at different concentrations to the binary mixture of TX100 + TX165, where the mole fraction of TX100 in the bulk phase, α, was equal to 0.8, at γ_{LV} of the binary mixture equal to 60 mN/m.

2.2. Measurements

The speed of sound as well as the densities of aqueous solutions of single surfactant and their ternary mixtures were simultaneously and automatically measured using a digital vibrating tube densitometer and the speed of the sound analyzer (Anton Paar DSA 5000 M) provided with automatic viscosity correction and two integrated Pt 100 thermometers. Both the speed of sound and the density are extremely sensitive to temperature, so it was kept constant within 0.001 K using a proportional temperature controller. The apparatus was first calibrated with triple-distilled water and dry air. The standard uncertainties in density measurements were estimated to be $\pm 2 \cdot 10^{-3}$ kg m^{-3} and for the speed of sound ± 0.1 m s^{-1}.

All viscosity measurements of the aqueous solution of the studied systems containing FSO100 were performed with the Anton Paar viscometer (AMVn) at 298, 303, 308, 313 and 318 ± 0.01 K with the precision of 0.0001 mPa·s and the uncertainty 0.3%.

3. Results and discussion

From Fig. 1 it results that the values of the speed of sound, u, as a function of the logarithm of surfactant concentration in the bulk phase (C) increase at the concentration higher than the critical micelle concentration (CMC) only in the case of aqueous solutions of nonionic hydrocarbon surfactants, TX100 and TX165. It means that micelles of TX100 and TX165 are more packed (structured) and less compressible than the corresponding monomeric phase. In the case of aqueous solution of nonionic fluorocarbon surfactants and their ternary mixtures of surfactants, M_1–M_4, the values of u increase in the concentration range corresponding to the saturated monolayer at the water–air interface [13] and next decrease at the concentrations higher than the values of "the second CMC" of studied solutions determined on the basis of the fluorimetric measurements [14]. Thus, the bulk properties of the studied fluorocarbon surfactants and their mixtures are quite different from those of TX100 and TX165 and suggest that the use of the Auerbach's relation for such a system may not be proper. This relation has the form:

$$u = \left(\frac{\gamma_{LV}}{6.33 \times 10^{-10} \rho} \right)^a \quad (1)$$

where γ_{LV} is the surface tension of the solution, ρ – the density and $a = 2/3$. Oswal et al. used the Auerbach's relation to estimate speed of sound of alkyl alkanoates [19] and alkyl amines [20]. Aminabhavi et al. [21] used the Auerbach's relation to estimate speed of sound of the binary mixtures of 2-methoxyethanol with aliphatic alcohols. Recently Blairs [22] has modified the Auerbach's relation for the estimation of unknown sound velocities of metallic liquids using available surface tension and density values. Eq. (1) predicts that a plot of log u against log γ_{LV}/ρ should be linear with the slope equal

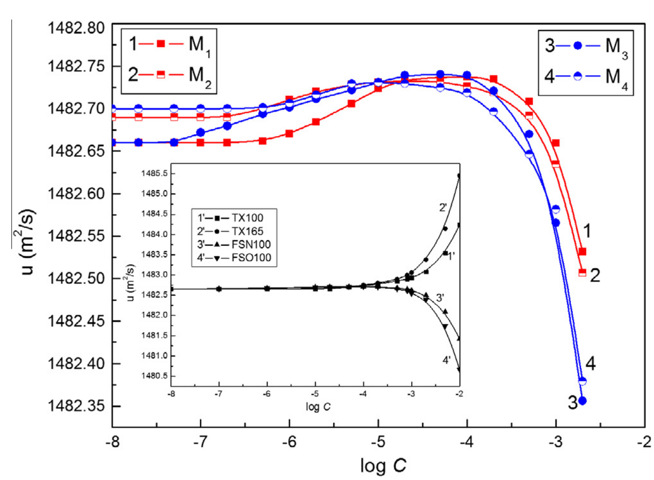

Fig. 1. A plot of the values of speed of sound (u) of aqueous solutions of the ternary mixtures of surfactants denoted as M_1 (curve 1), M_2 (curve), M_3 (curve 3) and M_4 (curves 4) as well as single surfactants TX100 (curve 1'), TX165 (curve 2'), FSN100 (curve 3') and FSO100 (curve 4') vs. the logarithm of the concentration of the added, third fluorocarbon surfactant or the concentration of a single surfactant, C.