Surface Activity of Sodium Salts of *alpha*-Sulfo Fatty Esters: The Air-Water Interface[1]

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Abstract

Adsorption at the air-water interface of sodium hexyl α-sulfopelargonate, sodium heptyl α-sulfopelargonate, sodium methyl α-sulfomyristate, and sodium methyl α-sulfopalmitate has been investigated.

The amount of surfactant adsorbed at the interface has been obtained by the application of a simple form of the Gibbs equation to surface tensions of aqueous solutions of varying surfactant ion concentration but at constant counterion (Na^+) concentration. Surface tensions were determined by using the drop-volume method. Counterion concentrations of 0.01 and 0.04N were used. Cross-sectional areas for the surfactant anions are in the range 44 to 59Å^2 (independent of concentration) and are consistent with close packing in which the carbon chains are perpendicular to the interface.

For each surfactant, increase in counterion concentration from 0.01 to 0.04N results in a surface-tension decrease of about 7.5 dyne/cm. This effect can be predicted by using bulk activity coefficients from the Debye-Hückel theory.

Dependence of surface tension on carbon chain length indicates that the carbon chains of the four compounds behave similarly at the air-water interface.

Introduction

THE OBJECTIVE OF THE STUDY is to investigate the adsorption of the sodium salts of various α-sulfo fatty esters from aqueous solutions. The preparation from animal fats of various sulfo-derivatives possessing surfactant properties has been reported extensively by Stirton and co-workers (1–8). They have surveyed both surface and bulk properties of aqueous solutions of compounds of the type $RCH(SO_3Na)COOR'$ and have found that the compounds are biodegradable. Also, the compounds behave as detergents (Terg-O-Tometer tests) when $R \geqslant C_{12}H_{25}$— and R′ is small, e.g., —CH_3, and as wetting agents (9,10) when R and R′ are of comparable length, e.g., $R = R' = C_7H_{15}$—.

It is of interest to study the surface activity of compounds representative of both the detergent and the wetting types, with a view to elucidating the basic differences in their behavior. For instance, the Draves test is widely used to measure the efficiency of wetting agents, but the criterion for success of a particular molecular species is by no means clear although diffusion and adsorption factors operate (11,12).

Normally, wetting and detergency processes involve a solid, and much can be learned about the manner in which surfactant molecules are oriented at a liquid-solid interface from the amount of heat evolved upon immersion of the solid into surfactant solutions of different concentrations (13–15) together with knowledge of the amount of surfactant adsorbed. At liquid-vapor (and liquid-liquid) interfaces the dependence of surfactant behavior on molecular structure, and upon ionic strength of the solution, can be elucidated by analysis of the surface tension data.

Thermodynamics of Surfactant Adsorption

The Gibbs adsorption equation has been used by several workers (16–25) to determine the amount of surfactant adsorbed from solution. The thermodynamics of adsorption from electrolyte solutions have been formulated by Guggenheim (26), and application to surfactant solutions has been carried out by, for example, Pethica (19). The complete form of the Gibbs equation, for a solution at constant temperature and pressure, containing solute species i, is

$$d\gamma = -RT\sum_i (\Gamma_i - m_i M_{H_2O}\Gamma_{H_2O})\, d(\ln a_i), \qquad [1]$$

where m and a are the molality and absolute activity, and $1000M_{H_2O}$ is the molecular weight of water. The term Γ_i is the *total* concentration of species i in the region of the interface. The surface concentration Γ'_i can be defined as

$$\Gamma'_i = \Gamma_i - m_i M_{H_2O}\Gamma_{H_2O}. \qquad [2]$$

Pethica, in particular, pointed out that an aqueous solution of A^+B^- (e.g., $A^+ = Na^+$, $B^- = RCH(SO_3^-)$-$COOR'$) would contain five principal species, A^+, B^-, H_3O^+, OH^-, and H_2O. With such a system Γ'_{B^-} cannot be obtained with certainty from a simple form of Equation 1. The presence of excess indifferent electrolyte A^+C^-, however, suppresses exchange at the interface between Na^+ and H_3O^+ so that only $d(\ln a_{B^-})$ need be considered in the summated terms of Equation 1. The indifferent electrolyte also compresses the double layer at the interface so that $m_{B^-}M_{H_2O}\Gamma_{H_2O}$ in Equation 2 is negligible compared with Γ_{B^-}, and Γ'_{B^-} can then be taken as the surface concentration of B^- in the charged monolayer at the surface. Furthermore, the activity coefficient (f given by a = mf) of one electrolyte is independent of concentration in the presence of excess concentration of another electrolyte (27), i.e., the ionic atmosphere of B^- is constant and $d(\ln f_{B^-})$ can be equated to zero. The combined result is that Equation 1 reduces to

$$d\gamma = -RT\Gamma'_B\, d(\ln m_{B^-}). \qquad [3]$$

Bulk surfactant concentrations of interest are of the order of 10^{-3} to 10^{-4}, and m_{B^-} can be equated to the molar concentration c_{B^-}. Under conditions of constant counterion concentration, changes in surface tension are entirely attributable to changes in bulk surfactant ion concentration, and the reciprocal of Γ'_B (moles/cm^2) can be used to obtain the area σ occupied by a surfactant ion at the interface.

The results reported herein are at concentrations in the vicinity of, and below, the critical micelle con-

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centration where plots of γ against $\ln c_{B^-}$ are linear, signifying according to Equation 3 that the amount of surfactant adsorbed is constant. The occurrence of a constant amount of surfactant adsorbed over a considerable range of concentration has been observed previously (21–23,25) for ionic surfactants and has been termed the region of saturation adsorption (25).

The thermodynamic arguments can be extended to provide an estimate of the effect of variation in counterion concentration upon actual surface-tension values. The surface-tension change $\gamma_2 - \gamma_1$, accompanying a change in counterion concentration from 1 to 2, is given (25) by integration of the Gibbs equation over this counterion concentration range:

$$\gamma_2 - \gamma_1 = -RT\Gamma'_{B^-} \int_1^2 (d \ln a_{A^+} + d \ln a_B). \qquad [4]$$

The activity coefficient of A^+B^- is related to the individual activity coefficients of A^+ and B^- by

$$f_\pm = (f_+ f_-)^{1/2}\text{; also } a_i = f_i m_i\text{, and } m_i \cong c_i \cdot$$

To integrate Equation 4 it is necessary to make the assumption that Γ'_{B^-} is independent of the change in total counterion concentration. Generally this assumption will be valid, provided there is a sufficient counterion concentration to satisfy the arguments leading to Equation 3 at the lowest counterion concentration used (Table I). Equation 4 then reduces to

$$\gamma_2 - \gamma_1 = -RT\Gamma'_B \left[\ln \frac{c_{A^+}(2)}{c_{A^+}(1)} + 2 \ln \frac{f_\pm(2)}{f_\pm(1)} \right] \cdot \qquad [5]$$

Activity coefficients have been calculated from the Debye-Hückel theory of electrolyte solutions.

Experimental Procedure

Materials

The four surfactants studied were prepared by Stirton et al. (2,5,6,7) and purified as follows.

Sodium hexyl α-sulfopelargonate $C_7H_{15}CH(SO_3Na)\text{-}COOC_6H_{13}$; abbrev. NaHexαSPelar, M.W. 344.5, was extracted with toluene, then recrystallized from ethanol and dried under vacuum.

Sodium heptyl α-sulfopelargonate $C_7H_{15}CH(SO_3\text{-}Na)COOC_7H_{15}$; abbrev. NaHepαSPelar, M.W. 358.5, was purified by extraction of aqueous alcoholic solution with diethyl ether. The ester was then crystallized from the alcoholic solution at −20C and recrystallized from absolute ethanol at −30C.

Sodium methyl α-sulfomyristate $C_{12}H_{25}CH(SO_3Na)\text{-}COOCH_3$; abbrev. NaMeαSM, M.W. 344.5, was crystallized twice from ethanol, then extracted with diethyl ether, and finally recrystallized from absolute ethanol.

Sodium methyl α-sulfopalmitate $C_{14}H_{29}CH(SO_3Na)\text{-}COOCH_3$; abbrev. NaMeαSPalm, M.W. 372.5, was twice crystallized from ethanol.

Sodium chloride, Baker Analyzed grade, was heated in a platinum crucible to 750C for three hours to remove surface active impurities.

Triply distilled water was used to prepare the solutions. The first distillation was from a block tin still. The second distillation was of dilute alkaline potassium permanganate solution from Pyrex glass. The water was then redistilled through a well-leached Pyrex apparatus. The surface tension of the water at 25C, obtained by using the drop-volume method, was 72.00 ± 0.05 dyne/cm, which compares well with the value in International Critical Tables of 71.97 ± 0.05 dyne/cm. The conductivity of the water in equilibrium with the atmosphere was approximately 1.1×10^{-6} mhos/cm.

Surface-Tension Determination

Few comparative studies are reported in the literature on methods of surface-tension determination, especially for surfactant solutions. The results of a study aimed at testing the reliability of methods of surface-tension determination have been reported elsewhere (28). The methods examined were the du Noüy ring, drop volume, Wilhelmy plate, and pendant drop. In brief, the conclusions reached were that the du Noüy method does not give reproducible values for surfactant solutions. The drop volume and Wilhelmy plate methods are reliable, and although the instruments gave slightly different values (at most 0.5 dyne/cm) of the surface tension of a given solution, the slopes of γ against ln c plots were identical. The pendant drop apparatus was rather crude, but, in spite of this, the results indicated that the method is also reliable for use with surfactant solutions. The drop-volume method is the most convenient to use and was employed to obtain the results reported herein (28), although the Wilhelmy plate apparatus was used to investigate the slow decrease in surface tension with time found with NaMeαSM and NaMeαSPalm solutions.

Results and Discussion

Aging

Before proceeding to the presentation and interpretation of the results of surface-tension determinations, it is necessary to discuss the decrease in surface tension with time which was found for NaMeαSM and NaMeαSPalm solutions by using the Wilhelmy plate method. Typically the surface tension decreased at the rate of about 0.1 dyne/cm per hour and continued for at least 24 hr. The phenomenon of aging, as it is often called, is not new (29,30), and many explanations have been suggested although evidence for a particular cause is often inconclusive.

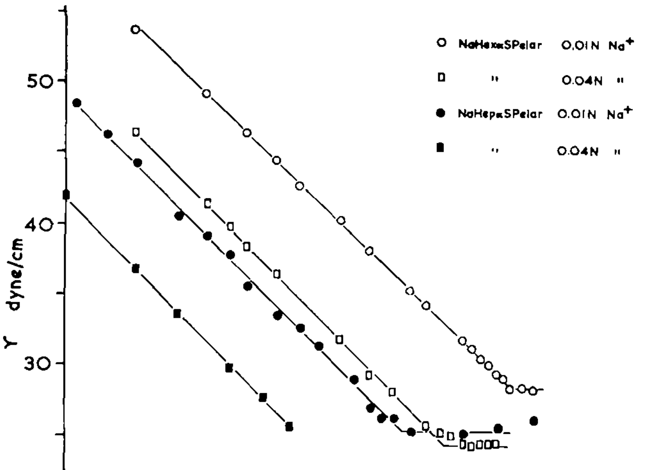

FIG. 1. Plots of surface tension (25C) against logarithm of molar concentration for solutions of sodium hexyl α-sulfopelargonate and sodium heptyl α-sulfopelargonate in 0.01N and 0.04N sodium ion concentrations.

A large number of experiments were conducted, both severally and collectively, to reduce or remove aging. The principal causes considered arise from: a) the presence of multivalent ions as impurities in the water and in the esters (31,32), b) impurities which are themselves surface-active (16), e.g., sodium α-sulfomyristic acid, c) slow attainment of equilibrium at the surface (33,34), d) contamination from the atmosphere, e) reorientation of the molecules in the monolayer (35), and f) slow hydrolysis (30).

The cause of aging could not be ascertained, nor was it possible to reduce the rate. There is insufficient evidence, from studying only four compounds, to suggest that aging occurs as a result of NaMeαSM and NaMeαSPalm molecules with one long chain but is inhibited when two chains are present. It is interesting to note that a plot of γ against ln c for NaMeαSM, obtained by extrapolating the γ against time (aging) curves to zero time, had a slope identical to that obtained by the drop-volume method.

Variation with Surfactant Concentration

Surface tensions of NaHexαSPelar, NaHepαSPelar, NaMeαSM, and NaMeαSPalm solutions in 0.01N and 0.04N sodium ion concentrations are given in Figures 1 and 2 as plots of γ against ln c. The portions of the plots in the concentration range below the cmc give the amount of surfactant adsorbed Γ'_{B^-} according to Equation 3, and the reciprocal of Γ'_{B^-} is the area σ occupied in the interface by a surfactant ion. Values of Γ'_{B^-} and of σ are given in Table I. The limits of precision on the surface-tension values lead to uncertainties of less than 1 Å^2/molecule on σ values, except for NaMeαSPalm in 0.04N sodium ion concentration, where the uncertainty is between 1 and 2 Å^2/molecule. The plots of γ against ln c are linear and have zero slope at concentrations above the cmc, which is a good indication of the purity of the compounds.

Molecular Cross-Sectional Areas

Scale models (1:10^8) of all compounds give cross-sectional areas of about 50Å^2/molecule if the model is oriented with the carbon chain(s) of all compounds out-stretched, closely-packed, and normal to the interface. It is reasonable to assume that the carbon chains are on the air "side" of the interface and that the polar groups are in the solution. A major factor, which cannot be accounted for in terms of scale models, is that the surfactant ions will have water molecules attached to the polar groups, which increase the cross-sectional area.

TABLE I

Amount of Saturation Adsorption and Areas for Adsorbed Surfactant from Equation 5

Compound	Na$^+$ conc. (N)	$\Gamma'_{B^-} \times 10^{10}$ (moles/cm^2)	σ (Å^2/molecule)
NaHexαSPelar	0.01	2.80	59
NaHexαSPelar	0.04	2.92	57
NaHepαSPelar	0.01	2.93	57
NaHepαSPelar	0.04	2.97	56
NaMeαSM	0.01	3.03	55
NaMeαSM	0.04	3.27	51
NaMeαSPalm	0.01	3.76	44
NaMeαSPalm	0.04	3.52	47

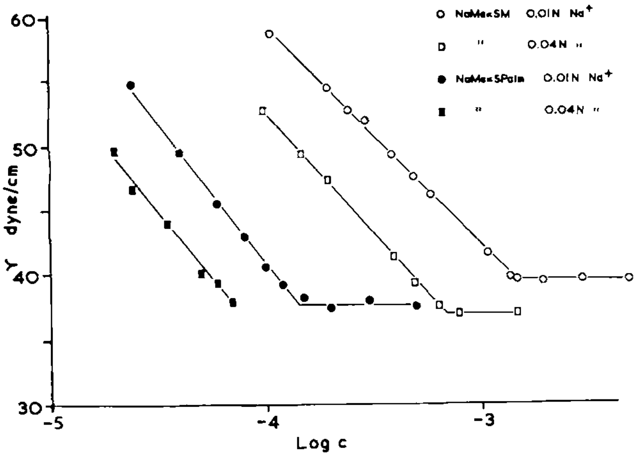

FIG. 2. Plots of surface tension (25C) against logarithm of molar concentration for solutions of sodium methyl α-sulfomyristate and sodium methyl α-sulfopalmitate in 0.01N and 0.04N sodium ion concentrations.

It is interesting to find that both carbon chains of NaHexαSPelar and NaHepαSPelar are able to pack closely together to give areas which are only slightly greater than those for NaMeαSM and NaMeαSPalm. The main conclusion from consideration of the cross-sectional areas is that the carbon chains of all four compounds behave in a similar manner at the interface, and on this basis there is no distinction between the wetting types (NaHexαSPelar and NaHepαSPelar) and the detergent types (NaMeαSM and NaMeαSPalm).

Influence of Length of Carbon Chain

The molecular species serve to demonstrate the influence of chain length upon the surface tension of a solution. There is a decrease in surface tension of about 10.5 dyne/cm, at a given surfactant concentration, from NaHexαSPelar to NaHepαSPelar, i.e., for the addition of one $-CH_2-$ group. The addition of two $-CH_2-$ groups to the carbon chain of NaMeαSM, which gives NaMeαSPalm, results in a surface-tension decrease of about 18.5 dyne/cm, i.e., almost twice the decrease found for the pelargonates. There is, therefore, added confirmation that the carbon chains of all four compounds behave similarly at the air-water interface.

It has long been recognized that there is cohesion between carbon chains at an air-water interface (36). (With oil-water interfaces such cohesion is absent so that comparison between air-water and oil-water interfaces can supply information about the contribution of the cohesive forces to the over-all behavior of a surfactant species.) In the absence of oil-water data it is interesting to make a rough calculation of the contribution of a methylene group to the surface tensions of the solutions by using Langmuir's interpretation (37) of Traube's rule (38). Traube found that, for the addition of a methylene group to a surface-active species, the concentration required to give a particular surface tension was reduced by approximately one-third. Langmuir (37) offered the explanation that the drop of one-third in concentration for each CH_2 group of a homologous series arises from the work w required to transfer one CH_2 group from the bulk solution to the interface. To a rough approximation, w is given by

$$w = RT \ln \frac{c_1}{c_2}, \qquad [6]$$

where c_1 and c_2 are the bulk concentrations, such that according to Traube's rule $c_1/c_2 \simeq 3$. The value of w is then about 640 cal/mole of CH_2 groups. Interactions of a cohesive nature are not included in this interpretation, and Traube's rule can only be really tested with such nonionizable solutes as alcohols.

For ionizable surfactants interaction between the polar groups should be included because this can be expected to be dependent upon the distance of separation of the surfactant ions. However it is instructive to assume that the contribution to the energy of desorption of a $-CH(SO_3^-)COO-$ group for each surfactant is constant under the experimental conditions.

For NaMeαSM at 0.01N Na^+ concentration, $\gamma = 50$ dyne/cm when $c_{B^-} = 3.7 \times 10^{-4}$M; for NaMeαSPalm, $\gamma = 50$ when $c_{B^-} = 3.8 \times 10^{-5}$M. The ratio of the bulk concentrations is 9.75, which agrees well with the expectation of 3^2 for the addition of two CH_2 groups. The energy of desorption of a CH_2 group given by Equation 8 is 676 cal/mole, which compares favorably with 640 cal/mole.

For NaHexαSPelar, $\gamma = 47.5$ when $c_{B^-} = 5.13 \times 10^{-4}$M; for NaHepαSPelar, $\gamma = 47.5$ when $c_{B^-} = 1.26 \times 10^{-4}$M, giving a concentration ratio of 4.1, as opposed to 3 if Traube's rule were obeyed. The corresponding energy of desorption is 835 cal/mole of CH_2.

It is possible that NaMeαSM and NaMeαSPalm give good agreement with Traube's rule because, with only one carbon chain per molecule, there is considerable freedom of the hydrocarbon chain and little cohesion between neighboring carbon chains. The cross-sectional areas (Table I) are then determined by the size of the polar groups and attached water molecules. With NaHexαSPelar and NaHepαSPelar however, each molecule has two carbon chains packed side by side, and the cross-sectional areas (shown in Table I to be slightly greater than those of the other two compounds) may arise from closely packed carbon chains, which have little freedom. The result is that cohesive forces operate between them.

Effect of Sodium Ion Concentration

The cross-sectional areas shown in Table I are not significantly affected by change in sodium ion concentration from 0.01N to 0.04N. The surface tension, for a given surfactant concentration, is greatly reduced by an increase in counterion concentration. A fourfold increase in ionic strength (I = total electrolyte concentration) produces a surface-tension decrease of 7 or 8 dyne/cm, which is apparently independent of molecular structure.

Changes in surface tension resulting from changes in sodium ion concentration have been calculated according to Equation 5. Activity coefficients for Na^+B^- were calculated by using the form of the Debye-Hückel equation which takes into account ionic size:

$$\log f_\pm = \frac{-0.509\sqrt{I}}{1 + 0.33 \times 10^8 a\sqrt{I}} \qquad [7]$$

TABLE II

Calculated and Observed Changes in Surface Tension Resulting from Changes in Counterion Concentration

Calculated			Observed	
$Å^2$	$\Gamma'_{B^-} \times 10^{10}$ moles/cm^2	$\gamma_2 - \gamma_1$ dyne/cm	$Å^2$	$\gamma_2 - \gamma_1$ dyne/cm
45	3.69	11.1	46	6.8
50	3.32	9.96	53	7.7
55	3.02	8.4	57	7.5
60	2.77	8.3	58	8.2

where a is the mean distance of approach of the ions. The constants in Equation 7 are for 25C.

The values of $\log f_\pm$ are the same for all four surfactants for a single value (taken as 3×10^{-8} cm) of a. The difference $\gamma_2 - \gamma_1$ in surface tension as given by Equation 5 will therefore depend on Γ'_{B^-} for a given ionic strength (Table I). Calculated values of $\gamma_2 - \gamma_1$ are given, together with experimentally observed values, in Table II. The following values were used in the calculations:

$a = 3 \times 10^{-8}$ $I = 0.01$ $\log f_\pm = 0.0463$

$a = 3 \times 10^{-8}$ $I = 0.04$ $\log f_\pm = 0.0848$

Agreement is considered to be satisfactory when it is remembered that the activity coefficients given by the Debye-Hückel equation are only approximate for the systems under investigation.

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