

## Surface properties of cationic polyelectrolytes hydrophobically modified

Hernán E. Ríos\*, Javier González-Navarrete, Víctor Vargas, Marcela D. Urzúa

Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Correo Central, Chile

### ARTICLE INFO

#### Article history:

Received 9 February 2011

Received in revised form 29 March 2011

Accepted 30 March 2011

Available online 7 April 2011

#### Keywords:

Amphipathic polyelectrolytes

Surface tension

Adsorption free energy

### ABSTRACT

Poly (N,N-dimethyl-N,N-diallyl ammonium) chloride, a highly hydrophilic polyelectrolyte, was hydrophobically modified and the surface properties of the resulting amphipathic polyelectrolytes were determined. The surface activity increases with the polyelectrolyte side chain length despite the ability of this type of polyelectrolyte to form hydrophobic micro domains in solution. The standard free energy of the adsorption process,  $\Delta G^{\circ}_{\text{ads}}$ , were a linear function of the number of carbon atoms in the lateral chain as well as their transfer and interfacial contributions to the adsorption process with  $-1.73 \text{ kJ mol}^{-1}$  of methylene group to  $\Delta G^{\circ}_{\text{ads}}$ . From the dependence of the surface tension with the temperature the  $\Delta S^{\circ}_{\text{ads}}$  was determined. The latter parameter was always positive regardless the polyelectrolyte side chain length, thus the main driving force to  $\Delta G^{\circ}_{\text{ads}}$  arises from the large positive  $\Delta S^{\circ}_{\text{ads}}$  values.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Amphipathic hydrophilic polyelectrolytes display in water solution two kinds of behavior depending on their hydrophobic/hydrophilic balance. The stabilization in the water phase is related with the trend of these systems to hypercoiling by hydrophobic interactions adopting a micelle-like structure with an inner apolar core and an outer polar crown exposed to the water. They have been considered “polysoaps” because their monomer structures resemble a simple detergent molecule. In aqueous solutions present a dissociation degree which depends on their concentration and linear charge density. Hydrophilic polyelectrolytes strongly interact with surfactants of opposite charge forming aggregates in solution [1] or films which can be spread onto water surface forming thin films [2]. The literature has been recently reviewed by Langevin [3,4]. Since these polyelectrolytes are water soluble, the formation of surface monolayers requires the presence of a surfactant of opposite charge. Neutral polymers of intermediate hydrophobic character are well-known to form Langmuir monolayers by spreading a relatively dilute polymer solution in an organic volatile solvent on top of a water subphase. After solvent evaporation, the surface tension reaches a constant value corresponding to a reproducible state of the monolayer which remains stable over several days [5].

If the amphipathic polyelectrolytes are hydrophobic, i.e., soluble in organic solvents, then they are able to form a quasi-reverse micelle systems with an inner polar core in this case. These “hydrophobic polysoaps” are soluble in organic solvents, and

behave in these solvents as non-ionic polymers with a very low or zero dissociation degree. This kind of polyelectrolytes can be spread at water surfaces forming monolayers. Recently, polyelectrolytes derived from poly(4-vinylpyridine) quaternized with n-tetradecylbromide at different quaternization degrees were studied at the air/water interface showing the adsorption isotherms (surface pressure-area) several phase transitions and critical areas whose magnitudes were dependent on the quaternization degree [6].

Regarding to their adsorption at interfaces, no matters if polyelectrolytes adsorption process is conducted from water to water/oil interface for hydrophilic polysoaps or from oil to oil/water interface for hydrophobic polysoaps; in both cases the phenomenon occurs spontaneously with a free energy decreasing. However, the adsorption mechanism seems to be different. In the former case, the polysoap is stabilized in the aqueous solution with their polar heads solvated by water and their hydrophobic moieties hydrated in an ordered ice-like structure. Thus, in this case the adsorption is entropically governed by the disorder created by the destruction of these ice-like structures as the polysoap extends their aliphatic chains to the oil phase. In the second case the adsorption it seems to be mainly determined by the enthalpy of hydration of the polar heads as the polyelectrolyte is adsorbed on the water/oil interface.

The behavior of these polyelectrolytes, hydrophilic or hydrophobic, and the thermodynamic implications of their adsorption at interfaces have been properly discussed by Babak and Boury [7]. Usually, the surface tension of polyelectrolyte solutions begins to decrease only when the ionic strength is high enough and the lateral repulsion of charged groups is shielded to a great extent, and. Another way to increase the polyelectrolyte surface activity consists in the hydrophobic mod-

\* Corresponding author.

E-mail address: [hrrios@uchile.cl](mailto:hrrios@uchile.cl) (H.E. Ríos).

ification of the main chain leading to the formation of polysoaps [8].

Therefore, these macromolecules can eventually migrate spontaneously at the air–water surface [9–12] or to a liquid–liquid interface [13–17], where their side chains extend to air phase, vertically or in a more extended conformation, or into the non-polar liquid whereas their polar groups are anchored onto water phase. As far as we know, the major part of these works have been focused to anionic systems and the surface properties of cationic hydrophilic amphipathic polyelectrolytes have been practically ignored in the literature as compared with studies dealing with surface and interfacial properties of hydrophilic anionic polyelectrolytes which have been reported [9–14]. Nevertheless, in both cases, anionic or cationic, their water solubility is determined by the balance between the polyelectrolyte molecular weight, i.e., the length of the main chain, the size of their lateral chains and the nature of the polar group. We believe that in cationic systems this balance seems to be very narrow being especially difficult to attain in order to obtain hydrophilic cationic polyelectrolytes.

We study some cationic systems but they were non-water soluble polyelectrolytes, thus their interfacial properties were studied from an organic solvent such as chloroform to a chloroform/water interface [15,17]. Considering both systems, anionic or cationic, the general features were the following: the adsorption process is always entropy dependent, no matters the kind of interface or the polyelectrolyte involved. Some effect of the polyelectrolyte molecular weight,  $M_w$ , was found [4], i.e., the adsorption process decreases as the  $M_w$  increases. In one case [13] the adsorption effectiveness, i.e., the minimum surface/molecule ratio at the interface, seems to play a less important role than the adsorption efficiency, i.e., a direct measurement the polyelectrolyte bulk concentration required to induce a particular effect at the interface. In general, the standard free energy of adsorption  $\Delta G^{\circ}_{ads}$  shows a linear dependence with the number of carbon atoms in the polyelectrolyte side chain. The contribution of each methylene group to  $\Delta G^{\circ}_{ads}$  is dependent on the type of polyelectrolyte monomer unit, the kind of interface and the solvent where the polyelectrolyte is soluble. Effectively, if the monomer is anionic and contains two carboxylate groups then the polyelectrolyte shows an apparently “anomalous” adsorption behavior [10]. In these polyelectrolytes the surface activity decreases as the side chain length increases on the contrary to that occurs with those containing only one carboxylate group in the monomer unit where the surface activity decreases abruptly as the length of the side chain increase. This phenomenon has been attributed to a polyelectrolyte desorption process due to electrostatic repulsion between two neighboring carboxylate groups at the interface or even to a micellization process when the length of the polyelectrolyte side chain is higher than twelve carbon atoms. The surface tension behavior suggests that the adsorption process is competitive with the polyelectrolyte “micellization” in the bulk [12]. As stated above considering water soluble cationic amphipathic polyelectrolytes little or nothing works have been reported. In fact, we studied the interfacial properties of several poly-(N-alkyl pyridinium) bromides [16] and poly-(2-dimethylamino) ethylmethacrylate-N-alkyl quaternized [17]. Both systems were non-water soluble, thus in both cases the adsorption process was studied from chloroform to chloroform/water interface and in all cases the interfacial activity increased as the polyelectrolyte side chain length decreases, on the contrary to what happens with surface properties of anionic polyelectrolytes.

Considering cationic hydrophilic polyelectrolytes the limited literature has been reviewed by Laschewsky [18]. The surface tension of an aqueous solution of a “tail-end” single cationic methacrylate monomer decreases with detergent concentration whereas the polyelectrolyte derived from it practically do not show surface activity and the surface tension is nearly that of

pure water, at least in the polyelectrolyte concentration range studied. The types of monomer geometries of the polar groups and properties of these “polysoaps” were extensively revised in the Laschewsky's work [18].

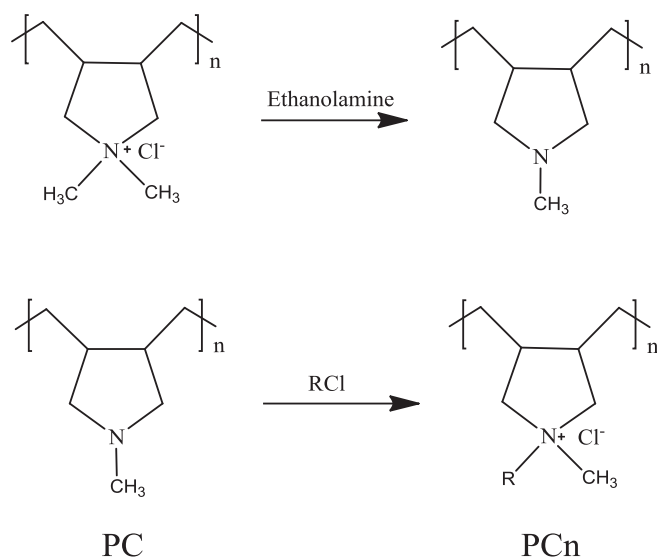
Thus the main aim of the present work is to study the surface properties of poly (N-n-alkylmethyldiallylammonium) chloride with n-alkyl = hexyl, octyl, decyl and dodecyl side chains are studied; a “head-type” cationic hydrophilic polysoap in the Laschewsky sense. In order to fulfill with the work's purpose it was necessary to modify this hydrophilic cationic polyelectrolyte with some side aliphatic chains in order to obtain water soluble amphipathic polyelectrolytes.

## 2. Experimental

Poly (dimethyl diallylammonium chloride) (CAS, 26062.79-3) low molecular weight type with an average molecular weight ranging from 100,000 to 200,000, was from Aldrich. Milwaukee, WI, USA. This chemical is used as an industrial flocculant and is released at 20% (w:w) water solution. This product was used as received and it was ultrafiltered through Millipore® polyethersulfone membranes in order to obtain, among others, a fraction with  $M_w$  ranging between 50,000 and 30,000.

This fraction was lyophilized and used without further purification. The average molecular weight was 29,000 with a  $M_w/M_n$  ratio of 1.76 which was obtained by GPC from the elution peak according to the classical heights/slices graphical method. A Merck-Hitachi L-6000A chromatograph equipped with a Shimadzu RID-6A refractive index detector and a Shodex OHpak KB-803 GPC column which it was calibrated with Pullulan® monodisperse standards, several polymaltotrioses from Shodex. The eluent was 0.40 M NaCl.

In order to modify the original polyelectrolyte, the method reported by Quina [19] was used. The latter is basically a selective demethylation of the hydrophilic polyelectrolyte followed by an exhaustive reaquaternization with n-alkylchlorides. The final products were water soluble and the exhaustive quaternization was corroborated by  $^1\text{H}$  NMR. The modified polyelectrolytes were named PC6, PC8, PC10 and PC12 for the hexyl, octyl, decyl and dodecyl derivatives, respectively. The following figure summarizes the mentioned method:



The final products (PC<sub>n</sub>) were obtained by heating at 60 °C a mixture of PC and the respective alkyl chloride in chloroform in a 1:1,2 mole ratio, respectively. The reaction time was 120 h. After that, the chloroform was extracted by rotovaporation and the sticky solids were dried under vacuum. Then they were dissolved in a

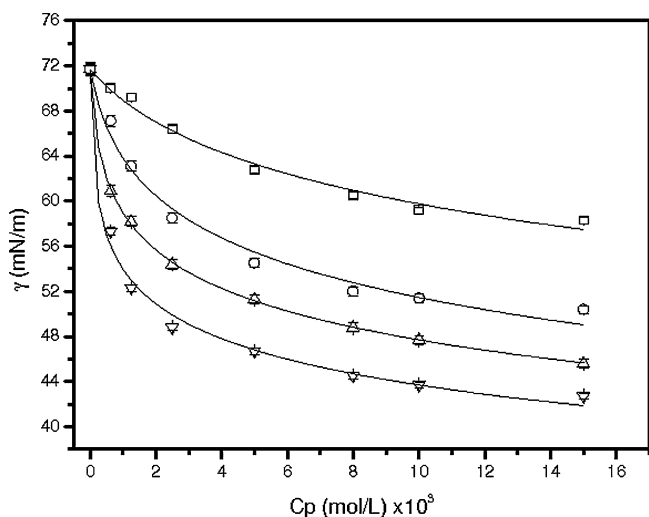


Fig. 1. Surface tension of amphiphilic polyelectrolytes. (□) PC6, (○) PC8 (Δ) PC10 and (▽) PC12 at 298.15 K.

50:50 ethanol/water mixture and ultrafiltered through a Millipore® polyethersulfone membrane of MWCO 1000. The polymer solution was washed with the above mentioned mixture and then with pure water until chloride was not detected in the eluted water by  $\text{AgNO}_3$ . The polymers (PC $n$ ) were finally freeze dried.

The quaternization degree was determined directly from the ratio of the number of hydrogen atoms of the experimental  $^1\text{H NMR}$  spectra of PC $n$ 's with the number of hydrogen atoms of a theoretical monomer unit of PC $n$ 's completely quaternized. The quaternization degrees were around 94% in all cases (see [Supplementary Material](#)).

The surface tension measurements were performed according to the Du Nöuy method in a Krüss K-8 interfacial tensiometer at 283.15, 298.15 and 308.15 K  $\pm 0.01^\circ$ . The solutions were prepared and kept at 25 °C in their respective volumetric flasks in a thermal bath before each measurement. Then it was poured into the measurement vessel. After approximately 5 min the thermal equilibrium was again restored and each measurement was done. No appreciable changes in surface tension ( $\gamma$ ) were detected after 1 h in all cases being the results highly reproducible. Each  $\gamma$  measurement was performed at least 5 times. Standard deviation in surface tension data measurements was  $\pm 0.33$ .

Bidistilled and ultrafiltered through Millipore® water with a specific conductivity of 0.2–0.3  $\mu\text{S cm}^{-1}$  and a surface tension  $\gamma^\circ$  of 72.5  $\text{mN m}^{-1}$  at 25 °C was used. All the reagents used were from Aldrich of the highest purity available.

### 3. Results and discussion

Fig. 1 shows the surface tension  $\gamma$  behavior of PC6, PC8, PC10 and PC12 solutions as a function of their bulk concentrations  $C_p$  in moles of monomers per liter at 298.15 K. As can be seen,  $\gamma$  strongly decreases as the side chain length increases. PC6 which has the shorter side length then is the more hydrophilic polyelectrolytes of the series studied here and consequently it shows the smaller surface activity contrary to PC12 which has the higher surface activity. This type of polyelectrolytes has a “normal” behavior in relation to their surface activity opposing to that occurs with poly(mono- $n$ -alkylmaleate- $\text{alt-N-vinylpyrrolidone}$ ) [12] sodium salts where the surface activity decreases as the polyelectrolyte side chain length increases. Apparently, the predominating trend of these cationic amphiphilic polyelectrolytes is to migrate to the surface in spite of their well known tendency to form hydrophobic micro domains in solution [20]. Obviously, at the equilibrium condition the polyelectrolyte is materially distributed between the surface and the bulk

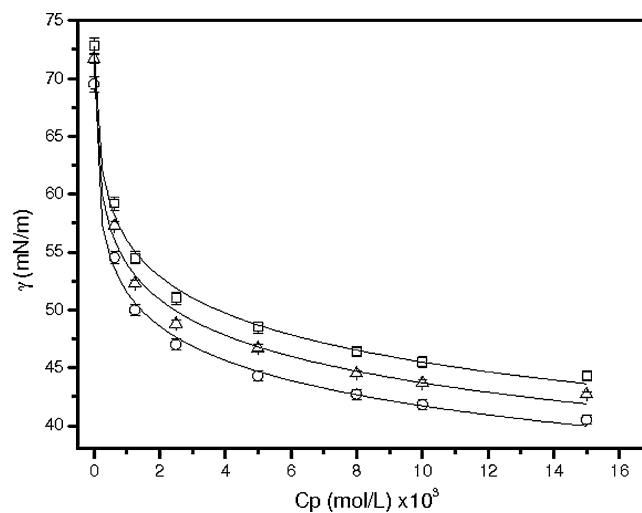


Fig. 2. Surface tension of PC12 at (□) 283.15 K, (Δ) 298.15 K and (○) 308.15 K.

Table 1  
Gibbs–Szyzkowski adsorption parameters.

T (K)	Polyelectrolyte	$A \times 10^4$	B	$\chi^2_{\text{red}}$
283.15	PC6	$53.2 \pm 0.72$	$0.288 \pm 0.004$	0.11
	PC8	$7.3 \pm 0.58$	$0.230 \pm 0.022$	0.93
	PC10	$1.5 \pm 0.022$	$0.165 \pm 0.006$	0.18
	PC12	$0.3 \pm 0.001$	$0.148 \pm 0.008$	0.45
298.15	PC6	$19.1 \pm 0.54$	$0.209 \pm 0.009$	0.36
	PC8	$3.8 \pm 0.32$	$0.197 \pm 0.019$	0.99
	PC10	$0.5 \pm 0.004$	$0.162 \pm 0.0002$	0.03
	PC12	$0.2 \pm 0.001$	$0.145 \pm 0.010$	0.67
308.15	PC6	$13.8 \pm 0.83$	$0.205 \pm 0.018$	0.89
	PC8	$2.5 \pm 0.005$	$0.188 \pm 0.008$	0.35
	PC10	$0.2 \pm 0.003$	$0.158 \pm 0.004$	0.11
	PC12	$0.2 \pm 0.005$	$0.141 \pm 0.007$	0.36

solution in an extent which depends on its nature, mainly of its side chain length and its polar head structure. In order to establish the entropy of the adsorption process, the effect of the temperature on  $\gamma$  was also determined. As an example, in Fig. 2 the  $\gamma$  versus  $C_p$  for PC12 at 283.15; 298.15 and 308.15 is shown. As can be observed,  $\gamma$  decreases with temperature for the same polyelectrolyte. This result is general, i.e. occurs in the three systems here studied and it may be explained as a dehydration process of the “hydrophobic ice-like water molecules” which are surrounding the apolar side chains as the temperature increases. The hydrophobic effect would be more pronounced and the polyelectrolyte could migrate more easily to the surface.

In order to quantify the thermodynamic parameters of the adsorption process, the classical treatment of Gibbs–Szyzkowski was applied [9,12,13]. The  $A, B$  adjustment parameters of this equation are summarized in Table 1. As stated,  $A$  values are related with the standard free energy of adsorption,  $\Delta G^\circ_{\text{ads}}$ , i.e., with the  $(\partial\gamma/\partial C_p)_T$  slopes. Therefore, the greater the slope, the higher the  $\Delta G^\circ_{\text{ads}}$  and the polyelectrolyte surface activity increases. On the other hand,  $B$  values should be constant for a homologous series where the solute is a single low molecular weight amphipathic molecule.  $B$  is related with the areas covered by the polar groups at the surface in its closest packing arrangement or with the minimum interfacial area/molecule ratio, thus  $B$  is associated with the limiting excess surface concentration. For this reason  $B$  should be constant if all the molecules are vertically oriented to the air phase at the surface. In this work monomers belong to a homologous series considering that there are two methylene groups of difference from one particular monomer to the following one. Results in

**Table 2**  
Coefficients of  $\Gamma$  equation.

PCn	$b$ (Å)	$T$ (K)	$\xi$	$d\text{Ln}C_p/d\text{Ln}a$	$K_i \times 10^{11}$
PC6	7.965	283.15	0.882	1.789	1.650
		298.15	0.894	1.808	1.584
		308.15	0.902	1.822	1.544
PC8	7.616	283.15	0.923	1.857	1.712
		298.15	0.935	1.878	1.645
		308.15	0.944	1.893	1.604
PC10	6.651	283.15	1.057	2.113	1.949
		298.15	1.071	2.142	1.875
		308.15	1.081	2.161	1.831
PC12	6.427	283.15	1.094	2.187	2.017
		298.15	1.108	2.216	1.941
		308.15	1.118	2.236	1.895

Table 1 show that not only  $A$  values decrease with temperature but also  $B$  values for the same polyelectrolyte system. There are some differences in the polyelectrolyte free energy of adsorption which depends of their side chain and also in the magnitude of the areas covered by monomer unit at the surface. In fact, the macromolecular nature of the polyelectrolyte induces some conformations of the monomer unit which probably are absent in amphipathic low molecular weight systems. Thus, monomer unit in polyelectrolytes could be spread covering an average area which depends on their size and conformation at the surface determined at least partially by their persistence length which could be very different.

Solid lines in Figs. 1 and 2 are the theoretical curves constructed with the  $A$ ,  $B$  values in the Szyszkowski equation:

$$\gamma = \gamma^\circ - \gamma^\circ B \log \left[ \left( \frac{C_p}{A} \right) + 1 \right] \quad (1)$$

where  $\gamma^\circ$  is the surface tension of pure solvent.

As can be verified, the theoretical curves are well fitted to the experimental data. The small magnitude of the maximum errors between experimental and theoretical data reflects the appropriateness of the Gibbs–Szyszkowski's treatment for accounting for the results not only in the anionic systems studied [9,14,16] but also in the present case.

In order to evaluate the excess surface concentration the following equation was used:

$$\Gamma = -\frac{Z_p Z_g}{Z_p + Z_g} \times \frac{1}{RT} \times \frac{d\gamma}{d\text{Ln}C_p} \times \frac{d\text{Ln}C_p}{d\text{Ln}a} \quad (2)$$

where  $Z_p$ ,  $Z_g$  are the polyion and the counterion valences, respectively and  $a$ , the mean ion activity. The Manning's theory [21] allows evaluate  $(d\text{Ln}a/d\text{Ln}C_p)$  as:

$$\frac{d\text{Ln}a}{d\text{Ln}C_p} = 1 - \left( Z_g \times \frac{\xi}{2} \right) \quad \text{if } \xi < |Z_g|^{-1} \quad (3)$$

and

$$\frac{d\text{Ln}a}{d\text{Ln}C_p} = \frac{1}{2} (Z_g \xi)^{-1} \quad \text{if } x > |Z_g|^{-1} \quad (4)$$

where  $\xi$  is given by:

$$\xi = \frac{\ell_\beta}{b} \quad (5)$$

here  $\ell_\beta$  is the Bjerrum length and  $b$  is the average distances between charges in the polyelectrolytes framework. The latter were calculated for the three systems considering as a model for the polyelectrolyte, an oligomer consisting on 4 monomer units. For the calculus of  $b$  distances, the program HyperChem Professional (Hypercube Inc., Gainesville, FL, USA) version 7.0 with the semi empirical calculation method AM1 was used. Table 2 summarizes

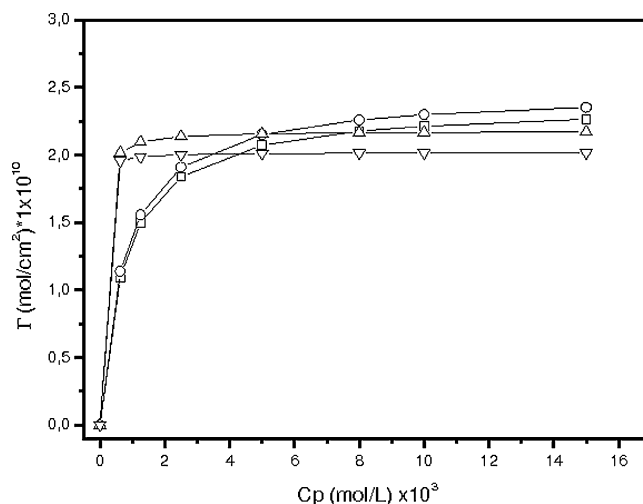


Fig. 3. Excess surface concentration versus  $C_p$ . (□) PC6, (○) PC8 (Δ) PC10 and (▽) PC12 at 298.15 K. Continuous lines correspond to  $\Gamma$  versus  $C_p$  curves according to Eq. (6).

the values of some of these parameters as a function of the temperature. Therefore, differentiating equation 1, in order to obtain the term  $(d\gamma/d\text{Ln}C_p)$ , Eq. (2) becomes:

$$\Gamma = \frac{K_i \gamma^\circ B C_p}{C_p + A} \quad (6)$$

where  $K_i$  is a constant depending on the type of polyelectrolyte and the temperature. Obviously, at lower  $C_p$ ,  $\Gamma$  varies linearly with  $C_p$  whereas at higher  $C_p$  values  $\Gamma$  becomes constant given by  $K_i \gamma^\circ B$ . At this condition,  $\Gamma = \Gamma^\infty$ , which is the limiting excess surface concentration and the surface should be completely saturated. With  $\Gamma^\infty$  values, the areas covered by monomer unit at the surface,  $\sigma$ , can be calculated as  $1/(N_A \Gamma^\infty)$  where  $N_A$  is the Avogadro number. The  $\Gamma$  behavior with  $C_p$  is shown in Fig. 3 and the  $\Gamma^\infty$  values together with the areas covered at the surface are summarized in Table 3. As can be seen in Fig. 3, the trend of the initial slopes follows the sequence:

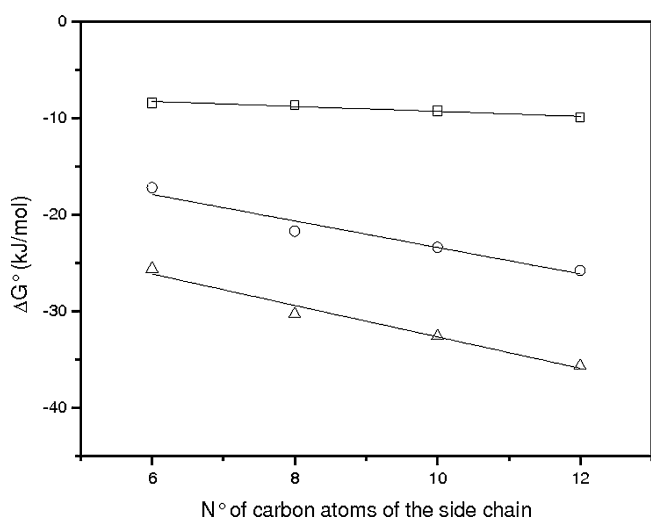
$$\left( \frac{d\Gamma}{dC_p} \right)_{\text{PC12}} > \left( \frac{d\Gamma}{dC_p} \right)_{\text{PC10}} > \left( \frac{d\Gamma}{dC_p} \right)_{\text{PC8}} > \left( \frac{d\Gamma}{dC_p} \right)_{\text{PC6}}$$

This behavior can be explained taking into consideration that the surface saturation requires more monomer units of those polyelectrolytes containing shorter side chains. On the other hand, at constant temperature  $\sigma$  values increase as the side chain size increases whereas for the same side chain length the  $\sigma$  values increase as the temperature increase suggesting that side chains are covering more extended areas as its thermal level increases. Moreover, the  $\sigma$  values here found are in a good agreement with those reported for cationic tetra methyl ammonium type detergents [22] and some copolymers of poly(4-vinylpyridine) partially quaternized [6].

In order to compare the relative adsorption efficiency, the  $pC_{20}$  values were determined. The  $C_{20}$  values were obtained by direct interpolation at 20 surface tension units lower than that of pure solvent, from the  $\gamma$  versus  $C_p$  curves. If  $C_{20}$  could not be determined directly, it was obtained by extrapolation from the linear part of plots of  $\gamma$  versus  $\text{Ln}(C_p)$  as it was explained before [12,14]. The  $pC_{20}$  values for the cationic amphipathic polyelectrolytes here studied are also summarized in Table 3. As can be seen, PC12 shows the higher value of  $pC_{20}$  in all the temperature range studied being the most efficient polyelectrolyte because it requires the lower bulk concentration to saturate the interface. On the other hand, for the same type of polyelectrolyte,  $pC_{20}$  increases as the temperature increase thus the hydrophobic effect increases with temperature

**Table 3**  
Limiting excess surface concentration, areas covered by monomer, PC<sub>20</sub> and standard free energy adsorption contributions.

T (K)	PCn	$\Gamma^\infty \times 10^{10}$ (mol cm <sup>-2</sup> )	$\sigma \times 10^{16}$ (cm <sup>2</sup> )	pC <sub>20</sub>	$-\Delta G^\circ_{\text{ads}}$ (kJ mol <sup>-1</sup> )	$-\Delta G^\circ_{\text{tr}}$ (kJ mol <sup>-1</sup> )	$-\Delta G^\circ_{\text{int}}$ (kJ mol <sup>-1</sup> )
283.15	PC6	3.46	48.0	1.09	21.2 ± 0.28	15.4 ± 0.20	5.8 ± 0.08
	PC8	2.86	58.0	1.92	26.9 ± 2.24	19.9 ± 1.57	7.0 ± 0.67
	PC10	2.34	71.0	2.26	30.3 ± 0.61	21.7 ± 0.30	8.6 ± 0.31
	PC12	2.17	76.4	2.67	33.1 ± 0.57	23.9 ± 0.07	9.2 ± 0.50
298.15	PC6	2.38	69.8	1.28	25.6 ± 0.93	17.2 ± 0.48	8.4 ± 0.45
	PC8	2.32	71.5	2.05	30.3 ± 2.19	21.7 ± 1.82	8.6 ± 0.37
	PC10	2.18	76.1	2.36	32.6 ± 0.31	23.4 ± 0.20	9.2 ± 0.11
	PC12	2.02	82.3	2.78	35.7 ± 0.51	25.8 ± 0.13	9.9 ± 0.38
308.15	PC6	2.20	75.6	1.25	26.8 ± 1.89	17.7 ± 1.10	9.1 ± 0.79
	PC8	2.10	79.0	2.06	32.0 ± 0.90	22.5 ± 0.50	9.5 ± 0.40
	PC10	2.01	82.6	2.57	35.4 ± 0.63	25.4 ± 0.38	10.0 ± 0.25
	PC12	1.86	89.4	2.96	38.1 ± 1.21	27.3 ± 0.68	10.8 ± 0.53



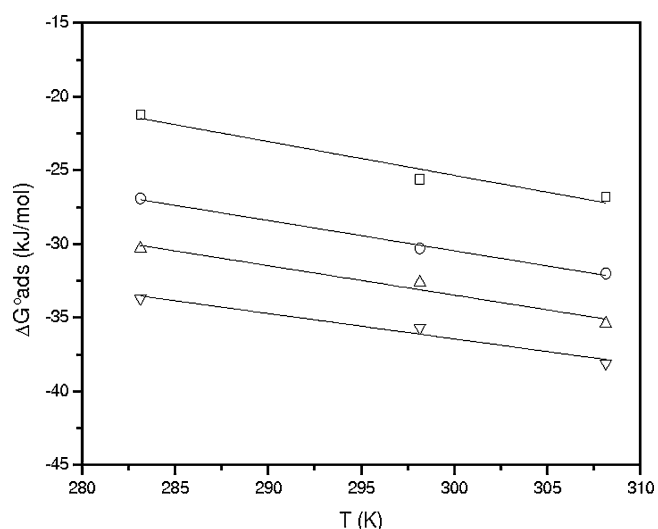
**Fig. 4.** Adsorption free energies versus the number of carbon atoms in the polyelectrolyte lateral chain. (Δ)  $\Delta G^\circ_{\text{int}}$ , (○)  $\Delta G^\circ_{\text{tr}}$  and (□)  $\Delta G^\circ_{\text{ads}}$ .

and consequently side chains adopt more freely conformations which cover greater average areas at the surface coherent with the  $\sigma$  observed trend.

The standard free energy of adsorption,  $\Delta G^\circ_{\text{ads}}$ , was determined according to the following equation [12]:

$$\Delta G^\circ_{\text{ads}} = -2.303RT[pC_{20} + 1.744] - 120.46\sigma \quad (7)$$

As can be seen, this equation shows that  $\Delta G^\circ_{\text{ads}}$  have two negative contributions: the first term is related with the standard free energy of transfer per mol of monomer unit from the bulk to the interface,  $\Delta G^\circ_{\text{tr}}$ . As stated before, this term is related with the adsorption efficiency which is a direct measure of the polyelectrolyte bulk concentration required to induce a determined effect at the interface, i.e., associated with pC<sub>20</sub>. The second free energy term,  $\Delta G^\circ_{\text{int}}$ , is related with the accommodation of the monomer at the interface, i.e., with the minimum area/molecule ratio at the interface. Consequently, the latter parameter has been considered as a direct measure of the effectiveness of the adsorption process. Both,  $\Delta G^\circ_{\text{tr}}$  and  $\Delta G^\circ_{\text{int}}$ , and also  $\Delta G^\circ_{\text{ads}}$  are linearly dependent on the number of carbon atoms in the polyelectrolyte side chain as can be seen in Fig. 4. The respective slopes are all negative and their magnitudes are a measure of the contribution by mol of methylene group to each free energy adsorption contribution:  $\Delta G^\circ_{\text{tr}}$ ,  $\Delta G^\circ_{\text{int}}$ , and  $\Delta G^\circ_{\text{ads}}$ . For instance, at 298.15 K,  $-1.63$  kJ mol<sup>-1</sup>;  $-1.375$  kJ mol<sup>-1</sup> and just  $-0.255$  kJ mol<sup>-1</sup> are found for  $d[\Delta G^\circ_{\text{ads}}]/dn$ ,  $d[\Delta G^\circ_{\text{tr}}]/dn$  and  $d[\Delta G^\circ_{\text{int}}]/dn$ , respectively. The former value reflects how spontaneous the adsorption process is. The second value reflects that methylene groups actually contribute



**Fig. 5.** Adsorption free energies versus temperature. (□) PC6, (○) PC8, (Δ) PC10 and (▽) PC12.

to stabilize the polyelectrolyte at the surface regardless the trend of this type of polyelectrolytes to form hydrophobic micro domains in solution as it was demonstrated by Wang and Engberts [20] by fluorescence studies. Probably, the polyelectrolyte adopts at the surface a conformation which is more favorable for the hydrophobic interactions that prevail in solution and at the surface as well. The third value represents that the packing of the polyelectrolyte at the air/water surface occurs spontaneously with a standard free energy contribution just  $-0.255$  kJ mol<sup>-1</sup> of methylene group. The latter reflects the process of the polyelectrolyte stabilization with its hydrophobic tails pointing to the air phase in an arrangement normal to the surface. The latter value reflects that methylene groups contribute spontaneously to cover the interface, vertically or in a more extended shape as the respective polyelectrolyte side chain size increases.

In Fig. 5 the dependence of  $\Delta G^\circ_{\text{ads}}$  versus the absolute temperature is shown. As can be seen, these plots are linear and from the respective slopes the standard adsorption entropies were obtained. In fact, in order to evaluate the standard entropy of adsorption the following equation was used:

$$\Delta S^\circ_{\text{ads}} = -\frac{d(\Delta G^\circ_{\text{ads}})}{dT} \quad (8)$$

These values, along with the standard enthalpies of adsorption, calculated as:

$$\Delta H^\circ_{\text{ads}} = -T^2 \frac{d(\Delta G^\circ_{\text{ads}}/T)}{dT} \quad (9)$$

**Table 4**  
Standard entropies and enthalpies of adsorption.

PCn	$T\Delta S^{\circ}_{\text{ads}}$ (kJ mol <sup>-1</sup> )	$\Delta H^{\circ}_{\text{ads}}$ (kJ mol <sup>-1</sup> )
PC6	68.6	44.9
PC8	61.4	32.1
PC10	59.6	26.9
PC12	51.5	15.5

are summarized in Table 4. The  $\Delta S^{\circ}_{\text{ads}}$  values are positive which reflects that polyelectrolyte are adopting at the interface a less ordered structure than in solution. As it was demonstrated by Wang and Engberst [20] this type of systems are able to form hydrophobic micro domains in solution and their ability increases as the side chain length increases. Thus, as polyelectrolyte migrate to the interface loose part of this ordered structure in an extent that depends on the side chain. Probably, at the interface the polyelectrolyte adopts an extended random coil with their polar piperidinium groups mainly pointed to water phase. Thus, the shorter the side chain, the smaller the ability to maintain the ordered structure at the interface.

On the other hand,  $\Delta H^{\circ}_{\text{ads}}$  values are positive for the three systems studied here. This behavior can be explained in terms of the desolvation degree of the hydrophobic water molecules which associated with the adsorption process. In fact, PC6, the more hydrophilic and the less compact polyelectrolyte should has the higher amount of hydrophobic water molecules solvating their side chains (because their hydrophobic micro domains are the less packed in solution), thus the greater  $\Delta H^{\circ}_{\text{ads}}$ . On the contrary, PC12, the more compact and the less hydrophilic polyelectrolyte, should has fewer “ice-like” water molecules solvating the apolar side chains, thus their adsorption at the surface is accompanied by the smaller water desolvation degree of the series.

#### 4. Conclusions

From the above results, it can be concluded that cationic amphipathic polyelectrolytes show an important surface activity as greater as anionic systems, regardless of their ability to form hydrophobic micro domains that eventually could stabilize the polyelectrolyte in bulk solution. Probably these polyelectrolytes adopt at the surface a conformation that allows it to keep away water, maximizing the hydrophobic interactions between the side aliphatic chains, in a large extent than hydrophobic micro domains do it in bulk solution. Moreover, comparing the magnitude of the areas covered by comonomer unit at the surface obtained with those determined with the Langmuir technique in polyelectrolytes with analogous structure, it was concluded that the limiting area and the surface pressure concepts are independent of the way, i.e., spreading or adsorption, that the polyelectrolyte monolayer was obtained [12,23].

The standard free energy of the adsorption process is mainly determined by their transference contribution from water to the surface as occurs in another polyelectrolyte systems being the main driving force of  $\Delta G^{\circ}_{\text{ads}}$ , the large positive entropy contribution associated with the adsorption at the surface. This work suggests an important application of these polyelectrolytes in the study of dispersions stabilization.

#### Acknowledgement

The financial support of Fondecyt, Research Project 1090092 is acknowledged.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2011.03.063.

#### References

- [1] B.A. Noskov, D.O. Grigoriev, S.Y. Lin, G. Loglio, R. Miller, Dynamic surface properties of polyelectrolyte/surfactant adsorption films at the air/water interface: poly(diallyldimethylammonium chloride) and sodium dodecylsulfate, *Langmuir* 23 (2007) 9641–9651.
- [2] V.M. Kuznetsov, A.V. Akentiev, B.A. Noskov, A.M. Toikka, Spread films of synthetic polyelectrolyte-surfactant complexes: dilational viscoelasticity and effect on water evaporation, *Colloid Journal* 71 (2009) 202–207.
- [3] D. Langevin, Complexation of oppositely charged polyelectrolytes and surfactants in aqueous solutions. A review, *Advances in Colloid and Interface Science* 147–48 (2009) (special issue 170–177).
- [4] D. Langevin, F. Monroy, Interfacial rheology of polyelectrolytes and polymer monolayers at the air–water interface, *Current Opinion in Colloid & Interface Science* 15 (2010) 283–293.
- [5] F. Monroy, F. Ortega, R.G. Rubio, M.G. Velarde, Surface rheology, equilibrium and dynamic features at interfaces, with emphasis on efficient tools for probing polymer dynamics at interfaces, *Advances in Colloid and Interface Science* 134–135 (2007) 175–189.
- [6] B. Miranda, H.M. Hilles, R.G. Rubio, H. Ritacco, D. Radic, L. Gargallo, M. Sferrazza, F. Ortega, Equilibrium and surface rheology of monolayers of insoluble polycations with side chains, *Langmuir* 25 (2009) 12561–12568.
- [7] V.G. Babak, F. Boury, Adsorption kinetics of hydrophobic polysoaps at the methylene chloride–water interface, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 243 (2004) 33–42.
- [8] B.A. Noskov, A.Yu. Bilibin, A.V. Lezov, G. Loglio, S.K. Filippov, I.M. Zorin, R. Miller, Dynamic surface elasticity of polyelectrolyte solution, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 298 (April (1–2)) (2007) 115.
- [9] H.E. Ríos, J.S. Rojas, I.C. Gamboa, R.G. Barraza, Polysoaps solutions: air–water interfacial properties, *Journal of Colloid and Interface Science* 156 (1993) 388–393.
- [10] R.G. Barraza, H.E. Ríos, Surface properties of aqueous solutions of poly(maleic acid-co-vinyl-*n*-alkyl) potassium salts, *Journal of Colloid and Interface Science* 209 (1999) 261–263.
- [11] M.D. Urzúa, W.J. Cabrera, H.E. Ríos, Surface properties of poly (N-monoalkyl maleamic acid-alt-styrene) sodium salts: effect of the molecular weight and the side chain length, *Journal of Colloid and Interface Science* 264 (2003) 284–289.
- [12] H.E. Ríos, C.K. Fonseca, C. Brito, M.D. Urzúa, W.J. Cabrera, Adsorption of poly (mono-*n*-alkylmaleate-alt-N-vinyl-2-pyrrolidone) sodium salts at air/water interface, *Journal of Macromolecular Science Part B: Physics* 45 (2006) 335–342.
- [13] H.E. Ríos, M.H. Aravena, R.G. Barraza, Amphipathic polyelectrolytes at the *n*-octane/water interface, *Journal of Colloid and Interface Science* 165 (1994) 259–263.
- [14] M.D. Urzúa, F.J. Mendizábal, W.J. Cabrera, H.E. Ríos, Interfacial properties of poly(maleic acid-alt-1-alkene) disodium salts at water/hydrocarbon interfaces, *Journal of Colloid and Interface Science* 281 (2005) 93–100.
- [15] R.G. Barraza, A.F. Olea, F. Martínez, I. Ruiz-Tagle, Adsorption of hydrophobically modified polyelectrolytes at the *n*-octane/water interface, *Journal of Colloid and Interface Science* 261 (2003) 559–564.
- [16] M.D. Urzúa, H.E. Ríos, Adsorption of poly(4-vinylpyridine) N-alkyl quaternized at the chloroform/water interface, *Polymer International* 52 (2003) 783–789.
- [17] H.E. Ríos, J.E. González-Navarrete, M.L. Peña, C.D. Sagredo, M.D. Urzúa, Adsorption of poly-2-(dimethylamino) ethylmethacrylate-N-alkyl quaternized at the water/chloroform interface, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 364 (2010) 61–66.
- [18] A. Laschewsky, Molecular concepts, self-organization and properties of polysoaps, *Advances in Polymer Science* 124 (1995) 1.
- [19] R.C. Bazito, F.L. Cassio, F.H. Quina, Synthesis and characterization of chiral [3,22]-ionenes, *Macromolecular Symposia* 229 (2005) 197–202.
- [20] G.J. Wang, J.B.F.N. Engberts, Fluorescence spectroscopic study of the aggregation behavior of non-cross-linked and cross-linked poly(alkylmethyl-diallylammonium bromides) having decyl, octyl, and hexyl side chains in aqueous solution, *Langmuir* 12 (1996) 652–656.
- [21] G.S. Manning, Cluster theory of polyelectrolytes solutions. II. Additivity Rules, osmotic pressure and Donnan equilibrium, *Journal of Chemical Physics* 43 (1965) 4260–4267.
- [22] M.J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd ed., John Wiley & Sons, NY, 1989, pp 70–80.
- [23] L.T. Gargallo, A. Leiva, L. Alegría, B. Miranda, A. González, D.D. Radic, Interfacial properties of poly(N-vinyl-2-pyrrolidone) at the air/water interface, *Journal of Macromolecular Science Part B: Physics* 43 (2004) 913–924.