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Effect of Counterions and Headgroup Hydrophobicity on Properties of Micelles Formed by Alkylpyridinium Surfactants. 2. Microcalorimetry

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We report the influence of counterions and headgroup hydrophobicity on the enthalpies and heat capacities of micelle formation by 1-alkyl-4-*n*-dodecylpyridinium surfactants in aqueous solution. For micelle-forming 1-alkyl-4-*n*-dodecylpyridinium iodide surfactants (alkyl = C_1−C_3), enthalpies of micelle formation show no trend with respect to 1-alkyl chain length. Changes in molecular architecture of the counterion, however, have a large influence on the thermodynamics of micelle formation. It is shown that next to solvation, London dispersion interactions, counterion (substituent)−water interactions, and the microenvironment of counterions adsorbed to micellar surfaces play an important role in determining the exothermicities of micelle formation. Isobaric heat capacities of micelle formation show that the formation of wormlike micelles for salicylate-containing cationic surfactants is due to a favorable microenvironment for salicylate counterions in the Stern layer of micelles.

Introduction

Many physicochemical properties show sudden changes when a characteristic concentration of surfactant is exceeded. This change is attributed to the formation of colloidal aggregates and occurs over a relatively small concentration range characteristic for the surfactant. Aggregation of surfactant monomers in aqueous solution can lead to a variety of aggregate structures including micelles, vesicles, and inverted structures. Depending on the molecular architecture of the surfactant, temperature, concentration, and added electrolyte, a particular aggregate morphology is favored.[1] This paper deals with the formation of micelles as a function of surfactant structure, with the emphasis on the molecular architecture of counteranions.

Micelle formation is the result of a delicate balance of molecular interactions, which determine the Gibbs energy of formation, size, and shape of the aggregates. Related to the Gibbs energy of micelle formation are the enthalpies of micelle formation, which yield fundamental information on micelle formation, i.e. interactions associated with the process of self-assembly. Isothermal titration microcalorimetry has been used to study the thermodynamics of micelle formation, i.e. $\Delta_{mic}H$ and $\Delta_{mic}C_p°$ of cationic,[2−8] anionic,[9−14] and nonionic[15] surfactants in aqueous solution.

In a typical isothermal microcalorimetric experiment, small aliquots of a concentrated surfactant solution (concentration ≫ cmc, e.g. 20 times the cmc, where cmc is the critical micelle concentration) are injected into a sample cell, which initially contains water or a surfactant solution below the cmc. Typical injection volumes are 10 μL, whereas the cell volume is 1.3 mL.

Figure 1 shows a typical enthalpogram for the dilution of a concentrated surfactant solution into the sample cell. At the beginning of the experiment the sample cell contains only water. Micelles are injected into the sample cell, which, for this surfactant, results in endothermic pulses of heat. The endothermicity in the premicellar region results from the breakup of micelles into monomers. After thermal equilibrium is reached, the next aliquot is injected. Subsequent aliquots result in an increase of surfactant concentration in the sample cell. After n aliquots the concentration in the cell approaches the cmc, and a change in pattern is recorded. After n +1 aliquots the micellar region is entered and the dilution enthalpy is determined by the concentration differences of the micellar solution in the syringe and in the sample cell, respectively.

Integration of the areas under the peaks (Figure 1) yields the dependence of heat of dilution on concentration. Figure 2 shows a plot of the heat of dilution versus concentration for surfactant **1** (Chart 1). Isothermal titration microcalorimetry provides both the enthalpy of micellization and the cmc. The difference between the

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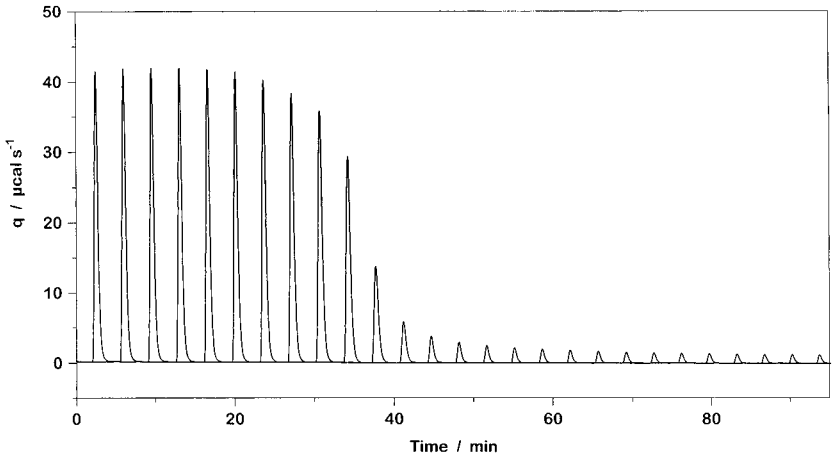

Figure 1. Titration of a micellar solution of surfactant **1** into water.

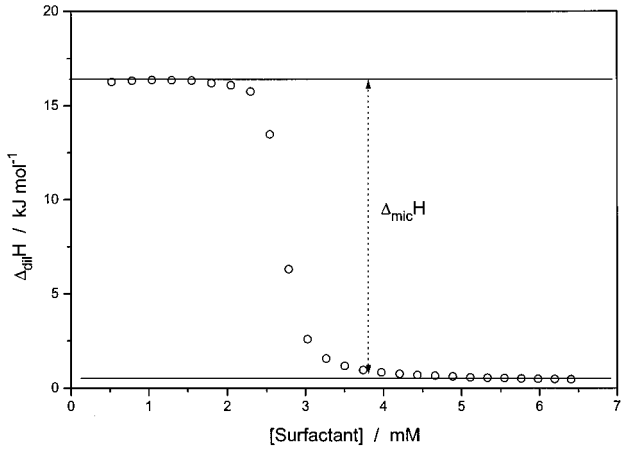

Figure 2. Enthalpy of dilution versus surfactant concentration for surfactant **1** at 30 °C.

two horizontal parts of the S-shaped curve (Figure 2) yields the enthalpy of micellization. The break in the S-shaped curve occurs at the cmc. Critical micelle concentrations, determined using isothermal titration microcalorimetry, are, within error limits, equal to cmc values found using conductometry.[16] Therefore, cmc values determined using isothermal titration microcalorimetry are not reported in this paper, and we refer to an earlier paper on the influence of counterions on the aggregation behavior of alkylpyridinium surfactants.[16] Previously,[17] we discussed the influence of 4-alkyl chain length, 4-alkyl chain branching, and counterion size on the enthalpies of micelle formation by 1-methyl-4-alkylpyridinium surfactants. The enthalpies of micelle formation become more exothermic upon increasing the 4-alkyl chain length, whereas no trend with respect to chain branching was observed.

Counterions adsorb to micellar surfaces and thereby alter electrostatic headgroup repulsions. Previously,[17] enthalpies of micelle formation were shown to become more exothermic upon decreasing the size of hydrated counterions, indicating the importance of solvation, i.e. the position of counterions with respect to micellar surfaces. This paper is aimed at showing that, besides solvation, specific counterion effects also strongly influence the thermodynamics of micelle formation. Specific counterion effects include London dispersion interactions between counterions and surfactant monomers in the aggregate, counterion (substituent)−water interactions, and interactions due to the microenvironment of counterions in the Stern layer.

With respect to surfactant structure the following features are discussed: (i) headgroup hydrophobicity, (ii) counterion hydrophobicity, and (iii) aromatic counterions.

The choice of amphiphiles was, in part, limited because of sometimes unfavorable Krafft temperatures.

Experimental Section

Titration Microcalorimetry. Enthalpograms were recorded using a Microcal Omega titration microcalorimeter (Microcal, Northampton, MA). All water was doubly distilled, and solutions were degassed before use. In a typical experiment the sample cell and reference cell were filled with water. The syringe contained a surfactant solution having a concentration approximately 20 times the cmc. The sample cell was stirred (350 rpm, unless stated otherwise) to ensure complete mixing. After thermal equilibrium had been achieved, the first aliquot was injected (5−10 μL). The heat absorbed or evolved was recorded, and subsequently the next aliquot was injected after thermal equilibrium had been reached (typically 210 s between injections and an injection time of 20 s). This procedure was repeated until the desired concentration range was covered. The results were analyzed using Omega software (Origin 2.9).

Synthetic Procedures. The synthesis and purity of the surfactants are described elsewhere.[16,18]

Results and Discussion

Influence of Micellar Size and Shape on the Enthalpy of Micelle Formation. In order to study the influence of micelle size on the recorded heats of injection, the surfactant concentration in the syringe was increased at constant injection volume. It is known that the size of micelles increases with increasing concentration.[19] Surfactant **1** has a cmc of 2.5 mM and forms wormlike micelles at concentrations above 45 mM (both at 30 °C).[19] The influence of the injection concentration on the enthalpies of micelle formation is shown in Table 1.

The enthalpy of micelle formation becomes more exothermic upon increasing surfactant concentration in the syringe. The results can be understood[19,20] in terms of a closer packing of surfactant monomers in an aggregate, resulting in stronger London dispersion interactions between the hydrophobic moieties and less water pen-

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Chart 1

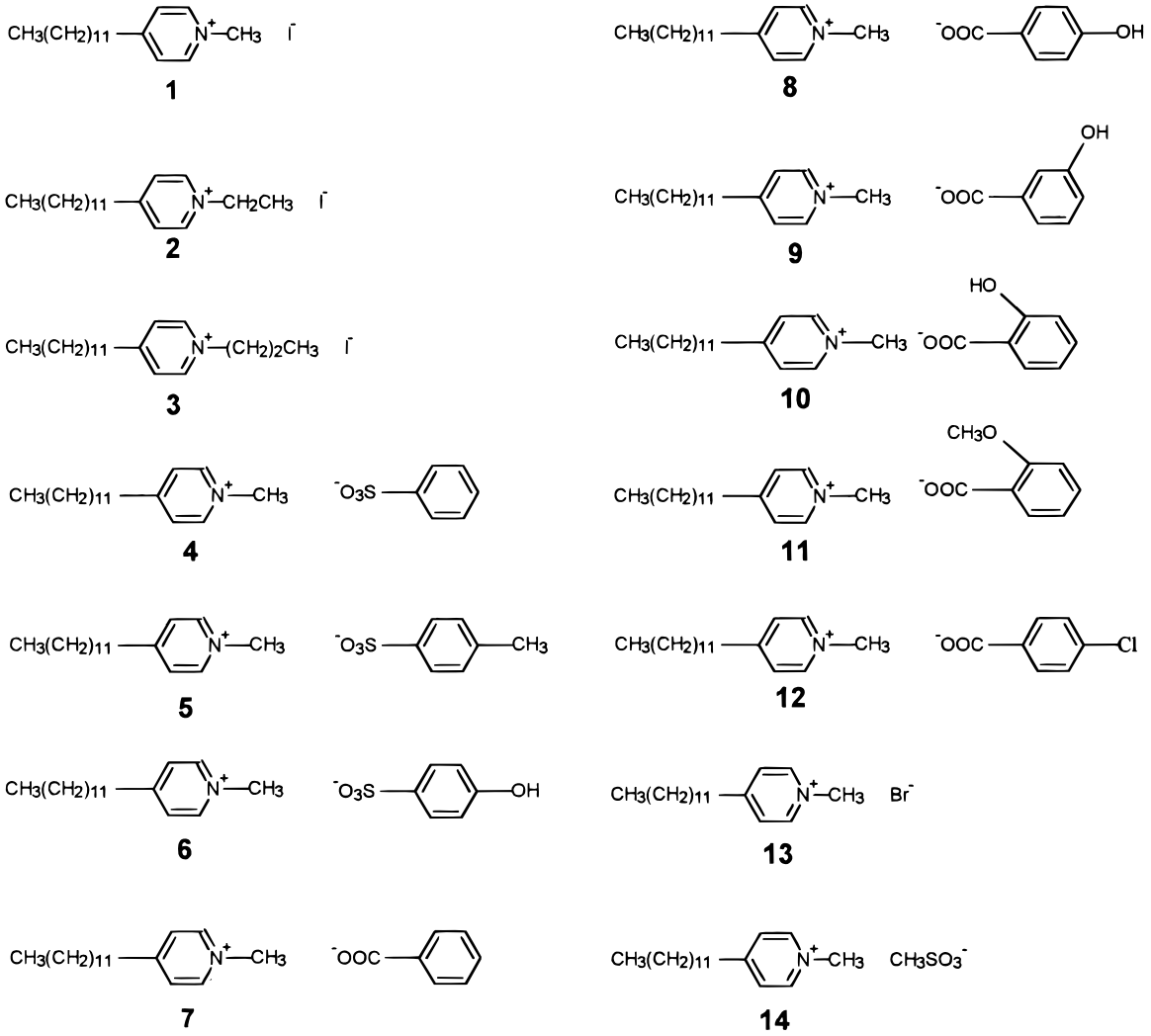

Table 1. Influence of Surfactant Concentration in the Syringe (Injection Concentration) on the Standard Enthalpy of Micellization for Surfactant 1 at 30 °C

injection concn (mM)	$\Delta_{mic}H^a$ (kJ mol^{-1})	injection concn (mM)	$\Delta_{mic}H^a$ (kJ mol^{-1})
35.1	−15.7	74.2	−16.9
50.1	−16.1	90.5	−17.1
61.2	−16.5		

[a] Estimated error: ±0.1−0.2 kJ mol^{-1}.

Table 2. Influence of Stirring Speed on the Measured Enthalpy of Micellization of Surfactant 1 at 30 °C

stirring speed (rpm)	$\Delta_{mic}H^a$ (kJ mol^{-1})	stirring speed (rpm)	$\Delta_{mic}H^a$ (kJ mol^{-1})
200	−15.9[b]	500	−16.4
350	−16.1	600	−16.0

[a] Injection concentration = 50 mM. [b] Estimated error = 0.2−0.5 kJ mol^{-1}, depending on the stirring speed.

etration between the headgroups. Increased headgroup repulsions are, in the case of ionic surfactants, partly balanced by an increase in counterion binding. Consequently, deaggregation is more endothermic (i.e. micelle formation is more exothermic).

Influence of Stirring Speed. Surfactants are surface-active materials. Therefore, adsorption of surfactants at the water−solid interface and at the water−air interface of the sample cell is possible. If adsorption had been significant in the present study, the measured enthalpy might be due not only to micelle formation but also to adsorption. Surfactants adsorbed at interfaces contribute to the observed heat effect, and less surfactant is, at a given concentration, available for the monomer−micelle equilibrium. The influence of stirring speed on the measured enthalpy of micelle formation is shown in Table 2. No trend was observed. Hence, complications due to adsorption were negligible.

In contrast to the injection concentration, the stirring speed does not play a significant role in the observed heat effects. Since shape and size of the injected micelles affect the observed heat effect, we decided to use a standardized experimental procedure, which involved an injection concentration of ca. 20 times the cmc and a stirring speed of 350 rpm.

Headgroup Hydrophobicity. 1-*n*-Alkyl-4-*n*-dodecylpyridinium iodide surfactants with a 1-alkyl chain having fewer than four carbon atoms form micelles in aqueous solution. When the 1-alkyl chain length is further increased, vesicles are formed.[19] The surfactants reported here all form micelles.[19] The 1-alkyl chains are located in the Stern layer[19,21,22] and are incompletely dehydrated upon micelle formation. Nusselder et al.[19] observed a weak dependence of the cmc ($\Delta_{mic}G°$) on the hydrophobicity of

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Table 3. Influence of Headgroup Hydrophobicity on the Enthalpy of Micellization

	$\Delta_{mic}H^a$ (kJ mol^{-1})			
surfactant	30 °C	40 °C	50 °C	60 °C
1[b]	−16.1	−21.0	−29.9	−29.4
2	−17.0	−22.7	−27.9	−32.0
3	−15.8	−21.3	−26.1	−30.4

[a] Estimated error: ±0.1−0.2 kJ mol^{-1}. [b] According to ref 17.

the 1-alkyl chain for surfactants **1**, **2**, and **3**, indicating stabilization of micelles due to the hydrophobicity of the 1-alkyl chain (e.g. a more negative standard Gibbs energy of micellization). Within error limits of the microcalorimeter, no dependence of $\Delta_{mic}H$ on headgroup hydrophobicity was observed (Table 3). Incomplete dehydration of the headgroup region and interactions between the 1-alkyl groups probably cancel upon micellization. The dependence of $\Delta_{mic}G$ on headgroup hydrophobicity is apparently an entropic effect.

Heat Capacities of Micellization as a Function of Counterion and Headgroup Hydrophobicity. Heat capacities of micellization are believed[7] to be primarily related to hydrophobic interactions. These heat capacities are a linear function[23] of the hydrophobic surface area of the monomers. This area is largely separated from contact with water upon micellization. Therefore, the heat capacities yield information about solute−solvent interactions. Hydrophobic groups are characterized by large and positive partial molar heat capacities, reflecting the temperature dependence of their hydration enthalpies. As a result, association of surfactants in water is accompanied by large negative heat capacities of micelle formation. For micellization of sodium *n*-dodecylsulfate, Sharma et al.[14] reported a heat capacity of micellization between −422 and −550 J mol^{-1} K^{-1} depending on the temperature range. Mehrian et al.[5] reported that heat capacities of micellization, for a series of alkylpyridinium chloride surfactants in water, are independent of temperature over the range 6−60 °C. A heat capacity of micellization of −382 J mol^{-1} K^{-1} is reported for *n*-decyl-, −462 J mol^{-1} K^{-1} for *n*-dodecyl-, and −621 J mol^{-1} K^{-1} for *n*-tetradecylpyridinium chloride upon micellization.

Bashford and Burchfield[24] studied the micellization of alkyltrimethylammonium bromide surfactants. Heat capacities of micelle formation are −320 (decyl), −409 (dodecyl), and −499 J mol^{-1} K^{-1} (tetradecyl). The changes in heat capacity of micellization per CH_2 group are identical within error limits and amount to −45 J mol^{-1} K^{-1}, independent of the nature of the headgroup.

The effect of surfactant structure (i.e. counterion and headgroup hydrophobicity) on the heat capacity of micellization of 1-*n*-alkyl-4-alkylpyridinium surfactants is summarized in Table 4. No clear trend is observed. The number of methylene groups exposed to water by water penetration influences the heat capacity of micellization; this might also add to the observed variation in $\Delta_{mic}C_p°$ values. Furthermore, heat capacities of micellization are independent of temperature in the range 30−60 °C. The enthalpies of micellization showed an excellent linear correlation with temperature (correlation coefficients > 0.996) for all surfactants examined.

Johnson and Olofsson[25] studied the heat capacities of micellization of *n*-hexadecyltrimethylammonium surfactants with *p*- and *o*-hydroxybenzoate counterions. It was observed that the heat capacities of micellization depended on the position of the hydroxy group relative to the carboxyl moiety in the hydroxybenzoate counterions. The results were explained[25] by assuming that salicylate anions penetrate between headgroups of the surfactant, while *p*-hydroxybenzoate anions remain in the Stern region. This difference would cause differences in aggregation behavior between surfactants with the different aromatic counterions. However, the data in Table 4 show that the heat capacities of micellization for surfactants **10** and **11** are similar, while **10** forms wormlike micelles and **11** forms spherical micelles. The degree of penetration of aromatic counterions between pyridinium headgroups was found to be similar for both surfactants, however.[16] The fact that Johnson and Olofsson[25] observed and interpreted a "trend", as discussed above, may be due to the fact that they studied a limited number of surfactants.

Surfactants **10** and **12** form long wormlike micelles, whereas the other surfactants form spherical micelles. Since the heat capacity of micellization is related to hydrophobic hydration, formation of long wormlike micelles, in the case of surfactants **10** and **12**, is attributed to "headgroup effects" rather than changes in alkyl chain−solvent interactions upon micellization. NMR data[16] indicate that the degree of penetration of aromatic counterions between the headgroups is not affected by the substitution pattern of the aromatic counterion. The heat capacities reported by Johnson and Olofsson[25] are therefore probably constant within the error limit of the heat capacities of micellization and are not influenced by differences in the degree of penetration (i.e. a difference in solvation). Headgroup effects and interactions which determine the unusual growth of micelles for surfactants **10** and **12** will be discussed in detail in a future paper.[26]

Influence of Aromatic Counterions on Enthalpies of Micellization of 1-Methyl-4-*n*-dodecylpyridinium Surfactants. All aromatic counterions reported in this paper penetrate between pyridinium headgroups in micelles formed by 1-methyl-4-*n*-dodecylpyridinium surfactants. The same degree of penetration is found,[16] although the microenvironments may be different (e.g. degree of water penetration and the size of the micelle). Upon micellization the counterions interact with surfactant monomers in the aggregate. Apart from counterion-surfactant interactions, counterion−solvent interactions should also be considered. The importance of these interactions is discussed below.

An increase in hydrophobicity of counterions produces an increase in exothermicity of enthalpies of micellization (compare **4** and **5**, Table 5) and of the aggregation numbers, whereas the degree of water penetration is smaller. These trends can be rationalized in terms of an increase in counterion−surfactant monomer interactions in the micelle.[1,20] Although the degree of water penetration (i.e. counterion−solvent interactions) will also affect the enthalpies of micellization, the dominant contribution to the enthalpies of micellization, however, is attributed to the enlarged hydrophobic surface area of the counterion exposed to the surfactant monomer.

When *p*-hydroxy substituents are present in the aromatic counterions, the role of water penetration between headgroups becomes more important.

Introduction of a hydroxy group at the para position leads to more exothermic enthalpies of micellization (compare **4** with **6** and **7** with **8**). Remarkably these effects are accompanied by a decrease in the degree of counterion binding.[16] Since the Stern region of micelles contains

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Table 4. Heat Capacities of Micellization[a] ($\Delta_{mic}C_p°$) as a Function of Surfactant Structure

surfactant	$\Delta_{mic}C_p°$ [b] (J mol^{-1} K^{-1})
1-methyl-4-*n*-dodecylpyridinium iodide (**1**)	−449
1-methyl-4-*n*-dodecylpyridinium bromide (**13**)	−469
1-methyl-4-*n*-dodecylpyridinium methanesulfonate (**14**)	−485
1-methyl-4-*n*-dodecylpyridinium benzenesulfonate (**4**)	−548
1-methyl-4-*n*-dodecylpyridinium toluenesulfonate (**5**)	−579
1-methyl-4-*n*-dodecylpyridinium 4-hydroxybenzenesulfonate (**6**)	−460
1-methyl-4-*n*-dodecylpyridinium benzoate (**7**)	−591
1-methyl-4-*n*-dodecylpyridinium 4-hydroxybenzoate (**8**)	−433
1-methyl-4-*n*-dodecylpyridinium 3-hydroxybenzoate (**9**)	−375
1-methyl-4-*n*-dodecylpyridinium salicylate (**10**)	−533
1-methyl-4-dodecylpyridinium 2-methoxybenzoate (**11**)	−558
1-methyl-4-*n*-dodecylpyridinium 4-chlorobenzoate (**12**)	−601
1-ethyl-4-*n*-dodecylpyridinium iodide (**2**)	−501
1-*n*-propyl-4-*n*-dodecylpyridinium iodide (**3**)	−484

[a] Upon plotting $\Delta_{mic}H$ vs T a straight line is obtained ($r > 0.996$ for all surfactants examined). [b] Estimated error: ±50 J mol^{-1} K^{-1}.

Table 5. Influence of Aromatic Counterions on the Enthalpy of Micellization of 1-Methyl-4-*n*-dodecylpyridinium Surfactants

	$\Delta_{mic}H$[a] (kJ mol^{-1})			
surfactant	30 °C	40 °C	50 °C	60 °C
4	−9.0	−14.9	−20.2	−25.5
5	−10.0	−16.5	−22.3	−27.4
6	−15.3	−20.6	−25.1	−29.1
7	−7.6	−14.2	−20.1	−25.5
8	−14.9	−19.7	−24.3	−27.8
9	−17.9	−22.1	−26.0	−29.1
10	−22.4	−28.1	−33.8	−38.3
11	−1.7	−7.8	−13.5	−18.4
12	−15.8	−22.5	−28.9	−33.7

[a] Estimated error: ±0.1−0.2 kJ mol^{-1}.

water, the hydroxy group is in a favorable environment, whereas the methyl group (in the case of surfactant **5**) is in a less favorable environment. This indicates a delicate balance between hydrophobic effects and counterion substituent−water interactions.

Moving the hydroxy substituent of the hydroxybenzoate counterion from para to meta to ortho in 1-methyl-4-*n*-dodecylpyridinium x-hydroxybenzoate surfactants leads to more exothermic enthalpies of micellization (compare **8**, **9**, and **10**). The strongly exothermic enthalpy of micellization for 1-methyl-4-*n*-dodecylpyridinium salicylate is due to the formation of wormlike micelles. Compared to surfactant **8**, surfactant **9** has a more exothermic enthalpy of micellization, because the hydroxy group is in a more favorable environment. Instead of interactions with water which has penetrated between the headgroups, the hydroxy group interacts with the water in the outer parts of the Stern region.

1-Methyl-4-*n*-dodecylpyridinium *p*-chlorobenzoate (**12**) also forms wormlike micelles, and the solutions are viscoelastic at 1.2 mM (the critical wormlike micelle concentration is 0.9 mM). The enthalpy of micellization is less exothermic than that for **10**, because the chloro group is relatively hydrophobic. Penetration of water into the region where the counterion is located means that the hydrophobic chloro substituent experiences unfavorable interactions with the water.

Introduction of an *o*-methoxy substituent in the counterion (**11**) leads to an increase in cmc, a decrease in the degree of counterion binding,[16] and a much less exothermic enthalpy of micellization, most likely due to increased electrostatic headgroup repulsions. The microcalorimetric curve type is B,[27] which means that ion-ion interactions are important in determining the thermodynamics of micellization. The optimal headgroup area is large, and headgroup repulsions are strong. Comparison of surfactants **11** and **10** shows that the *o*-methoxy group hampers micellization. In the case of **10**, micellization is facilitated by hydrogen bonding at the micellar surface. Formation of entangled networks of wormlike micelles by **10** and **12** will be discussed in a future paper.[26]

Conclusion

Changes in the structure of counterions considerably influence the thermodynamics of micelle formation.

The influence of (aromatic) counterion structure on the enthalpies of micelle formation is rationalized by taking hydration, London dispersion interactions, counterion (substituent)−water interactions, and the microenvironment of the counterion in the Stern layer into account. The most pronounced example of counterion effects involves 1-methyl-4-*n*-dodecylpyridinium salicylate surfactants. When dissolved in water, above the cmc, this surfactant forms extremely long wormlike micelles. The *o*-hydroxy group points into the outer parts of the Stern layer, and the counterion intercalates between pyridinium headgroups. Combination of favorable interactions and a favorable microenvironment, compared to other counterions (e.g. 3-hydroxybenzoate), leads to the most exothermic enthalpy of micelle formation of the surfactants examined in this study.

Isobaric heat capacities of micellization show that formation of extremely long wormlike micelles is due not to a drastic change in alkyl chain−water interactions but to a favorable microenvironment for the salicylate counterion in the Stern layer.

Microcalorimetry appears to be a very sensitive technique which probes the delicate balance of interactions when surfactants with slightly different counterions aggregate to form micelles in aqueous solution.

The fact that no trend in enthalpies of micelle formation is observed with respect to headgroup hydrophobicity is explained by assuming that incomplete dehydration of the headgroup region and interactions between the 1-alkyl groups cancel upon micelle formation.

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