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Interactions of short chain phenylalkanoic acids within ionic surfactant micelles in aqueous media

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Abstract: The solubilization and interactions of phenylalkanoic acids induced by the cationic surfactant, cetyltrimethylammonium bromide (CTAB) and the anionic surfactant sodium dodecyl sulfate (SDS) was investigated spectrophotometrically at 25.0 °C. The UV spectra of the additives (acids) were measured with and without surfactant above and below the critical micelle concentration (*cmc*) of the surfactant. The presence of an alkyl chain in phenylalkanoic acids was responsible for hydrophobic interactions resulting in a shift of the spectra towards longer wavelengths (red shift). The value of partition coefficient (K_x) between the bulk water and surfactant micelles and, in turn, the standard free energy change of solubilization (ΔG_p^\ominus) were also estimated by measuring the differential absorbance (ΔA) of the additives in micellar solutions.

Keywords: alkanolic acids; solubilization; *cmc*; CTAB; SDS.

INTRODUCTION

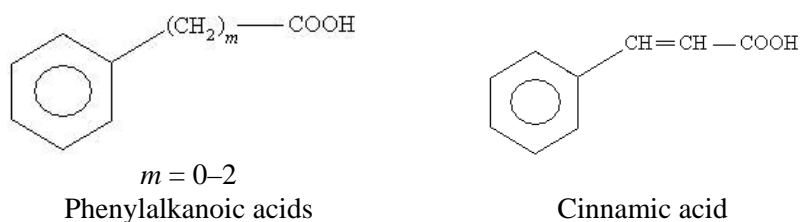
The augmented solubility of sparingly soluble solutes in water brought about by a surfactant micellar solution is well known as solubilization, a phenomenon that plays an important role in industrial and biological processes.^{1,2} The process of solute (additive) transfer from one medium to another is of widespread importance and characterized by a free energy change of transfer in relation to the partition coefficient. The solute transfer from one medium to another can be used to predict the solubilization of small molecules and anesthetic drugs in biological membranes.³

Amphiphilic additives containing a benzene ring are convenient to investigate spectrophotometrically.⁴ The physical behavior of the surfactant micelles can be envisaged as the construction of a model membrane to mimic a biological system. This experimental model is useful for studying the interaction of biolo-

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gical surfaces with the additive molecule.⁵ Phenylalkanoic acids and their derivatives are being used in pharmaceutical research. These compounds act as agonists for hPPARs (human peroxisome proliferator activated receptors), in particular the human PPAR α isoform, and are effective in the treatment of abnormal lipid metabolism, diabetes and other disorders.^{6,7}

In the past, the solubilization of various hydrophobic additives in aqueous micellized ionic surfactant systems were investigated.^{8–12} Recently, spectroscopic studies of diverse organic additives in different ionic surfactant systems were reported.^{13–15} In the current study, short chain phenylalkanoic acids in aqueous solution of anionic sodium dodecyl sulfate (SDS) and cationic cetyltrimethylammonium bromide (CTAB) surfactants were investigated. The additives studied were phenylmethanoic acid (PhMA), phenylethanoic acid (PhEA), 3-phenylpropionic acid (3-PhPA) and 3-phenylpropeonic acid or cinnamic acid (CA). The general structures of the additives are given below:



In this current study, the effect of increasing the alkyl chain length in acid molecules on their solubilization in cationic and anionic surfactant solutions was studied using UV spectroscopy. The incremental free energy change of transfer per methylene group, $\Delta G^{\ominus}(\text{CH}_2)$, and site of solubilization were evaluated and are discussed.

EXPERIMENTAL

Reagents

The CTAB and SDS were obtained from Sigma and Fluka, respectively. Phenylalkanoic acids ($\text{C}_6\text{H}_5(\text{CH}_2)_m\text{COOH}$, $m = 0-2$) and cinnamic acid were obtained from Merck. All chemicals were used without further purification. The water used throughout was distilled twice over alkaline permanganate in a Pyrex all-glass set-up.

Simple absorbance measurements

The UV absorption spectra of phenylalkanoic acids, each of concentration 1×10^{-6} mol dm^{-3} in aqueous solution, were measured at 25.0 ± 0.1 °C on a Hitachi double beam UV-220 type spectrophotometer equipped with 10 mm matched quartz cells. Then the absorption spectra of 1×10^{-6} mol dm^{-3} phenylalkanoic acid solution containing CTAB and SDS were taken at 25.0 °C using water as the blank.

Differential absorbance measurements

An additive solution (phenylalkanoic acid) of a particular concentration (1×10^{-6} mol dm $^{-3}$) was prepared. One portion of this solution was used as a solvent for SDS micellar solutions. Measurements were made at 25.0 ± 0.1 °C in such a way that a cuvette filled with an additive solution was set on the reference side and cuvette filled with SDS micellar solutions at the same additive concentration on the sample side of the instrument.

Conductance measurements

The specific conductance of twenty CTAB (1.29×10^{-4} to 13.5×10^{-4}) and SDS (1.14×10^{-3} to 12.0×10^{-3}) aqueous solutions were measured on a microprocessor conductivity meter (WTW), LF 2000/C at 25.0 °C. A water thermostat was used to control the temperature within ± 0.1 °C. The critical micelle concentration (*cmc*) was determined from plots of the specific conductance *versus* the concentration of the surfactant solution. The *cmc* values for SDS and CTAB in water were determined to be 8.0×10^{-3} and 9.0×10^{-4} mol dm $^{-3}$, respectively.

RESULTS AND DISCUSSION

The absorption spectra of a representative acid (PhMA) in water and at certain concentrations of SDS and CTAB are shown in Fig. 1. Surfactant solutions are known to cause a red shift in the spectra of organic additives. The effect of various concentrations (c_s) of CTAB and SDS on the maximum absorption wavelength (λ_{\max}) of the phenylalkanoic acids are shown in Figs. 2 and 3. In addition, the absorbance (*A*) for two representative acids, PhMA and 3-PhPA, are given in Tables I and II. It can be inferred from Figs. 2 and 3 that the UV spectra shift continuously to higher wavelengths. The increase in absorbance with increasing c_s is due to the increased number of additive molecules in the micellar phase.¹⁶ At surfactant concentrations above the *cmc*, the spectra no longer change with increasing c_s assuming all the additive molecules are taken into the micelles.

The value of red shift was greater for the more hydrophobic acid (3-PhPA) than the less hydrophobic acid (PhMA) in presence of both the surfactants. The more hydrophobic acid exhibited a larger red shift even at surfactant concentra-

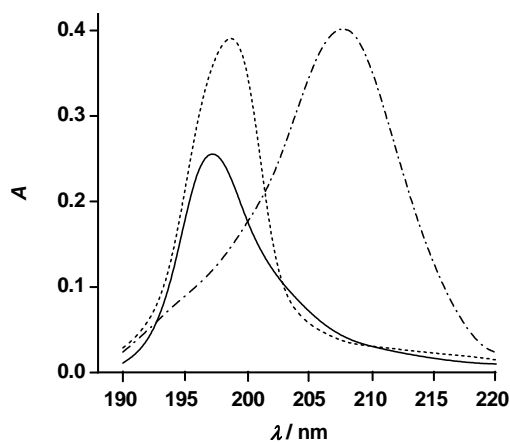


Fig. 1. Absorption spectra of PhMA in water (—), in 6.0 mmol dm $^{-3}$ SDS (···) and in 0.6 mmol dm $^{-3}$ CTAB (—·—).

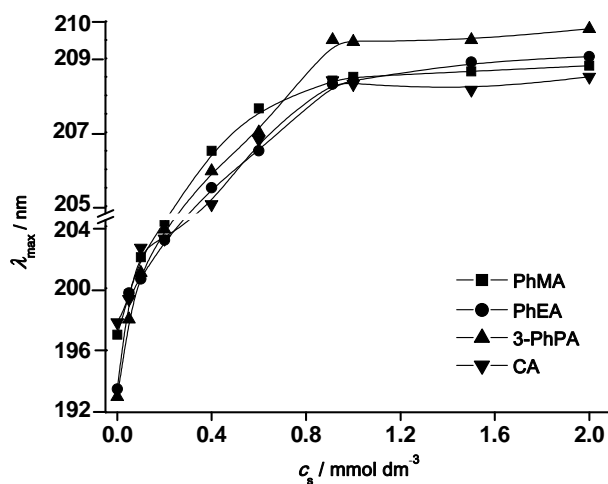


Fig. 2. Effect of increasing concentration of CTAB on the λ_{max} of phenylalkanoic acids.

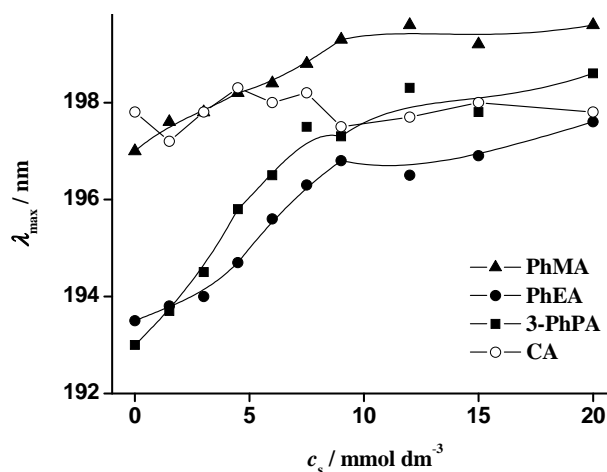


Fig. 3. Effect of increasing concentration of SDS on the λ_{max} of phenylalkanoic acids.

tions below their observed *cmc*. The shift also depends on the nature of charge (positive or negative) present on the surfactant head group. In the case of 3-PhPA, the value of red shift in the cationic surfactant (CTAB) was $\Delta\lambda_{\text{max}} = 16.9$ nm as compared to the anionic surfactant (SDS), where $\Delta\lambda_{\text{max}} = 5.6$ nm. Hence, the red shift for each acid in the anionic surfactant solutions was smaller. The red shifts in the spectra are generally representative of the interaction between surfactant and additive acid. The initial shifts represent the association between additive and monomeric surfactant, while the λ_{max} value becomes more uniform in the micellar region. The red shift also represents changes in the micropolarity around the orientated chromophore, due to which the energy of transition is reduced. The red shift in the case of acids could also be due to their conversion to anions, the bands of which are likely to appear at higher wavelength values compared to the un-

dissociated acids. The anions are attached significantly to cationic CTAB and the binding phenomenon could involve the parallel stacking of acid molecules with surfactant monomer, and later reorientation to incorporate them into the micelles as the *cmc* is reached. On the other hand, owing to the repulsive interaction between the acid anion and SDS head, the only possibility of interaction is through water bridging, hence the wavelength was not altered much with the anionic surfactant. As c_s is increased, there is a continuous change in the wavelength, initially due to complex formation or binding with monomeric surfactant and later due to appearance of premicellar aggregates and ultimately due to presence of polarity gradient offered by the organized solutions of the two surfactants.

TABLE I. Absorbance (A) of phenylalkanoic acids at various concentrations (c_s) of CTAB

$c_s / \text{mmol dm}^{-3}$	PhMA	3-PhPA
0.0	0.256	0.291
0.050	0.305	0.304
0.10	0.339	0.327
0.20	0.351	0.349
0.40	0.389	0.403
0.60	0.402	0.435
0.91	0.409	0.539
1.0	0.539	0.552
1.5	0.618	0.591
2.0	0.620	0.588

TABLE II. Absorbance (A) of phenylalkanoic acids at various concentrations (c_s) of SDS

$c_s / \text{mmol dm}^{-3}$	PhMA	3-PhPA
0	0.256	0.291
1.5	0.248	0.282
3.0	0.273	0.221
4.5	0.283	0.248
6.0	0.389	0.248
7.5	0.406	0.272
9.0	0.420	0.304
12	0.411	0.326
15	0.429	0.335
20	0.435	0.344

However, the λ_{max} values of the CA obtained in pure water are comparable to those obtained in the surfactant solutions of SDS. This means “no change in polarity” around the oriented chromophore of the CA or, in other words, the incapability of the CA molecules to penetrate into the SDS micelles. It was suggested that the anions of CA are incapable of penetrating into the SDS micelles owing to repulsive interactions between the negatively charged oxygen of the CA anion and the anionic head of SDS.¹⁷ Similar behavior was observed for cationic hemi-

cyanine dyes into CTAB micellar solutions.⁸ The CTAB, which contains positive head group, interacts with the negative charge present on the phenylalkanoic acid molecules. In turn, the acid molecules penetrate easily into the CTAB micelles.

The differential absorbances (ΔA) spectra of PhMA solutions in the presence of SDS at different concentrations are shown in Fig. 4. The ΔA values were obtained at the wavelength λ_{\max} , where the highest peak appears in the spectra. The shift of each peak with increasing c_s can be ignored within experimental error (± 0.5 nm). The λ_{\max} wavelengths for the respective acids are given in Table III. The increase in ΔA with increasing surfactant concentration is attributed to the increase in the number of solubilized additive molecules in the micellar phase, as observed for other additives.^{8-14,18}

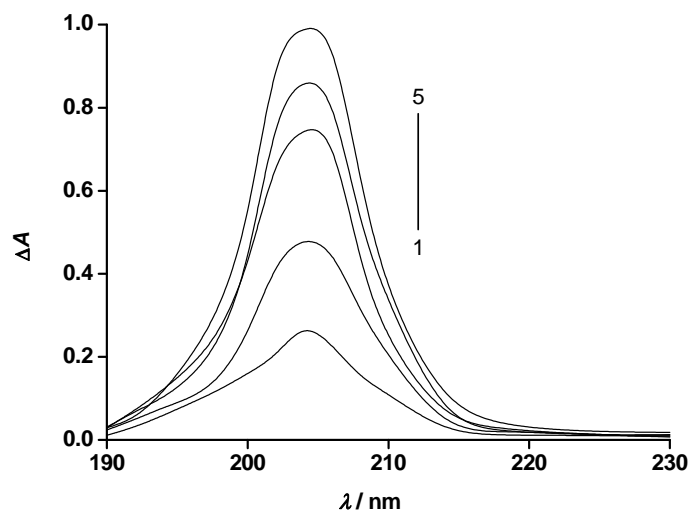


Fig. 4. Differential absorption spectra of PhMA in: 1) 18.0, 2) 36.0, 3) 54.0, 4) 72.0 and 5) 90.0 mmol dm⁻³ solutions of SDS.

The ΔA values of solutions of phenylalkanoic acids in the presence of various concentrations of SDS at 25.0 °C are shown in Fig. 5. In the pre-micellar region, ΔA is practically zero and increases for each acid with increasing concentration of SDS. ΔA was recorded at the respective maximum wavelength (λ_{\max}). Kawamura *et al.*,¹⁸ developed a relationship for the determination of the water-micelle partition coefficient, K_c .

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_{\infty} (c_a + c_s^{\text{mo}})} + \frac{1}{\Delta A_{\infty}} \quad (1)$$

where ΔA_{∞} represents the ΔA value at infinitive c_s , c_a is the concentration of additive and c_s^{mo} is the micellized concentration of the surfactant and is given by $c_s - cmc_0$ (cmc_0 is the *cmc* of the surfactant in water). The dimension of K_c in Eq.

(1) is $\text{dm}^3 \text{mol}^{-1}$, which is related to K_x as $K_c = K_x/n_w$, where n_w is the number of moles of water per dm^3 , *i.e.*, 55.5 mol dm^{-3} .

TABLE III. Values of λ_{max} and K_x for the added phenylalkanoic acids in SDS and CTAB solutions

Additive	SDS			CTAB ¹⁰		
	λ_{max}	K_x	$\Delta G_p^\ominus / \text{kJ mol}^{-1}$	λ_{max}	K_x	$\Delta G_p^\ominus / \text{kJ mol}^{-1}$
PhMA	204.3	1358	17.87	208.7	13123	23.49
PhEA	203.4	2204	19.07	211.6	34776	25.91
3-PhPA	203.8	3105	19.92	210.7	54851	27.04
CA	–	–	–	207.0	41658	26.35

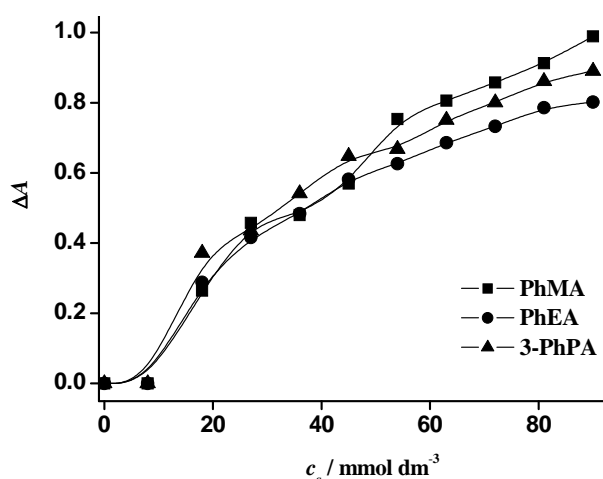


Fig. 5. Effect of the SDS concentration on the differential absorbance of phenylalkanoic acids.

The plots of $1/\Delta A$ against $1/(c_a + c_s^{\text{mo}})$ for phenylalkanoic acids at a certain concentration of additive ($c_a = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$) are presented in Fig. 6. The intercept and slope of the linear relationship in Eq. (1) give the values of ΔA_∞ and K_c . The values of K_x calculated from K_c are given in Table III.

The standard free energy change, ΔG_p^\ominus , of the transfer of the additives from bulk water to micelles is given by the relationship:

$$\Delta G_p^\ominus = -RT \ln K_x \quad (2)$$

where R is the general gas constant and T is the absolute temperature. The ΔG_p^\ominus values are summarized in Table III.

Free energy change per methylene group, $\Delta G^\ominus(\text{CH}_2)$, from water to micelles is obtained from straight-line plots using the following equation:

$$-\Delta G^\ominus(\text{CH}_2) = RT \frac{d \ln K_x}{dm} \quad (3)$$

where R and T are defined parameters and m refers to the number of methylene groups in alkyl chain of the acid molecules. The plots of $\ln K_x$ vs. m for both systems are shown in Fig. 7. The values of $\Delta G^\ominus(\text{CH}_2)$ evaluated from the plots are -1.03 and -1.77 kJ mol^{-1} for the SDS and CTAB system, respectively.

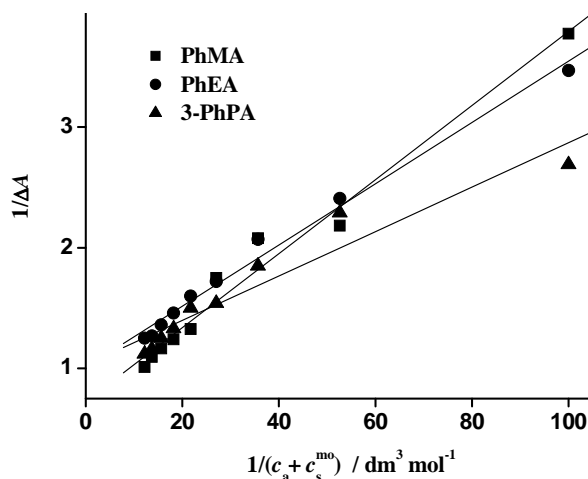


Fig. 6. Relationship between $1/\Delta A$ and $1/(c_a + c_s^{m0})$ for phenylalkanoic acids.

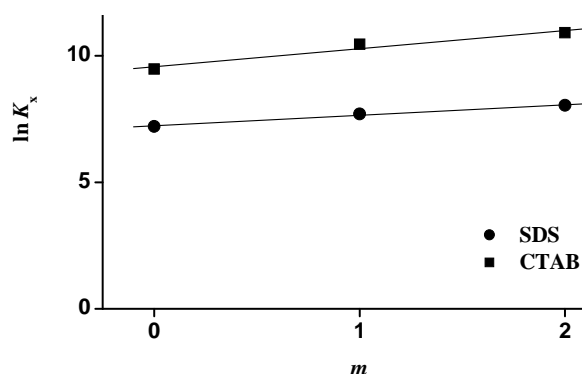


Fig. 7. $\ln K_x$ vs. the number of carbon atoms in hydrocarbon chain of phenylalkanoic acids.

The values of the free energy change per methylene group of transfer from water to ionic micelles were reported to be -1.3 kJ mol^{-1} for alkyl phenoxide ions and alkyl phenols, and -1.25 kJ mol^{-1} for benzoic acid and aniline.¹⁹ The free energy of transfer per CH_2 group of the same compounds from water to *n*-heptane was close to -3.76 kJ mol^{-1} . These results were taken to imply that the compounds were solubilized within an aqueous environment, such as near the micellar interface region.²⁰ It may be concluded from the above results that the solubilization site of phenylalkanoic acids in the ionic micelles was the water–micelle interface. The lower value of $\Delta G^\ominus(\text{CH}_2)$ in the CTAB system suggests that this system was more favorable for solubilization than the SDS system. The

negative value of $\Delta G^\ominus(\text{CH}_2)$ indicates that the solubilization of phenylalkanoic acids into micelles was a spontaneous phenomenon.

In view of the fact that the phenyl ring was common in the phenylalkanoic acids, the alkyl chain appears to be an important factor for the solubilization. The insignificant shifts in the λ_{max} of phenylalkanoic acids in SDS solutions show the presence of electrostatic repulsion between the anions of the acids and SDS. However, phenylalkanoic acids were expected to interact favorably with CTAB. The partition coefficients, K_x , obtained in CTAB micellar solutions were higher than those found for the SDS micellar solutions. The higher K_x values indicate stronger interaction and hence enhanced solubility of the acids in the CTAB micelles. It is recognized that aromatic acids counter ions are more efficient with cationic micelles.²¹ Furthermore, it was reported that CTAB micelles cause more ionization of aromatic acids, which leads to increase in the van der Waals association between the surfactant molecules and the additive molecules.²² It is suggested that additive molecule forms an ion pair with the surfactant monomer. The adhesion of this ion pair to the micellar surface enhances the incorporation of additive molecule at a later stage. Where hydrophobic interactions allow for parallel stacking of additive acids with monomeric surfactants¹³ and incorporation of acids into the micelles is in such a way that their hydrophobic part is directed inwards towards micellar core, both these factors change the polarity of microenvironment around the oriented chromophore and hence cause a red shift by lowering the energy of transition.

CONCLUSIONS

The differential absorbance of the phenylalkanoic acids increased with increasing surfactant concentration, indicating that the acid molecules absorbed light more favorably in the micellar phase than in the aqueous phase. However, cinnamic acid is incapable of penetrating into SDS micelles due to analogous charge. An increase in the hydrophobicity of the acid molecules affects an increase in the K_x values. Moreover, the solubilization site of phenylalkanoic acids in ionic micelles is the water–micelle interface.

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ИЗВОД

INTERAKCIJA KRATKOLANČANIH FENILALKANSKIH KISELINA SA MICELAMA
POVRŠINSKI AKTIVNIH SUPSTANCI U VODENOJ SREDINIKASHIF NAEEM¹, SYED W. H. SHAH², BUSHRA NASEEM³ и SYED S. SHAH²¹Central Analytical Facility Division, PINSTECH, PO Nilore, Islamabad 45650, ²Department of Chemistry, Hazara University, Mansehra, Pakistan и ³Department of Chemistry, Lahore College for Women University, Lahore, Pakistan

Растворљивост и интеракција фенилалканских киселина у присуству катјонске, цетил-триметиламонијум-бромида (СТАВ), и анјонске површински активне супстанце натријум-додецилсулфата (SDS) испитивана је спектрофотометријски на 25,0 °C. UV спектри адитива (киселина) су мерени без присуства и у присуству површински активних супстанци, испод и изнад критичне мицеларне концентрације (*cmc*). Присуство алкилног ланца у фенилалканским киселинама је одговорно за хидрофобну интеракцију и померај у спектру према већим таласним дужинама. Вредност партиционог коефицијента (K_x) између воде и мицеле површински активне супстанце и стандардна слободна енергија растварања (ΔG_p^\ominus) су такође одређени мерењем диференцијалне апсорбанције (ΔA) адитива у мицеларном раствору.

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