



Krafft temperature and thermodynamic study of interaction of glycine, diglycine, and triglycine with hexadecylpyridinium chloride and hexadecylpyridinium bromide: A conductometric approach



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ABSTRACT

Krafft temperature (T_k) and thermodynamics of micellization of Hexadecylpyridinium chloride (HPyCl) and Hexadecylpyridinium bromide (HPyBr) were carried out in the absence and in the presence of amino acids-glycine, diglycine and triglycine. Thermodynamic parameters of micellization – Gibbs free energy of micellization, enthalpy, entropy, free energy related with hydrophobic part and surface contribution were calculated from the specific conductance data. Transfer values of Gibbs free energy and enthalpy were also calculated. T_k of HPyCl and HPyBr were determined in aqueous as well as in presence of aqueous-glycine, diglycine and triglycine. Effect of polar head group, counter-ions, additives, T_k , and micellization parameters on micelle formation of the surfactants are the main points taken into consideration while explaining and interpreting the results to get an insight into the interactions of these additives with the cationic surfactants.

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1. Introduction

In pharmaceutical [1,2], industrial [3], biochemical [4,5], and cosmetic applications [6] surfactants find a significant place. Protein–surfactant interactions are important as they enhance the protein functional characteristics. Using conductivity [7,8], chromatography [7], axisymmetric drop shape analysis [9], fourier transform infrared spectroscopy (FTIR) [10–12], circular dichroism [13,14], fluorescence [15,16], and direct calorimetry [17–20], interaction between protein–surfactant were investigated. For oil–water or air–water interfaces protein–surfactants interact instantly [21,22] and thereby leading to considerable changes in the protein conformation [23,24]. Interactions of globular proteins with surfactants alter molecular characteristics of proteins affecting their binding capacities at interfaces owing to self-association. Proteins can be stabilized by surfactants in two ways: firstly surfactant molecules prevent adsorption of proteins by dominating the interface and secondly they may associate with the protein molecules, preventing their coagulation. In pharmaceutical formulations, the biotechnologists are using surfactants to minimize the loss of proteins due to interfacial and colloidal mechanisms [6]. Interaction of surfactants with the proteins is still a problem which needs further investigation. Understanding the nature and origin of protein–surfactant

interactions is important from academic as well as from industrial point of view.

Ionic surfactants have the affinity to form solid hydrates on precipitation from aqueous medium. The solubility of a material will often be observed to undergo a sharp, discontinuous increase at some characteristic temperature commonly referred to as the Krafft temperature [25]. As the temperature is increased, the solubility increases abruptly and as CMC concentration becomes equal to solubility micelles are formed. Moroi [26] defined the micellar temperature range as the range between Krafft point and Krafft temperature. Krafft temperature varies differently with two surfactants with similar structure, like charges in binary mixture of surfactants [27,28]. A shallow depression in the Krafft temperature is observed when the precipitate contains both the surfactants. Surfactants with dissimilar structures and counter-ions, a larger depression in Krafft temperature is detected [29]. Previously, it has been shown that the Krafft point of ionic surfactants (the Krafft temperature at the critical micelle concentration) can be changed by varying the counter-ion [30], or by increasing the degree of unsaturation [31], or branching [29] in the hydrocarbon chain. Using Krafft temperature measurements, surfactant–dendrimer interactions were found to be mainly electrostatic in nature [32]. Water-soluble dendrimers {poly (amidoamine)} and their derivatives were mainly investigated [33], but significant interactions in micellar system with poor and insoluble dendrimers showed a significant trend [34]. The thermodynamics of micellization processes of ionic surfactants with different additives received much attention in recent years as the thermodynamic

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parameters are powerful means for elucidating the mechanism of the micellization and effects of additives on the micellization process [35]. As is well known CMC is method dependent and the molecular structure, pressure, added electrolyte, and temperature play a significant role in micelle formation. The two important structural parameters which determine the effect on CMC are the chain length and chain branching of the surfactant. CMC usually increase upon increasing degree of branching and decrease upon increasing chain length [3,46]. Micellization in ionic surfactants is hampered by electrostatic head group repulsions and head group interactions are also influenced by the counter-ions, thus it will be interesting to investigate HPyCl and HPyBr in aqueous amino acids as these two ionic surfactants differ only in their counter-ions. HPyCl and HPyBr are used as antiseptic for killing bacteria and microorganisms. For instance, use of HPyCl in mouthwashes, toothpastes, lozenges, throat sprays, breath sprays, and nasal sprays has been well established. It has also been shown to be effective in preventing dental plaque and reducing gingivitis [36–38].

2. Materials and methods

2.1. Materials

Hexadecylpyridinium chloride (HPyCl), and hexadecylpyridinium bromide (HPyBr) both 98% from Sisco Research Laboratories Pvt. Ltd. Mumbai India (SRL) were used without further purification. Glycine 99% from Merck, Diglycine 99% from ACROS organic and Triglycine 99% from Sigma Aldrich (Scheme 1), these were used as such but dried over P_2O_5 .

2.2. Krafft temperature measurements

To determine Krafft temperature, T_k , clear aqueous solutions of surfactants, HPyCl and HPyBr in the absence and in the presence of glycine, diglycine and triglycine were prepared and placed in a refrigerator at 277.15 K for at least 24 h, where the precipitation of surfactant hydrated crystals occurred. The concentration of the surfactant as well as the additive were kept constant to determine the effect of different additives on the Krafft temperature of these surfactants. The temperature of the precipitated system was raised gradually in water bath Julabo MD Germany (maintaining the temperature within ± 0.02 K) under constant stirring, and its specific conductance was measured using Labindia Pico⁺ Conductivity meter. At each temperature, conductance was checked until it reached a steady value. The Krafft temperature was taken as the temperature where the conductance versus temperature plots showed an abrupt change in slope. This temperature was the same as that required to completely dissolve the hydrated solid surfactant.

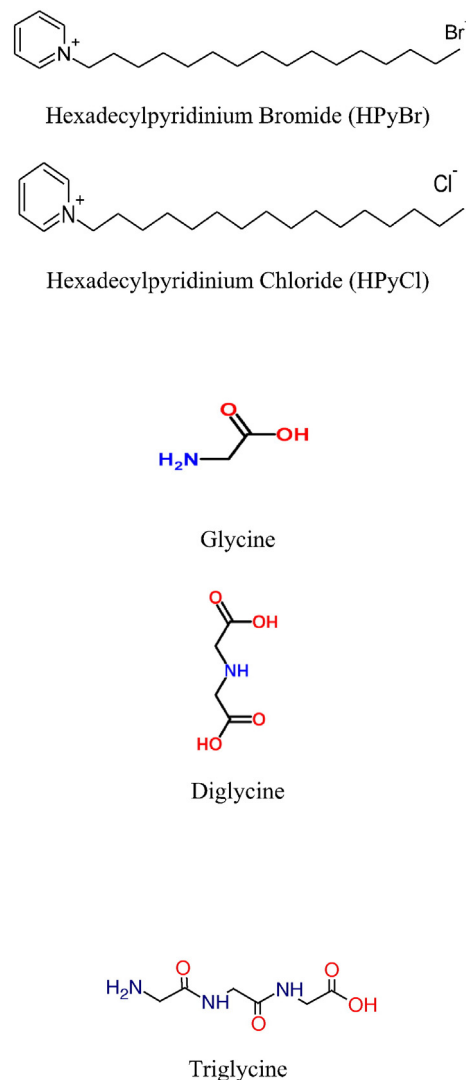
2.3. Conductivity measurements

Conductivities of solutions were measured by Labindia Pico⁺ conductivity meter having range of 0.01 $\mu\text{S}/\text{cm}$ to 199.9 mS/cm and accuracy 0.5%. The conductivity meter was first calibrated with 0.01 and 0.1 M KCl solutions at 298.15 K, the cell constant was found to be 0.995. Double distilled water having conductivity in the range 2–3 micro Siemens per centimeter was used to prepare the solutions. The stock solutions of HPyCl and HPyBr each were prepared in aqueous and in 0.02 M glycine, diglycine and triglycine solutions.

3. Results and discussion

3.1. Krafft temperature

Krafft temperature of the solutions of aqueous HPyCl, aqueous HPyBr, and their mixtures with 0.02 M glycine, diglycine and triglycine are shown in Figs. 1 and 2. From Fig. 1, it can be seen that conductance



Scheme 1. Chemical structures.

decreases in presence of glycine but increases in presence of diglycine and triglycine, this can be attributed to strong head group interactions in presence of di and triglycine which stabilize the surfactant crystal

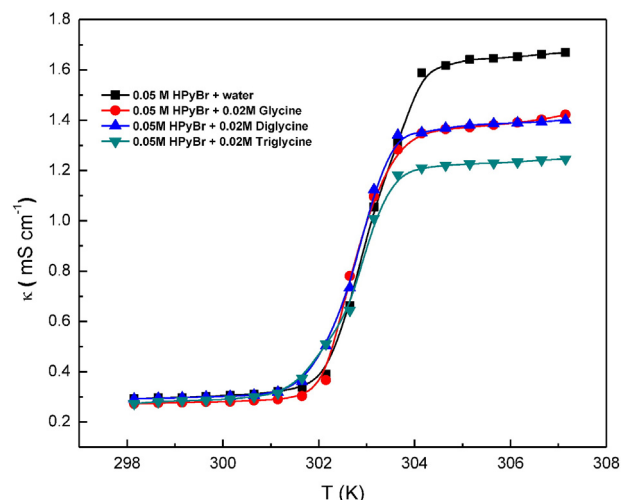


Fig. 1. Specific conductance (κ) vs Temperature (K).

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