

Counterion Effect on the Thermodynamics of Micellization of Alkyl Sulfates

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Thermodynamics of micelle formation of anionic surfactants was investigated by using isothermal titration calorimetry (ITC). Highly purified decyl and dodecyl sulfates have been used to analyze the effect of counterions (Li^+ , Na^+ , K^+ , and Cs^+) on critical micelle concentration (cmc) and enthalpy of micellization (ΔH_{mic}) determined between 10 and 60 °C. The enthalpy of micellization decreases strongly with increasing temperature and passes through zero (endothermic to exothermic processes), while the cmc versus temperature exhibits a minimum. At a given temperature and for a fixed chain length, the decrease of cmc and ΔH_{mic} in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ is related to the increase of the binding of counterions to micelles. The electrostatic repulsions between ionic headgroups, which prevent the aggregation, are progressively screened as the ionic character decreases with the size of the counterion. The heat of dilution of micelles is markedly dependent on temperature and is correlated with the temperature-dependent shape of micelles. The cmc concept has an exact meaning within the so-called phase separation model of micelle formation. Therefore, free energy and entropy were deduced from the cmc and enthalpy of micellization using this model by taking into account the counterion binding. The temperature changes of ΔS_{mic} indicate that the process of micellization is entropically driven. ΔG_{mic} is always negative (thermodynamically favored process) and slightly temperature and counterion dependent.

Introduction

The formation of a micelle from monomeric ionic surfactants results from a balance between (attractive) hydrophobic interactions between the hydrophobic tails of the amphiphiles, (attractive and repulsive) electrostatic interactions between their hydrophilic charged headgroups, as well as with and between the counterions. Micelles are more or less spherical and may adopt prolate (elongated cylindrical) or oblate (large, flat lamellar) shapes according to the properties of the molecules and the media involved. In aqueous solutions, where the hydrophobic chains of the micelle-forming surfactants are oriented toward the interior of the micelles, the solution-micelle interfacial region contains the headgroups and the electrical double layer that is divided into two parts: the Stern layer of strongly bound counterions and the diffuse layer of counterions. The strength and importance of the various interactions resulting in the micelle formation were analyzed by varying externally controllable factors, such as temperature and ionic strength, or the properties of the molecules (nature of ions or chain length). Relations between concentration and structure of the resulting micelles, in particular association number and shape, were found.^{1–4}

Many techniques have been applied to analyze the process of micellization by measuring changes in physical properties at the critical micelle concentration (cmc).^{1,2,4} Most commonly, the breaks in the electrical conductivity, surface tension, and light scattering have been used for this purpose. Especially the differences in cmc with respect to the nature of the counterions as well as the shape of micelles and the surface charge density have been investigated and appear to reflect the degree of binding of the counterions to the micelles. The degree of

counterion binding to micelles was measured by different experimental techniques, including ultrafiltration,⁵ specific-ion electrode,⁶ electric conductivity,^{7,8} NMR chemical shift,⁹ and Corrins–Harkins plot.¹⁰ The values usually depend on the method used; however, they show the same feature. For alkali alkyl sulfate surfactants, the large hydrated radii and low polarizability result in lowering the degree of binding and in increasing the cmc.^{7,11–15} The decrease of the surface potential of micelles with decreasing hydrated radius from Li^+ to Cs^+ is in agreement with the modification of the counterion binding.¹⁶ For a given counterion (Cs^+), the analysis of SANS and SAXS scattering profiles shows that the counterions are more dissociated in micelles of surfactants with C_{10} chains than with C_{12} chains.¹⁷ From a structural point of view, the effect of counterions has been well documented by Missel and co-workers for dodecyl sulfates in a salty solution of the same alkali-metal chloride. Quasi-elastic light scattering proves the tendency of micelles to grow from spherical to long rodlike structures in the order $\text{Li}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Cs}^+$ with a significant change in the aggregation number with temperature.¹⁸ It has been recently confirmed that the micellar growth of sodium dodecyl sulfate is larger when the counterion hydration is smaller (from Na^+ , K^+ , to Cs^+).¹⁹ The same set of alkyl sulfates was used to analyze the adsorption behavior at the air/water interface by neutron reflectivity and surface tension measurements.^{15,20} It confirms the larger area occupied by the smaller ion and the larger number of water molecules bound to the interface for Li^+ and Na^+ compared to Cs^+ .¹⁵

Among other techniques, calorimetry was mainly used to analyze the effect of headgroup, chain length, and temperature on the micellization of alkyl sulfate surfactants^{4,21–25} but only rarely to analyze the effect of counterions,¹² probably because this effect was expected to be very small. For alkyl sulfates and especially sodium dodecyl sulfate, some thermodynamical

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parameters were calculated at discrete temperatures either by means of calorimetric measurements^{4,12,25} or on the basis of theoretical considerations.^{8,12,13} Between 20 and 55 °C, calorimetric measurements showed an almost linear variation of the enthalpy of micelle formation of Li, Na, and K dodecyl sulfates.¹² The Gibbs free energy adopts similar values for all counterions.^{12,15}

Actually, the improvement of precision and sensitivity in calorimetric measurements allows the measurement of very small heat changes. This led us to reconsider the thermodynamics of micelle formation of decyl and dodecyl sulfate surfactants with different alkali counterions (Li⁺, Na⁺, K⁺, and Cs⁺) in pure water over a large temperature range. Our aim is to complete the understanding of the micellization of alkyl sulfates with new accurate calorimetric data using highly purified surfactants.

Experimental Section

Synthesis. Alkali decyl and dodecyl sulfates (Li⁺, Na⁺, K⁺, and Cs⁺) were prepared by sulfation of the long chain alcohol with chlorosulfonic acid.²⁶ The purity of decyl and dodecyl alcohol (puriss. grade, SIGMA-Aldrich, St. Louis, MO) was 99.7%, analyzed by GLC.^{27a} Decyl and dodecyl alcohol, respectively, dissolved in dried diethyl ether (MERCK, Darmstadt, Germany) was sulfated with a diethyl ether adduct of chlorosulfonic acid (synthesis grade, MERCK, Darmstadt, Germany) at 0 °C. Chlorosulfonic acid was distilled before use to remove water. The molar excess of chlorosulfonic acid in the sulfation reaction amounted to 10%. The obtained sulfuric acid half ester was neutralized with 2 N lithium, sodium, potassium, and cesium carbonate (synthesis grade, MERCK, Darmstadt, Germany), respectively, at 10 °C. The solid was filtered, dissolved in absolute ethyl alcohol (MERCK, Darmstadt, Germany), and filtered again to remove inorganic residues. Finally, the anionic surfactants were recrystallized several times from ethyl alcohol. The alcohol was purified by heating with a saturated potassium hydrate solution for 2 h and following distillation.

The purity of the prepared alkali alkyl sulfates was proved by a quantitative high-performance liquid chromatography (HPLC) method to detect traces of alkanols in alkyl sulfates.^{27b–29} The influence of long chain alcohols in alkyl sulfates on the adsorption and aggregation behavior in aqueous solution is generally known. The corresponding homologous alcohols possess surface activities that are stronger by more than 2 orders of magnitude compared to those of the alkyl sulfates themselves. Therefore, the used alkali decyl and dodecyl sulfates were extremely purified. The residual decyl and dodecyl alcohol, respectively, in the surfactants used in this work amounts to less than 0.01 mol %.

In the next sections, we will use the following abbreviations for the surfactants investigated: LiDeS, NaDeS, KDeS, and CsDeS for the decyl compounds and LiDS and NaDS for the dodecyl compounds with Li⁺, Na⁺, K⁺, and Cs⁺ as counterions.

Isothermal Titration Calorimetry. Critical micelle concentration (cmc) and enthalpy of micellization (heat of micelle formation) are measured with an isothermal titration calorimeter (Microcal Inc., Northampton, MA). Experimentally, these values are determined via the reverse process, i.e., demicellization. A concentrated surfactant solution (usually 10 times the cmc) is injected into the thermostated sample cell containing pure water (2.1 mL) in multiple steps of 2.5–10 μ L using a syringe with a capacity of 250 μ L at a constant stirring rate (400 rpm). At each step, the heat produced or consumed is measured as a

function of time (Figure 1a). The heat of each injection determined by integration of the heat flow peak after subtraction of a linear base line is divided by the injected mole number. It yields the heat of reaction per mole plotted versus the concentration of surfactant in the cell (Figure 1b). The heat flow plot can be divided into two concentration ranges where the reaction enthalpies are more or less constant. For the first injections, the final concentration in the sample cell is below the cmc. The heat change essentially stands for micellar dilution, demicellization, and dilution of monomers (whatever of these come from the micelle or from the equilibrium with micelles). The strong heat change indicates that the cmc in the sample cell has been reached. If more micelle solution is added, the micelles are no longer dissolved and the only heat now measured is caused by the dilution of micelles. This is the second range. The cmc corresponds to the concentration where the first derivative displays a minimum or maximum depending on the temperature (Figure 1c). At this concentration, the enthalpy of micellization is calculated as the heat difference between the two extrapolated lines as indicated in Figure 1d. In all systems investigated, the estimation of the enthalpy of demicellization is very accurate for temperatures 5 °C below or above the temperature where the enthalpy change approaches zero. In this peculiar case, the first derivative does not display a sharp peak and the determination of the cmc is less accurate or even impossible. In the present case, we have used a second-order polynomial function as an empirical relation between cmc and temperature in order to determine the temperature at which the cmc goes through a minimum.

Solubility. At a concentration of 10 times the cmc, potassium decyl and dodecyl sulfate are not completely soluble in water at room temperature. The solution contains hydrated crystals dispersed in a micellar phase. Above 28 °C, the potassium decyl sulfate solution is completely clear. The micellization of KDeS was thus investigated in the limited range between 30 and 50 °C. In the case of potassium dodecyl sulfate, which has a Krafft temperature of 34 °C at the cmc,⁴ it was impossible to investigate the micellization process since the temperature leading to a clear solution was too high (50 °C) and KDS precipitated at the top of the syringe, which is not thermostated. Although CsDeS has a smaller hydrated radius than KDeS, its solubility limit is much above the cmc⁷ and solutions are clear even at low temperatures down to 10 °C. This solubility gap encountered for potassium alkyl sulfates has already been reported.^{7,30} Missel has quantified this difference in solubility by measuring the temperature at which the solid phase is in equilibrium with the micellar phase. This temperature does not decrease continuously with the size of the counterion but follows the order LiDS < NaDS < CsDS < RbDS < KDS for the dodecyl series.¹⁸ This confirms our observation that KDeS has a lower solubility than CsDeS.

Results and Discussion

cmc and ΔH_{mic} . cmc and enthalpy of micellization determined according to the method described in Figure 1 are presented in Table 1 and Figures 2–5 for each alkyl sulfate series.

Our values of the cmc, determined by ITC measurements, are slightly larger than obtained in previous papers with the same surfactants.^{7,12,21,24,31} This difference arises mainly from the purity of surfactants, because the cmc is quite sensitive to surface active impurities even in trace amounts. They are also caused from the sensitivity of the methods used. For example, differences in cmc for alkylbenzenesulfonate are observed

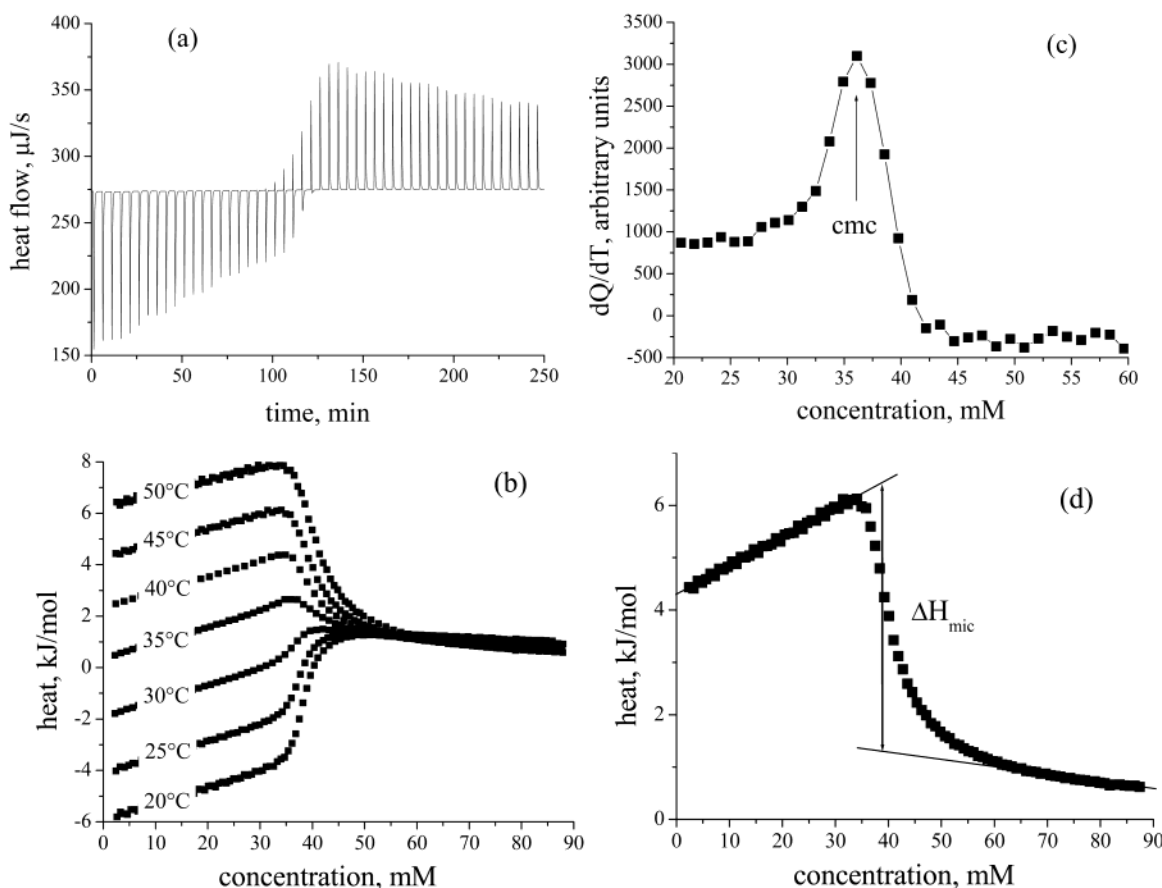


Figure 1. Determination of the cmc and enthalpy of micellization for LiDeS. (a) Heat flow versus time caused by 50 injections of 5 μL of LiDeS into 2.1 mL of water at 10 $^{\circ}\text{C}$. (b) Heat of reaction versus LiDeS concentration in the sample cell between 20 and 50 $^{\circ}\text{C}$. (c) First derivative of the heat of reaction at 10 $^{\circ}\text{C}$. The cmc is determined from the maximum of this curve. (d) Determination of the enthalpy of micellization at 45 $^{\circ}\text{C}$.

between calorimetric and electrical conductivity measurements.³¹ The cmc can differ up to 10% without significant modifications of the enthalpy as shown in Figure 5 for sodium dodecyl sulfate.

At a given temperature, the cmc decreases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ as previously obtained by numerous studies.^{7,12,15,16} This decrease was explained by considering the binding of counterions to micelles. The determination of partial volumes and calculations of the hydration of micelles indicated a very small change in hydration during micellization.⁷ This means that the hydration shell of cations limits the distance of closest approach. If the size of nonhydrated ions follows the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$, the size of hydrated ions is however in the reverse order as shown in Table 2.

The larger the hydrated radius, the further the ion is located from the surface of the negatively charged surfactant headgroups. Thus, Li^+ having the largest hydrated radius cannot approach the highly charged surface of the micelle as close as smaller ions. Therefore, it can neither screen the charge at the surface of micelles nor reduce the surface potential as effectively as the smaller ions.¹⁶ On the contrary, the hydrated Cs^+ cation has the smallest size and interacts more strongly with the oppositely charged heads. The smallest size of hydrated Cs^+ results in the highest extent of counterion binding comparing Li^+ , Na^+ , K^+ , and Cs^+ . The headgroup interactions (repulsive forces) are more screened, which favors micelle formation. Consequently, the cmc decreases when the size of the hydrated counterion decreases while the degree of counterion binding increases. The effect of counterion must not be reduced to electrostatic effects but also influences aggregate size and aggregation number as shown for the dodecyl series.^{17,18} CsDS

has the lowest cmc of alkali dodecyl sulfates and forms micelles with a rodlike shape and a large aggregation number.¹⁸

The plot of the cmc versus temperature has a parabolic shape, typical for ionic surfactants.^{2,33} The cmc decreases, reaches a minimum and increases again as the temperature raises (Figures 2 and 3). In the range between 10 and 60 $^{\circ}\text{C}$, the temperature dependence of the cmc is small (< 2 mM) and independent of the cmc values, even for surfactants with a low cmc such as alkali dodecyl sulfate surfactants. Several equations were proposed^{25,34} to describe the observed symmetrical parabolic curve, and we have used the following:

$$\ln(\text{cmc}) = aT^2 + bT + c$$

Fitting this equation to the experimental data points enables us to determine the temperature T_0 at which the cmc has a minimum. The position of this minimum has a thermodynamic significance. According to the pseudo-phase model, the free energy $\Delta G_{\text{mic}} = RT \ln(\text{cmc})$ is a linear function of temperature. Therefore, the minimum in cmc leads to a minimum in $(\Delta G_{\text{mic}}/T)$. According to the Gibbs–Helmholtz relation, the enthalpy of micellization is written as $\Delta H_{\text{mic}} = \Delta G_{\text{mic}} - T\delta(\Delta G_{\text{mic}})/\delta(T)$ or as $\Delta H_{\text{mic}}/T^2 = -\delta(\Delta G_{\text{mic}}/T)/\delta(T)$ and has to be zero at the temperature T_0 . Since the cmc of KDEs is measured in a reduced temperature range above 30 $^{\circ}\text{C}$, the temperature T_0 was only determined from the temperature dependence of the enthalpy of micellization, using a second-order polynomial function to describe the dependence of ΔH_{mic} on temperature ($T_0(\Delta H_{\text{mic}}) = 20.9$ $^{\circ}\text{C}$). All values determined from the cmc and enthalpy plots are presented in Table 3.

TABLE 1: Critical Micelle Concentrations (cmc's) and Enthalpies of Micellization of Alkyl Sulfate Surfactants Determined by ITC in Pure Water as a Function of Temperature^a

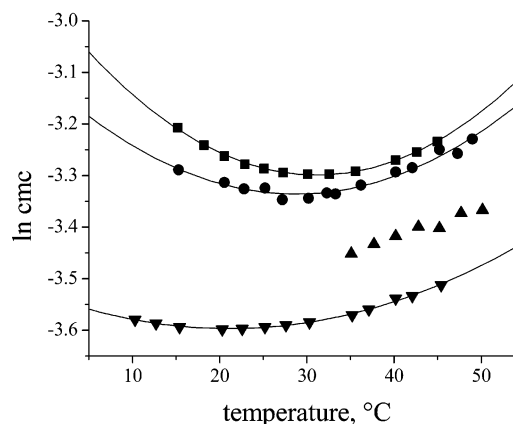
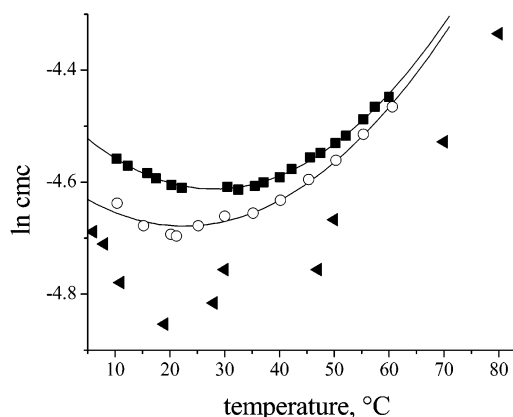
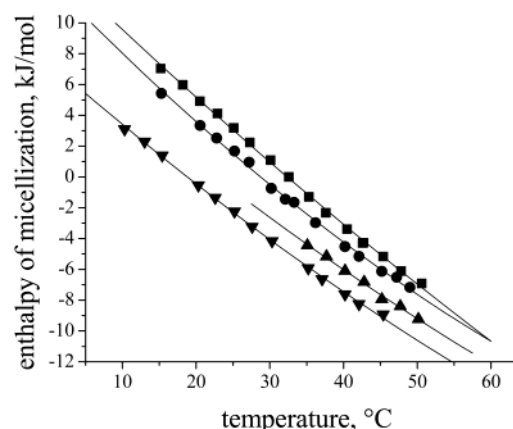
surfactant	<i>T</i> , °C	cmc, mM	ΔH , kJ mol ⁻¹	surfactant	<i>T</i> , °C	cmc, mM	ΔH , kJ mol ⁻¹
LiDeS ^b	15.2	40.5	7.04	LiDS ^b	35.2	28.1	-5.92
	18.2	39.1	5.97		37.1	28.45	-6.63
	20.55	38.3	4.92		40.2	29.1	-7.61
	22.9	37.7	4.12		42.1	29.2	-8.25
	25.1	37.4	3.18		45.4	29.8	-8.92
	27.3	37.1	2.23		10.3	10.48	9.64
	30.1	37.0	1.09		12.3	10.35	8.53
	32.6	37.0	0.00		15.9	10.22	6.50
	35.6	37.2	-1.29		17.5	10.12	5.65
	40.2	38.0	-3.39		20.3	10	4.09
	42.6	38.6	-4.29		22.2	9.95	3.06
	45.0	39.4	-5.17		25.2		1.48
					27.5		0.53
NaDeS	15.3	37.3	5.22	NaDS	30.5	9.97	-1.45
	20.3	36.4	3.30		32.5	9.92	-2.44
	22.1	35.9	2.77		35.5	9.98	-4.04
	25.4	36.0	1.51		37.1	10.05	-4.86
	27.1	35.2	0.81		40.1	10.14	-6.21
	30.1	35.3	-0.87		42.2	10.29	-7.22
	32.1	35.7	-1.38		45.6	10.51	-8.75
	36.2	36.2	-2.94		47.5	10.59	-9.52
	40.5	37.15	-4.21		50.2	10.78	-10.67
	42.1	37.45	-5.04		52.1	10.92	-11.49
	45.4	38.8	-6.29		55.3	11.25	-12.69
	47.3	38.5	-6.74		57.4	11.5	-13.56
					60	11.7	-14.29
KDeS	35.1	31.7	-4.45	NaDS	10.4	9.68	6.87
	37.7	32.3	-5.17		15.2	9.3	4.55
	40.2	32.8	-6.10		20.2	9.16	2.14
	42.8	33.4	-6.82		21.2	9.13	0.90
	45.2	33.3	-7.94		25.2	9.3	-0.51
	47.7	34.3	-8.40		30	9.46	-2.83
CsDeS	50.15	34.5	-9.20	NaDS	35.2	9.51	-5.27
	10.3	27.9	3.10		40.2	9.73	-7.74
	12.7	27.7	2.30		45.35	10.1	-9.72
	15.4	27.5	1.40		50.3	10.45	-11.63
	20.3	27.4	-0.54		55.3	10.95	-13.62
	22.6	27.4	-1.34		60.6	11.5	-15.49
	25.2	27.5	-2.24				
	27.6	27.6	-3.23				
	30.3	27.75	-4.16				

^a cmc values are obtained with an accuracy of ± 0.1 mM for alkali decyl sulfate and ± 0.05 mM for alkali dodecyl sulfate, whereas the accuracy of the enthalpy values is ± 0.03 kJ mol⁻¹ K⁻¹. ^b For LiDeS and LiDS, values correspond to the average of two independent measurements.

TABLE 2: Ionic Radius of Alkali Ions in a Crystal r_{cr} and in the Hydrated State r_{hyd} ³²

alkali	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
r_{cr} (Å)	0.59	0.99	1.37	1.52	1.67
r_{hyd} (Å)	3.40	2.76	2.32	2.28	2.28

The values deduced from the cmc and the enthalpy curves agree well. Using the pseudo-phase separation model, the free energy of ionic surfactants is written as $\Delta G_{mic} = RT(1 + f)\ln(\text{cmc})$ where f is the fraction of counterions bound to micelles. The Gibbs–Helmholtz relation can thus be rewritten as $-\Delta H_{mic}/T^2 = R(1 + f)\delta(\ln(\text{cmc}))/\delta T + R \ln(\text{cmc})\delta(1 + f)/\delta T$. When the enthalpy passes through zero at $T = T_0$, the minimum in cmc can occur at a different temperature since the counterion binding represented as the parameter f may be temperature dependent. This could lead to a shift in the minimum temperature T_0 and explain the larger difference observed for CsDeS. The temperature T_0 , at which the enthalpy of micellization changes sign, shifts to lower temperatures as the size of the

**Figure 2.** Logarithm of the cmc as a function of temperature for alkali decyl sulfates: (■) Li⁺, (●) Na⁺, (▲) K⁺, and (▼) Cs⁺.**Figure 3.** Logarithm of the cmc as a function of temperature for alkali dodecyl sulfates: (■) Li⁺, (○) Na⁺, and (▼) Na⁺ (data from Paula et al.²⁴).**Figure 4.** Enthalpy of micellization as a function of temperature for alkali decyl sulfates: (■) Li⁺, (●) Na⁺, (▲) K⁺, and (▼) Cs⁺.

hydrated counterion decreases. The difference in T_0 between Li⁺ and Na⁺ remains constant as the chain length increases.

The enthalpy of micellization is markedly temperature dependent as illustrated in Figures 4 and 5.

The enthalpy of micellization decreases by about 0.4 kJ/K for decyl surfactants and by about 0.5 kJ/K for dodecyl surfactants with increasing temperature. The formation of micelles is an endothermic process at low temperatures and an exothermic process at higher temperatures. At a given temperature, the enthalpy of micellization ΔH_{mic} decreases continuously in the order Li⁺ > Na⁺ > K⁺ > Cs⁺. Since the process of micelle formation consists mainly of (i) the destruction of water

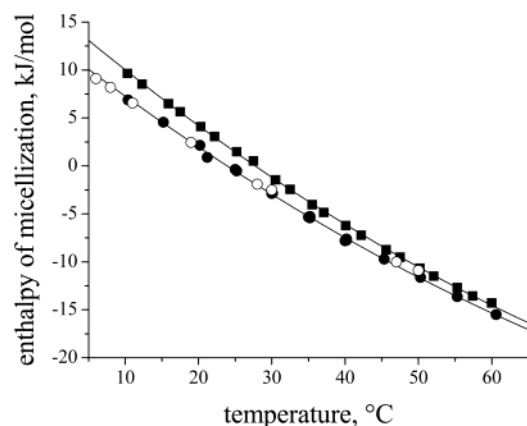


Figure 5. Enthalpy of micellization as a function of temperature for alkali dodecyl sulfates: (■) Li^+ , (●) Na^+ , and (○) Na^+ (data from Paula et al.²⁴).

TABLE 3: Temperature T_0 (°C) Associated with the Minimum in Critical Micelle Concentration and Zero Enthalpy Change

surfactant	LiDS	NaDS	LiDeS	NaDeS	CsDeS
$T_0(\text{cmc})$	28.1	22.9	31.2	29.0	21.1
$T_0(\Delta H_{\text{mic}})$	27.6	23.7	32.1	28.5	19.0

structure surrounding the hydrophobic part of surfactant when it escapes from water and aggregates as a liquid core inside the micelle and (ii) the dehydration of the polar part and its electrostatic interaction due to aggregation,¹² the decrease in ΔH_{mic} from Li^+ to Cs^+ results mainly from the heat required to overpass the electrostatic repulsion between headgroups. The electrostatic repulsions between ionic headgroups prevent the aggregation but are progressively screened as the degree of ionicity of the $\text{SO}_4^- \text{M}^+$ bond decreases with the size of the counterion and its polarizability. As the counterion binding decreases in the order $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ followed by increased electrostatic repulsions between headgroups, the energy required to overpass this repulsion is larger, indicating that the process is then more endothermic. The curves are regularly shifted to lower values on going from Li^+ to K^+ . Assuming the same increment for Rb^+ and Cs^+ , the micellization enthalpy for cesium decyl sulfate is found at values expected for rubidium decyl sulfate. As indicated in Tables 2 and 3, both the hydrated radius and the minimum temperature T_0 are similar for K^+ and Cs^+ , so that one can expect a much smaller increment for the bigger ions such as Rb^+ and Cs^+ . Finally, the characteristics of micellization are as follows: a change of the counterion for a given chain length is only accompanied by a vertical shift whereas an increase in chain length results in a change of the temperature dependence of the micellization enthalpy. At low temperatures ($T < 20$ °C), the chain length has almost no effect on the micellization enthalpy whereas at higher temperatures, increasing chain length decreases more strongly the enthalpy values (Figures 4 and 5).

The heat capacity $\Delta C_{p,\text{mic}}$ determined as $\Delta C_{p,\text{mic}} = (\partial \Delta H_{\text{mic}} / \partial T)_P$ is a linear function of T since ΔH_{mic} is described as a second-order polynomial function of temperature. From the variation of ΔH_{mic} with T (Figures 4 and 5), the heat capacity was determined for Li^+ , Na^+ , and Cs^+ counterions. It has been proposed that $\Delta C_{p,\text{mic}}$ is a linear function of the hydrophobic surface that gets exposed to water during the de-micellization process according to $\Delta C_{p,\text{demic}} = 33n_{\text{H}}(\text{J mol}^{-1} \text{K}^{-1})$ with n_{H} the number of hydrogen atoms at 25 °C.^{35,36} If only the hydrophobic chain would have an influence on the heat capacity,

TABLE 4: Experimental $\Delta C_{\text{mic}}(\text{exp})$ and Theoretical Values of the Heat Capacity Changes ($\Delta C_{\text{mic}}(\text{th}) = -33n_{\text{H}}$) in $\text{J mol}^{-1} \text{K}^{-1}$ at 25 °C for the Investigated Surfactants^a

surfactant	LiDS	NaDS	LiDeS	NaDeS	CsDeS
$\Delta C_{\text{mic}}(\text{th})$	-825	-825	-693	-693	-693
$\Delta C_{\text{mic}}(\text{exp})$	-534	-493	-448	-407	-362

^a The error bars are $10 \text{ J mol}^{-1} \text{K}^{-1}$ for dodecyl sulfates and $17 \text{ J mol}^{-1} \text{K}^{-1}$ for decyl sulfates.

the values should be the same for all counterions investigated at a given chain length and decrease only with decreasing chain length. However, the results shown in Table 4, where both expected values at 25 °C according to the theory and the experimental ones are presented, indicate that the counterion plays a certain role.

Results are in accordance with literature data ($\Delta C_{\text{mic}}(\text{NaDeS}) = -394 \text{ J mol}^{-1} \text{K}^{-1}$ and $\Delta C_{\text{mic}}(\text{NaDS}) = -516 \text{ J mol}^{-1} \text{K}^{-1}$ at 25 °C³⁷). The large difference between experimental and calculated values can be partially explained by a different number of hydrogen atoms exposed to water during micellization. If we compare the data for the same counterion but different chain lengths, the experimentally observed difference is $86 \text{ J mol}^{-1} \text{K}^{-1}$ instead of $132 \text{ J mol}^{-1} \text{K}^{-1}$. This indicates that the number of methylene groups which are still in contact with water molecules in the micelle decreases with decreasing chain length. The differences within one alkali alkyl sulfate series indicate an additional influence of the counterion. ΔC_p increases in the order $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$: the effect of the counterion has a positive contribution to the heat capacity ($41 \text{ J mol}^{-1} \text{K}^{-1}$ from Li^+ to Na^+ and $45 \text{ J mol}^{-1} \text{K}^{-1}$ from Na^+ to Cs^+). During the micellization process, the condensation of ions onto micelles reduces the number of water molecules in the solvation shell since the ions can share hydration water with the headgroups and the heat capacity associated with the dehydration process of counterions is positive.³⁸ However, as the size of the counterion increases, the latter binds more strongly to the headgroups and the number of water molecules expelled from the headgroups during micellization is smaller than for a smaller counterion. Consequently, the dehydration contributes positively to the heat capacity in the reverse order than observed experimentally. The compensation effect may arise from a change in aggregation number as suggested based on change in hydrodynamic radius ($R_h(\text{Li}^+) = 26.5 \text{ \AA}$, $R_h(\text{Na}^+) = 26.7 \text{ \AA}$, $R_h(\text{K}^+) = 124.1 \text{ \AA}$, and $R_h(\text{Cs}^+) = 182 \text{ \AA}$ between 40 and 45 °C with an alkalichloride salt concentration of 0.45 M).¹⁸

Heat of Dilution. Below the cmc, the curves of LiDeS shown in Figure 1a have a constant positive slope, indicating that the process of demicellization is dependent on the concentration of monomers already present in solution. This effect tends, however, rapidly to decrease with increasing hydrated radius, i.e., the increase in counterion binding and almost vanishes with increasing the chain length. Above the cmc, the process of dilution of the micellar solution is endothermic as for all ionic surfactants² and the heat of dilution appears to be almost constant. However, the plot of the heat of dilution versus temperature at a given concentration above the cmc (for example at 6-fold the cmc for the decyl sulfate set and twice the cmc for the dodecyl sulfate set as shown in Figures 6 and 7) shows a clear dependence of the heat of dilution on temperature.

It decreases with increasing temperature and reaches a minimum in the case of Li^+ and Na^+ counterions. It is noteworthy that the temperature, at which the heat of dilution has a minimum, seems to be identical for Li^+ and Na^+ and independent of chain length. This minimum seems also to occur for Cs^+ at higher temperatures. However, due to the strong

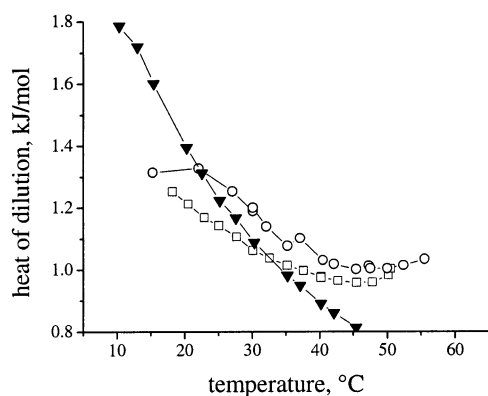


Figure 6. Heat of dilution of micelles as a function of temperature above the cmc for alkali decyl sulfates: (\square , 65 mM) Li^+ , (\circ , 70 mM) Na^+ , and (\blacktriangledown , 50 mM) Cs^+ .

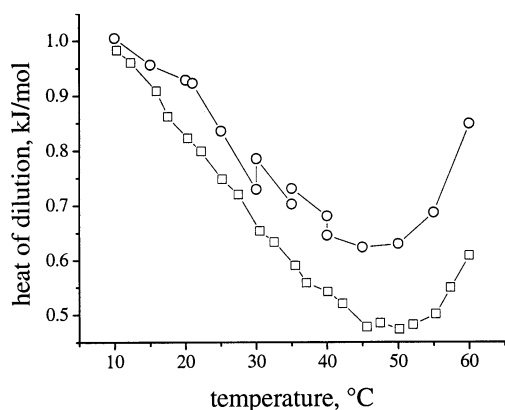


Figure 7. Heat of dilution of micelles as a function of temperature above the cmc for alkali dodecyl sulfates: (\square , 18 mM) Li^+ and (\circ , 18 mM) Na^+ .

exothermicity at temperatures above 45 °C, it was not possible to measure the heat changes over a larger temperature range. The strong temperature dependence of the heat of dilution of CsDeS micelles could result from the dehydration and/or the change in micelle shape due to dilution, providing the decrease in monomer concentration with temperature is comparable for all surfactants. The cation Cs^+ , having a smaller radius in the hydrated state than the other ions and thus a smaller hydration shell, may be more sensitive to dilution than Li^+ or Na^+ having a larger hydration shell. The second assumption of a change in shape agrees with the results of Missel.¹⁸ For the dodecyl sulfate series, the hydrodynamic radii of Li^+ and Na^+ as determined by quasi-elastic light scattering varies slightly with temperature, whereas those of KDS and CsDS decrease strongly with temperature. If one applies this result qualitatively to the decyl series, it means that the temperature strongly influences the growth of CsDeS micelles (sphere-to-rod transition) leading to a strong temperature dependence of the heat of dilution in contrast to LiDeS and NaDeS.

Thermodynamical Parameters. From the cmc and the enthalpy of micellization, the free energy and entropy can be determined. The entropy of micellization is easily calculated from the relationship: $T\Delta S_{\text{mic}} = -\Delta G_{\text{mic}} + \Delta H_{\text{mic}}$. The main problem lies in the determination of the free energy. Assuming a sufficiently large aggregation number ($m > 60$), an ideal behavior of monomers in water and no electrostatic effects, the pseudo-phase separation model leads to the following equation: $\Delta G_{\text{mic}} = RT \ln(\text{cmc})$. The use of this equation for ionic

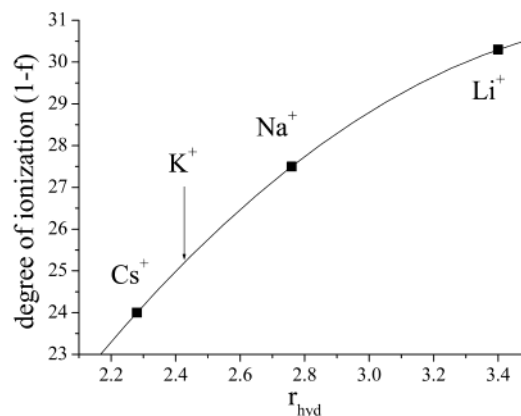


Figure 8. Degree of ionization ($1 - f$) versus the hydrated radius of the alkali counterion of dodecyl sulfate micelles. Values are taken from Mukerjee et al.⁷ except that for K^+ , which is determined by its hydrated radius (see Table 2).

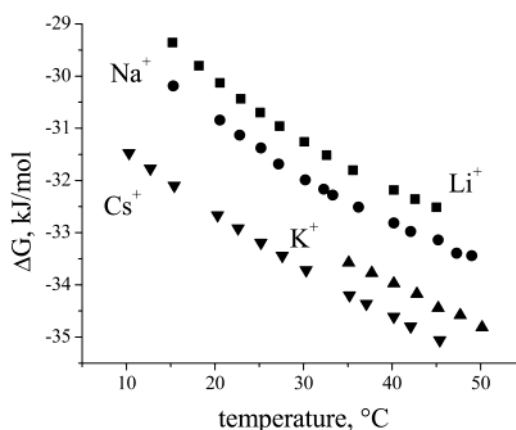


Figure 9. Free energy of micellization as a function of temperature for alkali decyl sulfates: (\blacksquare) Li^+ , (\bullet) Na^+ , (\blacktriangle) K^+ , (\blacktriangledown) Cs^+ .

surfactants assumes a state of complete dissociation, but not all counterions are free in the sense of having the same activity or mobility as those of a simple electrolyte. To take into account the electrostatic interactions between headgroups, we must include a term describing the counterion binding. It has been proposed to use the equation $\Delta G_{\text{mic}} = RT(1 + f)\ln(\text{cmc})$, where the cmc is written in fraction units and f refers to the fraction of counterions bound to a micelle, assuming it is temperature-independent.² The correct evaluation of the counterion binding is quite difficult since it depends on the method as proved for NaDS.³ We have here used the values of the ionization degree, defined as the fraction of counterions not bound to a micelle ($\alpha = 1 - f$), which are determined by electrical conductivity⁷ for LiDS, NaDS, and CsDS. In Figure 8, the values of the degree of ionization α are presented for Li^+ , Na^+ and Cs^+ versus the hydrated radius.⁷ They are valid for dodecyl sulfate surfactants and vary with the chain length.^{8,17} Due to the discrepancy in the literature data even for one method,³ we have considered those values as depending only on the counterions and not on the chain length. The value for K^+ was deduced using the hydrated radius given in Table 2. The values of the free energy and entropy are presented in Figures 9 and 10 for the decyl sulfate series and in Figures 11 and 12 for the dodecyl sulfate series as a function of temperature.

The change in counterion from Li^+ to Cs^+ produces nearly vertical shifts in the ΔG_{mic} curves toward more negative values indicating that the process becomes thermodynamically more favorable due to a decrease of the electrostatic repulsions

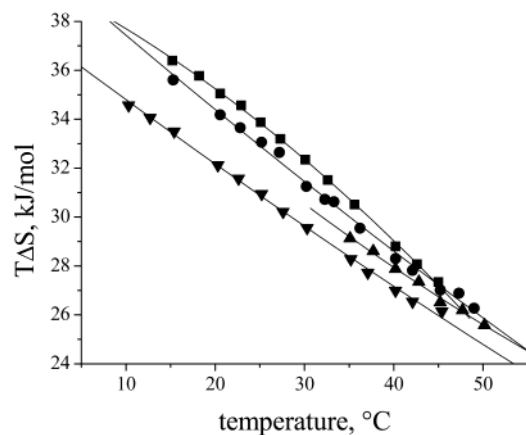


Figure 10. Entropy of micellization as a function of temperature for alkyl decyl sulfates: (■) Li^+ , (●) Na^+ , (▲) K^+ , (▼) Cs^+ .

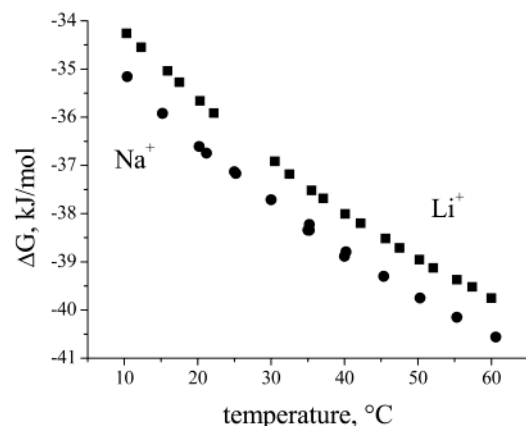


Figure 11. Free energy of micellization as a function of temperature for alkyl dodecyl sulfates: (■) Li^+ , (●) Na^+ .

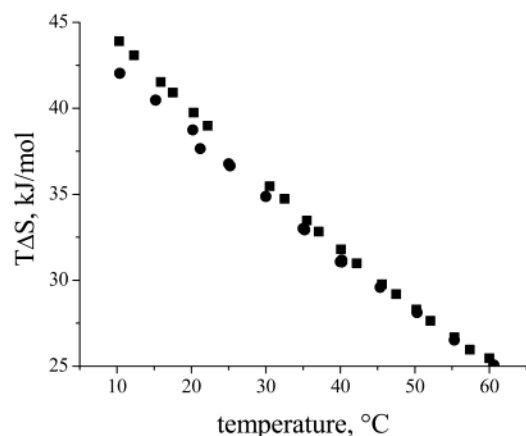


Figure 12. Entropy of micellization as a function of temperature for alkyl dodecyl sulfates: (■) Li^+ , (●) Na^+ .

between polar headgroups. Increasing temperature leads to a similar decrease in ΔG_{mic} for all the compounds investigated. ΔG_{mic} plots do not exhibit a pronounced minimum as the cmc curves (Figures 2 and 3) since the term RT is dominating and $\ln(\text{cmc})$ acts only as a correcting factor. Both the slight temperature dependence of the free energy and its negative values result from the dominating influence of the entropy term as shown in Figure 13 for LiDeS.

The entropy term ($T\Delta S_{\text{mic}}$) shows the same vertical shifts on going from Li^+ to Cs^+ as the enthalpy and the free energy. The shortening of the chain length leads to a more pronounced decrease of the entropy term. In the investigated temperature

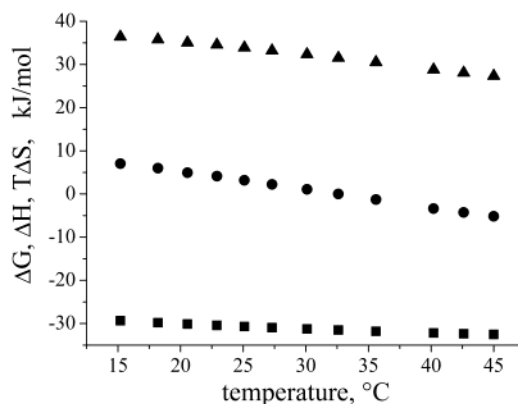


Figure 13. Thermodynamical parameters (▲) $T\Delta S$, (●) ΔH , and (■) ΔG of the micellization process for LiDeS as a function of temperature.

range, the micellization process turns to be entropically driven, i.e., the entropy is the controlling factor of micellization. From the large gain in entropy during micelle formation, it has been qualitatively concluded that the positive variation in entropy due to the destruction of the water structure around the hydrophobic part and due to the dehydration of the polar parts exceed the entropy decrease due to the association of surfactant molecules in a micelle and due to the binding of counterions to the micelles¹. Assuming the destruction of the water structure is the same for all compounds of the alkyl sulfate series, the decrease in entropy $T\Delta S_{\text{mic}}$ on going from Li^+ to Cs^+ is mainly associated to the dehydration of polar headgroups. As the hydration shell decreases from Li^+ to Cs^+ due to the larger polarizability of the ions, the change in entropy is smaller for ions with a smaller hydrated radius.

Conclusion

This study of the effect of counterions (Li^+ , Na^+ , K^+ , and Cs^+) on the micelle formation of decyl and dodecyl sulfates by isothermal titration calorimetry has shown that counterions affect the thermodynamics of micellization and their influence can be recorded by ITC. Critical micelle concentration (cmc) and enthalpy of micellization (ΔH_{mic}) decrease in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ at a given temperature and for a fixed chain length. This decrease is associated with the decrease of the counterion binding in the reverse order. The electrostatic repulsions between ionic headgroups, which prevent the aggregation, are progressively screened with the size of the counterion and the process of micelle formation is less endothermic and molecules aggregate already at a lower concentration. The cmc versus temperature reaches a minimum, while the enthalpy of micellization passes through zero.

The endothermic heat of dilution of micelles in the post-micellar region is strongly dependent on the temperature for the cation Cs^+ and correlates with the change in micelle shape. The use of the pseudo-phase separation model including the counterion binding shows that the variations of enthalpy and entropy of micellization compensate each other and the free energy ΔG_{mic} is only slightly dependent on counterions and temperature. A decrease in hydrated ionic radius and an increase in chain length produce nearly vertical shifts in the plot ΔG_{mic} versus temperature.

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