# First Evaluation of the Thermodynamic Properties for Spheres to Elongated Micelles Transition of Some Propanediyl- $\alpha$ , $\omega$ -bis(dimethylalkylammonium bromide) Surfactants in Aqueous Solution

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The apparent and partial molar enthalpies, apparent molar volumes, and adiabatic compressibilities at 298 K of the aqueous solutions of the cationic gemini surfactants propanediyl- $\alpha, \omega$ -bis(octyldimethylammonium bromide) (8-3-8) and propanediyl- $\alpha$ ,  $\omega$ -bis(dodecyldimethylammonium bromide) (12-3-12) have been measured as a function of concentration. The trends of the partial molar enthalpies versus concentration are the first well documented thermodynamic evidence of sphere to rod transition in the micellar phase, involving a detectable quantity of heat, and allow the determination of the change in enthalpy associated with this transition. The changes in enthalpies upon micellization and for the sphere to elongated micelles transition,  $\Delta H_{s-r}$ , have been obtained from the experimental data by using a pseudo-phase transition approach:  $-1.5 \text{ kJ mol}^{-1}$  for 8-3-8 and -3.9 kJ mol<sup>-1</sup> for 12-3-12. No evidence of the above transition is found in the trends of volumetric properties versus *m*. The apparent adiabatic molar compressibilities for the compounds under investigation are also reported here for the first time: a negative group contribution for the methylene group is evaluated, when the surfactants are present in solution as a single molecule, reflecting its solvation structure. In the micellar phase, the  $-CH_2$ - group contribution becomes positive. A value of  $1.17 \times 10^{-3}$  cm<sup>3</sup> bar<sup>-1</sup> mol<sup>-1</sup> for the change in adiabatic molar compressibility upon micellization is obtained. The lower values of the methylene group contributions to the volumetric properties for the monomers support the hypothesis of partial association of the chains before the cmc.

## Introduction

Research in the field of *gemini* surfactants, that is, surfactants in which at least two identical moieties are bound together by a spacer at the polar head level, has grown very quickly, due to the their advantages over the monomeric surfactants with respect to various applications. In fact, *gemini* surfactants show increased surface activity, a lower critical micelle concentration (cmc), and useful viscoelastic properties such as effective thickening.<sup>1</sup> Recently, many studies concerning the practical use of *gemini* molecules have appeared in the literature, showing that the first speculative interests were followed by practical applications.<sup>1-3</sup> Moreover, cationic bisquaternary ammonium surfactants show stronger biological activity than the corresponding monomers and are more active both on a molar and on a weight scale as far as germicidal activity and protein binding ability are concerned.<sup>2,4</sup>

Quite recently, the use of *gemini* surfactants as nonviral vectors in gene therapy has been proposed.<sup>5–7</sup> Although viral vectors are generally very efficient in delivering genes into a targeted cell, their use is not without the risk of adverse or immunogenic reaction, or replication, depending on the virus being used. As a result, nonviral vectors have in many cases

become a preferred means of gene delivery into eukaryotic cells. *Gemini* surfactants seem to be the most promising. $^{5-8}$ 

In the field of cationic surfactants, the structures bearing an ammonium headgroup were widely studied, due to their fast and simple synthetic pathway.<sup>3,9–17</sup> However, different and more tailored structures were prepared in recent years, showing the great interest connected with these kinds of molecules.<sup>18</sup> With the aim to collect chemicophysical data, useful to correlate the structure of surfactants with the transfection ability, we undertook the solution thermodynamic study of the simplest and best known cationic *gemini* surfactants, the bisquaternary ammonium bromides. These compounds have been extensively studied by Zana et al.<sup>3,9–17</sup> under the chemicophysical profile. Their results are a very convenient starting point for the interpretation of our thermodynamic data.

#### **Materials and Methods**

The surfactants propanediyl- $\alpha,\omega$ -bis(octyldimethylammonium bromide) (8-3-8) and propanediyl- $\alpha,\omega$ -bis(dodecyldimethylammonium bromide) (12-3-12) were prepared by us, by a general protocol similar to those found in the literature.<sup>19</sup>

**Propanediyl-** $\alpha$ , $\omega$ **-bis(octyldimethylammonium bromide)** (8-3-8). The *N*,*N*,*N*-octyldimethylamine (45.77 g, 0.291 mol) was dissolved in anhydrous ethanol and warmed at reflux. A solution of 1,3-dibromopropane (29.28 g, 0.145 mol) in ethanol was slowly added dropwise. The reaction was stopped after 20

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h. The solution was evaporated, and the solid residue was suspended twice in ethyl acetate, giving a white solid that was crystallized from methanol/ethyl acetate. The crystals were filtered on a buchner funnel under inert gas flux. The white needle crystals were very hygroscopic. Yield: 47.28 g (63%).  $R_f$ : 0.03 Al<sub>2</sub>O<sub>3</sub> (ethyl acetate/methanol 75:25). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ ): 0.87 (t, 6H, 2 CH<sub>3</sub>), 1.29 (m, 20H, 10 CH<sub>2</sub>), 1.67 (m, 4H, N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>), 2.17 (m, 2H, N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>N<sup>+</sup>), 3.06 (m, 12H, 4 N<sup>+</sup>CH<sub>3</sub>), 3.35 (m, 8H, 4 N<sup>+</sup>CH<sub>2</sub>). Anal. Calcd for C<sub>23</sub>H<sub>52</sub>Br<sub>2</sub>N<sub>2</sub>: C, 53.49; H, 10.15; N, 5.42. Found: C, 53.43; H, 10.19; N, 5.49.

**Propanediyl-** $\alpha$ , $\omega$ -bis(dodecyldimethylammonium bromide) (12-3-12). The N,N,N-dodecyldimethylamine (10.45 g, 0.049 mol) was dissolved in anhydrous ethanol and warmed at reflux. A solution of 1,3-dibromopropane (5.00 g, 0.025 mol) in ethanol was slowly added dropwise. The reaction was stopped after 24 h. The solution was refrigerated at 0 °C, and a solid mass was filtered. Further evaporation of the resulting ethanolic solution gave another crop of solid product. The solid was crystallized from ethanol/ethyl acetate. The crystals were filtered on a buchner funnel under inert gas flux. The white needle crystals were very hygroscopic. Yield: 11.60 g (75%).  $R_f$ : 0.03 Al<sub>2</sub>O<sub>3</sub> (ethyl acetate/methanol 75:25). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$ ): 0.86 (t, 6H, 2 CH<sub>3</sub>), 1.24 (m, 20H, 10 CH<sub>2</sub>), 1.77 (m, 4H, N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>), 2.66 (m, 2H, N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 3.38 (m, 12H, 4 N<sup>+</sup>CH<sub>3</sub>), 3.53 (m, 4H, 4 N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>-chain), 3.80 (m, 4H, 4  $N^+CH_2CH_2CH_2N^+$ ). Anal. Calcd for  $C_{31}H_{68}Br_2N_2$ : C, 59.22; H, 10.90; N, 4.46. Found: C, 59.18; H, 10.99; N, 4.40.

The solutions were prepared by weight using freshly boiled doubly distilled water, stored under nitrogen. Solution concentrations are expressed by molality, m (mol kg<sup>-1</sup>).

**Methods.** The enthalpies of dilution were measured by means of the Thermometric TAM 2277 (flow-mixing cell) microcalorimeter, equipped with a 221 Nano Amplifier instrument, at 298 K. The TAM thermostat (2277-011, from 5 to 90 °C) is stable to within  $\pm 0.1$  mK. The freshly prepared surfactant solutions, kept before injection at the experimental temperature by means of a Heto cryothermostatic bath, were diluted into the "mixing" measuring cell of the microcalorimeter in a 1:1 ratio by using CO<sub>2</sub>-free water. The injection of the solutions and of water into the calorimeter was done by means of a Gilson peristaltic pump, Minipuls 2, and their flows were determined by weight. Electrical calibrations were performed before and after each run.

The density, *d*, and sound velocity, *u*, of the solutions were measured by a Paar DSA 5000 oscillating U-tube density  $(\pm 0.000\ 001\ g\ cm^{-3})$  and sound velocity  $(\pm 0.1\ m\ sec^{-1})$  meter which measures to the highest accuracy in wide viscosity and temperature ranges. Temperature is controlled within  $\pm 1 \times 10^{-3}$  K. On the basis of an additional measuring cell made of stainless steel and on high resolution electronics, the sound velocity of the sample can be determined accurately. Both measuring cells are temperature controlled using a built-in solid state thermostat and two integrated Pt(100) platinum thermometers. The instrument was calibrated before each series of measurements by degassed bidistilled water ( $d_0 = 0.997\ 043\ g\ cm^{-3}$ ,  $u_0 = 1497\ m\ sec^{-1}$  at 298 K) and dry air ( $d = 0.001\ 169\ g\ cm^{-3}$  at  $P = 1\ bar$ ).

# Results

The experimental data have been expressed in terms of the apparent and partial molar quantities of the solute, as usual in solution thermodynamics, assuming infinite dilution as the reference state. Apparent and partial molar quantities were obtained from the experimental data using methods detailed elsewhere.<sup>20–25</sup>



**Figure 1.** Relative apparent molar enthalpies (full circles) and partial molar relative enthalpies (empty circles) of the 8-3-8 gemini surfactant as a function of surfactant molality.

For the sake of clarity, we recall that, with reference to the state of infinite dilution, the molar enthalpy of dilution,  $\Delta H_d$ , is given by

$$\Delta H_{\rm d} = L_{\Phi,\rm f} - L_{\Phi,\rm i} \tag{1}$$

where  $L_{\Phi}$  is the relative apparent molar enthalpy and the indexes f and i stand for the final (after dilution) and initial (before dilution) concentrations, respectively.

For ionic surfactant in the premicellar region, the relative apparent molar enthalpy can be expressed by means of a polynomial in  $m^{1/2}$ . Stopping the serial expansion at the third term, we obtain

$$L_{\Phi} = A_{\rm L} m^{1/2} + B_{\rm L} m + C_{\rm L} m^{3/2}$$
(2)

where  $A_{\rm L}$  is the limiting Debye-Huckel slope for relative enthalpies accounting for the long range electrostatic solutesolute interactions. The parameters  $B_{\rm L}$  and  $C_{\rm L}$  are obtained from the experimental points in the premicellar region by a leastsquares curve fitting.

In the micellar region, the apparent molar enthalpies are evaluated by means of eq 1, and when a value of  $L_{\Phi}$  versus *m* not experimentally measured is needed, by graphical interpolation.

The partial molar enthalpies,  $L_2$ , are determined by drawing the best curve for the apparent molar enthalpies versus *m* and then by calculating the partial molar quantities as  $\Delta(mL_{\Phi})/\Delta m$ from points interpolated at regular intervals.

The heats of dilution and apparent and partial molar enthalpies at 298 K, obtained by means of eqs 1 and 2, for the compounds under study are available as Supporting Information. In Figures 1 and 2, the plots of the apparent and partial molar enthalpies as a function of molality for the compounds under study are shown.

The apparent molar volumes,  $V_{\Phi}$ , and adiabatic compressibilities,  $K_{s,\Phi}$ , were calculated by means of the following equations<sup>26–29</sup>

$$V_{\Phi} = \frac{M}{d} - \frac{10^3 (d - d_0)}{m d d_0}$$
(3)

$$K_{s,\Phi} = \frac{M\beta_s}{d} - \frac{10^3(\beta_{s,0}d - \beta_s d_0)}{mdd_0}$$
(4)

where *d* is the density of the solution of molality *m*, *M* is the molecular weight of the surfactants,  $d_0$  is the density of the solvent, and  $\beta_{s,0}$  and  $\beta_s$  (in units of bar<sup>-1</sup>) are the coefficient of adiabatic compressibility of the solvent and of the solute,



**Figure 2.** Relative apparent molar enthalpies (full squares) and partial molar relative enthalpies (empty squares) of the 12-3-12 gemini surfactant as a function of surfactant molality.

respectively. The latter is calculated from sound velocity, u, and density data as

$$\beta_{\rm s} = 100/(u^2 d) \tag{5}$$

Experimental densities, sound velocities, and the data from eqs 3–5 are available as Supporting Information.

## Discussion

Only a few data have been published until now about the thermodynamics of gemini surfactant solutions, 17,25,30 and a lot of questions about their behavior are still open. For instance, it is not completely clear if the group contribution approach is valid also in the case of gemini surfactants and if it is possible to use the group contribution obtained from the study of monomers to predict the properties of gemini surfactant solutions. Moreover, it is known<sup>13,15</sup> that this class of surfactants undergoes structural transitions in solution from spherical to elongated micelles, but until now, in the literature, thermodynamic parameters for such transitions have not been reported. In general, as far as regular surfactants are concerned, phase transitions in solutions involve too small of an amount of heat to be detected by enthalpy measurements, but other second derivative thermodynamic properties seem to be more sensitive to structural transitions.<sup>21</sup> The reasons why we have chosen to perform measurements on two bisquaternary ammonium bromide surfactants having the same spacer, constituted by three methylene groups, and different chain lengths, namely, the dioctyl (8-3-8) and didodecyl (12-3-12) compounds, are the following: (i) the well documented sphere to rod transition for the compound 12-3-12<sup>13,15</sup> and for the compounds having a short spacer and ii) conductivity data<sup>14</sup> showing the different behavior between 8-3-8 and 12-3-12 in the premicellar region. In fact, some very interesting papers about aggregation number and shapes of micelles of the didodecyl compound as a function of the length of the spacer have appeared in the literature some time ago,<sup>13,15</sup> showing the structural changes of the 12-3-12 compounds as a function of concentration.

Time-resolved fluorescence quenching (TRFQ) techniques for the determination of the aggregation number and cryogenic transmission electron microscopy (cryo-TEM) for the direct visualization of the aggregates have been used. At concentrations close to the cmc, micelles of 12-3-12 are spherical with an aggregation number of 25; that is, about 50 dodecyl chains stick together. This number increases significantly with concentration, suggesting a change in shape toward elongated micelles, confirmed by the cryo-TEM images and by the trends in solution viscosity. Small angle neutron scattering (SANS) measurements

agree with the above observations. A cmc value of 55 mM and a degree of ionization of  $\alpha = 0.27$  for 8-3-8<sup>12</sup> and a cmc value of 0.91 mM for 12-3-12<sup>10,11</sup> are reported in the literature. In a previous paper,<sup>9</sup> a value of 20 mM has been also reported for 8-3-8. Conductivity data of 8-3-8 versus concentration, reported by Frindi et al.,<sup>12</sup> show a first break at 20 mM and a second break at 55 mM. The value of concentration at which the second break is occurring has been assumed to be the cmc, following the spectrofluorometric and ultrasonic absorption data. From our conductivity experiments, not reported here, a value of 56 mmol  $kg^{-1}$  for the cmc of 8-3-8 has been determined, in good agreement with the above-reported literature values, and we have used this value in the following calculations. The data obtained from an electrical conductivity study of the above compounds are interpreted in terms of ion pairing in the premicellar region for the 8-3-8 compound.<sup>14</sup> However, 12-3-12 behaves regularly as a strong electrolyte.

Apparent and Partial Molar Enthalpies. In general for ionic surfactants, as far as apparent and partial molar enthalpies as a function of concentration are concerned, the curves, after increasing in the premicellar region, tend to level off at concentrations above the cmc, where they are almost parallel. The lowering of the curves in the micellar region, proportional to the number of carbon atoms in the alkyl chain, is attributed to the electrostatic interactions in micellar solutions. The trends for the compounds under study, reported in Figures 1 and 2, show a very peculiar behavior. The curves of 12-3-12 at very low concentrations are positive, as expected. On the contrary, the trends of the apparent and partial molar enthalpy of 8-3-8 as a function of concentration in the premicellar region are different: notwithstanding the greater value of the cmc, they are always negative starting from the lowest concentrations examined. The explanation of this different and unusual behavior could be found in the predominant interactions in dilute solutions depending on the length of the hydrophobic tails, as already suggested from the interpretation of the conductivity data:8,14 for 8-3-8, ion pairing interactions involving exothermic processes are prevalent, while 12-3-12 behaves regularly. The partial molar enthalpies of the latter decrease sharply below the cmc to a first plateau, due to the formation of spherical micelles; then, a new smaller jump starting at a concentration greater than 0.020 m to a second plateau value at concentrations greater than 0.045 m is clearly seen. In the case of the dodecyl compound, the dilution enthalpies have been measured up to a concentration of 0.1 m: samples of greater concentration cannot be injected in our flow-mixing calorimetric cell, due to the very high viscosity, further evidence of a change in structure of the solution. The above-reported well documented change in shape of the micelles could offer a possible explanation of the observed behavior, the first jump being associated with the formation of spherical micelles and the second one with the transition from spherical to elongated micelles.

For 8-3-8, the first plateau ends at the cmc. Then, after a jump, corresponding to the formation of spherical micelles, a new plateau is reached. A less steep jump, centered around 0.15 m, is suggested to correspond to the formation of elongated micelles, in accordance with literature data.<sup>13,15</sup>

To obtain the enthalpy change upon micellization,  $\Delta H_M$ , we have applied a pseudo-phase transition model, in which the aggregation process is considered like a phase transition, taking place at equilibrium. In this model, it is assumed that, at the cmc, the partial molar properties present a discontinuity due to the formation of the pseudo-phase. The micellization parameters are obtained by extrapolating at the cmc the trends of partial



**Figure 3.** Apparent molar volume  $(cm^3 mol^{-1})$  of the 8-3-8 gemini surfactant as a function of surfactant molality. Also included are results from the fit of the experimental data by eq 6 (solid line).

molar properties before and after the cmc.<sup>20–25</sup> Rather sharp changes occur, in fact, around the cmc, but they are never discontinuous, especially for surfactants with short hydrophobic chains. Following this procedure, we have  $\Delta H_{\rm M} = -1.9$  kJ mol<sup>-1</sup> for 8-3-8 and  $\Delta H_{\rm M} = -16.9$  kJ mol<sup>-1</sup> for 12-3-12 for the formation of spherical micelles. The latter value is in good agreement with that predicted in ref 17b for 12-3-12 from the trends of micellization enthalpy of didodecyl compounds with even s, from 2 to 12, measured by titration calorimetry.

In the case of 12-3-12, but never for 8-3-8, the enthalpies of dilution have been also directly measured by means of titration calorimetry by Bai et al.,<sup>30</sup> in order to obtain the micellization enthalpy. Their values, according to the observation of Grosmaire et al.,<sup>17b</sup> are less exothermic than those found in the present study and in ref 17b and seem to not be very reliable. Moreover, the titration calorimetry data have never been expressed in terms of apparent and partial molar enthalpies, losing in this way, in our opinion, very interesting details on the systems under investigation. In the sphere to rod transition, in fact, a relevant quantity of heat seems to be involved. From the plots in Figure 1, according to the interpretation suggested above, the  $\Delta H_{s \rightarrow r}$  results are -1.5 kJ mol<sup>-1</sup> for 8-3-8 and -3.9kJ mol<sup>-1</sup> for 12-3-12. Some time ago, we observed a comparable trend for the partial molar enthalpies of an anionic surfactant, the potassium 4-(hexylcarbonil-amino)-2-hydroxybenzoate (KPAS-C<sub>7</sub>), in 0.02 m KOH solution.<sup>23,24</sup> At a surfactant concentration of  $\sim 0.14$  mol kg<sup>-1</sup>, a sudden change in slope suggested a structural transition in solution, tentatively attributed to a sphere to rod transition. At that time, we suggested, as a determining factor, the possibility of an intramicellar rearrangement of the hydrogen bonds between the -OH and the carboxylic group of the salicylic moiety from intramolecular to intermolecular hydrogen bonding. The results obtained by the study of 8-3-8 and 12-3-12 gemini compounds seem to support our hypothesis. In fact, when an intermolecular hydrogen bond is formed, the system looks like a sort of "gemini" surfactant with a very short spacer, similar to the 8-3-8 compound investigated here. This conformation could justify the observed sphere to rod transition. Moreover, the value of  $\Delta H_{s \rightarrow r}$  for KPAS-C<sub>7</sub>, around -1.5 kJ mol<sup>-1</sup>, is nicely comparable with that for 8-3-8.

**Volumes and Adiabatic Compressibilities.** We show in Figures 3 and 4 the trends of apparent molar volume for 8-3-8 and 12-3-12, respectively, and in Figure 5 the apparent molar adiabatic compressibilities as a function of concentration. The apparent molar volumes for m-s-m type gemini surfactants in aqueous solution have already been investigated by Wettig and Verral,<sup>26</sup> but in the present work, a greater number of experi-



**Figure 4.** Apparent molar volume ( $cm^3 mol^{-1}$ ) of the 12-3-12 gemini surfactant as a function of surfactant molality. Also included are results from the fit of the experimental data by eq 6 (solid line).



**Figure 5.** Apparent molar isentropic compressibilities  $(cm^3 mol^{-1} bar^{-1})$  of the 8-3-8 (circles) and of 12-3-12 (squares) gemini surfactants as a function of surfactant molality. Also included are results from the fit of the experimental data by eq 6 (solid line).

mental points has been determined in the same concentration range, to more carefully look for evidence for sphere to rod transition. Adiabatic compressibilities, on the contrary, are reported here for the first time. Despite the great care we have used in our experiments, the curves do not show peculiar behavior around the concentrations at which the sphere to rod transitions are expected. This means that the change in volume involved in such transitions, if present, is of the same order of magnitude as the experimental error. The change in volume upon micellization is primarily due to the change in structure of the water molecules involved in the hydrophobic effect<sup>31,32</sup> and to the change in electrostriction of the polar part of the molecule, modulated by the value of  $\alpha$ , the degree of ionization of the micelle: volumetric properties, such as volumes and compressibilities, are reflective, in fact, of the solute-solvent interactions. It is obvious that a great change in these interactions occurs when micelle formation begins. A further change in structure of the micelles, in which solute-solute van der Waals interactions are mainly involved, is expected to give rise to a smaller change in apparent molar volume of surfactant, if any. The same arguments are valid for compressibilities.

To extract micellization parameters, the volumetric data have been analyzed assuming a pseudo-phase transition model.<sup>12,26</sup> Following this model, the observed trends above the cmc can be described by the equation

$$X_{\Phi} = X_{\Phi,M} - (\operatorname{cmc}\Delta X_{\Phi,M})(1/m)$$
(6)

Here, *X* stands for the volume or for the adiabatic compressibility. Knowing the values for the cmc, the values of  $X_{\Phi,M}$ , the property in the micellar phase, and  $\Delta X_{\Phi,M}$ , the change in property upon micellization, can be obtained by a least-squares fit. In Table 1, the values so obtained, together with the values

TABLE 1: Values of  $X_{\Phi^{\circ}}$ , the Property at Infinite Dilution,  $X_{\Phi,M}$ , the Property in the Micellar Phase,  $\Delta X_{\Phi,M}$ , the Change in Property upon Micellization,  $X_{\Phi,cmc}$ , the Property at the cmc for the Compounds under Investigation

compound	X	$X_{\Phi}^{\circ}$	$X_{\Phi,\mathrm{M}}$	$\Delta X_{\Phi,\mathrm{M}}$	$X_{\Phi,\mathrm{cmc}}$	$cmc^a$
8-3-8	$V^b$ Ks <sup>c</sup>	437.3 -0.003 842	446.5(1) 0.013 05(10)	9.5(2) 0.016 33(10)	437.2(2) -0.003 29(10)	0.056
12-3-12	$V^b$ Ks $^c$	$571.2^d$ -0.005 36 <sup>e</sup>	579.6(2) 0.022 25(10)	11.7(2) 0.025 72(10)	567.8(2) -0.003 48(10)	0.000 91

<sup>a</sup> In units of mol kg<sup>-1</sup>. <sup>b</sup> In units of cm<sup>3</sup> mol<sup>-1</sup>. <sup>c</sup> In units of bar<sup>-1</sup> cm<sup>3</sup> mol<sup>-1</sup>. <sup>d</sup> From ref 26. <sup>e</sup> From the group contribution approach (ref 28).

of  $X_{\Phi,\text{cmc}}$ , the value at the cmc, obtained by

$$X_{\Phi,\rm cmc} = X_{\Phi,\rm M} - \Delta X_{\Phi,\rm M} \tag{7}$$

are reported. The good agreement between the experimental and computed data is shown in Figures 3-5, in which the solid line represents the computed function. The values of apparent molar volumes at the cmc and in the micellar phase agree very well with those found by Wettig and Verral.<sup>26</sup> Moreover, in the case of 8-3-8, the experimental value of  $X_{\Phi}^{\circ}$ , obtained by extrapolation to infinite dilution of the data below the cmc (reported in Table 1), is comparable to the values obtained by different group contribution approaches.<sup>26,33,34</sup> The group contribution of the methylene group to the change in apparent molar volume upon micellization, obtained from the comparison of 8-3-8 and 12-3-12, is smaller compared to those obtained from the study of normal surfactants.<sup>22</sup> The reduction of this group contribution in the case of gemini surfactants is confirmed by the data reported in ref 26, if the compounds with spacer 3, excluding 8-3-8, are considered. A possible explanation of this behavior is that the alkyl chains of the gemini surfactants are already associated in solution, as we suggested some years ago.<sup>25</sup>

The isentropic compressibilies (see Figure 5) show trends as a function of m, similar to those of volumes, with a sharp increase at the cmc, ending in a plateau in the micellar region, without showing peculiarities. Notwithstanding, it is generally accepted that properties second or higher order as derivatives of free energy are more sensitive to the transition in solution, but this is not the case for the compressibilities we have measured. Compressibility, as the other volumetric properties, is strictly associated with the structure of the hydration sphere of the molecule: the disruption of the rigid cavity hosting the hydrophobic moiety of the surfactant molecule, together with the reduction of the electrostriction due to the counterion binding in micelles, allows a greater change in volume with pressure. Once again, the analogy between the micellization process and the folding of proteins or polypeptides is very strict: proteins in the native state and folded polypeptides show positive compressibility. On the contrary, negative compressibilities are evaluated by the group contribution approach for the completely unfolded state and negative compressibilities are shown by the surfactants under investigation (see Table 1) below the cmc. It is generally accepted that the group contribution of  $-CH_2$  to the molar compressibility is negative  $(-1.9 \times 10^{-4} \text{ cm}^3 \text{ bar}^{-1})$  $mol^{-1}$  in ref 28 and  $-1.6 \times 10^{-4} cm^3 bar^{-1} mol^{-1}$  in ref 29) at infinite dilution. We have evaluated  $K_{s,\Phi}^{\circ}$  of 8-3-8 by extrapolating at infinite dilution the experimental trend below the cmc, and we have evaluated the value for 12-3-12 by applying the first of the above group contributions (Table 1). Both values are negative, as expected. In Table 1 are also reported the values of  $K_{s,\Phi,cmc}$ , the compressibility at the cmc, obtained by eq 7: they are negative and the lengthening of the hydrophobic chain lowers the values to a limited extent with respect to infinite dilution. In the micellar phase, the -CH<sub>2</sub>- group contribution becomes positive: from the data in Table 1, a value of  $1.17 \times$  $10^{-3}$  cm<sup>3</sup> bar<sup>-1</sup> mol<sup>-1</sup> can be obtained, lower than the value of

 $1.5 \times 10^{-3}$  cm<sup>3</sup> bar<sup>-1</sup> mol<sup>-1</sup>, reported in ref 27 for the change in adiabatic molar compressibility upon micellization of alkyltrimethylammonium bromide monomers. The lower value compared to the monomers could support the above-reported hypothesis of partial association of the chains before the cmc.

## Conclusions

The evaluation of the apparent and partial molar enthalpies at 298 K of aqueous solutions of the cationic gemini surfactants propanediyl- $\alpha, \omega$ -bis(octyldimethylammonium bromide) and propanediyl- $\alpha, \omega$ -bis(dodecyldimethylammonium bromide) as a function of concentration allows the determination, besides the enthalpy of micellization, of the change in enthalpy associated with the sphere to rod transition in the micellar phase, which has never been reported before. The changes in enthalpies upon micellization and for sphere to elongated micelle transition have been obtained from the experimental data by using a pseudophase transition approach. The sphere to rod transition appears to be an exothermic process, with the quantity of heat involved increasing with increasing chain length. The  $\Delta H_{s \rightarrow \tau}$  results are -1.5 kJ mol<sup>-1</sup> for 8-3-8 and -3.9 kJ mol<sup>-1</sup> for 12-3-12.

Moreover, the data reported here are a further contribution supporting the interpretation of a similar trend in the partial molar enthalpies of an anionic surfactant, the potassium 4-(hexylcarbonilamino)-2-hydroxybenzoate in 0.02 *m* KOH solution, previously studied by us: due to the formation of intermolecular hydrogen bonding, this surfactant can assume a structure very similar to that of gemini compounds. The value of  $\Delta H_{s \rightarrow r}$  is very similar to that for 8-3-8 and could support this hypothesis.

On the other hand, no evidence of the above transition is found in the trends of volumetric properties versus m, in the limits of the accuracy of the experimental methods used.

The group contribution approach, using the values obtained from the study of monomers, seems to not be suitable in the case of gemini compounds.

The adiabatic molar compressibilities, reported here for the first time, show a negative group contribution for the methylene group, when the surfactants are present in solution as monomers, reflecting its solvation structure. In the micellar phase, the  $-CH_2-$  group contribution becomes positive: a value of  $1.17 \times 10^{-3}$  cm<sup>3</sup> bar<sup>-1</sup> mol<sup>-1</sup> for the change in adiabatic molar compressibility upon micellization is obtained, lower than that of the alkyltrimethylammonium bromide monomers. The lower values of the methylene group contributions to the volumetric properties with respect to the monomers support the hypothesis of partial association of the chains below the cmc.

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**Supporting Information Available:** Tables collecting the molalities, m, enthalpies of dilution,  $\Delta H_d$ , apparent,  $L_{\Phi}$ , and partial,  $L_2$ , molar enthalpies of the 8-3-8 and 12-3-12 gemini surfactants, in water at 298 K; tables reporting the densities, d, apparent molar volumes,  $V_{\Phi}$ , sound velocities, u, coefficients of adiabatic compressibility,  $\beta_s$ , and isentropic compressibilities,  $K_{s,\Phi}$ , as a function of molality, m, of the 8-3-8 gemini surfactants, in water at 298 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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