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Effect of organic additives and temperature on the micellization of cationic surfactant cetyltrimethylammonium chloride: Evaluation of thermodynamics

Md. Sayem Alam [a,*], A. Mohammed Siddiq [a], V. Mythili [a], M. Priyadharshini [a], Nasim Kamely [a], Asit Baran Mandal [a,b,**]

[a] Industrial Chemistry Laboratory, Council of Scientific and Industrial Research (CSIR), Central Leather Research Institute (CLRI), Adyar, Chennai 600 020, India
[b] Chemical Laboratory, Council of Scientific and Industrial Research (CSIR), Central Leather Research Institute (CLRI), Adyar, Chennai 600 020, India

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ABSTRACT

In the present study, we report the effect of organic additives and temperature on the micellization of cationic surfactant cetyltrimethylammonium chloride (CTAC). The micellization behavior of CTAC was studied at different fixed temperatures and fixed concentrations of organic additives (viz., sugar and amino acid) in aqueous solutions. The critical micelle concentrations (*CMC*) of CTAC were measured by the conductivity and dye solubilization methods. The CMC values first increase with increasing temperature (up to 298 K) and then decrease with increasing temperatures; whereas the increasing trend was found to be with organic additive concentrations. The thermodynamic parameters (viz., standard Gibbs energy (ΔG_m^0), standard enthalpy (ΔH_m^0), and standard entropy (ΔS_m^0) of micellization of CTAC) are evaluated. The thermodynamic parameter values clearly indicate less stability of the CTAC solution in the presence of organic additives.

1. Introduction

A large number of molecules are amphiphilic (viz., surfactants, drugs, and polymers) in nature. These molecules contain two parts: (i) one oil preferring or water fearing part, referred to as lipophilic or hydrophobic and (ii) the other one is the water preferring part, hydrophilic. In aqueous environment, these amphiphilic molecules (viz., surfactants [1–8], drugs [9–16], and polymers [17–21]) can form a kind of self-organized molecular assembly above their *critical micelle concentrations* (*CMC*), which can be called as micelles. The self-assembly and the self-organization are natural and spontaneous processes occurring mainly through non-covalent interactions, such as van der Waals, hydrogen bonding, hydrophobic/hydrophilic, electrostatic, donor and acceptor, and metal–ligand coordination networks [22]. The interests in micelle solutions stem from their potential as functional molecular assemblies for use in many fields of pure and applied sciences. They can be used as models for several biochemical and pharmacological systems. Therefore, these solutions of amphipathic systems can solubilize water-insoluble substances (including certain medicines/drugs) in their hydrophobic cores [23].

The clouding is a well-known phenomenon and observed in nonionic surfactants; upon raising the temperature, the system becomes cloudy (from clear solution) and phase-separates at a well-defined temperature (i.e., cloud point, CP) [24,25]. Under special conditions ionic surfactants undergo phase separation [26–32]. Recently, researchers found that some amphiphilic drugs also undergo pH, concentration, and temperature dependent phase separation [33–46]. It was observed that their cloud point (CP) can vary with additives [33–46]. The thermodynamic parameters of some amphiphilic drugs in the presence of additives were evaluated [47–52].

In the present investigation, we report the effect of (i) organic additives (viz., sugar and amino acid), (ii) temperature on the micellization of the cationic surfactant cetyltrimethylammonium chloride, CTAC (see Scheme 1(A)); and also (iii) the thermodynamic parameters that are evaluated (in micellization) in the absence and presence of additives.

2. Materials and methods

2.1. Materials

CTAC (≥98%, Sigma, USA), 1-[4-(phenylazo)phenylazo]-2-naphthol, and Sudan III (see Scheme 1(B)) (≥98%, Sigma, USA) were used as

* Corresponding author.
** Correspondence to: A.B. Mandal, Industrial Chemistry Laboratory, Council of Scientific and Industrial Research (CSIR), Central Leather Research Institute (CLRI), Adyar, Chennai 600 020, India.
E-mail addresses: sayemalam@gmail.com, sayem@clri.res.in (Md.S. Alam) abmandal@hotmail.com, abmandal@clri.res.in (A.B. Mandal).

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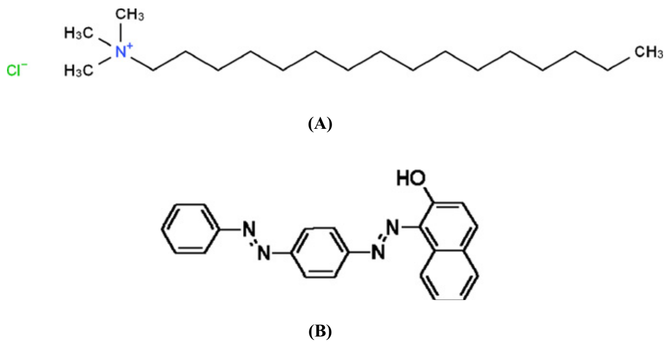

Scheme 1. The molecular structure of cationic surfactant (A) cetyltrimethylammonium chloride, CTAC (A) and water insoluble dye 1-[4-(phenylazo)phenylazo]-2-naphthol, Sudan III (B), used in the present study.

received. D-(−)-Fructose (≥99%), asparagine (≥99%), glutamic acid (≥99%), and L-arginine (≥99%) (all SRL, India) were used as received. All the solutions were prepared in Millipore water (used doubly distilled deionized water — specific conductivity 1–2 μS cm^{-1} at 25 °C).

2.2. Methods

2.2.1. Conductivity measurements

WTW Benchtop conductivity meter (model: inoLab® Cond 7110) and dip cell (cell constant = 1.0 cm^{-1}) were employed to perform the conductivity measurements at different temperatures (viz., 293.15, 298.15, 303.15 and 308.15 K). The stock solutions of surfactant (with or without a fixed concentration of additives) were prepared in (double distilled) Millipore water. The conductivity was measured by successive addition of concentrated solution in pure water (in the case of without additives) or in a fixed concentration of additive solutions. A break in the specific conductivity versus surfactant concentration curve signals the onset of the micellization process (Fig. 1). The uncertainties in the measured conductivity and *CMC* were ±0.5 μS cm^{-1} and ±0.1 mM, respectively.

2.2.2. Dye solubilization measurements

Dye solubilization experiments for the aqueous surfactant (CTAC) solutions (with and without additives) were performed at room temperature (~300 K). The sample solutions with Sudan III (see Fig. 2) dye (kept for 24 h) were filtered and then the spectra were recorded using a Varian UV–visible spectrophotometer (model: Carry 100).

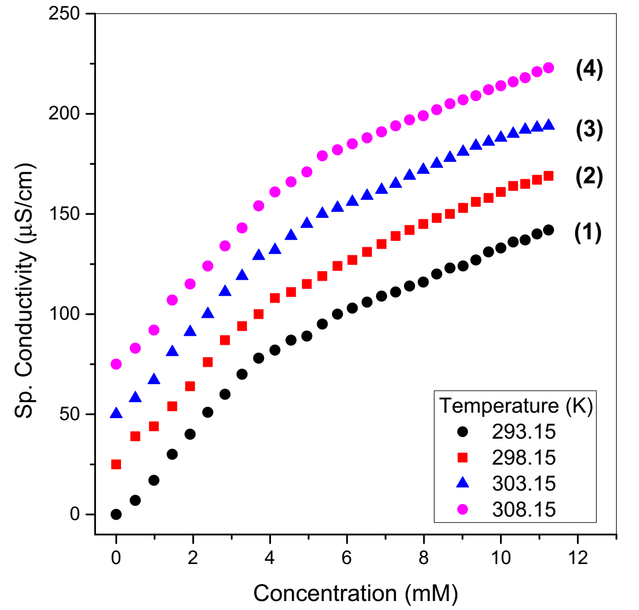

Fig. 1. Representative plots of specific conductance versus [CTAC] in the presence of 50 mM (fixed) arginine concentration at different fixed temperatures. Curves 2, 3, and 4 have been shifted by 25, 50, and 75 scale units (mS/cm), respectively.

3. Results and discussion

3.1. Micellization of CTAC in the absence and presence of organic additives

The *CMC* of CTAC in the absence and presence of fixed concentrations of additives (10, 20, 30 and 50 mM) were determined by conductivity method at different temperatures (293.15, 298.15, 303.15, and 308.15 K). Fig. 1 shows the representative plots of specific conductivity vs. [CTAC]. The *CMC* values of CTAC first increase (up to 298 K) and then decrease with increasing temperature (see Fig. 3); whereas, with

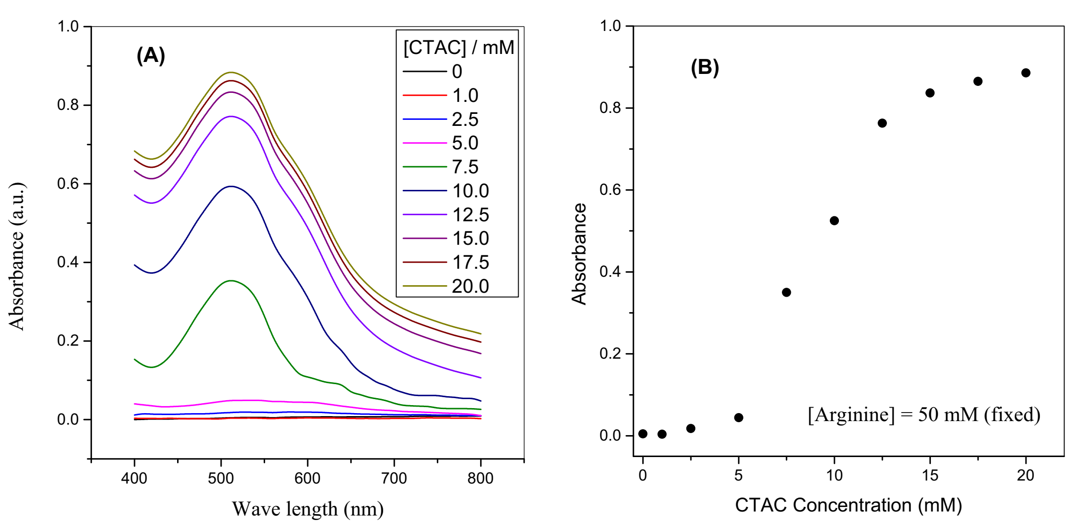

Fig. 2. The visible spectra of the dye Sudan III solubilized in aqueous 50 mM arginine solution containing different fixed concentrations of CTAC (A), and the corresponding plots (representative) of specific absorbance (at λ_{max} = 510 nm) versus [CTAC] at 298.15 K (B).