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Micellization behavior of cationic surfactant dodecyldimethylethylammonium bromide (DDAB) in the presence of papain

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Abstract

The effect of water-soluble, globular protein papain, on the cmc of a cationic surfactant dodecyldimethylethylammonium bromide (DDAB) in aqueous solution has been studied by using conductivity, viscosity and absorbance spectroscopy. The results obtained show that the interactions between surfactant and protein depend upon the concentration of protein and the temperature. The cmc values of DDAB have been estimated at various concentrations of papain as well as at different temperatures ranging from 283.15 to 303.15 K. The thermodynamic parameters of micellization have been determined from cmc values and an enthalpy–entropy compensation effect also observed for the systems. Thermodynamic parameters (ΔG_m°, ΔH_m° and ΔS_m°) for the micelle systems in the presence of papain have been obtained by applying the mass action model. Viscosity measurements have been performed to evaluate the rheological and conformational changes of protein–surfactant solution. To confirm the interactions between surfactant and protein, absorbance spectroscopy has been performed.

Keywords: Papain; DDAB; Conductivity; Viscosity; Physiochemical; Absorbance spectroscopy

1. Introduction

In spite of large difference between the molecular structure of protein and surfactant and their mechanism of adsorption, considerable work has been performed to explore the interactions between them [1–15]. The reason of taking much interest in such systems lies in their number of applications in industrial as well as biological processes [16,17]. Different types of physicochemical techniques like surface tension [18], conductivity [19–21], viscosity [22], etc. have been used to investigate the interactions between cationic and anionic surfactants with proteins. These interactions in aqueous media give rise to the formation of association structures, thereby modifying the solution and interfacial properties [23,24]. Hydrophobic and electrostatic interactions are two main driving forces for the association between surfactant and proteins. Generally, the binding of surfactant monomers to protein chain occurs at very low surfactant concentration, often one to three orders of magnitude below the cmc of surfactant. The study on the effect of proteins on the properties of surfactants provides important information for interactions between surfactants and proteins.

The thiol enzyme, papain is water-soluble globular protein obtained from the latex and unripe fruit of *Carica papaya* [25]. It is used medically as it has an anticoagulant effect and it has been claimed that the enzyme eliminates necrotic tissues in chronic wounds, burns and ulcers. It also has commercial importance in the brewery, food and in the textile industry. Papain has a single peptide chain of 211 residues folded into two parts that form a cleft, having molecular weight 23,000 Da. The molecule has one free SH group that is functional.

In comparison to anionic surfactant, the literature comprises of cationic surfactant and water-soluble protein is limited [26–30]. The aim of this paper is to investigate the effect of concentration of papain and temperature on micellization of cationic DDAB by physiochemical and spectroscopic methods. The thermodynamic parameters, ΔG_m°, ΔH_m° and ΔS_m° have been calculated from conductivity data. Viscosity and UV–vis absorption studies have also been carried out to investigate the

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conformational and rheological changes in papain in the presence of surfactant.

2. Experimental

2.1. Materials and methods

The cationic surfactant, dodecyldimethylethylammonium bromide (DDAB) used in this study was a product of Fluka (purity >99%) and was used as received. Papain, a crystalline powder, was a product of Himedia. Papain was dissolved in double distilled water and the pH was unadjusted. Double distilled water of specific conductance 2–3 $\mu S\,cm^{-1}$ was used in all preparations.

2.2. Conductometry

The conductivity measurements of surfactant in the absence as well as in the presence of papain were carried out with the help of digital conductivity meter operating at 50 Hz from Labindia. A dip type conductivity cell with a double walled jacket to circulate the thermostated water was used for all measurements. The conductivity cell was calibrated with standard KCl solutions, and the obtained cell constant was $1.02\,cm^{-1}$ [31]. The measurement of conductivity was carried out with an accuracy of ±3% and the degree of precision was greater than ±0.1%. All the solutions were prepared by weight in deionized water with an accuracy of $\pm 1 \times 10^{-4}$ g. The concentrated solution was progressively added to protein solution and conductance values were measured after thorough mixing at constant temperature. An automated thermostat bath from Julabo, Germany, was used for maintaining the temperature with an accuracy of ±0.01 K. The conductivity measurements were made at different temperatures, *viz.* 283.15–303.15 K for surfactant–protein binary systems, as a function of surfactant concentration.

2.3. Viscometry

The viscosity measurements were carried out at 298.15 K using Ubbelohde type suspended level capillary viscometer. The viscometer was calibrated using standard pure solvents. Three sets of readings for the flow times of solvents were recorded and the arithmetic mean was taken for the calculation of viscosity [32]. The viscometer constants, A and B, were estimated by solving the simultaneous equations of type:

$$\frac{\eta}{\rho} = At - \frac{B}{t} \quad (1)$$

where η, ρ and t represent viscosity, density and time of flow for solvent, respectively. The calculated values of A and B were 0.00777 and −0.06549, respectively. The precision of viscosity measurements was of ±0.25% and the accuracy was ±1%.

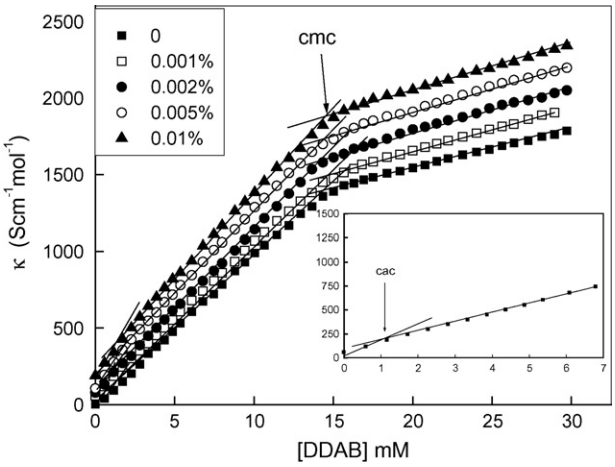

Fig. 1. Specific conductance (κ) vs. [DDAB] in the presence of various concentrations of papain (%, w/v) at 298.15 K. The inset figure shows the cac value of 0.001 (%, w/v) papain.

2.4. UV–vis spectrophotometry

The UV–vis spectrum of papain–DDAB solution was measured using a Jasco 530 Spectrophotometer. The absorption spectra of papain were taken in different surfactant concentrations at λ_{278}. The surfactant concentration was varied from 0 to 30 mM both in the sample and reference cell.

3. Results and discussion

3.1. Conductivity measurements

The formation of protein–micelle complex can give rise to gross conformational changes in the protein molecule. The measurement of solution conductivity provides a simple way to monitor such conformational changes, and hence the occurrence of protein–micelle association [19]. Fig. 1 exemplifies the variation of the specific conductance (κ) at constant papain

Table 1
Critical aggregation concentration (cac), critical micelle concentration (cmc), degree of binding (α), degree of association (γ) and various Gibbs energy parameters of DDAB at different concentrations of papain from conductivity measurements at 298.15 K

Papain (%, w/v)	cac (mol/l)	cmc (mol/l)	α	γ	ΔG°_{cac} KJ/mol	ΔG°_{m} KJ/mol	$\Delta G^{\circ}_{M,tra}$ KJ/mol	ΔG°_{Pr} KJ/mol
0.00		0.0139		0.74		−35.75		
0.001	0.0114	0.0142	0.070	0.68	−35.25	−34.43	1.32	−0.91
0.002	0.0115	0.0145	0.057	0.65	−34.69	−33.73	2.02	−0.95
0.005	0.0116	0.0147	0.035	0.64	−34.45	−33.47	2.28	−0.96
0.01	0.0117	0.0148	0.023	0.63	−34.20	−33.25	2.50	−0.95