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# Surface properties of poly($N$-monoalkylmaleamic acid-alt-styrene) sodium salts: effect of the molecular weight and the side chain length

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## Abstract

The surface properties of poly($N$-monoalkylmaleamic acid-alt-styrene) sodium salts are studied as a function of the molecular weight and the size of the linear alkyl lateral chain of the polyelectrolyte. The experimental results are well described by the Gibbs–Szyszkowski treatment. Both the surface tension behavior and the standard free energy of adsorption depend on the polyelectrolyte side chain and on the average molecular weight, $M_w$. An $M_w$-dependent contribution to the free energy of adsorption ranging from $-1.21$ to $-1.05$ kJ for mole of methylene groups is found. The area covered by monomer units increases with $M_w$ and the sizes of side chains are similar to those reported in small-molecule systems. The nature of the functional group amide in the side chain has practically no effect on the surface properties as compared with the ester group in this kind of polyelectrolytes.

*Keywords:* Surface properties; Poly($N$-monooctylmaleamic acid-alt-styrene) sodium salts; Molecular weight; Gibbs adsorption

## 1. Introduction

The surface properties of amphipathic polyelectrolytes are a topic of great interest from both basic and technological points of view [1,2]. This kind of polyelectrolyte is formed by a monomer unit which is structurally similar to a simple low-molecular-weight detergent molecule and for this reason it has been called polysoap. In a previous work [3] the behavior of the surface tension, $\gamma$, of synthetic polyelectrolytes derived from an alternating 1:1 poly(maleic acid-co-styrene) at the air–water interface was studied. The decrease of the surface tension was proportional to the side-chain length of the polyelectrolyte, whereas the results of the excess surface concentration, as well as the areas covered by monomer unit and the free energy of adsorption, were all comparable with those reported in small-molecule systems in spite of the high molecular weight of the solute. The influence of the nature of the monomer unit on the surface properties of several synthetic anionic and cationic polyelectrolytes was studied by Okubo [4]. The behavior is mainly determined by the hydrophobic character of the counterion in the case of cationic polyelectrolytes, whereas anionic polymers such as sodium polyacrylate and polystyrene sulfonate present low surface activity due to the incapacity of these polyelectrolytes to separate their hydrophobic and hydrophilic moieties at the surface.

As far as we know, few studies of the influence of the molecular weight on the surface properties of amphipathic polymers have been reported. The general view of high-molecular-weight samples is that this influence is minor if it exists. Nevertheless, for oligomers [5] below the concentration of intramolecular aggregation a remarkable influence of $M_w$ on surface properties seems to exist. On the other hand, Cao [6] reported that the equilibrium spreading pressures of monolayers of polyethylene oxide are dependent on its $M_w$, whereas the surface properties of bovine serum and human serum albumin, which have practically the same $M_w$ but different amino acid sequences, are dissimilar [7]. The aim of the present work is precisely to analyze the influence of the molecular weight of polyelectrolytes on the surface properties of a series of poly($N$-monoalkylmaleamic acid-

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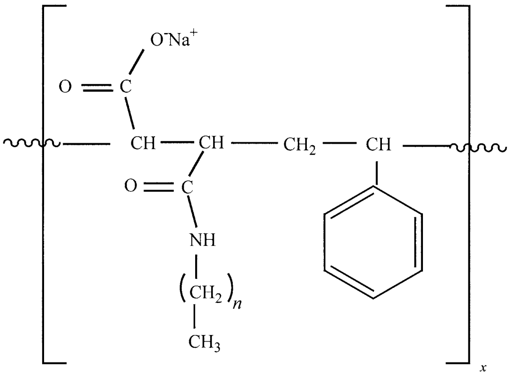
alt-styrene) sodium salts. The structure of the comonomeric unit is the following:



$n = 2, 7, 9, 11$

## 2. Experimental

Poly(maleic anhydride-alt-styrene), AM-alt-Sty, of $M_w$ 45,000 and 125,000 was synthesized by radical polymerization in anhydrous benzene at 55 °C under a nitrogen atmosphere, mixing an equimolar amount of maleic anhydride and styrene with $\alpha,\alpha$-azobisisobutyronitrile (0.3% mole with respect to the monomers) as initiator. The white solids obtained were filtered and washed in Soxhlet with anhydrous benzene in order to eliminate impurities and oligomers, and were dried under vacuum. The AM-alt-Sty polymer with $M_w$ 1600 was a commercial sample from Aldrich, Milwaukee, USA. The polyelectrolytes used here were named P16, P450, and P1250 for $M_w$ 1600, 45,000, and 125,000, respectively.

Poly($N$-monoalkylmaleamic acid-alt-styrene), AMNC$_n$-alt-Sty, with $n = 3$, 8, 10, and 12, was synthesized by refluxing AM-alt-Sty with the respective linear $n$-alkylamines in acetonitrile. Reactions were considered finished when the IR band of the carbonyl group of the maleic anhydride at 1825 cm$^{-1}$ disappeared completely and the IR band of the amide carbonyl group of 1625 cm$^{-1}$ appeared. In order to obtain the sodium salts, polymers were treated with aqueous 10 w/v% $NaHCO_3$ and the resulting solutions were finally dialyzed and lyophilized. Polyelectrolytes were characterized by IR and $C^{13}$ NMR spectroscopy.

The surface tension measurements were performed at 25 ± 0.01 °C according to the Du Noüy method in a Krüss Model K-8 interfacial tensiometer.

The average molecular weight of the synthesized polymers was estimated by solution viscosity measurements in THF at 30 °C using the relationship [8]

$$[\eta] = 5.07 \times 10^{-5}\,\mathrm{M}^{0.81}. \tag{1}$$

Bidistilled and ultrafiltered water with a surface tension of 71.0 dyn/cm was used. All other reagents used were of analytical grade.

## 3. Results and discussion

Figures 1a–1d show the dependence of the surface tension in the high-dilution zone as a function of polymer concentration, $m$, in moles of comonomer unit/l for all the polyelectrolytes studied here. These figures show the $\gamma$ behavior at constant side-chain length for the three different $M_w$. As can be seen, $\gamma$ decreases with the polyelectrolyte concentration until a plateau seems to be reached. Moreover, in all cases $\gamma$ is clearly dependent on the molecular weight of the polyelectrolyte; i.e., the slope $d\gamma/dm$ is more negative as the molecular weight of the polyelectrolyte decreases. On the other hand, at constant $M_w$ the $\gamma$ lowering is more pronounced as the side chain length increases as can be observed in Figs. 2a–2c. Similar behavior was found in aqueous solutions of poly(monoalkylmaleic acid-alt-styrene) sodium salts in the same range of concentration [3] keeping $M_w$ constant. These results reflect the fact that the surface properties are practically independent of the type of functional group of the polyelectrolyte amide or ester [3] connecting the side aliphatic chain with the main chain. However, there is a marked effect of $M_w$ on the polyelectrolyte surface activity for the same side chain.

In order to quantify and compare the adsorption process at the surface the Gibbs equation was used [4],

$$\Gamma = -\left[\left(|Z_p Z_g|\right)/\left(|Z_p| + |Z_g|\right)\right] RT \times (d\gamma/d\ln m)(d\ln m/d\ln a), \tag{2}$$

where $a$ and $m$ are the mean ion activity and the polyelectrolyte concentration, respectively. $Z_p$ and $Z_g$ are the polyion monomer unit and the counterion valences, respectively, and $R$ and $T$ have their usual meaning. The $(d\ln m)/(d\ln a)$ term was evaluated according to Manning's [9] theory by

$$d\ln a/d\ln m = \frac{1}{2}\left|Z_g^{-1}\right|(\xi^{-1}) \quad \text{if } \xi > 1, \tag{3}$$

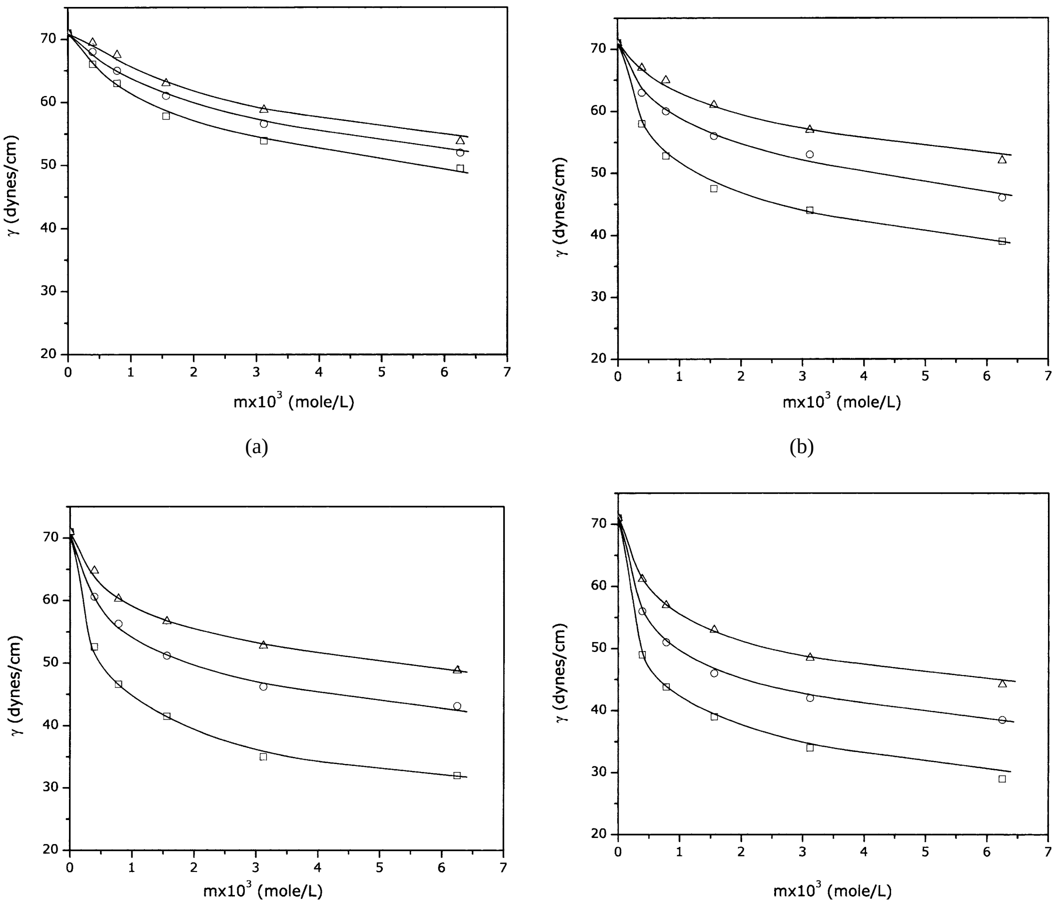
where $\xi$ is the linear charge density parameter, defined as

$$\xi = e^2/\varepsilon kTb. \tag{4}$$

In Eq. (4), $e$ is the proton charge, $\varepsilon$ the bulk dielectric constant of the solvent, and $b$ the average distance between charges on the polyelectrolyte chain. The latter value was calculated assuming that C–C–C bond angles and C–C bond distances were 109.5° and 1.54 Å, respectively. Then values of 5.03 Å, 1.418, and 2.836 were obtained for $b$, $\xi$, and $(d\ln m)/(d\ln a)$, respectively. Then, Eq. (2) becomes

$$\Gamma = -[1.418/RT](d\gamma/d\ln m). \tag{5}$$

Obviously, the surface excess values are dependent on the charge spacing $b$ and some error may be involved in its estimation: however, this calculated parameter should be very close to the actual distance between charges, considering the high dilution range where surface tension measurements were done. Some differences in $b$ might exist comparing



(a) (b)

(c) (d)

Fig. 1. Surface tension dependence on polyelectrolyte concentration at constant side chain length: (a) propyl, (b) octyl, (c) decyl, and (d) dodecyl derivatives. (□) P16, (○) P450, (△) P1250.

propyl derivatives of low $M_w$, which is nearly a semirigid rod polyelectrolyte as compared with the more coiled octyl, decyl, and dodecyl derivatives. The latter ones should have a similar conformation, and therefore analogous $b$, and it may be stabilized in solution, pointing its charges to water and their apolar residues probably forming hydrophobic microdomains distant from bulk water. The magnitude of the linear charge density parameter, $\xi = 1.418$, reflects that in the limit of infinite dilution at least 30% of the sodium counterions are condensed onto the polyion to give $\xi = 1$; thus the term $(d \ln m / d \ln a)$ in Eq. (2) is not the unity as occurs in single electrolytes. Manning's polyelectrolyte counterion condensation theory reasonably accounts for this fact.

At 25 °C, Eq. (5) results to be

$$\begin{aligned} \Gamma &= -[5.726 \times 10^{-11}](d\gamma / d \ln m) \\ &= -[5.726 \times 10^{-11}] m (d\gamma / dm). \end{aligned} \tag{6}$$

The slopes, $(d\gamma/dm)$, were evaluated by fitting the experimental data to the empirical Szyszkowski equation [10],

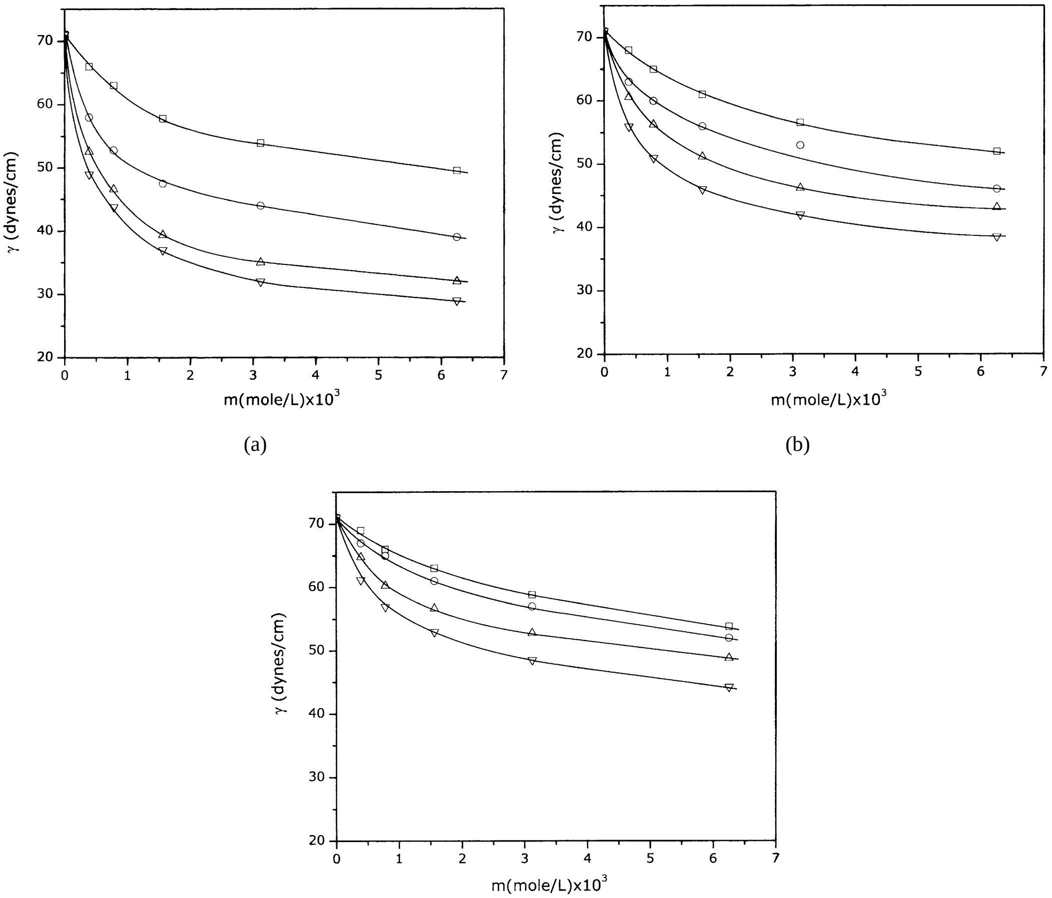
$$\gamma = \gamma_0 \{1 - B \log[(m/A) + 1]\}, \tag{7}$$

where $\gamma_0$ is the surface tension of the pure solvent and $A$, $B$ are two empirical adjustable parameters. In Table 1 are summarized the values of these parameters for the $\gamma$ adjustment for all the polymers here studied. The small magnitude of the maximum errors between experimental and theoretical data reflects the appropriateness of the Gibbs–Szyszkowski equations for accounting for the results in the present case as well. In Figs. 1a–1d the theoretical curve of $\gamma$ versus $m$ is also shown.

Table 1
Adjustment parameters of Gibbs–Szyszkowski equation

| $M_w$ | Side chain | $A \times 10^4$ | $B$ | Maximum error* |
|---|---|---|---|---|
| 1600 | Propyl | 3.9 | 0.249 | 0.28 |
| | Octyl | 0.7 | 0.229 | 0.28 |
| | Decyl | 0.2 | 0.217 | 0.72 |
| | Dodecyl | 0.1 | 0.206 | 0.76 |
| 45,000 | Propyl | 5.1 | 0.232 | 0.38 |
| | Octyl | 2.0 | 0.220 | 0.36 |
| | Decyl | 0.8 | 0.206 | 0.58 |
| | Dodecyl | 0.3 | 0.191 | 0.60 |
| 125,000 | Propyl | 7.3 | 0.229 | 0.48 |
| | Octyl | 3.8 | 0.201 | 0.78 |
| | Decyl | 1.5 | 0.192 | 0.30 |
| | Dodecyl | 0.7 | 0.190 | 0.36 |

* $|\gamma_{\text{theor}} - \gamma_{\text{expl}}|$.



(a) (b) (c)

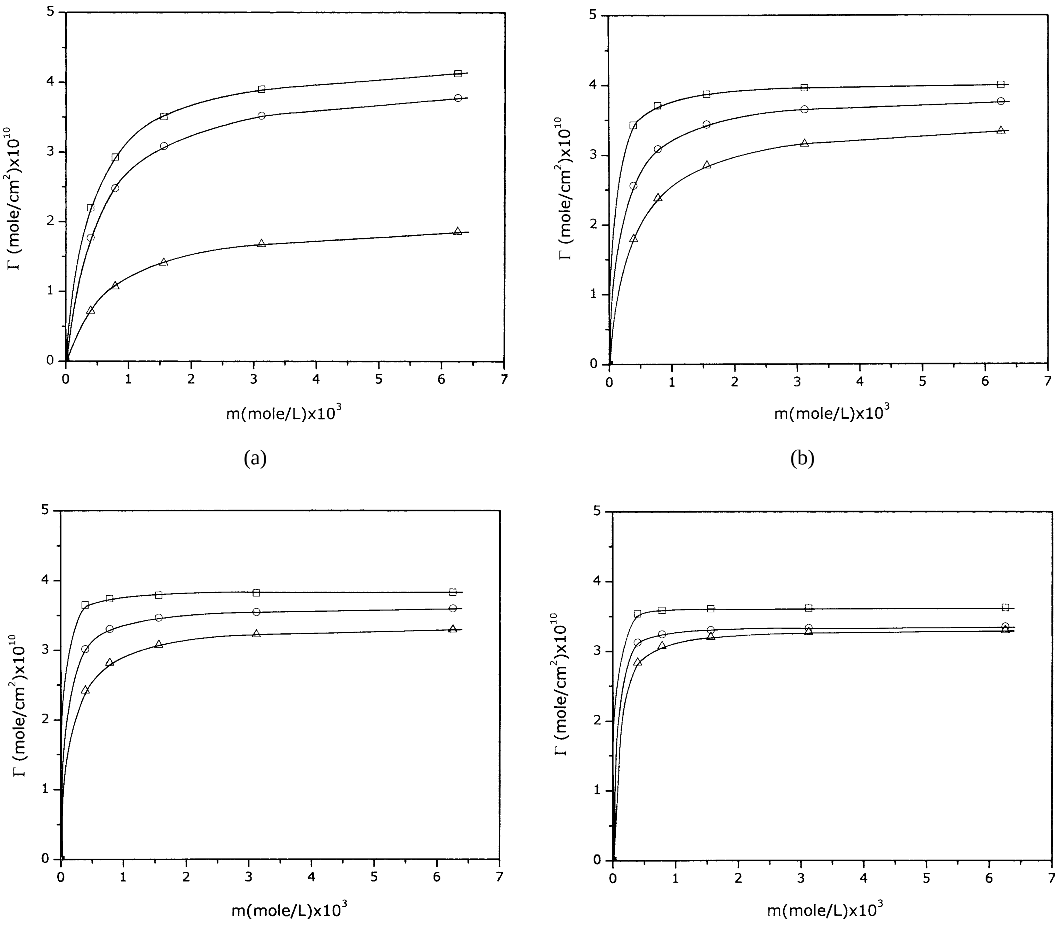
Fig. 2. Surface tension versus polyelectrolyte concentration at constant $M_w$: (a) P16, (b) P450, (c) P1250. (□) propyl, (○) octyl, (△) decyl, and (▽) dodecyl derivatives.

In Eq. (7), $A$ is a parameter related to the standard free energy of adsorption. $B$ is related to the average number of molecules per unit area at the surface in its closest packing arrangement (minimum surface area/molecule), i.e., with the limiting excess surface concentration. The $A$ and $B$ values are of the same order of magnitude as those reported in analogous systems [3] at the air/water surface and slightly higher than those reported at the $n$-octane/water interface [11].

Figures 3a–3d show the $\Gamma$ dependence on $m$ at constant side chain length for the three $M_w$ over the entire concentration range studied here. As expected, all these curves are Langmuir-type saturation profiles. The sequence of the initial slopes $d\Gamma/dm$ is the following:

$$(d\Gamma/dm)_{\text{dodecyl}} > (d\Gamma/dm)_{\text{decyl}} > (d\Gamma/dm)_{\text{octyl}} > (d\Gamma/dm)_{\text{propyl}}.$$

Thus, the surface saturation is reached more rapidly with polyelectrolytes containing longer side chains, i.e., chains that cover a larger area at the surface. Moreover, for the same side chain, $\Gamma$ depends on the molecular weight of the polyelectrolyte for the same $m$. In fact, the smaller the molecular weight, the higher the excess surface concentration and, consequently, the higher the $\Gamma_\infty$. Obviously, the P16 polyelectrolyte is nearly a semirigid rod; thus, it shows the greatest ability to extend its lateral chains at the surface due to its smaller steric hindrance as compared with the polyelectrolytes of higher molecular weight, which should have a quasi-random coil structure due to their higher $M_w$. The polyelectrolyte concentration where the plateau is reached follows the order determined by the side chain length. Similar $\Gamma_\infty$ are obtained for the P450 polyelectrolyte. In the case of the P1250 polyelectrolyte, some limitations to accommodate its aliphatic side chains at the surface might exist. In the bulk, this polyelectrolyte probably has a random coil structure with its polar carboxylate groups in contact with water and the side chains forming some of the inner hydrophobic microdomains mentioned above, which can be sensed by fluorescence studies. Obviously, propyl derivatives should have less ability to form these microdomains than octyl, decyl, and dodecyl derivatives. Therefore, the fluorescence of an appropriate hydrophobic probe could be enhanced in these microenvironments. At the surface its conformation must be compatible with a structure similar to a comb-like polyelectrolyte with its lateral chains exposed to the air phase and the polar groups in contact with the water phase. Thus, the adsorption process at the surface could



(a) (b)

(c) (d)

Fig. 3. Excess surface concentration: (a) propyl, (b) octyl, (c) decyl, and (d) dodecyl derivatives. (□) P16, (○) P450, (△) P1250.

involve a change in the polyelectrolyte conformation. The low surface activity of P1250 polyelectrolyte as compared with the other is a consequence of the incapacity of this polyelectrolyte to extend lateral chains freely to the air at the surface. Therefore, P1250 polyelectrolyte should maintain itself at the surface part of the conformation which it adopts in the bulk. It is important to state that this polymer has an average degree of polymerization of 615, as compared with only 220 for the P450 polyelectrolyte and just 8 for P16 polyelectrolyte, which probably has a semirigid rod conformation not only in the bulk water but also at the interface.

Table 2 summarizes the values of $\Gamma_\infty$ and the areas covered by the comonomeric unit at the surface, $\sigma$. The $\sigma$ values increase with the size of the polyelectrolyte lateral chain. As expected, longer side chains cover a major area at the surface, whereas their magnitudes are similar to those reported for simple low-molecular-weight detergents [12–14], carboxylic acids [15], and analogous polyelectrolytes [3].

The standard free energy of adsorption, $\Delta G^0_{\text{ads}}$, was calculated according to the expression [10]

$$\Delta G^0_{\text{ads}} = -2.303RT\big[\log(A) - 1.744\big], \tag{8}$$

and the values are summarized in Table 2. As can be seen, these values are all negative, reflecting the fact that the adsorption process occurs spontaneously. For the same $M_w$, $\Delta G^0_{\text{ads}}$ is more negative, as the lateral chain size increases. On the other hand, $\Delta G^0_{\text{ads}}$ is also more negative as the $M_w$ decreases at constant side-chain length. The magni-

Table 2
Limiting excess surface concentration, areas covered by comonomer units and standard free energies of adsorption

| $M_w$ | Side chain | $\Gamma_\infty \times 10^{10}$ (mol/cm$^2$) | $\sigma \times 10^{16}$ (cm$^2$) | $-\Delta G^0_{\text{ads}}$ (kJ/mol) |
|---|---|---|---|---|
| 1600 | Propyl | 4.39 | 37.8 | 29.4 |
| | Octyl | 4.50 | 41.0 | 33.7 |
| | Decyl | 3.84 | 43.2 | 36.8 |
| | Dodecyl | 3.63 | 45.7 | 38.5 |
| 45,000 | Propyl | 4.09 | 40.6 | 28.8 |
| | Octyl | 3.88 | 42.8 | 31.1 |
| | Decyl | 3.64 | 45.5 | 33.3 |
| | Dodecyl | 3.37 | 49.2 | 35.8 |
| 125,000 | Propyl | 4.04 | 41.1 | 27.9 |
| | Octyl | 3.54 | 46.8 | 29.5 |
| | Decyl | 3.38 | 49.0 | 31.8 |
| | Dodecyl | 3.35 | 49.5 | 33.7 |

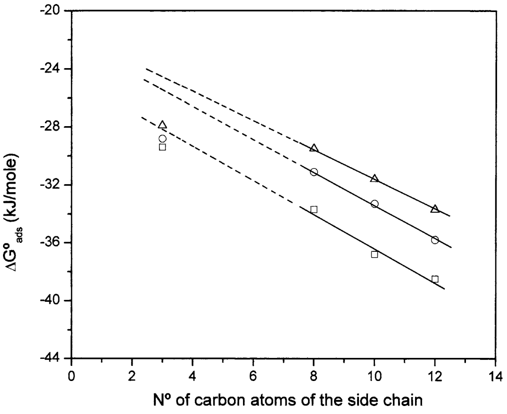


Fig. 4. Standard free energy of adsorption versus the number of carbon atoms in the lateral chain: (□) P16, (○) P450, (△) P1250.

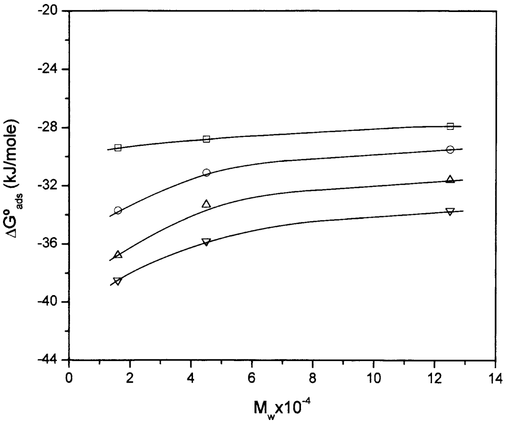


Fig. 5. Standard free energy of adsorption versus $M_w$: (□) propyl, (○) octyl, (△) decyl, and (▽) dodecyl derivatives.

tudes of $\Delta G^0_{\text{ads}}$ are comparable with values reported in similar systems [3]. In order to estimate the contribution of each methylene group to the total free energy of adsorption, $\Delta G^0_{\text{ads}}$ was plotted against the number of carbon atoms, $n$, in the lateral chain. As can be seen in Fig. 4, there is a linear behavior of $\Delta G^0_{\text{ads}}$ with $n$, at least for 8-, 10-, and 12-carbon derivatives in the three systems. Propyl polyelectrolytes deviate from the linear trend shown by the other polyelectrolytes. The linear adjustment considering only the octyl, decyl, and dodecyl polyelectrolytes yields $-1.21$, $-1.17$, and $-1.05$ kJ/mol for the contribution of each methylene group to $\Delta G^0_{\text{ads}}$ for the P16, P450, and P1250 polyelectrolytes, respectively. As expected, methylene groups desorb the polyelectrolyte from water. Keeping constant the polyelectrolyte side chain length, $\Delta G^0_{\text{ads}}$ was plotted against $M_w$ and the results are shown in Fig. 5. As can be observed, in all cases $\Delta G^0_{\text{ads}}$ is less negative as $M_w$ increases. However, the trend of these curves suggests the existence of a high-$M_w$ region where $\Delta G^0_{\text{ads}}$ becomes independent of $M_w$. This zone was not experimentally accessible due to polyelectrolyte solubility problems.

From the above results it can be concluded that the surface properties of such amphipathic polyelectrolytes are dependent on the polyelectrolyte $M_w$ from the thermodynamic and conformational points of view. Both the $\Delta G^0_{\text{ads}}$ and the $\sigma$ values are dependent on $M_w$. The $\sigma$ values increase with the size of the lateral chain. Thus, these side chains extend at the surface, covering larger areas and adopting a more extended conformation depending on their size. Finally, the amide group, with an NH group capable of interacting by hydrogen bonding with neighboring carbonyl moieties, seems to have no effect on the surface properties as compared with the ester groups of poly(monoalkylmaleic acid-alt-styrene) sodium salts.

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## References

[1] M. Hara, Polyelectrolytes, 1st ed., Dekker, New York, 1993.
[2] S.K. Tripathy, J. Kumar, H.S. Nalwa, Handbook of Polyelectrolytes and Their Applications, American Scientific Publishers, Stevenson Ranch, CA, 2002.
[3] H.E. Ríos, J.S. Rojas, I.C. Gamboa, R.G. Barraza, J. Colloid Interface Sci. 156 (1993) 388.
[4] T. Okubo, J. Colloid Interface Sci. 125 (1988) 387.
[5] A. Laschewsky, Adv. Polym. Sci. 124 (1995) 1–86.
[6] B.H. Cao, M.W. Kim, Faraday Discuss. 98 (1994) 245.
[7] T.J. Su, J.R. Lu, Z.F. Cui, R.K. Thomas, J. Penfold, J. Phys. Chem. B 102 (1998) 8100.
[8] N. Ohno, K. Nitta, S. Makino, N. Sugai, J. Polym. Sci. 11 (1973) 253.
[9] G.S. Manning, J. Chem. Phys. 51 (3) (1969) 924.
[10] M.J. Rosen, Surfactants and Interfacial Phenomena, 2nd ed., Wiley–Interscience, New York, 1989.
[11] H.E. Ríos, M.H. Aravena, R.G. Barraza, J. Colloid Interface Sci. 165 (1994) 259.
[12] F. van Voorst Vader, Trans. Faraday Soc. 56 (1960) 1067.
[13] M. Dahanakaye, A.W. Cohen, M.J. Rosen, J. Phys. Chem. 90 (1986) 2413.
[14] K. Shinoda, M. Hato, Hayashi, J. Phys. Chem. 76 (1972) 909.
[15] S. Ross, I.D. Morrison, Collloidal Systems and Interfaces, Wiley, New York, 1988.