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Adsorption of poly-2-(dimethylamino) ethylmethacrylate-N-alkyl quaternized at the water/chloroform interface

Hernán E. Ríos*, Javier González-Navarrete, María L. Peña, Claudio D. Sagredo, Marcela D. Urzúa

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

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The interfacial properties of poly-2-(dimethylamino) ethyl methacrylate-N-alkyl quaternized with octyl, decyl, dodecyl and tetradecyl bromide are studied from the chloroform to the water/chloroform interface. In order to estimate the entropy of the adsorption process, the interfacial tension was measured at several temperatures according to the Du Noüy method. The interfacial tension decrease is highly dependent on the hydrophilic–hydrophobic balance between the quaternary ammonium groups and the aliphatic side chains. The shorter the polyelectrolyte side chains the higher the interfacial activity. The excess interfacial concentrations, Γ, are determined according to the Gibbs–Szyszkowski equation and the areas covered by monomer unit at the interface σ are higher than those reported for condensed monolayers of single low molecular weight amphipathic molecules, such as alcohols and carboxylic acids. The free energies of adsorption, ΔG°_{ads}, reveal that the adsorption process is comparable to that occurring in small molecules systems. The linear dependence of ΔG°_{ads} with the number of carbon atoms on the side chain allows estimating the contribution per methylene side group between +0.32 and +0.39 kJ mol^{-1}. On the other hand, the contribution from the polar residue to ΔG°_{ads} ranges between −40.4 and −45.7 kJ mol^{-1}. The dependence of the interfacial tension with temperature suggests that entropy is the driving force factor determining the adsorption process.

1. Introduction

Water soluble amphipathic polyelectrolytes formed by monomers having polar heads and hydrophobic side groups are used in several industrial applications, such as to modify viscosity and stability properties of aqueous solutions and gels [1,2]. Usually, those which are water soluble have been named "hydrophilic polyelectrolytes" or polysoaps, due to their monomer structure resembles a simple detergent molecule. However, they do not show a critical micelle concentration (CMC), because each macromolecule can be considered as a "preformed micelle"; stabilized by hydrophobic interactions occurring into the microdomains that they form.

On the contrary, non-water soluble polyelectrolytes, which have been named "hydrophobic polyelectrolytes", behave as non-ionic polymers with a very low or zero dissociation degree in organic solvents. In these solvents they are probably stabilized as reverse micelles, with their non-polar side chains exposed to the solvent and a polar internal core, which probably accepts some water molecules.

The interfacial properties of amphipathic polyelectrolytes have been practically ignored in the literature. In a previous work [3] we studied the interfacial properties of poly(4-vinylpyridine) N-alkyl quaternized with hexyl, octyl and decyl bromide, at the water/chloroform interface with two major conclusions: the interfacial activity decreases as the side chain length increases and, entropy is the main driving force for the adsorption phenomenon. The interfacial activity of these hydrophobic polyelectrolytes at the water/chloroform interface leads us to propose a model to quantify ion exchange processes through interfaces with potential environmental applications [4].

On the other hand, some cationic derivatives of acrylate and methacrylate monomers such as dimethylamino ethyl methacrylates and acrylates N-alkylquaternized have been studied [5–7]. The monomers were water soluble but not the polymers derived from them [8]. However, some copolymers containing this type of monomer produce water soluble polymers. In fact, they have been recently used for synthesize cross-linked copolymers in order to be used as adsorbents of 4-nitrophenol [9]. The quaternization with short chain alkyl halides derived from dimethylamino ethyl methacrylate and acrylate moieties in block copolymers, yields water soluble copolymers which are able to form micelles. The literature has been extensively revised by Riess [10]. The selective betainization of 2-(dimethylamino) ethyl methacrylate residues in tertiary amine methacrylate diblock copolymers gen-

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* Corresponding author.
E-mail address: hrios@uchile.cl (H.E. Ríos).

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erate water soluble copolymers with a large surface activity [11]. The adsorption and desorption of phosphate and nitrate ions from a quaternary copolymer of polypropylene films, grafted with N,N-dimethylamino ethylmethacrylate, have been recently studied. The quaternizing agents in the latter case were 1-bromo octadecane, methyl iodide and benzyl chloride, in order to increase the ionic character of the film [12]. Recently, some conformational changes have been detected in poly(N,N-dimethylaminoethyl methacrylate) quaternized with benzyl chloride at different proportions. The resulting polycations undergo conformational transitions which are dependent on the polyion concentration, the nature of the counterion (SO_4^{2-} or $S_2O_8^{2-}$) and also on the polyelectrolyte linear charge density. The complexes polyelectrolyte-counterions are also able to remove Congo Red from aqueous solutions [13]. Thus, as it was suggested before, these polyelectrolytes could be used in solid state as potential physical barriers to trap organic pollutants, or in solution, to remove organic or inorganic anions through water/organic solvent interfaces.

Besides, the adsorption kinetics of hydrophobic polysoaps at the methylene chloride/water interface was also studied [14], showing that the adsorption process is characterized by several stages of adsorption with different typical relaxation times. It does not matters if polyelectrolyte adsorption process is conducted from water to the water/oil interface, for hydrophilic polysoaps, or from oil to the 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 [14]. In the late 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 governed by the entropy created by the destruction of ice-like structures, as the polysoap extends their aliphatic chains into the oil phase. In the late case, the adsorption is determined by the enthalpy of hydration of the polar heads, as the polyelectrolyte is adsorbed on the water/oil interface.

Consequently, the aim of the present work is to establish if enthalpy is actually the thermodynamic parameter which governs the polyelectrolyte adsorption process from bulk chloroform to the chloroform/water interface. For this purpose the interfacial activity of poly(N,N-dimethylaminoethyl methacrylate) quaternized with octyl, decyl, dodecyl and tetradecyl bromides, as a function of the polyelectrolyte concentration and temperature, was measured.

2. Experimental

2.1. Materials

The used polyelectrolytes were synthesized as previously described [5,8] and were characterized by IR, ^{1}H NMR and ^{13}C NMR. The polymer structure is consigned in Fig. 1. Bidistilled and ultrafiltered water, with a specific conductivity of 0.4–0.5 μS cm was used. All the other used reagents were of analytical grade. The polyelectrolytes were named C8, C10, C12 and C14, respectively. The polyelectrolyte concentration, *Cp*, was expressed as moles of monomer units/L.

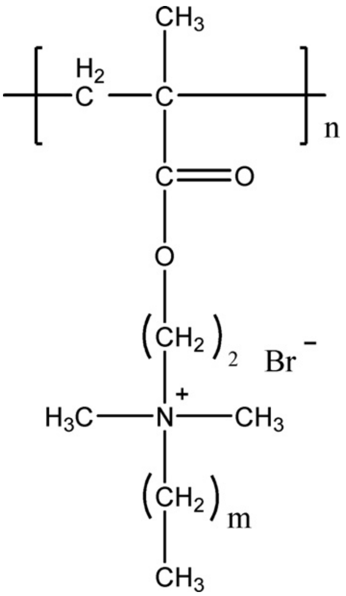

Fig. 1. Polyelectrolyte monomer unit. *m* = 7, 9, 11, 13.

2.2. Methods

The polyelectrolyte molecular weights were determined by GPC with Merck-Hitachi HPLC equipped with a HMW6E Waters Ultra Styragel column using chloroform as solvent and polystyrene form Waters, as standards for the column calibration. The interfacial tension measurements were performed in a Krüss K-8 interfacial tensiometer at 283.15, 298.15 and 313.15 K ± 0.1, according to the Du Nöuy method. The interfacial tensions between pure water/chloroform phases were 29.5, 28.8 and 27.4 mN/m at 283.15, 298.15 and 313.15 K, respectively. The surface tension measurements were performed at least 5 times after thermal equilibrium was reached (after 10–15 min); the results were highly reproducible. No time dependence on interfacial tension measurements was found, at least until 240 min after sample preparation. Viscosity measurements were performed at 298.15 K with a Desreux–Bischoff dilution viscometer in chloroform. The intrinsic viscosity [η] of the solutions was obtained by the classical extrapolation method of Huggins, η_{sp}/Cp versus *Cp* plot.

3. Results and discussion

In Table 1 are summarized some polyelectrolyte characterization data. As can be seen, the average molecular weight, *M*, increases as the side chain length increases as well as the intrinsic viscosity. Obviously, as the side chain increases, *M* should increases as well as the polyelectrolyte hydrodynamic volumes. The GPC chromatograms of these polyelectrolytes are very sharp, as much as of those of the standard, coherent with the low polydispersities reported in Table 1. Thus, it seems probably that polymerization process occurs in the micelle medium, each micelle acting as an independent reaction system and the resulting polyelectrolytes show nearly monodisperse molecular weights because it is well known that micelles of one kind have the same aggregation number (15). The octyl monomer, having the shorter aliphatic chain and the smaller ability to form micelles in water than the greater monomers, presents the smaller polyelectrolyte molecular weight (C8). On the contrary, the tetradecyl monomer, with the larger aliphatic chain of the series and the higher their molecular weight (C14), should have the greater capability to form micelles.

Fig. 2a–c shows the behavior of γ_{int}, in the high dilution range, as a function of *Cp* for the four polyelectrolytes studied here, at 283.15,

Table 1
Polyelectrolytes characterization data.

Polyelectrolyte	*M*	[η] (dL g^{-1})	Mw/Mn
C8	15,000	0.04	1.08
C10	29,000	0.17	1.04
C12	72,000	0.38	1.05
C14	91,000	0.46	1.06

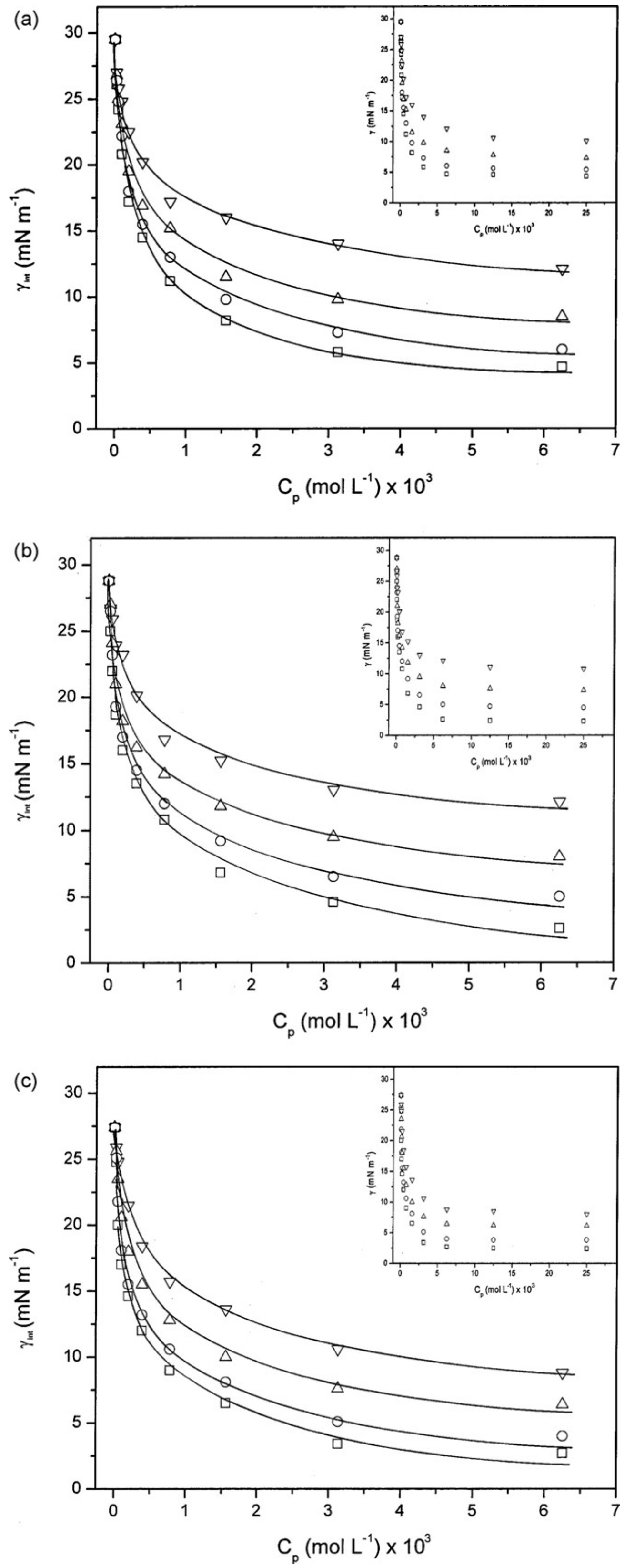

Fig. 2. Interfacial tension dependence with polymer concentration for (□) C8, (○) C10, (△) C12, and (▽) C14 at (a) 283.15 K, (b) 298.15 K, and (c) 313.15 K.

298.15 and 313.15 K, respectively. In these figures, the experimental data for γ_{int} versus *Cp*, in all the studied concentration range, are also shown. In all cases there is an important decrease of γ_{int} with *Cp*, reaching a plateau, which is slightly temperature dependent. In fact, as the temperature increases, the interfacial activity is more pronounced. On the other hand, at constant temperature, the value of *Cp* where the plateau is reached depends on the kind of polyelectrolyte. Moreover, the decrease of γ_{int} for these systems is more pronounced than that reported in anionic polyelectrolytes at the n-octane/water interface [15]. According to Fig. 2a–c, the interfacial activity follows the same order, as indicated for the derivative. In fact, at the high dilution, the general trend of the absolute values of $d\gamma_{\text{int}}/dCp$ follows the sequence 48000 for C14, 81900 for C12 99250 for C10 and 101700 for C8, whereas the interfacial activity follows the opposite tendency. The monomer units of these polyelectrolytes differ only in the length of their side chains, thus they have an increasing hydrophobic character from C8 to C14, since the polar group is the same in all of them, a quaternary ammonium group with bromide as counterion. In a solvent with low dielectric constant, such as chloroform, the ammonium groups are forming ion pairs with their counterions, with a very low dissociation degree. For this reason these systems have been considered hydrophobic polyelectrolytes [14] and the enormous interfacial activity here reported derives fundamentally form the hydrophilic character of their quaternary ammonium groups, which makes the polyelectrolyte to migrate spontaneously to the chloroform/water interface. Effectively, the γ_{int} behavior suggests that C14 is the most chloroform solvated polyelectrolyte, thus this polyelectrolyte should be predominantly stabilized in the bulk chloroform. On the other hand, the higher hydrophilic character of C8 is reflected in a greater γ_{int} decrease when compared with the other polyelectrolytes. Obviously, the interfacial tension behavior is dependent on factors such as the solvation degree, the hydrophilic–hydrophobic balance of the monomer unit, the strength of the ion pair between the bromide and the ammonium groups and if the polyelectrolyte transference occurs from an organic solvent to an organic solvent/water interface or from an aqueous solution to a water/organic solvent interface. A molecular description of these transference processes which certainly have some thermodynamic implications, has been appropriately described by Babak and Boury [14].

In order to quantify the adsorption process, the Gibbs equation was used to estimate Γ [16]:

$$\Gamma = -(RT)^{-1} Cp \left(\frac{d\gamma_{\text{int}}}{dCp} \right) \qquad (1)$$

Γ is the excess surface concentration and *R* and *T* have their usual meaning. Eq. (1) is usually applied for non-electrolyes. However, the hydrophobic polyelectrolytes here studied behave as non-electrolytes in a medium of low dielectric constant such as chloroform ($\varepsilon = 4.8$). In addition, the specific electric conductivity of the polyelectrolyte solutions was identical to that of pure chloroform revealing null dissociation degree. In order to evaluate the slopes, $d\gamma_{\text{int}}/dCp$, the experimental data of γ_{int} versus *Cp* were adjusted to the Szyszkowski's empirical equation:

$$\gamma_{\text{int}} = \gamma^{\circ}_{\text{int}} - \gamma^{\circ}_{\text{int}} B \,\text{Log} \left[\left(\frac{Cp}{A} \right) + 1 \right] \qquad (2)$$

Here $\gamma^{\circ}_{\text{int}}$ is the interfacial tension between pure phases, and *A*, *B* are two empirically adjusted parameters which are related to the standard free energy of adsorption, $\Delta G^{\circ}_{\text{ads}}$, and to the areas covered by molecules at the interface, respectively. Table 2 summarizes the values of *A*, *B* and their respective errors from the fitting to the experimental data shown in Fig. 2a–c. In general, at constant temperature, *A* increases as the polyelectrolyte side chain length increase. Therefore, the shorter the polyelectrolyte side chain, the higher the polyelectrolyte interfacial activity. In fact, C8 having the

Table 2
Empirical adjustment parameters of Szyszkowski's equation, limiting excess surface concentrations (Γ^{∞}), areas covered per molecule (σ) and standard free energies of adsorption, $\Delta G^{\circ}_{\text{ads}}$.

T (K)	Polímero	$A \times 10^6$	B	Error[a]	$\Gamma^{\infty} \times 10^{10}$ (mol cm^{-2})	σ (Å^2)	$-\Delta G^{\circ}_{\text{ads}}$ (kJ mol^{-1})
283.15	C8	1.30	0.341	0.88	4.27	38.9	37.8 ± 0.2
	C10	1.64	0.324	0.62	4.06	40.9	37.3 ± 0.1
	C12	1.89	0.294	0.55	3.68	45.1	36.9 ± 0.2
	C14	3.04	0.267	0.28	3.35	49.6	35.8 ± 0.2
298.15	C8	1.13	0.332	0.87	3.85	43.1	40.2 ± 0.3
	C10	1.43	0.323	0.87	3.75	44.3	39.6 ± 0.3
	C12	1.60	0.285	0.76	3.31	50.1	39.3 ± 0.1
	C14	2.79	0.265	0.47	3.07	54.0	37.9 ± 0.2
313.15	C8	1.01	0.343	0.74	3.61	46.0	42.5 ± 0.2
	C10	1.30	0.320	0.93	3.37	49.3	41.8 ± 0.3
	C12	1.55	0.286	0.53	3.01	55.2	41.4 ± 0.1
	C14	2.59	0.258	0.14	2.72	61.1	40.0 ± 0.1

[a] $\left|\gamma_{\text{exptl}} - \gamma_{\text{theor}}\right|$.

shorter side chain has greater hydrophilic character than C10, C12 and C14, respectively. On the other hand, at constant temperature, B decreases as the polyelectrolyte lateral chain length increases. Similar effect has been reported in pyridinium type hydrophobic polyelectrolytes, although in that case, the dependence is less pronounced than in the present work [3].

Differentiating Eq. (2) it is possible to obtain:

$$\frac{d\gamma_{\text{int}}}{dCp} = -\frac{\gamma^{\circ}_{\text{int}}B}{Cp + A} \tag{3}$$

This last equation can be related to Eq. (2) in order to get the Gibbs–Szyszkowski equation:

$$\Gamma = \frac{\gamma^{\circ}_{\text{int}}BCp}{RT(Cp + A)} \tag{4}$$

The dependence of Γ with Cp for all the systems here studied was plotted according Eq. (4) and the behavior is shown in Fig. 3 at 298.15 K. As can be seen, all these profiles are typical of saturation curves. At low Cp, Γ is nearly linear with Cp whereas at high Cp, Γ becomes practically independent on Cp reaching a plateau where the interface should be saturated. In these figures it can be observed that at the plateau, Γ follows the order C14 < C12 < C10 < C8. Obviously, fewer C14 polyelectrolyte monomers are required to cover the interface than C8 polyelectrolyte monomers due to the higher size of the C14 monomers.

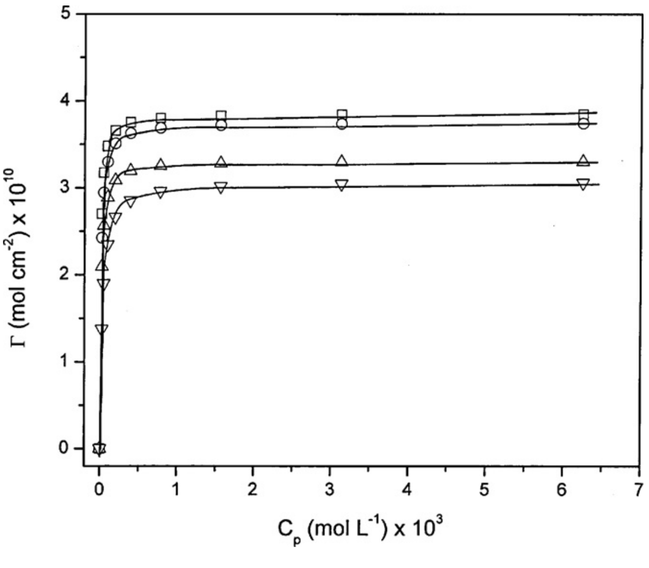

Fig. 3. Excess interfacial concentration for (□) C8, (○) C10, (△) C12, and (▽) C14 at 298.15 K.

If $Cp \gg A$, Eq. (4) becomes:

$$\Gamma^{\infty} = \frac{\gamma^{\circ}_{\text{int}}B}{RT} \tag{5}$$

and the areas covered by monomer unit at the interface, σ, is:

$$\sigma = (\Gamma^{\infty}N_a)^{-1} \tag{6}$$

The values of Γ^{∞} and σ at each temperature are summarized in Table 2. As can be seen the values of σ are greater than those reported from condensed films of single amphiphatic low molecular weight molecules, such as alcohols, carboxylic acids, and long chains p-phenols [17]. Evidently, the polyelectrolytes have some restrictions inherent to their structure which are not present in single molecules. In all cases, at constant temperature, σ increases as the polyelectrolyte side chain increase. Similar trends for σ have been reported in polyelectrolytes derived from poly(maleic acid-co-1-olefins) potassium salts [18], as well as poly (monoalkyl maleate-co-styrene) sodium salts [15], at the n-octane/water interface, and poly(monoalkylmaleate-alt-N-vinyl-2-pyrrolidone) sodium salts at the air/water interface [19]. The same trend for σ was reported on the adsorption of poly(4-vinyl pyridine) N-alkyl quaternized at the chloroform/water interface [3]. However, the effect of the size of the lateral chain in the latter case is smaller than that observed in the present work. Differences can be attributed to the cationic monomer structure, pyridinium in that case and quaternary ammonium in the present work.

Obviously, polyelectrolytes with larger side chains should cover a greater area at the interface. In fact, polyelectrolytes with shorter side chains adopt, at the interface, a more compact structure than those with larger side chains.

On the other hand, at constant side chain, the areas covered at the interfaces increases as the temperature increases, and the polyelectrolyte probably adopts a more loose structure. Thus, polyelectrolytes with shorter side chains are more packed at the interface with their lateral chains pointing to the chloroform phase, perpendicularly to the interface, and their polar heads in contact with the water phase where the solvation of the ammonium and bromide groups take place as it was stated by Babak and Boury [14]. The same phenomenon should occur with larger side chains polyelectrolytes with the chains disposed in a more flat conformation at the interface. In polyelectrolytes, the covered area by monomeric unit is an average area because of the monomeric units forming the polyelectrolyte is less free than simple low molecular weight amphipathic molecules. As stated above the polyelectrolyte has some limitations to accommodate the monomer units at the interface, which are inherent to the polymer structure.

As can be inferred from the negative values of the standard free energies of adsorption, $\Delta G^{\circ}_{\text{ads}}$ summarized in Table 2, in all cases

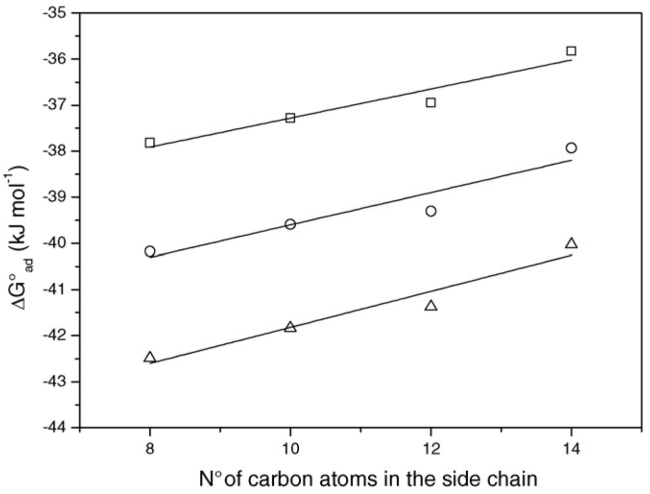

Fig. 4. Standard free energies of adsorption dependence with the number of carbon atoms in the side chain. (□) 283.15 K, (○) 298.15 K, and (△) 313.15 K.

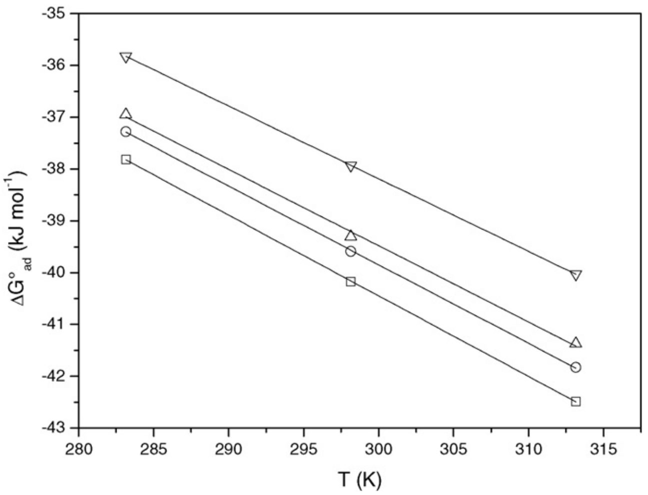

Fig. 5. Dependence of the standard free energies of adsorption with temperature, (□) C8, (○) C10, (△) C12, and (▽) C14.

the adsorption process occurs spontaneously. These values were determined according to the following equation [16]:

$$\Delta G^{\circ}_{\text{ads}} = 2.303RT[\text{Log}(A) - 1.09] \qquad (7)$$

1.09 is the decimal logarithm of the molal chloroform concentration. As can be observed, these $\Delta G^{\circ}_{\text{ads}}$ values become more negative as the polyelectrolyte side chain decreases. This fact is consistent with the greater hydrophilic character of the polyelectrolyte as their lateral hydrophobic chain decreases. These $\Delta G^{\circ}_{\text{ads}}$ values are similar than those reported in poly(4-vinylpyridine) N-alkyl quaternized with hexyl, octyl and decyl bromides pyridinium [3], however they are greater than those reported for polyelectrolytes derived from maleic anhydride in water/n-octane interface and at the water/hydrocarbon interfaces [16,18,20]. Nevertheless, in the last three cases the polyelectrolytes were water soluble and migrate from the aqueous solution to the water/organic solvent interface. In the present work the process is opposite to that described before. However, the observed $\Delta G^{\circ}_{\text{ads}}$ are in the same order of magnitude. Different from these $\Delta G^{\circ}_{\text{ads}}$ values are those reported by Olea et al., for poly-(maleic acid-alt-n-1-alquene) dipotassium salts, where probably adsorption competes with micellization [18].

The contribution per mol of methylene group to the total $\Delta G^{\circ}_{\text{ads}}$ was obtained plotting these values against the number of carbon atoms in the lateral chain of the monomer unit. Fig. 4 shows that this dependence is linear in all cases. From the slope and the intercept of these plots the contribution to $\Delta G^{\circ}_{\text{ads}}$ for methylene group and the polar group was, respectively, obtained. These values are summarized in Table 3. As can be observed the contribution to $\Delta G^{\circ}_{\text{ads}}$ per methylene group is small but positive in all the temperature range here studied, therefore, methylene groups do not contribute to the adsorption process reflecting that these groups are more stable in the bulk chloroform. On the other hand, the contribution of the polar group to $\Delta G^{\circ}_{\text{ads}}$ is negative. Thus, these groups contribute to the adsorption process at the interface, consistent with the more hydrophilic character they have. Moreover, for the same polyelectrolyte, the $\Delta G^{\circ}_{\text{ads}}$ values per methylene group are more positive as the temperature increases, which reflects how favorable become the interaction between non-polar methylene groups and chloroform, as the temperature increases. On the other hand, as the temperature increases, $\Delta G^{\circ}_{\text{ads}}$ values for the polar, 2-(dimethylamino) ethyl methacrylate bromide groups become more negative. Thus, temperature increases the adsorption process of these groups at the interface. This phenomenon can be explained in terms of an increase of the ion pair bromide-ammonium dissociation as the temperature increases producing a more hydrophilic behavior of these groups as they arrive to the interface.

In order to determine the standard entropy of the adsorption process by monomer unit, $\Delta S^{\circ}_{\text{ads}}$, the dependence of the $\Delta G^{\circ}_{\text{ads}}$ with temperature was plotted, as can be observed in Fig. 5. From the slopes of these curves the $\Delta S^{\circ}_{\text{ads}}$ were obtained and their values are summarized in Table 4. All these values are positive reflecting that the polyelectrolyte at the interface adopts a less ordered conformation than in the bulk solvent. In fact, this kind of polyelectrolytes behaves like a quasi-reverse micelle systems with their non-polar side groups solvated by chloroform molecules and an hydrophilic core which can contain water molecules. As polyelectrolytes migrate to the interface they loose this ordered structure and at the interface can adopt a random coil conformation with their polar groups mainly exposed to the water phase. However, the $\Delta S^{\circ}_{\text{ads}}$ values decreases as the lateral chain increases, thus the longer the lateral chain the higher the ability to maintain the bulk ordered quasi-reverse micelle structure at the interface. Similar trend and comparable values for $\Delta S^{\circ}_{\text{ads}}$ were found in poly(4-vinylpyridine) N-alkyl quaternized with hexyl, octyl and decyl bromides [3].

In fact, having the C8 polyelectrolyte the higher hydrophilic character of the series, its adsorption at a hydrophilic–hydrophobic interface from the bulk solvent is the most disordered process loosing almost completely its quasi-reverse micelle structure.

Table 3
Contributions to $\Delta G^{\circ}_{\text{ads}}$.

T (K)	$\Delta G^{\circ}_{\text{ads}}$ (kJ mol^{-1})[a]	$-\Delta G^{\circ}_{\text{ads}}$ (kJ mol^{-1})[b]
283.15	0.32	40.4
298.15	0.35	43.1
313.15	0.39	45.7

[a] Per mol of methylene group.
[b] Per mol of polar group.

Table 4
Thermodynamic adsorption parameters.

Polyelectrolyte	$T\Delta S^{\circ}_{\text{ads}}$ (kJ mol^{-1})	$\Delta H^{\circ}_{\text{ads}}$ (kJ mol^{-1})
C8	46.6	6.3
C10	45.2	5.7
C12	43.9	4.8
C14	39.6	3.9

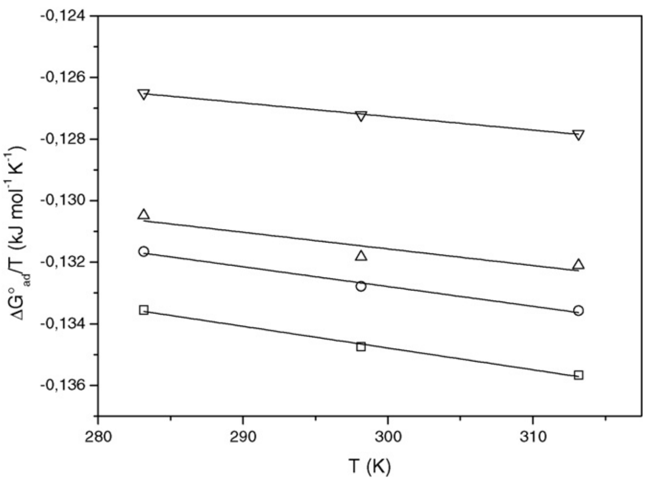

Fig. 6. Dependence of $\Delta G^\circ_{ads}/T$ with the temperature. (□) C8, (○) C10, (△) C12, and (▽) C14.

The standard enthalpies of the adsorption process ΔH°_{ads} were determined according to the following equation:

$$\Delta H^\circ_{ads} = -T^2 \frac{d(\Delta G^\circ_{ads}/T)}{dT} \tag{8}$$

Obviously, ΔS°_{ads} was considered constant in the temperature range here studied. The slopes $d(\Delta G^\circ_{ads}/T)/dT$ were obtained from plots of $\Delta G^\circ_{ads}/T$ versus T which, as can be seen in Fig. 6, are linear. The values of ΔH°_{ads} summarized in Table 4 are all positive. The adsorption process can be analyzed in terms of a balance between several effects. One of them, which involve some chloroform desolvation degree of the non-polar aliphatic side chains, is endothermic. Another process implying solvation of the polar ammonium groups and their bromide counterions at the interface by water molecules, is naturally exothermic; however to do this, water structure nearby the interface should be reorganized, which is an endothermic process. Finally, the rearrangement of the polyelectrolyte at the interface is a process which requires work for their occurrence. The sum of all these contributions results in a small positive enthalpy for the adsorption process in this case. Similar trend was reported in a poly(4-vinylpyridine) N-alkyl quaternized with hexyl, octyl and decyl bromides [3].

4. Conclusions

From the above results it can be concluded that the adsorption process results in a hydrophilic–hydrophobic balance of the polar and non-polar groups of the monomer structure. The contribution to ΔG°_{ads} per mol of methylene group is positive because aliphatic chains makes that the polyelectrolyte stays in the bulk chloroform, probably stabilized in a quasi-reverse micelle conformation. The solvation of the polyelectrolyte monomeric units could be altered by temperature, probably inducing conformational changes depending on their length. Finally, we can state that the main driving force contributing to the negative values of ΔG°_{ads} arises from the positive values of the standard entropy of adsorption, on the contrary to that proposed in literature [14]. The interfacial activity of these polyelectrolytes is a relevant property of these systems, which can be used as potential adsorbents of contaminant ions through interfaces.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2010.04.037.

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