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Micellization behavior of dodecylethyldimethylammonium bromide as a function of temperature and concentration

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ABSTRACT

Micellization behavior of aqueous solutions of dodecylethyldimethylammonium bromide has been studied as a function of concentration and temperature employing densiometry, viscometry, ultrasound velocity measurements and conductometry. Density data has been used to evaluate apparent molar volumes and apparent molar expansion of surfactant monomers and micelles. Isoentropic compressibility, apparent molar isoentropic compressibility and apparent molar compression values and various acoustic interaction parameters like molar sound velocity, acoustic impedance and Wada's constant, have also been calculated using ultrasound velocity data. Conductivity measurements have been used to evaluate the degree of counterion binding. All methods yielded almost similar critical micellar concentration values. The data was used to discuss thermodynamics of micellization based on phase separation and mass action models. Micellization process of the surfactant was found to be spontaneous.

1. Introduction

The study of surfactant systems has been a subject of research interests because of their technological, fundamental, pharmaceutical and biological considerations [1–3]. The size and shape of micelles can be controlled by varying surfactant structure and by changing solution conditions such as ionic strength, pH, overall surfactant concentration and temperature. In this regard, extensive studies [4–8] have been carried to investigate the aqueous solutions of alkyl (octyl, nonyl, decyl, dodecyl, tetradecyl and hexadecyl) trimethylammonium bromide as a function of concentration and temperature. The temperature dependence of critical micellar concentration (cmc) can be used to determine various thermodynamic properties like free energy, enthalpy and entropy of micellization. The application of surfactant systems in industrial, technological and pharmaceutical companies requires detailed understanding of their various physicochemical properties such as density, viscosity, cmc, geometry, size, ultrasound velocity, conductivity, and degree of counterion binding. The study of aqueous solutions of ionic surfactants has emerging applications in industries and pharmaceutical companies [9,10]. One important class of ionic surfactants known trialkylammonium halides, has been a subject of increasing interest and has been extensively exploited in treatment of pollutants and other compounds in many biological, pharmaceutical and environmental systems [11–13]. Though the studies on micellization behavior of these quaternium nitrogen-based surfactants [4–6,8,13] like haxadecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and dodecyltrimethylammonium bromide, are frequently available, there are only a few reports [13–17] of physicochemical studies of dodecylethyldimethylammonium bromide ($C_{12}EMe_2AB$). Further to our knowledge there is no report on the effect of temperature on the micellization properties of $C_{12}EMe_2AB$. The surfactant is an effective surface active compound and can conveniently interact with neutral and anionic surfactants/polymers forming solutions of different consistencies. It has antifungal properties and low cost of production. Therefore the present work aims at detailed investigation of the effect of temperature and concentration on micellization behavior of $C_{12}EMe_2AB$ with special focus on density, apparent molar volume, ultrasound velocity, isoentropic compressibility, viscosity, conductivity, cmc, degree of counterion binding and thermodynamics of micellization.

2. Experimental method

2.1. Materials

The surfactant $C_{12}EMe_2AB$ with purity 99% from Sigma was used without further purification. Triply-distilled water was used in all the experiments.

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2.2. Methods

2.2.1. Density measurements

The densities of aqueous solutions of $C_{12}EMe_2AB$ were measured using calibrated dilatometer. The dilatometer was filled up to a level slightly below the first calibrated mark and after weighing, it was immersed in the constant temperature bath. Temperature was increased slowly till the meniscus coincided with the mark. The temperature was recorded after the meniscus remained stationery at the mark for 15 min. A similar procedure was followed for all the subsequent marks on the stem. The densities obtained corresponding to each mark were least square fitted to the recorded temperatures ($\rho = a + bT$). The best fit parameters a and b were utilized to compute the densities of solutions at the required temperatures. The accuracy in the density measurement was ± 0.00001 g·cm^{-3}.

2.2.2. Viscosity measurements

The viscosity measurements of the surfactant solutions were done using Cannon Ubbelhold type suspended viscometer between 20 °C and 50 °C at 5° intervals. The constancy of temperature was achieved (within 0.02 °C) by circulating water from a HAAKE GH thermostat. The accuracy of viscosity measurement was within $\pm 10^{-6}$ Pa·s.

2.2.3. Ultrasound velocity measurements

The velocity of ultrasound waves in various surfactant solutions were measured by an Ultrasonic Interferometer (Mittal-M81). The measuring cell of the instrument is double walled and is specially designed to maintain the temperature of solutions constant. A fine micrometer screw provided at the top of the cell can raise or lower a disk shaped reflector plate by a known distance through the solution in the cell. If the distance traversed by the waves before reflection in the solution is equal to an integral multiple of half wavelengths, the current registered by the instrument is maximum. The displacement of the reflector plate as recorded by the micrometer for twenty such maxima was measured and the average displacement (L) per maximum was calculated. This gives the half wavelength of sound waves traveling in solution and the wavelength of ultrasonic waves given by $\lambda = L/10$ was used to calculate ultrasound velocity ($U = \lambda \times \nu$). Measurements were made at a frequency of 4 MHz in the given temperature range at 5 °C intervals with the precision of 0.1 m/s.

2.2.4. Conductivity measurements

The conductivity measurements of surfactant solutions were done using dip-type conductivity cell (Elico, EC-03) connected to a digital RLC meter (GR. 1695, USA) with an accuracy of $\pm 0.2\%$. The temperature of the surfactant solutions was kept constant within ± 0.05 °C. The specific conductivities were computed from the corresponding measured resistances of surfactant solutions.

3. Results and discussion

3.1. Density measurements

The experimental density values of aqueous solutions of $C_{12}EMe_2AB$ at various concentrations and temperatures are obtained and plotted versus surfactant concentration. The plots show an inflection point at each temperature corresponding to critical micellar concentration (cmc) [18]. A representative plot of density versus surfactant concentration at 308.15 K is shown in Fig. 1. However, such plots show no second inflection point indicating that size and shape of micelle remain constant in the investigated range of surfactant concentration and temperature [19–22]. The cmc values obtained are given in Table 2. The variation of density with concentration is expressed [23] as

$$\rho = \rho_0 + (1 - v_s\rho_0)C_s + (1 - v_m\rho_0)C_m \quad (1)$$

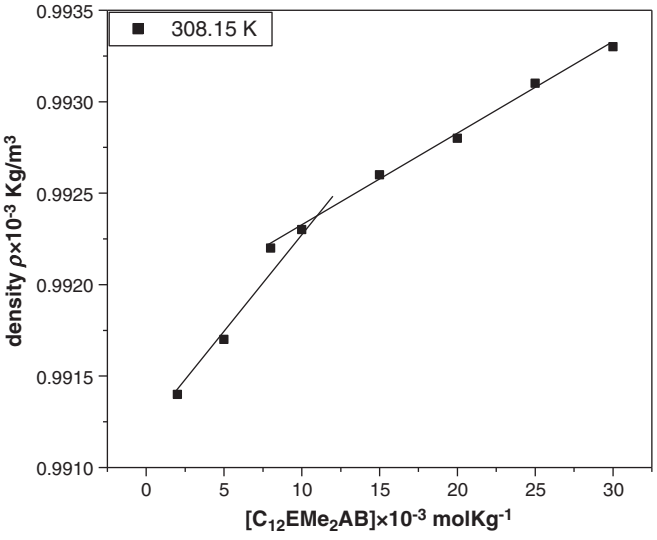

Fig. 1. Variation in the density of aqueous $C_{12}EMe_2AB$ solution with its concentration [$C_{12}EMe_2AB$] at 308.15 K.

where ρ and ρ_0 are the densities of surfactant solution and water respectively, v_s and v_m are the apparent specific volumes of monomers and micelles respectively and C_s and C_m are their corresponding concentrations in g/cm^3. Considering these apparent specific volumes to be independent of concentration, then $\rho_0 = \rho_0 + (1 - v_s\rho_0)C_s$ for premicellar region ($C_m = 0$) and for postmicellar region ($C_m = C - cmc$), $\rho = \rho' + (1 - v_m\rho_0)(C - cmc)$ where $\rho' = \rho_0 + (1 - v_s\rho_0)C_s$ and $(C - cmc)$ is the micellar concentration. Apparent molar volume is very significant to explain the micellization behavior as a function of concentration and temperature [23]. Apparent molar volume of surfactant ($V_s = v_s \times M$) and micelle ($V_m = v_m \times M$) calculated from the slopes of density versus surfactant/micelle concentration plots at different temperatures is given in Table 1. The observed increase in apparent molar volume with the increase in temperature (Fig. 2) is due to the relaxation of structured water engaged in solvation of the hydrocarbon chain, the head group, and the counterions. The behavior is in tune with the earlier findings for other surfactants [23,24]. The change in apparent molar volume upon micellization ($\Delta V_m = V_m - V_s$) calculated at different temperatures is given in Table 1. The values of ΔV_m found for $C_{12}EMe_2AB$ are positive in consistency with the earlier reported values for other surfactants [25–28]. This effect may primarily be due to breaking of structured icebergs around hydrophobic part of monomeric surfactants during micellization. A linear decrease of ΔV_m values with temperature increase was observed. However at higher temperatures, the contribution to ΔV_m was found to be lower which may be due to lower contribution of less structured icebergs. However it has been reported [23] that increase in temperature, increases degree of ionization, which shall increase ΔV_m. Therefore the effect of water molecules on ΔV_m has been suggested to compensate the increase in ΔV_m due to increase in degree of ionization on increase in temperature.

Table 1
Molar apparent volumes of dodecylethyldimethylethylammonium bromide as a function of concentration and temperature.

Temperature (K)	V_s	V_m	ΔV_m
	cm^{3}mol^{-1}		
298.15	165.03	249.20	84.17
303.15	172.59	255.11	82.52
308.15	205.77	273.48	67.71
313.15	243.01	288.31	45.30
318.15	278.24	302.61	24.37
323.15	297.38	317.94	20.56

Error limits in the measurements of V_s, and V_m are $\pm 4\%$, and ± 4 respectively.