Characteristics of mixed systems of phenol red and cetylpyridinium chloride

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ABSTRACT

Dye–surfactant systems known to exhibit two critical micelle concentrations (cmcs) are not many and the behavior of such systems in the mixed form has not been fully explored and reported. Phenol red (PR) and cetylpyridinium chloride (CPC) form one such dye–surfactant pair and its mixtures are studied here in the entire composition range using surface tension, conductance and UV–Visible spectroscopy methods. In this mixed system, mixed micelles are formed with one cmc in the region of $0 < \alpha_{CPC} < 0.5$, while mixed micelles as well as micelles of the surfactant alone are formed with two cmcs if $0.5 \leq \alpha_{CPC} < 1$ (α_{CPC} is the mole ratio of CPC to PR in solution). The mixture shows strong synergism in cmc with high negative value for interaction parameter. The bathochromic shift of the 432 nm band indicated hydrogen bonding between PR^- species in the region of $\alpha_{CPC} < 0.4$ and this hydrogen bonding weakened more in the presence of CPC due to ion pair formation than in the presence of a non-ionic surfactant TX-100. The relative amount of CPC in the mixture and the nature of the surfactant are found to influence the maximum wavelength of the PR^{2-} band also. The excess standard free energy of micellization has a linear correlation with the interaction parameter. Surface excess values of the individual components of the mixed system were evaluated. The compositions of the mixed micelle and the adsorbed layer reveal that some CP^+ monomers also aggregate/adsorb along with the CP^+–PR^- ion pairs.

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1. Introduction

Surfactants are molecules having hydrophilicity to a lesser extent and hydrophobicity to a larger extent such that on dissolving in water they undergo adsorption at the air–water interface followed by aggregation into micelles in the millimolar or submillimolar concentration region. Due to adsorption and aggregation properties, surfactants find widespread applications in chemical, biochemical, pharmaceutical and industrial fields. Adsorption and aggregation behavior of surfactants can be modified or tuned by adding additives of different types and also by varying the solvent properties.

Dyes are another type of molecules which also have hydrophobicity and tendency to adsorb and aggregate. However, the molecular structure and the relative extents of hydrophobicity and hydrophilicity in the molecule do not conform to consider dye as a surfactant. In comparison to surfactants, dyes micellize at relatively higher concentrations. Some of the dye molecules have structures such that they are able to form molecular aggregates (J and H aggregates) other than micelles. Dyes, besides being used largely for dyeing, are also used as indicators and sensors due to their halochromic nature. Both in dyeing and dye separation processes, surfactants are used as auxiliary agents along with dyes for better results. In dyeing processes surfactants are mainly used as wetting, dispersing and leveling agents, while in dye separation processes they are used as solubilizers. Therefore, for the textile and other coloring industries, understanding of the dye–surfactant interactions is very important. Several approaches are being used to study the dye–surfactant interactions. For example, dyes may be added as additives to surfactant solutions and changes in the surfactant behavior can be investigated. Secondly, changes in the behavior of dyes can be studied in the presence of surfactants. In the third approach, dye–surfactant mixtures are studied by treating them as mixed surfactant systems.

Cetylpyridinium chloride (CPC) and phenol red (PR) form a dye–surfactant system of opposite charges and it is reported to exhibit interesting spectral features [1–3]. CPC in the presence of PR is reported [3] to have two cmc values, the lower one is considered to be due to micellization of CP^+–PR^- ion pair and the higher one is attributed to the micellization of pure CPC. In the submicellar concentration range below the first cmc, PR^- forms ion pairs with CP^+ and in the concentration range above first cmc and below the second cmc, PR^- undergoes deprotonation to give PR^{2-} [1,3]. A few more dye–surfactant pairs are reported [4–7] to have similar aggregation behavior with two cmc values. Dye–Surfactant combinations may be studied using two types of mixing protocols, which we classify as 'protocol 1' and 'protocol 2'. In protocol 1, different measurements are made by adding varying amounts of surfactant to an aqueous solution containing a fixed amount of dye. Whereas

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in protocol 2 measurements are made by adding varying amounts of a mixture of surfactant and dye of a particular composition to water as it is done while studying mixed surfactants and the interaction between the two components of a mixture are analyzed using the approach like Rubingh's model [8]. The advantage of using mixing protocol 2 is that the entire composition range from mole fraction 0 to 1 of the components can be covered, which is not possible if mixing protocol 1 is adopted. In mixing protocol 1, measurements are essentially made at a fixed mole fraction of dye which is normally very low (~0.1). All the reported studies [3–7] on the dye–surfactant combinations known to exhibiting two cmc values, which are not many, were made using protocol 1. It would be interesting, due to the presence of two cmc values, to explore the behavior of such dye–surfactant pairs in the mixed state using protocol 2. Rashidi-Alavijeh et al. [5] however estimated the interaction parameter of congo red (CR) dye with different cationic surfactant systems by applying the Rubingh's model [8], but only at single composition of each dye–surfactant combination because they used mixing protocol 1. It is worth mentioning here that even in the case of surfactants known to have two cmc values, number of studies of such anionic + cationic mixed surfactant systems involving the second cmc is very limited [9–11]. Therefore, in this paper we have studied the surface and solution behavior of CPC + PR mixed system by making surface tension, conductance and absorbance measurements and the thermodynamics of mixed surfactant systems is applied to evaluate the interaction parameter. For comparison purpose, the TX-100–PR system has also been studied.

2. Materials and methods

PR was obtained from Himedia as its sodium salt. CPC was obtained from Fluka. Millipore grade water was used for preparing the solutions. The stock solutions of CPC + PR in water were prepared in different mole fraction ratios by weighing. Surface tension measurements were made by the Wilhelmy plate method using a K11 Krüss tensiometer and conductance measurements were made using Wayne Kerr B905 automatic precision bridge. For surface tension and conductance experiments, the required amount of water was taken in sample vessel or sample tube and into it known amounts of the CPC + PR stock solution were added, and after each addition surface tension or conductance was recorded. UV–Visible spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer. All experimental measurements were made at 25 °C using a circulation bath Julabo F12.

3. Results and discussion

3.1. Surface tension, specific conductance and cmc

The variation of surface tension (γ) and specific conductance (κ) of aqueous solutions of CPC + PR mixtures with mixture concentration (c_s) is shown in Figs. S1 and S2 (Supplementary material), respectively. The γ versus $\ln c_s$ plot (surface tension isotherm) of CPC solution ($\alpha_{CPC} \equiv \alpha_1 = 1$, α_{CPC} is the mole ratio of CPC to PR in solution) has the typical shape expected for a pure surfactant solution and the cmc was found to be equal to 9.0×10^{-4} M (M = mol dm^{-3}). From the specific conductance data the cmc value of CPC solution was found to be equal to 1.0×10^{-3} M. These values of cmc of CPC are in good agreement with the reported values [12–14]. The cmc value and the absence of surface tension minimum near the cmc in the surface tension isotherm ascertain that the CPC sample used in this study is pure. The surface tension isotherm and the specific conductance plot of PR solution ($\alpha_{PR} \equiv \alpha_2 = 1$, α_{PR} is the mole ration of PR to CPC in solution) provided that the cmc values of PR are equal to 23.0×10^{-3} and 21.3×10^{-3} M, respectively. The shapes of the surface tension isotherms of mixtures of $\alpha_{CPC} = 0.1$, 0.2 and 0.4 (i.e., $0 < \alpha_{CPC} < 0.5$) are similar to those of $\alpha_{CPC} = 1$, but surprisingly surface tension isotherms of $\alpha_{CPC} = 0.9$, 0.7 and 0.5 (i.e., $0.5 \leq \alpha_{CPC} < 1$) have different shapes near cmc. Therefore,

CPC + PR mixture shows a different type of aggregation behavior with two surface tension breaks when the mixture contains 50% or less than 50% PR. To highlight the different types of aggregation behavior in mixtures of $\alpha_{CPC} = 0.9$, 0.7 and 0.5, we have showed in Fig. 1 the shapes of surface tension isotherms near cmc using an expanded scale. The cmc values of the CPC + PR mixed systems are given in Table S1. The cmc values of the mixtures for data analysis have been taken as the averages of the values obtained from the surface tension and specific conductance data, and these average values are presented in Fig. 2.

In the mixtures of $\alpha_{CPC} = 0.9$, 0.7 and 0.5, after the first break, surface tension of the solution remains almost constant for a short range of concentration of the mixture and thereafter the surface tension slightly increases and then levels off. The slight increase in surface tension is to the extent of about 2.6, 2.0 and 1.0 mN m^{-1} in the mixtures of $\alpha_{CPC} = 0.9$, 0.7 and 0.5, respectively. Similar trend in the surface tension isotherms near the cmc has been reported [3–7] for single surfactants in the presence of fixed amounts of dyes. Shahir et al. [4] reported two breaks in the surface tension isotherm of tetradecyltrimethylammonium bromide (TTAB) in the presence of 2×10^{-5} M tartrazine (a food dye) which are similar to the breaks observed in surface tension isotherms of CPC + PR mixtures of $\alpha_{CPC} = 0.9$, 0.7 and 0.5. The two breaks in the surface tension isotherms of TTAB in the presence of tartrazine were considered to correspond to two cmc values, the first one due to the formation of dye rich micelles and the second one due to the formation of surfactant rich micelles [4]. The increase in surface tension in between the two breaks is explained as due to the replacement of the TTAB-tartrazine ion pairs at the surface monolayer by TTAB [4]. Similar explanations were given for the breaks found in the surface tension isotherms of CTAB (cetyltrimethylammonium bromide), TTAB, CPB (cetylpyridinium bromide) and CPC in the presence of fixed amount of CR [5]. Surface tension isotherms of sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) in the presence of neutral red (5×10^{-5} M) are reported [6] to pass through minimum and then maximum before finally becoming flat, while in the presence of 2.5×10^{-5} M of pararosaniline/crystal violet/ethyl violet/malachite green also the surface tension isotherms of SDS and SDBS have two break points, but without surface tension minimum [7]. Even the surface tension isotherm of CPC in the presence of 3.6×10^{-5} M PR is reported to exhibit two breaks [3]. Gohain et al. [3,6,7] also attributed the breaks in the surface tension isotherms of SDS, SDBS and CPC in the presence of different dyes to the formation of micelles of dye–surfactant ion pairs at the first break and to the micellization of surfactant alone at the second break. It may be noted that in all the above reported studies [3–7] mixing protocol 1 is adopted. For comparing the surface tension isotherm of CPC solution in the presence of fixed amount of PR with that of CPC + PR mixed systems, we measured the surface tension of aqueous CPC solution in the presence of 8×10^{-5} M of PR and its surface tension isotherm is shown in Fig. S1 and that near the cmc in Fig. 1. In the light of the above reported [3–7] aggregation behavior of dye–surfactant systems containing a fixed low amount of dye, the two breaks observed in the surface tension isotherms of CPC + PR mixed systems of $\alpha_{CPC} = 0.9$, 0.7 and 0.5 (Fig. 1) can be explained in the following manner: As we go on adding a mixture of CPC and PR to water, in the bulk there will be CP$^+$, PR$^-$, PR^{2-}, Cl$^-$, Na$^+$ and CP$^+$–PR$^-$ ion pairs, and at the air–water interface a monolayer of CP$^+$–PR$^-$ ion pairs will form. Since CP$^+$–PR$^-$ ion pairs will behave like a non-ionic surfactant [4–6], its surface activity will be relatively more and it will preferentially adsorb at the air–water interface. Along with the CP$^+$–PR$^-$ ion pairs, it is probable that some CP$^+$ monomers may also get adsorbed (refer Section 3.5). As the air–water interface gets saturated by the adsorbed CP$^+$–PR$^-$ ion pairs and CP$^+$ monomers, the first break in the surface tension isotherm appears and the non-ionic surfactant like ion pairs along with some CP$^+$ monomers (refer Section 3.3) will start aggregating to form mixed micelles. This process will continue on further addition of the CPC + PR mixture to produce more mixed micelles. In the mixed micellar phase,