

# The properties of a family of two-headed surfactant systems: the 4-alkyl-3-sulfosuccinates 2. Surface properties of alkyl sulfosuccinate micelles

Judith A. MacInnis, Greg D. Boucher, R. Palepu, and D. Gerrard Marangoni

**Abstract:** The micellar properties of a family of two-headed surfactants, the alkyl sulfosuccinates, were investigated employing fluorescence, ultra-violet spectroscopy, and acid–base titrations, as a function of the chain length of the surfactant. Polarity of the micellar interior was investigated using pyrene and the ionic probe 8-anilino-1-naphthalensulfonic acid ammonium salt (ANS). Pyrene  $I_1/I_3$  ratios were used to probe the microenvironment of the probe in the palisade layer of the micelle. The  $pK_a$  values of both of the anionic head groups were determined using acid–base titrations. Surface potential measurements were obtained from the measurement of the  $pK_a$  of the hydrophobic indicator, 7-hydroxycoumarin, at the sulfosuccinate micellar interface. All of these results were used to examine the surface properties of the alkyl sulfosuccinate micelles and the polarity of the micellar interior.

*Key words:* micellization,  $pK_a$ , surface potential, surface charge density, 7-hydroxycoumarin, pyrene.

**Résumé :** Faisant appel à la fluorescence, à la spectroscopie ultraviolette et à des titrages acide/base, on a étudié les propriétés micellaires d'une famille d'agents de surface à deux têtes, les sulfosuccinates d'alkyle, en fonction de la longueur de la chaîne de l'agent de surface. On a étudié la polarité de l'intérieur de la micelle en utilisant le pyrène et une sonde ionique, le sel d'ammonium de l'acide 8-anilino-1-naphthalène-1-sulfonique (ANS). On a utilisé les rapports  $I_1/I_3$  du pyrène pour évaluer le microenvironnement de la sonde dans la couche palissade de la micelle. On a déterminé les valeurs des  $pK_a$  des deux têtes ioniques à partir de mesures de  $pK_a$  de la 7-hydroxycoumarine, un indicateur hydrophobe, à l'interface micellaire du sulfosuccinate. On a utilisé l'ensemble de ces résultats pour étudier les propriétés superficielles des micelles de sulfosuccinate d'alkyle et la polarité de l'intérieur de la micelle.

*Mots clés :* micellisation,  $pK_a$ , potentiel de surface, densité de charge de surface, 7-hydroxycoumarine, pyrène.

[Traduit par la Rédaction]

## 1. Introduction

Micelles in ionic detergent solutions are generally considered to be excellent models for the study of colloidal and detergent properties due to the ease of creating stable colloidal aggregates with definite surface properties. There have been a number of papers in the literature describing the synthesis and micellar and solution properties of novel two-headed surfactant systems (1–4). However, much of this work has focused on the synthesis, critical micelle concentration values (cmc), and the degrees of counter ion binding ( $\beta$  values) of two-headed surfactants. Although the  $\beta$  values provide some information on the surface charge densities of the micelles, direct measurements of the surface properties of the two-headed surfactants are essential to evaluate the unique structure of the interface between water and the micelles of these two-headed surfactants (5–17). Surface potential mea-

surements using solubilized pH indicators have often been used to examine the properties of micelles and model lipid membranes. The micelle–water interface possesses properties that are distinctly different from those of the bulk solution and the micellar interior. Understanding the surface properties of micelles may play an important role in applications such as micellar catalysis, transport phenomena, anesthetic properties, and colloid stability in mixed electrolyte solutions, where surface micellar effects have been recognized as being important. Surface potential measurements may also shed some light on the hard-water tolerance of two-headed surfactants (3). The present paper involves the examination of a family of two-headed surfactants, the disodium 4-alkyl 3-sulfosuccinate surfactants (Fig. 1). These two-headed surfactants are of interest because the addition of a second negatively charged head group adjacent to an existing anionic surfactant increases the cmc and lowers the Kraft point of the two-headed surfactants (1–4). The alkyl sulfosuccinate surfactants have negatively charged sulfonate and carboxylate groups separated by two carbon atoms on the alkyl chain (4), and hence may also have interesting micellar properties as a function of the pH.

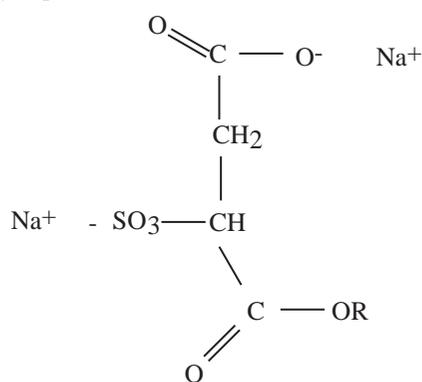
In this paper, the micellar surface properties and the micropolarity of a family of two-headed surfactants, the alkyl sulfosuccinates, were investigated using fluorescence

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**Fig. 1.** Structural formula of alkyl sulfosuccinate surfactants (R = alkyl group).



spectroscopy, ultra-violet spectroscopy, and acid–base titrations of surface solubilized indicator 7-hydroxycoumarin. As a first step in determining the micellar properties of the sulfosuccinate surfactants, as a function of pH, we have also determined the  $pK_a$  values of both of the anionic head groups of the alkyl sulfosuccinates, employing acid–base titrations. Pyrene  $I_1/I_3$  ratios and the luminescent intensities of ANS were used to determine the polarity of the microenvironment of the micelle. The measurement of the  $pK_a$  of hydrophobic indicator, 7-hydroxycoumarin, at the sulfosuccinate micellar surface, was used to determine the micellar surface potentials. All of these properties are discussed in terms of the influence of having two negatively charged head groups on the surfactant chain. Nuclear magnetic resonance spectroscopy was also used to investigate the location of a typical aromatic probe (benzene) in the surfactant micelles.

## 2. Experimental

The alkyl sulfosuccinates were synthesized using the following general procedure. Equimolar amounts of maleic anhydride and an alcohol were heated for 20 min, with constant stirring, in a 500 mL round bottom flask. An equimolar amount of an aqueous sodium metabisulfite solution was added, and the mixture was neutralized to  $\text{pH} \cong 7\text{--}9$ . The mixture was then allowed to reflux for 20–24 h. The progress of the reaction was monitored by running a UV spectrum on the reaction mixture to confirm the absence of the maleic anhydride double bond. The resulting surfactants were purified through Soxhlet extraction with diethyl ether for at least 72 h. The structures of these surfactants were confirmed by nuclear magnetic resonance and FT-IR spectroscopy.

The  $pK_a$  values of the respective anionic head groups were determined as follows. Aqueous surfactant solutions, with concentrations twice the critical micelle concentration, were titrated with standardized sodium hydroxide (0.10 M, Fisher Scientific A.C.S.) and were used to obtain the titration curve data. The pH of the solution was measured using a glass electrode and a Cole–Palmer Digi-Sens pH/mv meter. The electrode was calibrated using pH 4 and 10 buffer solutions (Fisher Scientific). The pH values were reproducible to  $\pm 0.15$  pH units.

The luminescence probing experiments to obtain the pyrene  $I_1/I_3$  ratios in the sulfosuccinate micellar interior were carried out as follows. Pyrene (Aldrich, 99%) was purified through sublimation and recrystallization (twice) with ethanol. The pyrene probe was held at a constant concentration of  $2 \times 10^{-5}$  M. A small amount of a pyrene–ethanol solution was placed in a small flask, and the solvent was allowed to evaporate, depositing the pyrene as a monolayer at the bottom of the flask.

The stock aqueous solution of the surfactant was added to the flask containing the pyrene; this solution was stirred overnight to ensure complete dissolution of the pyrene in the surfactant solution. Steady-state pyrene emission spectra were recorded on a Perkin–Elmer MPF-66 spectrophotometer, using an excitation wavelength of 338 nm and scanning the emission spectra from 350 to 500 nm. The intensities of the first and third peaks of the emission spectra were recorded and used to determine the  $I_1/I_3$  ratio and hence, an estimate of the micropolarity of the micellar interior.

The ANS polarity studies were carried out as follows: 8-anilino-1-naphthalenesulfonic acid ammonium salt was purchased from Aldrich and was used as received. A stock solution of the probe ( $10^{-5}$  M) was prepared in absolute ethanol. Micellar solutions of ANS were prepared by taking an aliquot of the stock solution and adding the surfactant solution. The resulting solutions were sonicated for 5 min. Fluorescence measurements were made using an excitation wavelength of 389 nm and the emission spectra was obtained from 400 to 525 nm.

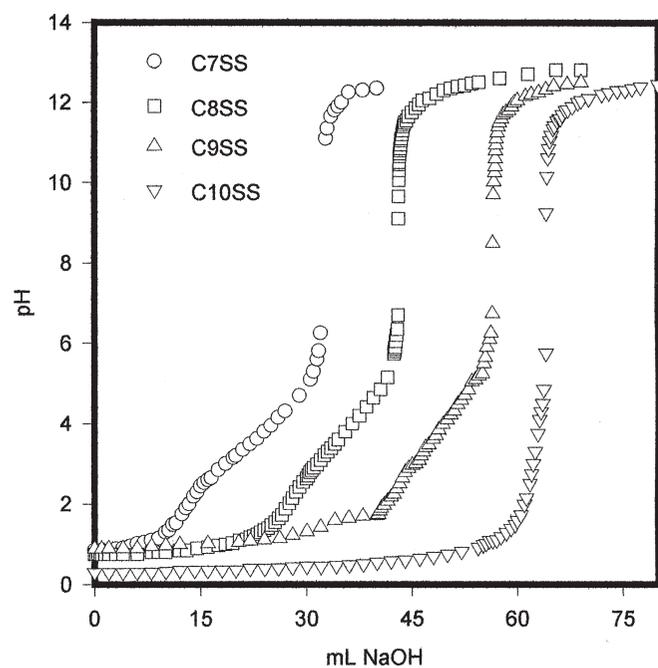
The nmr spectra ( $^1\text{H}$  and proton decoupled  $^{13}\text{C}$ ) were obtained on a Bruker AC-200.  $\text{D}_2\text{O}$  was used as a solvent for all of the sulfosuccinate experiments. The  $^1\text{H}$  spectra were referenced to the HOD peak ( $\delta = 4.81$  ppm), while the  $^{13}\text{C}$  chemical shift signals were referenced to the deuterium lock signal. Two sets of nmr experiments were carried out to determine the location of a typical aromatic probe (benzene) in the surfactant micellar interior.

(a) Benzene solubilization studies: The alkyl sulfosuccinate solutions were prepared, at a concentration of twice the critical micelle concentration. To 1 mL of each of these solutions was added 10 or 20  $\mu\text{L}$  of benzene (Aldrich), and the mixture was stirred for 30 min.

(b) Surfactant Studies: At least five solutions, up to twice the critical micelle concentration were prepared in  $\text{D}_2\text{O}$ . To 1 mL of each of these solutions was added 10 mL of benzene.

Surface potential measurements were carried out as follows. Sodium dodecyl sulfate (Aldrich, 99%) was recrystallized twice from absolute ethanol. The nonionic surfactant octaethylene glycol decyl ether ( $\text{C}_{10}\text{E}_8$ ) was supplied by Fluka and was used without further purification. The acid–base indicator 7-hydroxycoumarin was obtained from Aldrich Chemical Co. and was used without further purification. The pH was adjusted by NaOH (A.C.S. Reagent Fisher Scientific) or HCl (A.C.S. Reagent Fisher Scientific). NaCl (A.C.S. Fisher Scientific) was used to adjust the ionic strength of the surfactant solutions. Solutions were titrated from high pH to low pH by the addition of small amounts of NaOH or HCl solutions (0.10 M). After the addition of either NaOH or HCl the pH of the solution was recorded, and the degree of ionization of the indicator was

**Fig. 2.** Sodium hydroxide titration curves of the alkyl sulfosuccinate surfactants.



**Table 1.**  $pK_a$  values of alkyl sulfosuccinates.

No. of carbons	Sulfonate group	Carboxylate group
7	1.51	4.86
8	1.66	5.15
9	1.74	5.21
10	1.85	5.39

obtained by measuring the intensities of the peak at 373 nm as a function of pH using the HP 8450A diode array spectrophotometer.

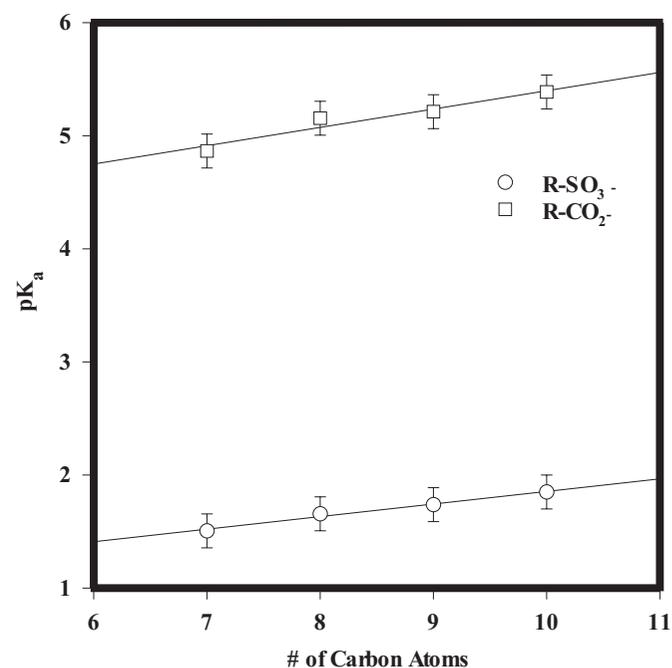
### 3. Results

#### 3.1. $pK_a$ determination

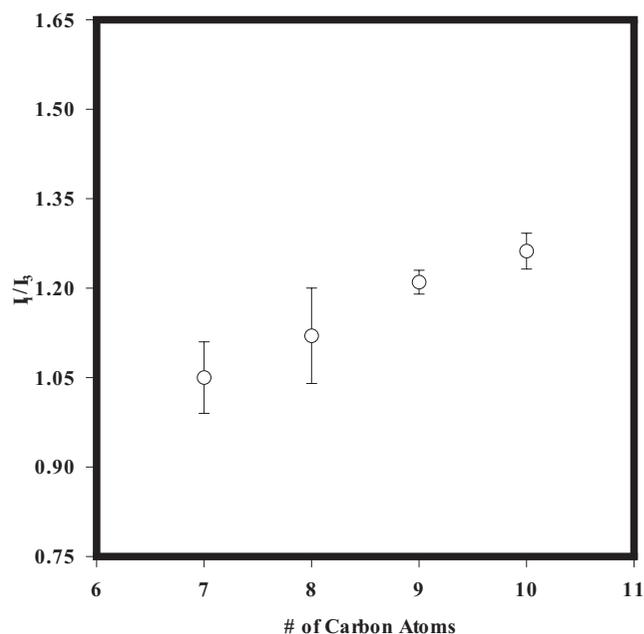
Aqueous solutions of the alkyl sulfosuccinates were prepared at twice the critical micelle concentration, and the resulting solutions were titrated using 0.1 M NaOH. The  $pK_a$  values for the carboxylate and the sulfonate anionic head groups were determined from the apparent breaks that occur in the titration curves (Fig. 2), and these values are given in Table 1.

The  $pK_a$  values (Fig. 3) increase with increasing carbon number for both the carboxylate and sulfonate head groups. There is an observed dependence on increasing chain length for the  $pK_a$  values, and these values are in agreement with the literature values. These  $pK_a$  values depend slightly on the alkyl chain length (18). Hence, we can clearly see from Fig. 1 that when the pH is high (>9.6), the sulfosuccinates are in the form of two-headed anionic surfactants. Varying the pH of the solution should change the properties of the sulfosuccinate micelles as the degree of ionization of the ionizable carboxylate head group is changed; this is currently under investigation.

**Fig. 3.**  $pK_a$  values of the alkyl sulfosuccinate surfactants, as a function of carbon number.



**Fig. 4.** Pyrene  $I_1/I_3$  ratios of alkyl sulfosuccinates.



#### 3.2. Fluorescence studies

##### 3.2.1. Pyrene

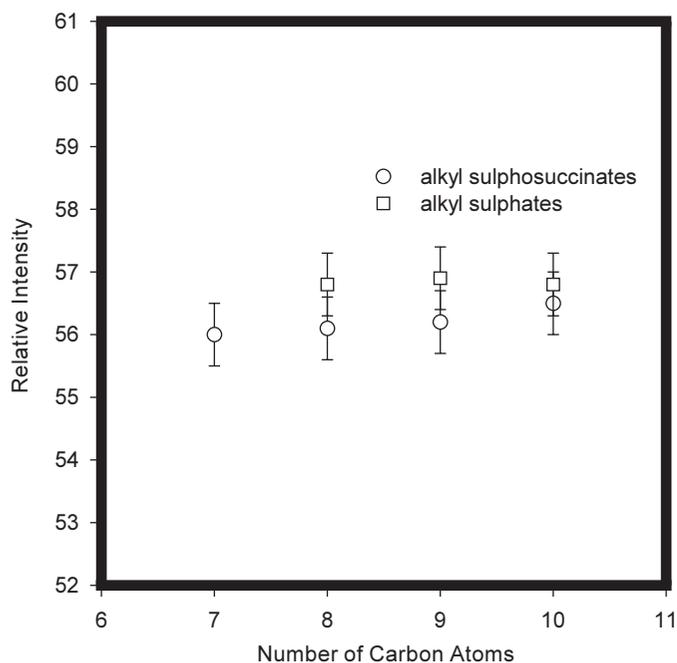
The pyrene  $I_1/I_3$  ratios were determined for the alkyl sulfosuccinates (Fig. 4) and are given in Table 2.

##### 3.2.2. 8-Anilino-1-naphthalenesulfonic acid ammonium salt

To verify the polarity of the microenvironment, the photophysical behavior of an ionic probe, ANS, was investigated with the two-headed surfactants under study. The relative intensity of the probe in the presence of the alkyl

**Table 2.** Aggregation numbers ( $N_s$ ), size of sulfosuccinate micelles, and  $I_1/I_3$  pyrene ratios.

No. of carbons	$N_s^a$	$R$ (Å)	$a_0$ (Å <sup>2</sup> )	$v/a_0l_c$	$I_1/I_3$
7	12±3	8.52	76.01	0.16	1.05 ± 0.06
8	20±5	10.50	69.27	0.19	1.12 ± 0.09
9	29±4	12.32	65.76	0.21	1.21 ± 0.02
10	42±5	14.38	61.87	0.23	1.26 ± 0.03
Water	—	—	—	—	1.81 ± 0.04

<sup>a</sup>Reference 1.**Fig. 5.** Relative intensity ANS + alkyl sulfosuccinate surfactants and ANS + alkyl sulphate surfactants.

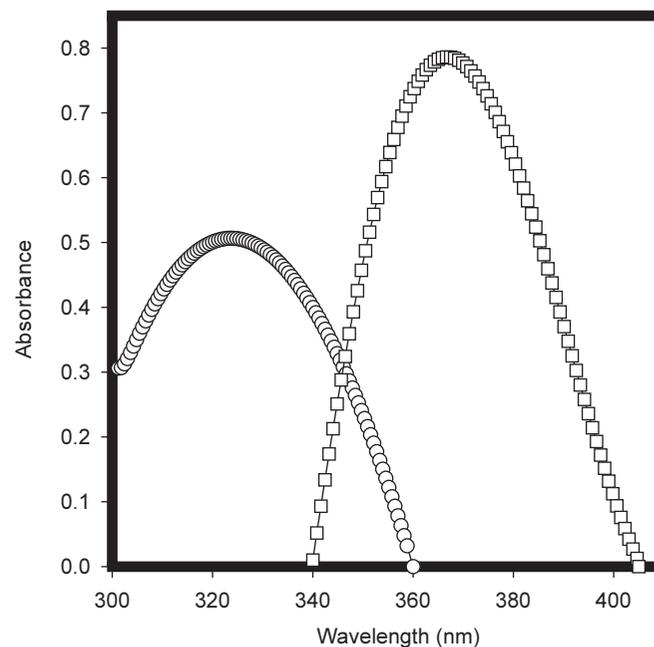
sulfosuccinates and the alkyl sulphate surfactants is shown in Fig. 5.

### 3.3. Surface potential measurements

The measurement of the surface potential of a micellar system will provide information on the surface charge density – surface potential relationships for these novel two-headed surfactants. 7-Hydroxycoumarin and its derivatives have been used, in the literature, to investigate the interfacial microenvironment of a large number of monolayers (8–12). The electrostatic surface potential of a charged interface can be calculated using the following expression:

$$[1] \quad \Psi_0 = \frac{2.303RT}{F} (pK_a^i - pK_a^{obs})$$

where  $\Psi_0$  is the surface potential,  $pK_a^{obs}$  is the apparent  $pK_a$  value of the 7-hydroxycoumarin at the charged surface,  $pK_a^i$  is the apparent  $pK_a$  of the 7-hydroxycoumarin at the surface when  $\Psi_0 = 0$  and  $F$ ,  $R$ , and  $T$  are the Faraday constant, the universal gas constant, and the absolute temperature, respectively. The  $pK_a$  values of 7-hydroxycoumarin are a function of the dielectric constant of the medium. The  $pK_a^i$  of the indicator is determined from the  $pK_a^{obs}$  in the presence of a nonionic surfactant. The nonionic surfactant micelle acts as

**Fig. 6.** UV/vis adsorption spectrum for 7-hydroxycoumarin in aqueous solution at a pH of 2.0 ( $\lambda_{max} = 320$  nm) and a pH of 10.0 ( $\lambda_{max} = 370$  nm).

a zero potential reference state for determining the  $pK_a^i$  values of 7-hydroxycoumarin in anionic micelles. The absorption spectrum of 7-hydroxycoumarin was obtained as a function of pH; the UV spectrum shows two characteristic peaks that are pH dependent (Fig. 6).

The protonated 7-hydroxycoumarin ( $pH < 6$ ) exhibits an intense absorption band with  $\lambda_{max}$  at 324–330 nm, with a log  $\epsilon \sim 4.1$ . In basic solution ( $pH > 8$ ) the absorption band that appears at  $\lambda_{max}$  365–370 nm, with log  $\epsilon \sim 4.2$ , is assigned to the anionic form of the indicator that is formed from the dissociation of the acidic phenolic proton at position seven (19).

The results for the  $\lambda_{max}$  of the acid form and the  $\lambda_{max}$  of the anionic form of the indicator are in excellent agreement with the literature. The absorbance spectrum (1.0 cm cells) of a  $6.0 \times 10^{-5}$  M solution as a function of pH at 370 and 320 nm is given in Fig. 7.

The observed  $pK_a$  for 7-hydroxycoumarin was determined from the absorption spectra using the following equation:

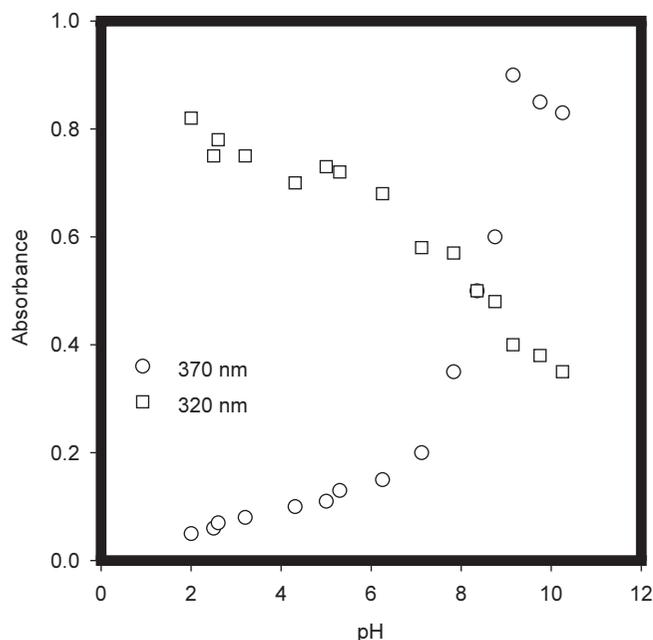
$$[2] \quad pK_a = pH - \log \left( \frac{\alpha}{100 - \alpha} \right)$$

where  $\alpha$  is the percentage of 7-hydroxycoumarin that has been ionized. The maximum absorbance of the 7-hydroxycoumarin at the  $\lambda_{max}$  of the probe, as a function of the solution pH, was taken as the 100% ionization value and the minimum absorbance as the 0% ionization value. At least six different values between 0 and 100 were examined for each solution.

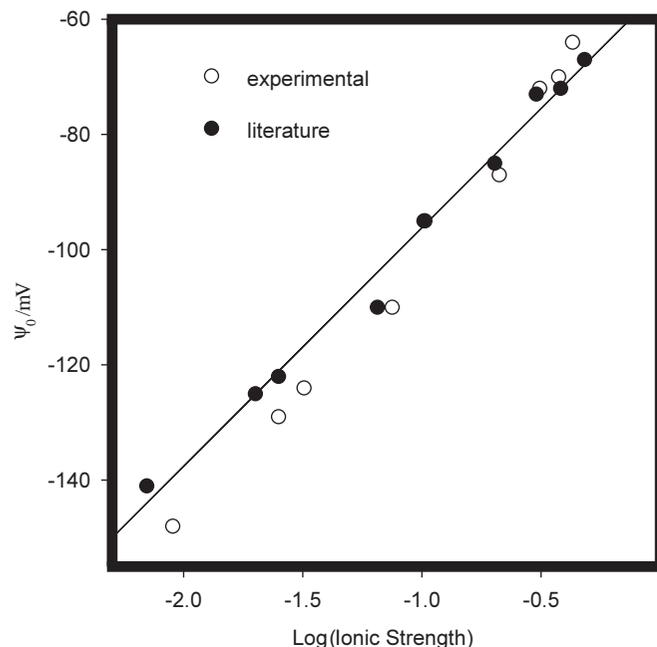
For the alkyl sulfosuccinate surfactants the ionic strength,  $I$ , of the bulk solution is given by

$$[3] \quad I = 10^{(pH_i - 14)} + [NaCl] + cmc + 1/2(\Sigma Z^2 cmc)$$

**Fig. 7.** Absorbance of 7-hydroxycoumarin as a function of pH at 320 and 370 nm.



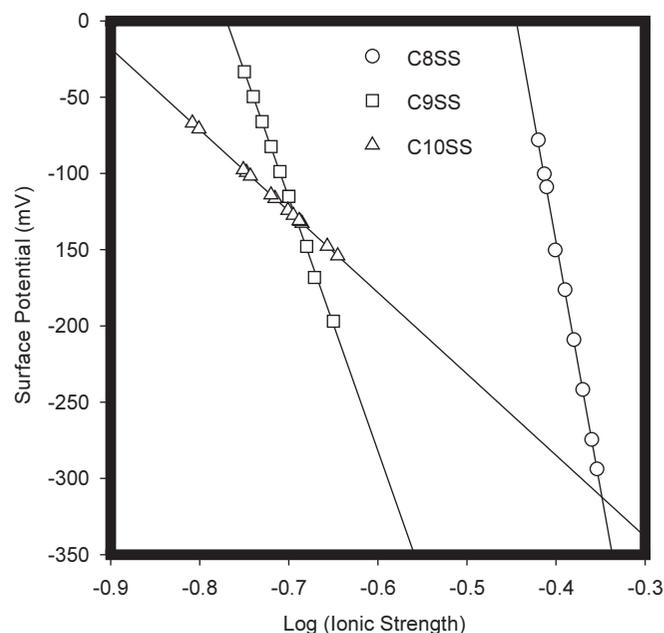
**Fig. 8.** Surface potentials of sodium dodecyl sulphate at various ionic strengths.



where  $pH_i$  is the initial pH,  $[NaCl]$  is the concentration of added NaCl, and the last term is due to the contributions of the negatively charged head groups ( $Z = -2$ ). This equation neglects the contribution to the ionic strength from the micelles and the dissociated counter ions (6).

The experimental surface potentials of 0.02 M SDS solutions, of varying ionic strength, were determined using the above method. The measured values for SDS are in excellent agreement with those reported in the literature. These are shown in Fig. 8. The potentials were calculated using

**Fig. 9.** Surface potentials of the alkyl sulfosuccinates at varying ionic strength.



**Table 3.** Surface charge densities of the alkyl sulfosuccinates.

No. of carbons	$N_s^a$	$R$ (Å)	$\beta^a$	$\sigma_0$ (C/m <sup>2</sup> )
7	12	8.52	0.60	$-0.061 \pm 0.005$
8	20	10.50	0.66	$-0.058 \pm 0.005$
9	29	12.32	0.70	$-0.053 \pm 0.005$
10	42	14.38	0.87	$-0.025 \pm 0.005$

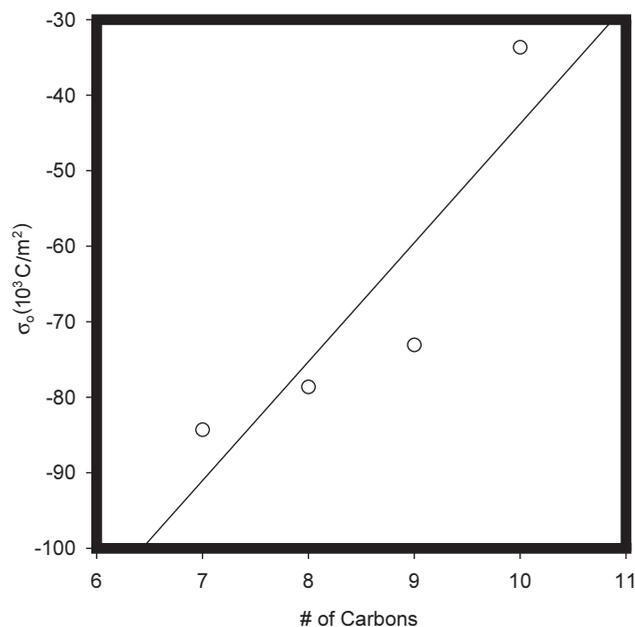
<sup>a</sup>Reference 1.

eq. [1] based on the  $pK_a$  of 7-hydroxycoumarin, in  $5 \times 10^{-3}$  mol/L  $C_{10}E_8$ , of  $9.12 \pm 0.15$  ( $pK_a^0$ ). This value was found to be constant by up to an ionic strength of 4 M NaCl. The experimental surface potentials for the alkyl sulfosuccinates are shown in Fig. 9, and as both the un-ionized and ionized forms of the indicator partition into the micellar phase and reside within the interfacial region of the anionic micelles (8, 9, 11, 12), the differences between  $pK_a^i$  and  $pK_a^0$  should reflect the difference in the surface potential of the two-headed surfactants vs. the nonionic reference micelle. The above expression assumes that the dielectric constant of the medium directly surrounding the probe is relatively the same in both micellar systems. This has been verified for SDS and DTAB micelles (8, 12, 14) and should be a reasonable assumption for the sulfosuccinate micelles.

The surface charge density was calculated using the following equation:

$$[4] \quad \sigma_0 = \frac{-eN_s(1-\beta)}{4\pi a^2}$$

where  $N_s$  is the aggregation number, and  $\beta$  is the fraction of surfactant ions in the micelle that are electrically neutralized by the specific binding of a counter ion. These values are given in Table 3 (Fig. 10).

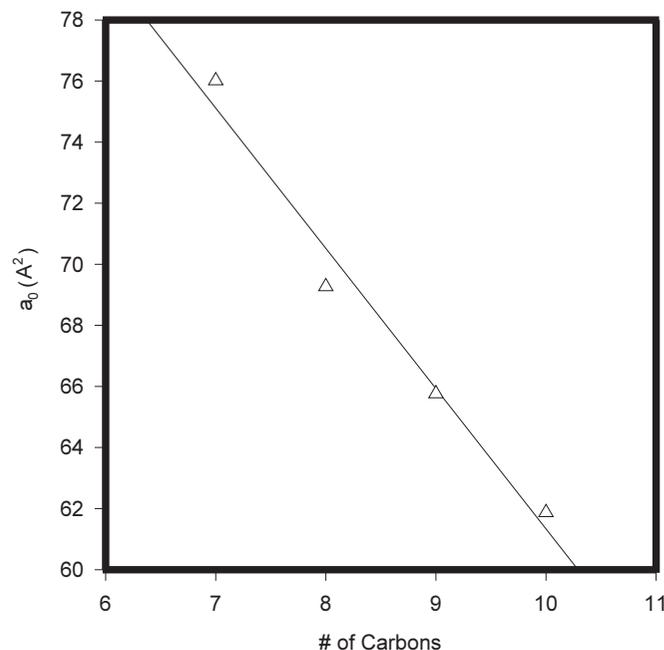
**Fig. 10.** Surface charge density of the alkyl sulfosuccinates.

#### 4. Discussion of results

The  $pK_a$  values of the sulfonate and carboxylate head groups of the alkyl sulfosuccinates increase as the number of carbons is increased on the hydrocarbon chain (Table 2, Fig. 3). The titration of the alkyl sulfosuccinates produces a curve that is similar to that of a weak acid titrated with a strong base. The break points that occur in the curve are due to the neutralization of the carboxylate and sulfonate head groups. The  $pK_a$  values are in good agreement with those for the aliphatic carboxylic acids (18). The  $pK_a$  values for the sulfonic acid group is slightly higher than the  $pK_a$  values for benzenesulfonic and toluenesulfonic acids (18). There is also an observed dependence on increasing chain length for the  $pK_a$  values, which is in reasonable agreement with the literature.

The use of luminescence probing experiments to determine a number of important properties of surfactant micelles is well established (19–29). The ability of pyrene to sense the polarity of its microenvironment is also well established (22–29). Since the pyrene  $I_1/I_3$  ratios reflect the polarity of the microenvironment around the probe, it can, therefore, detect changes in polarity in micelles. Analysis of the pyrene  $I_1/I_3$  ratios (Table 2, Fig. 4) gives information about the polarity of the microenvironment surrounding the solubilized probe in the micelle. It is known that pyrene is solubilized in the palisade layer of micelles, near the polar head groups, where it senses a relatively high polar environment (30). In the present study, it is evident that the pyrene senses a very similar degree of polarity in the microenvironment surrounding the probe in all of the sulfosuccinate micelles. This may be attributed to the inability of the pyrene to penetrate deeply into the micelle, and hence the pyrene senses the same degree of polarity due to the location of the pyrene near the micelle–water interface.

The surface area per head group for the sulfosuccinate micelles has been estimated as follows. The hydrophobic chain

**Fig. 11.** Surface area per head group alkyl sulfosuccinates.

volume of the micelle ( $v$ ) and the critical chain lengths ( $l_c$ ) were obtained using Tanford equations (30):

$$[5] \quad v = 27.4 + 26.9n \text{ (}\text{\AA}^3\text{)}$$

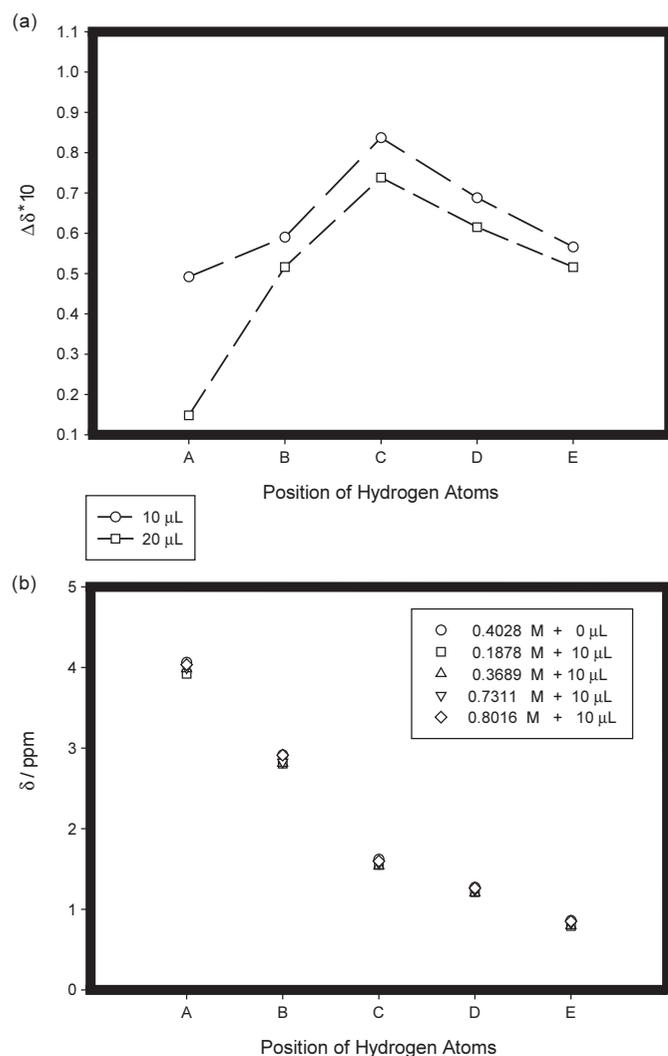
$$[6] \quad l_c = 1.5 + 1.265n \text{ (}\text{\AA}\text{)}$$

where  $n$  is the number of carbon atoms of the chain. The micellar radius,  $r$ , and the surface area per head group ( $a_0$ ) were obtained assuming spherical shape. The aggregation numbers were determined by fitting the C-13 measurements to the mass action model (1). The values of  $r$  and  $a_0$  ( $(4\pi r^2)/N_{\text{agg}}$ ) along with the critical packing parameter ( $v/(a_0 l_c)$ ), which is a parameter-controlling micelle shape, are presented in Table 3 (30). The increase in the critical packing parameter indicates the formation of larger spherical micelles; however, we estimate that the surface area per head group decreases linearly with an increase in carbon number. This is shown in Fig. 11.

The ionic probe, ANS, has been known to interact with anionic micelles such as sodium dodecyl sulphate (31). The spectral behavior of ANS is interesting because the emission properties are sensitive not only to the polarity of the microenvironment but to the microviscosity of the environment of the probe. ANS is almost nonfluorescent in aqueous solutions, but it exhibits a fluorescence enhancement upon binding to the micellar surface. This fluorescence enhancement is due to the polarity-dependent twisted intramolecular charge transfer (TICT) (32). When the ANS molecules are transferred from the highly polar aqueous media to the relatively nonpolar micellar surface, the reduction in polarity and the increase in microviscosity leads to a decrease in the rate of the TICT process. Inhibition of nonradiative TICT pathways results in an increase of the emission quantum yield lifetime.

In examining Fig. 5 it can be seen that the members of the alkyl sulfosuccinate family experience the same polarity in the microenvironment surrounding the ANS probe. The same

**Fig. 12.** (a) Changes in proton chemical shifts upon addition of benzene (C8SS). (b) Changes in proton chemical shifts upon increasing surfactant (C8SS) concentration (benzene concentration = 10  $\mu\text{L}/\text{mL}$ ).



is also true for the alkyl sulfate surfactants. These results agree with those obtained from the pyrene polarity study.

Before we discuss the surface potentials of the sulfosuccinate surfactants, certain facts must be considered when examining the use of a probe for surface potential measurements. To calculate the surface charge density the radius of the micelle hydrophobic core is needed. Because of changes at the micelle surface, its shape is not known exactly (22, 23); also the exact position of the 7-hydroxycoumarin at the micelle surface is also not known. If the indicator resides outside the micelle surface it will sense a surface potential lower than the true value (1). There have been extensive nmr studies carried out with aromatic molecules solubilized in SDS micelles (33) in the literature. These studies have indicated that the aromatic molecules with ionizable hydroxy groups sit in the plane of the sulphate head groups in the SDS micelle. Therefore, it is rea-

**Table 4.** Changes in proton chemical shift (ppm) due to added benzene ( $\mu\text{L}$ , in parentheses).

Hydrogen position	$\delta$ (0)	$\Delta\delta \times 10$ (+10)	$\Delta\delta \times 10$ (20)
<i>(a) C7SS</i>			
Alpha	4.0187	0.4920	0.1480
Beta	2.9144	0.5900	0.5160
C	1.6208	0.8370	0.7380
D	1.2715	0.6880	0.6150
CH <sub>3</sub>	0.8042	0.8092	0.5160
<i>(b) C8SS</i>			
Alpha	4.0876	0.4180	0.7140
Beta	2.8923	-0.3690	-0.3200
C	1.6355	0.7870	0.8110
D	1.3010	0.8110	0.8110
E CH <sub>3</sub>	0.8706	0.5650	0.5900
<i>(c) C10SS</i>			
Alpha	3.9769	-0.2460	-0.3470
Beta	2.8923	-0.7380	-0.3440
C	1.5013	-0.6045	-0.1625
D	1.2543	0.2700	0.6390
E CH <sub>3</sub>	0.8436	0.3200	0.6150

sonable to assume in our present investigation that the 7-hydroxycoumarin indicator will also sit in this plane and hence, respond to the true surface potential.

Although the locus of solubilization may not be the same for benzene and other aromatic molecules (pyrene or 7-hydroxycoumarin), one should be able to obtain a fairly reasonable qualitative estimate of the location of aromatic molecules in the sulfosuccinate surfactant micelle interior from the nmr studies of benzene solubilized in the alkyl sulfosuccinate micelles. It can be seen from Fig. 12(a) that the magnitude of the alpha proton chemical shift (i.e., head group region) are greater than those of the other proton shifts, that occur due to added benzene (Table 4), suggesting that the benzene is residing in the head group region of the micelle. The second area of the nmr study involved keeping the benzene concentration constant and increasing the surfactant concentration. From this study it was concluded that the proton chemical shifts are not influenced by the increasing surfactant concentration (Fig. 12(b)). These studies indicate, in the range of ion concentrations studied, that the benzene is located within the head group region of the surfactant micelle. From this we can conclude that the acid-base indicator 7-hydroxycoumarin should also be located in the same region of the micelle.

It is clear from the surface potential values, in the anionic sulfosuccinate micelles, that these surfactants must have relatively low degrees of counter ion binding, as the surface potential values are two to three times larger than those of sodium dodecyl sulphate at comparable ionic strengths. In addition, the dependence of the surface potential on ionic strength is significantly different for these two-headed surfactants vs. the single-headed surfactants. In the case of the two-headed surfactants, the  $\psi_0$  values decrease with an increase in ionic strength, whereas for the single-headed surfactants, the  $\psi_0$  values increase with increasing ionic strength. This may indicate a significant difference in the properties of two-headed surfactant micelles, as a function

of increasing salt concentration, vs. single-headed surfactant micelles like sodium dodecyl sulphate.

It is also important to note that the differences in the surface potential values between the members of the alkyl sulfosuccinate family are due to several important factors:

1. The various micellar solutions have different ionic strengths due to the fact that the members of the sulfosuccinate family have different cmc values.
2. The degree of counter ion binding is different for each member of the sulfosuccinate family.
3. The sulfosuccinate micelles may have slightly different sizes and shapes.

## 5. Conclusions

It has therefore been shown that the alkyl sulfosuccinate surfactants exhibit characteristics that are distinctive of a family of surfactants that contain two negatively charged head groups.

The micellar properties of these two-headed anionic surfactants have therefore been shown to be influenced by the pH of the solution. Also the presence of this second negatively charged head group affects not only the polarity of the microenvironment of the micelle, but it also increases the surface potential of the head-group region.

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