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Adsorption of amphiphilic polysaccharides onto polystyrene latex particles

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Abstract

Adsorption properties of hydrophobically modified carboxymethylpullulans (HMCMP) with different degree of modification of alkyl chains (C8) onto polystyrene latex particles have been investigated. Hydrophobic interactions between the grafted alkyl chains and the surface are responsible for the adsorption of these polymers. Their adsorption isotherms are Langmuir type, therefore, there is only a monolayer of adsorbed polymer chains. Variations of plateau adsorbed amounts and adsorbed layer thicknesses show a competition between the number of anchors (alkyl chains) and size of loops. Desorption of adsorbed polymer chains has been tested in three different media (0.1 M NaCl, pure water and 0.01 M NaOH). The greater desorbed amount has been obtained in 0.01 M NaOH (hydrolysis of ester bonds).

Keywords: Amphiphilic polysaccharide; Latex particles; Adsorption

1. Introduction

Polysaccharides are of growing interest as they show many unique properties such as biocompatibility, biodegradation, biological activity. They are particularly useful for the rheological control, stabilization and emulsification of suspension. For specific applications and particularly when the polymer solution is the continuous phase for a suspension of dispersed solid particles, surface-active amphiphilic polymers can be very useful to optimize the properties of the suspension by a suitable control of the chemical structure and/or physical features. In this context, the grafting of alkyl groups variable in length and in quantity allows to envisage a whole range of amphiphilic systems with adaptative properties. Hydrophobically modified polymers are often used in this manner in aqueous-based dispersions [1,2] and to prevent adsorption of proteins by changing the nature of the adsorbing substrate surface [3–6].

Few systematic studies on adsorption of amphiphilic polysaccharides at the solid–liquid interface are reported in the literature [7,8] contrary to synthetic amphiphilic polymer [9–12]. Therefore, the aim of this work was to study the adsorption characteristics of a series of model amphiphilic polysaccharides onto latex particles.

The polysaccharides considered here are hydrophobically modified carboxymethylpullulans (HMCMP) with different degree of modification of octyl chains (C8). In a recent article [13] the solution properties in salt medium of these samples were studied by means of viscometry and flow field-flow fractionation with on-line coupling multi-angle laser light scattering (F4/MALLS). In dilute solution polymer/polymer hydrophobic interaction increases with degree of modification of C8. At lower degree of modification, the main species in solution are composed of isolated chains, the conformation of which is close to that the non-amphiphilic precursor. However, some aggregates of polymer chains are present in solution and aggregation trend increases with the degree of modification. For higher degree of modification ($\approx 30\%$ of octyl chains per anhydroglucose units), compact structure formed of isolated polymer chains has been identified due to intramolecular hydrophobic associations. We have shown that a competition between intramolecular and intermolecular associations could explain the metastability of the solution [14].

We report here the adsorption of such HMCMP with

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Table 1
Characteristics of PS latex particles

Sample	Diameter (nm)[a]	Zeta potential (mV)[b]	% latex particles (wt)
Latex A	375±5	−37±1	8.52
Latex B	95±1	−42±1	11.61

[a] Determined by PCS measurements after filtration (filter: 0.45 μm).

[b] Determined in pure water.

different degree of modification of octyl group onto polystyrene (PS) latex particle.

2. Experimental section

2.1. Materials

2.1.1. Polymers

Pullulan (a flexible, neutral and linear polysaccharide) was purchased from Hayashibara Biochemical Laboratory (Okayama, Japan). The different products used hereafter were commercially available and used without further purification. Water was from a Milli-Q water reagent system.

Synthesis of carboxymethylpullulan (CMP) and hydrophobically modified carboxymethylpullulans (HMCMP) has been described by Duval et al. in a previous work [15,16]. The octyl pendant groups are grafted onto carboxylic acid functions of the CMP (initial $DS_{COOH} \sim 1$) through ester links. As described previously, the sodium salt of carboxymethylpullulan (CMP, Na^+) was synthesized in water/isopropanol medium by reacting the hydroxyl groups of pullulan with sodium chloroacetate in the presence of sodium hydroxide. For the synthesis of HMCMP, an aqueous solution of CMP, Na^+ was transformed into its acidic form (CMP, H^+) by percolating through a cationic resin (Amberlite IRN-77, H^+ form) and then neutralized by tetrabutylammonium hydroxide (Bu_4N^+, OH^-) up to pH7. After freeze-drying, the CMP, Bu_4N^+ was dissolved in dimethylsulfoxide (DMSO) at 40 °C. Octyl bromide was added and the reaction continued at the same temperature with magnetic stirring for a night. An excess of LiCl was added to convert HMCMP, Bu_4N^+ into the lithium salt form (HMCMP, Li^+) that precipitated in DMSO and was remove by filtration. HMCMP, Li^+ was washed and precipitated twice in ethanol. After filtration and drying, an aqueous solution of HMCMP, Li^+ was allowed to dialyse against pure water for 7 days until complete removal of Chloride. Finally the polymer was freeze-dried [15,16].

A $\bar{M}_n$ of 170,000 g mol^{-1} with a polydispersity index (I_p) of 1.9 were found for the synthesized CMP using size exclusion chromatography on-line coupled with multi angle laser light scattering (SEC/MALLS). The samples were coded as CMP–*x*–C8 with *x* the degree of modification (number of alkyl chains per 100 anhydroglucose units). *x* was determined by measuring the quantity of octanol (gas chromatography) after total saponification of the ester groups of CMP–*x*–C8 sample [15,17].

2.1.2. Latex particles

Two polystyrene latex particles varying by their sizes (A and B) were synthesized by emulsifier-free emulsion polymerization of styrene and sodium styrene sulfonate using potassium persulfate as initiator according to Juang and Krieger [18]. Latexes are slightly charged (less than 1% of sodium styrene sulfonate with regard to the amount of styrene introduced during synthesis) to allow stabilization of the particles in aqueous media. Their characteristics are reported in Table 1. The particles were spherical and quite homogeneous in size as indicated by scanning electronic microscopy (SEM).

Turbidity measurements [8,19] have shown that PS latex particles flocculate at NaCl concentration of 10^{-1} M due to screening of electrostatic repulsions.

2.2. Methods

2.2.1. Preparation of solutions

Solutions were prepared by dissolving polymer in Milli-Q water then, after stirring, ionic strength was adjusted. Adsorption of charged polymer onto charged latex particles needs the presence of a low ionic strength to screen electrostatic repulsion This point will be discussed below.

2.2.2. Adsorption isotherms

Adsorption isotherms were determined as follows: 8 g of polymer solution was added to 2 g of concentrated latex dispersion. The solid/liquid ratio (*S*/*L*) was fixed at 1.7×10^{-2} g of latex/g of solution for all the experiments (see below). The resulting solutions were magnetically stirred at 25 °C for 30 h (see below). After adsorption, the samples were centrifuged at 15,000 rpm for 1 h (Sigma laborzentrifugen 2K15) and a part of supernatant, containing non-adsorbed polymer, was taken. It has been verified that no free polymer was eliminated during the centrifugation step. The adsorbed amount (Γ) was determined from the difference between the initial polymer concentration and the concentration in the supernatant, determined using a total organic carbon analyzer (TOC-Vcsn, Shimadzu, Japan). A such method allows the determination of Γ with acceptable uncertainty (less than 10%).

The adsorption isotherms were established by using the latex particles of 375 nm (sample A). With latex particles of smaller size, the centrifugation of adsorbed particles is difficult.

2.2.3. Adsorbed layer thickness

Photon correlation spectroscopy (PCS) was used for determining the adsorbed layer thickness (δ_H) from the measurement of the mean diffusion co-efficient (D_t) of bare and polymer-coated particles. The apparent hydrodynamic radius (R_H) was calculated from the diffusion coefficient of

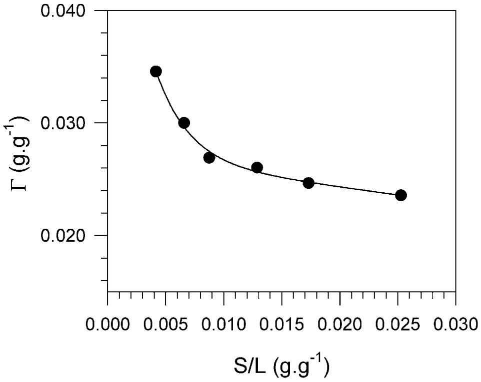

Fig. 1. Influence of the *S*/*L* ratio on CMP-23-C8 adsorbed amount (T = 25 °C, 0.1 M NaCl medium, $C_{\text{pinitial}} = 1.4$ g L^{-1}).

translation (D_t) by application of the Stokes–Einstein equation:

$$R_H = \frac{kT}{6\pi\eta D_t}$$

where k is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the dispersion medium. The Stokes–Einstein equation provides a direct method for determining the mean hydrodynamic radius of a collection of colloidal particles undergoing Brownian motion. The apparent adsorbed layer thickness was obtained from the difference of apparent R_H of polymer-covered and bare particles [20–22].

For analysis, the initial latex dispersion (cf. Table 1) is diluted with a factor 1000 and the polymer concentration is about 1 g L^{-1}, the whole at the desired salinity. Latex and polymer solutions are filtered through 0.45 μm membrane. After 2 days of stirring, the dispersion was analyzed with a Macrotron photogoniometer AMTEC (SEMATECH, Paris, France) fitted with a 5 mW He–Ne laser ($\lambda = 633$ nm) and a RTG correlator at a scattering angle of 90°.

The layer thicknesses were measured using both synthesized latex particles but the precision has been found better with the smaller latex particles (i.e. latex B). This point will be particularly discussed in the following (Section 3.1.3).

2.2.4. Electrokinetic measurements

Zeta potentials were determined with a Zetasizer 3000 (Malvern Worcestershire, UK). In the case of polymer-coated particles, they were centrifuged first and redispersed in 0.1 M NaCl medium in order to remove non-adsorbed polymer.

2.2.5. Desorption measurements

Desorption measurements were realized as follows: solutions of polymer were allowed to adsorb, in 0.1 M NaCl at 25 °C, as described for the adsorption measurements (see above), then centrifuged. Supernatants were removed from centrifugation tubes; insoluble parts (latex + adsorbed polymer) were washed quickly with twice 5 mL of 0.1 M NaCl, and then put again in suspension in the tested medium. After magnetically stirring (24 h at 25 °C), suspensions were centrifuged and the supernatants were collected. The adsorbed amount after desorption was determined by measuring the concentration of polymer in the new supernatant with a total organic carbon analyzer.

3. Results and discussion

3.1. Adsorption measurement

Before realizing an adsorption isotherm the effect of different parameters (time, *S*/*L* ratio, size of particles) on adsorption of HMCMP was determined.

Adsorption properties of HMCMP were performed in 0.1 M NaCl to ensure adsorption. Indeed, in water, the electrostatic repulsions between anionic latex particles and anionic HMCMP prevent any adsorption. Adsorption of polymer onto latex surface decreases with pH until the value of 5, where a plateau is reached. Based on this result, pH has been fixed to 5 for which all carboxylic groups are ionized and adsorption becomes independent of the pH.

3.1.1. Kinetics of adsorption

The amount of adsorbed polymer (expressed as Γ in milligram of adsorbed polymer per gram of latex particles) has been measured as a function of time (results not shown) at pH = 5 and $S/L = 1.7 \times 10^{-2}$ g g^{-1}. The kinetics of adsorption was very fast and a plateau was already reached after less than 1 h of contact (full adsorption level).

For a convenient reason, a contact time between polymer and latex particles of 30 h has been chosen in order to determine the levels of adsorption.

3.1.2. Influence of the solid/liquid ratio

Many studies have shown the influence of the solid/liquid ratio on the levels of adsorption [9,10,23]. Fig. 1 represents the evolution of adsorbed amount for CMP-23-C8 as a function of the solid/liquid ratio (*S*/*L*) in 0.1 M NaCl for an initial concentration of polymer high enough ($C_{\text{pinitial}} = 1.4$ g L^{-1}) to obtain plateau adsorbed amount. It is found that Γ decreases when *S*/*L* ratio increases then reaches a plateau. This trend has been observed for several systems [9,10] and is explained by the formation of polymer bridges between latex particles, then flocculation of these particles and, therefore, decrease the adsorption surface. When *S*/*L* ratio decreases, there are less polymer bridges since, the distance between particles increases, therefore, the available surface for adsorption increases.

In what follows the amount of polymer adsorption was measured a *S*/*L* ratio of 1.7×10^{-2} g g^{-1} i.e. on the plateau.

Table 2
Adsorbed polymer layer thickness for two different polymers and particles ($T=25$ °C, 0.1 M NaCl)

Polymer	CMP-11-C8		CMP-24-C8	
Latex	B	A	B	A
δ_H (nm)	37	56	26	35
$\delta_{H,\mathrm{eff}}$ (nm)	73	74	42	41

See the text for details.

3.1.3. Influence of size particles on the adsorption of HMCMP

In this work two different sizes of particles were used in order to study the adsorption properties of HMCMP. Latex particles of large size (i.e. 375 nm) were used for the determination of the adsorbed amount of polymer. This choice has been done to make easier the recovery of coated particles upon centrifugation. On the other hand, latex particles with smaller size (i.e. 95 nm) were used for measuring the adsorbed polymer layer thickness.

To know if the particle radius has an effect on their adsorption properties, the thickness of adsorbed layer of two polymers was determined for the two different particles in 0.1 M NaCl medium (Table 2). We can notice that the thickness increases when the particle radius increases as reported by several authors [24–27]. Garvey et al. [26] have explained this fact on geometrical considerations by assuming that the surface and the volume occupied by an adsorbed polymer molecule is independent of the curvature radius. So when the particle radius decreases, an adsorbed polymer molecule can occupy more space laterally and since, volume is constant, thickness of the adsorbed layer decreases. In order to test this explanation, we have calculated an effective layer thickness $\delta_{H,\mathrm{eff}}$ corresponding to adsorption on an equivalent flat surface using the following equation [25]:

$$\delta_{H,\mathrm{eff}} = \frac{(R_H + \delta_H)^3 - R_H^3}{3 \times R_H^2}$$

where R_H is the hydrodynamic particle radius. The obtained values are reported in Table 2.

We can notice that values of $\delta_{H,\mathrm{eff}}$ do not depend on hydrodynamic particle radius which could mean that particle size has only geometrical influence on HMCMP adsorption. However, the above equation is strictly valid if adsorbed polymer amount is independent of the particle radius. This hypothesis is usually checked [25,26] except for adsorption of tribloc co-polymers (PEO)–(PPO)–(PEO) on latex [24].

The verification has shown that the size of the latex particles induces geometrical differences but do not change the adsorption process. Consequently, whatever the used latex particles, i.e. larger for adsorbed polymer amount and smaller for adsorbed polymer thickness, the correlation between such obtained results is relevant.

3.2. Influence of the hydrophobic modification on the adsorption properties of HMCMP

3.2.1. Adsorption isotherms

Useful information on the adsorption can be obtained from the adsorption isotherms which represent the plot of adsorbed amount (Γ) as a function of equilibrium polymer concentration in the supernatant (C_s) at the equilibrium state and controlled temperature.

All the adsorption isotherms are non-linear in concentration and may be described by Langmuir isotherms: the level of adsorption first increases after which it levels off (plateau). (Fig. 2). Scatchard type analysis adequately account for the isotherms behaviour [28]:

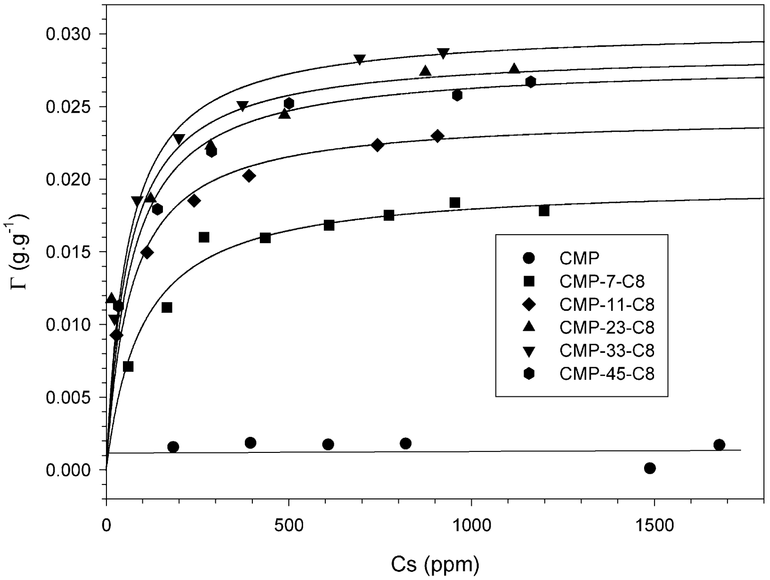

Fig. 2. Adsorption isotherms of CMP and CMP-x-C8 in 0.1 M NaCl medium at 25 °C ($S/L=1.7\times10^{-2}$ g g^{-1}), fitted with the Langmuir model.

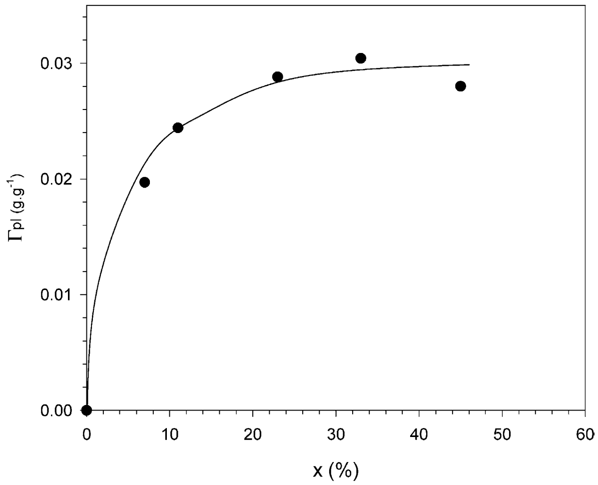

Fig. 3. Values of Γ_{pl} deduced from the Scatchard linearisation for HMCMP in 0.1 M NaCl medium at 25 °C ($S/L = 1.7 \times 10^{-2}$ g g^{-1}).

$$\frac{C_s}{\Gamma} = \frac{1}{K \times \Gamma_{pl}} + \frac{C_s}{\Gamma_{pl}}$$

with C_s: equilibrium polymer concentration; Γ: adsorbed amount; Γ_{pl}: plateau adsorbed amount; K: affinity constant between polymer interaction sites and latex interaction sites.

On Fig. 2 it can be seen that Langmuir's model is perfectly adapted to describe the isotherms. Consequently it appears that adsorption is limited to monolayer formation onto latex surface. This monolayer adsorption has also been observed for systems based on similar amphiphilic polymers [23,29,30], whereas for other amphiphilic polymers notably those with a block repartition of hydrophobic groups, it has been evidenced a multi-layer adsorption [9,10]. Therefore, it seems that the repartition of amphiphilic groups on the hydrophilic backbone is a parameter of great importance for the adsorption process.

All the isotherms have a high affinity, i.e. at low concentration Γ rises sharply while at higher concentration it reaches a plateau. The level of adsorption at the plateau Γ_{pl} (determined from the Scatchard analysis) depends strongly on the number of octyl groups up to $x = 20\%$ then a plateau is obtained for higher x indicating that the latex surface is saturated with polymer (Fig. 3).

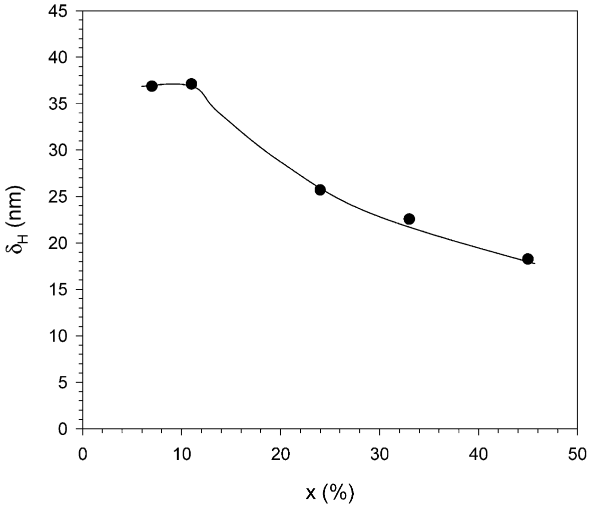

Fig. 4. Values of δ_H for HMCMP in 0.1 M NaCl medium at 25 °C.

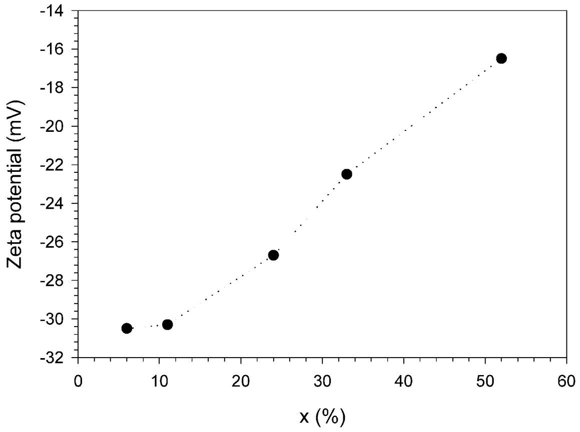

Fig. 5. Variation of zeta potential as a function of degree of modification in 0.1 M NaCl medium at 25 °C ($S/L = 1.7 \times 10^{-2}$ g g^{-1}).

Useful information was hoped from the analysis of the constant K of the above equation, which is related to polymer/surface affinity. Unfortunately K is obtained with a poor precision.

3.2.2. Thickness of the adsorbed layer

The thickness of the adsorbed layer, which is comprised between 20 and 40 nm values close to the gyration radius of polymer chains in solution [13], continuously decreases from $x = 11\%$ (Fig. 4). Such a behavior is close to the case of adsorption of hydrophobically modified polyacrylates onto hydrophobic surfaces [12].

Turbidity measurements have shown that no flocculation occur (even in the presence of salt) for the lower concentrated adsorbed PS suspensions. On the contrary, naked PS particles largely flocculate in the presence of 0.1 M NaCl due to the screening of electrostatic repulsion between particles. For the more concentrated latex suspensions we must notice that flocculation of particles occur due to polymer bridging (see *S/L* ratio influence).

3.2.3. Zeta potential measurements

Fig. 5 presents variations of zeta potential of 375 nm diameter latex particles with adsorbed CMP-*x*-C8 layers as a function of the octyl grafting rate in 0.1 M NaCl medium. We can notice that the zeta potential of latex particles increases with the grafting rate. This behavior can be explained by the reduction of the charge density rate (via ester bonds) of HMCMP as the grafting rate increases.

3.2.4. Discussion

It is currently though that an adsorbed flexible coil polymer exists as a series of trains, loops and tails. The trains are sequences of polymer segments that are in contact

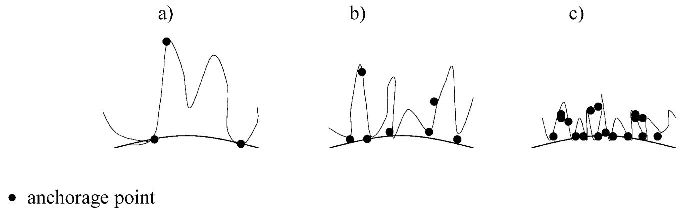

Fig. 6. Schematic representation of adsorption of CMP-x-C8 onto latex particles as a function of the degree of modification ($T=25$ °C, 0.1 M NaCl medium), (a) $0<x<15$, (b) $15<x<30$, (c) $30<x<50$.

with the surface. The loops are the parts of polymer chain between two trains, whereas tails are at the end of the chains.

The data reported in Figs. 3 and 4 can be explained by considering that there is competition between the number of alkyl anchoring groups (trains) and the size of polymer loops. For the lower degree of modification ($5<x<15\%$), the number of anchors is low, therefore, the loop size and the thickness of adsorbed polymer layer are important. For higher degree of modification ($x\approx 20$–40%) the number of anchors increases thus explaining higher level of adsorption. Moreover the loop size decreases and, therefore, the thickness too. For degree of modification of about 40%, the adsorbed polymer amount does not increase anymore that may indicate a saturation of the surface in anchors. In the same time, the thickness of adsorbed polymer layer decreases. This may be explain by a loop size decreases, but one can also involved intra and/or intermolecular hydrophobic associations between alkyl chains of absorbed polymer which decrease still further the adsorbed polymer layer thickness (Fig. 6). This explanation is consistent with the work of Poncet et al. [12] in the case of adsorption of hydrophobically modified polyacrylates onto hydrophobic surfaces.

We have reported in a recent article [13] that sample with highest level of octyl groups (CMP-45-C8) exists under compact conformation due to hydrophobic intramolecular associations. If any conformational change occurs during adsorption, the main alkyl moieties should remain involved in intramolecular association and consequently the number of alkyl anchor onto latex surface should be low. As a consequence in a such case, we should observe an increase of Γ_{pl}. But on the contrary our results evidence that Γ_{pl} reaches a plateau for degree of modification above 20–25%. This result indicate a saturation of the latex surface which appears consistent with a large number of anchor point even for polymer with a compact conformation in solution (i.e.HMCMP-C8-45). This result seems to indicate that an opening of such polymer chain (HMCMP-C8-45) occurs during adsorption. From a thermodynamic point of view, it can be argued that polymer chains prefer to adsorb onto solid surface rather than remain in compact conformation in solution.

3.3. Stability of the adsorbed polymer layer

The stability of adsorbed polymer layer is an important characteristic for potential applications. Most workers report that polymer adsorption is irreversible. This reversiblility of polymer adsorption was evaluated from 'desorption isotherms' after soaking the latex particles for 24 h in three different media.

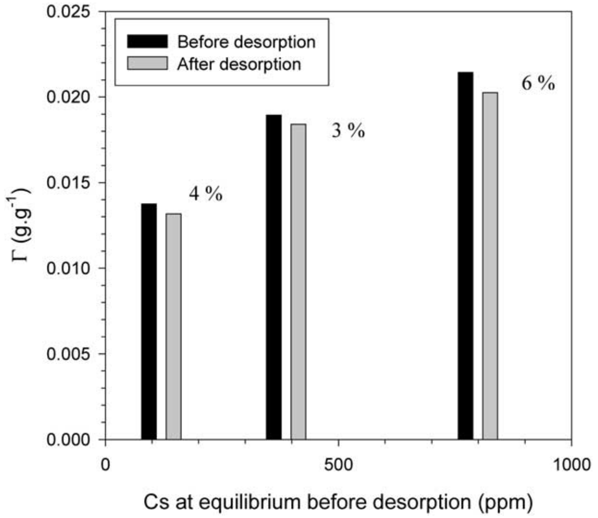

Fig. 7. Desorption in 0.1 M NaCl of CMP-11-C8 (24 h of desorption after 30 h of adsorption in 0.1 M NaCl 25 °C).

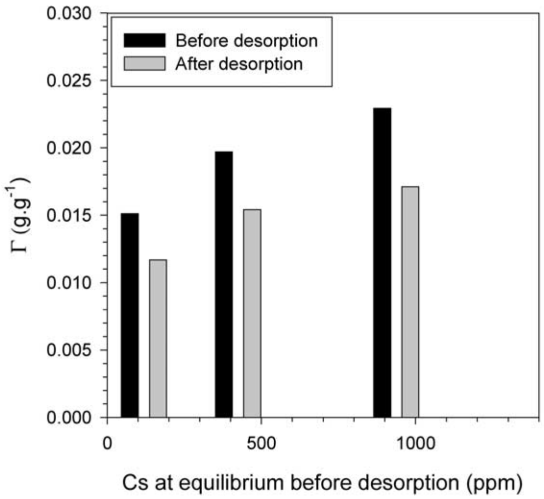

Fig. 8. Desorption in pure water of CMP-11-C8 (24 h of desorption after 30 h of adsorption in 0.1 M NaCl, 25 °C).

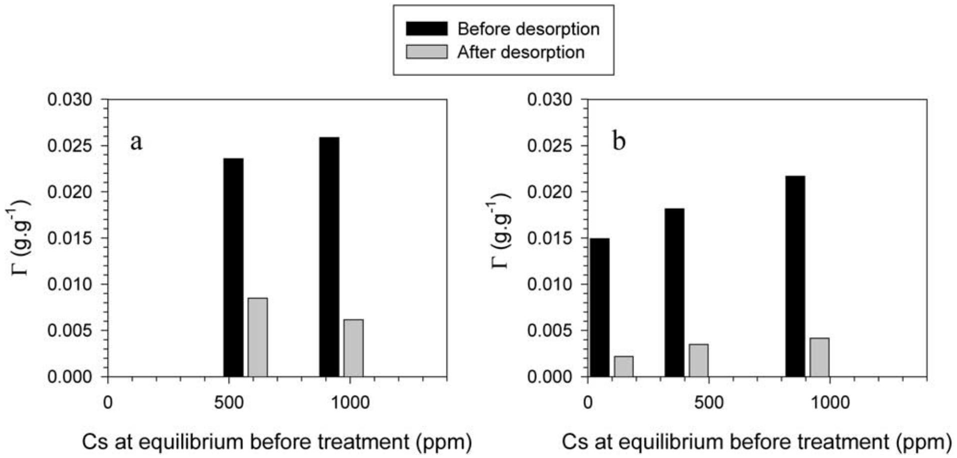

Fig. 9. Desorption in 0.01 M NaOH medium of CMP-23-C8 (a) and CMP-11-C8 (b) (24 h of treatment after 30 h of adsorption in 0.1 M NaCl, 25 °C).

3.3.1. *In 0.1 M NaCl*

Fig. 7 compares the adsorbed amount after 24 h of desorption in 0.1 M NaCl of CMP-11-C8 with adsorbed amount before desorption, for three initial equilibrium concentrations. As it can be seen, less than 10% of desorbed polymer has been observed in the adsorption medium; this correlates well with data reported from different systems [31,32].

3.3.2. *In pure water*

In pure water, electrostatic repulsion between carboxylate functions are greatly increased and we have demonstrated that any measurable adsorption of CMP-*x*-C8 occurs in this medium, therefore, it can be assumed that desorption should be favored.

Fig. 8 represents the adsorbed amount after 24 h of desorption in pure water of CMP-11-C8. We found about 20% of desorbed chain after 24 h in pure water. No more evolution has been seen after 4 days of desorption (results not shown). This weak desorption should be the consequence of a competition between hydrophobic interactions (which favor adsorption) and electrostatic repulsions (responsible for desorption). Desorption of polymer bearing different amount of C8 groups have shown similar tendency.

3.3.3. *In 0.01 M NaOH*

A previous study in our laboratory [33] has shown that in 0.01 M NaOH, ester bonds of CMP-*x*-C8 are fully hydrolyzed in few hours while the polysaccharide backbone is not degraded. After this hydrolysis, the CMP precursor is getting back.

Fig. 9(a) presents CMP-11-C8 amount still adsorbed after 24 h of such alkaline treatment (0.01 M NaOH). It can be seen that the amount of desorption is increased in comparison with the two previous studied media. This desorption should be attribute to the saponification of ester bonds. Consequently polymer in the form of CMP has not affinity towards surface anymore and is, therefore, released into the medium. Nevertheless saponification seems not to be complete and may depend on initial grafting rate of HMCMP. This is evidenced in the Fig. 9(a) for which much more CMP-23-C8 remains adsorbed on the latex surface than CMP-11-C8 (Fig. 9(b)). Adsorption of HMCMP should slow down the saponification of ester bonds for accessibility reasons.

4. Conclusion

In this paper several aspects of amphiphilic polysaccharide (HMCMP) adsorption at a solid/liquid interface have been discussed. The adsorption of HMCMP on polystyrene latex particles can occur through hydrophobic interaction and can be described by Langmuir isotherms. The difference between the level of adsorption and the layer thickness of HMCMP differing by their degree of modification of octyl groups can be argued by a competition between the number of anchors and the size of the loops. The 'hydrophobic induced adsorption' is limited by electrostatic repulsion due to ionic charges on latex surface and polymer. This adsorption is clearly irreversible in pure water and in 0.1 M NaCl. The desorption observed in 0.01 M NaOH is the consequence of hydrolysis of ester bounds between octyl groups and polysaccharide backbone.

Further work is in progress on the rheological properties of latex particles—amphiphilic polymer systems.

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