

Effect of Water-Soluble Polymers on the Surface Properties of 3-(Dimethyldodecylammonio)Propanesulfonate in Aqueous Solutions

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Using surface tension measurements the interaction between 3-(dimethyldodecylammonio)propanesulfonate, DPS, and poly(vinylpyrrolidone), PVP, poly(acrylic acid sodium salt), PAC, and poly(sodium 4-styrenesulfonate), PSS, has been studied. No interaction between PVP and PAC and the surfactant was observed, while a significant interaction with PSS was detected. The dependence of the equilibrium surface tension on the surfactant concentration is interpreted by means of the phase transition model (*Langmuir* 1991, 7, 1055). Dynamic surface tension of DPS solutions in the absence and presence of polymers was determined by using the drop-volume tensiometer. The surfactant adsorption kinetics on the interface is a diffusion-controlled process. Two asymptotic solutions, at long times and at short times, to the classic Ward and Tordai equation were used to fit dynamic results. At long times there is evidence of the intermolecular attractions between the surfactant molecules at the interface in good agreement with the equilibrium surface tension results.

Introduction

Surfactant–polymer mixtures are commonly utilized in many practical applications, because mixtures often provide more desirable properties than the pure surfactants.^{1–3} Nonionic water-soluble polymers and ionic surfactants are the most investigated polymer–surfactant systems. In these mixtures an important question that remains to be solved is the role of surfactant charge on the tendency to interact with polymers. It is known that there is a strong interaction between uncharged polymers and anionic surfactant;^{4–6} cationic surfactants interact only weakly with poly(ethylene oxide)⁷ or poly(vinylpyrrolidone)⁷ while for more hydrophobic polymers such as hydroxypropylcellulose,⁸ poly(propylene oxide),⁴ or poly(ethylene glycol)⁹ significant interactions were detected. Several theories have been developed to explain this behavior. The most popular one considers that the headgroups of cationic surfactants are larger than the anionic ones, reducing the access of the polymer to the surface of the micelles.¹⁰ However, results obtained by systematic modification of the kind and size of the headgroups showed that the interaction between ionic surfactants and polymers can be related with the polymers hydration shell.^{4,11}

It has been observed that the interaction takes place when the surfactant concentration is higher than a value referred to as *cac*, critical aggregation concentration. At this concentration starts the surfactant adsorption on the polymer chain in the form of aggregates. Once the polymer is saturated with the surfactant, the excess of surfactant molecules forms free micelles, and at higher surfactant concentrations polymer-bound aggregates coexist with free micelles.¹²

To study the role of the surfactant charge on the polymer–surfactant interaction, we have studied the interaction between a zwitterionic surfactant 3-(dimethyldodecylammonio)propanesulfonate, (DPS), whose hydrophilic polar heads carry both a negative and a positive charge, and water-soluble polymers. The polymers selected are the following: poly(vinylpyrrolidone), PVP, poly(acrylic acid sodium salt), PAC, and poly(sodium 4-styrenesulfonate), PSS.

The interaction was studied by determining the cmc of micelles in the absence and the presence of polymers by using surface tension measurements.

On the other hand, several technological processes use surfactant solutions under nonequilibrium conditions. In these applications, the dynamic surface tension is an important property which allows to obtain kinetic information of the surfactant adsorption at the interface. Therefore the dynamic surface tensions of dilute solutions of surfactant without and with different concentrations of polymers were obtained. The static and dynamic surface tensions are analyzed according to different models described in the literature.

Experimental Section

Materials. 3-(Dimethyldodecylammonio)propanesulfonate, DPS, from Fluka, was used without further purification. The surfactant showed no minimum in the surface tension–concentration plot (Figure 1), confirming its purity. Poly-

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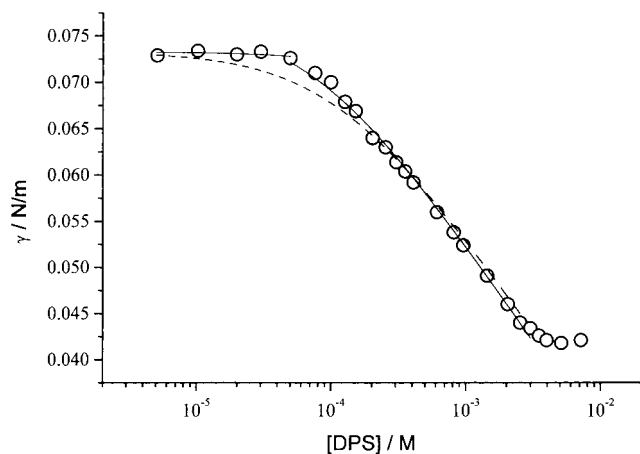


Figure 1. Equilibrium surface tension values of DPS aqueous solutions. Dotted line is calculated according to the Langmuir model, eq 5, and solid lines are calculated according to the phase transition model, eqs 6 and 7 and parameters in Table 2.

(vinylpyrrolidone) fractions, PVP (MW = 10 000 g/mol) and poly(acrylic acid sodium salt), PAC (MW = 20 000 g/mol) fractions were from Fluka. Poly(sodium 4-styrenesulfonate), PSS (MW = 75 000 g/mol) was from Aldrich. The molecular weights were provided by the manufacturers. The pH of pure DPS and mixtures containing PVP and PSS polymers was 5.3–6.0, while pH = 9.5 is measured in PAC solutions.

The solutions were prepared with water obtained after treatment with a Milli-Q system from Millipore and presented a conductivity of around 0.3 $\mu\text{S}/\text{cm}$.

Surface Tension Measurements. The measurements of the equilibrium and the dynamic surface tensions were carried out with a drop tensiometer TVT-1 from LAUDA, Germany,¹³ using one syringe of 5 mL. The steel inner radius of the capillary used for measurements of the equilibrium surface tensions was 1.08 mm, and that corresponding for measuring the dynamic surface tension was of 1.345 mm.

The drop tensiometer TVT-1 presents three different modes of measurements: the dynamic measuring mode, the classic version of the drop-volume method applicable to the measurement of the static and dynamic surface tensions of pure liquids, and the standard and quasi-static modes for the measurement of the static and dynamic surface tensions of surface active agents, respectively.

In this work the equilibrium surface tensions were carried out with the so-called standard mode and the dynamic ones with the quasi-static mode. In the former the drop formation consists of different stages. At the beginning the drop is formed with a rather high speed. Then the dosing rate decreases automatically with increasing drop volume. By this measuring mode hydrodynamic influences are avoided because the final dosing rate just before the drop detachment is always very low. The quasi-static mode consists of a two-step process: in the first one, a drop with a certain volume is quickly formed at the capillary. This volume must be smaller than the critical volume according to the actual interfacial tension at the drop surface and the drop will remain at first at the tip of the capillary. In the second step, while keeping the drop volume constant, the interfacial tension decreases as a result of adsorption and after a time it reaches a value corresponding to the critical volume and the drop detaches. The time interval between the drop formation and detachment is measured, and the next drop is formed by the same principle.

All measurements were performed at 25.00 ± 0.01 °C. The temperature in the tensiometer was controlled with a low-temperature thermostat RM 6 from LAUDA. The value of the equilibrium surface tension of water using the standard method is (73.3 ± 0.8) mN/m. This value slightly differs from the literature value. Discrepancy is probably due to the measuring mode, standard mode, designed for systems containing surface-active agents. We use this value for comparative purposes to study the

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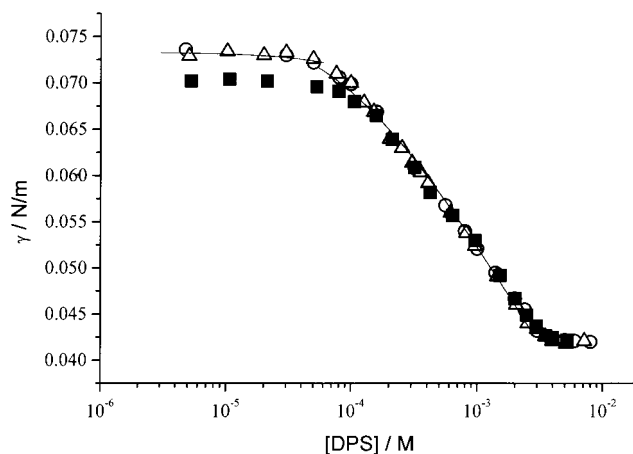


Figure 2. Effect of addition of polymers on equilibrium surface tension values of DPS aqueous solution: circles, DPS; triangles, DPS and 0.05% PAC; squares, DPS and 0.05% PVP. The line is calculated according to the phase transition model, eqs 6 and 7 and PAC parameters in Table 2.

effect of the addition of surfactant and polymer-surfactant mixtures on the water surface tension. Therefore, it is necessary to compare results obtained in the same experimental conditions. When the classic dynamic mode was used, the value obtained was (71.6 ± 0.5) mN/m, in excellent agreement with the water surface tension found in the literature.¹⁴

Results and Discussion

Determination of the Critical Micelle Concentration by Surface Tension Measurements. The study of the interaction between DPS and polymers was carried out by determining the critical micelle concentration, of micelles in the absence and the presence of polymers.

The critical micelle concentration, cmc, was obtained by the surface tension method using the drop tensiometer TVT-1 from Lauda. Surface tension decreases rapidly with increasing surfactant concentration before reaching a near plateau region. The measured surface tension values are plotted as a function of the surfactant concentration, and the cmc is estimated from the break point in the resulting curve. The curve corresponding to the pure surfactant DPS is plotted in Figure 1. The cmc of the pure DPS surfactant was 3.66 mM, in agreement with the value found in the literature.¹⁵

The experiments were repeated to determine the cmc of micellar aggregates containing polymers. The addition of these polymers to DPS aqueous solutions induces two different behaviors as a function of the kind of polymer. When PVP and PAC were added, the trend of equilibrium surface tension/surfactant concentration curves is similar to that in the absence of polymers; i.e., only a discontinuity in these curves was detected (Figure 2). The cmc values of micelles containing 0.05% (w:w) PVP and 0.05% (w:w) PAC are 3.7 and 3.4 mM, respectively. These values agree with that of the pure DPS; thus, it can be concluded that there is no interaction between these polymers and DPS.

In contrast when different concentrations of poly(sodium 4-styrenesulfonate), PSS, were added, the curves present different regions with three break points (T_1 , T'_2 , and T_2), Figure 3. This behavior has been observed in other mixtures^{16–18} and was interpreted as follows:¹⁸ below T_1 ,

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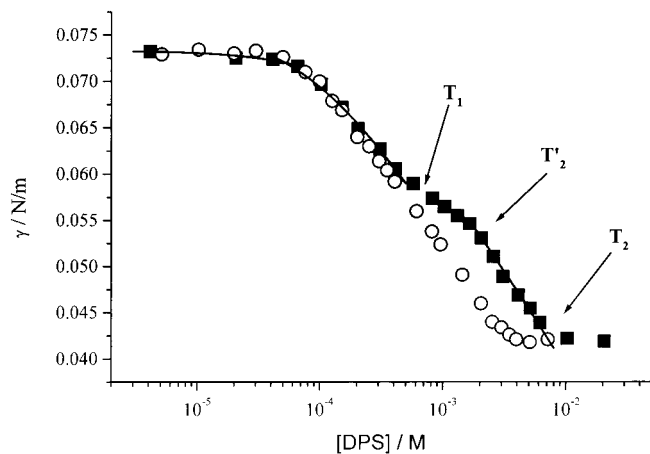


Figure 3. Effect of addition of 0.05% PSS on equilibrium surface tension values of DPS aqueous solution: circles, DPS; squares, DPS and 0.05% PSS. The lines are calculated according to the phase transition model, eqs 6 and 7 and parameters in Table 2.

Table 1. Cmc Values of 3-(Dimethyldodecylammonio)propanesulfonate in the Presence of Different PSS Concentrations

% PSS	T_1 /mM	T_2 /mM
0.05	0.67	7.66
0.075	0.70	10.3
0.1	0.68	11.4
0.12	0.67	13.8

the polymer and surfactant molecules are supposed to be free in solution, and at T_1 surfactant concentration starts the adsorption on the polymer chain. This concentration is usually lower than the critical micelle concentration of pure surfactant, cmc, and is named cac. The T_1 values obtained at different PSS concentrations are listed in Table 1. As can be seen in the table, this value is independent of PSS concentration. It is assumed that just above T_1 all the surfactant added binds to the polymer and the free surfactant concentration remains constant at a value of T_1 . In the intermediate region between T'_2 and T_2 the concentration of free surfactant increases from T_1 to cmc¹⁸ and T_2 corresponds to the polymer saturation and to the formation of surfactant micelles in the bulk. T'_2 has been detected by other authors^{17–19} and was defined as the stoichiometric concentration for binding.¹⁸ According to this model, $T_2 - \text{cmc}$ is the amount of bound surfactant.¹⁸ To confirm this fact, we represent T_2 vs the polymer concentration, Figure 4. As can be seen in the figure, T_2 linearly varies with the polymer content, and from the slope, the number of monomer surfactant molecules needed to saturate the polymers was calculated; we found a value of 580 ± 70 . From this value the surfactant molecules/polymer repeat unit ratio is calculated to be around 1.5. The intercept, $(3.8 \pm 0.9) \times 10^{-3}$ M, agrees to the cmc of the surfactant in water.

Results may indicate that the interaction could be electrostatic in origin, even though no interaction between DPS and poly(acrylic acid sodium salt) was observed. In this case the weak protonation of the carboxylate group, detected by the increase of pH (9.5), seems prevents the interaction between DPS and PAC.

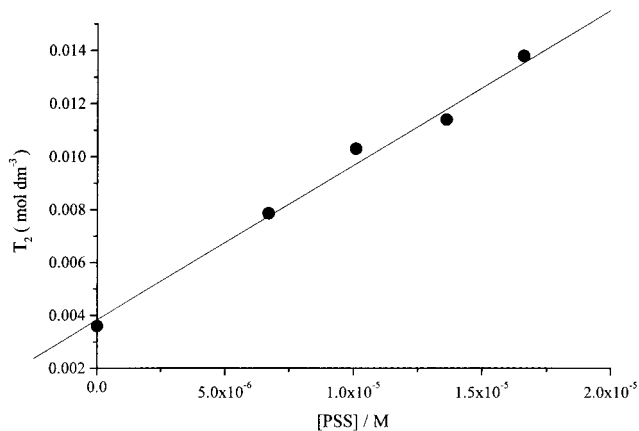


Figure 4. Dependence of T_2 with PSS concentration.

Interpretation of the Equilibrium Surface Tension Data. As is well-known from the dependence of the equilibrium surface tension on surfactant concentration, the surface excess concentration of surfactant adsorbed at the interface, Γ_∞ , and the minimum area per molecule, A_{\min} , can be calculated by using the Gibbs adsorption equation:

$$\Gamma = -(RT)^{-1}(d\gamma/d \ln C) \quad (1)$$

According to eq 1 the slope of the curve γ vs $\ln C$ is proportional to Γ . However, the surface tension curves corresponding to the surfactant without and with polymers show that at a distinct concentration referred as critical, C_c , the concentration at the interface increases greatly with a little change in both the surface tension and the bulk concentration. At surfactant concentrations lower than C_c , the surface tension curve exhibits a plateau, induction period. After sufficient adsorption, the addition of surfactant molecules is not possible without large changes in surface tension; then the surface tension decreases rapidly signaling the end of the induction period. This behavior has been observed by other authors.^{20–22} The origin of this induction period is attributed to cohesive forces²³ and cannot be interpreted by the Gibbs adsorption model. Therefore different models have been developed to explain this behavior.

Molecular adsorption on the fluid surface is usually interpreted by using the Langmuir adsorption isotherm. This model considers that the adsorption occurs onto a particular site and the energetic barrier for transfer of the surfactant between sites is much larger than the thermal energy. The rates of adsorption and desorption in this model are given by

$$d\Gamma/dt = \beta \exp(-E_a/RT) C_s(\Gamma_\infty - \Gamma) - \alpha \exp(-E_D/RT) \Gamma \quad (2)$$

where C_s is the sublayer concentration, β , α , E_a , and E_D are the preexponential factors and the energies of activation for adsorption and desorption, respectively, and t denotes time. This model assumes that the activation energies are independent of the surface coverage. From eq 2 it can be obtained that

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$$\Gamma/\Gamma_\infty = C/(C + a) \quad (3)$$

where a represents the concentration at which 50% of Γ_∞ has been reached, and is given by

$$a = (\alpha/\beta) \exp[(E_a - E_D)/RT] = k_D/k_a \quad (4)$$

k_D and k_a represent the desorption and adsorption rate constants, respectively; C is the bulk surfactant concentration. By combination of eqs 1 and 3 the so-called Langmuir–Szyszkowski equation is obtained:

$$\gamma = \gamma_0 - RT\Gamma_\infty \ln(1 + C/a) \quad (5)$$

where γ_0 is the surface tension of the solvent. In this case we use the value obtained in this work, 73.3 mN/m.

The pure DPS experimental results have been fitted to eq 5, and the best fitting parameters are the following:

$$\Gamma_\infty = 3.7 \times 10^{-6} \text{ mol/m}^2$$

$$a = 0.00012 \text{ mol/dm}^3$$

Figure 1 shows the experimental results along the surface tension values calculated from eq 5 and the fitting parameters. As can be seen from the figure, the Langmuir model cannot adequately interpret the induction period. This fact was expected because this model does not consider intermolecular attractive forces to explain the cooperative behavior detected around the critical surfactant concentration, C_c . The model developed by Lin,²⁴ the phase transition model, interprets this behavior by intermolecular attractions which lead to the formation of a liquid phase from a gaseous state. Prior to the critical surface coverage intermolecular attractions are not significant and the adsorption state is essentially gaseous. Therefore the adsorption may be described by the Langmuir model. At the critical coverage the expanded liquid begins to develop on the surface coexisting with the gaseous monomer phase. When more surfactant is added to the system, the expanded liquid grows at the expense of the gaseous phase with the surface tension and the bulk sublayer concentration constants. The addition of more surfactant molecules leads to the complete disappearance of the gaseous phase and the surface is uniformly covered by the liquid phase. The model assumes that the monomer exchange between this phase and the subsurface of the bulk is also described by a Langmuir isotherm. According to these assumptions the equilibrium surface tension is related to the bulk surfactant concentration by the following equations:

$$C < C_c: \quad \gamma(C) = \gamma_0 - \Gamma_\infty RT \ln(1 + C/a_m) \quad (6)$$

$$C > C_c: \quad \gamma(C) = \gamma_0 - \Gamma_\infty RT \ln\{(a_1 + C)(a_m + C_c) / (a_1 + C_c)a_m\} \quad (7)$$

where a_m and a_1 are the parameters of the Langmuir isotherm corresponding to the surfactant adsorption from the gaseous phase and from the bulk, respectively. The parameters obtained in the fitting procedure of the experimental results to eqs 6 and 7 are given in Table 2. Figure 1 shows the good agreement between experimental results corresponding to pure DPS and eqs 6 and 7.

In the case of polymer–surfactant mixtures the experimental results were also fitted to these equations,

Table 2. Best Fitting Parameters for 3-(Dimethyldodecylammonio)propanesulfonate Aqueous Solution in the Absence and Presence of Polymers

% polymer	$\Gamma_\infty, 10^6$ mol/m ²	$a_m, 10^3$ mol/dm ³	$a_1, 10^3$ mol/dm ³	$C_c, 10^5$ mol/dm ³
0	3.8 ± 0.5	0.8 ± 0.3	0.082 ± 0.004	4.2 ± 0.3
0.05% PVP	3.8 ± 0.8	1.0 ± 0.5	0.098 ± 0.006	8.7 ± 0.5
0.05% PAC	3.9 ± 0.6	0.5 ± 0.2	0.092 ± 0.004	4.2 ± 0.4
0.05% PSS				
$C < T_1$	3.8 ± 0.7	0.35 ± 0.06	0.099 ± 0.004	5.2 ± 0.4
$C > T_2$	3.8 ± 0.7	0.35 ± 0.06	0.261 ± 0.006	5.0 ± 0.3
0.075% PSS				
$C < T_1$	3.7 ± 0.6	0.27 ± 0.02	0.11 ± 0.02	5.0 ± 0.1
$C > T_2$	3.7 ± 0.6	0.27 ± 0.02	0.200 ± 0.005	5.0 ± 0.2
0.10% PSS				
$C < T_1$	3.9 ± 0.8	0.5 ± 0.1	0.127 ± 0.009	5.6 ± 0.7
$C > T_2$	3.9 ± 0.8	0.5 ± 0.1	0.430 ± 0.004	5.5 ± 0.5
0.12% PSS				
$C < T_1$	3.8 ± 0.6	0.500 ± 0.009	0.132 ± 0.006	4.6 ± 0.4
$C > T_2$	3.8 ± 0.6	0.500 ± 0.009	0.522 ± 0.008	5.4 ± 0.9

and the best fitting parameters are summarized in Table 2. In mixtures containing PSS polymer the three regions of these curves were fitted. The first region corresponds to surfactant concentrations lower than C_c , so was fitted to eq 6. The second one is the region comprised between $C_c < C < T_1$, and the third region is between T_2 and T_2 ; both regions were fitted to eq 7. Figures 2 and 3 show good agreement between the experimental results and those calculated from eqs 6 and 7 using the fitting parameters of Table 2.

Examination of the fitting parameters shows the following: (i) the maximum surface excess concentration, Γ_∞ , is not affected by the addition of polymers. We found an average value of 3.8×10^{-6} mol/m². From this value it is possible to calculate the minimum area per molecule at the surface, A_{\min} , using the following relation: $A_{\min} = (N\Gamma_\infty)^{-1}$; N is Avogadro's number. The value found in this work is 0.44 nm². This value suggests that the orientation of the surfactant molecules is almost perpendicular to the surface.²⁵ (ii) The critical concentration, C_c , remains constant at a value of around 5×10^{-5} M when polymers are added, except in the case of PVP, which increases until 8.7×10^{-5} M. The weak surface-active nature of PVP (the surface tension value of its aqueous solution is 70 mN/m) can be responsible of this behavior. (iii) The parameter a_m is not affected by the addition of polymers. The a_1 parameter presents similar behavior when PVP and PAC polymers are added, while it increases with the addition of PSS, and the effect is more pronounced in the $C > T_2$ range.

Interpretation of the Dynamic Surface Tension.

The dynamic surface tensions of solutions containing different surfactant concentrations without and with polymers were obtained by using the quasi-static method. In all cases the surfactant concentration was below its cmc to avoid the effect of the diffusion of micellar aggregates. Figure 5 shows some of these results.

The main theoretical model to analyze the dynamic surface tension curves considers the dynamic adsorption at the interface as a diffusion-controlled process.²⁶ The equation obtained according to this model is the classic equation of Ward and Tordai,²⁶ which cannot be solved analytically; as a consequence, the experimental results are not fitted to this equation. However, asymptotic solutions at long and at short times were obtained and have been successfully applied to ionic and nonionic

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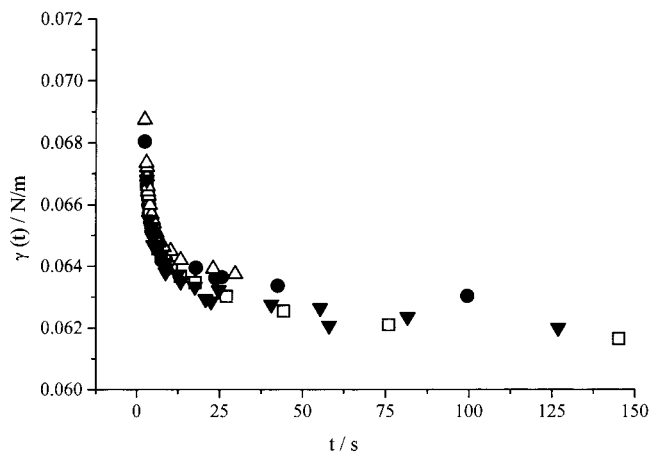


Figure 5. Dynamic surface tension data for solutions of 0.1 mM DPS dissolved in (●) water, (□) 0.05% PAC, (△) 0.05% PSS, and (▼) 0.05% PVP.

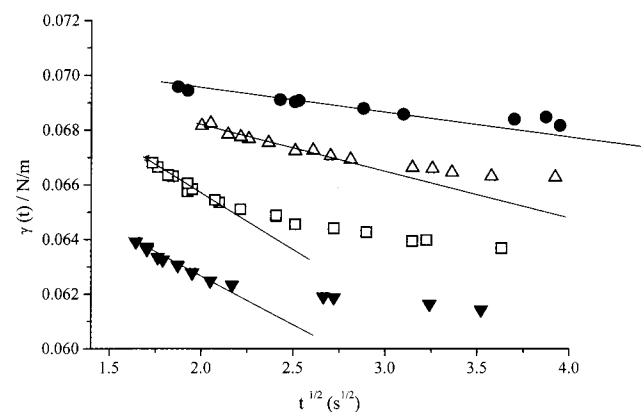


Figure 6. Dynamic surface tension data plotted vs $t^{1/2}$. The lines are least-squares fits to the data as $t \rightarrow 0$: (●) DPS 0.04 mM; (□) DPS 0.1 mM and PAC 0.05% (w:w); (△) DPS 0.064 mM and PSS 0.05%; (▼) DPS 0.15 mM and PVP 0.05%.

surfactants.²⁷ In particular for nonionic surfactants the equations in the form of derivatives are the following:

$$\left[\frac{d\gamma(t)}{dt^{1/2}} \right]_{t \rightarrow \infty} = \Gamma^2 RT C (\pi/4D)^{1/2} \quad (8)$$

$$\left[\frac{d\gamma(t)}{dt^{1/2}} \right]_{t \rightarrow 0} = -2RT(D/\pi)^{1/2} \quad (9)$$

where D represents the diffusion coefficient of the surfactant. The validity of these equations is tested as applied to pure DPS solutions and to mixtures of DPS and polymers.

Asymptotic Solution at Short Times. To fit experimental results to eq 9, the dynamic surface tension was plotted vs $t^{1/2}$. Figure 6 shows some results corresponding to DPS aqueous solutions without and with polymers. As can be seen in the figure, results are linear at short times as expected for a diffusion process. From slopes the diffusion coefficients were calculated. These values are in Table 3. Examination of values shows that the addition of polymers does not modify the diffusion coefficient of DPS, except in the case of PVP.

Taking into account that dynamic surface tension measurements correspond to solutions in which monomer surfactant molecules are predominant, results indicate

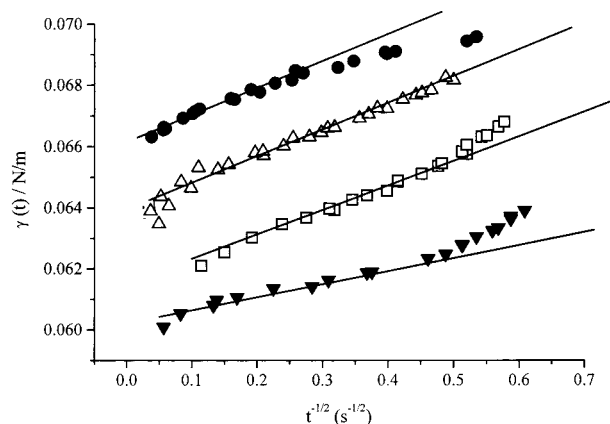


Figure 7. Dynamic surface tension data plotted vs $t^{-1/2}$. The lines are least-squares fits to the data as $t \rightarrow \infty$: (●) DPS 0.04 mM; (□) DPS 0.1 mM and PAC 0.05% (w:w); (△) DPS 0.064 mM and PSS 0.05%; (▼) DPS 0.15 mM and PVP 0.05%.

Table 3. Diffusion Coefficients of DPS in Aqueous Solutions without and with Polymers Obtained from the Ward and Tordai Asymptotic Solutions at Short Times and at Long Times

% polymer	$(D, 10^{10}/\text{m}^2/\text{s})$	
	$t \rightarrow 0$	$t \rightarrow \infty$
0	1.77 ± 0.08	7.7 ± 0.5
0.05% PVP	0.85 ± 0.02	26 ± 0.4
0.05% PAC	1.78 ± 0.09	28 ± 0.2
0.05% PSS	1.6 ± 0.1	20 ± 0.5
0.075% PSS	1.7 ± 0.1	27 ± 0.2
0.10% PSS	1.4 ± 0.2	29 ± 0.2
0.12% PSS	1.2 ± 0.1	34 ± 0.3

that the diffusion of DPS monomers is not affected by the addition of PAC and PSS. In the case of PVP the diffusion coefficient weakly decreases with regard to that of pure DPS.

Asymptotic Solution at Long Times. Dynamic surface tension values plotted vs $t^{-1/2}$ are some curves represented in Figure 7. The data are linear at long times (short $t^{-1/2}$ values), indicating that the process is also diffusion-controlled at long times, eq 8. The lines are fitted, and from the slopes the D values are calculated. These values are collected in Table 3. Examination of the diffusion coefficients at long and short times shows the following: (i) the D values at long and short times do not agree and, in all cases, the diffusion coefficients obtained at short times are lower than those at long times; (ii) the difference between these D values is always greater when polymers are present in solution. These results indicate that the surfactant monomer molecules are diffused to the interface more quickly at long times. This fact could be due to the existence of the intermolecular attractions when the interface is sufficiently occupied. This is consistent with results obtained by equilibrium surface tension measurements. These attractive forces can be responsible for the increase of the diffusion coefficient at long times. The addition of water-soluble polymers increases the surfactant intermolecular attractions at the interface as compared with those at the air-water interface.

Conclusions

The surface tension measurements of 3-(dimethyldecylammonio)propanesulfonate aqueous solutions without and with the polymers poly(vinylpyrrolidone), PVP, poly(acrylic acid sodium salt), PAC, and poly(sodium 4-styrenesulfonate), PSS, support the existence of inter-

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actions between DPS surfactant and PSS. The results obtained in this work show that the interaction starts at a surfactant concentration, c_{ac} , lower than the cmc of pure surfactant. The c_{ac} value is independent of the polymer concentration. Above this concentration the surfactant binds to the polymer and, after polymer saturation, the free surfactant concentration increases until it reaches the cmc of aqueous surfactant and pure surfactant micelles are obtained. The dependence of the equilibrium surface tension with the surfactant concentration is interpreted by means of the phase transition model. The dynamic surface tensions of DPS solutions without and with different polymer concentrations indicate that the sur-

factant adsorption kinetics is a diffusion-controlled process. The diffusion coefficients and the equilibrium surface tension show the existence of intermolecular attractions between surfactant molecules at the interface even in pure surfactant solutions.

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