



Spectral characterization and colloidal properties of 1-hexadecylpyridinium chloride in aqueous binary mixtures of different glycols

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ABSTRACT

The influence of various water–glycol mixed solvents on the self-assembly of 1-hexadecylpyridinium chloride (CPyCl) was investigated using electrical conductivity and spectroscopic measurements. Temperature studies were performed in aqueous mixtures of ethylene, diethylene, triethylene and tetraethylene glycols (abbreviated as EG, DEG, TEG and TeEG, respectively). The correlation among critical micellization concentration (cmc) and degree of ionization (β) was discussed in term of thermodynamic parameters or the changes in the Gibbs free energy, enthalpy and entropy upon micelle formation (ΔG_m^0 , ΔH_m^0 and ΔS_m^0). The differences in the Gibbs energies of micellization of CPyCl between water and binary solvents were determined to evaluate the influence of the cosolvent. This study allowed us to conclude that the ability of glycols to act, as a structure breaker and its interaction with the surfactant hydrophilic groups are the controlling factors of the micellization process. The effect of cosolvents on the size of the aggregates was analyzed by means of density measurements. Micellar micropolarity and solute solvent parameters were examined spectrophotometrically using methyl orange (MO) as a probe. The increase in micellar microviscosity was revealed from fluorescence measurements. The mechanism of docking of surfactant and the probe molecules in the system were obtained by using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy.

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1. Introduction

Due to their amphiphilic nature, surfactants have applications in a wide variety of fields [1,2]. Surfactants are used as additives in pharmaceutical formulations [3], to enhance the solubilization of hydrophobic compounds [4], as catalysts [5], as detergents [6], etc. Such important roles are related to their ability to form aggregates (micelles) when concentration of surfactant in aqueous solution exceeds critical micelle concentration (cmc). 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 phenomena in nonaqueous media. The term “solvophobic interaction” has been coined to describe the micelle formation in polar organic solvents [7]. Notwithstanding the recognition of the importance of “water structure” in the micelle formation in aqueous surfactant solutions, no significant attempt seems to have been made to investigate the role of “structuredness” which may exist in many polar organic solvents due to the presence of one or more potential hydrogen bonding centers in their molecules. Most of the major studies on solvophobic effect [8–10] have so

far involved *n*-alkyltrimethylammonium bromide or chloride surfactants and focused on the influence of chain length of surfactants in aqueous binary solvent mixtures. Penfold et al. [11] studied the micelle formation of monododecyl octaethylene glycol (C₁₂E₈) and monododecyl hexaethylene glycol (C₁₂E₆) in water mixed with ethylene glycol, sorbitol or glycerol using small angle neutron scattering. They found that the size of the micelle increased with the addition of cosolvent. This behavior was attributed to a decreasing hydration of the polyoxyethylene groups due to the interaction between water and the cosolvent causing a reduced curvature in the micellar aggregates. Rodriguez and coworkers [12] have carried out the micellar-catalyzed reaction in water–EG solutions. Nagarajan et al. [13] have developed theoretical models to predict the aggregation behavior of surfactants in polar organic solvents and in aqueous-organic mixed solvent media. Recently, we have reported [14] an investigation on the micellar properties of cationic surfactant 1-hexadecylpyridinium chloride (CPyCl) in water–*N,N*-dimethylformamide mixtures. A reduction in the hydrodynamic micelle radius was observed that was attributed to a decrease in the aggregation number. Evidence for the formation of a thicker solvation layer, consistent with the participation of the cosolvent in micellar region was also found.

In the present work, changes in the cmc and micellar ionization degree, aggregation number and the polarity of the interfacial

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region of CPyCl in aqueous solution of ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (TeEG) have been reported. Glycols have been selected in order to discriminate between their additive effect on the micellization of CPyCl with respect to the increase in their alkyl chain length. The gradual replacement of water with polar solvents (glycols) allows one to explore a wide bulk phase polarity range and their influence on the micellization. The purpose of the work is to shed more light on finding a way of fitting together all the obtained conductometric and spectroscopic experimental data in different aqueous mixtures of glycols for a given CPyCl surfactant.

2. Materials and methods

2.1. Materials

The cationic surfactant, 1-hexadecylpyridinium chloride (CPyCl, $\geq 98\%$) and ethylene glycol (EG, 98%), diethylene glycol (DEG, 98%), triethylene glycol (TEG, 99%) and tetraethylene glycol (TeEG, 99.1%) were purchased from Fluka. The solvatochromic probe, Methyl Orange (MO) was from British Laboratories (purity $\geq 99\%$). D₂O was from Aldrich with purity greater than 99%. Triply distilled water with conductivity $< 3 \mu\text{s}$ was used in experiments.

2.2. Methods

2.2.1. UV-vis absorption spectroscopy

Absorption spectra were taken over the range of 200–550 nm using a Jasco V 530 UV-vis spectrophotometer. All the spectra were taken at 298.15 K. In addition MO was chosen as absorption probe for studying an empirical measure of solvent polarity (E_T). These spectra were recorded against a blank consisting of an aqueous solution or water-glycol micellar solution of concentration comparable to that of the assay solution. The MO concentration was kept at 2.5×10^{-5} M.

2.2.2. Fluorescence measurements

To estimate the micellar micropolarity, the fluorescence emission spectra of MO in CPyCl solution were obtained on an instrument from Shimadzu RF-540, Japan, using a quartz cuvette. Measurements were duplicated and the mean value was used. The excitation and emission band slits were fixed at 5 nm.

2.2.3. Density measurements

The micellar aggregation numbers (N_{agg}) were obtained using density measurement (detail is given in supplementary data) on an instrument from Mettler DA-310 densitometer.

2.2.4. Zeta potential

The zeta potential measurements of the CPyCl in pure water and in different water-glycol were measured at 298.15 K on a Zeta potential from Malvern Instruments (Zen 3600), using Laser-Doppler electrophoresis light scattering method.

2.2.5. Conductivity titration

The electrical conductivity was measured in a thermostatic glass cell using a Pico digital conductivity meter operating at 50 Hz from Lab India instruments with an absolute accuracy of $\pm 3\%$ and precision of $\pm 0.1\%$. An automatic thermostated bath from Julabo was used for maintaining the temperature within ± 0.01 °C. The conductivity cell was calibrated with standard KCl solution, and the obtained cell constant was 1.02 cm^{-1} .

2.2.6. FTIR spectroscopy

FTIR spectra were recorded in the frequency range of 4400–350 cm^{-1} with help of Perkin-Elmer (RX1) FTIR spectrophotometer to investigate the association of surfactant with MO molecules.

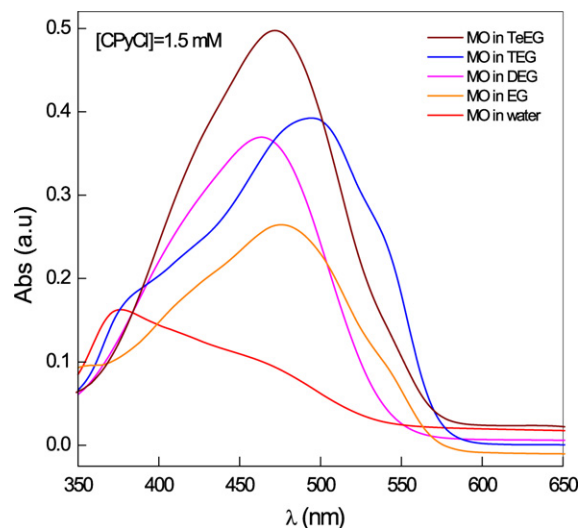


Fig. 1. UV absorption spectra of MO in different glycols (30 wt%) with 1.5 mM CPyCl.

2.2.7. ¹H NMR spectroscopy

The location and association behavior of MO in micellar media was determined by studying the differences in chemical shift in the ¹H NMR spectra of the aqueous surfactant systems with and without an adequate concentration of the MO molecules using Bruker Avance FT-NMR (400 MHz) spectrophotometer.

3. Results and discussion

3.1. Spectroscopic analysis

The variations of the CPyCl micellar interfacial region polarity caused by the presence of glycols in the bulk phase of micellar solution have been made using UV-visible spectroscopic studies. Fig. S1 in supplementary material shows the UV spectrum of CPyCl with concentration of 1.5 mM in different weight percentages of DEG. The intense band centered at about 213 and 258 nm in the spectrum of CPyCl was assigned to $\pi-\pi^*$ electronic transition involving the pyridinium ring. The absorbance intensity increases with increase in DEG content. The linear relationship between the absorbance at $\lambda_{\text{max}} = 258$ nm as a function of different concentrations of CPyCl in different wt% of glycols is also summarized in Fig. S2 (supplementary data). Comparison of different glycols indicate that the absorption band of CPyCl (at 258 nm) is unaffected by the presence of the different glycols. The intensity of the band increases with increase in CPyCl concentration, however its location is independent of the concentration (Fig. S2).

To obtain insight into the interfacial region polarity caused by the presence of glycols in the bulk phase of micellar solution, Methyl Orange (MO) was chosen as an absorption probe. The choice of the probe was dictated due to great sensitivity of absorption spectra to the polarity of their microenvironment [15]. Moreover, the MO probe satisfies the procedural requirement of being soluble in a wide variety of media due to its structure and ionic character [16,17]. Fig. 1 shows MO's electronic absorption band in 30% content of different glycols (5% data is represented in Fig. S3 supplementary material). In neutral aqueous solutions, MO exhibited an absorbance maximum (λ_{max}) at 462 ± 1 nm, in agreement with the literature [18]. The band has a hump at the high frequency side of the absorption maximum in water, while in the binary solvent mixture, the hump is on the low frequency side. In the presence of organic solvents, the electronic spectra of azo dyes like MO have a superposition of a $\pi-\pi^*$ and $n-\pi^*$ transition [19]. It has been proposed that, as the polarity of the medium increases, the $\pi-\pi^*$ transition shifts to the visible region and the

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