• Technical

Studies of Ester-Containing Surfactants: Effect of Position of Ester Group on Surface Tension

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ABSTRACT

The properties in aqueous solution of the series of sodium sulfoalkyl alkanoates of general formula $C_nH_{2n+1}COO(CH_2)_mSO_3Na$ (where n = 9,10, and 11; m = 2,3, and 4) have been investigated by measurements of surface tension. According to the Gibbs absorption isotherm equation, the slope of the curves of the surface tension vs. logarithm concentration gives the amount of surfactant adsorbed. The surface tension of sodium 4-sulfobutyl ester derivatives was lower than that of sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives in the region below the critical micelle concentration. The areas occupied/molecule for sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives were in the range 51-56 Å^2, which agreed with the value 50 Å^2 obtained for the sodium dodecyl sulfate. However, the values of the areas occupied/molecule for sodium 4-sulfobutyl ester derivatives were 63-65 Å^2, which was large compared with that of sodium dodecyl sulfate. The effect of the ester group in the sodium 4-sulfobutyl ester derivatives on the orientation of the molecule at the air-water interface is different from the effect of the ester group in the sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives on the orientation of the molecule at the air-water interface.

INTRODUCTION

In previous papers (1,2), a series of sodium sulfoalkyl alkanoates, $RCOO(CH_2)_jSO_3Na$, was prepared by the reaction of sodium isethionate, propane soltone, and butane sultone with normal fatty acids of 10-, 11-, and 12-carbon atoms. The effect of the position of the ester group on some surface active and colloidal properties of these surfactants in aqueous solution was investigated. The results of these investigations demonstrated that the critical micelle concentration (CMC) of these surfactants increases when the ester group moves toward the more central position of the hydrocarbon chain. The Kraft point, stability to hydrolysis, and other bulk properties were influenced strongly by a change of the position of the ester group. However, the results of these investigations did not reveal satisfactorily the physical-chemical properties of the surfactant solutions. Therefore, to supplement knowledge regarding the effect of the position of the ester group on the physical-chemical properties of sodium sulfoalkyl alkanoates, including the ester group, this article describes the surface active properties of a series of these surfactants. Specifically, the surface tensions of aqueous solutions of the surfactants were measured. Furthermore, the amount of surfactant adsorbed at the air-water interface was estimated from the slope of the surface tension vs. logarithm of concentration curves. The relation between the molecular structure of these surfactnats and area occupied/molecule is discussed and compared with that of sodium dodecyl sulfate (SDS).

In the present experiment, the surface tension was measured in systems with no added salt, which were adopted by Robins and Thomas (3). The addition of salt remarkably affects the micellar properties of the solution, and the latter are influenced by the ester group in the alkyl chain of the surfactants.

EXPERIMENTAL PROCEDURES

Materials

The sodium 2-sulfoethyl alkanotate, 3-sulfopropyl alkanotate, and 4-sulfobutyl alkanoates, $RCOO(CH_2)_2SO_3Na$, $RCOO(CH_2)_3SO_3Na$, and $RCOO(CH_2)_4SO_3Na$, were prepared from corresponding fatty acids or sodium alkanotates (capric, undecylenic, and lauric acid) of a high purity by reaction with sodium isethionate, propane sultone, and butane sultone, according to the method described in the papers previously mentioned. The products were recrystallized three times from methanol or ethanol and then extracted with petroleum ether for 200 hr to remove traces of unreacted fatty acid. Each pure material was obtained as a white, flake powder. The sodium sulfoalkyl alkanoates prepared are as follows: sodium 2-sulfoethyl caprate and laurate (9C-2 and 11C-2); sodium 3-sulfopropyl caprate, undecylate and laurate (9C-3, 10C-3, and 11C-3); and sodium 4-sulfobutyl caprate and laurate (9C-4 and 11C-4).

SDS was prepared from dodecyl alcohol and chlorosulfonic acid by the method of Dreger, et al., (4). The product was recrystallized five times from ethyl alcohol and then extracted with petroleum ether for 200 hr.

The purity of the compounds was ascertained by IR spectra and also from results of elemental analysis. Analysis of these compounds for carbon and hydrogen gave the calculated values for their composition within ±0.3%.

Method

The surface tensions of aqueous solutions of the surfactants were measured by using a Wilhelmy plate apparatus described in a previous paper. All the measurements were conducted at 30±0.5 C. The water used in preparing the solutions was prepared by passage through an ion exchange resin column and then by distilling from dilute alkaline potassium permanganate solution in a Pyrex glass vessel. The surface tension of the water was 72±0.1 dyne/cm at 25 C, and the specific conductivity of the water was 1.1×10^{-6} mho/cm at 25 C.

RESULTS AND DISCUSSION

The surface tension of aqueous solutions of the seven surfactants containing ester groups is shown in Figure 1 as a

TABLE I

Critical Micelle Concentration and Surface Active Properties

		Surface tension and adsorption		
Surfactants	CMC[a] x 10^3 (mol • $l.^{-1}$)	γ at CMC (dyne • cm^{-1})	Γ x 10^{10} (mole • cm^{-1})	Area • $Molec.^{-1}$ $Å^2$
$C_9H_{19}COO(CH_2)_2SO_3Na$	20.5	39.1	3.22	51.7
$C_9H_{19}COO(CH_2)_3SO_3Na$	16.0	41.3	3.20	52.0
$C_9H_{19}COO(CH_2)_4SO_3Na$	10.4	41.1	2.54	65.5
$C_{10}H_{21}COO(CH_2)_3SO_3Na$	6.6	41.5	3.19	52.1
$C_{11}H_{23}COO(CH_2)_2SO_3Na$	4.6	38.8	3.08	54.1
$C_{11}H_{23}COO(CH_2)_3SO_3Na$	3.7	41.1	2.99	55.6
$C_{11}H_{23}COO(CH_2)_4SO_3Na$	2.2	42.3	2.63	63.2
$C_{12}H_{25}OSO_3Na$	6.4	38.1	3.31	50.2

[a]CMC = critical micelle concentration.

function of the logarithm of their molar concentration. All curves of surface tension against concentration show an abrupt inflection at the point which correspond to the CMC values obtained by the electro conductivity method in a previous paper (1). The CMC values of these surfactants are shown in Table I.

It is evident from Figure 1 and Table I, that the surface tension at the same molar concentration in the range below the CMC and the CMC value of a series of sodium sulfoalkyl alkanoates decreased with the increase in the length of the hydrocarbon chain. However, a comparison of the decrease/methylene group in the fatty acid portion and the decrease/methylene group situated between sulfonate and ester group on the CMC showed that the former was larger than the latter. For the comparison of the surface tension at the same molar concentration in the range below the CMC, the decrease/methylene group was similar. Namely, the decrease of the surface tension at the same molar concentration in the range below the CMC and the CMC value of the surfactants, whose methylene groups inserted between the sulfonate and ester group were constant, i.e., 9C-3, 10C-3, and 11C-3, were larger than that of the surfactants with the same number of carbon atoms in the fatty acid portion, i.e., 11C-2, 11C-3, and 11C-4 and 9C-2, 9C-3, and 9C-4. This result suggests that the surface active and colloidal property of the methylene unit situated between sulfonate and ester group is lower than that of the methylene unit in the fatty acid portion.

The comparison of the surface tension curves of the surfactants which has the same number of carbon atoms in the fatty acid, i.e., 11C-2, 11C-3, and 11C-4 and 9C-2, 9C-3, and 9C-4, shows that the slope of sodium 4-sulfobutyl ester derivatives are remarkably less than that of the sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives at the straight portion near the CMC. It is widely known that decrease of the surface tension in the region below the CMC indicates the adsorption of the surfactant molecule at air-water interface and that, in the region above the CMC, the surfactant molecule is packed closely at the surface of solution (5). Accordingly, the slope of the straight portion near the CMC suggests a saturated adsorption of the surfactant molecule at air-water interface.

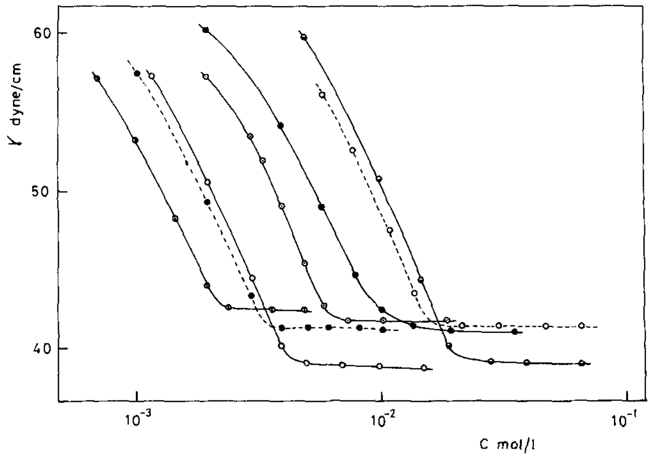

FIG. 1. Surface tension of aqueous solution of sodium sulfoalkyl alkanoates: 11C-4 (——●——), 11C-3 (--●--), 11C-2 (——○——), 10C-3 (——⊙——), 9C-4 (——●——), 9C-3 (--○--) and 9C-2 (——⊖——).

The amount of adsorption of surfactant Γ at the air-water interface can be calculated by applying the Gibbs adsorption isotherm equation:

$$\Gamma = -\frac{1}{2RT} \times \frac{\partial\gamma}{\partial \ln C}$$

where γ is the surface tension and C is the molar concentration. $\partial\gamma/\partial \ln C$ values were obtained from linear portion of surface against logarithm concentration curve in region near the CMC. Area A occupied per surfactant molecule is calculated from the amount of surfactant adsorbed by $A = 1/N\Gamma$: where N is the Avogadro number. The amount of the saturated adsorption and area occupied/surfactant molecule of sodium sulfoalkyl alkanoates series are shown in Table I. The surface tension of SDS also is included in Table I for comparison.

As is evident from the Table I, the area occupied/molecule for sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives were in the range 51-56 $Å^2$, which agrees with the value ca. 50 $Å^2$ obtained for SDS. These values almost coincided with the theoretical value obtained from the model molecular structure. On the other hand, the area occupied/molecule for sodium 4-sulfobutyl ester derivatives was 63-65 $Å^2$, which was large compared with the values of area occupied/molecule for sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives. That is, in the region near the CMC, the number of molecules of sodium 4-sulfobutyl ester derivatives to give saturated adsorption is less than that of molecules of the sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives at the air-water interface.

The interpretation of these data can be made by suggesting a difference of orientation of the surfactant molecules at the air-water interface. Sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives with the shorter methylene chain situated between the sulfonate and ester group are perpendicular to the air-water interface, which agrees with orientation of ordinary surfactants, such as SDS. On the other hand, for the sodium 4-sulfobutyl ester derivatives, it can be considered that a longer methylene chain situated between the sulfonate and ester group has a specific inclination at the surface of aqueous solution. Therefore, by comparison with the sodium 2-sulfoethyl and 3-sulfopropyl ester derivatives, the sodium 4-sulfobutyl ester derivatives should give a loose-packing in the region near and above the CMC.

For a series with the same number of carbon atoms in the surfactants, i.e., 9C-4, 10C-3, and 11C-2, moving the ester group from the terminal position to a more central position in the hydrocarbon chain increased the CMC value and also increased the surface tension at the same molar concentration in the region below the CMC. The phenomenon is explained below.

For a given number of carbon atoms, moving the ester group from the ionic head to a more central position in the hydrocarbon chain reduced the hydrophobic nature of the hydrocarbon chain, because the affinity of the ester group for water increases. Thus, it might be expected that the ester group further removed from the sulfonate would increase the CMC and would increase the solubility of the surfactant in water. Accordingly one may consider that surface activity of the surfactant is lower.

To put it differently, these results can be explained by considering the surface active and collodial property of the methylene unit situated between sulfonate and ester group to be lower than that of the metylene unit in the fatty acid portion.

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