

# Micellization Enthalpy of Some Alkylsulfobetaines in Aqueous Solution

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Microcalorimetric measurements on (octyldimethylammonio)- and (dodecyldimethylammonio)propanesulfonate aqueous solutions have been carried out at 25 °C to shed light on their thermodynamic properties. These neutral surfactants exhibit critical micellar concentration values higher than expected. A comparative analysis of enthalpic results for the two compounds has been made, taking into account both volumetric and activity findings. It was concluded that strong interactions of the hydrophilic head group with solvent molecules and structural hindrance of the surfactant polar groups must be the main factors controlling the thermodynamics of micellar aggregation.

## Introduction

As pointed out by several authors,<sup>1-4</sup> the thermodynamic behavior of alkylbetaines is peculiar. Although their zwitterionic properties might lead one to believe that the higher homologous compounds could easily form molecular aggregates like micelles, these amphiphiles show unexpectedly high critical micellar concentrations (cmc) compared to the nonionic homologues.

Our previous research on alkylsulfobetaines was carried out to achieve a deeper knowledge of their physicochemical properties in solution and to analyze such changes when micellization processes,<sup>5,6</sup> or higher molecular aggregation phenomena,<sup>7</sup> occur. The results have been interpreted in terms of hydrophile-lipophile balance, HLB.<sup>8</sup>

The thermodynamic aspect involved in the transition from solution to colloid phase was mainly considered by examining the change in the free energy with temperature. Unfortunately, the changes in cmc with temperature were not significant. Thus, the calculated enthalpic and entropic changes had a large uncertainty.

In order to obtain more accurate thermodynamic information for the micellization process of (alkyldimethylammonio)propanesulfonates, calorimetric measurements have been performed. (Octyldimethylammonio)propanesulfonate (B<sub>8</sub>DAPS) and (dodecyldimethylammonio)propanesulfonate (B<sub>12</sub>DAPS) were selected. Since the hydrophile-lipophile balance of the two betaines

is quite different, a useful comparison can be made between the thermodynamic behavior of the two surfactants.

## Experimental Section

(A) **Materials.** (Dodecyldimethylammonio)propanesulfonate, B<sub>12</sub>DAPS, and (octyldimethylammonio)propanesulfonate, B<sub>8</sub>DAPS, Calbiochem, were purified as previously reported.<sup>5,6</sup>

Water was deionized by using Millipore columns and degassed. Its electrical conductivity was about 10<sup>-7</sup> Ω<sup>-1</sup> cm<sup>-1</sup>, at 25 °C.

The solutions were prepared by weight, allowed to stay at room temperature, and used within 2 weeks.

(B) **Methods.** The integral enthalpies of dilution, ΔH<sub>id</sub>, were measured at 25 °C with an LKB 2107-121 flow microcalorimeter. The apparatus setup is described in the literature.<sup>9</sup> The minimum detector sensitivity is ±0.05 μV/μW, minimum heat effect is 1 μW, and reproducibility is 1%. The calorimeter is equipped with an LKB peristaltic pump and a recorder. Each run requires at least 3 cm<sup>3</sup> of solution.

The heat of dilution of sucrose was chosen as a standard.<sup>10</sup> Measurements were carried out by taking into account the suggestions of Fortier et al.<sup>11</sup>

For the highly diluted solutions, supplementary measurements were performed by an LKB 2107 batch calorimeter.<sup>12</sup> The temperature stability was 0.01 °C, the detector stability and sensitivity were 0.005 μV and 0.1 μV/μW, respectively, and the accuracy of calibration resistors was 0.002%.

Freezing point depressions, ΔT, were measured by a Knauer apparatus equipped with a digital display. The accuracy on ΔT is to within 0.002 °C. The apparatus was calibrated with standard NaCl solutions.<sup>13</sup>

Density measurements on B<sub>8</sub>DAPS solutions were performed by an A. Paar apparatus, calibrated with standard NaCl solutions<sup>14</sup> according to the methods previously reported.<sup>5</sup> The

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**Table I.** Molality ( $m$ ) and Osmotic Coefficient ( $\Phi$ ) for (Octyldimethylammonio)propanesulfonate, B<sub>8</sub>DAPS, from Cryoscopic Measurements

$m$ , mol kg <sup>-1</sup>	$\Phi$	$m$ , mol kg <sup>-1</sup>	$\Phi$
0.1314	1.0195	0.8971	0.6103
0.1583	0.9776	1.0660	0.5349
0.2200	0.9846	1.2441	0.4772
0.3564	1.0061	1.4325	0.4321
0.4453	0.9323	1.5924	0.4043
0.6871	0.7437	1.7182	0.3623

**Table II.** Molality ( $m$ ) and the Apparent Molal Volume ( $\Phi_V$ ) for (Octyldimethylammonio)propanesulfonate, B<sub>8</sub>DAPS, at 25 °C

$m$ , mol kg <sup>-1</sup>	$\Phi_V$ , cm <sup>3</sup> mol <sup>-1</sup>	$m$ , mol kg <sup>-1</sup>	$\Phi_V$ , cm <sup>3</sup> mol <sup>-1</sup>
0.091 07	246.6 ± 0.8	0.7289	251.9 ± 0.2
0.185 40	244.7 ± 0.5	0.7625	250.1 ± 0.2
0.393 93	241.7 ± 0.3	0.8956	253.4 ± 0.1
0.438 59	245.4 ± 0.3	1.4966	254.2 ± 0.1
0.655 77	249.7 ± 0.2		

accuracy on density measurements was within 10<sup>-6</sup> g cm<sup>-3</sup> and  $d_0 = 0.997\ 047$  g cm<sup>-3</sup> was used as the density of water at 25 °C.

### Results

The osmotic coefficients,  $\Phi$ , for B<sub>8</sub>DAPS solutions, listed in Table I, were calculated according to the equation<sup>15</sup>

$$\Phi = \Delta T(0.5377 + (2.68 \times 10^{-4})\Delta T)/m \quad (1)$$

where  $m$  is the molality.

The density of solutions,  $d$  (g cm<sup>-3</sup>), was obtained by the equation

$$d = (1/A)(\tau^2 - B) \quad (2)$$

where  $\tau$  is the oscillation period of a wave traveling through the measured sample and  $A$  and  $B$  are calibration constants.

The apparent molal volumes,  $\Phi_V$ , were calculated as

$$\Phi_V = [1000(d_0 - d)]/(mdd_0) + PM/d \quad (3)$$

where  $PM$  is the solute molecular weight.

The partial molar volumes,  $\bar{V}_2$ , were obtained, for B<sub>8</sub>DAPS, according to

$$\bar{V}_2 = \Phi_V + m(d\Phi_V/dm) \quad (4)$$

The  $\Phi_V$  and  $\bar{V}_2$  values are listed in Table II and shown in Figure 2.

Due to the large uncertainty on  $\Phi_V$  values at low surfactant content, only a few selected points were reported and the  $\Phi_V$  vs  $m$  function below the cmc was linearized. The abscissa of the function is very close to the value inferred by assuming an additivity rule for the limiting partial molar volumes of sulfobetaines.<sup>5</sup>

The integral enthalpies of dilution,  $\Delta H_{id}$ , for C<sub>8</sub>DAPS and C<sub>12</sub>DAPS are reported in Table III.

The  $\Delta H_{id}$  values are related to the apparent molal enthalpies,  $\Phi_L$ , through the equation

$$\Delta H_{id} = Q/n = \Phi_{L,f} - \Phi_{L,i} \quad (5)$$

where  $Q$  is the measured heat and  $n$  the number of solute moles. The subscripts  $f$  and  $i$  refer to the final and initial concentration, respectively.

In the premicellar range,  $\Phi_L$  values fit the relationship

$$\Phi_L = Bm + Cm^2 \quad (6)$$

The quadratic form reported in the above equation is truncation of a power-law series. Higher terms were not included since the agreement between experimental  $\Delta H_{id}$  values and the ones calculated by eq 6 is to within the experimental accuracy ( $\pm 1.5\%$ ).

**Table III.** Molality ( $m$ ), Dilution Enthalpy ( $\Delta H_{id}$ ) from  $m$  to  $m/2$ , and Apparent Molal Enthalpies ( $\Phi_{L,i}$ ) for (Octyldimethylammonio)propanesulfonate (B<sub>8</sub>DAPS) and (Dodecyldimethylammonio)propanesulfonate (B<sub>12</sub>DAPS) at 25 °C

B <sub>8</sub> DAPS			B <sub>12</sub> DAPS		
$m$ , mol kg <sup>-1</sup>	$\Delta H_{id}$ , J mol <sup>-1</sup>	$\Phi_{L,i}$ , J mol <sup>-1</sup>	$m$ , mol kg <sup>-1</sup>	$\Delta H_{id}$ , J mol <sup>-1</sup>	$\Phi_{L,i}$ , J mol <sup>-1</sup>
0.1140	302.4	-528	0.002 502	95.3	+314
0.2356	648.2	-1256	0.003 004	128.0	+181
0.3220	1187	-1877	0.003 506	370.0	+14.9
0.5044	2089	-3443	0.004 011	720	-278.4
0.5283	2319	-3771	0.005 015	971	-657
0.6535	2661	-4573	0.006 005	1296	-1114
0.6798	2550	-4570	0.007 012	1393	-1386
0.7592	2236	-4573	0.008 003	1451	-1719
0.9279	2157	-5237	0.009 025	1212	-1812
1.2235	1708	-5950	0.010 03	1141	-1910
1.2403	1809	-6226	0.014 04	834	-2219
1.5993	1609	-6509	0.016 05	722	-2321
1.9182	1383	-6782	0.018 09	659	-2430
2.0727	1340	-7140	0.020 06	571	-2491
2.5060	932	-6930	0.024 66	436	-2566
			0.039 98	265.0	-2496
			0.050 14	205.7	-2480

**Table IV.** Coefficients  $B$  and  $C$  of Equations 6 and 8 for B<sub>8</sub>DAPS and B<sub>12</sub>DAPS, for Concentrations below the Cmc, at 25 °C

	B <sub>8</sub> DAPS (0 < $m$ < 0.40)	B <sub>12</sub> DAPS (0 < $m$ < 0.0036)
$B$ , J mol <sup>-2</sup> kg	$-3.98 \times 10^3$	$+4.49 \times 10^6$
$C$ , J mol <sup>-3</sup> kg <sup>2</sup>	$-5.74 \times 10^3$	$-1.29 \times 10^8$

The coefficients  $B$  and  $C$  of eq 6 were obtained<sup>15</sup> as intercept and slope by fitting  $\Delta H_{id}/(m_f - m_i)$  vs  $(m_f + m_i)$ . In fact

$$\Delta H_{id} = \Phi_{L,f} - \Phi_{L,i} = B(m_f - m_i) + C(m_f^2 - m_i^2) \quad (7)$$

The relative partial molal enthalpies  $L_2$ , were calculated by the relationship

$$L_2 = d(\Phi_L m)/dm = 2Bm + 3Cm^2 \quad (8)$$

The constants  $B$  and  $C$  for B<sub>8</sub>DAPS and B<sub>12</sub>DAPS are reported in Table IV.

### Discussion

The  $\Phi$  values of diluted (octyldimethylammonio)propanesulfonate solutions are close to unity. Up to about 0.4 mol kg<sup>-1</sup>, B<sub>8</sub>DAPS behaves as monodispersed solute and weak deviation from ideality may be interpreted in terms of solute-solvent long range interactions.

Stronger deviations are observed above 0.4 mol kg<sup>-1</sup>, Figure 1. On the basis of the previous surface tension measurements,<sup>6</sup> it was postulated that B<sub>8</sub>DAPS forms micellar aggregates above this concentration. The marked decrease of the  $\Phi(m)$  function, shown in Figure 1, similar to that observed for other surfactants,<sup>16,17</sup> suggests aggregation processes.

The  $\Phi$  data reported in Table I have been used to calculate the mean activity coefficients,  $\gamma$ , through the equation<sup>18</sup>

$$\ln \gamma = (\Phi - 1)\{1 + 1/M_0 \int_{m=0}^m (dm/m)\} \quad (9)$$

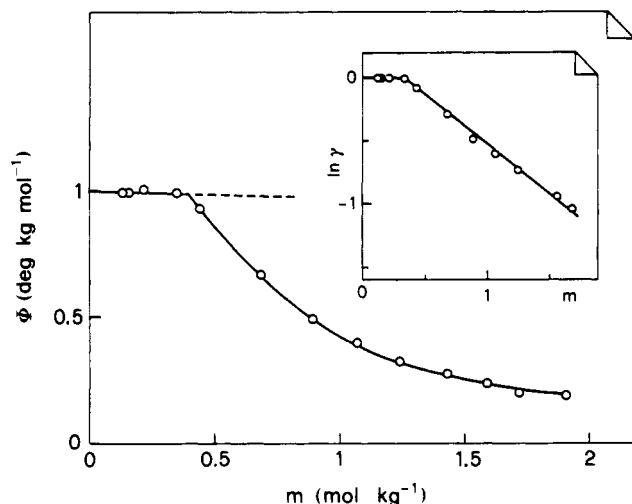
where  $M_0$  is the solvent molecular weight.

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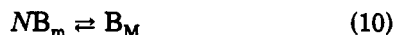


**Figure 1.** Osmotic coefficients,  $\Phi$ , of  $B_6$ DAPS solutions from cryoscopic data, vs the surfactant molality,  $m$ . The inset shows the logarithm of activity coefficients,  $\gamma$ , plotted against  $m$ .

Self-consistent activity coefficients can be obtained by replacing the limit  $m = 0$  in eq 9 with a reference concentration.<sup>19</sup> In the case of  $B_6$ DAPS, the lower limit has been taken equal to  $0.05 \text{ mol kg}^{-1}$ . The function  $\ln \gamma(m)$  for  $B_6$ DAPS is the inset in Figure 1.

The smooth decrease of  $\gamma(m)$  is in accordance with a gradual molecular aggregation. The system should evolve from the monodispersed solution to the micellar phase through several equilibrium steps. In this case, the micellization of  $B_6$ DAPS may be interpreted on the basis of the mass-action law.<sup>20,21</sup>

If  $B_m$  and  $B_M$  indicate the monomeric and micellar species, respectively, and  $N$  the aggregation number, the following relationship may be written:



This equilibrium reaction depends on the constant  $K_e$ .

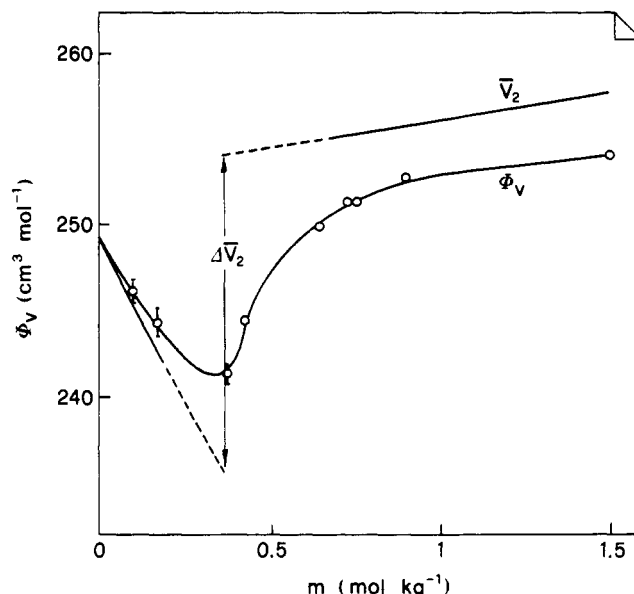
$$K_e = [B_M]/[B_m]^N \quad (11)$$

As reported,<sup>5</sup> reliable values for  $K_e$  and for average aggregation number can be estimated from cryoscopic data. Accordingly,  $K_e = 70$  and  $N = 13$  have been calculated for  $B_6$ DAPS. These values indicate that the surfactant forms relatively small micelles that coexist over a wide range of concentration with appreciable amounts of surfactant in the monomeric state.

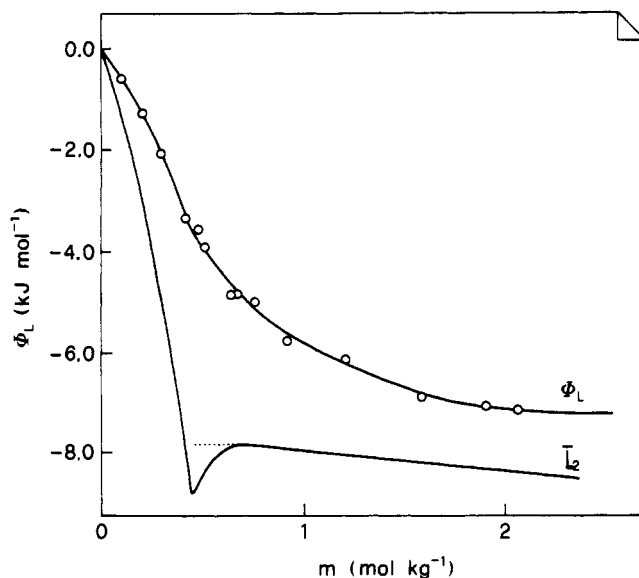
This picture finds further support on the apparent molar volume and partial molar volume of  $B_6$ DAPS (Figure 2). In agreement with most organic solutes,<sup>22,23</sup>  $\Phi_V$  values decrease with increasing the solute concentration because of the packing of the water molecules surrounding the surfactant tails. The  $\Phi_V$  function reaches a minimum when the molality approaches the cmc.

At the cmc, an increase of  $\bar{V}_2$  values has been observed. From the comparison of  $\bar{V}_2$  values for  $B_6$ DAPS with that of higher homologues,<sup>5</sup> we can postulate that few water molecules are squeezed out during the micellization process.

Solute-solvent interactions have an appreciable influence on the enthalpic behavior of  $B_6$ DAPS. At low



**Figure 2.** Apparent molal volume,  $\Phi_V$ , and the partial molal volume,  $\bar{V}_2$ , of  $B_6$ DAPS aqueous solutions, at  $25^\circ\text{C}$ , as a function of the molal concentration,  $m$ .



**Figure 3.** Apparent molal enthalpy,  $\Phi_L$ , and the relative molal enthalpy,  $L_2$ , as a function of  $B_6$ DAPS molal concentration,  $m$ , at  $25^\circ\text{C}$ .

concentrations,  $L_2$  values decrease with increasing surfactant content (Figure 3). This feature, which is typical of organic solutes with strong hydrophilic sites, can be related to the breaking of water structure.

From a thermodynamic point of view, these "structure breaking" effects may overcome the hydrophobic interactions between the short alkyl chains.<sup>24</sup>

On approaching the cmc, significant changes in the enthalpic behavior occur. By extrapolation of the linear segments of the premicellar and postmicellar  $L_2$  function to the cmc, the enthalpy of micellization at  $25^\circ\text{C}$ ,  $\Delta H_{\text{mic}} = 0.4 \text{ kJ mol}^{-1}$ , can be estimated.

Above 49% (w/w) ( $m = 2.6 \text{ mol kg}^{-1}$ ), the calorimetric measurements become unreliable because of the occurrence of a liquid crystalline phase. The existence of this mesophase is consistent with microscopic observations and NMR measurements.<sup>7</sup>

The calorimetric behavior of  $B_{12}$ DAPS is quite different

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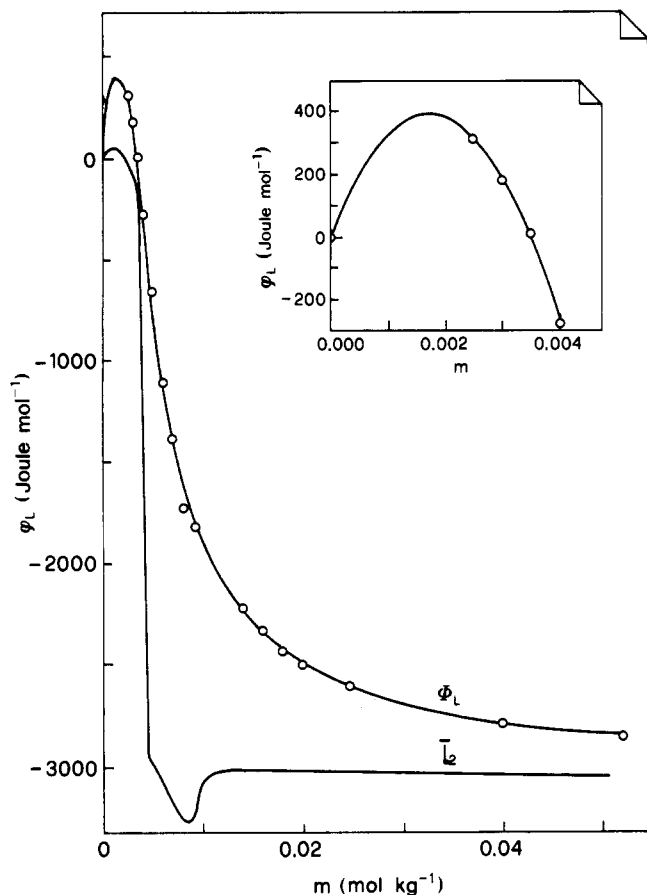
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**Figure 4.** Apparent molal enthalpy,  $\Phi_L$ , and the relative molal enthalpy,  $L_2$ , as a function of  $B_{12}$ DAPS molal concentration,  $m$ , at 25 °C. The inset shows the trend of  $\Phi_L$  vs  $m$  for very diluted solutions.

(Figure 4). Below the cmc the  $\Phi_L$  values of this surfactant increase up to a maximum. Some years ago, Levine and Wood<sup>25</sup> studied the  $L_2$  dependence on solute concentration for a series of tetraalkylammonium salts and showed that  $L_2(m)$  becomes more positive with increasing number of carbon atoms in the molecule. Further evidence of a relationship between tail length and partial molal enthalpy may be seen from other literature data.<sup>26</sup> This phenomenon might be related to the strong interactions between the hydrophobic solute and solvent (clathrate structures around the hydrocarbon tails), with consequent gain in enthalpy at high concentrations.

The cmc of  $B_{12}$ DAPS is below  $4 \times 10^{-3} m$ .<sup>5,6</sup> Above this concentration, both  $\Phi_L$  and  $L_2$  values steeply decrease with increasing solute concentration. In this case the micellar aggregation is perhaps more similar to a phase transition<sup>27-29</sup> than to an equilibrium process. It occurs with a loss of large amounts of water, and the strong hydrophobic interactions between the tails give rise to relatively large micelles with aggregation numbers of about 70.<sup>30</sup> The enthalpy of micellization is negative at 25 °C and significant:  $\Delta H_{mic} = -3000 \text{ J mol}^{-1}$ .

Above the cmc,  $L_2$  values are nearly constant. This result is in line with a presumed low polydispersity of  $B_{12}$ DAPS micelles.<sup>31</sup>

**Table V.** Enthalpy of Micelle Formation ( $\Delta H_{mic}$ ), the free energy ( $\Delta G_{mic}$ ), and the entropy ( $\Delta S_{mic}$ ) for the Micellization Process of (Octyldimethylammonio)propanesulfonate ( $B_8$ DAPS), (Dodecyldimethylammonio)propanesulfonate ( $B_{12}$ DAPS), Sodium Octyl Sulfate ( $NaC_8S$ ) and Dodecyl Sulfate ( $NaC_{12}S$ ), and Hexaethylene Glycol Octyl Ether ( $C_8E_6$ ) and dodecyl Hexaethylene Glycol Dodecyl Ether ( $C_{12}E_6$ ) at 25 °C

	$\Delta H_{mic}$ , kJ mol <sup>-1</sup>	$\Delta G_{mic}$ , kJ mol <sup>-1</sup>	$T\Delta S_{mic}$ , kJ mol <sup>-1</sup>	ref
$NaC_8S$	+1.5	-15.0	+16.5	35
$B_8$ DAPS	+0.4	-12.1	+12.5	<sup>a</sup>
$C_8E_6$	+18.0	-21.3	+39.3	21
$NaC_{12}S$	+0.4	-21.3	+21.8	33
$B_{12}$ DAPS	-3.0	-23.5	+20.5	<sup>a</sup>
$C_{12}E_6$	+16.3	-33.0	+49.3	19

<sup>a</sup> This work.

The absolute values for the free energy of micellization,  $\Delta G_{mic}^\circ$ , were obtained from

$$\Delta G_{mic}^\circ = RT \ln X_{mic} \quad (12)$$

where  $X_{mic}$  is the mole fraction at the cmc,  $\Delta G_{mic}^\circ(B_8\text{-DAPS}) = -12.1 \text{ kJ mol}^{-1}$  and  $\Delta G_{mic}^\circ(B_{12}\text{DAPS}) = -23.5 \text{ kJ mol}^{-1}$ .

Despite the electroneutrality of their hydrophilic sites, alkylsulfobetaines exhibit a thermodynamic behavior which is closer to that of their ionic homologues than to their nonionic ones.<sup>32</sup> In Table V are compared our values with those obtained for sodium alkanesulfates<sup>33-35</sup> and for alkyl hexaethylene glycol alkyl ethers.<sup>21</sup>

$\Delta G_{mic}^\circ$  is the resulting sum of two distinct thermodynamic contributions,  $\Delta H_{mic}^\circ$  and  $-T\Delta S_{mic}^\circ$

$$\Delta G_{mic}^\circ = \Delta H_{mic}^\circ - T\Delta S_{mic}^\circ \quad (13)$$

At 25 °C the enthalpic variation for  $B_8$ DAPS micellization is small, positive, and scarcely influent on the free energy of micelle formation. The micellar stability is ensured by a significant entropic gain, due to the collapse of water clathrate structures at the polar-apolar interface and to an increase in the rotational freedom of alkyl chains in the micellar core.

Concerning  $B_{12}$ DAPS, the micellar aggregation is favored by a significant enthalpic contribution ( $-3.0 \text{ kJ/mol}$ ) at 25 °C due to hydrophobic interactions much larger than those observed for  $B_8$ DAPS solutions. Moreover, the entropic contributions are large and significant at 25 °C. Perhaps, interactions between the dipoles of the polar head groups involve, to some extent, solvation water and reduce the overall entropic gain of the process.<sup>36</sup>

Other factors, such as the steric hindrance of the large highly solvated head groups, could affect negatively the stability of these zwitterionic micelles.

In the above interpretation, thermodynamic effects, related to the change of solvent structure around the micelles have not been considered. These could play also an important role, but any speculation about them cannot be unambiguously supported by the present data.

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