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A CALORIMETRIC INVESTIGATION OF MICELLE FORMATION IN AQUEOUS SODIUM DODECYLSULFATE SOLUTIONS

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ABSTRACT

The thermodynamics of molecular association in aqueous sodium dodecylsulfate (NaDDS) solutions at 25 °C is investigated using isothermal titration, adiabatic titration and conventional calorimetry. The resulting heat effect due to micelle formation at the critical micelle concentration (c.m.c.) is 0.52±0.04 kcal/mole. The equilibrium constant, enthalpy and entropy change values for the interaction of Na^+ with the sulfate group at the micelle surface are calculated from the thermometric titration data. No measurable interaction between Na^+ and DDS^- below the c.m.c. is observed. The degree of ionic dissociation as a function of NaDDS concentration is calculated and discussed.

INTRODUCTION

Aqueous solutions of ionic surfactants offer a system for investigating the thermodynamics of complex association equilibria. In these solutions, monomer is in a stable, reversible equilibrium with an aggregation of monomer units, the micelle. In the micelle the hydrocarbon chains orient themselves away from the water and the polar groups are at the micelle surface. The ionic surface may be expected to exert a high electrostatic field in the region of the micelle and result in a strong attraction of the counter ion for the micelle surface. In addition, interaction between the monomer units and the counter ion may also be significant.

The critical micelle concentration (c.m.c.) for aqueous sodium dodecylsulfate (NaDDS) solutions has been determined by many investigations and the value, 0.0081±0.0001 mole/liter, is well established. However, the calorimetrically determined values previously reported for the heat associated with the micellization process differ by as much as 1 kcal/mole[1-3]. The degree of ionic dissociation of the micelle in the region of the c.m.c. has been determined by several investigators[4-8] but no equilibrium constants or enthalpy change for the interaction of the micelle and its counter ion have been previously reported. The present work reports equilibrium

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constants, enthalpy and entropy change values for the formation of micelles and the binding of Na^+ ions in the aqueous NaDDS solutions calculated from adiabatic and isothermal calorimetric titration data.

EXPERIMENTAL

Materials

Two samples of NaDDS were used in these experiments. Sample I was a highly purified material previously prepared and characterized in these laboratories[9]. Sample II was a reagent grade (99.0%) product obtained from the Britisch Drug House, Ltd., London. The c.m.c.'s of Sample I and II determined by the surface tension method (at 25.0°C) were 8.1[9] and 5.0 mmoles/liter, respectively. Neither sample was found to give a minimum in the plot of surface tension *versus* concentration. This indicates the absence of unreacted alcohols, *i.e.*, n-dodecanol. The depression of the c.m.c. found for Sample II is probably due to the presence of inorganic salts and/or C_{14} or higher alcohol sulfate impurities. Bakers ,Analytical Reagent' grade NaCl was used to study the interaction between Na^+ and DDS^- below the c.m.c. Freshly distilled water was used in the preparation of all solutions and all solutions were stored and used under a pure nitrogen atmosphere.

Calorimetric runs

The calorimetric data were obtained using Tronac Inc. precision constant temperature environment (adiabatic) and isothermal titration calorimeters. Both these instruments are automated, similar in design to those previously described by Christensen *et al.*[10,11]. Interaction between Na^+ and DDS^- ions below the c.m.c. was studied using the isothermal titration calorimeter by adding a 1.0 *M* NaCl solution to 90 ml of a 1 m*M* NaDDS solution. Interaction between the counter ion and micelle was studied using the adiabatic titration calorimeter by dilution of 0.4 *M* NaDDS solutions of Samples I and II into 50 ml of water. Four duplicate runs were made for each sample. Similar runs were made for Sample I using a conventional adiabatic calorimeter. In these experiments several NaDDS solutions above the c.m.c. were diluted to a final NaDDS concentration below the c.m.c., 3.5 m*M*. At least three calorimetric measurements were made for each concentration. In all cases the initial temperature of the solutions in the calorimeter was 25.00°C and the attainment of equilibrium appeared to be essentially instantaneous. It was observed, however, that significant concentration of impurities (0.1% isopropanol or acetone) resulted in severe kinetic problems as the surfactant is diluted. In these cases a rapid exothermic reaction followed by a very slow and erratic endothermic reaction was observed. Thus it is imperative that all glassware and the calorimeter reaction vessel be rinsed with distilled water and dried under nitrogen before preparing any solutions.

Calculations

Model and assumptions

The anions in NaDDS solution tend to form aggregates containing *n* monomer

(m) units. If no ion-pairing occurs at the micelle surface then the equilibria may be written as

$$n\mathrm{DDS}^-(\mathrm{m}) \rightleftharpoons (\mathrm{DDS}^-)_n(\mathrm{M});\ K_\mathrm{M},\ \Delta H^\circ_\mathrm{M},\ \alpha = 1.0 \tag{1}$$

where n represents the number of monomer dodecylsulfate ions, M represents the micelle, α is the degree of ionic dissociation, $(n-z)/n$, where z is the number of counter ions paired with the sulfate groups at the micelle surface, K_M is the equilibrium constant and $\Delta H^\circ_\mathrm{M}$ is the heat of micellization.

Upon micelle formation, significant ion-pairing may occur between the Na^+ counter ions and the sulfate groups at the micelle surface, thus

$$(z\mathrm{Na}^+ + z\mathrm{DDS}^-)\ (\mathrm{M}) \rightleftharpoons (\mathrm{NaDDS})\ (\mathrm{M});\ K_\mathrm{p},\ \Delta H^\circ_\mathrm{p} \tag{2}$$

where K_p is the equilibrium constant and $\Delta H^\circ_\mathrm{p}$ is the heat of ion-pairing at the micelle surface. Appreciable ion-pairing implies the change at the c.m.c. is

$$n\mathrm{Na}^+(\mathrm{m}) + n\mathrm{DDS}^-(\mathrm{m}) = [(\mathrm{Na}_z(\mathrm{DDS})_n)^{-(n-z)} + (n-z)\mathrm{Na}^+](\mathrm{MU});$$
$$K_\mathrm{M},\ \Delta H^\circ_\mathrm{M},\ \alpha \neq 1.0 \tag{3}$$

where MU represents the micellar unit, involving both bound and free gegenion. Above the c.m.c. the process occurring as the surfactant is diluted is essentially,

$$[(\mathrm{Na}_z(\mathrm{DDS})_n)^{-(n-z)} + (n-z)\mathrm{Na}^+] \rightleftharpoons [(\mathrm{Na}_{z'}(\mathrm{DDS})_n)^{-(n-z')} + (n-z')\mathrm{Na}^+] \tag{4}$$

Thus the incremental dilution of micelles only changes α, the degree of ionic dissociation of the counter ion with the sulfate groups of the micelle surface.

The following experimental observations and assumptions were employed in our calculations of the heat of micellization, equilibrium constants and degree of ionic dissociation[12]: (*1*) the activity coefficient of the Na^+ and DDS^- monomer (m) ions not associated with the micelle may be computed using an extension of the Debye–Hückel expression of the form[13]

$$\log\gamma = \frac{-Z^2A\sqrt{\mu}}{1+B\mathring{a}\sqrt{\mu}} + CZ^2\mu \tag{5}$$

where γ is the calculated activity coefficient, μ the ionic strength, Z the valence, and $\mathring{a}$ the "effective" ion diameter. A and B are functions of the temperature and solvent dielectric constant[13] and C is an empirical parameter. Since the value of $\mathring{a}$ for the DDS^- ion is not known we used the value given for SO_4^{2-} ion of 4.0 Å[14]. A value of 0.2 for C was used in these calculations[15]; (*2*) the activity coefficient of the DDS^- anions associated in the micelle (M) is assumed to be independent of the total NaDDS concentration[16]; (*3*) above the c.m.c. further addition of NaDDS increases the number of micelles while the monomer concentration increases only insignificantly. However, we do not imply that the activity coefficient of the monomer above the c.m.c. is constant[16]; (*4*) although the effective radius of the micellar unit (MU) is expected to decrease with increasing micelle concentration[16], the number of monomer units comprising the micellar unit, anions plus their counter ions, are assumed unchanged. This assumption is supported by the fact that the amount of solubilizate dissolved per mole of NaDDS above the c.m.c. remains constant over the concentration range of 0.008 to 0.6 M[17]. The above assumptions are made by most investigators of the micellization process, and are consistent with available experimental evidence.

ΔH_M°, ΔH_p° and log K_p values

The ΔH_M° values were calculated from the difference in the slopes of the calorimetric titration curves[18] in the region just above and just below the c.m.c. The c.m.c. and ΔH_M° values were used to correct the heat of dilution data for formation of monomer units during the titration. The resulting heat (Q_c) values are related then only to changes in the amount of Na$^+$ ion-paired at the micelle surface as expressed in Eqn. (4). The heat (Q_c) measured is then

$$Q_c = ([\mathrm{NaDDS}](\mathrm{M})_{(f)} V_{(f)} - [\mathrm{NaDDS}](\mathrm{M})_{(i)} V_{(i)})\, \Delta H_p^\circ = \Delta n \Delta H_p^\circ \tag{6}$$

where (f) refers to the final diluted solutions, (i) refers to the initial titrant solution, V is the corresponding volume and Δn is the change in the number of moles of [NaDDS](M) during the dilution process. Combining Eqns. (6) and (2) with Eqns. (7) and (8)

$$[\mathrm{Na}^+](\mathrm{Total}) = [\mathrm{Na}^+](\mathrm{m}) + [\mathrm{NaDDS}](\mathrm{M}) \tag{7}$$

$$[\mathrm{DDS}^-](\mathrm{M, Total}) = [\mathrm{DDS}^-](\mathrm{M}) + [\mathrm{NaDDS}](\mathrm{M}) \tag{8}$$

the expressions for total gegenions and micelle associated sulfate, results in an expression for Q_c in terms of K_p, ΔH_p° and [Na$^+$](Total), which may be solved for K_p and ΔH_p° by least squares methods[18,19]. The [DDS$^-$](M, Total) expression in Eqn. (8) is not equal to the total sulfate present in the solution but differs from the total by the concentration of monomer present. Thus below the c.m.c. [DDS$^-$](M, Total) = 0 and above the c.m.c. [DDS$^-$] (M, Total) = [DDS$^-$](Total) − c.m.c.

The mathematical treatment of data is as follows: the best K_p and ΔH_p° values for the reaction may be calculated by least squares analysis of Eqn. (6). The error square sum over the x data points is given by Eqn. (9)

$$U(K_p, \Delta H_p^\circ) = \sum_{j=1}^{x} (Q_{c,j} - \Delta H_p^\circ \Delta n_j)^2 \tag{9}$$

and the best values of K_p and ΔH_p° for a given calorimetric titration are those which minimize the function $U(K_p, \Delta H_p^\circ)$, that is those which satisfy Eqns. (10 and (11):

$$\frac{\partial U}{\partial \Delta H_p^\circ} = 0 = \sum_{j=1}^{x} Q_{c,j} \Delta n_j - \Delta H_p^\circ \sum_{j=1}^{x} (\Delta n_j)^2 \tag{10}$$

$$\frac{\partial U}{\partial K_p} = 0 = \sum_{j=1}^{x} (Q_{c,j} - \Delta H_p^\circ \Delta n_j)\, \Delta H_p^\circ \frac{\partial \Delta n_j}{\partial K_p} \tag{11}$$

Eqn. (10) may be directly solved for ΔH_p° if K_p, and, thereby, the Δn_j values are known. Eqn. (11) is a nonlinear expression in K_p and must either be solved by trial and error or by some iterative technique. A complete and accurate solution of Eqns. (10) and (11) involves five steps[19]: (*1*) assumption of an initial K_p value; (*2*) calculation of the concentration of each species in the reaction vessel at each data point using the assumed value of K_p; (*3*) calculation of the value of ΔH_p° using Eqn. (10); (*4*) evaluation of the error square sum, U, to establish how well the K_p and ΔH_p° values fit the experimental data; (*5*) recalculation of sets (*2*), (*3*) and (*4*) using new values of K_p until the best set of K_p and ΔH_p° values are obtained[19]. Since activity coefficient corrections for micelle bound sulfate groups were not made, and assumed to be constant the resulting K_p value is therefore a pseudo-thermocdynamic constant of the form:

$$K_p = \frac{a_{(\mathrm{NaDDS})(\mathrm{M})}}{a_{\mathrm{Na}^+}[\mathrm{DDS}^-(\mathrm{M})]} \tag{12}$$

and will differ from the true thermodynamic K_p value by the activity coefficient of the $\mathrm{DDS}^-(\mathrm{M})$ species. Since the actual micelle concentration in the solutions used is less than 1 m*M* this correction may be smaller than the uncertainties in the calculated $\log K_p$ values for the two detergent samples.

Log K_M and α values

Using the experimentally obtained c.m.c. and calculated K_p value the degree of ionic dissociation of micelles near the c.m.c. can be calculated. The $\log K_M$ values were then computed using the equation derived by Phillips[20]

$$-\log K_M = \left(2-\alpha-\frac{1}{n}\right)\log(\text{c.m.c.}) \tag{13}$$

where n is the number of dodecylsulfate units ($n = 57$)[16] per micelle. Values of α were calculated at total surfactant concentrations of 9, 10, 11 and 12 m*M* and extrapolated to the c.m.c. value of 8 m*M*.

EXPERIMENTAL RESULTS

The heat produced when 1.0 *M* NaCl was added to 90 ml of 1 m*M* NaDDS solutions could be quantitatively accounted for by the heat due to dilution of the titrant[21]. We, therefore, conclude that there is no significant interaction between Na^+ and monomeric DDS^- (m) ions below the c.m.c. Conductivity[22,23] and potentiometric[24] studies of NaDDS solutions below the c.m.c. give similar results in support of this conclusion.

Titration calorimetry

The titration calorimetry results obtained by dilution of a 0.4 *M* NaDDS solution into 50 ml of water, are shown in Fig. 1. A significant change in the rate of heat production in the region of the c.m.c. is indicated for both samples of NaDDS. The c.m.c.'s obtained from the intercepts of the slopes are 8.0±0.9 mM for Sample I and 5.0±0.7 mM for Sample II. The ΔH_M° values due to micelle formation obtained from the titration curves are 0.52±0.04 and 0.41±0.05 kcal/mole for Samples I and II, respectively.

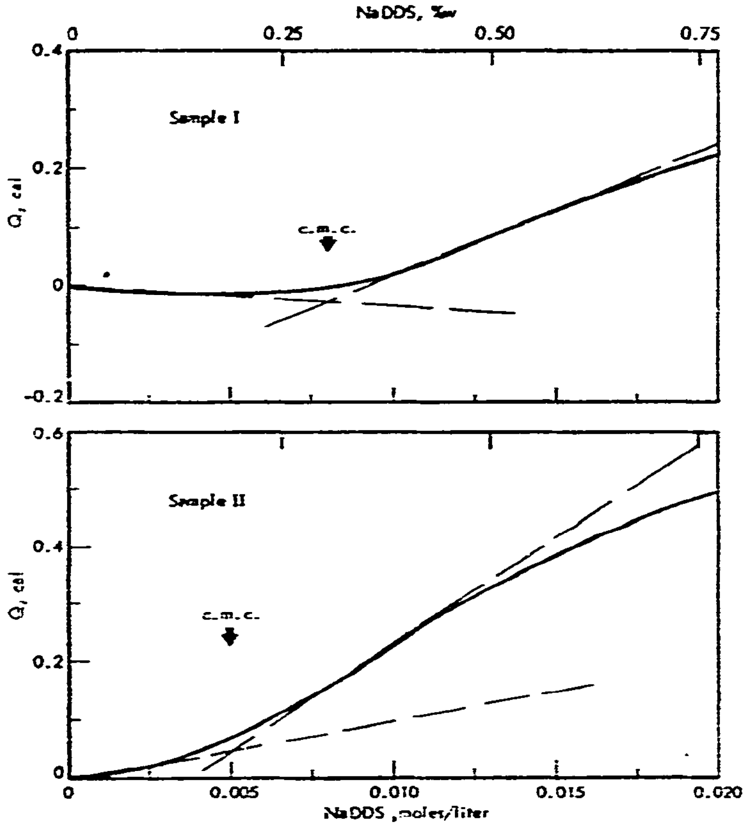

Fig. 1. Plot of Q vs. final NaDDS concentration for dilution of a 0.4M NaDDS solution into 50 ml of H_2O in the region of the c.m.c.

It is known from previous studies that interaction between Na^+ ion and the sulfate groups at the micelle surface is not stoichiometric[4-8] and the nonlinearity of the titration curves given in Fig. 1 above the c.m.c. can be ascribed to changes in the amount of Na^+ associated with the sulfate group on the micelle surface as the total surfactant concentration is increased. The log K_p, ΔH_p° and ΔS_p° values for the interaction of Na^+ with $DDS^-(M)$ given in Table I were calculated from the thermometric titration data in the region where the final surfactant concentration varies from 0 to 40 mM NaDDS. Figs. 1 and 3 were composed from a smooth fit to over one hundred data points each. The standard deviation between runs in Q_c is less than ±0.03 cal.

TABLE I

LOG K, $\Delta H°$ AND $\Delta S°$[a] VALUES ASSOCIATED WITH MICELLE (M) FORMATION AND COUNTER ION, Na^+, INTERACTION WITH THE SULFATE (SO_4) GROUP AT THE MICELLE SURFACE AT 25 °C

Reaction[b]	*Sample*[c]	*Log K_M*	*ΔH°_M (kcal/mole)*	*ΔS°_M (gibbs/mole)*
(1) $(nNa^+ + nDDS^-)(m) = [(Na_zDDS_n)^{-(n-z)}](M) + (n-z)Na^+$	I	3.62±0.1	0.52±0.04	18.3±0.3
	II	3.97±0.1	0.41±0.04	19.5±0.3
		LogK°_p	*ΔH°_p*	*ΔS°_p*
(2) $[(zNa^+ + zDDS^-)](M) = [Na_zDDS_z](M)_{(p)}$	I	2.50±0.15	−1.09±0.14	7.8±0.5
	II	1.43±0.2	−1.14±0.09	2.7±0.6

[a] Standard state, hypothetical one molar solution (valid at $\mu = 0$). All concentration units are moles/liter. [b] Reaction (1) is valid only for formation of the micelle at the c.m.c., see text. Reaction (2) is for ion-pairing at the micelle surface, see text. [c] Sample I, a highly purified sodium dodecylsulfate sample[9]; Sample II obtained from the British Drug House, Ltd.

Conventional calorimetry

The results of the conventional calorimetric studies for Sample I are shown in Fig. 2. Extrapolation of the data to the c.m.c. yields the heat effect due to dissociation of the micelle. The value obtained is 0.51 kcal/mole, in excellent agreement with the thermometric titration results for the same sample.

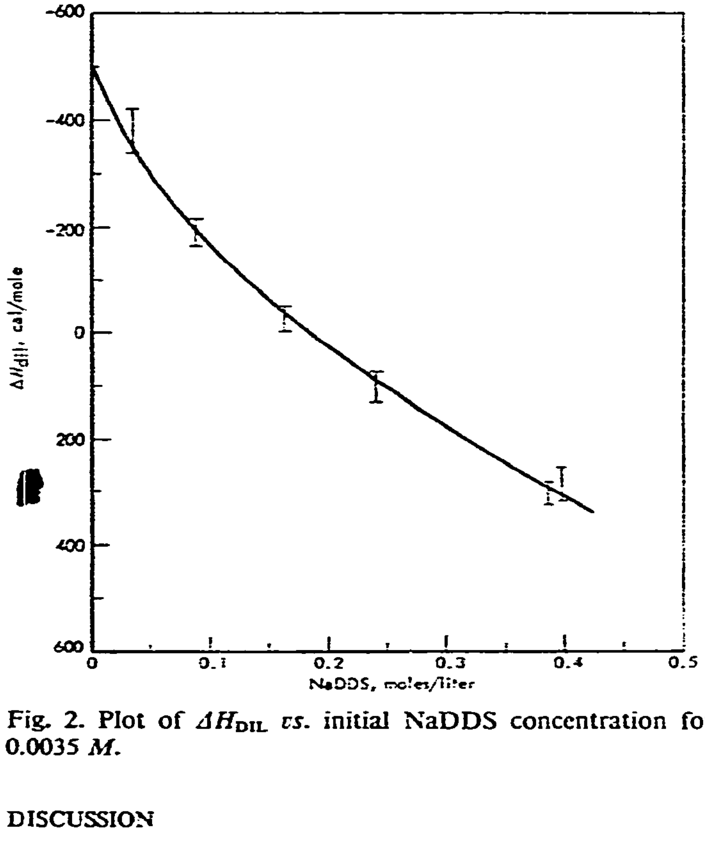

Fig. 2. Plot of ΔH_{DIL} *vs.* initial NaDDS concentration for dilution to a final concentration of 0.0035 M.

DISCUSSION

Critical micelle concentration

The c.m.c.'s determined by calorimetry for the pure Sample I (8.1 mM) and the reagent grade Sample II (5.0 mM) are in excellent agreement with the values obtained by surface tension measurements[9].

Heat of micellization, $\Delta H^{\circ}_{\mathrm{M}}$

The only calorimetrically determined values for the heat of micellization of NaDDS (Table II) with which present results can be directly compared are the value of 0.09 kcal/mole reported by Skinner *et al.*[1] and the value of −0.45 kcal/mole reported by Benjamin[2]. The value reported by Skinner *et al.*[1] differs from our value because they assumed that the micellization process could be approximated by the process of diluting a NaDDS solution at twice the c.m.c. to a NaDDS concentration corresponding to the c.m.c.[1]. A ΔH° value for the same process may be calculated from our data to be 0.16 kcal/mole, in better agreement with the value reported by

TABLE II

COMPARISON OF THE HEATS OF MICELLIZATION OF SODIUM ALKYL SULFATES AT 25°C

Number of carbon atoms	*C.m.c. (mmoles/liter)*	$\Delta H_{\text{M}}^{\circ}$ *(kcal/mole)*	*Method*
8	not given	0.8	calorimetry[3]
10	not given	0.5	calorimetry[3]
12	not given	−0.45 (26.5°C)	calorimetry[2]
12	8.0	0.49[a]	calorimetry[1]
12	8.0	0.52	present study

[a] Corrected for interaction of Na^+ ion with the micelle, see text.

Skinner. The results of this study, however, indicate that interaction between the Na^+ counter ion and the micelle contributes significantly to the process represented by Eqn. (4). Using the K_p and ΔH_p^c values given in Table I to correct the value reported by Skinner *et al.*[1] for ion-pairing yields 0.49 kcal/mole for $\Delta H_{\text{M}}^{\circ}$, in good agreement with the value of 0.52 kcal/mole obtained in the present work. The difference between our value and that given by Skinner *et al.*[1] is then due to differences in the interpretation of the data.

A ΔH_{M}^{c} value is estimated to be 0.2 kcal/mole by extrapolation of values reported by Goddard *et al.*[3] for the n-C_8 and n-C_{10} sulfates. This extrapolated value is lower than our value of 0.52 kcal/mole. The value of 0.6 kcal/mole obtained from measurements by Flockhart and Ubbelohde[25] of the variation of the c.m.c. with temperature is in reasonable agreement with the present calorimetrically determined value.

The results given in Table I indicate that both the $\Delta H_{\text{M}}^{\circ}$ and ΔS_{M}^{c} values contribute about equally to the lowering of the c.m.c. for Sample II as compared to Sample I.

Interaction of Na^+ with dodecyl-SO_4^- group

The present results show that the affinity of the dodecyl sulfate anions for the Na^+ counter ion is significantly larger for micelle bound anions than for free monomer anions. Comparison of the present results for Sample I given in Table I with previously reported values for the interaction of Na^+ ion with SO_4^{2-} ion[14] (log $K = 0.65$, $\Delta H^c = -0.49$ kcal/mole and $\Delta S^\circ = 1.3$ gibbs/mole) suggests that the high affinity of the micelle for the counter ion is primarily an entropy effect and that water molecules in the vicinity of the micelle are highly ordered by the micellar charge. Thus while the ΔH_p^c value for the interaction of Na^+ ion with the sulfate groups on the micelle surface is only −0.60 kcal/mole more exothermic than the corresponding value for SO_4^{2-} ion, the corresponding $-T\Delta S_p^c$ contribution to the interaction is −1.95 kcal/mole more exothermic. The relative ΔS_p^c values indicate that more disorder is introduced to the system when a neutral micelle is formed than when the $NaSO_4^-$ ion pair is formed. This is to be expected since in the formation of the neutral micelle all charged ions are removed from the solution and solvation of the NaDDS(M) micelle heads can only occur through dipole–dipole interactions. The difference in the logK_p values for interaction of Na^+ with the micelle surface for the two samples is entirely an entropy effect, the ΔH_p° values being equal for the two samples. The difference in the ΔS_p° values for the interaction of Na^+ ions with DDS^- (M) anions between the pure and impure sample indicates that the impurities give rise to a less highly ordered charged micelle surface.

Degree of ionic dissociation of micelle

There are no previously reported values with which the log K_p, ΔH_p° and ΔS_p° values for the interactions of Na^+ with DDS^-(M) ions at the micelle surface can be directly compared. A correlation between the experimental values of the heat of dilution and the corresponding species present in the calorimeter calculated from the c.m.c. and logK_p values shown in Table I is given in Fig. 3. As Fig. 3 indicates, the

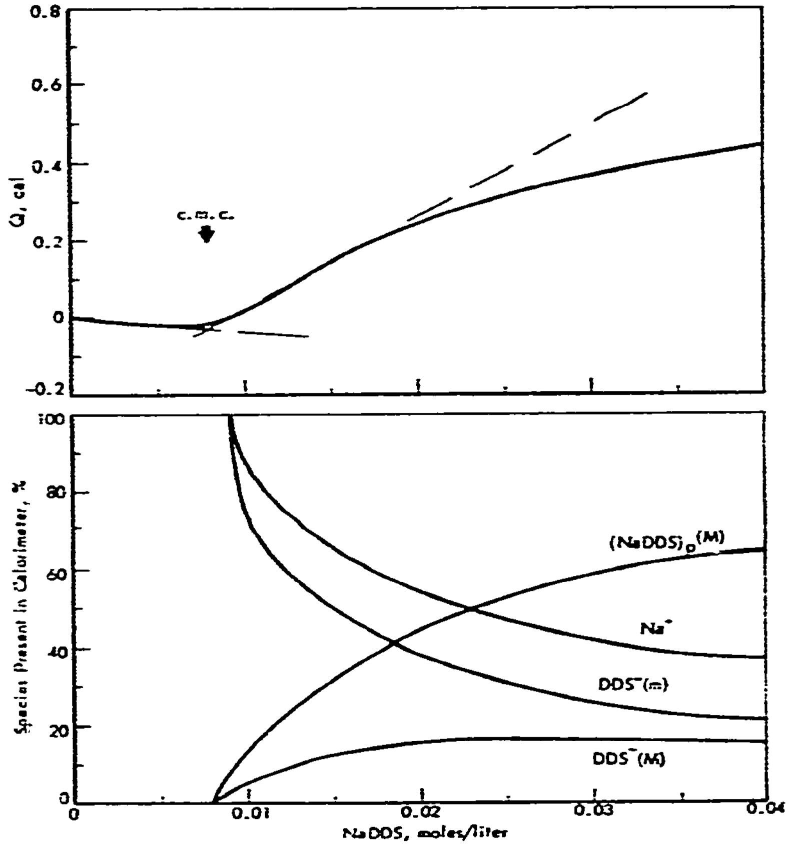

Fig. 3. Plot of Q *vs.* NaDDS concentration for dilution of 0.4M NaDDS into 50 ml of H_2O and the corresponding species distribution present in the calorimeter reactor vessel.

relative amounts of free Na^+ ion and Na^+ associated with the micellar DDS^-(M) groups vary rapidly in the region close to the c.m.c. but remain relatively constant above ~0.03 M NaDDS. Several investigators have determined the degree of dissociation, α, of NaDDS micelles[4–8]. The variation of α with total NaDDS concentration calculated from the present results is given in Fig. 4. The effective charge of NaDDS micelles in the region of the c.m.c. has been previously determined by electrophoresis[4] and light scattering[5] data and an α value for the Na^+ counter ion associated with the sulfate group at the micelle surface is calculated from these data to be 0.29[4] and 0.18[5] respectively. The corresponding value calculated from the present results is 0.29, in agreement with the electrophoresis data[4]. Using Na^+ ion sensitive membrane electrodes an α value near the c.m.c. has been measured by several investigators[6–8]. The average of the reported values is 0.23 ± 0.04 and is in agreement with the values given in Fig. 4 over the concentration range of 0.01 to 0.05 M in which the EMF measurements were made[6–8].

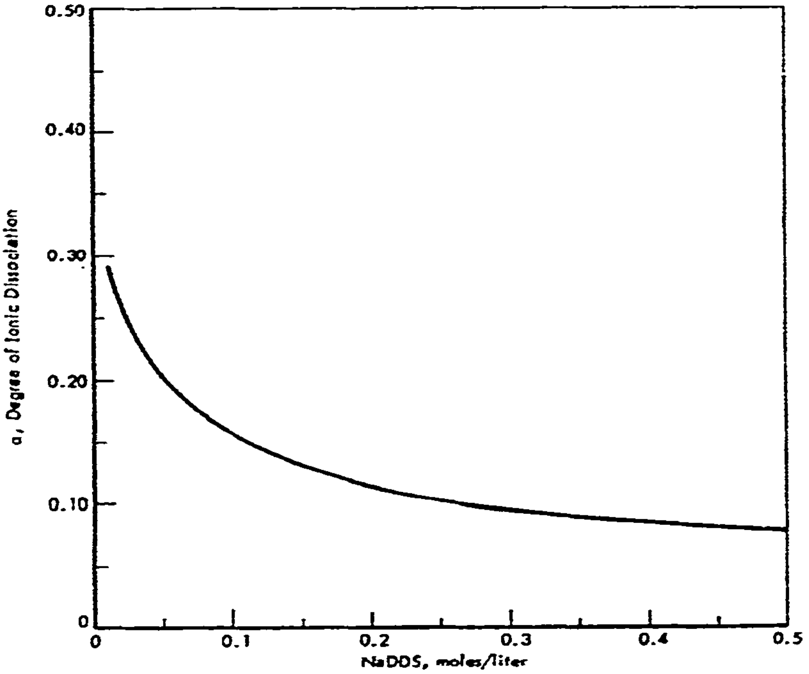

Fig. 4. Calculated variation of α with concentration for NaDDS solutions.

X-ray[26–28] density[28,29] differential ultrasonics[30] and spectrophotometric[31] studies on aqueous micellar solutions confirm that the micelle interior is liquid hydrocarbon. Spectrophotometric studies of solubilization[17] also indicate that regular solution theory can be applied to the micelle interior. The results of the EMF studies[6–8] and those results here indicate that the micelle surface may be treated as an aqueous electrolyte solution. Thus experimentally the micelle can be treated as a two phase system.

Contribution of the hydrocarbon chain

It is instructive to compare the $\log K_M$, ΔH°_M and ΔS°_M values for micelle formation with the corresponding values for removal of a n-alkane from water. The experimental and calculated $\log K_M$, ΔH_M° and ΔS_M° values given in Table I are valid only at the c.m.c. where $\alpha = 0.29$ (for the pure material). The thermodynamic quantities associated with the micellization process where n DDS^-(m) anions combine to form a fully charged micelle with no ion-pairing at the micelle surface are presented in Table III. The thermodynamic quantities associated with the hypothetical reaction where n Na^+ and n DDS^- (m) combine to form a neutral micelle with complete surface ion-pairing are also given in Table III. In the calculation of the $\log K_M$ values, n and the c.m.c. are given the values of 57 and 8.1 mM/liter, respectively. The ΔH_M° values given in Table III were corrected to values valid at either $\alpha = 0$ or $\alpha = 1$ using the ΔH_p^c value to correct for association or dissociation of the counter ion. Thus for example correcting the ΔH_M° value for $\alpha = 0.29$ to $\alpha = 0$ involves the association of 0.29 moles of Na^+ ion per mole of micelle. And the calculated ΔH_M° value is given by

$$\Delta H_M^\circ\ (\alpha = 0) = \Delta H_M^\circ\ (\alpha = 0.29) + 0.29\ (\Delta H_p^\circ) \tag{14}$$

TABLE III

LOG K_M, ΔH_M°, ΔS_M° AND α VALUES FOR THE REACTION $(nNa^+ + nDDS^-)(m) = [(Na_zDDS_n)^{-(n-z)} + (n-z)Na^+](M)$ AND ESTIMATED VALUES OF LOG K, ΔH° AND ΔS° FOR THE REMOVAL OF NORMAL PARAFFINS (C_{10} AND C_{12}) FROM WATER AT 25°C

	α[a]	$\log K_M^\circ$	ΔH_M° (kcal/mole)	ΔS_M (gibbs/mole)
NaDDS	1.00[b]	2.05	1.29	14
	0.29	3.62	0.52	18
	0.00[b]	4.15	0.20	20
		$\log K$	ΔH°	ΔS°
C_{10}		6.38[c]	−0.2[c]	28[c]
C_{12}		6.85[c]	−0.7[c]	29[c]

[a] Degree of dissociation, $\alpha = (n-z)/n$. [b] Hypothetical reaction, n and c.m.c. are given the values 57 and 8.1 mM/liter, respectively. [c] Estimated values, refer to text.

The $\log K$, ΔH° and ΔS° values for the removal of n-alkane from water were estimated using data reported by Schéraga and Néméthy[32] for C_1 and C_4 and data determined by Baker summarized by Fetterly[33] for n-C_{18}. Values for both C_{10} and C_{12} were obtained by interpolation of the above data. These values are given in Table III. Since the micelle surface is probably hydrated to a depth of about 2 methylene groups[34] the n-C_{10} values were used to compare with those obtained in our study.

Comparison of the values for DDS^-(M) at $\alpha = 1$ with those for C_{10} indicates that the lower K_M value for the charged micelle, as compared to C_{10} is due to both the ΔH_M° and ΔS_M° contributions to the micellization process. The ΔH_M° value for formation of the totally charged micelle can be viewed as a sum of three terms: (*1*) removal of the hydrocarbon chain from water. By comparison with the values for the paraffins this contribution should be slightly exothermic; (*2*) the electrostatic energy required to bring the charge sulfate heads together. For an aqueous solution this effect will also be exothermic[35]; and (3) changes in hydration of the sulfate group as the micelle is formed. Since the overall ΔH°_M value is endothermic, contribution (3) must be endothermic and large. This may be explained if the total number of water molecules associated with the first hydration sphere of the sulfate group decreases as the micelle is formed. A similar argument for ΔS°_M yields the conclusion that the electrostriction of the water by the sulfate group increases as the micelle is formed. Thus, although the solvation in the immediate vicinity of the sulfate group is reduced, the charged micelle appears to interact with the solvent over a very large volume. This would be expected since the total micelle charge is large.

Since nothing is quantitatively known about the thermodynamics for interaction of Na^+ with monomer dodecyl sulfate, it is difficult to draw exact conclusions on solvation of the neutral micelle. However, the $\log K_M$, ΔH°_M and ΔS°_M values given in Table III indicate that as the micelle charge decreases due to ion-pairing at the surface the micelle behaves more like the n-alkanes as expected.

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