

## Thermodynamics of the Hydrophobic Effect

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A thermodynamic theory is developed describing the transfer process of nonpolar substances from water to their pure state and the micellization process. The basis of the theory is the consideration, experimentally supported, that to a first-order approximation the change in the standard molar entropy ( $\Delta S^\circ$ ) can be considered proportional to the standard molar heat capacity ( $\Delta C_p^\circ$ ) with proportionality constant,  $r$ , independent of the temperature and the pressure. In general it is found that the value of the magnitude of  $r$  decreases with the size of the solute molecule until a limiting value. This level of approximation is sufficient to predict observations such as linear plots between  $T\Delta S^\circ$  and  $\Delta H^\circ$ , reduced behavior for surfactants with the temperature, and an important part of accepted phenomenology in the literature about the hydrophobic effect.

### 1. Introduction

Hydrophobic effect and hydrophobic interaction have been subjects of intense research in the second half of the twentieth century. This field of research is interesting for the physics of intermolecular interactions<sup>1,2</sup> because its theoretical basis<sup>3–5</sup> is not yet stabilized compared with other interactions (London dispersion, van der Waals interaction, ion–ion, ion–dipole, dipole–dipole...) and because hydrophobic properties are important to association phenomena in the aqueous environment, such as the formation of micelles, protein folding, and molecular recognition.<sup>6</sup>

“Hydrophobic substances are defined as substances that are readily soluble in many nonpolar solvents, but only sparingly soluble in water, distinct from substances that have generally solubility in all solvents because they form solids with strong intermolecular cohesion”.<sup>7</sup> From a macroscopic point of view, this effect is defined by the phenomenology of solution of nonpolar compounds in water. At room temperature, the dissolution process is slightly favored by enthalpy, but strongly opposed by a large, negative change in entropy<sup>8,9</sup> and large positive heat capacities of solution. This peculiar balance between enthalpy and entropy leads to an extraordinary temperature dependence of the thermodynamic behavior, such as solubility minima and lower critical solution temperatures.<sup>10</sup>

The microscopic description commonly accepted is in terms of a distortion of the local tetrahedral structure<sup>11</sup> of water around the nonpolar solutes. In the environment surrounding the substance, the hydrogen bonds between the water molecules are energetically disfavored, adopting a different organization.<sup>12</sup> These structures are usually named<sup>13</sup> “iceberg structures”, “flickering clusters”, or “clathration shells” (polyhedral cages similar to those found in crystalline hydrates formed by some small nonpolar molecules) and they are characterized by a diminution of the entropy around the substances. The hydro-

phobic interaction is caused by the withdrawal of hydrophobic substances from the aqueous solution.<sup>2</sup>

In 1967, Arnett et al.<sup>14</sup> suggested a linear correlation between the variation of the standard molar entropy of solution ( $\Delta S^\circ$ ) and the change in standard molar heat capacity of solution ( $\Delta C_p^\circ$ ) at 298.1 K for a set of alcohols. Another linear correlation was suggested by Kresheck in 1975 from a plot of the standard molar enthalpy ( $\Delta H^\circ$ ) versus the standard molar entropic contribution ( $T\Delta S^\circ$ ) for a set of ionic and nonionic surfactants in several media. Sturtevant,<sup>16</sup> in a work on the different origins of the large heat capacity and entropy changes observed for processes involving proteins, calculated the ratio  $\Delta S^\circ/\Delta C_p^\circ$  at 298.1 K for a set of hydrocarbons. He obtained a mean value of  $-0.263 \pm 0.046$ , and suggested that this value is constant for all hydrocarbons. On the other hand, from cmc<sub>0</sub> (the minimal critical micelle concentration and  $T_0$  (the temperature at the minimum), La Mesa<sup>17</sup> found that plotting  $(\text{cmc} - \text{cmc}_0)/\text{cmc}_0$  against  $|(T - T_0)/T_0|$  for an assortment of surfactants gave points falling close to a single curve represented by the empirical equation

$$\frac{\text{cmc}}{\text{cmc}_0} - 1 = \left| \frac{T}{T_0} - 1 \right|^\gamma \quad (1)$$

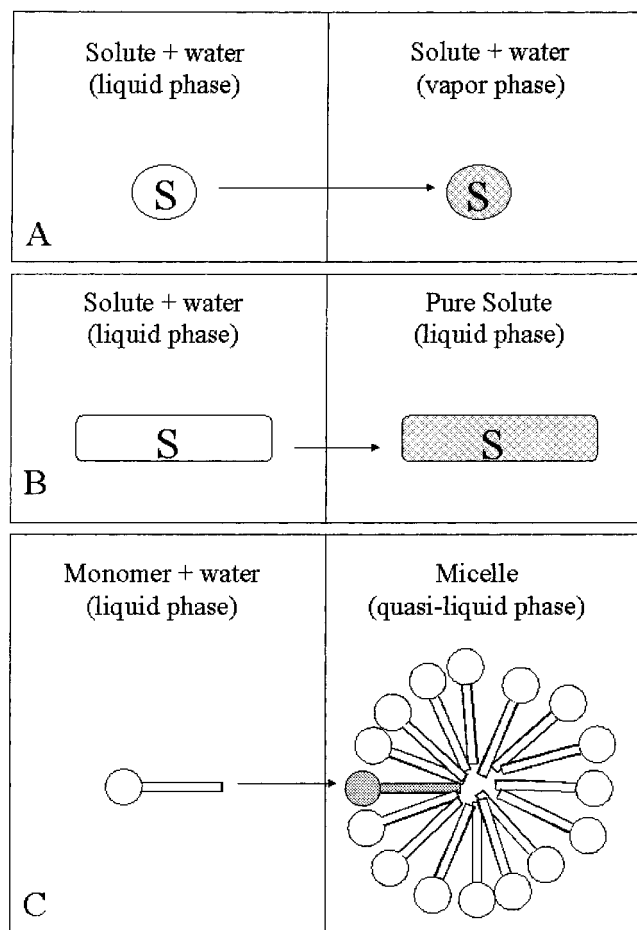
with  $\gamma = 1.74 \pm 0.03$ . The exponent has no obvious physical meaning, and it is not clear why this relation works as well as it does or what is the main source of the deviations of data points from the curve. Three years later, Muller<sup>18</sup> used this observation to develop a method of calculation in which the variation of heat capacity is considered a constant, and obtained a mean value of  $-0.247 \pm 0.037$  for the ratio  $\Delta S^\circ/\Delta C_p^\circ$  at 298.1 K for a set of surfactants.

In this paper, the link between these observations is found. The interest in establishing a relation between them is that it is possible to develop formally a macroscopic theory for the process of transfer of nonpolar solutes and micelle formation. The present point of view is encouraging because one can formally arrive at an important part of the commonly accepted phenomenology of nonpolar aqueous solution and micelle

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**Figure 1.** (A) Transfer process of molecule of nonpolar solute in aqueous solution to the mixture with its pure compound in the vapor phase and water vapor. (B) Transfer process of molecule of condensed nonpolar solute in water dissolution to its pure compound. (C) Transfer process of surfactant molecule from water dissolution to micelle.

formation. But it is intriguing in the sense that the understanding depends on an expression as simple as:  $\Delta S^\circ = r\Delta C_p^\circ$ .

As we will see later, there are other routes, but we have preferred to start the exposition from the experimental fact.

## 2. Theory

The three processes that are shown in Figure 1 will be studied. The first (Figure 1A) is the transfer process of a nonpolar molecule of solute to the vapor phase from the aqueous solution. If the size of the nonpolar solute molecule is increased enough, it stays in the liquid state at room temperatures and pressures. In this case (Figure 1B), the transfer process is from the aqueous solution to pure solute in the liquid phase. The monomers of surfactant molecules have one part of the molecule (circle in Figure 1C) that is hydrophilic and another part that is hydrophobic (rectangle in Figure 1C). These substances form micellar aggregates in aqueous solution above a cmc. The architecture of this aggregate is shown in Figure 1C. The hydrophobic parts of the monomer are normally hydrocarbon chains fitted within the aggregate, forming the so-called hydrocarbon core. The hydrophilic parts are in contact with the water molecules, forming the micelle surface. Some authors<sup>7</sup> think that the hydrocarbon core of micelles is in a quasi-liquid state. The difference between this quasi-liquid state and the liquid bulk state is that the hydrocarbon chains in the micelle are fixed and approximately perpendicular to the headgroup in the micelle surface. In the bulk liquid state, the two extremes of the

hydrophobic chain could move freely. In this work, the micellization process will be studied like a transfer process of surfactant monomer from the aqueous solution into the micelle.

We will assume the following notation for simplicity: in the case of nonpolar solutes  $\Delta G^\circ$  and  $\Delta H^\circ$  will represent the variation in the standard thermodynamic parameters of transfer from water, and in the case of amphiphiles, they will represent the variation in the thermodynamic parameters of micelle formation. Then, Taylor's expansion of  $\Delta G^\circ = \Delta G^\circ(\Delta H^\circ)$  around  $\Delta H^\circ = 0$  is as follows:

$$\Delta G^\circ(\Delta H^\circ) = \Delta G^\circ(0) + \left(\frac{\partial \Delta G^\circ(0)}{\partial \Delta H^\circ}\right)_P \Delta H^\circ + \left(\frac{\partial^2 \Delta G^\circ(0)}{\partial \Delta H^{\circ 2}}\right)_P \Delta H^{\circ 2} + \dots \quad (2)$$

Neglecting the term of second order and because:

$$\left(\frac{\partial \Delta G^\circ}{\partial \Delta H^\circ}\right)_P = \left(\frac{\partial \Delta G^\circ}{\partial T}\right)_P \left(\frac{\partial T}{\partial \Delta H^\circ}\right)_P = -\frac{\Delta S^\circ}{\Delta C_p^\circ} \quad (3)$$

one gets the relation:

$$\Delta G^\circ = -r\Delta H^\circ + \Delta G_0^\circ \quad (4)$$

where  $\Delta G_0^\circ \equiv \Delta G^\circ(\Delta H^\circ = 0)$  and  $r$  is a constant defined by:

$$\Delta S^\circ = r\Delta C_p^\circ \quad (5)$$

The first-order Taylor's expansion of  $T\Delta S^\circ$  as a function of  $\Delta H^\circ$  around  $\Delta H^\circ = 0$  is:

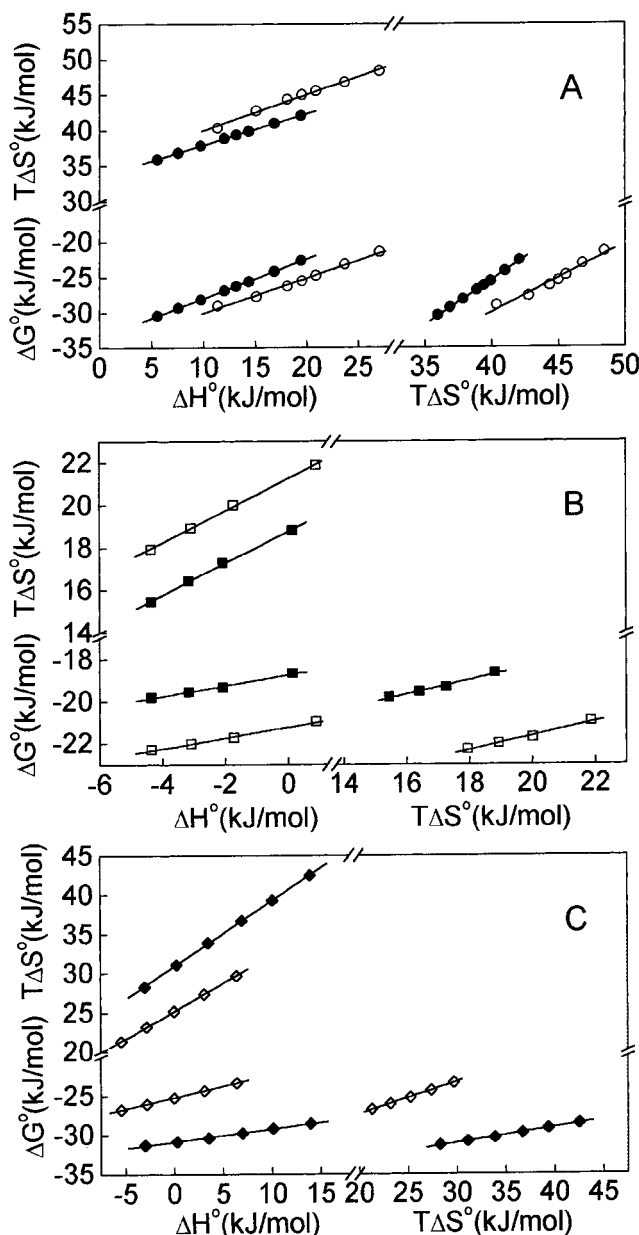
$$T\Delta S^\circ = (1+r)\Delta H^\circ + T_0\Delta S_0^\circ = (1+r)\Delta H^\circ - \Delta G_0^\circ \quad (6)$$

where  $T_0$  is the temperature at which  $\Delta H^\circ = 0$ ,  $\Delta S_0^\circ = \Delta S^\circ(T_0)$  and then  $\Delta G_0^\circ = -T_0\Delta S_0^\circ$ . Similarly for  $\Delta G^\circ = \Delta G^\circ(T\Delta S^\circ)$  around  $T\Delta S^\circ = 0$  is:

$$\Delta G^\circ = -\frac{r}{1+r}T\Delta S^\circ + \Delta G_0^\circ \quad (7)$$

where  $\Delta G_0^\circ \equiv \Delta G^\circ(T\Delta S^\circ = 0)$ .

Plots of  $\Delta G^\circ$  as a function of  $\Delta H^\circ$ ,  $\Delta G^\circ$  as a function of  $T\Delta S^\circ$ , and  $T\Delta S^\circ$  as a function of  $\Delta H^\circ$  for two gases, two condensed nonpolar solutes, one nonpolar surfactant, and one cationic surfactant are shown in Figure 2. The values of solution for methane and ethane were calculated by Rettich<sup>19</sup> et al. using a high-precision apparatus of the Benson–Krause type and the van't Hoff method. The data of  $\Delta H^\circ$  for benzene and toluene were measured by Gill et al.<sup>20</sup> and the data of  $\Delta G^\circ$  were calculated from solubility data measured by Bohon and Clausen.<sup>40</sup> The values of  $\Delta H^\circ$  for a dodecyldimethylphosphine oxide were measured by Kresheck<sup>21</sup> and the values of  $\Delta G^\circ$  were calculated from the values of cmc reported in this work. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the nonyltrimethylammonium bromide were calculated from the data of  $\Delta C_p^\circ$  measured by Musbally et al.<sup>36</sup> and using the constant of integration reported in this work. In Table 1 the results of the linear fits of Figure 2 are shown. The value of  $r$  is independent of the equation used. This result implies that the ratio between  $\Delta C_p^\circ$  and  $\Delta S^\circ$  can be considered a constant independent of temperature but dependent on the substance. On the other hand, the value of  $\Delta G_0^\circ$  calculated with eqs 4 and 6 are very similar, confirming the idea that these plots can be interpreted by a Taylor's expansion to a first order of approximation.



**Figure 2.** Linear correlations from eq 2 ( $\Delta G^\circ$  versus  $\Delta H^\circ$ ), eq 3 ( $\Delta G^\circ$  versus  $T\Delta S^\circ$ ), and eq 4 ( $T\Delta S^\circ$  versus  $\Delta H^\circ$ ). In Figure 2A, the experimental data were taken from ref 18 (methane  $\bullet$ , ethane  $\circ$ ). In Figure 2B, the experimental data of  $\Delta H^\circ$  were taken from ref 19 and the values of  $\Delta G^\circ$  and  $\Delta S^\circ$  were calculated from ref 38 (benzene  $\blacksquare$ , toluene  $\square$ ). In Figure 2C, the experimental data of  $\Delta H^\circ$  for dodecylmethylphosphine oxide ( $\blacklozenge$ ) were taken from ref 20 and the values of  $\Delta G^\circ$  and  $\Delta S^\circ$  were calculated from data of this reference. For nonyltrimethylammonium bromide ( $\diamond$ ) the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated, respectively, from the eqs 8 and 11 using a linear fit for data ( $\Delta C_p^\circ$ ) reported in the ref 36 (the values of  $T_0$ ,  $\ln x_0$ ,  $\Delta C_{p0}^\circ$  were taken from the same reference).

The expression for  $\Delta C_p^\circ$  as a function of temperature is now obtained by substitution of eq 5 into the Maxwell's equation:

$$\left(\frac{\partial \Delta S^\circ}{\partial T}\right)_P = \frac{\Delta C_p^\circ}{T} \quad (8)$$

and by integration with the initial condition  $\Delta C_p^\circ(T = T_0) = \Delta C_{p0}^\circ$ :

$$\Delta C_p^\circ(\theta) = \Delta C_{p0}^\circ \theta^{1/r} \quad (9)$$

where  $\theta = T/T_0$  is a reduced temperature. The expression of  $\Delta S^\circ$  as a function of  $\theta$  is given by eqs 5 and 9, and the identity  $\Delta S_0^\circ = r\Delta C_{p0}^\circ$ :

$$\Delta S^\circ(\theta) = r\Delta C_{p0}^\circ \theta^{1/r} = \Delta S_0^\circ \theta^{1/r} \quad (10)$$

Integrating the expression:

$$\left(\frac{\partial \Delta H^\circ}{\partial \theta}\right)_P = T_0 \Delta C_p^\circ \quad (11)$$

with initial condition  $\Delta H^\circ(\theta = 1) = 0$ :

$$\Delta H^\circ(\theta) = \frac{r}{1+r} T_0 \Delta C_{p0}^\circ (\theta^{1/r+1} - 1) \quad (12)$$

The expression of  $\Delta G^\circ$  as a function of the temperature is:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -\frac{r}{1+r} T_0 \Delta C_{p0}^\circ (r\theta^{1/r+1} + 1) \quad (13)$$

Apparently,  $r$  cannot take the value  $-1$ , but applying the L'Hopital rule, one can see that there is no problem for  $r$  tending to  $-1$  in the eqs 12 and 13.

**2.1. Nonpolar Solutes.** Supposing ideal behavior, the chemical potentials of a component,  $s$ , in mixtures with a medium  $\alpha$  and with a medium  $\beta$  are given by:

$$\mu_s^\alpha = \mu_s^{\alpha 0} + RT \ln x_s^\alpha \quad (14)$$

$$\mu_s^\beta = \mu_s^{\beta 0} + RT \ln x_s^\beta \quad (15)$$

where  $\mu_s^\alpha$  and  $\mu_s^\beta$  are the chemical potential of the component  $s$  in the mediums  $\alpha$  and  $\beta$ ;  $\mu_s^{\alpha 0}$  and  $\mu_s^{\beta 0}$  are the standard chemical potential of the component  $s$  in the mediums  $\alpha$  and  $\beta$ ; and  $x_s^\alpha$  and  $x_s^\beta$  are the concentration in mole fraction units of solute  $s$  in a medium  $\alpha$  and  $\beta$ , respectively.

In the thermodynamic equilibrium at constant pressure and at constant temperature between this mixtures:  $\mu_s^\alpha = \mu_s^\beta$ . The variation in standard Gibbs free energy of transferring 1 mol of solute  $s$  from the medium  $\alpha$  into the medium  $\beta$  is calculated from the Nernst distribution law:<sup>22-24</sup>

$$\Delta G^\circ \equiv \mu_s^{\beta 0} - \mu_s^{\alpha 0} = RT \ln x \quad (16)$$

where  $x$  is the coefficient of Nernst defined by:

$$x = \frac{x_s^\alpha}{x_s^\beta} \quad (17)$$

When the transfer process of nonpolar solutes from aqueous solution to a vapor phase is considered, eq 17 will be used because the vapor solute is in a mixture with the water vapor. For bigger solute molecules, the transfer process is to a medium formed by pure solute<sup>7,25</sup> in liquid state ( $x_s^\beta = 1$ ) and then:

$$x = x_s^\alpha \quad (18)$$

Equating eqs 13 and 16, the expression for  $\ln(x)$  as a function of reduced temperature is given by:

$$\ln x(\theta) = -\frac{r}{1+r} \frac{\Delta C_{p0}^\circ}{R} \left( r\theta^{1/r} + \frac{1}{\theta} \right) \quad (19)$$

**TABLE 1: Results of Linear Fits ( $y = a + bx$ ), Correlation Coefficient, and Constant  $r$  for the Transfer Process of Some Nonpolar Solutes in Vapor Phase Using Equations 4, 6, and 7<sup>a</sup>**

equation	$a$	$b$	correlation coefficient	$r$	reference	number of points
nitrogen						
4	$-34.601 \pm 0.053$	$0.6103 \pm 0.0047$	0.9997	$-0.6103 \pm 0.0047$	38/50	11
6	$34.601 \pm 0.053$	$0.3897 \pm 0.0047$	0.9993	$-0.6103 \pm 0.0047$	38/50	11
7	$-88.7 \pm 1.2$	$1.563 \pm 0.031$	0.998	$-0.6098 \pm 0.0047$	38/50	11
				$r = -0.6101 \pm 0.0047$		
methane						
4	$-33.529 \pm 0.041$	$0.5571 \pm 0.0031$	0.9999	$-0.5571 \pm 0.0031$	19	8
6	$33.531 \pm 0.0043$	$0.4425 \pm 0.0032$	0.9998	$-0.5575 \pm 0.0032$	19	8
7	$-75.7 \pm 0.6$	$1.258 \pm 0.016$	0.9995	$-0.5571 \pm 0.0031$	19	8
				$r = -0.5572 \pm 0.0032$		
ethane						
4	$-34.95 \pm 0.39$	$0.494 \pm 0.019$	0.996	$-0.494 \pm 0.019$	19	7
6	$34.98 \pm 0.40$	$0.505 \pm 0.020$	0.996	$-0.495 \pm 0.020$	19	7
7	$-68.5 \pm 3.4$	$0.963 \pm 0.076$	0.98	$-0.491 \pm 0.020$	19	7
				$r = -0.493 \pm 0.020$		

<sup>a</sup> The experimental data were taken from the bibliography.

In this case also there is no problem with  $r = -1$ . Differentiating eq 19 once with respect to  $\theta$ , it is easy to show that  $\ln x(\theta)$  reaches an absolute extreme at  $\ln x_0$  when,

$$\ln x_0 \equiv \ln x(\theta = 1) = -r \frac{\Delta C_{p0}^\circ}{R} = -\frac{\Delta S_0^\circ}{R} \quad (20)$$

Differentiating equation 19 twice:

$$\left( \frac{d^2 \ln x(\theta)}{d\theta^2} \right)_{\theta=1} = -\frac{\Delta C_{p0}^\circ}{R} \quad (21)$$

Until now we did not know the sign of  $\Delta C_p^\circ$ . If it is positive (negative)  $\ln x(\theta)$  goes through a maximum (minimum) when  $\theta = 1$ .

**2.2. Micelle Formation.** “The concept of a “critical concentration” for the formation of micelles from free amphiphile is inexact but convenient”.<sup>7</sup> In fact, one must consider a cmc as a concentration range or transition zone that separates two regions of concentrations. Below this region the monomer is free in solution and above this region an amount of monomer stays free in solution and the remainder forms micellar aggregates. If micelle formation was a separation in a distinct phase, the free monomer and the micelles would coexist only at one concentration of surfactant. The change in a physicochemical property  $\phi$  as a function of surfactant concentration is used to determine this interval. It is customary to define a single concentration within this transition region as a cmc, which is normally determined by graphical methods. This value depends on the experimental technique used because the response of different physicochemical properties as a function of surfactant concentration is not the same. However, as long as measurements are derived from data reasonably close to this transition zone, the ambiguity in the cmc generally does not exceed 1 or 2%.<sup>26</sup> From the theoretical point of view, the situation is not very different: each author defines the cmc depending on the mathematical convenience of defining the transition region. For example, in the electrostatic cell model,<sup>27</sup> the cmc is defined as the total surfactant concentration in which the monomer forming micelles is 3% of the total surfactant concentration. In the pseudo-separation model,<sup>28</sup> the cmc is defined as a saturation concentration for single solute particles. Phillips,<sup>29</sup> in his estimation of  $\Delta G^\circ$  for micelle formation, defines the cmc as the total surfactant concentration,  $x_t$ , that gives a maximum in

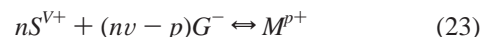
the curvature of  $\phi$  as a function of total surfactant concentration:

$$\left( \frac{d^3 \phi}{dx_t^3} \right)_{x_t = \text{cmc}} = 0 \quad (22)$$

It is interesting to observe that in a strict mathematical sense, the cmc in eq 22 is defined like an extremum in the curvature of  $\phi$  as function of the total concentration. Then it is possible to determine experimentally the cmc like a maximum or inflection point in the curvature depending on the physicochemical property chosen. For example, using the surface tension, the cmc appears as a maximum in the curvature and using titration calorimetry, it appears as an inflection point.<sup>21</sup>

An analogous derivation to Phillips's will be applied in this work, with the modification that the valence  $v$  of surfactant monomer will be considered; for monovalent monomer,  $v$  is equal to 1, and for nonionic surfactant,  $v$  and net charge of its micelles are equal to zero.

The mass action model is based on the supposition that the micelle is a species in thermodynamic equilibrium with its monomers, without loss of generality:



where  $G^-$ ,  $S^{v+}$ ,  $M^{p+}$  represent the counterion, surfactant monomer, and micelles of aggregation number  $n$  and net charge  $p$ . The micellization constant with the supposition of ideal behavior is written as:

$$K_m = \frac{x_m}{x_g^{nv-p} x_s^n} \quad (24)$$

where  $x_m$ ,  $x_s$ , and  $x_g$  are the concentration in mole fraction units of micelles, surfactant monomers, and counterion, respectively.

The change in standard Gibbs free energy of formation of whole micelles is given by:

$$\Delta \hat{G}^\circ = -RT \ln K_m \quad (25)$$

But we are not interested in this quantity. More useful is the Gibbs free energy of transfer of the monomer into the micelle per mole of surfactant ( $\Delta G^\circ$ ). Keeping in mind that this is not completely true because micelle formation is a cooperative



process, one can approach  $\Delta G^\circ$  from:

$$\Delta G^\circ = \frac{\Delta \hat{G}^\circ}{n} = -\frac{RT}{n} \ln K_m \quad (26)$$

To calculate  $K_m$ , the mass balances for total surfactant concentration ( $x_t$ ) and counterions ( $x_g$ ), respectively, are expressed as

$$x_t = x_s + nx_m \quad (27)$$

$$x_g = vx_s + px_m \quad (28)$$

and one can assume that  $\phi$  depends on concentration approximately as follows:

$$\phi = ax_s + bx_m \quad (29)$$

where  $a$  and  $b$  are proportionality constants. Simultaneously solving eqs 22, 26, 27, 28, and 29 with the assumption<sup>29,30</sup> that  $px_m \ll vx_s$  when the total surfactant concentration is equal to the cmc, the following equilibrium constant  $K_m$  can be obtained:

$$\frac{1}{K_m} = nv^{\frac{n(v+1)-p}{n(v+1)-p-2}} \times \left\{ \frac{[n(v+1)-p][2n(v+1)-2p-1]}{[n(v+1)-p-1][2n(v+1)-2p+2]} x \right\}^{n(v+1)-p-1} \quad (30)$$

In this case,  $x$  represents the total concentration of surfactant at the cmc. To apply this equation, the degree of ionization of the micelles ( $\alpha = p/vn$ ) must be calculated by some experimental method.<sup>30–32</sup>

Some authors suggest that eqs 26 and 30 must be used to calculate  $\Delta G^\circ$  when the aggregation number is low.<sup>30,33,34</sup> If the aggregation number is larger ( $>20$  or  $25$ ), eq 26 tends to a limiting value (which depends on temperature, pressure, and the substance), and then it is possible to use the “high aggregation number approximation”:<sup>29,33</sup>

$$n \gg p \Rightarrow n(v+1) \gg p \quad (31)$$

Equation 30 goes to

$$-\frac{\ln K_m}{n} = \left(v - \frac{p}{n}\right) \ln v + \frac{\ln 2 + 2 \ln n}{n} + \frac{\ln(v+1)}{n} + \left((v+1) - \frac{p}{n} - \frac{1}{n}\right) \ln x \quad (32)$$

Neglecting the second, third, and factor  $1/n$  of the fourth term,

$$\Delta G^\circ = (1 + v\beta)RT \ln x + v\beta RT \ln v \quad (33)$$

where  $\beta$  is the degree of counterion binding to the micelles ( $\beta = 1 - \alpha$ ). Because for  $v = 1$ ,  $\ln v$  is equal to 0 and

$$\lim_{v \rightarrow 0} v\beta RT \ln v = 0 \quad (34)$$

equation 33<sup>33</sup> is consistent with the expression obtained by Phillips<sup>29</sup> and other authors<sup>35</sup> for monovalent surfactants and for nonionics surfactants.

It is interesting to observe in eq 33 that:

$$\Delta G^\circ \leq 0 \Rightarrow x \leq e^{-(v\beta/(1+v\beta)) \ln v} \quad (35)$$

which, for valences  $\geq 2$ , results in a thermodynamic restriction in cmc values.<sup>33</sup>

For simplicity we will study the cases where  $v = 0$  and  $v = 1$ :

$$\Delta G^\circ = (1 + v\beta)RT \ln x \quad (36)$$

Equating eqs 13 and 36, the expression for  $(1 + v\beta) \ln(x)$  as a function of reduced temperature is given by:

$$(1 + v\beta) \ln x(\theta) = -\frac{r}{1+r} \frac{\Delta C_{p0}^\circ}{R} \left( r\theta^{1/r} + \frac{1}{\theta} \right) \quad (37)$$

A small and systematic shift between the experimental value of  $\ln x(T)$  obtaining by experiment and the value calculated by eq 37 is expected. For nonpolar solutes,  $\ln x(T)$  corresponds to a well-defined concentration. But as shown later, the cmc of surfactants depends on given criteria and, on the other hand, the value of  $\beta$  is dependent on the experimental method employed. Also, if eq 37 is employed as a fitting function, the fitting parameter  $\Delta C_{p0}^\circ$  will be dependent on the experimental method used to measure  $\beta$  and  $\ln x(T)$ .

Differentiating the function  $(1 + \beta)\ln(x)$  in eq 37 with respect to  $\theta$  one time, it is easy to show that  $(1 + \beta)\ln x(\theta)$  reaches an absolute extreme at  $(1 + \beta_0)\ln x_0$  when,

$$(1 + v\beta_0) \ln x_0 \equiv (1 + v\beta(1)) \ln x(1) = -r \frac{\Delta C_{p0}^\circ}{R} = -\frac{\Delta S_0^\circ}{R} \quad (38)$$

Differentiating eq 37 twice:

$$\left( \frac{d^2}{d\theta^2} ((1 + \beta) \ln x(\theta)) \right)_{\theta=1} = -r \frac{\Delta C_{p0}^\circ}{R} \quad (39)$$

In the case just presented, we have the same problem as in eq 21 because we do not know the sign of  $\Delta C_{p0}^\circ$ .

It is interesting to keep in mind that for nonionic surfactants ( $v = 0$ ), the function  $\ln x(\theta)$  reaches the extreme  $\ln x_0$  when  $\theta = 1$ . But, differentiating the function  $\ln x(\theta)$  in eq 36 for ionic surfactants ( $v = 1$ ) and regarding the variation of  $\beta$  with the temperature, the extreme is  $\ln x^*$  when the temperature is  $\theta = \theta^*$  ( $T^* = \theta^* T_0$ ).

**2.3. Thermodynamic Regions.** From eqs 20 and 38 and because  $\ln x_0$  is less than zero,  $\Delta S_0^\circ$  must be positive. Experimentally, it is found that the curves of solubility of the nonpolar solutes and cmc of the surfactants as a function of the temperature have a minimum and, from eqs 20 and 38,  $\Delta C_{p0}^\circ$  must be negative. This result combined with eq 5 indicates that  $r$  is negative. It is interesting to observe that if we introduce the hypothesis that  $r < 0$  into the theory, the condition of minima in the curves of solubility and cmc and a negative sign for  $\Delta C_{p0}^\circ$  is obtained.

Because  $r$  is negative, the function  $f(\theta) = \theta^{1/r}$  is a decreasing positive function. By eq 9,  $\Delta C_p^\circ$  is an increasing negative function with the temperature (its magnitude decreases with the temperature). This is in agreement with the experimental results.<sup>21,36,37</sup> From eq 10,  $\Delta S^\circ$  is shown to be a decreasing positive function with the temperature.

By eq 11 and keeping in mind that  $\Delta C_p^\circ < 0$ ,  $\Delta H^\circ$  is a decreasing function with the temperature. Then, because  $\Delta H^\circ(\theta = 1) = 0$ ,  $\Delta H^\circ$  is positive for  $\theta < 1$  and negative for  $\theta > 1$ . On the other hand, from eq 40 and because  $\Delta S^\circ$  is positive,  $\Delta G^\circ$  is a decreasing function with the temperature and its magnitude is an increasing function with the temperature.

$$\left( \frac{\partial \Delta G^\circ}{\partial \theta} \right)_P = -T_0 \Delta S^\circ \quad (40)$$

It is possible to calculate the region of temperature in which  $\Delta G^\circ$  is less than zero using eq 13 and the condition  $\Delta G^\circ < 0$ . In the interval of temperatures  $0 < \theta \leq \theta_1$ , where

$$\theta_1 = \left(\frac{-1}{r}\right)^{r/1+r} \quad (41)$$

$\Delta G^\circ$  is positive and the studied process cannot occur (thermodynamically inaccessible region). At the reduced temperature  $\theta_1$ ,  $\Delta G^\circ(\theta_1) = 0$  and  $T\Delta S^\circ = \Delta H^\circ = -T_0\Delta C_{p0}^\circ$ . If  $r$  is positive, the temperature  $\theta_1$  would not exist and then  $\Delta G^\circ$  would be negative for all temperatures.

It is interesting to study the interval of temperatures in which  $T\Delta S^\circ$  is the main contribution to  $\Delta G^\circ$ . Using eqs 10 and 12, if  $|\Delta H^\circ| < T\Delta S^\circ$  ( $-T\Delta S^\circ \leq \Delta H^\circ \leq T\Delta S^\circ$ ) and noting that  $f(\theta) = \theta^{1/r+1}$  is an increasing function if  $r < -1$  and a decreasing function if  $r > -1$ , one arrives at the interval  $\theta_1 < \theta < \theta_2$  (entropic driven region) where

$$\theta_2 = \left(\frac{1}{2+r}\right)^{r/1+r} \quad (42)$$

At the reduced temperature  $\theta_2$ ,  $\Delta H^\circ = -T\Delta S^\circ = -r/(1+r)T_0\Delta C_{p0}^\circ$ , and  $\Delta G^\circ = -2r/(1+r)T_0\Delta C_{p0}^\circ$ . For  $\theta_2 < \theta$  (enthalpic driven region), the enthalpy is the main contribution to  $\Delta G^\circ$ .

Because eqs 41 and 42 must be simultaneously satisfied for the value of  $r$  of a given substance, one can find the bounds of  $r$  ( $-2 < r < 0$ ) from the study of mathematical domain of the functions  $\theta_1(r)$  and  $\theta_2(r)$ .

#### 2.4. Linear Relations between $\Delta G^\circ$ , $\Delta H^\circ$ , $T\Delta S^\circ$ , and $\Delta V^\circ$ .

If the assumption that  $r$  is independent of pressure is considered in eq 5,

$$\left(\frac{\partial \Delta S^\circ}{\partial P}\right)_T = r \left(\frac{\partial \Delta C_p^\circ}{\partial P}\right)_T \quad (43)$$

and keeping in mind the relation

$$\left(\frac{\partial \Delta S^\circ}{\partial P}\right)_T = -\left(\frac{\partial \Delta V^\circ}{\partial T}\right)_P \quad (44)$$

where

$$\left(\frac{\partial \Delta V^\circ}{\partial T}\right)_P = \Delta V^\circ \Delta \alpha^\circ \quad (45)$$

and where  $\Delta V^\circ$  and  $\Delta \alpha^\circ$  are the changes in the standard molar volume and the standard molar expansion coefficient, respectively, and the relation

$$\left(\frac{\partial \Delta C_p^\circ}{\partial P}\right)_T = \frac{\partial}{\partial T} \left\{ \left(\frac{\partial \Delta H^\circ}{\partial P}\right)_T \right\}_P = \frac{\partial}{\partial T} \{ \Delta V^\circ (1 - T\Delta \alpha^\circ) \}_P \quad (46)$$

one arrives at the following equation of Bernoulli:

$$\left(\frac{\partial \Delta \alpha^\circ}{\partial T}\right)_P - \frac{1}{rT} \Delta \alpha^\circ = -(\Delta \alpha^\circ)^2 \quad (47)$$

Solving this differential equation with the initial condition  $\Delta \alpha^\circ(T_0) \equiv \Delta \alpha_0^\circ$ :

$$\frac{1}{\Delta \alpha^\circ(T)} = \frac{r}{1+r}T + \left(\frac{1}{\Delta \alpha_0^\circ} - \frac{r}{1+r}T_0\right)\left(\frac{T}{T_0}\right)^{-1/r} \quad (48)$$

Inserting eq 48 in eq 45 and by integration with the initial condition  $\Delta V^\circ(T_0) \equiv \Delta V_0^\circ$ :

$$\frac{\Delta V^\circ(\theta)}{\Delta V_0^\circ} = 1 + \frac{r}{1+r}T_0\Delta \alpha_0^\circ(\theta^{1/r+1} - 1) \quad (49)$$

Using eq 49 and the relations in eqs 10, 12, and 13, one arrives at the following interesting results:

$$T\Delta S^\circ(\Delta V^\circ) = (1+r)\frac{\Delta C_{p0}^\circ}{\Delta \alpha_0^\circ}\left(\frac{\Delta V^\circ}{\Delta V_0^\circ} - 1\right) + T_0\Delta S_0^\circ \quad (50)$$

$$\Delta H^\circ(\Delta V^\circ) = \frac{\Delta C_{p0}^\circ}{\Delta \alpha_0^\circ}\left(\frac{\Delta V^\circ}{\Delta V_0^\circ} - 1\right) \quad (51)$$

$$\Delta G^\circ(\Delta V^\circ) = -r\frac{\Delta C_{p0}^\circ}{\Delta \alpha_0^\circ}\left(\frac{\Delta V^\circ}{\Delta V_0^\circ} - 1\right) - T_0\Delta S_0^\circ \quad (52)$$

### 3. Results and Discussion

The study of the parameter  $r$  was made by linear plots (Figure 2) and by plots of the solubility or cmc as a function of the temperature. The experimental data of solubility in water ( $q$ ) as a function of the temperature of diatomic gases ( $H_2$ ,  $N_2$ ,  $O_2$ ), and saturated hydrocarbon gases in water solution (methane and ethane) was taken from the bibliography,<sup>38</sup> where  $q$  is defined as the weight of gas in grams dissolved in 100 g of water when the pressure of gas plus that of the water is one atmosphere. The mole fraction of solute dissolved in water at temperature  $T$  was calculated by:

$$x_s^w = \frac{1}{1 + \frac{M_s}{M_w} \times \frac{100}{q}} \quad (53)$$

where  $M_s$  and  $M_w$  are the molar weight of solute and the water molecule, respectively. The constant of Nernst was calculated by the following equation, where Dalton's and Raoult's laws were used to calculate the mole fraction of solute in vapor phase  $x_s^g$ :

$$\ln x = \ln \left( \frac{x_s^w}{x_s^g} \right) = \ln \left( \frac{x_s^w}{1 - (1 - x_s^w)P_w^\circ} \right) \quad (54)$$

where  $P_w^\circ$  is the vapor pressure of pure water at the temperature  $T$ . These values are tabulated in the bibliography.<sup>39</sup> For nitrogen, eqs 53, 54, and 16 were used in the calculation of  $\Delta G^\circ$  in Table 1. The solubilities in water of some condensed solutes (benzene, toluene, ethylbenzene, propylbenzene, *m*-xylene, and *p*-xylene) were taken from the bibliography<sup>40</sup> and the constant of Nernst was calculated from:

$$\ln x = \ln x_s^w \quad (55)$$

In the study of  $r$  for surfactants using plots of cmc against the temperature, 12 data sets of the cmc as a function of the temperature available in the bibliography were used; the cationic surfactants series of alkyltrimethylammonium bromides<sup>41</sup> (C8-TAB, C10-TAB, C14-TAB) and the *N*-dodecylpyridinium bromide.<sup>42</sup> The sodium alkylsulfate<sup>43</sup> series (SOS, SDeS, and SDS) and the sodium 4-(alkyl)benzenesulfonate series (*p*-(3-nonyl)benzenesulfonate,<sup>45</sup> *p*-(5-decyl)benzenesulfonate,<sup>44</sup> and *p*-(3-dodecyl)benzenesulfonate<sup>45</sup>) are anionics. The *N*-decyl-*N*-

**TABLE 2: Results of Linear Fits ( $y = a + bx$ ), Correlation Coefficient, and Constant  $r$  for the Transfer Process of Some Nonpolar Solutes in Liquid Phase Using Equations 4, 6, and 7<sup>a</sup>**

equation	$a$	$b$	correlation coefficient	$r$	references	number of points
benzene						
4	$-18.753 \pm 0.058$	$0.254 \pm 0.020$	0.994	$-0.254 \pm 0.020$	40a/20	4
6	$18.753 \pm 0.058$	$0.746 \pm 0.020$	0.9993	$-0.254 \pm 0.020$	40a/20	4
7	$-25.09 \pm 0.61$	$0.338 \pm 0.036$	0.99	$-0.253 \pm 0.020$	40a/20	4
4	$-18.752 \pm 0.037$	$0.257 \pm 0.012$	0.997	$-0.257 \pm 0.012$	40b/20	4
6	$18.752 \pm 0.037$	$0.743 \pm 0.012$	0.9997	$-0.257 \pm 0.012$	40b/20	4
7	$-25.22 \pm 0.39$	$0.345 \pm 0.023$	0.996	$-0.256 \pm 0.013$	40b/20	4
				$r = -0.255 \pm 0.020$		
toluene						
4	$-21.241 \pm 0.046$	$0.251 \pm 0.016$	0.996	$-0.251 \pm 0.016$	40a/20	4
6	$21.241 \pm 0.046$	$0.749 \pm 0.016$	0.9995	$-0.251 \pm 0.016$	40a/20	4
7	$-28.34 \pm 0.57$	$0.334 \pm 0.029$	0.992	$-0.250 \pm 0.016$	40a/20	4
4	$-22.13 \pm 0.19$	$0.249 \pm 0.092$	0.93	$-0.249 \pm 0.092$	40b/20	3(1)
6	$22.13 \pm 0.19$	$0.751 \pm 0.092$	0.993	$-0.249 \pm 0.092$	40b/20	3(1)
7	$-29.1 \pm 3.3$	$0.31 \pm 0.16$	0.89	$-0.237 \pm 0.093$	40b/20	3(1)
				$r = -0.248 \pm 0.093$		
ethylbenzene						
4	$-25.019 \pm 0.026$	$0.2116 \pm 0.0069$	0.9995	$-0.2116 \pm 0.0069$	40a/20	3
6	$-25.019 \pm 0.026$	$0.7883 \pm 0.0069$	0.99996	$-0.2117 \pm 0.0069$	40a/20	3
7	$-31.73 \pm 0.25$	$0.268 \pm 0.011$	0.9991	$-0.2113 \pm 0.0068$	40a/20	3
4	$-25.27 \pm 0.19$	$0.236 \pm 0.080$	0.95	$-0.236 \pm 0.080$	40b/20	3(1)
6	$25.27 \pm 0.19$	$0.764 \pm 0.079$	0.99	$-0.236 \pm 0.079$	40b/20	3(1)
7	$-32.7 \pm 3.2$	$0.29 \pm 0.29$	0.91	$-0.225 \pm 0.078$	40b/20	3(1)
				$r = -0.222 \pm 0.080$		
propylbenzene						
4	$-28.69 \pm 0.24$	$0.254 \pm 0.080$	0.95	$-0.254 \pm 0.080$	40b/20	3
6	$28.69 \pm 0.24$	$0.746 \pm 0.080$	0.994	$-0.254 \pm 0.080$	40b/20	3
7	$-38.0 \pm 3.9$	$0.32 \pm 0.14$	0.91	$-0.242 \pm 0.080$	40b/20	3
				$r = -0.250 \pm 0.080$		

<sup>a</sup> The experimental data were taken from the bibliography.

dimethylglycine<sup>46</sup> is zwitterionic, and the decylpentaoxyethylene glycol ether<sup>47</sup> and the dodecyldimethylphosphine oxide<sup>21</sup> are nonionic.

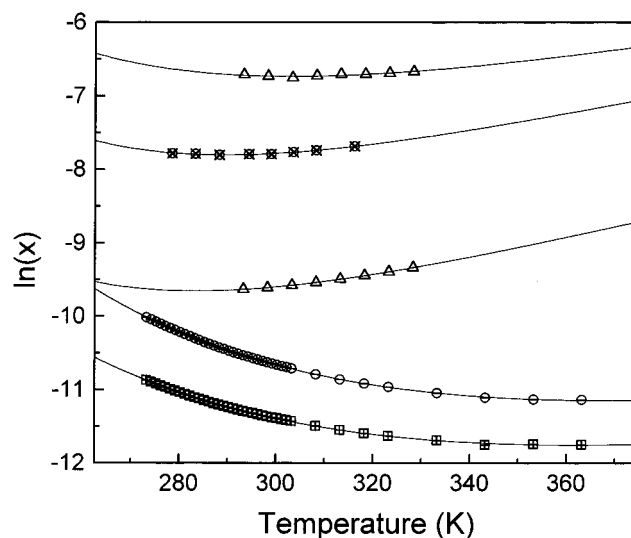
The data were fitted to the following expression, which follows from eqs 19 and 20 for nonpolar solutes and eqs 37 and 38 for surfactants:

$$\ln x = \frac{1}{1+r} \ln x_0 \left( r \left( \frac{T}{T_0} \right)^{1/r} + \frac{T_0}{T} \right) \quad (56)$$

The use of the eq 56 implicates the assumption of the “high aggregation numbers approximation”. For ionic surfactants, the use of this equation also implicates the assumption that  $\beta$  is independent of the temperature ( $\beta \approx \beta_0$ ) and then,  $T_0 \approx T^*$  and  $\ln x_0 \approx \ln x^*$ .

Table 2 shows the results of fitting the eq 56 to experimental data. In Figure 3 the experimental values of  $\ln x(T)$  as a function of the temperature for some substances (methane, nitrogen, benzene, C10-TAB, and C14-TAB) with their corresponding fits are shown. For nonpolar solutes,  $\Delta C_{p0}^\circ$  was calculated from eq 20 and for surfactants,  $\Delta C_{p0}^\circ$  was calculated from eq 38 using constant values of  $\beta$  available in the bibliography.<sup>48</sup> Using these values, in Figure 4 the theoretical predictions of eq 12 are shown to be in excellent agreement with the experimental values of  $\Delta H^\circ$  for these substances.<sup>19,20,49–51</sup> The theoretical plot of  $\Delta H^\circ$  for dodecyldimethylphosphine oxide was calculated using calorimetric data of ref 21.

It is possible to think that the calculation of  $r$  from plots of solubility or cmc against the temperature can mask differences and trends due to the least squares method and/or the approximations used in fitting the curves. In the calculation of  $r$  by linear plots (Figure 1), two experimental techniques are used because  $\Delta G^\circ$  is calculated from solubility or cmc measurements



**Figure 3.** Fits of eq 42 to the experimental solubility of nonpolar solutes and cmc values of surfactants in aqueous solution as a function of the temperature; data taken from bibliography. Symbols are defined in Table 4.

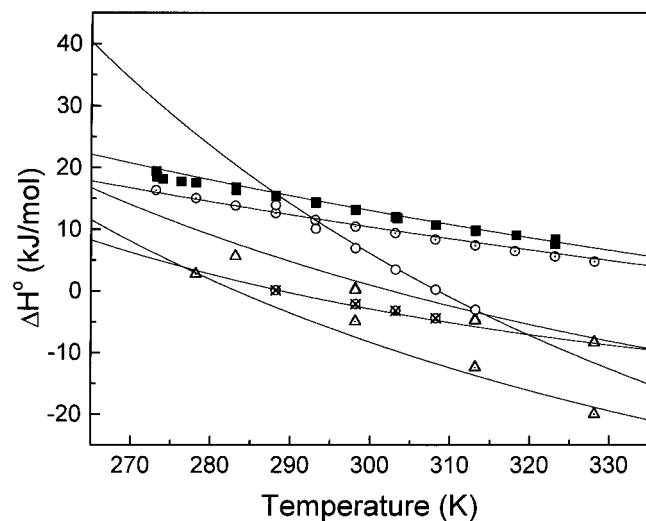
and  $\Delta H^\circ$  is directly measured by calorimetry. Only in the case of the gases (Table 1) were high precision data calculated by the van't Hoff method used. In the case of liquid nonpolar solutes and surfactants, only values of  $\Delta H^\circ$  from calorimetry were used. The reason for this procedure is because using values from two techniques, there are no internal correlations introduced in the data sets by the curve fitting used in the calculations.

From Table 1 it is evident that  $r$  decreases in magnitude when the size of the solute molecule increases. From Tables 2 and 3, it is evident that  $r$  presents a constant behavior independent of

**TABLE 3: Results of Linear Fits ( $y = a + bx$ ), Correlation Coefficient, and Constant  $r$  for the Micelle Formation Process of Some Surfactants Using Equations 4, 6, and 7<sup>a</sup>**

equation	$a$	$b$	correlation coefficient	$r$	references	number of points
dodecyltrimethylphosphine oxide (nonionic)						
4	$-30.887 \pm 0.037$	$0.1642 \pm 0.0047$	0.998	$-0.1642 \pm 0.0047$	21	6
6	$30.887 \pm 0.57$	$0.8358 \pm 0.0047$	0.99994	$-0.1640 \pm 0.0048$	21	6
7	$-36.95 \pm 0.24$	$0.1963 \pm 0.0067$	0.998	$-0.1641 \pm 0.0047$	21	6
				$r = -0.1641 \pm 0.0048$		
nonyltrimethylammonium bromide (cationic)						
4	$-25.181 \pm 0.014$	$0.2893 \pm 0.0035$	0.9998	$-0.2893 \pm 0.0035$	36	5
6	$-25.181 \pm 0.014$	$0.7107 \pm 0.0035$	0.99996	$-0.2893 \pm 0.0035$	36	5
7	$-35.43 \pm 0.18$	$0.4069 \pm 0.0069$	0.9996	$-0.2892 \pm 0.0035$	36	5
				$r = -0.2893 \pm 0.0035$		
decyltrimethylammonium bromide (cationic)						
4	$-28.87 \pm 0.13$	$0.303 \pm 0.023$	0.997	$-0.303 \pm 0.023$	41/51a	3
6	$28.87 \pm 0.13$	$0.697 \pm 0.023$	0.9995	$-0.303 \pm 0.023$	41/51a	3
7	$-14.4 \pm 1.2$	$0.433 \pm 0.047$	0.994	$-0.302 \pm 0.023$	41/51a	3
				$r = -0.303 \pm 0.023$		
dodecyltrimethylammonium bromide(cationic)						
4	$-35.62 \pm 0.13$	$0.213 \pm 0.014$	0.998	$-0.213 \pm 0.014$	41/51a	3
6	$35.62 \pm 0.13$	$0.786 \pm 0.014$	0.9998	$-0.214 \pm 0.014$	41/51a	3
7	$-45.28 \pm 0.65$	$0.271 \pm 0.022$	0.997	$-0.213 \pm 0.014$	41/51a	3
				$r = -0.213 \pm 0.014$		
tetradecyltrimethylammonium bromide (cationic)						
4	$-41.94 \pm 0.13$	$0.1974 \pm 0.021$	0.999	$-0.1974 \pm 0.0091$	41/51a	3
6	$41.94 \pm 0.13$	$0.8026 \pm 0.021$	0.99994	$-0.1974 \pm 0.0091$	41/51a	3
7	$-52.24 \pm 0.46$	$0.246 \pm 0.032$	0.998	$-0.1964 \pm 0.0091$	41/51a	3
				$r = -0.1974 \pm 0.0091$		
hexadecyltrimethylammonium bromide (cationic)						
4	$-48.17 \pm 0.41$	$0.197 \pm 0.021$	0.994	$-0.197 \pm 0.021$	41/51a	3
6	$48.17 \pm 0.41$	$0.803 \pm 0.21$	0.9997	$-0.197 \pm 0.021$	41/51a	3
7	$-59.9 \pm 1.1$	$0.244 \pm 0.32$	0.991	$-0.196 \pm 0.021$	41/51a	3
				$r = -0.197 \pm 0.021$		
sodium dodecylsulfate (anionic)						
4	$-37.909 \pm 0.040$	$0.2303 \pm 0.0095$	0.997	$-0.2303 \pm 0.0095$	43b/51b	5
6	$37.090 \pm 0.040$	$0.7696 \pm 0.0095$	0.9998	$-0.2304 \pm 0.0095$	43b/51b	5
7	$-49.23 \pm 0.58$	$0.299 \pm 0.016$	0.996	$-0.2302 \pm 0.0095$	43b/51b	5
				$r = -0.2303 \pm 0.0095$		

<sup>a</sup> The experimental data were taken from the bibliography.



**Figure 4.** Experimental values of  $\Delta H^\circ$  as a function of the temperature and theoretical predictions of eq 12 using the results of Table 2. Identical results for benzene, C10-TAB, and C14-TAB are obtained using  $r = -0.239$  in the theoretical prediction of eq 12. In the case of dodecyltrimethylphosphine oxide the parameters ( $\Delta C_{p,0}^\circ = -673.6 \pm 8.9 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T_0 = 308.5 \pm 5.7 \text{ K}$ ) were taken from the linear fit in the direct calorimetric data of  $\Delta H^\circ$ . The experimental data were taken from the bibliography (see text). Symbols are defined in Table 4.

the size. Identical qualitative behavior is found in Table 4. A study in detail of the results in Table 2 reveals the effect of using data from different references in the calculation of  $r$  in

the case of the benzene, toluene, and ethylbenzene. In the two latter cases it is observed that the second digit depends on the reference of the data set of the solubility. In the case of the sodium dodecylsulfate in the Table 4, this effect reaches the first significant digit. Comparing the results obtained by the two methods, in the case of gases (Tables 1 and 4), only the first significant digit is maintained and is independent of the reference of the data. An identical result is obtained in the comparison of the data in Tables 2 and 4 for the benzene derivatives. In the case of surfactants, the differences are bigger because of the imprecision of the concept of cmc and the consideration of a  $\beta$  that is independent of the temperature in the calculations. On the other hand, quantitatively it is not clear from the available data if  $r$  increases or decreases with the size of the solute molecule in Tables 2, 3, and 4 because the fluctuations are not big enough to determine some type of trend. For the benzene derivatives, the mean value using linear plots (Table 2) is  $-0.244 \pm 0.015$  (standard deviation) and that calculated from the plots of solubility against the temperature is  $-0.252 \pm 0.026$ . The value obtained by Sturtevant<sup>16</sup> for a set of hydrocarbons at 298.15 K is  $-0.263 \pm 0.046$ . For surfactants, the mean value using linear plots (Table 3) is  $-0.228 \pm 0.051$  and that determined from plots of the cmc against the temperature is  $-0.233 \pm 0.051$ . The calculated value by Muller<sup>18</sup> for surfactants at 298.15 K is  $-0.247 \pm 0.037$ . In the case of the benzene derivatives, it is only possible to get the first digit free of error. An identical result is obtain for the surfactants. Using only values free of error in the result, the value obtained in the two cases is the same ( $r = -0.2$ ). The possible differences between



**TABLE 4: General Results Using Equation 56 and Experimental Data Sets of Solubility of Nonpolar Solutes in Water and cmc of Surfactants as Function of the Temperature<sup>a</sup>**

compound	symbol	$r$	$T_0$	$\ln x_0$	number of points
Nonpolar solutes					
gases					
hydrogen	■	$-0.940 \pm 0.017$	$335.07 \pm 0.58$	$-11.2443 \pm 0.0015$	39
nitrogen	⊙	$-0.6635 \pm 0.0079$	$361.47 \pm 0.67$	$-11.7517 \pm 0.0031$	39
oxygen	⊞	$-0.6316 \pm 0.0041$	$367.33 \pm 0.40$	$-11.1467 \pm 0.0020$	39
methane	⊖	$-0.5663 \pm 0.0034$	$366.96 \pm 0.96$	$-11.1420 \pm 0.0021$	39
ethane	⊕	$-0.4651 \pm 0.0066$	$374.9 \pm 1.0$	$-11.1207 \pm 0.0081$	39
liquids					
benzene	⊗	$-0.227 \pm 0.022$	$289.02 \pm 0.72$	$-7.8013 \pm 0.0032$	8
toluene	⊕	$-0.2450 \pm 0.0094$	$289.66 \pm 0.27$	$-9.0183 \pm 0.0020$	12
ethylbenzene	⊞	$-0.290 \pm 0.019$	$289.93 \pm 0.40$	$-10.2614 \pm 0.0033$	8
<i>p</i> -xylene	+	$-0.268 \pm 0.034$	$289.9 \pm 1.1$	$-10.3154 \pm 0.0035$	9
<i>m</i> -xylene	×	$-0.231 \pm 0.029$	$290.23 \pm 0.66$	$-10.3309 \pm 0.0074$	8
Surfactants					
noionic surfactants					
decylpentaerythritol glycol ether	●	$-0.227 \pm 0.030$	$323 \pm 4.1$	$-11.322 \pm 0.033$	8
dodecyltrimethylphosphine oxide	○	$-0.170 \pm 0.029$	$305.2 \pm 1.2$	$-12.0547 \pm 0.0061$	6
zwitterionic surfactants					
<i>N</i> -decyl- <i>N,N</i> -dimethylglycine	▽	$-0.274 \pm 0.030$	$316.09 \pm 0.81$	$-7.8385 \pm 0.0047$	8
cationic surfactants					
octyltrimethylammonium bromide	▲	$-0.298 \pm 0.68$	$320.9 \pm 3.0$	$-5.3127 \pm 0.0038$	8
decyltrimethylammonium bromide	△	$-0.279 \pm 0.090$	$302.8 \pm 2.5$	$-6.7321 \pm 0.0063$	8
tetradecyltrimethylammonium bromide	▲	$-0.261 \pm 0.012$	$283.3 \pm 1.2$	$-9.6531 \pm 0.0052$	8
<i>n</i> -dodecylpyridium bromide	⬆	$-0.173 \pm 0.014$	$288.2 \pm 1.3$	$-8.5163 \pm 0.0045$	6
anionic surfactants					
sodium octylsulfate	◇	$-0.1806 \pm 0.0079$	$300.43 \pm 0.32$	$-6.0463 \pm 0.0027$	11
sodium decylsulfate	◇	$-0.2324 \pm 0.0052$	$300.09 \pm 0.16$	$-7.4317 \pm 0.0013$	11
sodium dodecylsulfate <sup>a</sup>	◆	$-0.2312 \pm 0.0070$	$297.45 \pm 0.22$	$-8.8212 \pm 0.0021$	11
sodium dodecylsulfate <sup>b</sup>	◆	$-0.1297 \pm 0.0062$	$299.09 \pm 0.15$	$-8.8323 \pm 0.0013$	7
<i>p</i> -(3-nonyl)benzenesulfonate	▼	$-0.300 \pm 0.044$	$293.54 \pm 3.1$	$-8.5902 \pm 0.0076$	8
<i>p</i> -(3-dodecyl)benzenesulfonate	▽	$-0.221 \pm 0.044$	$295.6 \pm 3.3$	$-8.830 \pm 0.011$	7
<i>p</i> -(5-decyl)benzenesulfonate	▽	$-0.2173 \pm 0.0099$	$297.92 \pm 0.77$	$-9.1324 \pm 0.0023$	8

<sup>a</sup> Data from ref 43a. <sup>b</sup> Data from ref 43b.

the substances or between the two processes, if they exist, are in the second significant digits; but, it is not possible to determine these values with assuredness (free of error) with the available data. Because it is not possible to make distinctions between the substances and processes, we will take the mean value of  $r$  ( $= -0.239 \pm 0.054$ ), which is the mean value obtained in this work for surfactants and nonpolar liquids with the biggest error of the considered values.

If a value for  $r$  independent of substance is considered in the theory, then eqs 9, 10, 12, and 13 and eqs 19 and 37 can take the followings “reduced forms”:

$$\frac{\Delta C_p^\circ}{\Delta C_{p0}^\circ} = \theta^{1/r} \quad (57)$$

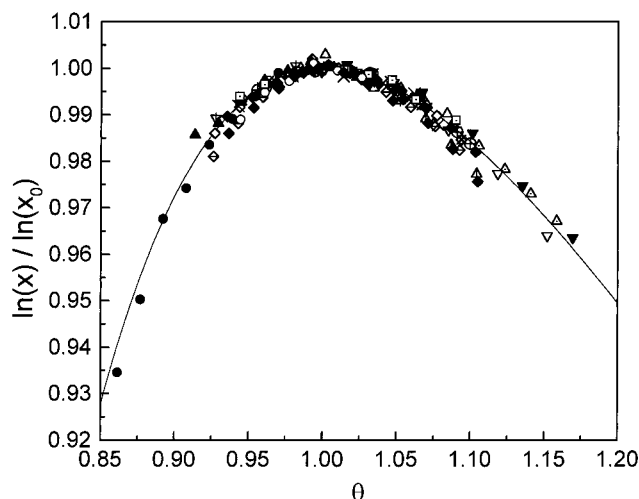
$$\frac{\Delta S^\circ}{\Delta C_{p0}^\circ} = r\theta^{1/r} \quad (58)$$

$$\frac{\Delta H^\circ}{T_0 \Delta C_{p0}^\circ} = \frac{r}{1+r} (\theta^{1/r+1} - 1) \quad (59)$$

$$\frac{\ln x}{\ln x_0} = \frac{1}{1+r} \left( r\theta^{1/r} + \frac{1}{\theta} \right) \quad (60)$$

$$\frac{\Delta G^\circ}{\Delta G_0^\circ} = \frac{1}{1+r} (r\theta^{1/r+1} + 1) \quad (61)$$

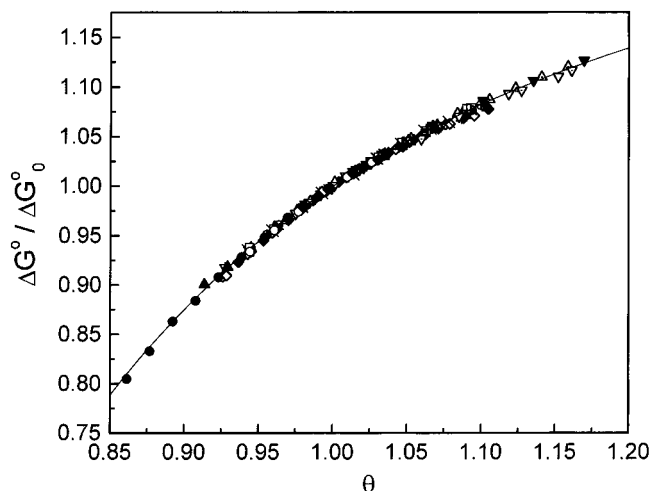
Because  $\beta$  varies little with the temperature, in eqs 60 and 61 it was assumed that  $(1 + \beta)/(1 + \beta_0) \approx 1$ . The firsts members of eqs 57, 58, 59, 60, and 61 are independent of substance,



**Figure 5.** Experimental values of  $\ln(x)/\ln(x_0)$  from the solubility of condensed nonpolar solutes and cmc values of surfactants as a function of the reduced temperature and theoretical prediction of eq 46, with  $r = -0.239$ . The experimental data were taken from the bibliography (see text). Symbols are defined in Table 4.

because in the second members,  $r$  was supposed to be independent of substance and  $\theta$  is a reduced temperature. This fact could induce a possible common behavior in all the nonpolar solutes and surfactants.

In Figure 5, the experimental values of  $\ln x(\theta)/\ln x_0$  versus the reduced temperature and the theoretical prediction of eq 60 with  $r = -0.239$  are shown. The  $\ln x(T)$  values were taken



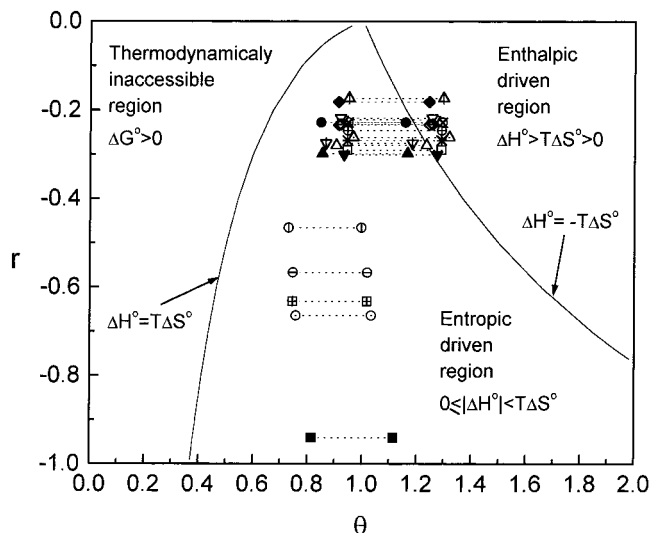
**Figure 6.** Experimental values of  $\Delta G^\circ/\Delta G^\circ_0$  of transfer process of condensed nonpolar solutes and micellization process of surfactants as a function of the reduced temperature and theoretical prediction of eq 45 with  $r = -0.239$ . The experimental data were calculated from eq 47. Symbols are defined in Table 4.

from the bibliography and  $\ln x_0$  values are from Table 2. The scattering of the data at high and low values of  $\theta$  is due to the imprecision in the calculation of the minima because for these data sets, the minimum was out of the temperature intervals studied by the authors. It is surprising that the function  $\ln x/\ln x_0$  has a “reduced behavior”; however, it is not possible to have another similar “reduced equation” independent of substance for  $x/x_0$ . On the other hand, because  $r$  is constant, the value for  $\ln x/\ln x_0$  only depends on the value of  $\theta$ ; but, this does not mean that  $\ln x/\ln x_0$  will be the same for all substances at the temperature  $T$  because this reduced temperature  $\theta$  corresponds to temperature  $T = \theta T_0$ . Moreover, in a substance with low  $T_0$ , the amount  $\ln x/\ln x_0$  changes faster than for other substance with larger  $T_0$ .

In general, the solubility of nonpolar solutes at constant temperature in aqueous solution depends on the molecular surface of the substance.<sup>7</sup> The cmc<sup>52,53</sup> depends on the nature of the headgroup, on the nature of the counterion, and on the length of the hydrocarbon chain. The nonionic surfactants usually have much lower cmc values than the ionic surfactants. For the same hydrocarbon chain, variations in the cmc were found when the size of headgroup was changed. On the other hand, for the same headgroup, the logarithm of cmc varies linearly with the alkyl chain length. Other modifications to the hydrocarbon chain (such as introducing branching, double bonds, or polar functional groups along the chain) usually lead to increases in the cmc, but the introduction of a benzene ring is equivalent to adding  $\sim 3.5$  methylene groups to the chain length. One possible explanation of the global “reduced behavior” is all the effects are balanced in the following sense: for nonpolar solutes and nonpolar surfactants, the value of  $T_0$  is such that the ratio between  $\ln(x_0)$  and  $\Delta C_{p0}/R$  is  $r$ . In the same way, but including the effect of the counterion binding to micelle, the value of  $T_0$  for ionic surfactants is such that the ratio between  $(1 + \beta_0)\ln(x_0)$  and  $\Delta C_{p0}/R$  is the same constant  $r$ .

In Figure 6 the experimental values  $\Delta G^\circ/\Delta G^\circ_0$  and the theoretical prediction of eq 61 with  $r = -0.239$  are shown. The experimental values of  $\Delta G^\circ/\Delta G^\circ_0$  were calculated from:

$$\frac{\Delta G^\circ}{\Delta G^\circ_0} = \frac{(1 + \beta)RT \ln x}{(1 + \beta_0)RT_0 \ln x_0} \approx \theta \frac{\ln x}{\ln x_0} \quad (62)$$



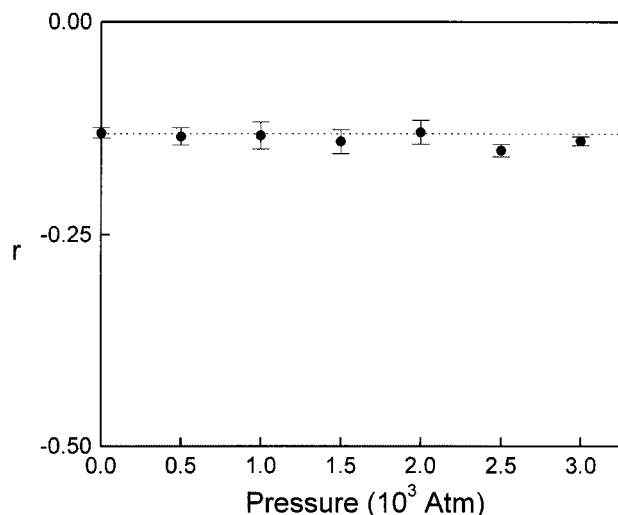
**Figure 7.** Plots of the thermodynamically inaccessibility region, entropic-driven region, and enthalpic-driven region. The points on the left-hand side are the reduced temperature of the melting point of water ( $273.15/T_0$ ) and the points on the right-hand side are the reduced temperature of boiling point of the water ( $373.15/T_0$ ) for each compound studied in this work. Symbols are defined in Table 4.

The self-association of amphiphiles in aqueous solution into micellar aggregates is accounted for by the hydrophobic effect, but the frequent preference for formation of relatively small micelles, with aggregation numbers of the order of 100 or less, requires the existence of an opposing contribution to  $\Delta G^\circ$  that prevents the growth of aggregates to a larger size.<sup>7</sup> If the favorable and opposing contributions to aggregation are namely  $\Delta G^\circ_{HP}$  and  $\Delta G^\circ_S$ , respectively, then

$$\Delta G^\circ = \Delta G^\circ_{HP} + \Delta G^\circ_S \quad (63)$$

The term  $\Delta G^\circ_{HP}$  is the hydrophobic contribution that has its origin in the interactions of the transfer process of the hydrocarbon chain of the monomer from the water to the micelle core. The other term,  $\Delta G^\circ_S$ , is the opposite contribution,<sup>54</sup> also known as the surface contribution because it has its origin in the surface effects in the micelle. Because the “reduced behavior” of  $\Delta G^\circ$  is the same for the transfer process of nonpolar solutes and for the micelle formation of surfactants, it is easy to think that the contribution of the interface effects in micelle formation should not be important. If this was true, the main contribution to  $\Delta G^\circ$  would be  $\Delta G^\circ_{HP}$ . This point of view is dangerous because to calculate  $\Delta G^\circ$ , only the nature of alkyl chain will be important. In other words because the logarithm of cmc is proportional to  $\Delta G^\circ$  (eq 36), all surfactants with the same hydrocarbon chain would have the same cmc. This supposition is not true because the cmc of nonionic surfactants is usually much lower than the cmc of the ionic surfactants. The following explanation seems more realistic: because the effects of the nature of the headgroup, the counterion, and the length of the hydrocarbon chain are balanced in the “reduced behavior” of  $\ln(x)/\ln(x_0)$  as a function of the reduced temperature  $\theta$ , the parameter  $\Delta G^\circ/\Delta G^\circ_0 = \theta \times \ln(x)/\ln(x_0)$  must also have “reduced behavior”. For this reason, there exists a mechanism for balancing the contributions to  $\Delta G^\circ$ .

In Figure 7 the thermodynamically inaccessible region, the entropic-driven region, and the enthalpic-driven region are plotted with the reduced temperatures of melting and boiling points of water for each compound studied in this work. All of nonpolar gases have their transfer process in the entropical-



**Figure 8.** Plot of the parameter  $r$  as a function of the pressure for sodium dodecyl sulfate in aqueous solution. These values were calculated from experimental data of ref 43b.

driven region. Above  $T_0$ , the transfer process of condensed nonpolar solutes studied and the micellization of surfactants is in the entropic-driven region. The enthalpic-driven region does not start immediately after  $T_0$ . Below this temperature, these process are still in the entropic-driven region and it is necessary to increase the temperature enough to go into the enthalpic-driven region.

In Figure 8 the plot of  $r$  versus the pressure in the range of 0 to 3000 atm for sodium dodecyl sulfate is shown. These values were calculated using the cmc data from ref 43b. The mean value obtained in this case is  $-0.1365 \pm 0.0075$ . However, it is surprising that no variation in this parameter is found when the pressure is changed. The linear relations between  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $T\Delta S^\circ$  with  $\Delta V^\circ$  predicted by eqs 50, 51, and 52 are compared with the experimental values from ref 36 for the nonyltrimethylammonium bromide in Figure 9.

#### 4. Conclusions

In this study, the Taylor's expansion of  $\Delta G^\circ = \Delta G^\circ(\Delta H^\circ)$ ,  $\Delta G^\circ = \Delta G^\circ(T\Delta S^\circ)$ , and  $T\Delta S^\circ = T\Delta S^\circ(\Delta H^\circ)$  were used. For example, for  $\Delta G^\circ = \Delta G^\circ(\Delta H^\circ)$  and for any process that is carried out in conditions of constant temperature and pressure, it is always possible to make the following expansion around the same  $\Delta H^\circ = \Delta H^\circ_c$ :

$$\Delta G^\circ(\Delta H^\circ) = \Delta G^\circ(\Delta H^\circ_c) + \left( \frac{\partial \Delta G^\circ(\Delta H^\circ)}{\partial \Delta H^\circ} \right)_P (\Delta H^\circ - \Delta H^\circ_c) + \left( \frac{\partial^2 \Delta G^\circ(0)}{\partial \Delta H^{\circ 2}} \right)_P (\Delta H^\circ - \Delta H^\circ_c)^2 + \dots \quad (64)$$

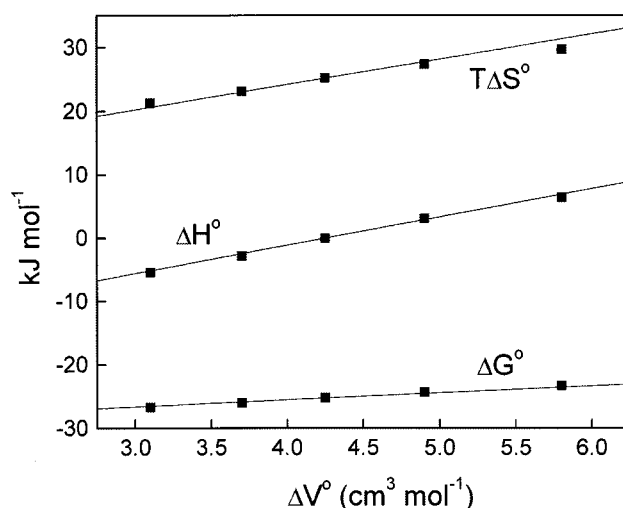
If the contribution of the second-order term

$$\left( \frac{\partial^2 \Delta G^\circ}{\partial \Delta H^{\circ 2}} \right)_P = -\frac{1}{T\Delta S^\circ} \left\{ \left( \frac{\partial \Delta C_p^\circ}{\partial \Delta S^\circ} \right)_P - \frac{\Delta C_p^\circ}{\Delta S^\circ} \right\} \quad (65)$$

is neglected, then

$$\left( \frac{\partial \Delta C_p^\circ}{\partial \Delta S^\circ} \right)_P - \frac{\Delta C_p^\circ}{\Delta S^\circ} \approx 0 \quad (66)$$

and eq 5 is obtained as a solution of the differential eq 66. In general, and for any process that is carried out at constant pressure and temperature, it is always possible to use eq 64 in



**Figure 9.** Linear relations between  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $T\Delta S^\circ$ , and  $\Delta V^\circ$  for nonyltrimethylammonium bromide using data of ref 36. The values of the ordinate axis were taken from Figure 2 and the values of  $\Delta V^\circ$  directly from reported data in ref 36. The parameter  $\Delta\alpha_0^\circ$  was estimated from the slope of a linear fit of  $\Delta V^\circ$  data as a function of the temperature and the values of the parameters  $\Delta C_p^\circ$  and  $T_0$  were taken from the data reported in this reference.

an interval around  $\Delta H^\circ_c$ . If the expansion truncated at first order is sufficient to describe the process in some interval of temperatures it is equivalent to suppose a  $r$  value independent of the temperature.

In this study, the Taylor's expansions were centered around  $\Delta H^\circ = 0$  because this fact is verified in general by the processes that involve the hydrophobic effect. If the relation in eq 66 is not equal to zero, it might be inferred that a more realistic description would be obtained. However, such a description would lead to greater mathematical complexity with little gain in physical insight. In the literature, the definition of the hydrophobic effect relates largely to its phenomenology<sup>7</sup> that includes (1) the low solubility of nonpolar solutes in water and the low cmc of surfactants; (2) the curves of the solubility and the cmc as a function of temperature commonly display a minimum; (3)  $\Delta C_p^\circ$  is large and negative; (4)  $\Delta S^\circ$  is large and positive; and (5)  $\Delta H^\circ$  changes sign at the characteristic temperature.

The theory presented to describe the hydrophobic effect requires only the following hypotheses to derive the aforementioned phenomenology: (1)  $\Delta S^\circ = r\Delta C_p^\circ$ , with  $r < 0$  constant at all temperatures and pressures; (2)  $\Delta H^\circ = 0$  at the characteristic temperature  $T_0$ ; and (3) the magnitude of  $\Delta S^\circ$  is large.

The first hypothesis is equivalent to supposing that  $\Delta C_p^\circ < 0$  or that there is a minimum in the curves of the solubility and the cmc as a function of the temperature. On the other hand, the third hypothesis is equivalent, using eqs 20 and 38, to supposing that the magnitude of  $\Delta C_p^\circ$  is large or the solubility (or the cmc) are low. The linearity of the plots of  $\Delta H^\circ$  versus  $T\Delta S^\circ$ <sup>15</sup> (and the linearity of the new plots of  $\Delta G^\circ$  versus  $\Delta H^\circ$  and  $\Delta G^\circ$  versus  $T\Delta S^\circ$ ) is predicted by substituting the relation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  in the following form of eq 5:

$$-\left( \frac{\partial \Delta G^\circ}{\partial T} \right)_P = r \left( \frac{\partial \Delta H^\circ}{\partial T} \right)_P \quad (67)$$

A consequence of a constant  $r$  independent of the pressure are the linear plots of the thermodynamic parameters as a function of  $\Delta V^\circ$ , and the consequence of the independence of

$r$  for large molecules is the reduced behavior of  $\ln(x)$ ,<sup>17</sup>  $\Delta C_p^\circ$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ .

The situation commonly accepted is that the solubility of nonpolar solutes is "entropy driven" or "entropy controlled"<sup>7,13</sup> because at room temperatures,  $\Delta H^\circ$  changes its sign and contributes only slightly in this region to  $\Delta G^\circ$ . In this theory, as we have shown, this fact can be considered as fortuitous (the contribution of  $\Delta H^\circ$  can be greater than the entropic contribution in some intervals of temperature), and the main role played by the entropy in this case is the relation  $\Delta S^\circ = r\Delta C_p^\circ$ .

In the opinion of some authors,<sup>7,13</sup> the driving force of micelle formation is the hydrophobic effect. For other authors, the driving force below  $T_0$  is the hydrophobic effect and above  $T_0$  it is the London dispersion force<sup>55</sup> because  $\Delta H^\circ$  is negative. One result of this work is that the transfer process of nonpolar solutes has the same value of  $r$  (within the experimental error) as that of the micellization of surfactants. Because of this similarity, surfactants follow the same "reduced behavior". This result should not be taken to mean that the alkyl chain contribution is the dominant contribution to  $\Delta G^\circ$  in micelle formation, but that the two contributions, the alkyl and surface contributions, are balanced to maintain a constant value of  $r$ .

One problem in computer simulations is how to check or to validate the results about the hydrophobic effect. The thermodynamic theory presented here contains the phenomenological aspects of the hydrophobic effect, focusing the attention on three points as already explained. Therefore, this theory can be used as a tool to validate the results of future works using computer simulations.

Finally, to determinate the validity range of this approximation high precision data of  $\Delta G^\circ$  and  $\Delta H^\circ$  or  $\Delta S^\circ$  and  $\Delta C_p^\circ$  as a function of the temperature in a large interval of temperatures are needed. On the other hand, the constancy of  $r$  with the pressure is surprising, indicating that this approximation also works in a large interval of pressures. If only an error free result is considered ( $r = -0.2$ ), it is possible to conclude that the absolute value of variation of the standard heat capacity is one order of magnitude bigger than the variation of the standard entropy. This qualitative result is independent of the process (transfer or micelle formation process) and independent of the substance when the solvent is water. If the solvent is different than water, the value of  $r$  can be different. For example, for the micellization process of dodecyltrimethylphosphine oxide in deuterium,<sup>21</sup>  $r$  is  $-0.0418 \pm 0.0070$ , which is one order of magnitude less than the calculated value for water (Table 3).

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