Introduction

There are many reasons why most studies related to the self-assembly of surfactant systems have been conducted in aqueous media. From these investigations a number of properties of great interest for their technical applications are now fairly well known. However, the appearance of certain applications of surfactants in areas such as lubrication or cleaning operations, which require water-free or water-poor media, has stimulated interest in the surfactant aggregation phenomenon in nonaqueous media. Among these media, strongly polar solvents with properties resembling those of water, such as ethylene glycol (EG), glycerol and formamide, have been used [1, 2]. In recent years, investigations of surfactant aggregation in nonaqueous polar solvents have focused mainly on two aspects: what is required from a solvent for amphiphilic assembly, and what

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Received: 13 December 1998
Accepted in revised form: 25 February 1999

Abstract The aggregation behaviour of tetradecyltrimethylammonium bromide in ethylene glycol–water mixtures across a range of temperatures has been investigated by electrical conductivity measurements. The critical micelle concentration (cmc) and the degree of counterion dissociation of micelles were obtained at each temperature from plots of differential conductivity, \( \frac{\partial \kappa}{\partial c} \), versus the square root of the total concentration of the surfactant. This procedure not only enables us to determine the cmc values more precisely than the conventional method, based on plots of conductivity against total concentration of surfactant, but also allows straightforward determination of the limiting molar conductance and the molar conductance of micellar species. The equilibrium model of micelle formation was applied to obtain the thermodynamics parameters of micellization. Only small differences have been observed in the standard molar Gibbs free energies of micellization over the temperature range investigated. The enthalpy of micellization was found to be negative in all cases, and it showed a strong dependence on temperature in the ethylene glycol poor solvent system. An enthalpy–entropy compensation effect was observed for all the systems, but whereas the micellization of the surfactant in the solvent system with 20 wt% ethylene glycol seems to occur under the same structural conditions as in pure water, in ethylene glycol rich mixtures the results suggest that the lower aggregation of the surfactant is due to the minor cohesive energy of the solvent system in relation to water.

Key words Critical micelle concentration – Thermodynamics properties – Tetradecyltrimethylammonium bromide – Ethylene glycol–water binary mixtures

Thermodynamics of micellization of tetradecyltrimethylammonium bromide in ethylene glycol–water binary mixtures
structural properties the aggregates formed in these media have. In order to obtain answers to these questions, a usual and obvious approach is the gradual replacement of water with other polar solvents, as this allows one to explore a wide range of polarities (so that the surfactant tails could experience a range of solvophobicities). In this way, several studies of surfactant aggregation have been carried out using solvents such as glycerol [3-5], formamide [6–11] and EG [5, 12–22], to name only a few. In relation to the physical properties of the solvent needed for amphiphilic aggregation to occur, previous studies indicate that these solvents must have three characteristics in common: a high cohesive energy, a high dielectric constant and a high hydrogen-bonding ability [15]. In particular, it must be pointed out that some authors [23] have proposed that the last point, namely, the ability for hydrogen-bond formation is a necessary condition for surfactant aggregation.

As already mentioned a large number of studies have been performed where water is gradually substituted with another polar solvent. This methodology has a double objective: it allows a simple characterization of the system, and it is possible to investigate the possibility of a chosen experimental technique to provide significant and easily interpretable data [2]. In addition, since the micellization process is most often revealed by the surfactant concentration value at which the aggregation takes place, i.e. the so-called critical micelle concentration (cmc), it is important to have appropriate procedures to obtain reliable cmc values in these media. On the other hand, a lot of information on the strength and nature of solvent–surfactant and solvent–solvent interactions can be obtained from the thermodynamic properties of micellization. These properties can be derived from a study of surfactant aggregation as a function of temperature. This kind of information provides a further understanding of the so-called solvophobic effect as opposed to the hydrophobic effect [23].

In this paper, we present the results obtained in an experimental study of the aggregation behaviour of tetradecyltrimethylammonium bromide (TTAB) in EG–water mixtures at different temperatures. Previously, two studies on the same system have been reported. Backlund et al. [13] investigated the aggregation and the phase behaviour of TTAB in water, EG and their respective mixtures at 30 °C. Gharibi et al. [16] have also carried out electrochemical studies associated with micellization of TTAB, among other cationic surfactants, in the same solvent mixtures at 25 °C. Unlike these investigations the aim of this work is the study of the influence of temperature in the micellization process of TTAB in different EG–water mixtures. In this investigation we have carried out conductivity measurements up to 60 wt% EG in the binary mixtures and in the temperature range 25–45 °C. The cmc values, degree of counterion dissociation (β), limiting molar conductance (Λ0) and molar conductance of micelles (ΛM) corresponding to each temperature were obtained by using a new approach recently proposed by Sugihara and coworkers [24–26]. From the cmc values as a function of temperature, and considering the equilibrium model for micelle formation, we have obtained the corresponding thermodynamic parameters of micellization.

Experimental

The surfactant TTAB was obtained from Sigma Chemical Co. and was used without any pretreatment. EG (spectrophotometric grade, >99%) was from Aldrich and was used as received. Water was doubly distilled (Millipore).

Conductometric measurements were made with a Crison model microCM 2202 digital conductivity meter using a dip-type cell of cell constant 1.03 cm⁻¹. All measurements were done in a jacketed vessel, which was maintained at the appropriate temperature (±0.1 °C) with a Mendingen E1 temperature bath. Specific conductivity values of each set containing 15–20 different concentrations at a fixed solvent composition (expressed as EG/water ratio in weight percent) were measured at different temperatures. The surfactant molar concentrations were converted to the molar fraction scale by using density values of solvents and solutions. These densities were measured with an Anton-Paar DMA 58 density meter. This apparatus determines the density value by placing the sample in a U-shaped tube and measuring the period of oscillation of this tube. The instrument was calibrated with air and water over the temperature range investigated. The temperature was maintained within ±0.01 °C.

The cmc values at each solvent composition were determined by using two different procedures. First, we used the conventional method based on the plot of conductivity (κ) against surfactant total concentration (c). In this plot we have fitted by least-squares analysis the conductivity–concentration data above and below the break point with a correlation coefficient greater than 0.9995. Second, in accordance with Sugihara and coworkers [24–26], we have plotted the derivative (Δκ/Δc) versus √c. From these plots, which show a reverse sigmoidal curve, the cmc values are taken as the inflection point, i.e. as the centre of the reverse sigmoid.

Results and discussions

Degree of counterion dissociation and cmc

The determination of the cmc for each solvent composition at different temperatures was first carried out by plotting specific conductivity (κ) against total concentration of surfactant (c). Figure 1 shows a number of these plots at different temperatures and at fixed solvent composition. From these plots the degree of counterion dissociation (β) was also obtained as the ratio between the slope of the postmicellar region (Sβ) to that of the premicellar region (S0). However, as the temperature and concentration of EG increased, we found that a smaller curvature appeared around the cmc; consequently the cmc and β values obtained are affected to a greater uncertainty. Therefore we decided to use a new approach that has recently been applied successfully in a