J. Chem. Thermodynamics 105 (2017) 337–344

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Conductometric and fluorescence probe analysis on molecular interactions between cationic surfactants in aqueous medium of glycyl dipeptide: Concentration and temperature effect

S. Chauhan *, Santosh Kumari, Kuldeep Singh

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla 171005, India

ARTICLE INFO

Article history:
Received 21 April 2016
Received in revised form 14 October 2016
Accepted 27 October 2016
Available online 29 October 2016

Keywords:
Aggregation
Critical micelle concentration
CTAB/DTAB
Glycyl dipeptide
Micellization

ABSTRACT

The effect of cationic micelles of cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) on interactions of glycyl dipeptide in aqueous medium have been studied in varying concentrations (0.001, 0.005 and 0.010 mol·kg^{-1}) at different temperatures (293.15 K to 293.15 K). The conductivity method has been employed to determine critical micelle concentration, *CMC* i.e. point of aggregation and the results have been discussed in terms of glycylglycine–CTAB/DTAB hydrophobic and electrostatic interactions in aqueous medium. The obtained *CMC* values reveal the fact that the micellization tendency of the surfactant increases in the presence of glycyl dipeptide. The *CMC*'s of CTAB and DTAB have been found to decrease from 0.87 to 0.66 mmol·kg^{-1} and 14.2–13.7 mmol·kg^{-1} respectively as the [Glycyl dipeptide] increased from 0.001 to 0.010 mol·kg^{-1}. The temperature dependence of the *CMC* values has been established in terms of ion–ion, ion–polar and hydrophobic–hydrophobic group interactions around the hydrophobic part of surfactants. Furthermore, the standard thermodynamic parameters of micellization have been evaluated and interpreted which enable to grasp fully the ion–ion/ion–hydro philic interactions existing in the present ternary (surfactant–dipeptide–water) system. In addition, the pyrene fluorescence technique has been used to study the change of micropolarity produced by the interactions of surfactants with glycyl dipeptide and the aggregation behaviour (*CMC* determination) of surfactants.

1. Introduction

Proteins are the most distinctive chemical compounds found in living cells. Dietary proteins are reduced into their constituting units i.e. dipeptides and amino acids. On the basis of mechanism involved in uptake process the dipeptides are absorbed more swiftly than the amino acids [1]. Peptides play an important role in fundamental physiological and biochemical processes, and are indispensable to many aspects of biomedical research especially in pharmaceutical industries, because of their wide applications in drug production which continues to edging towards biological arena [2,3]. The biological importance of proteins can be understood from their ability to act as a hormones and transmitters in central nervous system of living beings [4]. Moreover, small peptides such as glycyl dipeptides are the crux of building units of complex protein molecules and referred as water structure influencing molecules due to their significant effect on the aqueous system [5]. Thus, the peptides possessing more complex structure than that of amino acids may be used as model compounds to study the solution behavior of proteins (complex three dimensional structures) and their systematic study can provide valuable information about their behaviour in solution and insight into the complex structure of proteins.

The addition of solutes such as electrolytes, surfactants, salts or other bio–molecules to the peptide solution change their hydration behavior invoking their ability to bind other molecules [6]. But, the peptide–surfactant system continues to be an important and growing area of research due to their pervasive utilization in biosciences, food and cosmetic industry, drug delivery, detergency, and biotechnological processes [7]. Nevertheless, the nature of solvent plays a crucial role and affects the stability of peptide–surfactants mixture by distributing itself between aqueous and micellar phase or piled up both at polar head groups and inside the micelle hydrophobic core [8]. The physicochemical properties of surfactants in aqueous/non–aqueous medium in the presence of different additive such as salts, electrolytes or other bio–active molecules, have been studied to facilitate the knowledge of their

* Corresponding author.
E-mail address: scschauhan19@gmail.com (S. Chauhan).

http://dx.doi.org/10.1016/j.jct.2016.10.045
0021-9614/

solution/micellar behaviour and interactions between the mixture components [9,10]. All the same, hydrophobic and electrostatic interactions have been proposed to be the main driving forces which are accountable for the affiliation between surfactants and bio–active molecules in solution.

Owing to the facts considered above, a number of researchers have investigated the effect of electrolytes and surfactants on physicochemical properties of peptides [11–21]. However, an exhaustive survey of literature reveals that no report is so far available on the micellar properties of the Cetyltrimetylammonium bromide (CTAB) and Dodecyltrimetylammonium bromide (DTAB) in presence of glycyl dipeptides except for the work of Singh et al., [22], who have depicted only volumetric properties of some amino acids and two peptides (diglycine and triglycine) in aqueous surfactant solutions at T = 298.15 K. Therefore, in order to extract information on micellar behavior of surfactants in presence of peptides, the cationic surfactants CTAB and DTAB in aqueous solutions of glycyl dipeptide have been considered in the present work. Furthermore, with an eye to get better insight into different types of interactions which are responsible for the variations in the micellization behaviour of these surfactants, the effect of concentration of glycyl dipeptide (0.001, 0.005 and 0.010 mol·kg^{-1}) and temperature (293.15 K – 313.15 K) have also been studied for the mixture which is helpful to control the strength of protein–surfactant interactions in practical applications. The zwitter ionic structure of glycylglycine/glycyl dipeptide and molecular structures of CTAB, and DTAB are shown in the Scheme 1.

2. Experimental details

2.1. Material

The deionised distilled water with conductivity (2–3) $\times$ 10^{-6} S·cm^{-1} and pH of 6.8 to 7.0 at T = 298.15 K, obtained from a Millipore–Elix system was used for all experiments. CTAB and DTAB of AR grade have been obtained from Himedia Pvt. Ltd. (India) and recrystallized from ethanol by following the procedure reported elsewhere [9,23]. The glycyl dipeptide has been purchased from Spectrochem Pvt. Ltd. (India) and has been used as such without any additional treatment. Pyrene (A.R. grade) which has been used as fluorescent probe, was obtained from Merck (Germany) was used without further purification. A summary of provenance and purity of the sample used have also been provided in Table 1.

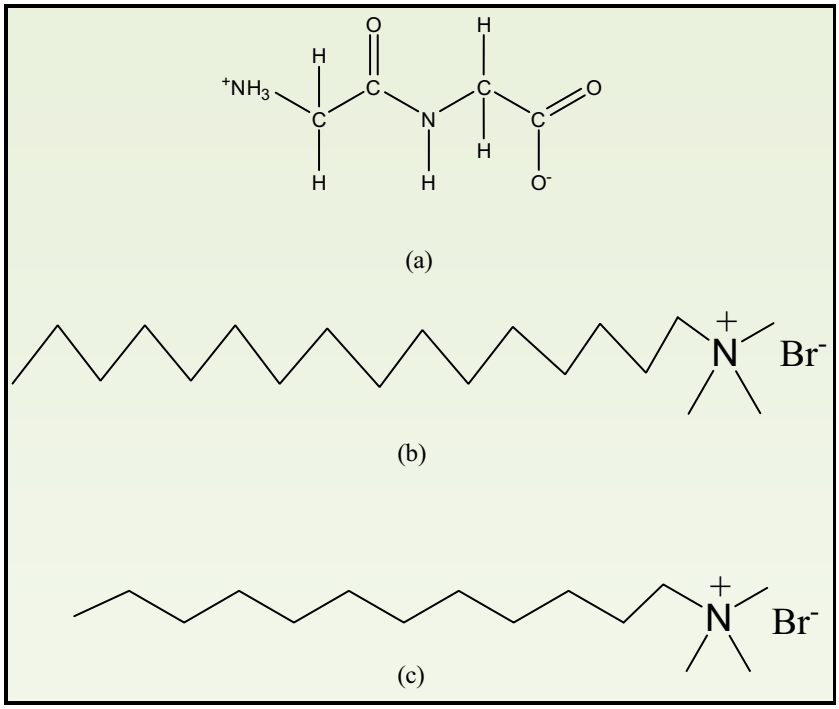
2.2. Methods

2.2.1. Conductivity measurements

Stock solutions of glycyl dipeptide (0.001, 0.005, and 0.010 mol·kg^{-1}) have been prepared in water and used as solvent for the preparation of different CTAB (0.1–2.0 mmol·kg^{-1}) and DTAB (1–30 mmol·kg^{-1}) concentrations. All solutions have been prepared by using Shimadzu balance with a precision of ±0.0001 g. Conductivity measurements have been carried out with digital conductivity meter Cyberscan CON 510, whose working principle and procedure has already been explained in our previous study [24]. The instrument works on AC (feeding voltage 110/120V and frequency 50/60 Hz) with operational frequency of 1 kHz. The temperature has been maintained constant at ± 0.1 K by circulating thermostated water through double walled conductivity vessel containing the solution. The relative uncertainty in electrical conductivity measurements was estimated to be $u_r(\kappa)$ = 5%.

2.2.2. Fluorescence measurements

The fluorescence probe study of CTAB and DTAB solutions was done with LS–55 Perkins Elmer Fluorescence Spectrophotometer, whose working principle and procedure has already been explained elsewhere [24]. For analysis of samples, a 10 mm path length quartz cuvette was filled with the appropriate solutions. The excitation wavelength was kept at 334 nm and the emission was recorded at (373 and 384) nm. The excitation and emission slits were kept at (8.0 and 2.5) nm, respectively. The experimental



Scheme 1. (a) Zwitter ionic structure of glycylglycine [$C_4H_8N_2O_3$] and molecular structure of (b) CTAB, [$C_{16}H_{33}N^+(CH_3)_3$ Br^-] and (c) DTAB [$C_{12}H_{25}N^+(CH_3)_3$ Br^-].