



Interactions of 2,2,2-trifluoroethanol with aqueous micelles of Triton X-100

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ABSTRACT

The effect of 2,2,2-trifluoroethanol (TFE) on micellar properties of Triton X-100 (TX-100) in aqueous solutions was investigated by cloud point (CP), viscosity, surface tension, and fluorescence techniques. The critical micelle concentration (CMC) values of the corresponding mixtures were obtained by the pyrene 1:3 ratio method and by surface tension data using the pendant drop technique. All the techniques provided about the same values for the CMC. Up to 0.83 M TFE increased the CMC by 30%. The small increase in the CMC is consistent with a slight increase in the solubility of the TX-100. Fluorescence measurements indicate that the TFE decreased the aggregation number by about 30%. The CP decrease and the intrinsic viscosity increase with TFE concentration are consistent with a preferential interaction of TFE with TX-100 micelles. TFE molecules form hydrophobic domains in the micellar layer palisade because they hydrogen bond with the oxyethylene group in TX-100. The intrinsic viscosity data are consistent with an increase in micelle hydrodynamic radius owing to the presence of TFE.

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1. Introduction

In many technical processes, such as foaming, wetting, emulsification, solubilization, and detergency, the surfactants are the main components in the formulation. However, the micellar properties of nonionic surfactants, such as the CMC, the micelle aggregation number, and the liquid–liquid equilibrium, etc., may be modified by the presence of solutes.

Among additives to surfactant solutions, alcohols hold a special place because they are the most common cosurfactants added to nonionic hydrocarbon surfactants to generate microemulsions. The effect of alcohols on micelle formation is a matter of interest from theoretical and practical points of view [1–3]. Alcohols are surface-active and self-associate when they are sufficiently soluble in water. Thus alcohols alone act as surfactants and they influence the behavior of other surfactants when combined with them [2].

Higher molecular weight and increasing concentration of alcohol further depress the CMC [1,2]. Most of the papers [3,4] and references therein deal with the effect of alcohols on micellization of ionic surfactants. However, the ternary systems nonionic surfactant/alcohol/water are interesting from academic and practical points of view for a variety of possible applications in the pharmaceutical, cosmetic, and food industries and as well as in processes of biotechnology, nanotechnology, etc. [5].

The most widely used alcohol to promote the formation of secondary structure in polypeptides and proteins is 2,2,2-trifluoroethanol (TFE) on account of its ability to substantially increase secondary structure and to alter the folding–unfolding kinetics of proteins. As a result, it is a cosolvent commonly employed in biophysical and biotechnological investigations [6,7]. The mechanism by which TFE affects the solubility and stability of proteins still remains unclear [7]. Although TFE is fully miscible with water at any ratio, the molecule forms microscopic clusters in aqueous solutions. Chitra and Smith [8], using the Kirkwood–Buff analysis, have found significant aggregation of TFE molecules in water near 30 vol%. Aggregation of TFE molecules has also been observed by X-ray scattering and NMR experiments [9–11]. The presence of TFE in TFE/water mixtures has the potential to affect ionic, hydrogen-bonding, and hydrophobic interactions. TFE strongly stabilizes the α -helical and β -sheet structures of many soluble and amphiphilic peptides by reducing solvation of the backbone amide groups, thus destabilizing extended coil conformations [12]. TFE has also been proposed to associate with apolar side chains, providing a nonaqueous matrix for hydrophobic collapse of polypeptides.

In addition to the practical interest of TFE/water mixtures, TFE has interesting physicochemical properties due to the presence of a hydrophobic CF_3 group that imparts a degree of hydrophobic character. On the other hand, the electron-withdrawing effect of the CF_3 group renders the TFE more acidic than ethanol, which favors hydrogen bonding.

Certain properties of nonionic surfactant solutions may be used to study the effect of the TFE on the mixtures TFE/water because

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micelle formation and liquid–liquid phase equilibrium are determined by the counterbalance of hydrophilic/hydrophobic interactions in these systems. Nonionic poly(oxyethylene) surfactants with general formula $R-(OCH_2-CH_2)_mOH$ exhibit a variety of solution phenomena in water, where m refers to the number of oxyethylene units and R the hydrophobic block in the molecule. A characteristic feature of many nonionic surfactant solutions is the presence of the so-called cloud point (CP) curves. This type of surfactants in aqueous solutions show a lower consolute temperature (LCST); i.e., they phase separate at an increased temperature. The origin of the CP phenomenon has been discussed by many authors [13–20]. The LCST is due to changes in the interaction energy between poly-oxyethylene groups and water as a function of temperature. The LCST has been also interpreted within the context of the Flory–Huggins theory of polymer solutions [15,16]. Here the profile of the CP with respect to surfactant concentration is determined by the enthalpic and entropic interaction parameters. It is also believed that clouding arises due to the attractive intermicellar interaction van der Waals attractive potential and water-mediated potential [21]. The CP can be modified by the presence of additives and shifted to higher or lower temperatures depending on the chemical nature of additive [22–24].

In this work we studied the effect of TFE on micellization of TX-100. TX-100 is a polydisperse nonionic surfactant of p -(1,1,3,3-tetramethylbutyl)phenoxy polyoxyethylene glycols containing an average of 9.5 oxyethylene units per molecule. This surfactant has been widely used to study properties of nonionic micellar solutions [25–28]. Various experimental techniques have been used to characterize the micelles of this surfactant [25–28]. Small-angle neutron scattering (SANS) studies suggest oblate ellipsoidal shape for the micelles of TX-100 in heavy water [21]. The micelle aggregation number of this surfactant in water at room temperature is about 100 [25–28]. However this parameter may change with temperature [25] and in the presence of additives such as electrolytes [27], ionic liquids [29,30], and other substances [31].

The micelle aggregation number that is determined from different techniques may be different for the approximation involved in the determination method [3]. Fluorescence quenching data for micelle characterization are less affected by the interactions in the system or deviations from the ideal behavior. Time-resolved fluorescence quenching [32–35] and steady-state fluorescence quenching are commonly used to determine the CMC and the micelle aggregation number [29,30,35,36]. The quenching effect of TFE on derivatives containing the 9-oxo-imidazol[1,2- α]purine skeleton has also been studied [37]. The objective of this work is to use cloud point, viscosity, surface tension, and fluorescence quenching data to study the effect of TFE on some properties such as CMC, micelle aggregation number and liquid–liquid equilibrium in TX-100 solutions. The results will be used to interpret the change of interactions originated by TFE in the systems studied. Our results may be useful in studies of aqueous solutions of peptides and proteins in the presence of TFE because similar interactions are involved in these systems.

2. Experimental

2.1. Materials

Triton X-100 (molecular weight = 625 g/mol) was obtained from E. Merck, Germany. Pyrene, Coumarin 153, and TFE (Sigma–Aldrich 99.9%) were used as received. Water was purified using a Millipore Milli-Q system having pore size 0.22 μm and resistivity $\geq 18.2 \text{ M}\Omega\text{cm}$ and was used for the preparation of all solutions.

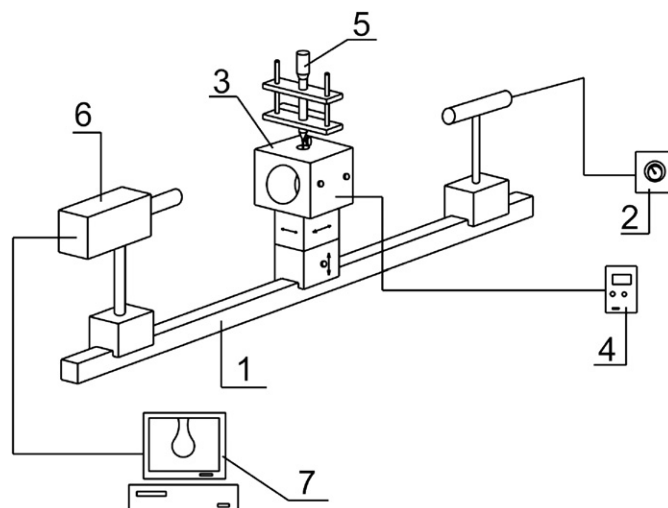


Fig. 1. Schematic pendant drop tensiometry apparatus: 1, optical rail; 2, regulated fiber optic illuminator; 3, environmental chamber and quartz cuvette inside; 4, temperature control system; 5, system for suspending the drop; 6, CCD camera; and 7, image digitizer and computer.

2.2. Methods

2.2.1. Cloud point

The CP measurements were performed by visual observation of the samples. After the samples were heated above the clouding temperature, the CP was taken as the temperature at which the last visible sign of cloud disappeared on cooling. The reproducibility of the results was $\pm 0.3^\circ\text{C}$.

2.2.2. Surface tension measurements by the pendant drop method

The theory of the pendant drop method of determining the surface tension has been described in detail by various authors [38–41]. This technique relies on a shape analysis by fitting the drop shape coordinates to the Young–Laplace equation. In addition to the analysis by full drop profile fitting, a relation can be used to determine the surface tension from the characteristic diameters [40,41].

The experimental setup for surface tension measurements used in this work is a homemade automatic pendant drop tensiometer developed by one of the authors [42]. A block diagram of the experimental setup is shown in Fig. 1. The system used for suspending the drop inside the environmental chamber includes a specially fabricated syringe pump. A steel needle with a flat tip is connected via Luer fittings through a chrome-plated brass one-way stopcock valve to a Gilmont Instruments GS-1200 micrometer syringe (2 ml). The valve helps to keep the drop volume constant. Image acquisition and analysis hardware/software coupled to the video camera is employed to process a series of droplet images.

Water used for surface tension measurements was purified using Millipore Milli-Q and then doubly distilled in quartz. The steel needle, the glass syringe barrel, and the connecting valve were ultrasonically cleaned and then rinsed with acetone, ethanol, and water and dried in an air stream. A small amount of solution was left at the bottom of the cuvette to create a saturated environment. To obtain the equilibrium surface tension, a sequence of 10 images was acquired at time intervals of 300 s for each concentration of TX-100 [41].

The video signal of the pendant drop that is formed at the tip of the needle was acquired by a National Instruments PCI-1407 image acquisition frame grabber card. The system acquired images with 640×480 pixels and 256 gray levels. Image analysis and control were done with a LabVIEW software user interface.

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