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Thermodynamic properties of surfactant sodium n-heptyl sulfonate in water and in aqueous solutions of poly(ethylene glycol) at different temperatures

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ABSTRACT

The volumetric, compressibility and electrical conductivity properties of sodium n-heptyl sulfonate (C_7SO_3Na) in pure water and in aqueous poly(ethylene glycol) (PEG) solutions were determined at different temperatures below and above the micellar composition range. At each temperature, the infinite dilution apparent molar volumes of the monomer and micellar state of C_7SO_3Na in aqueous PEG solutions respectively are smaller and larger than those in pure water. However, the values of the infinite dilution apparent molar isentropic compressibility of both monomer and micellar states of C_7SO_3Na in aqueous PEG solutions are larger than those in pure water. Thermodynamic parameters of micellization of investigated surfactant in water and in aqueous solutions of PEG at different temperatures were estimated and it was found that the micelle formation process is endothermic and therefore, this process must be driven by entropy increase. The calculated Gibbs free energies of micellization for aqueous PEG solutions are more negative than those for pure water and become more negative by increasing temperature. The variation of the critical micelle concentration (CMC) of C_7SO_3Na in water and in aqueous PEG solutions with temperature was obtained and a comparison between the CMC of C_7SO_3Na obtained from different thermodynamic properties was also made.

1. Introduction

It has been generally recognized that studies of thermodynamic and transport properties of surfactants are important to understand their behavior in solutions [1]. Therefore, the limited interest of scientists working in this field for direct measurement of some fundamental solution properties, such as the activity and osmotic coefficients, enthalpy and volume changes on dilution, electrical conductivity, transport numbers, etc., is somewhat surprising. These properties are indispensable to test various theories and models of surfactant solutions [2]. One of the important properties of surfactants is the association of their amphiphilic molecules into micellar aggregates in aqueous solutions. This association leads to a reduction of the energetically unfavorable contact between water and the apolar parts of the amphiphilic molecules while the polar groups are still solvated by water [3]. Micelles are thermodynamically stable aggregates. Their size, shape and charge (for ionic surfactant) may be modulated by other components and/or by varying the surfactant concentration, temperature, pressure, and so on. The surfactant concentration where the micelles start to form is known as the critical micelle concentration, abbreviated to CMC. The CMC is the single most important characteristic of a surfactant, useful *inter alia* in consideration of the practical use of surfactants. The CMC can be influenced by different factors such as chemical structure of surfactant (type of surfactant (ionic or non-ionic), alkyl chain length, head groups, valency of the counterion and different groups on alkyl chain), temperature, pressure and cosolute. There are a very large number of physicochemical properties which are sensitive to surfactant micellization. The most common and generally applicable techniques are surface tension, solubilization, equivalent conductivity, osmotic pressure, turbidity, magnetic resonance, fluorescence spectroscopy, self diffusion, density, sound velocity, viscosity, apparent or partial molar volume, isentropic or adiabatic compressibility, ultracentrifugation, vapor pressure, activity, osmotic coefficients and calorimetery measurements. In fact, CMC is not an exactly defined quantity, which causes difficulties in its determination [4]. For long-chain amphiphiles, an accurate determination is straightforward and different techniques give the same results. However, for short-chain, weakly associating amphiphiles, this is not the case and great care must be taken not only in the measurements but also in evaluating the CMC from experimental data.

The interaction between polymers and surfactant in aqueous solutions has also become a very interesting topic for widespread application such areas as oil recovery, colloid stability, surface modification, wetting, and the physiological transport and metabolism of lipids and their interaction with proteins as well as theoretical studies and has been investigated for several decades and

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extensively documented [5]. Surfactants may bind cooperatively to non-ionic water-soluble polymers to form micelle–polymer complexes [6–8], and these interactions are largely confined to anionic surfactants. With the addition of polymer, surfactant aggregates form on polymer chain when surfactant concentration reaches to a critical level (critical aggregation concentration, CAC), which is usually lower than the CMC of polymer-free surfactant solution. Among all the mixed polymer-surfactant systems, sodium alkyl sulfates [CH_3–$(CH_2)_{n-1}$–SO_4Na], especially sodium dodecyl sulfate ($C_{12}SO_4Na$), are the most used anionic surfactants. Sodium alkyl sulfonates [CH_3–$(CH_2)_{n-1}$–SO_3Na] are one of the most important class of anionic surfactants which can form micelles in aqueous solution and also may interact with water-soluble polymers such as poly(ethylene glycol) (PEG) in aqueous solution. Some limited thermodynamic properties for binary aqueous solutions of some sodium alkyl sulfonates have been reported in the literature [3,4,9–18]. Regarding to the mixed polymer–surfactant systems, only a few investigations involved sodium alkyl sulfonate [15,19–23] and all of them are related to the effect of polymer on the CMC of the surfactant, and in fact there is no any information in the literature about the comparison between the effect of water-soluble polymers on the thermodynamics properties of aqueous solutions of sodium alkyl sulfonates below and above their CMCs.

In this study, in order to study the effect of PEG and temperature on the apparent molar volume and isentropic compressibility as well as the conductivity behavior of the monomer and micellar state of C_7SO_3Na and therefore make a thorough analysis of the interactions between C_7SO_3Na and PEG, the apparent molar volume and isentropic compressibility of C_7SO_3Na in water and in aqueous solutions of PEG were determined at different temperatures from the accurate measurements of density and ultrasonic velocity. Furthermore, the electrical conductivity of these solutions was determined at different temperatures below and above the micellar composition range. From these data the variation of the critical micelle concentration (CMC) in pure water and in aqueous PEG solutions with temperature was obtained and a comparison between the CMC of C_7SO_3Na obtained from different investigated thermodynamic properties was made.

2. Materials and methods

2.1. Materials

Sodium n-heptyl sulfonate (C_7SO_3Na) (purity>99%) and poly(ethylene glycol) (PEG) were obtained from Merck and were used without further purification. PEG had a nominal molecular weight of 6000. The manufacturer has characterized this polymer with charge/lot number S35317 203. The used double distilled water for the preparation of the solutions was deionized.

2.2. Methods

2.2.1. Volumetric measurements

The density and sound velocity of the mixtures were measured at different temperatures with a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with proportional temperature control that kept the samples at working temperature within $\pm 10^{-3}$ K. The apparatus was calibrated with double distilled deionized, and degassed water, and dry air at atmospheric pressure. Densities and ultrasonic velocities can be measured to $\pm 10^{-6}\,g\,cm^{-3}$ and $\pm 10^{-2}\,m\,s^{-1}$, respectively, under the most favorable conditions. The uncertainties of density and ultrasonic velocity measurements were $\pm 3\times 10^{-6}\,g\,cm^{-3}$ and $\pm 10^{-1}\,m\,s^{-1}$, respectively.

2.2.2. Electrical conductivity measurements

Conductance measurements were carried out on a digital conductivity meter (Metrohm model 712) with a sensitivity of 0.1% and a dipping-type conductivity cell with platinized electrodes with a cell constant of $0.824\,cm^{-1}$ at a frequency of 1 MHz. The cell constant was calibrated with aqueous KCl solutions. The measurements of conductivities of the C_7SO_3Na solutions were carried out by continuous dilution of a concentrated solution into water or aqueous solutions of PEG. The conductivity was recorded when its fluctuation was less than 1% within 2 min. The temperature was controlled with a precision of 0.02 K.

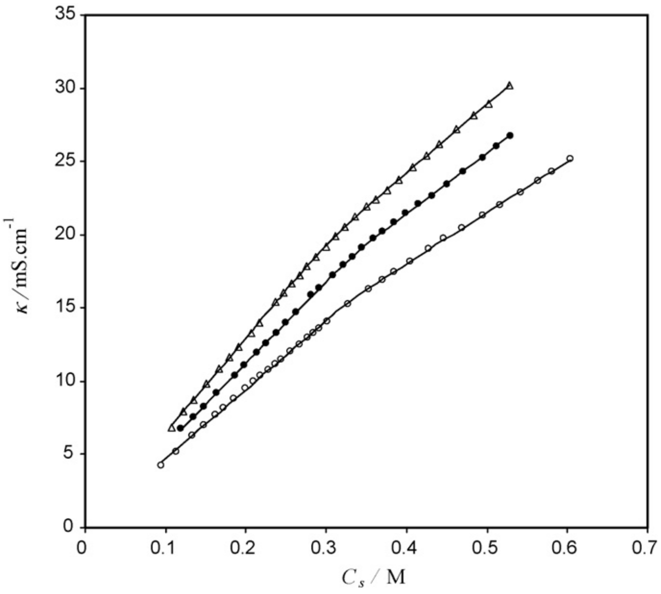

Fig. 1. Effect of the variation of C_7SO_3Na concentration on the specific conductivity in aqueous solution: (○) 298.15 K; (●) 308.15 K; (△) 313.15 K. The line shows the result of the nonlinear least-squares fit of the experimental data to Eq. (1).

3. Results and discussion

In the present work, two sets of experiments were carried out in order to describe thermodynamic properties of binary aqueous C_7SO_3Na solutions and ternary $C_7SO_3Na + PEG + H_2O$ solutions at different temperatures. For the first set of experiments, the density and ultrasound measurements for C_7SO_3Na in pure water and in aqueous solutions of PEG at different surfactant concentrations were made at 288.15, 293.15, 298.15, 303.15 and 308.15 K to study the variation in apparent molar volumes and compressibilities, with surfactant concentration and temperature. For the second set of experiments, the electrical conductivities for C_7SO_3Na in pure water and in aqueous solutions of PEG have been determined experimentally at 298.15, 308.15 and 313.15 K.

3.1. Conductivity measurements

Conductivity measurements are commonly used in the study of ionic micellar solutions. For nearly all ionic surfactants in aqueous solution, there is a substantial change of slope at the onset of aggregation. Experimental data of specific conductivities, κ, for C_7SO_3Na in water and in aqueous solutions of 2 wt% PEG are given in Table I of the Supporting information. The small conductivity of solvent was subtracted from the measured data. Representative results are displayed in Fig. 1 for C_7SO_3Na + water systems at different temperature. It is apparent that the gradual increase of the surfactant concentration leads to two readily distinguishable linear dependencies. In the low concentration domain the rise of κ is due to the growing number of free $C_7SO_3^-$ and Na^+ ions, whereas the break in the plot originates from the onset of micellization. Above the CMC the augmentation of the specific conductivity has a smaller slope