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Thermodynamics of Cationic and Anionic Surfactant Interaction

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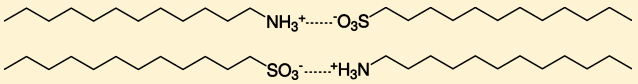
ABSTRACT: The interaction between positively and negatively charged linear surfactants is an interesting system for the understanding of the fundamental interplay of hydrophobic and ionic forces in lipid membranes and proteins. We used isothermal titration calorimetry to dissect the Gibbs free energies, enthalpies, entropies, and heat capacities of interaction into hydrophobic and ionic contributions for alkylamine interaction with alkyl sulfates and alkane sulfonates. Dependence on aliphatic chain length, surfactant concentration, temperature, and ionic strength provided a detailed thermodynamic description of this interaction. Reactions of surfactants with tails longer than approximately 10 carbon atoms were primarily driven by enthalpy changes arising from solid-phase interactions between aliphatic tails. Entropic contributions were small relative to enthalpic ones. Contributions of methylene groups were additive. The binding reaction can yield a solid or liquid complex, depending on temperature. Thermodynamic dissection yielded the parameters of the phase transition.



Thermodynamics of aggregation into solid (mod), kJ/mol

	Hydrophobic	Electrostatic	
$\Delta_b G$	-67	+29	(0.33 mM)
$\Delta_b H$	-106	-7	(any conc.)
$T\Delta_b S$	-39	-36	(0.33 mM)

INTRODUCTION

The combination of hydrophobic, ionic, and steric interactions determines the structures of biological macromolecules and assemblies. The thermodynamics of hydrophobic interactions have been studied for many years,[1−5] as have the thermodynamics of ionic interactions, electrostatic effects, and the role of water in these interactions.[6−8] Despite significant progress in this area of research, many fundamental questions remain unanswered, and it is important to understand the most simple model systems. One such system is the interaction between positively and negatively charged linear surfactants. Dissection of the hydrophobic and ionic contributions to the thermodynamics of surfactant interactions is the main goal of this paper.

Interaction between cationic and anionic surfactants in aqueous solution leads to various systems of great importance for both basic science and technological applications. It has been observed that equimolar mixtures of such detergents as sodium dodecyl sulfate (SDS, $C_{12}OSO_3^-$) and dodecyl ammonium chloride (DDAC, $C_{12}NH_3^+$) form stoichiometric complexes that may or may not coprecipitate, while the excess of one or the other component may lead to the formation of mixed micelles. Phase behavior,[9] the structure[10] and formation[11] of stoichiometric coprecipitate, mixed micelles, vesicle formation,[12] and other aspects of cationic and anionic surfactant mixtures have been studied extensively.

In this paper, we focus on the energetics of stoichiometric coprecipitate formation when alkylammonium detergents are mixed with alkylsulfate or alkyl sulfonate detergents. Extensive isothermal titration calorimetry (ITC) data are presented as functions of surfactant alkyl chain length, surfactant concentration, solution ionic strength, and temperature, yielding the main thermodynamic parameters of the interaction process. Our primary interest is to determine the contribution of the various functional groups—methylene, ammonium, and sulfonate or sulfate—to the overall thermodynamic parameters of surfactant binding, including the Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS), and heat capacity (ΔC_p) changes. By doing so, we determine energetic contributions of hydrophobic interactions between aliphatic tails and electrostatic (ionic) interactions between ammonium and sulfate headgroups.

It has been shown that interaction of oppositely charged surfactants with long aliphatic tails yields a large exothermic ΔH.[11,13] However, the physical reason for this large ΔH is unclear. It is currently thought that the exothermicity mainly results from the electrostatic interaction between oppositely charged ions.[14] Here, we present evidence that the large exothermic ΔH arises from aliphatic chain interaction and not from electrostatic forces. These results further extend and confirm the finding that hydrophobic interactions between long aliphatic chains in water are driven by a large exothermic ΔH and opposed by a relatively small ΔS.[15−17] These results are somewhat unexpected in light of the usual understanding of the hydrophobic effect which states that the enthalpy of hydrophobic interactions is near zero and the positive entropy is the driving force of the hydrophobic effect.[1] However, they are understandable when it is taken into account that aqueous aggregates of long chain aliphatic compounds have tightly packed and ordered aliphatic interiors,[10] maximizing favorable energetic interactions and lowering the entropy.

MATERIALS AND METHODS

Chemicals. The following surfactants were purchased from Acros Organics (Morris Plains, NJ: 1-800-ACROS-01; Geel, Belgium: +32 14 57 52 11): undecylamine (98%), dodecylamine hidrochloride

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(99%), tridecylamine (98%). From Sigma Chemical Co. (P.O. Box 14508, St. Louis, MO 63178, 314-771-5750): 1-decanesulfonic acid, sodium salt (98%), dodecylsulfate, sodium salt (99%). From Aldrich Chem. Co. (P.O. Box 355, Milwaukee, WI 53201, 414-273-3850): 1-dodecanesulfonic acid, sodium salt (99%). From Pfaltz Bauer Inc. (375 Fairfield Ave, Stamford, CT 06902): 1-nonanesulfonic acid, sodium salt (98%). Nonylamine (≥97%) was obtained from Fluka, Sigma-Aldrich (CH-9471 Buchs, 081/75525 11). All substances were used without further purification. Solutions were prepared using distilled Milli-Q water, which was boiled to remove dissolved CO_2. Solutions of alkylamines were kept in tightly sealed containers to minimize the chances of reaction with atmospheric CO_2.

Isothermal Titration Calorimetry. All experiments were performed with a Microcal (Northampton, MA) Micro Calorimetry System (MCS) calorimeter in the temperature range 25−65 °C with the cooling circulating bath temperature kept constant at 17 °C. The ITC unit was calibrated using its built-in electronic heat pulse generator and validated by reaction NaI + $AgNO_3$ → AgI↓. The enthalpy change determined in five experiments, $\Delta H = -109.4 \pm 1.8$ kJ/mol, was very close to that found in the literature, $\Delta H = -110.9$ kJ/mol.[18] Prior to experiment, the cell was carefully washed multiple times and prerinsed with a portion of the same surfactant solution. Reactant solutions were cooled at least 5° below experimental temperature to ensure quick equilibration of the calorimeter. The cell (1.3438 mL) was loaded with a solution of 0.33 mM and the syringe with 5 mM of oppositely charged surfactants unless specified otherwise. Titration was performed in 40 injections of 6.25 μL at intervals of 180 s, with a 250 μL injection syringe. At least 180 s of data was collected prior to the first injection to check the stability of the baseline. There were cases when the baseline did not return to the preinjection level after the injection (as in Figure 1). Increasing the intervals between injections did not affect the integral enthalpies of interaction.

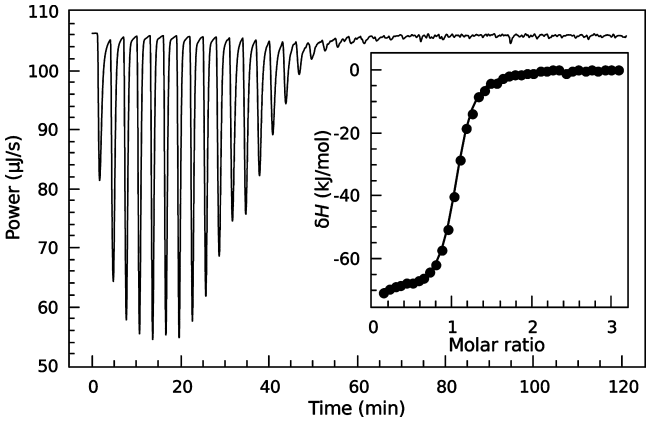

Figure 1. Raw ITC data of decane sulfonate (0.33 mM in the cell) titration by dodecylammonium (5 mM in the syringe) at 25 °C. The process is highly exothermic with the stoichiometry of approximately one cationic surfactant bound to one anionic surfactant (this example was fit with a stoichiometry of 1.03).

RESULTS

Reactions between cationic alkylammonium hydrochlorides and anionic alkyl sulfates and sulfonates have been shown to go through several stages.[11] Initially, when there is a large excess of one surfactant over the other, mixed micelles are formed. When the charge ratio approaches unity, a stoichiometric coprecipitate may be formed. Eventually, if there is a large excess of the other surfactant at the end of reaction, oppositely charged mixed micelles may form. In our ITC experiments, we usually could assign all heats to the formation of the stoichiometric coprecipitate.

Figure 1 shows typical ITC raw data (integrated curve is shown in the inset) of sodium decane sulfonate titration with dodecylammonium chloride. Exothermic peaks develop until the reaction comes to completion at the stoichiometric ratio of one cation added per one anion, and no further heat develops afterward. This indicates that one positive surfactant molecule binds per one negative surfactant molecule, consistent with the determination of precipitate composition from previous studies.[11] As the reaction proceeds, aggregate clusters form and precipitate out of aqueous solution.

The critical micelle concentration (cmc) for dodecylammonium chloride is approximately 14.7 mM.[19] A majority of our experiments (except where dependence on concentration was investigated) were performed with 5 mM dodecylammonium chloride concentration in the syringe. The cmc of decane sulfonate is even greater. Thus, before the beginning of the reaction, neither positive nor negative surfactants formed any micelles in the syringe or in the cell and there was no heat associated with micelle breakup during titration.

Most ITC curves were obtained by titrating negative surfactant in the cell with positive surfactant in the syringe. A series of experiments with different orders of titration was also carried out. Figure 2 compares the reaction of decane sulfonate

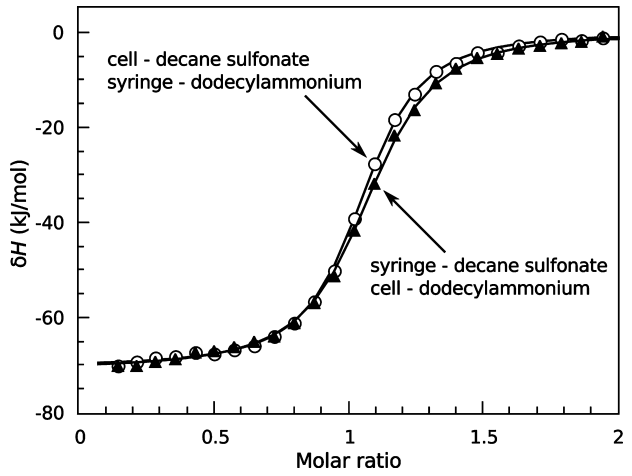

Figure 2. Dependence on the order of titration: cell − decane sulfonate, syringe − dodecylammonium (open circles); cell − dodecylammonium, syringe − decane sulfonate.

binding to dodecylammonium when the negative surfactant is in the cell and the positive in the syringe (open circles) with that when the negative surfactant is in the syringe while the positive is in the cell (solid triangles). The obtained reaction parameters from ITC curves are listed in Table 1, showing that there is no significant dependence on the order of titration.

Table 1. Dependence on the Order of Titration: Reaction Parameters Obtained from ITC Experiments

cell	syringe	ΔH^{obs}	K_b^{fit}	N_{fit}
$C_{10}H_{21}SO_3^-$ (0.33 mM)	$C_{12}H_{25}NH_3^+$ (5 mM)	−70.69	1.47×10^5	1.03
$C_{12}H_{25}NH_3^+$ (0.33 mM)	$C_{10}H_{21}SO_3^-$ (5 mM)	−70.93	1.96×10^5	1.05

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MODEL

The reaction between the fully dissolved negatively and positively charged detergents can be arbitrarily divided into two stages. In the first stage, an ion pair is formed between two oppositely charged ions, but the tails remain fully dissolved and do not interact with each other:

$$R_1NH_3^+ + R_2SO_3^- \leftrightarrow R_1NH_3^+\cdots R_2SO_3^- \quad (1)$$

where R_1 and R_2 are linear aliphatic chains of any length and may be different for oppositely charged detergents. Hereafter, the parameter $m = R_1 + R_2$ will be used to denote the total number of carbon atoms in both aliphatic chains. In the second stage, the electrically neutral and highly hydrophobic complex forms an aggregate of very large (indefinite) size ν which precipitates out of aqueous solution:

$$\nu(R_1NH_3^+\cdots R_2SO_3^-) \leftrightarrow (R_1NH_3^+\cdots R_2SO_3^-)_\nu\downarrow \quad (2)$$

The overall process need not be so neatly divided, however, for thermodynamic analysis to be valid.

Reaction 1 could be similar in energetics to the process of ion pair formation in ammonium sulfate aqueous solution. The energetics of the second reaction could be similar to the process of alkane aggregation and precipitation from aqueous solution. Because the solubility of ammonium sulfate is much higher than that of alkane with more than 20 carbon atoms, the probability of finding nonaggregated ion pairs is very small. We now consider Gibbs free energies of ammonium sulfate crystallization and alkane precipitation from aqueous solution to determine the extent to which their sum represents the Gibbs free energy of the reaction of alkylammonium with alkane sulfonate:

$$\Delta_A G = \Delta_A G_{ion} + \Delta_A G_{alk} \quad (3)$$

where $\Delta_A G_{ion}$ is the Gibbs free energy of ionic interaction and $\Delta_A G_{alk}$ is the Gibbs free energy of interaction of alkane tails.

The Gibbs free energy of ammonium sulfate aggregation at 1 M reference state is equal to

$$\Delta_A G_{ion} = -RT\ \ln(A_{ion}) = RT\ \ln(S_{ion}) \quad (4)$$

where S_{ion} and $A_{ion} = 1/S_{ion}$ are the ammonium sulfate solubility and aggregation parameter, respectively. For concentration C values other than 1 M, the Gibbs free energy can be estimated as

$$\Delta_{agg} G_{ion} = -RT\ \ln(A_{ion} C) \quad (5)$$

The Gibbs free energy of hydrophobic alkane aggregation can be obtained from the following equation:[15,17]

$$\Delta_{agg} G_{alk} = -RT\ \ln(A_{alk} C) = -RT(m\ \ln(\Delta w) + \ln(w_0) + \ln(C)) \quad (6)$$

where Δw is an increase in aggregation upon addition of one methylene (CH_2) group and is equal to 4.241.[15] The parameter w_0 is an empirical coefficient and is equal to 1.32 for n-alkanes.[15]

As an example, let us consider the reaction of decane sulfonate with dodecylammonium (see Figure 5). For this case, the concentration is C = 0.33 mM, S_{ion} = 4.1 M at T = 25 °C,[20] and A_{ion} = 0.244 M^{-1}; thus, from eq 5, one estimates the value of $\Delta_{agg} G_{ion}$ = 23.4 kJ/mol. The hydrophobic portion of the system can be estimated from eq 6 and is equal to −59.6 kJ/mol. For this particular system, the summation of ionic and hydrophobic contributions yields the model-predicted value $\Delta_{agg} G$ = −36.2 kJ/mol. The experimentally observed Gibbs free energy of the above-mentioned system obtained by ITC was equal to −30.6 kJ/mol. Therefore, there is a reasonable match between the model-predicted and observed Gibbs free energies.

On the one hand, the difference between the predicted and measured value is significant, since the standard deviation of the measured value did not exceed 1 kJ/mol. However, on the other hand, the discrepancy of approximately 5 kJ/mol is surprisingly small, since neither the approximation of ammonium and sulfonate ionic headgroups in surfactants as inorganic ammonium sulfate nor the approximation of aliphatic tails as alkanes can be expected to represent surfactants and their energetics precisely.

Detailed analysis of our experimental results shows this discrepancy of approximately 5 kJ/mol for all studied surfactant systems. We assign this difference to the approximation of headgroups by ammonium sulfate and adjust the Gibbs free energy of ionic interaction in the surfactant system by this value. Within the accuracy of our data, it was not feasible to determine the dependence of the ionic contribution on concentration. Therefore, we introduce the constant factor $B = 4.03 \times 10^{-5}$, which is approximately equal to the concentration adjusted by the 5 kJ/mol discrepancy.

Next we derive the association constant K_b^{mod} of the model, based on the aggregation reactions 1 and 2. The ionic and hydrophobic components can be written as

$$A_{ion} = \frac{1}{B}\frac{[R_1NH_3^+\cdots R_2SO_3^-]}{[R_1NH_3^+][R_2SO_3^-]} \quad (7)$$

and

$$A_{alk} = \frac{1}{C}\frac{[R_1NH_3^+\cdots R_2SO_3^-\downarrow]}{[R_1NH_3^+\cdots R_2SO_3^-]} \quad (8)$$

respectively. The molar concentration C comprises all forms of detergent that were added to the calorimeter cell. Making use of eqs 7 and 8, we express the overall association constant K_b^{mod} of subsequently occurring reactions 1 and 2 as follows:

$$K_b^{mod} = \frac{[R_1NH_3^+\cdots R_2SO_3^-\downarrow]}{[R_1NH_3^+][R_2SO_3^-]} = A_{ion} B A_{alk} C \quad (9)$$

Dependence on Concentration. The association constant does not depend on the concentrations of reacting molecules in a simple reaction, where one ligand molecule binds to one acceptor molecule and the resultant complex remains dissolved in solution. However, if the binding reaction is followed by an aggregation reaction (which is the case for oppositely charged detergents), then the apparent binding constant depends linearly on the surfactant concentration in the cell. This is because the apparent binding constant reflects a dissolution−precipitation reaction which depends on surfactant concentration.

Figure 3 shows ITC curves of dodecylammonium binding to decane sulfonate at three different concentrations of decane sulfonate in the cell. As predicted by the model, the enthalpies of all reactions were identical within the experimental error. If the fits of these curves are obtained using a single site binding model (without aggregation taken into account), the ratios of

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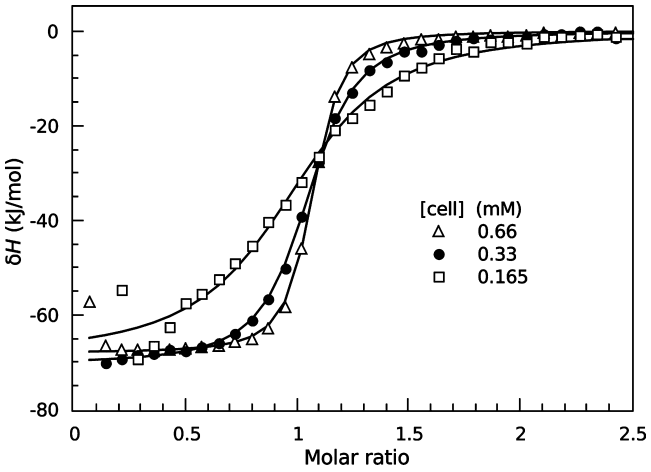

Figure 3. Dodecylammonium binding to decane sulfonate at 0.66 (open triangles), 0.33 (solid circles), and 0.165 (open squares) decane sulfonate concentrations in the cell. Dodecylammonium concentrations in the syringe were 10, 5, and 2.5 mM, respectively. The resultant enthalpies and stoichiometries of the reaction at all concentrations are the same. However, the steepness of the ITC curves or the apparent aggregation equilibrium constant differs by the factor equal to the differences between concentrations.

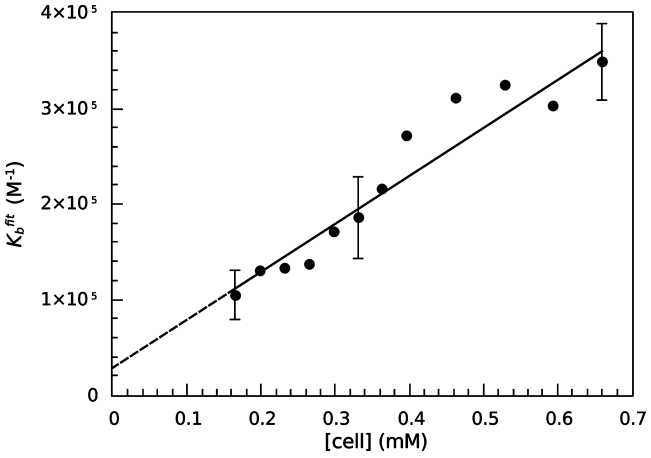

Figure 4. Dodecylammonium binding to decane sulfonate at 25 °C: the observed binding constant dependence on decane sulfonate concentration in the cell.

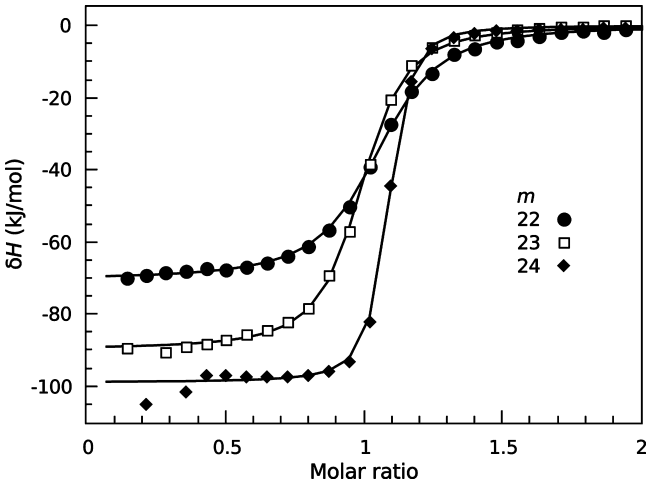

Figure 5. Dodecylammonium binding to alkane sulfonate of varying aliphatic chain length. Filled circles − decane sulfonate, open squares − undecane sulfonate, and filled diamonds − dodecane sulfonate.

apparent binding constants K_b^{fit} obtained at different concentrations are approximately the same as the ratio of these concentrations (see Table 2 for more details).

Figure 4 shows the observed binding constant dependence on the concentration of surfactant in the calorimeter cell. The dependence is approximately linear within the error of the experiment.

Dependence on Alkyl Chain Length. Dodecylammonium was titrated to three alkane sulfonates of varied chain length: decane sulfonate, undecane sulfonate, and dodecane sulfonate. The integrated ITC curves are presented in Figure 5. Thermodynamic parameters of surfactants containing various numbers of carbon atoms are summarized in Table 3.

The model formulated above predicts that the association constants for octane sulfonate and decane sulfonate reactions with octylammonium are equal to 4.69×10^1 and 8.43×10^2 M^{-1}, respectively. Such weak interactions were not observable by ITC at our experimental concentrations. In titration calorimetry, the range where K^{fit} can be reliably estimated is quite narrow and spans only about 3 orders of magnitude.[21] Only the constants K^{fit} that fell between about 10^4 and 10^7 M^{-1} could be measured. Overall, the fitted binding constant K_b^{fit} was close to the modeled association constant K_b^{mod} from eq 9 (see Table 3).

Gibbs free energies were increasingly more negative upon increasing aliphatic chain length of the surfactant in all tested series of surfactants. Methylene group contribution to the association process was equal to the methylene group contribution to alkane aggregation (−3.58 kJ/mol)[17] within our experimental error. This value appears to be universal where aggregation reactions take place.

Enthalpies of Aggregation. The enthalpies of stoichiometric aggregate formation followed the same trend as the Gibbs free energies: the longer the tail, the greater (more negative, more exothermic) the enthalpy. For example, the enthalpy of nonane sulfonate reaction with dodecylammonium was −59.2 kJ/mol, while the enthalpy of dodecylammonium−dodecylsulfonate complex formation reached a value of −84.2 kJ/mol. These enthalpies could not be predicted as precisely as Gibbs free energies by summing the enthalpies of alkane aggregation and ammonium sulfate crystallization. However,

Table 2. The ITC Curve Fitting Parameters of Dodecylammonium Binding to Decane Sulfonate at Three Different Surfactant Concentrations in the Cell[a]

C (mM)	ΔH^{fit} (kJ/mol)	N^{fit}	K_b^{fit} (M^{-1})	K_b^{mod} (M^{-1})
0.66	−70.9 ± 3.7	1.01 ± 0.03	$(3.5 \pm 0.4) \times 10^5$	5.5×10^5
0.33	−70.5 ± 5.2	0.98 ± 0.05	$(1.9 \pm 0.4) \times 10^5$	2.4×10^5
0.165	−72.7 ± 15.9	0.99 ± 0.03	$(1.1 \pm 0.3) \times 10^5$	1.4×10^5

[a]Binding constants K_b^{fit} obtained from experimental data fits are compared to binding constants K_b^{mod} obtained from the model (see eq 9).

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Table 3. Thermodynamic Parameters of Stoichiometric Coprecipitate Formation between Alkane Sulfonate and Alkylammonium as a Function of Aliphatic Chain Length m[a]

			$\Delta_{agg}G$ (kJ/mol)			$\Delta_{agg}H$ (kJ/mol)			
m	K_b^{fit} (M^{-1})	K_b^{mod} (M^{-1})	fit	mod	alk	obs	mod	alk	$T\Delta_{agg}S$ (kJ/mol)
21	3.3×10^4	6.4×10^4	−25.8	−27.5	−56.0	−37.4	−97.4	−90.8	−11.6
22	1.8×10^5	2.7×10^5	−30.0	−31.0	−59.6	−67.5	−102.6	−96.0	−37.4
23	2.6×10^5	1.2×10^6	−30.9	−34.6	−63.2	−81.9	−107.8	−101.2	−51.0
24	1.3×10^6	4.9×10^6	−34.9	−38.2	−66.8	−91.1	−113.0	−106.4	−56.3

[a]Experimental and calculated Gibbs free energies, enthalpies, and entropies were obtained at 25 °C.

the values could be rationalized in a similar fashion and provide information about the structure and phase of the surfactant complex.

The enthalpy of alkane aggregation into a solid phase at 25 °C can be estimated by an empirical equation[17]

$$\Delta_{agg}H_{alk} = -5.2m + 18.41 \quad (10)$$

where m is the number of carbon atoms in the aliphatic chains of both surfactant molecules. Since the enthalpy of ammonium sulfate crystallization is equal to −6.62 kJ/mol,[22] the estimated aggregation enthalpy of decane sulfonate titration with dodecylammonium (m = 22) would be equal to $-6.62-5.2 \times 22 + 18.41 = -102.6$ kJ/mol. The ionic contribution would be −6.62 kJ/mol, and the contribution from aliphatic tail association into a solid paraffin-like complex would be −96 kJ/mol (Table 3). The observed enthalpy is equal to −67.5 kJ/mol, which is approximately two-thirds of the predicted value. Such an observation indicates that aliphatic tails cannot interact as tightly in the surfactant complex as in pure alkane due to the bulkiness of the sulfonate headgroup. The number of carbon atoms that can form a true solid-like structure can be estimated from the observed and predicted enthalpy. For example, for decane sulfonate titration with dodecylammonium, it appears that there are $(67.5-6.62)/5.2 \approx 12$ carbon atoms out of the total of 22 in the system that form a solid-like structure. The estimate is very approximate and simplified, but we can definitely say that at least a portion of aliphatic chains in the system are solid-like. The enthalpy of liquid-like $C_{22}H_{46}$ alkane aggregation would be only −18.3 kJ/mol, which could by no means account for the much larger observed exothermic enthalpy.

It is interesting to compare alkyl sulfates with alkane sulfonates. Gibbs free energies quite precisely add up, indicating that the oxygen atom between the head and aliphatic tail in alkyl sulfates should be considered part of the headgroup. However, the enthalpies of alkyl sulfate reaction with alkylammoniums were systematically less exothermic when compared with alkane sulfonate reactions with alkylammoniums. For example, decane sulfonate−dodecylammonium produced −67.5 kJ/mol, while decyl sulfate−dodecylammonium produced only −46 kJ/mol. These differences might be attributed to the distinct phase and solubility behavior of both species.[23]

The entropies of surfactant complex formation are the least precisely determined thermodynamic parameters, because they were obtained by subtracting Gibbs free energies from enthalpies. Values obtained experimentally for various aliphatic tail lengths are listed in Table 3. We can at least qualitatively conclude that entropies are increasingly negative with the increase of surfactant aliphatic tail length. Analysis of the thermodynamic parameters showed that association of the oppositely charged alkylammonium and aliphatic sulfonate (sulfate) surfactants is an enthalpy driven and entropy opposed process. Large exothermic enthalpy primarily arises due to aliphatic tail association. The entropy has a negative ionic contribution and both negative and positive alkane contributions whose relative magnitudes depend on alkane chain length. It is usually assumed that the entropy drives hydrophobic interactions. Here we observe that entropy is negative when solid-phase aggregate is formed and may be positive only if liquid-phase aggregate is formed. The observation is similar to that previously described for aliphatic amine aggregation.[16]

Dependence on Temperature. The enthalpies of decane sulfonate reaction with dodecylammonium at various temperatures are shown in Figure 6a. ITC experiments of the enthalpy dependence on temperature were performed in the range 25−69 °C. From Figure 6a, one can see an abrupt change in enthalpy at approximately 49 °C which indicates a solid-to-liquid phase transition. Approximation of aggregate formation as that of an alkane of appropriate length ($C_{22}H_{46}$) is surprisingly precise. The results are in good agreement with the data available from the literature:[24] both the phase transition temperature and the enthalpy change between two phases are very similar, as shown in Figure 6a and b.

The slopes of the fitted lines in Figure 6a allow us to estimate constant pressure heat capacities of aggregation for both phases in $C_{10}SO_3^-$ + $C_{12}NH_3^+$ (approximated as $C_{22}H_{46}$) system. Values of specific heat in solid and liquid phases were approximately C_p(solid) = −1.56 kJ/mol K^{-1} and C_p(liquid) = −0.23 kJ/mol K^{-1}, respectively.

Dependence on Salt Concentration. In order to determine the effect of salt (NaCl) on aggregation reaction, dodecylammonium was titrated to decane sulfonate at various salt concentrations ranging from 0 to 1.0 M. There was no effect of NaCl on the ITC curves up to 0.2 M. However, some impact on the curves was observed at higher salt concentrations, as shown in Figure 7.

The observed decrease of the absolute enthalpy of binding between surfactants at high salt concentration may indicate electrostatic shielding by sodium and chloride ions. However, it may also be explained by weak ion binding to surfactant headgroups at high salt concentration. The ions may have to unbind the surfactant headgroups before the oppositely charged surfactants could bind each other.

DISCUSSION

In this paper, we have described the thermodynamics of oppositely charged surfactant stoichiometric complex formation for a series of surfactant systems with varying aliphatic chain length. The reactions occurring in these systems allow us to investigate thermodynamic additivity rules for various functional groups of the system.[15,26] The application of these rules

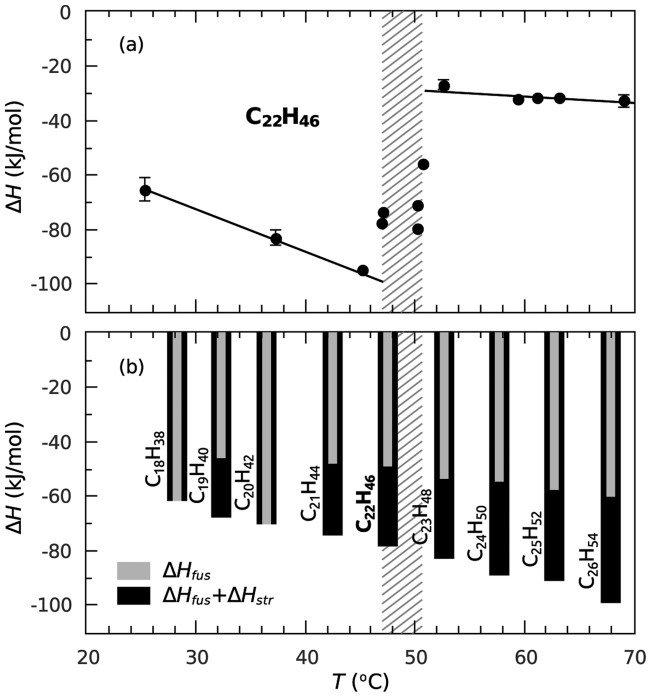

Figure 6. (a) Enthalpy dependence on temperature for decane sulfonate reaction with dodecylammonium. (b) Enthalpies of phase transitions of alkanes containing various numbers of carbon atoms (from 18 to 26): narrow gray bars represent the enthalpy changes of solid-to-liquid phase transition (ΔH_{fus}), while black bars represent the sum of enthalpy changes ΔH_{fus} + ΔH_{str}, where ΔH_{str} is related to structural rearrangements of molecules in the solid phase. The gray patterned column marks the temperature interval at which both the structural and solid-to-liquid phase transitions in $C_{22}H_{46}$ occurs. (Temperature and enthalpy data taken from refs 24 and 25.)

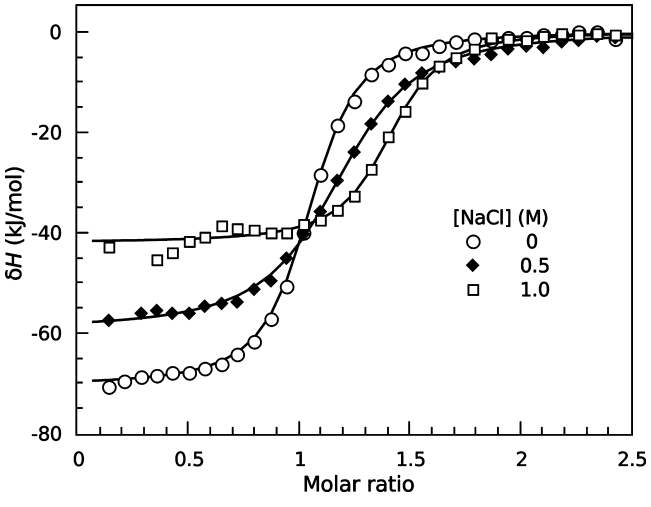

Figure 7. Dodecylammonium binding to alkane sulfonate at various concentrations of NaCl in the cell and syringe: 0 M (open circles), 0.5 M (solid diamonds), and 1.0 M (open squares).

help to answer the most important questions of this study: whether the amino and sulfonate surfactant headgroup behavior can be approximated as ammonium sulfate dissolution–crystallization reaction, and whether the aliphatic tail behavior can be approximated by alkane dissolution–aggregation equilibria.

Gibbs free energies of surfactant complex formation were nicely predicted by the model for all studied systems, including dependencies on aliphatic chain length, surfactant concentration, and temperature. Ionic headgroups opposed the association reaction, and this opposition could be overcome only by long aliphatic chains (of at least 10 carbon atoms). However, Gibbs free energies did not provide significant information about the structure of the complex, nor about its phase.

Enthalpies of oppositely charged surfactant interactions were highly exothermic primarily due to tail association. However, such reactions developed only up to about two-thirds of the predicted value using additivity rules. This result suggests that not all CH_2 groups of aliphatic tails formed the solid phase contacts and the packing was not as tight as in solid alkanes where there are no bulky ionic headgroups.

We found no studies concerning the structure of our investigated surfactant systems, apart from chemical composition.[11] Therefore, we developed a schematic model of surfactant packing using crystallographic data[10] of the most similar available structure—that of *O*-lauroylethanolamine–dodecylsulfate. *O*-Lauroylethanolamine was modified to dodecylammonium and the resulting structure optimized using the semiempirical quantum chemistry program MOPAC. During the optimization, decylsulfate molecules as well as dodecylammonium headgroups were frozen assuming no qualitative difference in hydrogen bonding. Figure 8 shows

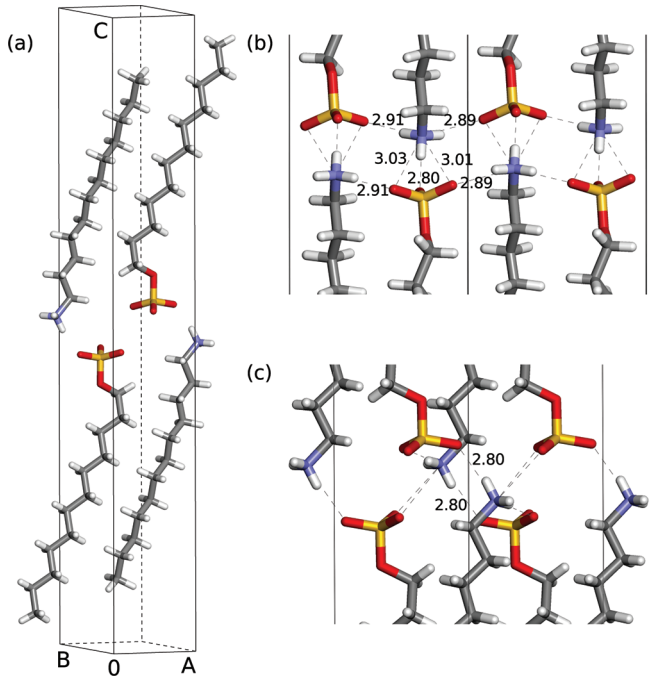

Figure 8. Packing diagrams of dodecylamine complex with dodecyl sulfate: (a) crystalline lattice unit cell; (b and c) orthogonal enlarged views of the hydrogen bonding network with the distances between ionic headgroups. The model was built according to the structure of the *O*-lauroylethanolamine complex with dodecylsulfate.[10]

the modeled structure of dodecylamine bound to dodecyl sulfate. The oppositely charged ionic headgroups bind to each other stoichiometrically as determined by ITC. Aliphatic tails form a well-packed layer of parallel hydrophobic tails.

Association between charged polymers such as poly(sodium acrylate)-*b*-poly(acrylamide)[27] or DNA[28] with positively charged detergents was found to be primarily entropy-driven.

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This entropy drive has been assigned to the release of counterions from the polymer. However, association reactions between oppositely charged long-chain aliphatic surfactants were found to be enthalpy-driven and entropy-opposed. All such systems formed electrostatically neutral complexes that usually coprecipitated from aqueous solution. This exhibits the importance of electrostatics in the association between oppositely charged species.

The enthalpy could be assigned primarily to aliphatic tail association, but the entropy had compensating contributions from headgroups and tails. It was thought earlier that the large exothermic enthalpy arises due to ion pair formation in such systems.[14] We believe that the enthalpy is primarily due to chain packing. Furthermore, our observations expand the conventional understanding of the hydrophobic effect, which states that the entropy drives hydrophobic interactions. Instead, here we confirm our earlier findings with alkylamines,[16] that long aliphatic chain association in water is an enthalpy-driven and entropy-opposed process.

The same reaction may be carried out at higher temperatures, above the fusion temperature. Then, as demonstrated for dodecylammonium binding to decane sulfonate, the thermodynamics of binding may be significantly different. The enthalpy change equals only −30 kJ/mol instead of nearly −100 kJ/mol, making the overall enthalpy contribution significantly smaller. Therefore, it may be concluded that, if aliphatic chains are unable to form a solid phase, the enthalpic contribution will be much smaller than if the solid phase is formed.

CONCLUSIONS

Association and aggregation reactions between long-chain aliphatic surfactants at temperatures below the fusion temperature are enthalpy-driven and entropy-opposed. The dominating enthalpy contribution is primarily due to aliphatic chain packing.

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Notes

The authors declare no competing financial interest.

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