

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231681111>

# Thermodynamic Study of the Aggregation Behavior of Sodium n-Hexyl Sulfate in Aqueous Solution

ARTICLE *in* LANGMUIR · AUGUST 1999

Impact Factor: 4.46 · DOI: 10.1021/la981759f

---

CITATIONS

40

---

READS

17

4 AUTHORS, INCLUDING:



Félix Sarmiento

University of Santiago de Compostela

158 PUBLICATIONS 2,485 CITATIONS

SEE PROFILE



Víctor Mosquera

University of Santiago de Compostela

170 PUBLICATIONS 3,114 CITATIONS

SEE PROFILE

# Thermodynamic Study of the Aggregation Behavior of Sodium *n*-Hexyl Sulfate in Aqueous Solution

María J. Suárez, José L. López-Fontán, Félix Sarmiento, and Víctor Mosquera\*

*Grupo de Física de Coloides y Polímeros, Departamento de Física Aplicada y Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*

*Received December 30, 1998. In Final Form: April 14, 1999*

The self-association of sodium *n*-hexyl sulfate (SHS) in aqueous solution has been examined at 25.0 and 35.0 °C. The critical micellar concentration (cmc) and the degree of counterion binding,  $\beta$ , were determined by conductivity measurements at 25.0 °C. Both quantities were used to calculate the standard Gibbs energy change on micellization. The standard enthalpy change on aggregation was measured by microcalorimetry at the same temperature. Good agreement has been found when comparing with the properties of other sodium alkyl sulfates. Densities were measured at the same temperatures. The apparent molal volumes and partial molal volumes have been evaluated at concentrations above and below the cmc. The change in partial molal volumes in the formation of micelles has been evaluated from these measurements. Ultrasound velocity measurements were used to obtain the cmc in water. Apparent adiabatic compressibilities were calculated from a combination of density and ultrasound velocity measurements. Surface tension was measured at a temperature of 25.0 °C. Surface properties were calculated from these data.

## Introduction

Continuing with the study on the thermodynamic properties of aqueous surfactants of short hydrocarbon chain length, the self-association of sodium *n*-hexyl sulfate (SHS) in aqueous solution has been investigated. In a previous study,<sup>1</sup> we investigated the physicochemical properties of aqueous solutions of the surfactant hexyltrimethylammonium bromide (C<sub>6</sub>TAB). The study showed that C<sub>6</sub>TAB forms small aggregates at a critical micellar concentration (cmc). In this paper, we have extended the study to the properties of aqueous solutions of sodium *n*-hexyl sulfate.

Several authors have reported systematic thermodynamic studies on the micellar behavior of the sodium *n*-alkyl sulfate series with *n* = 8, 10, and 12. Brun et al.<sup>2</sup> reported on the partial molal volumes and isentropic partial molal compressibilities of sodium dodecyl sulfate. Bloor et al.<sup>3</sup> studied the adiabatic compressibilities of sodium decyl and dodecyl sulfate and made a theoretical treatment which enables the micellar compressibility to be evaluated from these data. Musbally et al.<sup>4</sup> performed a thermodynamic study of the surfactants sodium, octyl, decyl, and dodecyl sulfate.

Thermodynamic models used in this work have been applied before to amphiphilic molecules which aggregate to low aggregation number, such as the aforementioned C<sub>6</sub>TAB and the surface-active drugs chlorhexidine diglucuronate<sup>5</sup> and propranolol hydrochloride.<sup>6</sup> We have validated the models comparing theoretical and experimental

thermodynamic parameter values. In all cases acceptable concordance was found. With such encouraging results, in this study we have extended the work on SHS by a detailed examination of the thermodynamic properties of its aqueous solutions. Preliminary evidence suggesting the possibility of self-association of sodium *n*-hexyl sulfate was obtained from the apparent solubilization of the water-insoluble dye Sudan IV by concentrated aqueous solutions of SHS. As far as we are aware, the aggregation characteristics of this surfactant have not previously been reported.

## Experimental Section

Sodium *n*-hexyl sulfate (purity  $\geq$  99%) from Lancaster (No. 6245) was used without further purification. Sodium chloride was of Analar Grade. All concentrations were determined by weight using double-distilled and sometimes, when necessary, triple-distilled degassed water.

Conductance at 25.00 °C was measured by using a conductivity meter (Kyoto Electronic Type C-117), the cell of which was calibrated with KCl solutions in the appropriate concentration range. The cell constant was calculated using molar conductivity data for KCl published by Shedlovsky<sup>7</sup> and Chambers et al.<sup>8</sup> SHS solutions of known concentration were progressively added to water using an automatic pump (Dosimat 665 Metrohm). The measuring cell was immersed in a thermostat bath, maintaining the temperature control to within  $\pm 0.01$  °C. The automatic pump and the temperature control were achieved using a Hewlett-Packard Vectra computer.

Enthalpy measurements were made at 25.0 °C with an LKB 10700 batch microcalorimeter, which utilizes the twin-vessel principle, each vessel being divided into two compartments.<sup>9</sup> The

\* To whom correspondence should be addressed. E-mail: fmvictor@usc.es.

(1) Mosquera, V.; del Río, J. M.; Attwood, D.; García, M.; Jones, M. N.; Prieto, G.; Suárez, M. J.; Sarmiento, F. *J. Colloid Interface Sci.* **1998**, *206*, 66.

(2) Brun, T.; Høiland, H.; Vikingstad, E. *J. Colloid Interface Sci.* **1978**, *63*, 89.

(3) Bloor, D. M.; Gormally, J.; Wyn-Jones, E. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1915.

(4) Musbally, G. M.; Perron, G.; Desnoyers, J. E. *J. Colloid Interface Sci.* **1974**, *48*, 494.

(5) Sarmiento, F.; del Río, J. M.; Prieto, G.; Attwood, D.; Jones, M. N.; Mosquera, V. *J. Phys. Chem.* **1995**, *99*, 17628.

(6) Mosquera, V.; Ruso, J. M.; Attwood, D.; Jones, M. N.; Prieto, G.; Sarmiento, F. *J. Colloid Interface Sci.* **1999**, *210*, 97.

(7) Shedlovsky, T. *J. Am. Chem. Soc.* **1932**, *54*, 1411.

(8) Chambers, J. F.; Stokes, J. M.; Stokes, R. H. *J. Phys. Chem.* **1956**, *60*, 985.

(9) Wadso, I. *Acta Chem. Scand.* **1968**, *22*, 927.

microcalorimeter was frequently calibrated electrically during the course of the study. In the most sensitive range used for measurements ( $30 \mu\text{V}$ ), the mean sensitivity of the detectors in the heat sinks of the two vessels was  $14.66 \pm 0.32 \mu\text{W } \mu\text{V}^{-1}$  (i.e.,  $\pm 2.2\%$ ). The two detector sensitivities differed by only  $0.37\%$ , which is less than the standard deviation of the sensitivity measurements of the two detectors; i.e., the vessels were matched. These sensitivities were also determined using the enthalpy of dilution of aqueous solutions of urea as reported by Gucker and Pickard,<sup>10</sup> obtaining excellent agreement with the electrical calibration.

The reaction vessel was charged with 2 mL of SHS solution of concentration twice the critical concentration and 2 mL of water. The reference vessel was charged with 2 mL of water in both compartments. On mixing, the final concentration of SHS is the critical micellar concentration, and as a result the enthalpy of demicellization is obtained.

The densities were measured at 25.0 and 35.0 °C with an Anton Paar DMA 60/602 densimeter with a resolution of  $\pm 10^{-6} \text{ g cm}^{-3}$ . The temperature control was maintained within  $\pm 0.005$  °C, giving rise to uncertainties in density of ca.  $\pm 1.5 \times 10^{-6} \text{ g cm}^{-3}$ . The temperature was kept by a HETO proportional temperature controller and checked with an Anton Paar DT 100-30 digital precision thermometer. The densimeter was calibrated at each temperature with air at known pressure and water, where the density of air-saturated water was assumed to be 0.997 043 and 0.994 030  $\text{g cm}^{-3}$  at 25.0 and 35.0 °C, respectively.

Ultrasound velocity was measured at 25.0 °C at a frequency of 2 MHz using a NUSonic Model 6380 concentration analyzer (NUSonic Inc.) with a temperature transducer connected to a Hewlett-Packard 3455A digital microvoltmeter. Errors in ultrasound velocity measurements can arise mainly from variations of temperature. Since temperature control was  $\pm 0.005$  °C, and the sound velocity transducer was connected to a Hewlett-Packard 3437A multimeter, the output of which was assessed continuously by a computer giving an accuracy in the velocity of  $\pm 0.01 \text{ m/s}$ , the uncertainties in the measurement of ultrasound velocity were ca.  $\pm 0.05 \text{ m/s}$  at molalities above the critical concentration. Measurements on more dilute solutions were subject to increased error associated with the adsorption of SHS from solution onto walls of the cell.

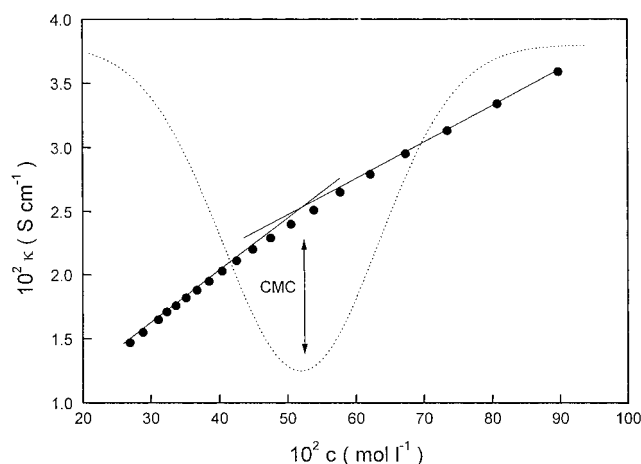
The surface tension was measured by the Wilhelmy plate method using a Krüss K12 processor tensiometer. Liquid samples were prepared in a glass vessel. To ensure that the glassware used in the measurements and preparation of the solutions were scrupulously clean, a solution of sodium hydroxide in ethanol was used. The temperature of the sample was kept constant at  $25.0 \pm 0.1$  °C by circulating thermostated water around the vessel. All samples were allowed to settle and the temperature reached a constant in that time. Sets of measurements were taken at 20–30 min intervals until measured values were constant. A platinum plate was used. Before each measurement, the plate was cleaned by heating it to red-hot stage with an alcohol burner.

## Results and Discussion

**Critical Micelle Concentration and Thermodynamics of Micellization.** Figure 1 shows a plot of specific conductivity,  $\kappa$ , as a function of molar concentration,  $c$ , for aqueous solutions of SHS. To calculate the cmc we have employed the definition of Phillips<sup>11</sup> which is in widespread use.<sup>12</sup> In agreement with Phillips, the cmc is defined by

$$\left( \frac{d^3 \kappa}{dc^3} \right)_{c=\text{cmc}} = 0 \quad (1)$$

The dashed line in Figure 1 shows the second derivative of the conductivity–concentration curve, and the minimum value corresponds to the critical micellar concentra-



**Figure 1.** Specific conductivity,  $\kappa$ , of SHS in water as a function of molar concentration. The dotted line represents the second derivative of the conductivity–concentration curve.

tion.<sup>13</sup> This value coincides with the intersection point of the two linear segments of the conductivity–concentration curve, corresponding to the monomeric and aggregate forms of the surfactant. A value of  $0.517 \text{ mol dm}^{-3}$  ( $0.559 \text{ mol kg}^{-1}$ ) was obtained.

An approximate value of the degree of counterion binding  $\beta$  was calculated from the relationship

$$\beta = 1 - \alpha = 1 - (S_2/S_1) \quad (2)$$

$\alpha$  is the degree of ionization, which was determined from the ratio of the mean gradients of conductivity against concentrations plots above ( $S_2$ ) and below ( $S_1$ ) the cmc.<sup>14</sup> A value of  $\alpha = 0.7$  was obtained.

Values (per mole of monomer) of the standard Gibbs energy change,  $\Delta G_m^\circ$ , on aggregation were calculated from the following expression, as predicted from the mass-action model (Mosquera et al. and references cited within).<sup>6</sup>

$$\Delta G_m^\circ = (1 + \beta)RT \ln x_{\text{cmc}} \quad (3)$$

where  $x_{\text{cmc}}$  is the cmc expressed in units of mole fraction. The obtained value of  $\Delta G_m^\circ$  was  $-14.8 \text{ kJ mol}^{-1}$ .

The experimental value measured for the change in standard enthalpy on aggregation,  $\Delta H_m^\circ$ , was  $5.4 \pm 0.5 \text{ kJ/mol}$ . The change in the standard entropy of micellization can, hence, be obtained from

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \quad (4)$$

giving a value of  $\Delta S_m^\circ = 68 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$ . Positive values of  $\Delta H_m^\circ$  and  $\Delta S_m^\circ$  are taken as evidence of hydrophobic interaction.<sup>15</sup>

In Figure 2 we show the change of the standard enthalpy,  $\Delta H_m^\circ$ , against the number of carbons  $n_c$  for a series of sodium alkyl sulfates.<sup>16–20</sup> This plot was fitted

(13) Pérez-Rodríguez, M.; Prieto, G.; Rega, C.; Varela, L. M.; Sarmiento, F.; Mosquera, V. *Langmuir* **1998**, *14*, 4422.

(14) Evans, H. C. *J. Chem. Soc.* **1956**, 579.

(15) Nusselder, J. J.; Engberts, B. F. N. *J. Colloid Interface Sci.* **1992**, *148*, 353.

(16) Kresheck, G. C.; Hargraves, W. J. *J. Colloid Interface Sci.* **1974**, *48*, 481.

(17) Goddard, E. D.; Hoeve, C. A. J.; Benson, G. C. *J. Phys. Chem.* **1976**, *80*, 905.

(18) Paredes, S.; Tribout, M.; Ferreira, J.; Leonis, J. *Colloid Polymer Sci.* **1976**, *254*, 637.

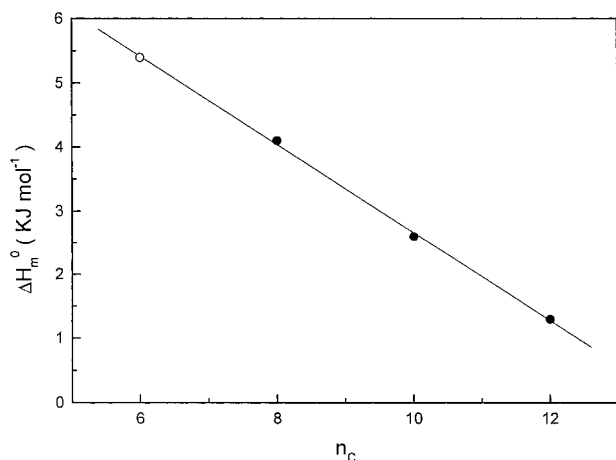
(19) Eatough, D. J.; Rehfeld, S. J. *Thermochim. Acta* **1971**, *2*, 443.

(20) Sharma, V. K.; Bhat, R.; Ahluwalia, J. C. *J. Colloid Interface Sci.* **1987**, *115*, 396.

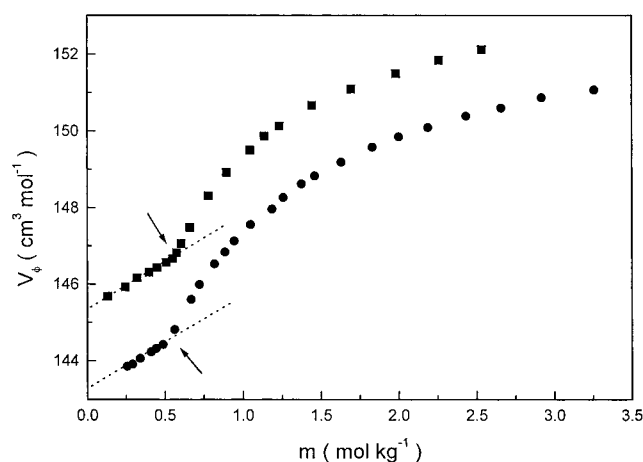
(10) Gucker, F. T.; Pickard, H. B. *J. Am. Chem. Soc.* **1940**, *62*, 1464.

(11) Phillips, J. N. *Trans. Faraday Soc.* **1955**, *51*, 561.

(12) Moroi, Y.; Matsuura, R. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 333.



**Figure 2.** Change in standard enthalpy of micellization,  $\Delta H_m^0$ , of sodium *n*-alkyl sulfate as a function of hydrocarbon chain length,  $n_c$ . (○) value from this work, (●) values from refs 14–18.



**Figure 3.** Apparent molal volumes,  $V_\phi$ , of sodium *n*-hexyl sulfate in water at 25 °C (●) and 35 °C (■). Dotted lines are values from the Debye–Hückel limiting law.

to an equation such that

$$\Delta H_m^0 = a_0 + a_1 n_c \quad (5)$$

and the following values were obtained:  $a_0 = 9.7 \pm 0.1$  and  $a_1 = -0.71 \pm 0.01$  with a correlation coefficient of 0.999 65. It is clear that SHS confirms eq 5, and the applicability of the empirical expression is for the homologous series  $6 \leq n_c \leq 12$ .

**Apparent and Partial Molal Volumes.** From the density data, apparent molal volumes,  $V_\phi$ , of the surfactant in water was computed using the expression<sup>8</sup>

$$V_\phi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{m\rho\rho_0} \quad (6)$$

where  $m$  is the molality of the solutions,  $M$  is the molecular weight of the surfactant, and  $\rho$  and  $\rho_0$  represent the densities for the solutions and pure water, respectively. Figure 3 shows  $V_\phi$  at 25.0 and 35.0 °C as a function of the molality. For each temperature the concentration dependence of  $V_\phi$  is similar to that of other surfactants.<sup>2,21–23</sup>

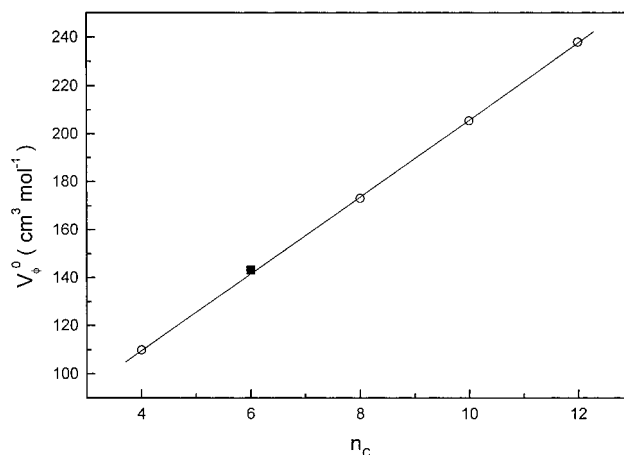
(21) De Lisi, R.; Ostiguy, C.; Perron, G.; Desnoyers, J. E. *J. Colloid Interface Sci.* **1979**, *71*, 147.

(22) De Lisi, R.; Perron, G.; Desnoyers, J. E. *Can. J. Chem.* **1980**, *58*, 959.

**Table 1.** Parameters of Eq 7 and Standard Deviation  $\sigma$

$t/^\circ\text{C}$	$A_v/\text{cm}^3 \text{ kg}^{1/2} \text{ mol}^{-3/2}$	$V_\phi^\circ/\text{cm}^3 \text{ mol}^{-1}$	$B_v/\text{cm}^3 \text{ kg} \text{ mol}^{-2}$	$\sigma$
25.0	1.87 <sup>a</sup>	$143.22 \pm 0.02$	$1.56 \pm 0.06$	0.000 16
35.0	1.96 <sup>a</sup>	$145.37 \pm 0.02$	$1.40 \pm 0.06$	0.000 42

<sup>a</sup> Debye–Hückel limiting slopes from ref 23.



**Figure 4.** Apparent molal volume at infinite dilution,  $V_\phi^\circ$ , and at a temperature of 25 °C, as a function of hydrocarbon chain length. (■) value from this work, (○) values from ref 4.

$V_\phi$ , in the premicellar region increases until the cmc and levels off slowly at a higher concentration. This indicates the presence of a clear cmc of 0.48 and 0.55 mol kg<sup>-1</sup> at 25.0 and 35.0 °C, respectively.

The volumes of micellization increase in magnitude with the surfactant chain length, and are consistent with a large decrease in hydrophobic character during micellization.

In the premicellar region  $V_\phi$  was fitted to molality by the equation<sup>24</sup>

$$V_\phi = V_\phi^\circ + A_v m^{1/2} + B_v m \quad (7)$$

where  $V_\phi^\circ$  is the apparent molal volume at infinite dilution,  $A_v$  is the Debye–Hückel limiting law coefficient and  $B_v$  is an adjustable parameter which measures the deviation from the limiting law. Values of  $V_\phi^\circ$  and  $B_v$  obtained, with the standard deviations for each temperature, are given in Table 1.

The temperature dependence of  $V_\phi^\circ$  is similar to that of other surfactants: the apparent molal volume at infinite dilution, in general, increases with temperature.<sup>25</sup> Figure 4 shows apparent molal volumes at infinite dilution,  $V_\phi^\circ$ , for some alkyl sulfates.<sup>4</sup> The increase of  $V_\phi^\circ$  with the number of carbons fitted the linear equation

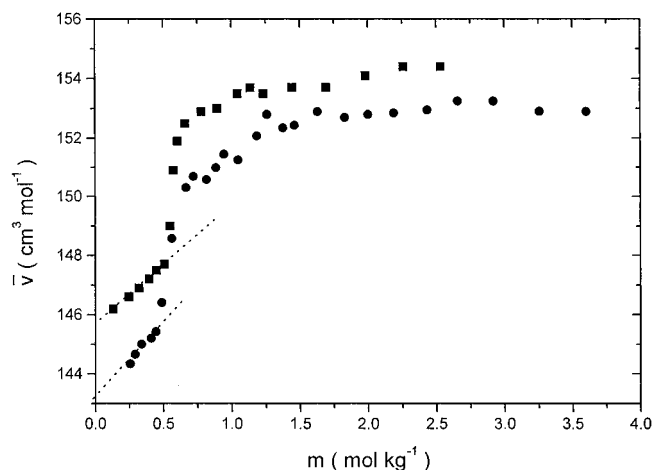
$$V_\phi^\circ = b_0 + b_1 n_c \quad (8)$$

with  $b_0 = 46 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$  and  $b_1 = 15.9 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$  and with a correlation coefficient of 0.999 91. It is clear that, here also, SHS confirms the empirical expression (8), and its applicability is for the homologous series  $6 \leq n_c \leq 12$ .

(23) Desnoyers, J. E.; Roberts, D.; De Lisi, R.; Perron, G. *Solution Behaviour of Surfactants*; Plenum Press: New York, 1982; Vol. 1.

(24) Desnoyers, J. E.; De Lisi, R.; Ostiguy, C.; Perron, G. *Solution Chemistry of Surfactants*; Plenum Press: New York, 1979; Vol. 1.

(25) Desnoyers, J. E.; Perron, G.; Roux, A. H. *Surfactant Solutions: New Methods of Investigation*; Marcel Dekker: New York, 1987.



**Figure 5.** Partial molal volumes,  $\bar{V}$ , of sodium *n*-hexyl sulfate in water at 25 °C (●) and 35 °C (■). Dotted lines are values from the Debye–Hückel limiting law.

**Table 2. Partial Molal Volumes of the Premicellar Region,  $\bar{V}_s$ , and the Micelle,  $\bar{V}_m$ , and the Change in Partial Molal Volume in Micelle Formation,  $\Delta\bar{V}$**

$t/^\circ\text{C}$	$\bar{V}_s/\text{cm}^3 \text{ mol}^{-1}$	$\bar{V}_m/\text{cm}^3 \text{ mol}^{-1}$	$\Delta\bar{V}/\text{cm}^3 \text{ mol}^{-1}$
25.0	$145.2 \pm 0.2$	$152.8 \pm 0.2$	$7.6 \pm 0.5$
35.0	$147.8 \pm 0.2$	$153.8 \pm 0.2$	$6.0 \pm 0.5$

The adjustable parameter  $B_v$  is related to a pair interaction<sup>24</sup> and is equivalent to the second virial coefficient. This parameter has been studied systematically for volumes.<sup>4,22,25</sup> For SHS,  $B_v$  is positive and decreases with temperature. The positive values indicate a degree of dimerization in the premicellar region.<sup>4</sup>

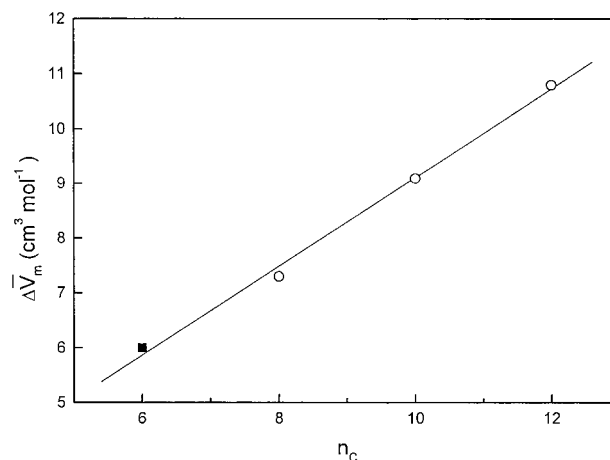
The partial molal volumes,  $\bar{V}$ , have been computed from  $V_\phi$  by the equation<sup>25</sup>

$$\bar{V} = V_\phi + m \left( \frac{\partial V_\phi}{\partial m} \right)_{T,P} \quad (9)$$

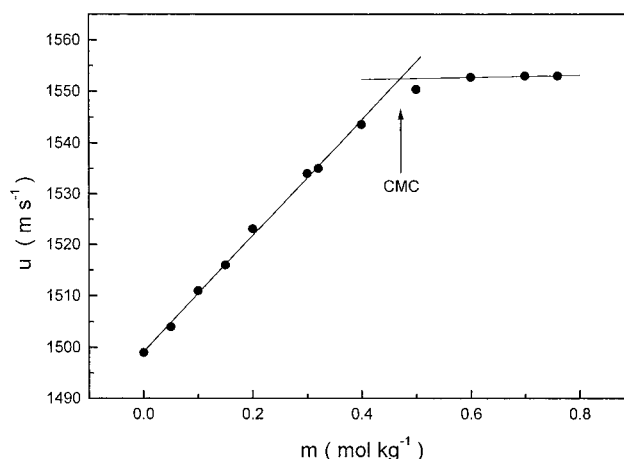
If  $V_\phi$  is known as a function of  $m$ ,  $\bar{V}$  can be calculated. Unfortunately, in the region where micellization occurs,  $V_\phi$  changes very rapidly, and it is nearly impossible to represent  $V_\phi$  by some polynomial in  $m$ . Therefore, it is often convenient to rewrite the eq 9 in the form

$$\bar{V} = \frac{d(V_\phi m)}{dm} \approx \frac{\Delta(V_\phi m)}{\Delta m} \quad (10)$$

for constant temperature and pressure. So, it is possible to determine  $\bar{V}$  graphically from a plot of  $\bar{V}$  against the mean molality. Figure 5 shows the values of  $\bar{V}$  so obtained at various molal concentrations and at 25.0 and 35.0 °C. Concentration and temperature dependence of  $\bar{V}$  are similar to those of other surfactants.<sup>24</sup> The initial break in the curves is taken as the cmc. This graph can be used to calculate the change in the apparent molal volume during micellization,  $\Delta\bar{V} = \bar{V}_m - \bar{V}_s$ , where the micelle apparent molal volume,  $\bar{V}_m$ , represents the linear part of  $\bar{V}$  beyond the cmc and is extrapolated to the cmc. The difference between this value of  $\bar{V}_m$  and the value of the one corresponding to the premicellar region,  $\bar{V}_s$ , is taken as  $\Delta\bar{V}$ . These values are given in Table 2 for both temperatures. As it has been observed with other surfactants,  $\Delta\bar{V}$  generally decreases as the temperature increases and increases with chain length.<sup>22</sup> Figure 6



**Figure 6.** Micellar partial molal volume change,  $\Delta\bar{V}$ , as a function of hydrocarbon chain length. (■) value from this work, (○) values from ref 4.



**Figure 7.** Ultrasound velocity of SHS in water as a function of molality at 25 °C. The arrow denotes the cmc.

shows the increase of  $\Delta\bar{V}$  with the number of carbons of some alkyl sulfates.<sup>4</sup> This curve was fitted to the equation

$$\Delta\bar{V} = d_0 + d_1 n_c \quad (11)$$

with  $d_0 = 1.0 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$  and  $d_1 = 0.81 \pm 0.03 \text{ cm}^3 \text{ mol}^{-1}$  and with a correlation coefficient of 0.998. Sodium *n*-hexyl sulfate conforms to eq 11, and the applicability of the empirical expression is for the homologous series  $6 \leq n_c \leq 12$ .

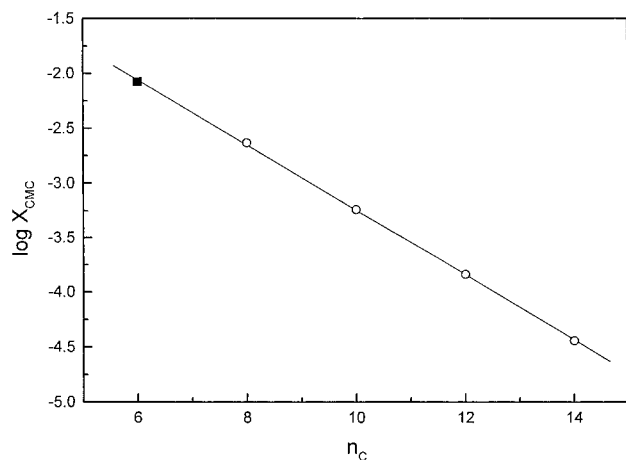
**Sound Velocity and Apparent Adiabatic Compressibility.** The dependence of the sound velocity,  $u$ , of the surfactant solutions at a temperature of 25 °C on the concentration,  $m$ , is shown in Figure 7. The two linear segments of the plot, corresponding to the monomeric and micellar forms of the surfactant, intersect at the cmc, showing a clear and a well-defined break. A value of  $0.471 \text{ mol kg}^{-1}$  was obtained by this means.

Figure 8 shows the plot of log molar fraction of the cmc,  $\log x_{\text{cmc}}$  vs number of carbon atoms,  $n_c$ , in the alkyl chain for a series of *n*-alkyl sulfates.<sup>26</sup>  $\log x_{\text{cmc}}$  was fitted to the linear equation

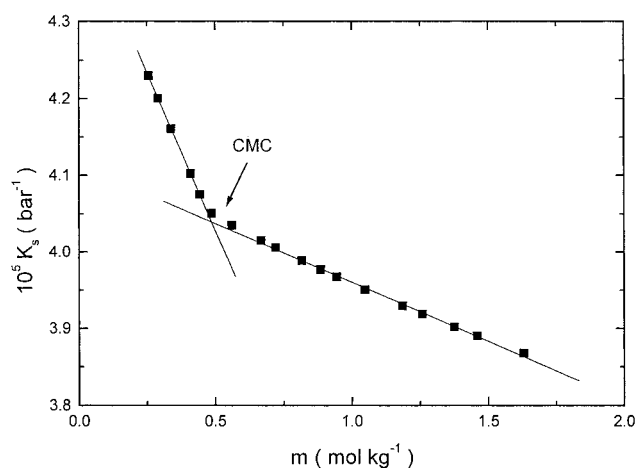
$$\log x_{\text{cmc}} = e_0 + e_1 n_c \quad (12)$$

where  $e_0 = -0.30 \pm 0.03 \text{ mol kg}^{-1}$  and  $e_1 = -0.294 \pm 0.003$





**Figure 8.** Logarithm of the molar fraction of the critical micelle concentrations (cmc) of sodium *n*-alkyl sulfates in water at 25 °C as a function of hydrocarbon chain length. (■) value from ultrasound velocity measurement, (○) values from ref 24.



**Figure 9.** Adiabatic compressibility,  $k_s$ , of SHS in water as a function of molality.

$\text{mol kg}^{-1}$ . The correlation coefficient of 0.9998 shows that there is very good agreement with the linear relationships between  $\log x_{\text{cmc}}$  and the number of carbon atoms of the alkyl chain, for the homologous series  $6 \leq n_c \leq 14$ .

The total adiabatic compressibility,  $k_s$ , of a liquid is given by

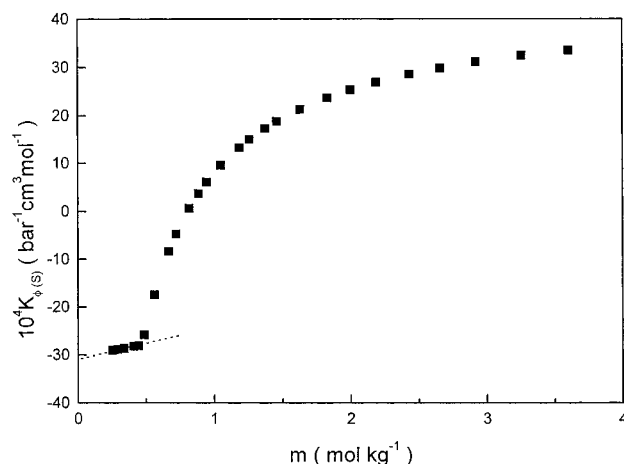
$$k_s = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S = \frac{1}{\rho u^2} \quad (13)$$

where  $V$ ,  $p$ , and  $S$  refer to volume, pressure, and entropy, respectively. Thus the adiabatic compressibility of a solution may be calculated by measurement of sample density,  $\rho$ , and the sound velocity,  $u$ , through the solution. A plot of  $k_s$  against concentration is shown in Figure 9.

The isentropic apparent molal compressibility,  $K_{\phi(S)}$ , can be calculated from ultrasound measurements:<sup>27</sup>

$$K_{\phi(S)} = \frac{1000(k_s - k_s^0)}{m\rho_0} + k_s V_\phi \quad (14)$$

$k_s$  and  $k_s^0$  are the isentropic coefficients of compressibility of the solution and solvent, respectively.  $K_{\phi(S)}$  can be calculated at each concentration by eq 14, giving a plot of



**Figure 10.** Isentropic apparent molal compressibility,  $K_\phi$ , of SHS in water as a function of molality.

**Table 3.** Apparent Molal Isentropic Compressibilities at Infinite Dilution,  $K_{\phi(S)}^\infty$ , of the Premicellar Region,  $K_{\phi(S)}^\infty$ , and of the Micelle,  $K_{\phi(S)}^m$ , and the Change in Partial Molal Compressibility in Micelle Formation,  $\Delta K_{\phi(S)}$ , for SHS and SDS

	$10^4 K_{\phi(S)}^\infty / \text{cm}^3 \text{bar}^{-1} \text{mol}^{-1}$	$10^4 K_{\phi(S)}^\infty / \text{cm}^3 \text{bar}^{-1} \text{mol}^{-1}$	$10^4 K_{\phi(S)}^m / \text{cm}^3 \text{bar}^{-1} \text{mol}^{-1}$	$10^4 \Delta K_{\phi(S)} / \text{cm}^3 \text{bar}^{-1} \text{mol}^{-1}$
SHS	-30	-27	35	62
SDS <sup>a</sup>	-66	-47	100	146

<sup>a</sup> Values from ref 2.

$K_{\phi(S)}$  vs concentration similar to the apparent molal volume plots (Figure 10).

As for the volumes, the change in partial molal isentropic compressibility of micellization,  $\Delta K_{\phi(S)}$ , can be evaluated by

$$\Delta K_{\phi(S)} = K_{\phi(S)}^m - K_{\phi(S)}^\infty \quad (15)$$

where  $K_{\phi(S)}^m$  is the apparent molal adiabatic compressibility of the micelle and  $K_{\phi(S)}^\infty$  the one of the disperse phase. Table 3 shows a comparison between the values obtained in this work for  $K_{\phi(S)}^m$ ,  $K_{\phi(S)}^\infty$ , and the values of sodium dodecyl sulfate (SDS)<sup>2</sup> as well as the apparent molal isentropic compressibility at infinite dilution,  $K_{\phi(S)}^\infty$ .

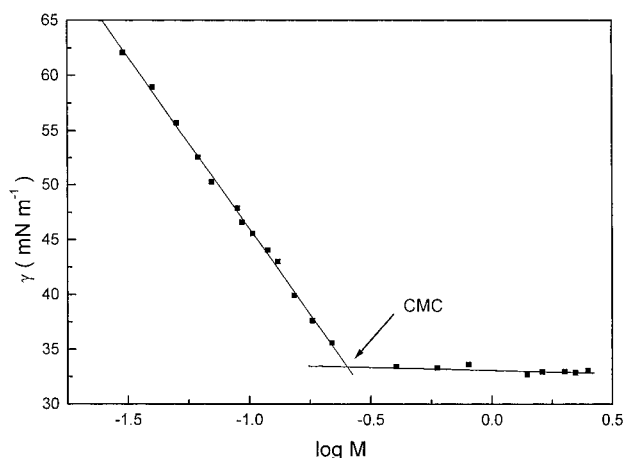
Previous studies of  $K_{\phi(S)}$  have shown that this quantity is large and negative for ionic compounds in water, positive for mainly hydrophobic solutes, and intermediate, small and negative, for uncharged hydrophilic solutes such as sugars.<sup>28,29</sup> It can be seen that at infinite dilution the isentropic partial molal compressibility,  $K_{\phi(S)}^\infty$ , of the single dispersed surfactant presented here confirms these ideas. The values are negative but higher than the ones for SDS and thus closer to the values of hydrophilic solutes. However, the  $K_{\phi(S)}^\infty$  values are positive, but smaller than the values of SDS that are large and positive, and such large and positive values have previously only been encountered for alcohols in a nonaqueous solvent, propylene carbonate.<sup>30</sup> In this case it was suggested that the absence of interaction forces other than van der Waals forces between solute and solvent resulted in such high compressibilities. It seems that the same explanation is valid in the case of micelles, and it seems to confirm the

(28) Høiland H.; Vikingstand E. *J. Chem. Soc., Faraday Trans. 1* **1976**, 72, 1441.

(29) Franks, F.; Ravenhill, J. R.; Reid, D. S. *J. Solution Chem.* **1972**, 1, 3.

(30) Høiland H. *J. Solution Chem.* **1977**, 6, 291.

(27) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold: New York, 1958.



**Figure 11.**  $\gamma$ - $\log c$  plot: points, experimental values; solid lines, regression lines for  $c > \text{cmc}$  and  $c < \text{cmc}$ , respectively.

idea that the interior of micelles resembles liquid hydrocarbons.<sup>31</sup> In our case, the value of SHS is nearly one-third of the value of SDS, confirming that the hydrocarbon chain must be more in contact with the solvent, so there is a large exposure of alkyl chains to the solvent and the interior of the aggregate, we think, is as far from the micellar state as SDS.

**Maximum Surface Excess Concentration and Minimum Surface Area per Molecule.** Typical plots of surface tension,  $\gamma$ , of aqueous solutions vs log molarity, bulk phase concentrations, are shown in Figure 11. The surface tension data were used to calculate maximum surface excess concentration,  $\Gamma$ , of the surfactant at the aqueous solution-air interface according to eq 16:<sup>32</sup>

$$\Gamma = -\frac{1}{4.61RT} \left( \frac{\partial \gamma}{\partial \log c} \right)_T \quad (16)$$

The slope of the linear portion of the curve of  $\gamma$  vs  $\log$ -(molarity) below the cmc was determined by the method of least mean squares with a correlation coefficient of

**Table 4. Maximum Surface Excess Concentration and Minimum Area Per Molecule**

	$10^6 \Gamma / \text{mol m}^{-2}$	$10^2 A^a / \text{nm}^2$
$n\text{-C}_6\text{H}_{13}\text{SO}_4^- \text{Na}^+$	2.7	60.5
$n\text{-C}_{10}\text{H}_{21}\text{SO}_4^- \text{Na}^+$	2.9 <sup>a</sup>	57 <sup>a</sup>
$n\text{-C}_{12}\text{H}_{25}\text{SO}_4^- \text{Na}^+$	3.1 <sup>a</sup>	53 <sup>a</sup>

<sup>a</sup> Values from ref 30.

0.9988. The minimum surface area per surfactant head-group at the aqueous solution-air interface,  $A$ ,  $\text{nm}^2/\text{molecule}$ , is then calculated from the equation<sup>32</sup>

$$A = \frac{10^{18}}{N_A \Gamma} \quad (17)$$

where  $N_A$  is Avogadro's number. Values of  $\Gamma$  and  $A$  calculated in this work are presented in Table 4. Comparing with the values of other alkyl sulfates,<sup>29</sup> we can see that  $\Gamma$  augments with increasing alkyl chain length and  $A$  decreases.

The value of the cmc calculated by surface tension was  $0.253 \text{ mol dm}^{-3}$  ( $0.263 \text{ mol kg}^{-1}$ ). This value is quite lower than the values calculated by other methods ( $0.559$  and  $0.471 \text{ mol kg}^{-1}$  for conductivity and ultrasound, respectively). For concentrations below but near the cmc, the slope of the curve  $\gamma$  vs  $\log m$  is essentially constant, indicating that the surface concentration has reached a constant maximum value.

### Summary

Our investigation has shown that SHS in aqueous solutions forms aggregates at a cmc which is predicted from the linear relationship between the cmc and the number of carbon atoms in the alkyl chain of other compounds in the homologous series of  $n$ -alkyl sulfates. We have shown that there is premicellar aggregation below the cmc. Measurements of the thermodynamic properties on micellization have led to the proposal of an organized micellar structure with large exposure of alkyl chains to the solvent.

**Acknowledgment.** We thank the Xunta de Galicia for financial support.

LA981759F

(31) Tanford, C. *The Hydrophobic Effect*, 1st ed.; Wiley: New York, 1973.

(32) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John Wiley: New York, 1978.