

# The effect of added alcohols on the micellization process of sodium 8-phenyloctanoate

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**Abstract**  $^1\text{H}$  NMR chemical shifts were examined for mixtures of sodium 8-phenyloctanoate (Na- $\omega$ -PhOct) in deuterated aqueous solutions of varying compositions of ethoxylated alcohols. In addition, diffusion-oriented spectroscopy experiments (DOSY) were performed on selected compositions to obtain the diffusion coefficients of the ethoxylated alcohols in the mixed micelles. As expected, the alcohol/surfactant systems exhibit behavior typical to that of an anionic surfactant/alcohol system, in that the critical micellar concentrations and aggregation numbers decrease with increasing alcohol concentration in the mixed solvent. The  $^1\text{H}$  NMR aromatic solute induced shifts (ASIS effects) on the alcohol and surfactant protons give significant information on the locations of the alcohol groups in the mixed micelle. All these results are interpreted in terms of the structure of the alcohol/surfactant systems as a function of their composition.

**Keywords** Alcohol · Surfactant · Mixed micelles · Ring current shifts · NMR · Solubilization

## Introduction

The dependence of the variation of the critical micellar concentration (CMC) values of surfactants on the structure of the surfactant has been the subject of numerous publications and compilations [1–4]. In the case of mixed micelles, the structure of the additive has a marked effect on the dependence of the CMC values on the additive

concentration. One of the key factors in determining how the additive affects the formation of mixed micelles is whether or not the compound is likely to be located in the micelles or in the intermicellar solution. Hydrophilic substances, like dioxane and urea, markedly increase the CMC at high concentrations [5–10], whereas hydrophobic substances, such as hydrocarbons, have been found to lower the CMC for many amphiphiles [11, 12]. The effect of normal linear alcohols has been studied in detail, and it has been observed that the lowering of the CMC values of alcohol/surfactant mixed micelles with increasing additive concentration is initially linear [1, 13–29]. The effect increases significantly as the chain length of the alcohol increases.

Ethoxylated alcohols are an interesting class of cosurfactants in that they interact differently with anionic and cationic micelles [25, 27, 30], which parallels the manner in which nonionic polymers [e.g., poly(ethylene) oxide] interact with sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB). In the case of the anionic micelles, the equilibrium properties of the mixed aggregates (CMC values, aggregation numbers, and distribution coefficients) depend on the number of ethylene oxide ( $-\text{CH}_2\text{CH}_2\text{O}$  or EO) groups in the alkoxyethanol at constant alcohol concentrations. Marangoni and Kwak [25] have interpreted this in terms of the contribution of the EO groups to hydrophobic effects; these influences are noticeably absent in the case of cationic surfactant/alkoxyethanol.

NMR techniques have been shown to provide excellent insights into the study of micelle formation at the molecular level. One-dimensional (1D) and two-dimensional (2D) techniques can be used to determine standard micellar properties like CMC values and aggregation numbers, as well as to examine the locus of solubilization of the alcohol in the mixed micelles [31]. Carbon 13 ( $^{13}\text{C}$ ) NMR chemical

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shifts have been shown to provide information on the conformations of the chains comprising the micelles [32–34];  $^{13}\text{C}$  relaxation rate measurements as a function of magnetic field strength have been used to determine the motions of the alkyl chains comprising the micelles and the headgroup regions [35–38]. NMR ring current shift measurements of phenyl groups attached to surfactant chains have been used to examine the structure of phenyl-containing surfactants and the locations of aromatic and nonaromatic solubilizes in the interior of surfactant micelles [11, 39–43].

In this paper, the effects of ethoxylated alcohols on the micellization process of sodium 8-phenyloctanoate will be investigated. CMC values and aggregation numbers of the mixed aggregates will be obtained from  $^1\text{H}$  chemical shifts. The partition coefficients have been calculated from the diffusion coefficients obtained via 2D diffusion-oriented spectroscopy (DOSY) experiments. Comparison of the NMR aromatic solute induced shifts (ASIS) effects of the  $^1\text{H}$  chemical shifts on the alcohol and surfactant backbone allow for a determination of the location of the alcohol ethoxylated groups in the surfactant micelles. All these results are interpreted in terms of the contributions of the EO groups to hydrophobic effects.

## Experimental

### Materials

Sodium 8-phenyloctanoic acid was purchased from Lancaster (97% pure). The alcohols were used as described previously [25]. The alcohols are referred to in terms of the length of the alkyl chain and the number of alcohol ethoxylated groups, i.e., 1-butanol is  $\text{C}_4\text{E}_0$ , ethylene glycol mono-*n*-butyl ether is  $\text{C}_4\text{E}_1$ , diethylene glycol mono-*n*-butyl ether is  $\text{C}_4\text{E}_2$ , and triethylene glycol mono-*n*-butyl ether is  $\text{C}_4\text{E}_3$ .

### Methods

Bulk solutions of sodium 8-phenyloctanoate (typically  $>0.1\text{ M}$ ) were prepared by dispersing the acid in  $\text{D}_2\text{O}$  and adding NaOD dropwise until it was dissolved completely. The final pH was adjusted to a value between 10 and 11 to prevent the hydrolysis of the carboxylate surfactant in the NMR tubes.  $\text{D}_2\text{O}$  was purchased from CDN isotopes and was 99.9% pure. Samples of differing concentrations were made up in the NMR tubes directly by pipetting appropriate amounts of a stock surfactant solution and  $\text{D}_2\text{O}$ , respectively. The alcohol/ $\text{D}_2\text{O}$  water mixed solvent systems were prepared on a molarity basis; the surfactant solutions were made up directly in the mixed solvent. The concentration of

the alcohol in the mixed solvent is reported in terms of moles of alcohol per liter of mixed solvent. The concentration of the surfactant solutions is reported as the moles of surfactant per liter of the mixed solvent system.

The 1D NMR spectra ( $^1\text{H}$ ) for the  $\omega$ -phenyloctanoate surfactant system as a function of surfactant concentration were obtained on both the Bruker AC-200 at St. F.X. University operating at 200.13 MHz for protons and a Bruker AVANCE-500 at the Atlantic Region Magnetic Resonance Centre (ARMRC) at Dalhousie University. All  $^1\text{H}$  spectra were referenced to the HOD peak, which was assigned a value of  $\delta=4.630\text{ ppm}$ . The diffusion experiments (DOSY) were performed on the AVANCE-400 spectrometer at StFX University. All experiments were carried out at  $25\text{ }^\circ\text{C}$  (298 K). A typical  $^1\text{H}$  NMR spectrum is given in Fig. 1.

## Results and discussion

### CMC determination

The CMC values for all the alcohol/surfactant mixed micelles were determined from the breaks in the plots of the  $^1\text{H}$  chemical shifts vs the inverse surfactant concentration. The CMC of the surfactant system without any alcohol added was found to be 54.5 mM, in excellent agreement with our previous paper [25]. A sample plot of the  $^1\text{H}$  chemical shifts vs the inverse surfactant concentration is given in Fig. 2 for the  $\omega$ -phenyloctanoate surfactant system in the presence and absence of added alcohol. We can

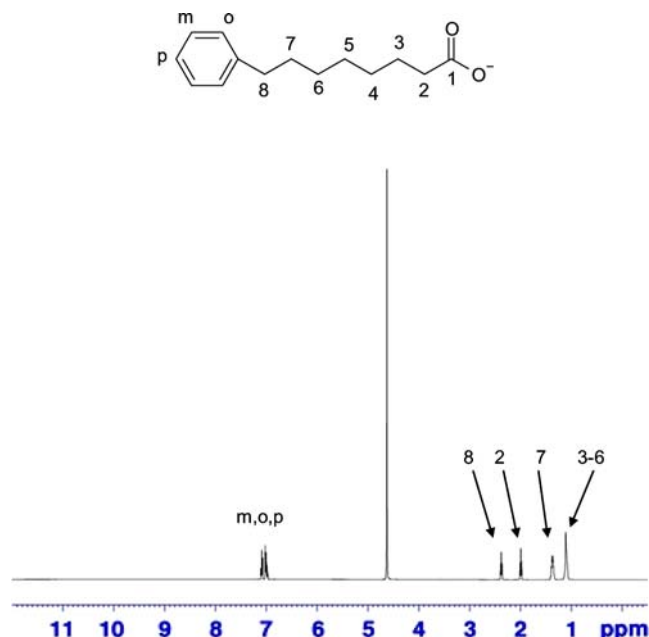
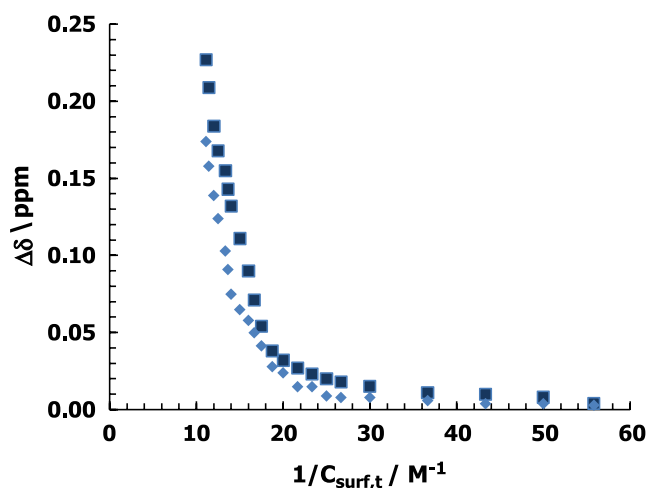
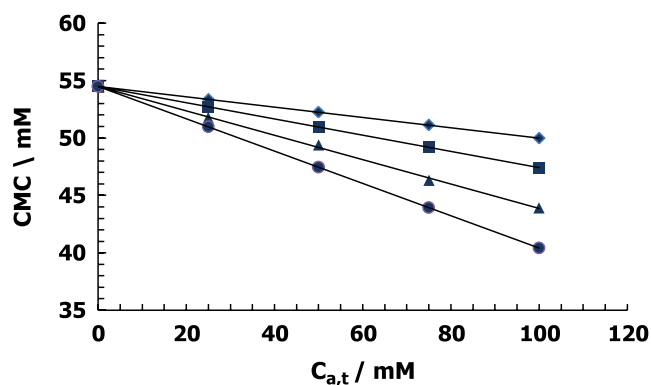


Fig. 1  $^1\text{H}$  NMR spectrum of sodium 8-phenyloctanoate



**Fig. 2** Sample plot of  $^1\text{H}$  NMR chemical shifts vs inverse surfactant concentration for the C-8 of sodium 8-phenyloctanoate in water (diamonds) and 0.10 M  $\text{C}_4\text{E}_0$  (squares)

clearly see from the plot that the addition of alcohol indeed lowers the CMC as expected; Fig. 3 gives the variation in CMC values relative to the concentration of alcohol added. We can see from Fig. 3 that, for all the mixed surfactant systems, the addition of up to 100 mM of alcohol decreased the CMC in a linear fashion. Again, we clearly see that, at the same concentration of alkoxyethanol, the CMC values of the mixed micelles decrease in the direction of increasing numbers of alkoxyethanol groups in the cosurfactant, in excellent agreement with the previous literature [25, 27, 44, 45]. The increased interactions of the alkoxyethanols with other anionic surfactants have been postulated to be due to the hydrophobic effects. As the four different alcohols investigated share a common four-carbon-long backbone, any differences among mixed systems are due entirely to the ethylene oxide (EO) groups or lack thereof (i.e., the  $\text{C}_4\text{E}_0$  cosurfactant). Manabe and Koda [45] investigated a series of homologous alkoxyethanols and SDS surfactants.



**Fig. 3** CMC values of sodium 8-phenyloctanoate/alkoxyethanol mixed micelles as a function of the alcohol concentration in the mixed solvent.  $\text{C}_4\text{E}_0$  (diamonds),  $\text{C}_4\text{E}_1$  (squares),  $\text{C}_4\text{E}_2$  (triangles),  $\text{C}_4\text{E}_3$  (circles)

They also observed a decrease in the CMC values of the SDS/alkoxyethanol mixed micelles as the number of EO groups in the alcohol was increased. Marangoni and Kwak [25] also found that CMC values of the anionic sodium decyl sulfate (SDecS)/alkoxyethanol mixed micelles decreased as the concentration of the alcohol was increased. Their results indicated that the dependence of the CMC value on the alcohol concentration (i.e., the  $-\text{dCMC}/\text{d}C_a$  values) increased in a consistent fashion as the number of EO groups in the alcohol was increased. In the present case, a similar trend was observed with the  $\text{C}_4\text{E}_0/\text{ph-C}_8\text{Na}$ ,  $\text{C}_4\text{E}_1/\text{ph-C}_8\text{Na}$ ,  $\text{C}_4\text{E}_2/\text{ph-C}_8\text{Na}$ , and  $\text{C}_4\text{E}_3/\text{ph-C}_8\text{Na}$  systems. The decreased CMC values at constant alcohol concentration for the alcohols containing more EO groups may indicate (1) these alcohols are more hydrophobic in nature than those that have less EO groups or (2) the more bulky EO groups are more efficient at screening electrostatic interactions, leading to a decrease in the electrostatic contribution to the Gibbs energy of micelle formation and, hence, a decreased CMC value. According to Marangoni and Kwak [25], these decreases in the CMC values must be interpreted in terms of the decrease in the Gibbs energy of the system due to hydrophobic interactions, which also manifests itself in terms of increased partitioning of the ethoxylated alcohols as the number of EO groups is increased. They noted that, for the cationic DTAB/alkoxyethanol mixed systems, no additional decrease in CMC values upon the addition of extra EO groups on the alcohol were observed, and the partition constants of the ethoxylated alcohols did not change as the number of EO groups in the alcohol increased.

The dependence of the CMC value on the alcohol concentration (the  $-\text{dCMC}/\text{d}C_a$  values) may be used to estimate the Gibbs energy of transfer of hydrophobic solutes from the aqueous phase to the micellar interior. The rates of change,  $-\text{dCMC}/\text{d}C_a$ , can be related to the free energy of transfer of the alcohol hydrophobic group from the aqueous phase to the micellar phase [15]

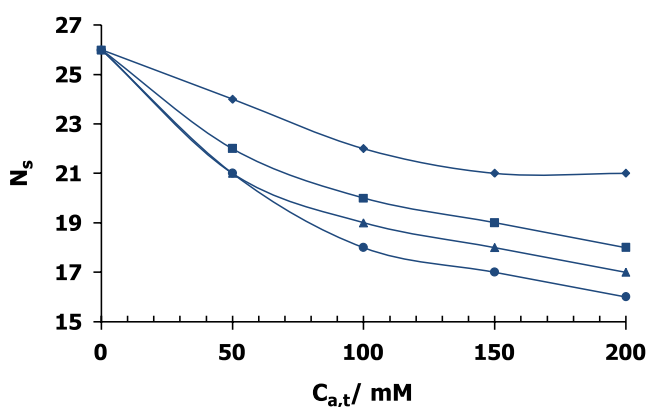
$$\ln \left[ -\frac{\text{dCMC}}{\text{d}C_{a,t}} \right] = C_G + \frac{w}{k_B T} \quad (1)$$

where  $w$  is the transfer free energy of the alcohol hydrophobic group from the aqueous to the micellar phase and  $C_G$  is a constant related to the free energy of micellization of the pure surfactant micelles. For the  $\text{ph-C}_8\text{Na}$  systems, the  $-\text{dCMC}/\text{d}C_a$  values were found to increase in the order  $\text{C}_4\text{E}_0 < \text{C}_4\text{E}_1 < \text{C}_4\text{E}_2 < \text{C}_4\text{E}_3$ . The values were as follows: 0.045 for  $\text{C}_4\text{E}_0$ , 0.0712 for  $\text{C}_4\text{E}_1$ , 0.100 for  $\text{C}_4\text{E}_2$ , and 0.141 for  $\text{C}_4\text{E}_3$ . As the series of ethoxylated alcohols used in the present paper has a constant alkyl chain length, any differences in the  $\text{dCMC}/\text{d}C_a$  values are likely due to the hydrophobicity of the EO groups and the

increased partitioning of the more hydrophobic alcohols into the micelles. The estimate of the transfer free energy of the EO group,  $w_{EO}$ , can be calculated from the dependence of the  $-d\text{CMC}/dc_a$  values on the number of EO groups in the alcohol. From the  $-d\text{CMC}/dc_a$  values it was determined that  $w_{EO}$  is  $-0.38 \pm 0.12$  RT or, approximately,  $-0.94 \pm 0.20$  kJ mol $^{-1}$ , which compares well to the Gibbs transfer energy of the EO group calculated previously [25].

#### Aggregation parameters

$^1\text{H}$  chemical shifts were fitted to a mass action model to extract the aggregation number of the surfactant,  $N_s$ , as in a previous publication [46] mass-action model are given in Table 1 and plotted in Fig. 4 as a function of the total alcohol concentration. The values obtained from fitting the  $^1\text{H}$  chemical shifts to the mass action model are given in Table 1. We observe from Table 1 that, without any added alcohol, the aggregation number for the ph-C $_8$ Na was found to be  $26 \pm 2$ , which is identical to the value reported by Gao et al. for the  $\omega$ -phenyloctanoate system [42]. As the concentration of alcohol in the mixed solvent system was increased, the surfactant aggregation numbers steadily decreased, in exactly the same fashion as was observed above with the CMC values. As expected, the surfactant micelles are made up of fewer monomer units and are decreasing in size with increasing alcohol content (within the limited concentration range studied here). There does appear to be an effect of decreasing aggregation number in the direction of increasing number of alcohol ethoxylate groups, but the effect is much less pronounced than in previous papers [25, 47], likely due to the small size of the aggregates. These findings can be attributed to the increased hydrophobicity and the reduction of charged head group repulsions due to the introduction of these neutral polar molecules into the mixed micelles.



**Fig. 4** Surfactant aggregation numbers ( $N_s$ ) of sodium 8-phenyloctanoate/alkoxyethanol mixed micelles as a function of the alcohol concentration in the mixed solvent.  $C_4E_0$  (diamonds),  $C_4E_1$  (squares),  $C_4E_2$  (triangles),  $C_4E_3$  (circles)

**Table 1** Aggregation numbers ( $N_s \pm 2$ ) for sodium 8-phenyloctanoate/alkoxyethanol mixed micelles as a function of the total alcohol concentration

$C_{a,t}$ (M)	$C_4E_0$	$C_4E_1$	$C_4E_2$	$C_4E_3$
0	26	26	26	26
50	24	22	21	21
100	22	20	19	18
150	21	19	18	17
200	21	18	17	16

#### DOSY experiments to determine partition coefficients

The alcohols  $C_4E_0$ ,  $C_4E_1$ ,  $C_4E_2$ , and  $C_4E_3$  are found to act as penetrating additives in the ph-C $_8$ Na micelles. As such, the partitioning of alcohols between micelles and bulk water is a very important parameter that helps to determine the physicochemical properties of the mixed surfactant-alcohol systems. The  $p$  value of the solubilize between the aqueous and micellar phases is defined as follows

$$p = \frac{C_{a,\text{mic}}}{C_{a,t}} \quad (2)$$

where  $C_{a,\text{mic}}$  is the concentration of alcohol in the micellar phase and  $C_{a,t}$  is the total concentration of alcohol. NMR techniques have been used extensively for the purpose of determining the distribution of solubilizates between the free (aqueous) and bound (micelle) phases. As an example, Carlfors and Stilbs [40] determined the partition coefficients,  $K_x$ , for aliphatic  $n$ -alcohols in aqueous solutions of sodium decanoate above the CMC by the Fourier transform NMR pulsed-gradient spin-echo self-diffusion method. Their results indicated that the partitioning of the alcohol between D $_2$ O and sodium decanoate micelles was directly dependent on the number of alcohol methylene groups and that the transfer Gibbs energy per CH $_2$  group was  $-2.5$  kJ/mol. Similar results were obtained by Gao et al. [35] using an alternate NMR method to determine solubilize distribution in the micellar phase, the NMR-paramagnetic relaxation enhancement experiment. In this technique, the changes in the spin-lattice relaxation times ( $T_1$ ) of the alcohol in the surfactant and surfactant-free solutions are compared in the presence and absence of paramagnetic ions. These relations are used to estimate the  $p$  value of the alcohol. Marangoni and Kwak [25] used this method to determine the  $p$  values for a series of alkoxyethanols with cationic and anionic surfactants. Their results indicated that the alcohol EO groups were contributing to the hydrophobic interactions in anionic micelles and that the transfer Gibbs energy per EO group was  $-1.0$  kJ/mol.

Diffusion-oriented spectroscopy (DOSY) experiment can be used to obtain the diffusion coefficients with which the

**Table 2** Diffusion coefficients and calculated transport properties of alkoxyethanols into the interior of sodium 8-phenyloctanoate micelles

Parameter/alcohol	C <sub>4</sub> E <sub>0</sub>	C <sub>4</sub> E <sub>1</sub>	C <sub>4</sub> E <sub>2</sub>	C <sub>4</sub> E <sub>3</sub>
$D_{\text{obs}}$	$5.25 \times 10^{-10}$	$3.90 \times 10^{-10}$	$2.63 \times 10^{-10}$	$2.21 \times 10^{-10}$
$D_{\text{mic}}$	$7.08 \times 10^{-11}$	$7.08 \times 10^{-11}$	$7.08 \times 10^{-11}$	$7.08 \times 10^{-11}$
$D_{\text{aq}}$	$7.94 \times 10^{-10}$	$6.92 \times 10^{-10}$	$6.31 \times 10^{-10}$	$6.03 \times 10^{-10}$
$p$	$0.37 \pm 0.04$	$0.49 \pm 0.04$	$0.66 \pm 0.04$	$0.73 \pm 0.03$
$K_x$	$121 \pm 24$	$184 \pm 28$	$343 \pm 36$	$476 \pm 24$
$\Delta G_t^\circ (\text{kJ} \cdot \text{mol}^{-1})$	$-11.9 \pm 0.4$	$-12.9 \pm 0.4$	$-14.5 \pm 0.3$	$-15.3 \pm 0.4$

partition coefficients of the alcohols can be obtained. In these experiments, the 2D DOSY technique is used to determine the observed diffusion coefficients of the alcohol in the presence and absence of the surfactant micelles. If the diffusion of the alcohol between the bulk phase and the micelles is fast on the NMR timescale, the observed diffusion coefficient,  $D_{\text{obs}}$ , is the weight averaged diffusion coefficient for the mixed surfactant-alcohol sample at a concentration above the CMC. Hence, the binding degree,  $p$ , of the alcohol to the micelles can be determined using the following equation:

$$D_{\text{abs}} = pD_{\text{mic}} + (1 - p)D_{\text{aq}} \quad (3)$$

$D_{\text{aq}}$  represents the diffusion coefficient of free additive in bulk water (D<sub>2</sub>O); this is determined using a solution of the alcohol in bulk D<sub>2</sub>O in the absence of added surfactant.  $D_{\text{mic}}$  represents the diffusion coefficient for the micellar bound additive in the micelle;  $D_{\text{mic}}$  is determined in a separate experiment by measuring the diffusion coefficient of a small amount of decanol in a 250-mM ph-C<sub>8</sub>Na solution, which is approximately five times its CMC value. Decanol is a long linear alcohol that is known to partition almost completely in the micelle; as such, the diffusion of decanol should be equal to the diffusion coefficient of the micelle in solution. The previous equation can be rearranged to give:

$$p = \frac{D_{\text{abs}} - D_{\text{aq}}}{D_{\text{mic}} - D_{\text{aq}}} \quad (4)$$

The mole fraction of the alcohol in the micelle phase is now given by

$$X_{\text{mic}} = \frac{pC_{\text{a,t}}}{(pC_{\text{a,t}}) + C_{\text{s,mic}}} \quad (5)$$

in which  $C_{\text{a}}$  is the concentration of alcohol and  $C_{\text{s,mic}}$  is the concentration of surfactant in micellar form. The mole fraction of the alcohol in the aqueous phase is

$$X_{\text{aq}} = \frac{(1 - p)C_{\text{a,t}}}{49.93} \quad (6)$$

where 49.93 is the number of moles of D<sub>2</sub>O in 1,000 mL. The mole fractions are used to determine the partition coefficient

$$K_x = \frac{X_{\text{mic}}}{X_{\text{aq}}} \quad (7)$$

Finally, the partition coefficient can be used to determine standard free energies of transfer of the additives,  $\Delta G_t^\circ$ , from the aqueous phase to the micellar phase

$$\Delta G_t^\circ = -RT \ln K_x \quad (8)$$

$T$  and  $R$  are the absolute temperature and gas constant, respectively.

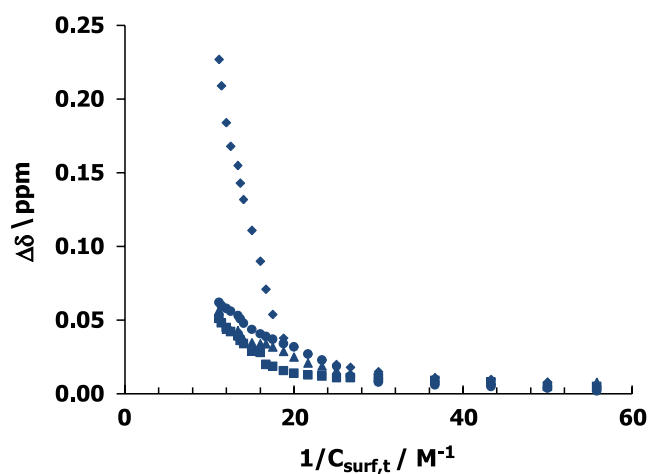
The diffusion coefficients and the partition coefficients of the mixed systems are given in Table 2. We note from Table 2 that the partition constants of the ethoxylated alcohols increase in the order C<sub>4</sub>E<sub>0</sub> < C<sub>4</sub>E<sub>1</sub> < C<sub>4</sub>E<sub>2</sub> < C<sub>4</sub>E<sub>3</sub>, indicating again that the alcohols with the larger number of EO groups partition more favorably in the interior of anionic micelles. From the calculated data, we see that the C<sub>4</sub>E<sub>3</sub> molecules are substantially more solubilized within the micellar interior than any of the other alcohols studied. Therefore, the EO groups are found to have a significant contribution to the hydrophobic interactions of mixed alkoxyethanol/ph-C<sub>8</sub>Na systems as they increase the solubilization of ethoxylated alcohols into surfactant micelles, in excellent agreement with previous literature [25, 44]. The  $K_x$  values and the Gibbs transfer energies of the alcohol are also given in Table 2. We clearly see that the  $K_x$  values increase in the direction C<sub>4</sub>E<sub>0</sub> → C<sub>4</sub>E<sub>3</sub>. The Gibbs transfer energies decrease in a fairly regular fashion from C<sub>4</sub>E<sub>0</sub> → C<sub>4</sub>E<sub>3</sub>; the slope of the plot of the Gibbs transfer energies vs number of EO groups yields an estimate of the transfer Gibbs energy per EO groups of  $-1.2 \pm 0.3$  kJ/mol, which compares well to the previous literature value [25].

#### Proton ASIS effects

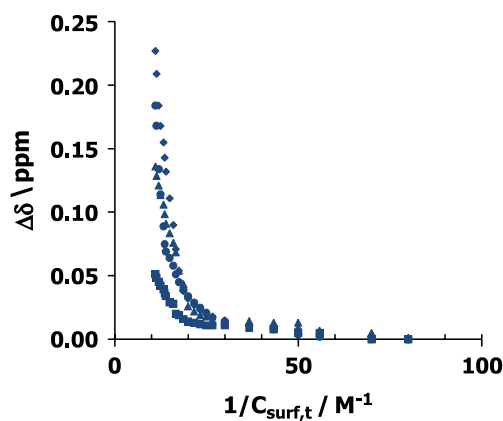
The presence of the benzene ring in the interior of the  $\omega$ -phenyloctanoate micelles leads to substantial ASIS shifts for the protons on the carbon backbone of the



$\omega$ -phenyloctanoate surfactant. Due to the solubilization of the alcohol in the micellar interior, ASIS-effect shifts will be observed for the alcohol molecules as well, and can help to locate the alcohol groups in the micellar interior. In the  $\omega$ -phenyloctanoate surfactant system, the observed changes in  $^1\text{H}$  chemical shifts are mainly due to the intermolecular ring current effect resulting from the terminal phenyl group. If the phenyl groups have an average location near the micellar palisade layer, significant ring current shifts would be observed for the protons near the headgroup of the surfactant and the alcohol protons adjacent to the surfactant head group, i.e., the  $\text{C}_1$  and  $\text{C}_2$  methylene protons of the alcohol. If the  $\omega$ -phenyl groups reside primarily in the core of the micelle, ring current shifts will only be observed for the protons near the end of the alcohol chains. In Fig. 5, the  $^1\text{H}$  chemical shifts of the  $\text{C}_1$  protons of 0.10 M  $\text{C}_4\text{E}_0$  and 0.10 M  $\text{C}_4\text{E}_3$  in the presence of increasing amount of the  $\omega$ -phenyloctanoate surfactant are plotted. The chemical shifts of the protons attached to carbons 2 and carbon 8 are also plotted in Fig. 5. We can clearly see that the magnitudes of the chemical shift changes of the protons directly attached to the carbons atoms in the  $\alpha$ -position from the hydroxyl group are very similar in magnitude between the monohydroxy alcohol (the  $\text{C}_4\text{E}_0$ ) and the ethoxylated alcohol examined here ( $\text{C}_4\text{E}_3$ ). This indicates that the averaged location of the protons on the  $\alpha$ -carbons is in the micellar headgroup region and that these protons sense a molecular environment similar to that of the  $\text{C}_2$  protons (the  $\alpha$ -carboxylate protons) in the surfactant headgroup. In Fig. 6, the chemical shift differences for the  $\omega$ - $\text{CH}_3$  protons of 0.10 M  $\text{C}_4\text{E}_0$  and 0.10 M  $\text{C}_4\text{E}_3$  cosurfactants are plotted for the same alcohol concentrations as a function of increasing concentration of the  $\omega$ -phenyloctanoate surfactant. When



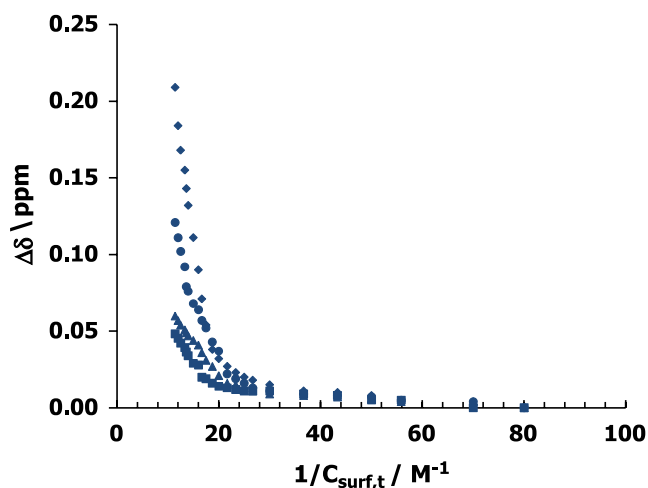
**Fig. 5**  $^1\text{H}$  chemical shifts of sodium 8-phenyloctanoate/0.10 M  $\text{C}_4\text{E}_0$  mixed micelles as a function of the inverse surfactant concentration.  $\text{C}_8$  (surfactant) (diamonds),  $\text{C}_2$  (surfactant) (squares),  $\text{C}_1$  ( $\text{C}_4\text{E}_0$ ) (triangles),  $\text{C}_1$  ( $\text{C}_4\text{E}_3$ ) (circles)



**Fig. 6**  $^1\text{H}$  chemical shifts of sodium 8-phenyloctanoate/0.10 M  $\text{C}_4\text{E}_1$  mixed micelles as a function of the inverse surfactant concentration.  $\text{C}_8$  (surfactant) (diamonds),  $\text{C}_2$  (surfactant) (squares),  $\omega$ - $\text{CH}_3$  ( $\text{C}_4\text{E}_0$ ) (triangles),  $\omega$ - $\text{CH}_3$  ( $\text{C}_4\text{E}_3$ ) (circles)

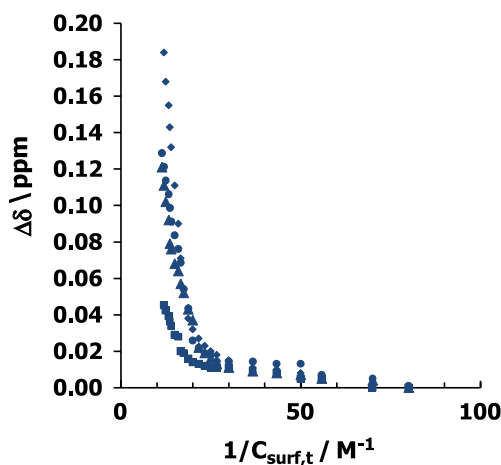
we examine these chemical shifts in Fig. 6, we observe larger chemical shift changes for both sets of  $\omega$ - $\text{CH}_3$  protons, consistent with their expected locations, i.e., buried more deeply in the micellar interior. These substantial low-frequency shifts (large ring current effects), comparable to the chemical shift changes for the  $\text{C}_8$  protons, are much larger than those of the  $\text{C}_2$  protons of the surfactant, indicating that, in the micelle, the methyl groups of both alcohols are on average in close proximity to the protons of the phenyl rings. The larger shifts observed for the  $\omega$ - $\text{CH}_3$  protons of the  $\text{C}_4\text{E}_3$  are due to (a) the fact that these protons are buried further in the micellar interior and b) the higher partition coefficient of the ethoxylated alcohol vs the monohydroxy alcohol.

Information about the average location of the EO groups in the ethoxylated alcohols in the mixed micelles can be obtained from the chemical shifts of the EO protons located on the carbons directly attached to the initial ether linkage in the alcohols (the  $\text{EO}_a$  protons) plotted in Figs. 7 and 8, respectively. If the EO groups reside predominantly in the surface palisade region only, i.e., in close proximity to the  $\text{C}_2$  and  $\text{C}_3$  surfactant methylene groups, very small ring current shifts will be observed. However, if the EO groups penetrate further into the interior of the micelle, we will observe substantial ring current shifts as the groups will be in closer proximity to the surfactant phenyl rings on the ends of the surfactant chains. When we examine Figs. 7 and 8, we first see that, for the  $\text{EO}_a$  protons on both  $\text{C}_4\text{E}_1$  and  $\text{C}_4\text{E}_3$ , substantial low-frequency shifts are observed in both cases, indicating that these protons are located beyond the micellar palisade layer, again in close proximity to the phenyl rings on the end of the surfactant chain. We note that, as more EO groups are added to the alcohol, the magnitude of the low-frequency shifts increases due to increased solubilization of the alcohol in the micellar



**Fig. 7**  $^1\text{H}$  chemical shifts of sodium 8-phenyloctanoate/0.10 M  $\text{C}_4\text{E}_2$  mixed micelles as a function of the inverse surfactant concentration.  $\text{C}_8$  (surfactant) (diamonds),  $\text{C}_2$  (surfactant) (squares),  $\text{EO}_a$  ( $\text{C}_4\text{E}_1$ ) (triangles),  $\text{EO}_a$  ( $\text{C}_4\text{E}_3$ ) (circles)

interior and the fact that these protons are penetrating more deeply in the micellar interior. In Fig. 8, when we examine the magnitude of the low-frequency shifts for the  $\text{EO}_a$  proton resonance on the  $\text{C}_4\text{E}_3$  alcohol, we see its chemical shift difference is higher than that of the terminal methyl group of the monohydroxy alcohol (the  $\text{C}_4\text{E}_0$ ) and, indeed, approaches that of the  $\text{C}_8$  carbon of the surfactant. These large, high-frequency shifts of the proton resonances of  $\text{EO}_a$  groups clearly indicate that these EO groups are, on average, located beyond the micellar palisade region deep in the interior of the mixed micelles. Additionally, given the fact that the chemical shift change for the  $\text{EO}_a$  groups for the  $\text{C}_4\text{E}_3$  is larger than that of the  $\omega\text{-CH}_3$  groups of the  $\text{C}_4\text{E}_0$ , we



**Fig. 8**  $^1\text{H}$  chemical shifts of sodium 8-phenyloctanoate/0.10 M  $\text{C}_4\text{E}_3$  mixed micelles as a function of the inverse surfactant concentration.  $\text{C}_8$  (surfactant) (diamonds),  $\text{C}_2$  (surfactant) (squares),  $\omega\text{-CH}_3$  ( $\text{C}_4\text{E}_0$ ) (triangles),  $\text{EO}_a$  ( $\text{C}_4\text{E}_3$ ) (circles)

can postulate that these EO groups at least are in an environment similar to that of the  $\omega\text{-CH}_3$  groups of the  $\text{C}_4\text{E}_0$ .

It is clear then from the NMR ASIS experiments that some of the EO groups are penetrating inside the surfactant micelles and are contributing to hydrophobic interactions. In our previous work on the calorimetry of surfactant/alkoxyethanol mixed micellar systems [48], we postulated that the presence of water molecules in the region slightly beyond the palisade layer allows the EO groups to maintain some favorable hydrogen bonding interactions in addition to the hydrophobic contacts between  $\text{CH}_2$  groups in the alcohol and surfactant backbone when the EO groups transfer to the micelles. The NMR results give direct evidence that these groups are located in the interior of the micelles; their ability to retain some water contacts as the mixed micelles form is a significant contribution to the driving forces for the formation of the mixed micelles.

## Conclusions

NMR chemical shift data were used to determine CMC values, aggregation parameters, and partition coefficients of alkoxyethanol/Na- $\omega$ -PhOct mixed systems. CMC values decreased in a linear fashion upon the addition of alcohol, which suggested that the ethoxylated species became solubilized inside the micelles. The aggregation numbers derived from the application of the mass action model to the  $^1\text{H}$  chemical shifts were found to decrease with increasing alcohol concentration, and there appeared to be a dependence of the surfactant aggregation number on the number of EO groups in the alcohol at constant alcohol concentration. The partition coefficients calculated for each of the four alcohols were found to increase in the order of  $\text{C}_4\text{E}_0 < \text{C}_4\text{E}_1 < \text{C}_4\text{E}_2 < \text{C}_4\text{E}_3$ . This showed that the EO groups increased the solubilization of alcohols into the surfactant micelles, suggesting that these groups contribute to hydrophobic interactions. The CMC values of the mixed micelles decreased upon increasing the number of EO groups on the alcohol molecule at a constant alcohol concentration, which is consistent with an increase in the hydrophobicity of the alcohol due to the increase in the number of EO groups in the molecule. The NMR ASIS experiments clearly showed that the ethylene groups are penetrating into the interior of the  $\omega$ -phenyloctanoate micelles and that the degree of penetration depends on the number of EO groups present in the alcohol head group region.

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