

Surface Tension for Aqueous Solutions of Sodium 1-Dodecanesulfonate

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A study has been carried out on the modification of surface tension in aqueous solutions of the collector sodium 1-dodecanesulfonate, at temperature of 293.15 K and pH between 4 and 10. The results of this study show that the surface tension varies very slightly when the pH in the medium of flotation bath is changed. The critical micelle concentration has been identified, and certain thermodynamic quantities associated with the adsorption of sodium 1-dodecanesulfonate in the solution–air interface were also obtained. Moreover, the values for the molecular limiting area range between (38 to 49) Å² per molecule and standard adsorption energy between (–29.00 to –29.61) kJ·mol^{–1}, at pH between 4 and 10.

Introduction

The variations in surface tension in a flotation bath due to the presence of the surface agents and the modification of pH is of great importance as regards the wetting phenomenon, owing to the influence both exert on the flotability of solid particles during flotation. The modification of surface tension in surfactant solutions has been examined more systematically over the past two decades, with greater attention being given to reagent purity.^{1–4}

The level of purity required of sodium 1-dodecanesulfonate (DSS) is most often defined in terms of the measured surface chemical behavior; however, it is generally accepted that very low levels of a surface active impurity may drastically affect the result.

The surface tension was measured as functions of pH and concentration, and thermodynamic quantities were evaluated by applying the thermodynamic treatment developed previously.⁵ The concentration range of the DSS applied in the present paper is that generally used for the surfactant as a flotation agent.

Materials and Methods

Commercially available DSS purchased from Merck (R.12146) described as 99+ % pure was used. In a previous work,⁶ a minimum in the curve of the surface tension versus concentration was found for this material, indicative of the active superficial effect of the impurities; for this reason, the DSS was purified by the means of three successive crystallizations of dissolutions of the solute in bidistilled water of resistivity of 10 MΩ·cm (Mili-Q quality) and crystallization at 50 °C.

The purified DSS was dissolved in bidistilled water of resistivity of 10 MΩ·cm (Mili-Q quality); the solute was weighed on a Mettler AJ-150 scale with an accuracy of ± 0.1 mg, and the desired solution volume was obtained by successive dilutions since the concentrations of the agent used are very small. In all cases, the solutions were prepared before the experiments were carried out to avoid possible alterations in the surface agents and hence changes in their properties over time. In all cases, the measurements for surface tension were carried out using solutions of constant ionic strength (10^{–2} mol·L^{–1} of NaCl). These measurements were performed 60 min after the preparation of the solutions, thus ensuring that values

Table 1. Surface Tension of Aqueous Solutions of Sodium 1-Dodecanesulfonate at 293.15 K

<i>c</i> /mol·L ^{–1}	σ /mN·m ^{–1}						
	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
1.4 × 10 ^{–5}	68.7	68.7	68.7	69.3	69.0	69.1	68.5
7.3 × 10 ^{–5}	65.2	68.0	68.2	68.9	68.8	68.6	68.0
1.4 × 10 ^{–4}	59.6	62.9	66.9	66.9	66.5	67.3	67.1
6.2 × 10 ^{–4}	53.6	56.8	58.2	59.0	58.9	58.8	58.1
1.0 × 10 ^{–3}	49.7	52.2	52.6	52.8	52.9	53.8	54.0
5.0 × 10 ^{–3}	40.5	41.1	40.3	40.0	40.5	40.3	40.8
6.0 × 10 ^{–3}	37.1	37.5	38.0	38.1	38.2	38.9	38.6
7.0 × 10 ^{–3}	36.0	36.2	37.0	37.2	37.5	38.4	38.0
8.0 × 10 ^{–3}	36.4	36.5	37.3	37.3	37.7	38.5	38.3
8.5 × 10 ^{–3}	36.3	36.5	37.2	37.3	37.7	38.6	38.3
9.0 × 10 ^{–3}	36.3	36.8	37.2	37.3	37.8	38.6	38.4

obtained for surface tension were steady-state values in accordance with Loznetsova et al.⁷ The uncertainty of DSS concentration was estimated to be within ± 0.1 × 10^{–5} mol·L^{–1}.

NaOH and HCl, supplied by Merck and Probus, respectively, were used as pH modifiers; in both cases small aliquots of 4 mol·L^{–1} solutions were used to reach the desired pH easily. pH measurements were performed with a Crison 2001 pH-meter having an uncertainty of 0.01.

The surface tension measurements were performed using the plate method,⁵ utilizing a Kruss K10 digital tensiometer, with an accuracy of ± 0.1 mN·m^{–1} and a platinum plate measuring (20 × 10 × 0.1) mm. The solution whose surface tension was to be measured was placed in the duly thermostated flask at 293.15 K, using a thermostat that allows consistent constant temperature regulation to ± 0.1 °C. Eleven determinations of surface tension were carried out for each solution, the average being taken from the last 10. Each value reported was an average of 10 measurements, where the maximum deviation from the average value was always less than 0.3 %. The uncertainty of the measurements was ± 0.15 mN·m^{–1}.

Results and Discussion

Surface tension for aqueous solutions of DSS are shown in Table 1, according to pH at surfactant concentrations between (1.4 × 10^{–5} and 9 × 10^{–3}) mol·L^{–1} and at *T* = 293.15 K. The values show that surface tension varies very slightly when pH in the medium is modified. The lowest values for surface tension are generally found in acid mediums, although there is no great difference when compared with neutral or alkaline mediums.

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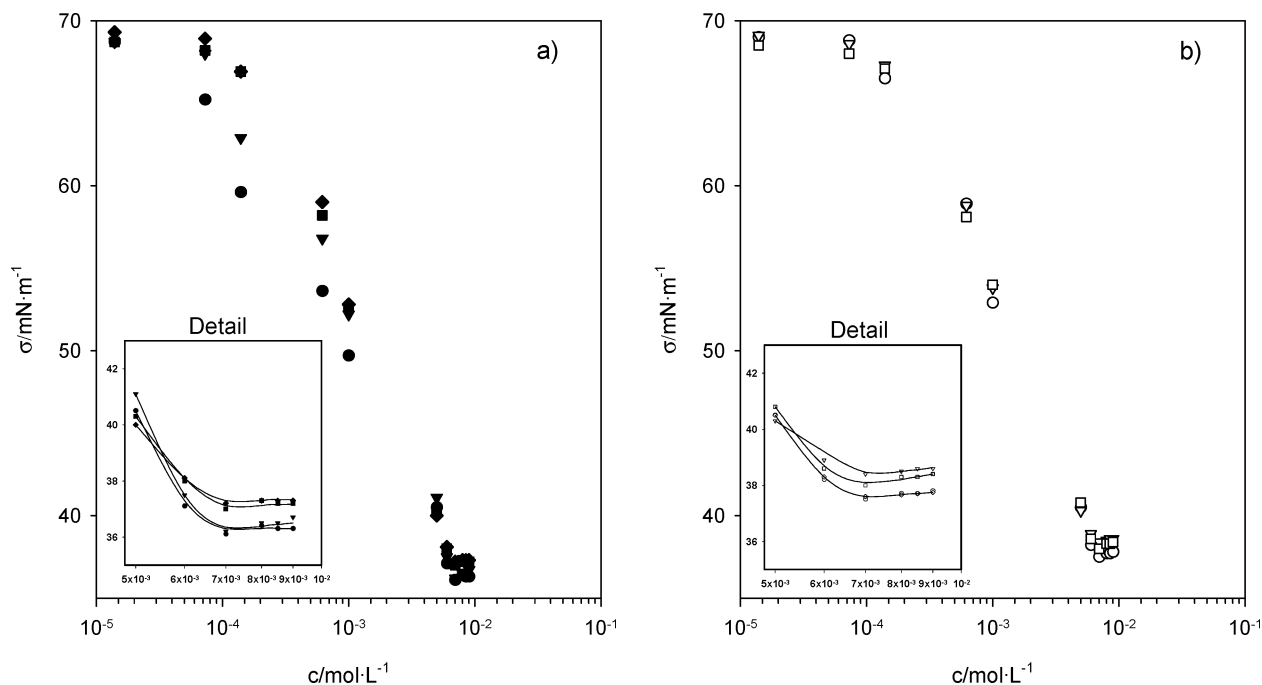


Figure 1. Surface tension vs molar concentration curves for sodium 1-dodecanesulfonate: (a) ●, pH 4; ▼, pH 5; ■, pH 6; ◆, pH 7; (b) ○, pH 8; □, pH 9; ▽, pH 10.

These results are very similar to those found in a recent study⁴ with sodium dodecyl sulfate (SDS), under the same experimental conditions. The results found with DSS are very different from that found in a previous work⁵ with sodium oleate, since the aqueous solutions of this collector are found strongly influenced by the pH of the flotation bath, above all in alkaline means.

Figure 1 shows the variation in surface tension of aqueous DSS solutions at various pH and different agent concentrations at temperature of 293.15 K. Surface tension is seen to decrease considerably when the surface active concentration is increased. The drop in surface tension as concentration is increased reveals the surfactant nature of DSS and, according to Centellas,⁸ is a characteristic of soaps, detergents, and surfactants. The area with constant surface tension was revealed, being the critical micelle concentration (cmc) of $7 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ for the range of pH between 4 and 10. This finding agrees with the cmc values reported by various authors, such as $5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ for Cabrerizo⁹ and $9.8 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ for Mukerjee and Mysels.¹⁰

Applying the thermodynamic treatment of adsorption at the liquid–gas interface in the presence of excess electrolyte, the Gibbs adsorption isotherm allows us to determine the values of surface excess concentration, Γ :

$$d\sigma = -yRT \Gamma d(\ln c) \quad (1)$$

where Γ represents the surface excess concentration, R is the universal gas constant, T is the absolute temperature, c is the molar concentration of the surface agent within the solution, σ is the surface tension, and $y = 1 + c/(c + c_{\text{NaCl}})$. Using eq 1, Γ may be calculated by adjusting the values for σ versus the $\ln c$ to a third-degree polynomial. Once the parameters for the polynomial have been obtained, the value of $-d\sigma/d(\ln c)$ is determined at different points of the polynomial.

From the DSS adsorption isotherm representations at pH 4, 6, 8, and 10 (Figure 2), it may be seen that in all cases the amount adsorbed increases as the surface agent concentrations is raised. Also, it may be seen that saturation is not reached;

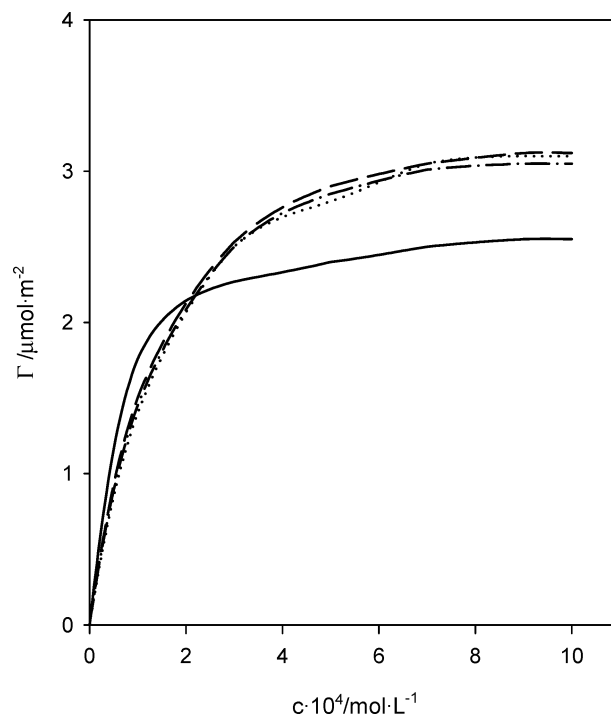


Figure 2. Surface excess concentration vs molar concentration curves at 293.15 K for sodium 1-dodecanesulfonate: —, pH 4; - - -, pH 6; ····, pH 8; - · - ·, pH 10.

however, from $6 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ of DSS, it increases very slightly. Because of this, it can be considered that the value of saturation (Γ constant) is found very near to $3.1 \text{ mol}\cdot\text{m}^{-2}$ at pH 6, 8, and 10 and at $2.6 \text{ mol}\cdot\text{m}^{-2}$ at pH 4. The results reported by Perea¹¹ for similar systems mainly agree with those obtained in this study.

Several kinds of equations of state have been proposed^{12–16} to describe the ionic surface agent monolayer adsorbed at the solution–air interface. The importance of these equations centers on the fact that they may be used to calculate thermodynamic magnitudes associated with adsorption.

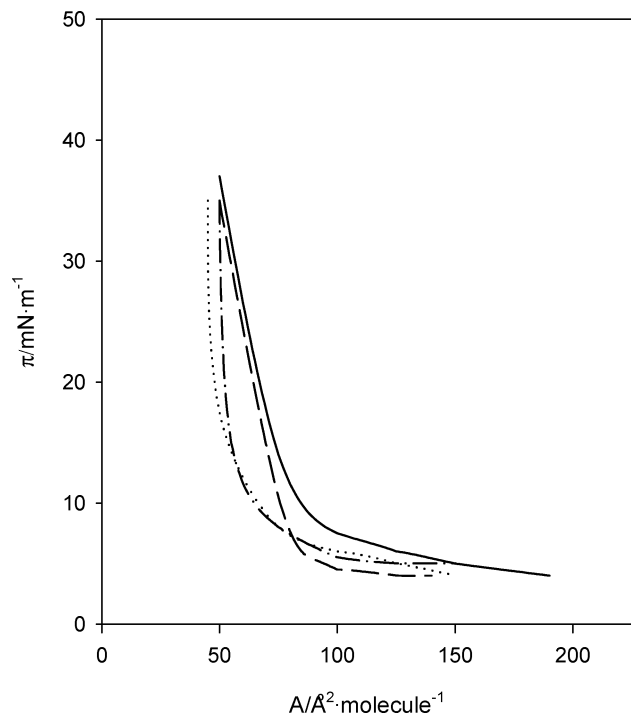


Figure 3. Surface pressure vs molecular area curves at 293.15 K for sodium 1-dodecanesulfonate: —, pH 4; - - -, pH 6; ···, pH 8; - · - ·, pH 10.

Surface pressure in a monolayer is

$$\pi = \sigma_o - \sigma \quad (2)$$

where σ_o is the surface tension of pure water and σ is the surface tension of the surfactant solution. Thus, the molecular area (A) is defined by the expression

$$A = 1/\Gamma N_A \quad (3)$$

where N_A is Avogadro's number. The experimental relationship between surface pressure (π) and molecular area (A) for the DSS solution–air interface at 293.15 K (Figure 3) was calculated from the data represented in Figure 2.

For an ideal monolayer, it has been established⁸ that

$$\pi A = kT \quad (4)$$

where k is the Boltzmann constant and T is the absolute temperature. However, ideal behavior undergoes a series of deviations based on the fact that molecules are dimensional entities and give rise to mutual interactions, which are that much greater when surfactants have a molecular charge. For this reason, real equations of state should be used, such as the equation proposed by Davies¹⁴ for a monolayer charged at the solution–air interface:

$$(\pi - \pi_s - \pi_r)(A - A_0) = kT \quad (5)$$

where A_0 is the molecular limiting area in the monolayer at high surface pressures, π_s is the contribution of surface pressure due the cohesion of van der Waals forces between surfactant hydrocarbonated chains, and π_r is the contribution of surface pressure due the repulsion of the polar groups of the adsorbed ions. The value of π_r is determined by

$$\pi_r = -6.03\sqrt{C_1} + 2kT/A \quad (6)$$

where C_1 is the concentration of the electrolyte in solution. The

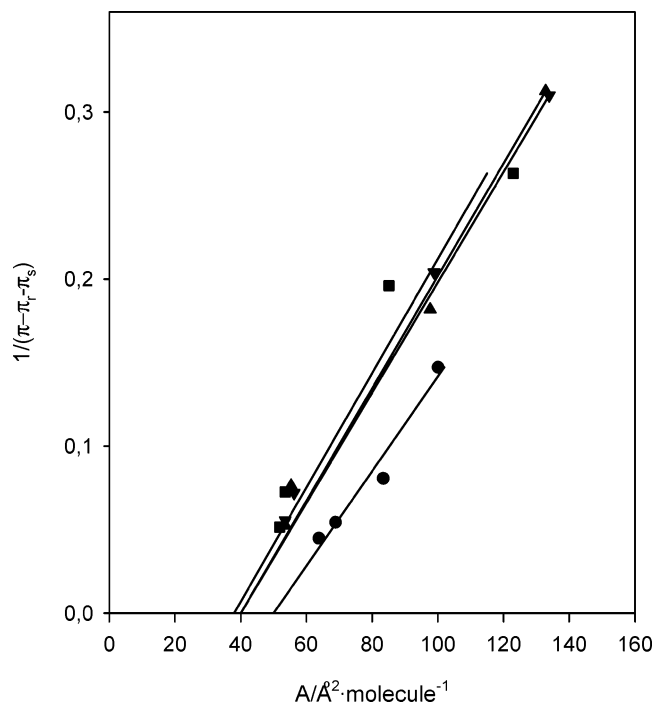


Figure 4. $1/(\pi - \pi_r - \pi_s)$ vs molecular area curves at 293.15 K for sodium 1-dodecanesulfonate: ●, pH 4; ■, pH 6; ▲, pH 8; ▼, pH 10.

Table 2. Values for A_0 , $\text{\AA}^2 \cdot \text{molecule}^{-1}$, Obtained from Equation 9 and Shown Graphically in Figure 4

	pH			
	4	6	8	10
eq 9	49	38	40	40
Figure 4	50.0	28.5	34.9	34.7

value of π_s is calculated from the empirical equation proposed by Tajima et al.:¹²

$$\pi_s = -K/A \quad (7)$$

where K , the proportionality constant, is determined by the equation proposed by Cabrerizo:⁹

$$K = (\phi - 1)kT + MkTA \quad (8)$$

where ϕ is the ordinate at source of the oblique asymptote and M is the slope of this asymptote, if $(\pi - \pi_r)kT$ is plotted against A .

Therefore, eq 5 becomes

$$(\pi + 6.03\sqrt{C_1} - 2kT/A - (\phi - 1)kT/A - MkT)(A - A_0) = kT \quad (9)$$

Values for A_0 at pH 4, 6, 8, and 10 were also obtained graphically, where by $1/(\pi - \pi_r - \pi_s)$ was plotted against A (Figure 4) where π_s is the contribution of surface pressure due the cohesion of van der Waals forces between surfactant hydrocarbonated chains, and π_r is the contribution of surface pressure due to the repulsion of the polar groups of the adsorbed ions. If linear dependence is deduced from this representation at the range of concentrations used, the value of the molecular limiting area (A_0) would be obtained by extrapolating to $1/(\pi - \pi_r - \pi_s) = 0$. The values for A_0 at pH 4, 6, 8, and 10 obtained by both procedures are given in Table 2.

So, the values calculated graphically at pH 4, 6, 8, and 10 are (50.0, 28.5, 34.9, and 34.7) $\text{\AA}^2 \cdot \text{molecule}^{-1}$, respectively. It may, therefore, be deduced that in some cases there is agreement between the values for A_0 , although in others there is a considerable difference between the analytical and the graphical

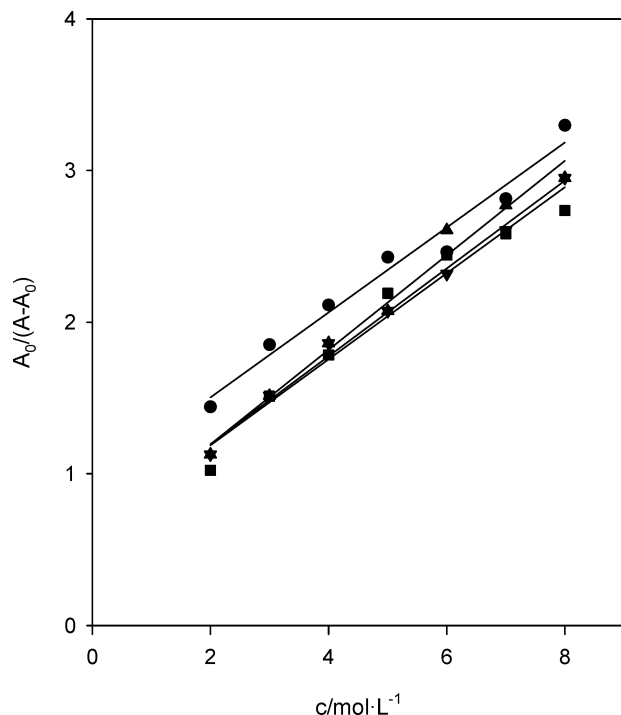


Figure 5. $A_0/(A - A_0)$ vs molar concentration curves at 293.15 K for sodium 1-dodecanesulfonate: ●, pH 4; ■, pH 6; ▲, pH 8; ▼, pH 10.

values. In this study, however, the value obtained from eq 2 was consistently used to fix a value for A_0 for the calculation of free standard adsorption energy. The finding agrees with the A_0 values reported by Perea¹¹ for SDS, (50 to 70) $\text{\AA}^2 \cdot \text{molecule}^{-1}$, while Cabrerizo⁹ gives a value of 21.3 $\text{\AA}^2 \cdot \text{molecule}^{-1}$. Likewise, the found values for A_0 in this work for DSS are very similar to those obtained for SDS (ionic surfactant similar to DSS) by various authors, such as 38 $\text{\AA}^2 \cdot \text{molecule}^{-1}$ by Tajima et al.;¹² 31 $\text{\AA}^2 \cdot \text{molecule}^{-1}$ by Padday;¹⁷ 50 $\text{\AA}^2 \cdot \text{molecule}^{-1}$ by Cook and Talbot;¹⁸ 40 $\text{\AA}^2 \cdot \text{molecule}^{-1}$ by Wilson et al.;¹⁹ and 44 $\text{\AA}^2 \cdot \text{molecule}^{-1}$ by Hines.³

Stern's adsorption model was used to calculate free standard adsorption energy at the DSS solution–air interface, $\Delta G_{\text{ads}}^\circ$. This model assumes that the adsorbed molecules are immobile and that adsorption occurs on specific areas of the surface, which is, in turn, homogeneous from the energy point of view. The equation thus obtained is

$$\frac{A_0}{A - A_0} = \frac{c}{55.5} \exp\left(-\frac{\Delta G_{\text{ads}}^\circ}{RT}\right) \quad (10)$$

where A_0 is calculated from eq 9, R is the constant for ideal gases, T is absolute temperature, and c is the molar concentration of the surface agent. $\Delta G_{\text{ads}}^\circ$ is obtained simply if, there is a linear relationship when plotting $A_0/(A - A_0)$ against c (Figure 5). Representations for the four pH values studied at 293.15 K are given in Figure 5 where a clear linear relationship for all four cases is seen. This allows values for $\Delta G_{\text{ads}}^\circ$ to be obtained through the slope, and these are (−29.00, −29.40, −29.61, and −29.44) $\text{kJ} \cdot \text{mol}^{-1}$ at pH 4, 6, 8, and 10, respectively. Adsorption

at the solution–air interface is also seen to cause a decrease in free energy for DSS. This indicates that the surfactant molecules will be adsorbed and arranged at this interface in such a way that the chains move away from the aqueous phase. Contrary to sodium oleate, however, the variation in pH in the DSS solution does not modify free standard adsorption energy substantially. The value given by Cabrerizo⁹ of $-29.90 \text{ kJ} \cdot \text{mol}^{-1}$ for DSS agrees with that found in the present study.

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