Micellization and mixed micellization of alkylxylenesulfonates — a calorimetric study

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Abstract

The effects of the position of sulfonate and of methyl groups on the aromatic ring of isomerically pure alkylxylenesulfonates on micellization and mixed micellization have been investigated using microcalorimetry and surface tension measurements. It was observed that the position of the sulfonate with respect to the alkyl chain is more critical than that of the methyl groups in determining the surfactant behavior in solution. Steric constraints to the packing of the molecules are proposed to be the main mechanism for the differences in the micellization of the surfactants. Calorimetric studies suggested that entropy was the main driving force for micellization. The mixed micellization of two structurally different alkylxylenesulfonates was found to be non-ideal. Regular solution theory adequately fits the data and microcalorimetry was used to verify the validity of the thermodynamic assumptions of the theory.

Introduction

Surfactants are increasingly used in processes such as flotation, detergency, enhanced oil recovery, paint formulation, lubrication and microelectronics [1–5]. Also, surfactant assemblies such as micelles have potential applications in novel separation and reaction schemes such as magnetic isotope separation and polymer synthesis [6,7]. An understanding of the solution behavior of surfactants, and in particular micellization, is important for improving the efficiency of the above processes.

Among the different factors that influence micellization, the surfactant structure plays an important role [8–14]. The effect of different structural variations in alkyl chain length, branching of the alkyl chain and the addition of functional groups on

micellization has been studied previously for a number of surfactants. An important structural variation is the position of the functional groups on the aromatic ring of surfactants containing a benzene ring. Studies on the effect of the position of functional groups in the aromatic ring on the properties of surfactants are limited [15,16]. Bolsman and Daane [15] have studied the stability of microemulsions using alkylxylenesulfonates, and have monitored resulting performance characteristics such as optimal salinity, solubilization parameter and interfacial tension. They observed that the surfactant with the sulfonate group in the ortho position with respect to the alkyl chain had lower optimal salinity, higher interfacial tension and lower solubility in water than surfactants with the sulfonate group in the para or meta positions. However, they used commercial grade surfactants with isomeric purity of only about 75%. Thus, even

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though they observed differences in properties with changes in the position of the sulfonate group, the effect of other isomers present cannot be excluded. In fact, in most of the studies on the effect of surfactant structure, the purity of the surfactant in terms of its isomers is not high. This could lead to erroneous conclusions since it is known that impurities even in small amounts can mask the effect of structural variations [8]. Using isomerically pure alkylxylenesulfonates, we have shown that the surfactant with the sulfonate group in the para position is more surface active, has a lower CMC and adsorbs onto alumina to a greater extent than the surfactant with the sulfonate group in the meta position [17]. Recently, Varadaraj et al. [18] have also observed the same behavior with alkylxylenesulfonates with the sulfonate group in the para and ortho position.

In this work, the effects of the position of sulfonate and methyl groups on the benzene ring of isomerically pure alkylxylenesulfonates on micellization and mixed micelle formation have been studied using surface tensiometry and microcalorimetry.
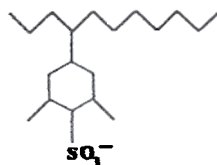
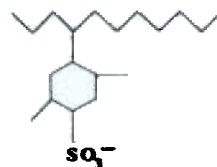## Experimental

Materials

Surfactants
4C11 2,4-*meta*-xylenesulfonate (Meta), 4C11 3,5-*para*-xylenesulfonate (Para1), 4C11 2,5-*para*-xylenesulfonate (Para2) and 4C11 4,5-*ortho*-xylenesulfonate (Ortho) obtained from ARCO Oil and Gas · Company were used in this work. The counterion for all the surfactants was Na. All the surfactants were specified to be at least 97% isomerically pure and were used as received. The structures of these surfactants are shown below:
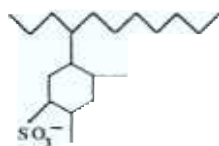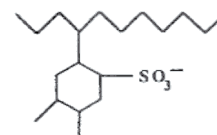

Meta   Para1

Para2   Ortho

Experimental conditions

All the experiments were carried out at 43°C and at a constant ionic strength of 0.03 kmol m^{-3} NaCl.

Methods

Surface tensiometry
Surface tension was measured using a water-jacketed du Nuoy ring tensiometer set to the test temperature.

Microcalorimetry
Calorimetric experiments were performed using a LKB 2107 differential microcalorimetry system. The calorimeter consists of a rotating block placed inside an air bath maintained at a constant temperature. The block consists of a sample cell and a reference cell. Each cell has two compartments. Mixing of the reactants is achieved by rotating the block. The temperature difference is then measured using thermopiles attached to each cell. The outputs of the thermopiles associated with each vessel are connected in opposition to one another, so that any electromotive force common to both vessels is nullified. The resulting output voltage is thus a measure of the reaction heat alone. This signal is amplified and is passed on to a digital read-out system and integrator/printer. The output is then calibrated for the reaction heat using a calibration heater built into each vessel.

For the enthalpy of micellization, the heat of dilution of a micellar solution to its premicellar concentration was measured. The heat of dilution

of the monomers was measured separately and was subtracted from the total reaction heat to obtain the heat of micellization.

The excess enthalpy of mixed micelle formation was measured by mixing concentrated micellar solutions of the two surfactants. Solutions of equimolar concentration were used for each measurement, so that the mixture composition was determined by the relative solution volumes.

Results and discussion

Surface tension

Surface tension data provide information on the adsorption of surfactants at the liquid/air interface and also on surfactant interactions in solution. The CMC of Meta, Para1 and Para2 were determined from the break in the surface tension curves (Fig. 1). The ortho-xylenesulfonate precipitated in the presence of 0.03 kmol m^{-3} NaCl and this result is discussed in the next section. Absence of a minimum in the curves indicates that the surfactants are pure. It can be seen from the figure that Para1 is more surface active than Meta and Para2. Also, Para1 and Para2 have a lower CMC and a larger lowering of surface tension at CMC than Meta. The difference in the surface activity and the CMC of the surfactants is attributed to:

(1) different hydrophobicities of the alkyl chains due to the inductive effect of the sulfonate group;

(2) different steric constraints arising from the positions of the sulfonate and methyl groups to the packing of the molecules at the interface and in micelles.

The relative hydrophobicities of the three surfactants were measured using reverse-phase high performance liquid chromatography [19]. The retention times of the alkylxylenesulfonates along with a series of isomerically pure linear alkylbenzenesulfonates (LABS) were determined. The different retention times of the surfactants arise purely from the hydrophobic interaction of the surfactants with the column. A plot of the alkyl chain length vs the logarithm of the retention time of LABS (Fig. 2) is linear. From the retention times of the alkylxylenesulfonates, their relative hydrophobicities were determined in terms of effective alkyl chain length. The results show that the two para-xylenesulfonates have the same effective chain length while the meta-xylenesulfonate is less hydrophobic by 0.5 CH$_2$ group.

From Fig. 1, the slopes of the lines on the low concentration side of the break for Meta, Para1 and Para2 were calculated to be -17.1 mN m^{-1}, -21.7 mN m^{-1} and -15.3 mN m^{-1}, respectively. Using these values in the Gibbs adsorption equation, the area per molecule for Meta, Para1 and
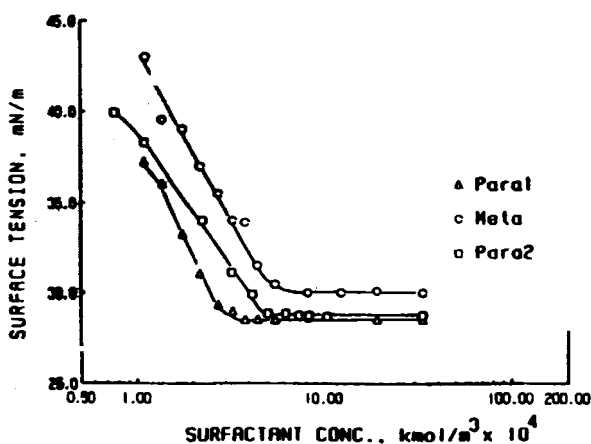

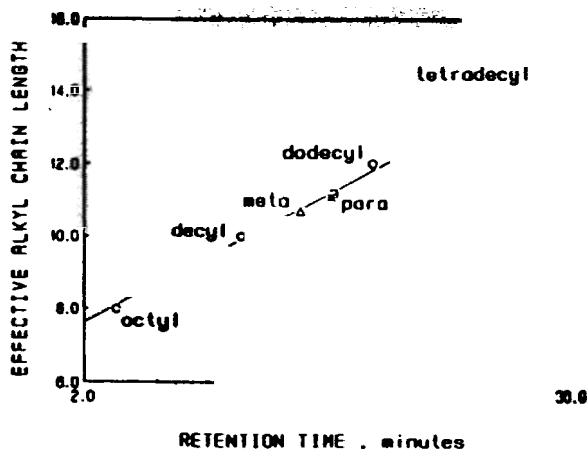Fig. 1. Surface tension of alkylxylenesulfonate solutions.

Fig. 2. Relative hydrophobicity of alkylxylenesulfonates.

Para2 was calculated to be 0.6 nm², 0.46 nm² and 0.66 nm², respectively. The area per molecule of Meta and Para2 is similar. The higher surface activity of Para2 as compared to Meta is therefore due to its higher hydrophobicity. However, the area per molecule of Para1 is smaller than that of Para2. Thus, even though the hydrophobicities of Para1 and Para2 are similar, Para1 is more surface active due to lower steric constraints to the packing of the molecules at the interface and in the micelles. The reason for the precipitation of the ortho-xylenesulfonate is due to the inability of the molecules to pack in the micelles due to high steric constraints. Since the surfactant monomers cannot pack into the micelles and also since it is unfavorable for them to remain in the aqueous phase, the surfactant precipitates out.

Mixed micelle formation

The effect of the position of the sulfonate and methyl groups on the benzene ring on the behavior of these surfactants in mixtures was investigated by measuring the mixed micelle formation of meta-xylenesulfonate and para-xylenesulfonate (Para1).

Surface tension was used to measure the CMC of the mixtures of the two surfactants and the results are given in Fig. 3. Also, the theoretical CMC values for the different mixtures calculated
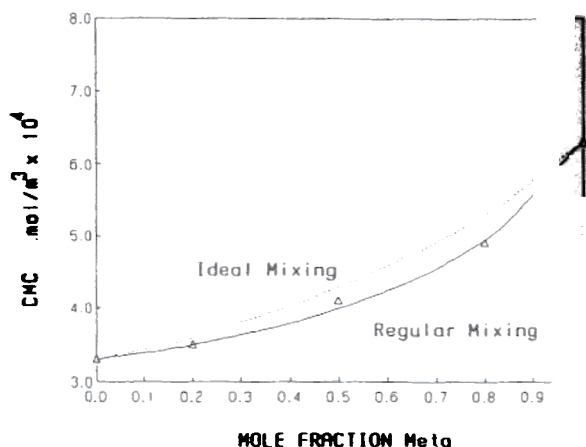
Fig. 3. CMC of mixtures of para-xylenesulfonate (Para1) and meta-xylenesulfonate (Meta).

using the ideal solution and regular solution theories are shown in the figure and it can be seen that the system shows a small negative deviation from the ideal behavior. This is interesting because mixtures of similar surfactants normally show ideal behavior [20,21]. Regular solution theory fits the data well with an interaction parameter (W) of −0.28. The deviations from ideality can be attributed to the difficulty in packing of the molecules in the mixed micelles [22]. Even though regular solution theory adequately fits the data, the validity of the thermodynamic assumptions for the system had to be verified [23]. Microcalorimetry was used to verify the assumptions and the results are discussed below.

Enthalpy of micellization

Calorimetry has been used extensively to study micellization of surfactants and has proved to be a valuable tool for understanding the formation and structure of micelles [24–26]. For example, based on their study of heat capacity, Mazer and Olofsson [26] found that the major contribution to the heat capacity change for micelle formation of dodecyl sulfate arises from changes in the alkyl chain and that the changes in the head group capacity are of secondary importance. In his work on the micellization of polyoxyethylene glycol dodecyl ethers, Olofsson [27] observed that the enthalpy of micellization corresponds to the dehydration of between 2 and 2.5 ethylene oxide groups implying that the rest of the ethylene oxide groups remain in full contact with water. Interestingly, the contribution of the alkyl chain to dilution enthalpy was zero while it dominated the entropy of micellization.

The calorimetric data for the three alkylxylene-sulfonates are given below.

Enthalpy of micellization of para-xylenesulfonate (Para1)

The heat of dilution data of premicellar and micellar Para1 solutions are given in Tables 1 and

TABLE 1

Heat of dilution of premicellar solutions

$10^4 C_{initial}$ (kmol m^{-3})	$10^4 C_{final}$ (kmol m^{-3})	ΔH_{dil}^a (cal mol^{-1})
3.11	2.02	−120
3.11	2.56	−116
3.11	2.10	−118

^{a}Average value is −118 cal mol^{-1}.

2, respectively. In these tables $C_{initial}$ and C_{final} represent the initial and final concentrations of the solutions, respectively, ΔH_{dil} and ΔH_m represent the enthalpies of dilution and micellization, respectively and Q_{dil} represents the heat of dilution.

The dilution of premicellar solutions results in an exothermic heat change of −118 cal mol^{-1}, and this heat results from the dilution of sulfonate monomers. For the dilution of micellar solutions, demicellization accounts for the bulk of the heat change, which for Para 1 is endothermic. The micellization enthalpy (ΔH_m) values are given in the fourth column of Table 2 and show excellent consistency with a mean value of −1091 cal mol^{-1}.

Enthalpy of micellization of meta-xylenesulfonate (Meta)

The heat of dilution results of premicellar and micellar Meta solutions are given in Tables 3 and 4, respectively.

The mean heat of monomer dilution is −36 cal mol^{-1}. Applying this correction to data obtained with demicellized solutions and using a CMC of

TABLE 2

Heat of dilution of micellar solutions

$10^4 C_{initial}$ (kmol m^{-3})	$10^4 C_{final}$ (kmol m^{-3})	$10^4 Q_{dil}$ (cal)	ΔH_m^a (cal mol^{-1})
5.77	2.80	3.93	−1041
8.92	2.80	5.44	−1084
1.13	2.58	4.87	−1148

^{a}Average value is −1091 cal mol^{-1}.

TABLE 3

Heat of dilution of premicellar solutions

$10^4 C_{initial}$ (kmol m^{-3}]	$10^4 C_{final}$ (kmol m^{-3})	ΔH_{dil}^a (cal mol^{-1})
6.22	4.96	−33
6.22	4.97	−39

^{a}Average value is −36 cal mol

TABLE 4

Heat of dilution of micellar solutions

$10^4 C_{initial}$ (kmol m^{-3})	$10^4 C_{final}$ (kmol m^{-3})	$10^4 Q_{dil}$ (cal)	ΔH_m^a (cal mol^{-1})
9.96	5.67	4.94	−745
9.96	5.68	4.74	−720
12.0	6.01	9.31	−858

^{a}Average value is −774 cal mol$^-$

$6.3 \cdot 10^{-4}$ kmol m^{-3}, the above data yield a mean ΔH_m of −774 cal mol^{-1}.

Enthalpy of micellization of para-xylenesulfonate (Para2)

The heat of dilution data of premicellar and micellar Para2 solutions are given in Tables 5 and 6, respectively.

The mean heat of monomer dilution is −354 cal mol^{-1}. Applying this correction to the data obtained with demicellized solutions and using a CMC of $5.3 \cdot 10^{-4}$ kmol m^{-3} yields a mean ΔH_m of −1671 cal mol^{-1}.

TABLE 5

Heat of dilution of premicellar solutions

$10^4 C_{initial}$ (kmol m^{-3})	$10^4 C_{final}$ (kmol m^{-3})	ΔH_{dil}^a (cal mol^{-1})
2.86	1.43	−363
2.86	1.42	−348
3.98	1.98	−365
3.98	2.00	−344

^{a}Average value is −354 cal mol^{-1}.

TABLE 6

Heat of dilution of micellar solutions

$10^4 C_{initial}$ (kmol m^{-3})	$10^4 C_{final}$ (kmol m^{-3})	$10^4 Q_{dil}$ (cal)	ΔH_m^a (cal mol^{-1})
10.6	5.2	5.3	−1652
10.6	5.1	5.0	−1677
8.52	4.3	4.96	−1685

^{a}Average value is −1671 cal mol^{-1}.

The free energy of micellization ΔG according to the phase separation model [28] is given by

$$\Delta G = 2RT \ln(\text{CMC}) \tag{1}$$

where CMC is the critical micelle concentration expressed in mole fractions, R is the gas constant and T is the absolute temperature.

The entropy of micellization ΔS is then calculated from the following equation

$$\Delta S = (\Delta H - \Delta G)/T \tag{2}$$

The values for the thermodynamic parameters of micellization for the three surfactants are shown in Table 7.

There is no particular trend in the enthalpy and entropy of micellization with the CMC of the surfactants. Both the enthalpy and entropy are favorable for the micellization of the surfactants. The enthalpies of the more hydrophobic *para*-xylenesulfonates are more exothermic than those of the *meta*-xylenesulfonate. However, these differences are very small when compared to the micellization entropy of the surfactants which is the main driving force for the micellization. The positive entropy change arises from the removal of water

TABLE 7

Thermodynamic parameters of micellization

Surfactant	ΔH (cal mol^{-1})	ΔG (cal mol^{-1})	ΔS (cal K^{-1} mol^{-1})
Para1	−1091	−15226	45
Meta	−774	−14407	43
Para2	−1671	−14626	41

molecules structured around the hydrocarbon chain.

Excess enthalpy of mixed micelle formation

Mixed micellization of the *meta*-xylenesulfonate and *para*-xylenesulfonate (Para1) showed negative deviations from ideal solution theory and it was found that regular solution theory adequately fitted the mixed CMC data. However, it has been shown that in certain systems, thermodynamic assumptions of the regular solution theory are not valid, even though the theory fits the surface tension data well [22,23]. Therefore, it was considered important to verify the validity of the assumptions prior to using the theory.

Regular solution theory is based on the assumption that the excess Gibbs free energy of mixing is given by

$$\Delta G_{mix} = X_1 X_2 WRT \tag{3}$$

where X_1 and X_2 are the mole fractions of the two surfactants in the mixed micelle and W is the interaction parameter. Regular solution theory also assumes that the excess entropy and volume of mixing are zero and hence the excess enthalpy of mixing is given by

$$\Delta H_{mix} = X_1 X_2 WRT \tag{4}$$

The excess enthalpy of mixed micelle formation of the two surfactants in this study at various surfactant compositions is shown in Fig. 4. The fact that the excess enthalpy of mixing is non-zero at all compositions suggests that the mixtures are non-ideal and the exothermic value indicates that the deviations are negative with respect to ideal mixing. An interaction parameter $W = -0.21$ fits the calorimetric data and it compares well with $W = -0.28$ obtained from the surface tension data. This indicates that the assumption of the regular solution theory (excess entropy of mixing is zero) is valid for the system of *meta*-xylenesulfonate and *para*-xylenesulfonate (Para1).
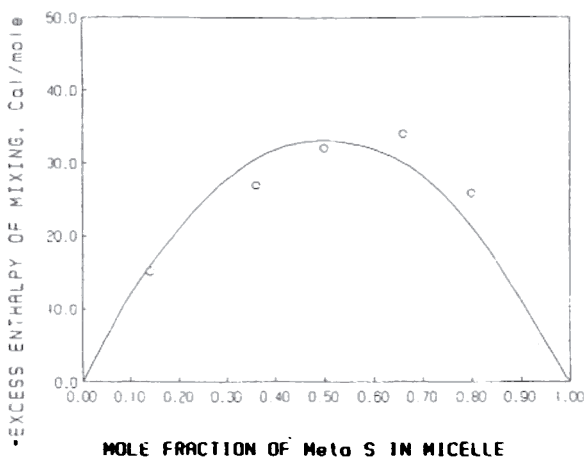
Fig. 4. Excess enthalpy of mixing of *para*-xylenesulfonate (Para l) and *meta*-xylenesulfonate (Meta).

Summary

The position of sulfonate and methyl groups on the benzene ring of alkylxylenesulfonates is shown to play an important role in determining the properties of these surfactants. The surfactant with the sulfonate group in the para position is more hydrophobic and has a lower CMC than the surfactant with the sulfonate group in the meta position. The surfactant with the sulfonate group in the ortho position precipitated in the presence of 0.03 kmol m^{-3} NaCl. The two *para*-xylenesulfonates with different positions of the methyl groups, though having the same hydrophobicity, have different surface activity and CMC values. This suggested that the steric constraints to the packing of the molecules at the liquid/air interface and in the micelles is the main mechanism for the observed differences in the behavior of the structurally different alkylxylenesulfonates. The position of the sulfonate group is found to be more critical than those of the methyl groups on the benzene ring in determining the behavior of the surfactants.

Microcalorimetric studies showed that enthalpy and entropy are favorable for micellization and entropy is the main driving force for the micellization of the surfactants.

The mixed micellization of *meta*-xylenesulfonate

and *para*-xylenesulfonate (Para l) is non-ideal. Regular solution theory fits the data well with an interaction parameter of −0.28. Microcalorimetric measurements of the excess enthalpy of mixed micelle formation showed that the thermodynamic assumptions of the theory are valid for the surfactant system studied.

Acknowledgments

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