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Aggregation, adsorption, and clouding behaviors of Triton X-100 in formamide

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ABSTRACT

The critical micelle concentration (cmc) of TX-100 in formamide (FA) was determined from surface tension measurements as functions of temperature and NaCl concentration. At 25 °C, cmc was also determined by the fluorescence method. For the sake of comparison, micellization parameters of TX-100 were also determined in water. cmc, aggregation number, and standard free energy of micellization in FA are about 400 times higher, 10 times lower, and 2 times higher than in water, respectively. On increasing the temperature, cmc in FA shows a slight increase, whereas in water it decreases. The logarithm of relative cmc decreases linearly with added NaCl concentration in both FA and water, and the rate of this decrease is surprisingly equal in the two solvents. Micellization of TX-100 is exothermic in FA, but endothermic in water. The cloud point (CP) of TX-100 was determined in FA + water medium and that in pure FA was estimated to be ∼233 °C when [TX-100] = 0.15 mol kg^{-1}. Surface excess values of TX-100 were calculated from Gibbs and Langmuir adsorption isotherms. Values of standard free energy of adsorption calculated from the Rosen–Aronson equation and from the Langmuir adsorption isotherm are comparable. The ratio of the surface tension of the solvent to that at the cmc has been demonstrated as a novel scale for measuring solvophobicity.

1. Introduction

Molecules having both solvophobicity and solvophilicity characters toward a particular solvent undergo adsorption and aggregation in that medium. Such molecules, known as surfactants, have wide-ranging applications and therefore their properties are studied extensively. Solvophobicity or solvophilicity of a molecule is determined by the nature of its interaction with a solvent and consequently the latter plays a key role in the adsorption and micellization behavior of surfactants. Micellization behaviors of surfactants are therefore investigated in different solvent media, for, e.g., (i) water in the absence and presence of various types of additives that alter the water structure, (ii) nonaqueous polar solvents including ionic liquids, (iii) mixed solvents containing water and organic polar solvent, and (iv) nonpolar organic solvents. For example, recent works of Eastoe and co-workers [1–5] illustrate the profound effects of solvent properties on aggregation and adsorption of surfactants.

TX-100 (Triton X-100, polyethylene glycol *tert*-octylphenyl ether) is a nonionic surfactant having several biochemical applications and its micellization characteristics in water are well-documented [6–13]. Micellization studies of TX-100 in a few mixed solvents containing water and organic polar solvent are also reported [14–19]. However, to our knowledge no report is available about its micellization behavior in pure organic polar solvents. The purpose of this work is therefore to study the aggregation, adsorption, and clouding behaviors of TX-100 in FA and compare it with that in water. Formamide (FA) was chosen because most of the studies in this solvent are devoted to ionic surfactants [20–26] only. Exploring FA more for the micellization studies of nonionic surfactants [26–28] is worth taking up in view of the recent publications which indicate that there is still much interest in the aggregation behavior of surfactants in organic polar solvents and their aqueous mixtures [1–5,29–32]. Moreover, we recently reported [33] that the ratio of the initial to the limiting surface tension at the cmc of a surfactant may provide a new scale to express solvophobicity, and to test this proposition TX-100 in FA is a good candidate.

2. Materials and methods

In this study TX-100 (Sigma), FA (Fluka, assay ⩾99.5%), pyrene (Fluka, assay ⩾97%), cetylpyridinium chloride (CPC; Sigma, assay ⩾99%), and sodium chloride (E. Merck, assay ⩾99%) were used without further purification. Surface tension measurements were made by the Wilhelmy plate method using K11 Krüss tensiometer. Hitachi F4500 FL spectrophotometer was used to record the fluorescence emission intensities of pyrene in the absence and presence of CPC as quencher. Density of the solutions was measured whenever needed by using an Anton Paar DMA 5000 density meter. Haake DC10 circulation bath was used for maintaining the

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temperature. Milli-Q grade water was used for preparing aqueous solutions. The cloud point (CP) was determined as the temperature at which clouding starts while heating and as the temperature where the solution becomes clear while cooling. An average of the two temperatures obtained while heating and cooling was taken as the CP. The experimental values of CP were reproducible within ±1 °C.

3. Results and discussion

3.1. Critical micelle concentration

Representative plots of surface tension of TX-100 in FA at 25 °C in the absence and presence of NaCl are shown in Fig. 1. For the purpose of comparison, such plots in water are also shown in Fig. 1. In water, surface tension plots show no minimum. In FA, on the other hand, surface tension minimum is observed and the surfactant concentration corresponding to the minimum is taken to be the cmc. From Fig. 1 the values of limiting surface tension of TX-100 at the cmc are found to be 31.1 and 29.5 mN m^{-1} in water and FA, respectively. In view of the large difference in the surface tension values of water (72 mN m^{-1}) and FA (58.5 mN m^{-1}), the limiting surface tension of TX-100 at the cmc appears to have a weak dependence on the nature of solvent, which is similar to the observation reported in other solvents [4,33].

We determined first the cmc values of TX-100 in water at different temperatures from the surface tension data and compared them with the reported [10,13–19,34] values as shown in Fig. 2 and Table S1 (supplementary material). Good agreement is found between the present and most of the reported [10,13–19,34] values of cmc. The values of cmc of TX-100 in FA determined from the surface tension data at different temperatures are also shown in Table S1 and Fig. 2. The cmc of TX-100 in FA at 25 °C was also determined by the fluorescence method and was found to be close to the value obtained from the surface tension data (Table S1). To determine cmc from the fluorescence method, we fitted the experimental values of the ratio (I_1/I_3) of emission intensities of pyrene at 374 (I_1) and 384 (I_3) nm to a sigmoid-type equation (Fig. S1; supplementary material) adopting the treatment suggested by Aguiar et al. [35]. The details of the data fitting are given elsewhere [33]. The value of cmc is taken as the concentration of TX-100 corresponding to the center of the sigmoid.

The cmc of TX-100 in FA is found to be about 400 times higher than that in water, which indicates reduced solvophobicity of TX-100 in FA. Such high values of cmc in FA were also reported [26,27] for polyethylene glycol dodecyl ethers ($C_{12}E_5$ and $C_{12}E_6$). On increasing the temperature, the cmc shows a small increase in FA, while in water it decreases. With the addition of NaCl, cmc decreases in both FA and water (Fig. 3). Two opposing effects operate in a surfactant solution on increasing the temperature: (i) the degree of solvation of the head group decreases, which favors micellization and (ii) the ordered structure of solvent molecules around the solvophobic tails breaks, which disfavors micellization. In water, the first effect is so predominant that phase separation or clouding of TX-100 occurs at a relatively low temperature (see Section 3.4). Thus, decrease in cmc with increase in temperature in water is attributed to the decrease in the degree of hydration. In FA, which has two centers (oxygen and nitrogen) for hydrogen bonding, the energy needed for desolvation is more and hence within the temperature range covered in this study a significant decrease in the degree of solvation does not seem to take place. This is reflected in a very high CP for TX-100 in FA (see Section 3.4). Therefore, the second effect noted above may be predominant in FA, thereby causing an increase in cmc with increase in temperature. On the other hand, on adding NaCl due to extensive hydration/solvation of the ions a salting-out effect operates in water [11] as well as FA causing reduction in cmc of TX-100 in both these solvents.

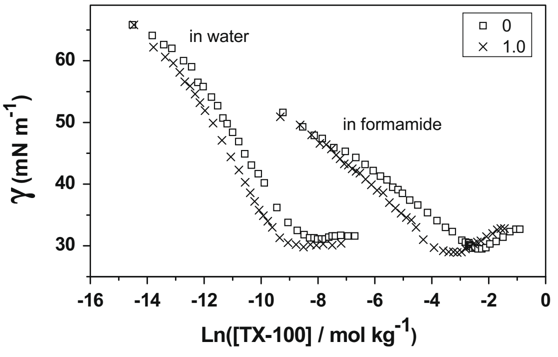

Fig. 1. Representative plots of surface tension of TX-100 in FA and water at 25 °C in the absence and presence of NaCl. Concentrations of NaCl in mol kg^{-1} are indicated in the inset.

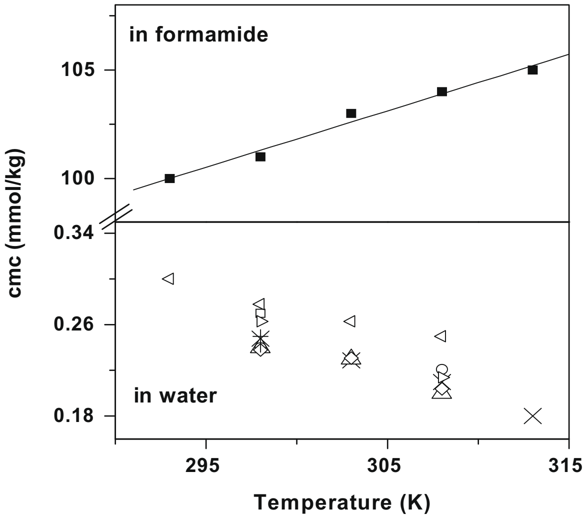

Fig. 2. Variation of cmc of TX-100 with temperature in FA and water. The reported values of cmc in water are from Refs. [10] (+), [14] (○), [15] (◇), [16] (□), [17] (△), [18,19] (|), [13] (◁), and 34 (▷). ■ and × indicate the present experimental values.

The variation of cmc of nonionic surfactant with the concentration of added electrolyte (c_e) is generally expressed by a linear equation of the form [10,36], ln cmc = $a_1 - b_1c_e$, where a_1 and b_1 are constant terms. Mukerjee [36] theoretically derived this linear equation and it is used here in the form

$$\ln(\text{cmc}/\text{cmc}_0) = -b_1c_e, \qquad (1)$$

where cmc_0 refers to the cmc in the absence of NaCl. Eq. (1) describes satisfactorily the dependence of cmc on NaCl concentration in both

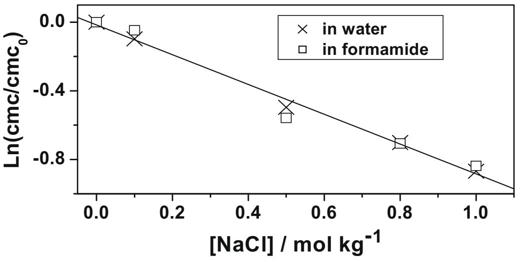

Fig. 3. Variation of logarithm of cmc of TX-100 in FA and water with NaCl concentration at 25 °C (cmc_0 refers to cmc in the absence of NaCl).