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Investigations on micellization and surface properties of sodium dodecyl sulfate in aqueous solutions of triflupromazine hydrochloride at different temperatures

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ABSTRACT

Micellization behavior of sodium dodecylsulfate (SDS) has been studied in the presence of phenothiazine drug triflupromazine hydrochloride (TFP) in the concentration range (0.01–0.50 mM) in water as well as in aqueous solutions of ethanol (1–10%, v/v) using conductivity and surface tension measurements. Critical micelle concentration (CMC), degree of micelle dissociation (β), Gibbs free energy of micellization (ΔG^{o}_{mic}), standard enthalpy (ΔH^{o}_{mic}) and entropy (ΔS^{o}_{mic}), maximum surface excess concentration (Γ_{max}), minimum area per surfactant molecule (A_{min}), Gibbs free energy of adsorption (ΔG^{o}_{ads}) and packing parameter (p) have been calculated from the above measurements. CMC values decrease with concentration of ethanol as well as of TFP in water. However in aqueous ethanol solutions, CMC values of SDS do not follow a regular decrease with TFP concentration. Surface parameters, Γ_{max} and A_{min} indicate comparatively less availability of surfactant molecules at the air–water interface in the presence of additives. The p values suggest that the micellar shape remains the same in the studied concentration range of TFP as well as ethanol. ^{1}H NMR spectroscopy has also been employed to acquire an idea about the nature of molecular interactions prevailing among the reacting species from the changes in chemical shift observed.

1. Introduction

The rigid tricyclic group of phenothiazine drugs which imparts the hydrophobic character to molecule is used for understanding correlation between molecular structure and physicochemical properties as well as for exploring interactions of drugs with other molecules [1]. These drugs having much pharmaceutical importance due to their local antibiotic, anesthetic, tranquilizing and antidepressant actions, have a property to form small aggregates in aqueous solutions [2]. The interaction of these drugs with biological membranes as a part of their action is a well known fact and has complemented the recent advances in drug delivery and drug targeting [3]. Use of micelles as drug carriers is beneficial over employing other alternatives due to their potential utilization as models for biochemical systems along with solubilization of feebly soluble drugs [4]. Drug solubility as well as bioavailability are the two most important factors which are to be considered while the choice of a suitable carrier is made [5,6]. Instead of using a single method to control varying parameters in drug delivery and targeting, combined effect of two or more may provide additional benefits and drug binding as well as solubility may be well optimized. Such an attempt has been made earlier by Li et al. by using the method of pH control combined with cosolvents, surfactants and complexants [7]. Also in some recent reports, in the study of interactions of micelles with lipophillic organic molecules, use of SDS micelles as carrier is combined with the use of cosolvents such as methanol, ethanol and propanol [8,9]. Phenothiazine drugs are used as their hydrochloride salts and studies on their interactions with surfactant micelles have been carried out by various workers. Most of these studies are based on the mixed micellization of these drugs with surfactants taking into account the aggregation properties of drugs [10–12]. It is well known that pharmacological effects of these drugs are manifested at very low concentration where self aggregation is not important, further the excess amount of drug has side effects besides its action like psychotic illness, overstimulation as well as other disorders in the body. So it would be better to choose the drug concentration where molecules do not aggregate as well as which is suitable from physiological point of view and to manifest its interactions with micelles from the change in micellization properties of surfactants along with other thermodynamic properties. Triflupromazine hydrochloride (TFP) is an important drug (Fig. 1) among phenothiazines being used as antipsychotics. Interactions of TFP with SDS in the presence of various pharmaceutically important cosolvents such as ethanol and ethylene glycol, have been studied by Gokturk and Var using UV–Visible spectroscopy only at one concentration (1.0×10^{-5} M) of drug [13]. Therefore in light of the above, conductivity, surface tension and NMR spectroscopy techniques have been used to study the interactions between TFP and SDS taking aqueous solutions

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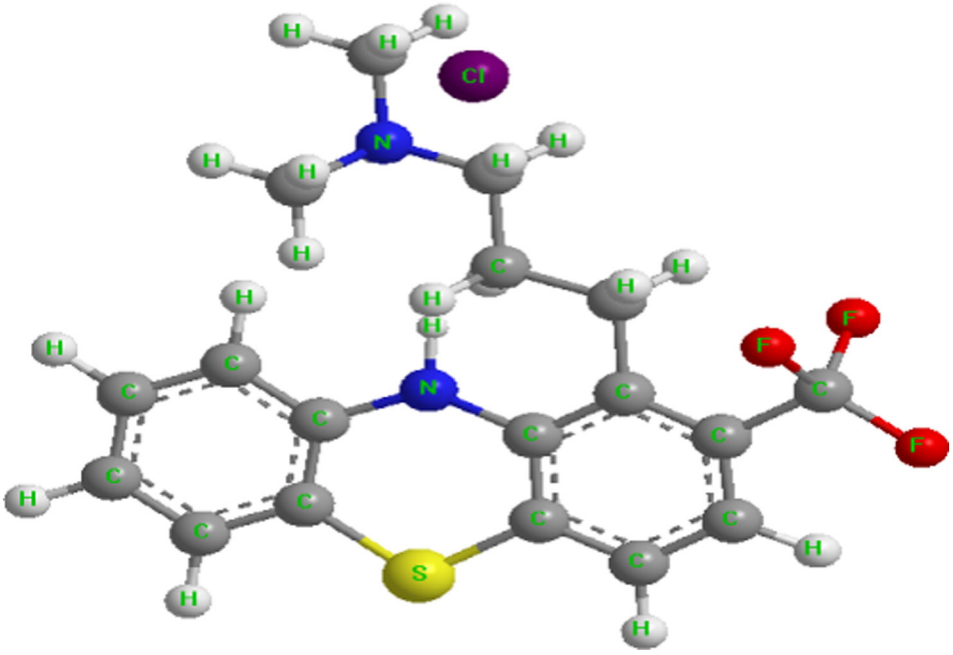

Fig. 1. Structure of triflupromazine hydrochloride.

of ethanol as the medium. Various micellar as well as thermodynamic parameters have been derived from these studies. The effect of a range of drug concentrations (0.01–0.50 mM, where aggregation of drug is not important) has been studied on the micellization behavior of SDS. Concentration range of cosolvent (ethanol) studied is (1–10%, v/v), which is acceptable pharmaceutically as well as biologically.

2. Experimental section

2.1. Materials

SDS and TFP used in experiments were supplied by Sigma Aldrich (USA) having purity higher than 99%. The CHNO analysis of the chemicals has been done to confirm this using FLASH 2000 Organic Elemental Analyzer, USA. The % compositions obtained experimentally for the elements are (parenthesis contain the ideal value calculated) SDS; [C% = 49.44 (49.93), H% = 7.97 (8.67), O% = 22.14 (22.19)], TFP; [C% = 52.17 (52.8), H% = 3% (3.14), N% = 4.39 (4.40), O% = 9.87 (10.06)]. These were dried over anhydrous $CaCl_2$ in vacuum desiccator before use. Absolute ethanol was purchased from Sisco Research Laboratories (India). Solutions were prepared in second stage Milli-Q water having specific resistance of 18.2 M ohm cm. The solutions were prepared using Mettler balance having an accuracy of 0.01 mg. The standard uncertainty in the molarity on an average is 2.4×10^{-6} M.

2.2. Methods

2.2.1. Conductivity measurements

Conductivity measurements were carried out with a digital conductivity meter (Systronics-306) at a fixed frequency of 50 Hz using a dip type cell with double walled glass jacket. The conductivity meter was calibrated using KCl solution ([KCl] = 0.10 mol L^{-1}, κ = 12.82 mS cm^{-1}) [14]. The temperature of the cell was maintained within 0.01 K. The reproducibility of the conductivity measurements was within ±0.2%.

2.2.2. Surface tension measurements

The ring detachment method was used to measure the surface tension (γ) values of the aqueous solutions of surfactants with a Kruss Easy Dyne Tensiometer from Kruss Gmbh (Hamburg, Germany). The Platinum ring used for the measurements was cleaned by washing with Milli-Q water followed by drying with acetone. Surface tension of Milli-Q water i.e. 72.0 mN m^{-1} at 298.15 ± 0.1 K [15] was used for calibrating the instrument. Final surface tension value reported is an average of at least 3 measurements. The accuracy in the measurement of surface tension with tensiometer is ±0.2 mN m^{-1}.

2.2.3. Nuclear magnetic resonance spectroscopy

^{1}H NMR spectra have been obtained employing a Bruker (AVANCE-III, HD 500 MHz) spectrometer at probe temperature of 300.15 K. D_2O has been used as lock solvent and its signal at 4.65 ppm was taken as the internal reference for the other nuclei. NMR spectra of pure SDS (5 mM) and TFP (5 mM) as well as of their mixtures have been studied in 9:1 (w/w) H_2O–D_2O solution. The chemical shift (δ) in ppm for pure components and mixtures has been reported and discussed in terms of various interactions.

3. Results and discussion

3.1. Effect of ethanol on micellization behavior of SDS using conductivity measurements

Conductivity (κ) measurements were performed for determining CMC values of SDS in aqueous solutions of drug (0.00, 0.01, 0.05, 0.10, 0.20, 0.50 mM) in water as well as in aqueous ethanol solutions (1–10%, v/v) over a temperature range (288.15–318.15 K). The κ values of SDS solution increase with temperature, but decrease with ethanol content in the medium (Fig. 2). CMC values correspond to the break in the conductivity versus concentration curve representing monomeric and micellar surfactant zone. The ratio of slopes in post micellar region (S_2) to premicellar region (S_1) is a measure of degree of ionization of the surfactant (β). Before discussing the drug effect on the micellar properties of SDS, it would be more appropriate to have insights about the change in micellar properties with ethanol concentration. The variation of κ for surfactant solution is consistent with the variation of β as both show a decrease with ethanol content and an increase with temperature. The addition of alcohol to water changes the water structure and dielectric constant, thus ability of the medium to loosen the bond of any electrovalent compound in it decreases. Additionally penetration of alcohol molecules in the palisade layer of the micelle affects the