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Properties of aqueous solutions of nonionic surfactants, Triton X-114 and Tween 80, at temperatures from 293 to 318 K: Spectroscopic and ultrasonic studies

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ABSTRACT

The speed of sound, density and refractive index of aqueous solutions of the nonionic surfactants, p-(1,1,3,3-tetramethylbutyl) phenoxypoly(ethyleneglycol) Triton X-114 (TX114) and polysorbate 80, Tween 80, have been measured over the entire range of concentration at 293, 298, 303, 308, 313 and 318 K under atmospheric pressure. Steady state fluorescence measurements have been also made using pyrene as a probe. From the experimental data the quantities such as critical micelle concentration (CMC), apparent dielectric constant, hydration number, isentropic compressibility, apparent specific adiabatic compressibility of a solute, intermolecular free length, acoustic impedance and molar sound number were determined. The variation of these parameters with concentration and temperature was discussed in terms of intermolecular interactions in the solution of a given surfactant.

1. Introduction

One of the key properties of surfactants responsible for their wide application in modern technologies [1–3] is their ability to form aggregates in solution above the critical micelle concentration (CMC) [4]. In aqueous media, the so-called direct micelles are formed due to a hydrophobic effect, with nonpolar fragments of surfactant molecules isolated within the micellar interior and polar head groups facing towards bulk water. Micelles are thermodynamically stable aggregates. Their size, shape and charge (for ionic surfactant) can be modulated by other components and/or by varying the surfactant concentration, temperature, pressure, and so on. Temperature has a significant effect on the supramolecular arrangement of surfactants in aqueous solution, especially nonionic ones, whose compatibility with water depends on the extent of hydration of the hydrophilic parts of molecules, which are particularly sensitive to temperature changes [4,5].

The nonionic surfactants belonging to the Tween series (polysorbates), find their application in food, bio-technical, pharmaceutical, industrial, domestic, chemical and bio-chemical areas [6–8]. Commercially available Tweens have predominantly 20 ethylene oxide groups attached to the sorbitan headgroup, with different long-chain saturated carboxylic acids, from lauric to stearic, and unsaturated oleic acid. Tweens are clear and non-odorous liquids at room temperature. Their low toxicity and acceptable degree of bio-degradability are responsible for their extensive utility [9]. All these utilities of polysorbates in various walks of life have encouraged us to study less explored properties of aqueous solutions of one of these compounds, Tween 80, with an intention to gather information on the nature of interactions between its molecules and water at different temperatures. It was also interesting to compare the obtained results with those of Triton X-114, one of the most explored surfactants in the separation methods based on the cloud point extraction [10–12]. For this purpose measurements of speed of sound, density and refractive index of aqueous solutions of p-(1,1,3,3-tetramethylbutyl) phenoxypoly (ethyleneglycol) Triton X-114 (TX114) and polysorbate 80, Tween 80, were performed over wide temperature and concentration ranges. Moreover, properties of the solutions were studied by means of steady state fluorescence measurements. On the basis of the obtained results the nature of molecular interactions in solutions at different concentrations and temperatures depending on the kind of medium, extent of solvation in solution, structure and size of the surfactant molecule were discussed.

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2. Experimental

Aqueous solutions of Triton X-114 (TX114) and Tween 80 (Sigma-Aldrich) were prepared in the concentration range from 10^{-6} to 10^{-2} M using doubly distilled and deionized water obtained from a Destamat Bi18E distiller.

The speed of sound as well as densities of aqueous solutions of studied surfactants at the temperatures 293, 298, 303, 308, 313 and 318 K were simultaneously and automatically measured using a digital vibrating tube densitometer and the speed of sound analyzer (Anton Paar DSA 5000 M) provided with automatic viscosity correction and two integrated Pt 100 thermometers. Both the speed of sound and 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 triply-distilled water and dry air. The standard uncertainties in density measurements were estimated to be $\pm 2 \times 10^{-3}$ kg·m^{-3} but for the speed of sound ± 0.1 m·s^{-1}.

The refractive index of studied solutions was measured by Abbemat 550 Performance Plus (Anton Paar). The apparatus was first calibrated with triply-distilled water. The precision of the refractive index and temperature measurements given by the manufacturer are ±0.00002 and ±0.03 K, respectively.

All speed of sound/density and refractive index measurements were made for 3 samples of two set measurements. Next for a given concentration of surfactant and temperature, the average value of speed of sound, density and refractive index was calculated and used for other calculations and discussion.

Steady state fluorescence measurements at different temperatures were made using a Hitachi F-2700 Fluorescence Spectrometer with a pyrene ($C = 2 \times 10^{-6}$ M) as a luminescence probe. Fluorescence excitation was done for pyrene at 335 nm, and the emission spectra were recorded in the range of 350–600 nm at a scan speed of 300 nm/min. The excitation and emission slit widths were 2.5 nm.

3. Results and discussion

Pyrene is a typical bioprobe for evaluating the interactions between various biomolecules because its emission property distinctly depends on the distance between two pyrene rings. The ratio of intensity of the first (I_1) and third (I_3) vibronic peaks, i.e., I_1/I_3, of the pyrene fluorescence emission spectrum is known as the "Py scale" [13]. In the presence of surfactants this ratio is considered to be the index of micropolarity of the system; i.e., it gives an idea of the microenvironment in the micelle [14,15]. A low value of this ratio (<1) is generally taken as pyrene having nonpolar surrounding, whereas a higher value (>1) is taken as the pyrene with the polar surrounding [16]. As follows from Figs 1 and 2 for the studied solutions of TX114 and Tween 80 at all concentrations the ratio proves to be greater than 1 and initially decreases very slowly because the surfactant molecules adsorption at the air-water interface indicates a small change in polarity in the bulk. A decrease in the I_1/I_3 ratio with the increase in TX114 and Tween 80 concentrations at a given temperature indicates the presence of pyrene in the nonpolar region in the bulk due to the aggregation of surfactant monomers in the bulk. Taking into account the values of I_1/I_3 for TX114 and Tween 80, it is possible to determine their CMC using the procedure proposed by Zana et al. [17,18]. According to this method the CMC values can be obtained from the interception of extrapolation of a rapidly varying part of the plot and the nearly horizontal part at a high surfactant concentration. Because the $I_1/I_3 = f(C)$ curves (C – concentration of the surfactant in the bulk phase) for the studied surfactants are sigmoid in nature, the values of CMC can be also calculated using the Sigmoid – Boltzman equation (SBE) [19,20]. Table 1 presents the values of CMC of TX114 and Tween 80 determined from the intersection points on the $I_1/I_3 = f(C)$ curves as well as those of CMC_1 and CMC_2 from the SBE equation according to the procedure of Aguiar et al. [21]. This Table shows that the obtained values of CMC and CMC_1 for TX114 are close to the literature data [7,22], but in the case of Tween 80 only those of CMC_1 are comparable because the others are much higher [23–26]. In addition, for Tween 80 both CMC, CMC_1 and CMC_2 values increase with the increasing temperature (T), which is in contrast with the literature data [23,24]. In the case of TX114 the values of CMC increase up to T = 298 K and then decrease but those of CMC_1 and CMC_2 increase with T. Generally, the CMC of nonionic detergents decreases with the increasing temperature [4]. It should be remembered that the effect of temperature on the CMC values of surfactants in aqueous solution is found to be quite complex. Hydrophobic interactions are considered to be responsible for micelle formation. The temperature increase disrupts hydration of hydrophilic groups of the surfactant favouring micellization and breaks down the structured water

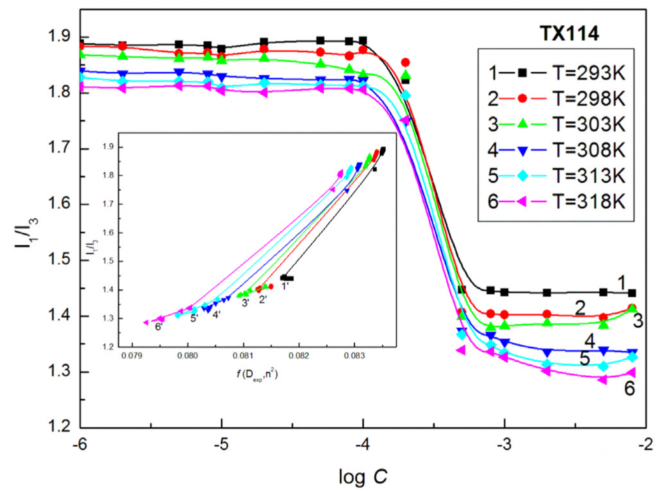

Fig. 1. A plot of the values of I_1/I_3 of aqueous solutions of TX114 vs. log C (curves 1–6) and vs. $f(D_{exp}, n^2)$ (curves 1′–6′) at T = 293 K (curves 1 and 1′), 298 K (curves 2 and 2′), 303 K (curves 3 and 3′), 308 K (curves 4 and 4′), 313 K (curves 5 and 5′) and 318 K (curves 6 and 6′).

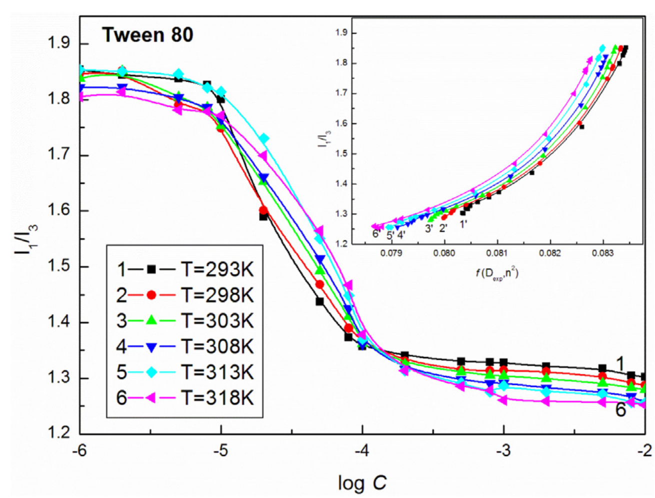

Fig. 2. A plot of the values of I_1/I_3 of aqueous solutions of Tween 80 vs. log C (curves 1–6) and vs. $f(D_{exp}, n^2)$ (curves 1′–6′) at T = 293 K (curves 1 and 1′), 298 K (curves 2 and 2′), 303 K (curves 3 and 3′), 308 K (curves 4 and 4′), 313 K (curves 5 and 5′) and 318 K (curves 6 and 6′).