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ORIGINAL CONTRIBUTION

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Coupling between polymer adsorption and colloidal particle aggregation

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Abstract Studies of the adsorption of high molecular weight polymers on colloidal latex and silica particles and their subsequent flocculation were carried out. Neutral polyethylene oxide samples with both a narrow and a broad molecular weight distribution were used together with low charged cationic copolymers. The influence of the particle concentration and polymer dose on the flocculation were systematically investigated under quiescent conditions.

Equilibrium bridging only occurred with polyelectrolyte, even in very dilute suspensions, at high particle coverage. In contrast to this, non-equilibrium bridging occurred with both neutral polymer and polyelectrolytes but only for more concentrated suspensions and small amounts of adsorbed polymer. Polymer adsorption in dilute suspensions, which did not show particle aggregation was measured an electrophoretic technique. In more concentrated suspensions, where flocculation takes place, we found that aggregation prevents further polymer adsorption and induces both an excluded volume and a surface effect. The consequences on the shape of the isotherms differ according to the aggregation mechanism.

A significant decrease of the amount, Γ, of adsorbed polymer is observed with non-equilibrium bridging. When both mechanisms simultaneously contribute to the aggregation, the value of Γ depends on their relative importance. In the intermediate range of copolymer dose their respective contributions are critically sensitive to the details of the mixing step and stirring, leading to non reproducible experimental results.

Key words Polymer adsorption – flocculation – bridging – zeta potential – colloidal particles

Introduction

Neutral polymers and polyelectrolytes are often used in industrial processes in order to control the stability and/or the flocculation of colloidal dispersions. This practical application has prompted numerous experimental and theoretical studies on the polymer adsorption and on the stability of colloidal suspensions modified by polymer adsorption on the particles [1, 2].

Polymer adsorption

Adsorption of both neutral polymers and polyelectrolytes on particles of opposite charge is usually characterized by a high affinity isotherm. In the case of polymers with a narrow molecular weight distribution the equilibrium concentration is often too small to be detected. Thus the adsorption process is controlled by the polymer dose Ci/S, where Ci is the initial polymer concentration and S is the total surface of particles per unit volume. In the case of polymolecular neutral polymers, the more rounded shape of the isotherm curves has been attributed to the preferential adsorption of larger chains [3]. Adsorption is still controlled by Ci/S, but the maximum adsorption is reached in excess of polymer. In the case of polyelectrolytes, this exchange of shorter chains by the larger ones only occurs for polymers of low molecular weight and low charge density [4].

Polymer chains are known to change their conformation after adsorption on a particle surface. After equilibrium has been reached the macromolecules adopt at low surface coverage, a flat conformation leading to a very thin polymer layer of thickness δ_h. Near particle saturation, loops and tails can develop and δ_h increases. The thickness δ_h of polyelectrolytes is sensitive to the ionic strength. Electrostatic interactions determine the kinetics of the adsorption/reconformation of polyelectrolytes, while only diffusion phenomena contribute to the adsorption of neutral polymers. As particle surfaces become more fully covered, the rate of further adsorption is reduced [5]. The polymer adsorption is usually irreversible upon dilution owing to the existence of multiple contact points between polymer and adsorbents.

Stability of colloidal suspensions

The addition of polymer into colloidal suspensions can produce flocculation. Usually, there is an optimal flocculation concentration (o.f.c.) of polymer for which the flocculation is especially efficient. Higher quantities of polymer lead to steric stabilization, further amplified by electrostatic repulsion if the polymer layer contains charged groups. The efficiency of flocculation by neutral polymers is very sensitive to their molecular weight. A small amount of high molecular weight polymer induces particle bridging as soon as the thickness of polymer layer is larger than the minimum distance of approach between the particles, which is approximately twice the Debye–Hückel length of the system. Because of the flat conformation of chains at low particle coverage, it is likely that bridging flocculation can also occur when polymer chains are in an extended non-equilibrium conformation. Gregory [5] suggested that this non-equilibrium mechanism could explain why bridging is especially efficient in concentrated suspensions. Pellsers et al. [6] have shown that non-equilibrium flocculation is predominant in salt free suspensions. The flocculation range is sensitive to the molecular weight for a given particle concentration. At the o.f.c. the efficiency of flocculation increases with particle concentration [6]. Both equilibrium and non-equilibrium bridging mechanisms are involved in the flocculation of suspensions, but their relative contribution is not well understood.

Highly charged chains adopt a very flat conformation, due to their high affinity for the particle surface. The aggregation is then described by a charge neutralisation mechanism: below saturation, the particle surface has a mosaic pattern of positively and negatively charged regions which produce extensive irreversible aggregation. The value of the o.f.c. does not depend on the molecular weight of added polymer. It corresponds to a value of ζ-potential of the particles close to zero when the ratio n_+/n_- approaches 1, n_+ being the number of charges on the adsorbed polymer and n_- the number of charges carried by the particles. On the other hand, low charged polymers can develop thicker layers than neutral polymers as the neutral segments do not adsorb onto the particle surface, and hence they can induce particle aggregation by bridging. Bridging flocculation is observed for polymer charge density below 15% [7]. A combination of particle bridging and neutralization is expected for intermediately charged polymers.

Tanaka et al. [8] have suggested that flocculation might make a part of the particle surface inaccessible to polymer and thus reduce the effective amount adsorbed by the suspension. This effective value was found to decrease when the particle concentration in the suspension increases in excess of high molecular weight polyelectrolytes [8].

These mechanisms describe correctly polymer adsorption and particle aggregation in dilute suspensions. But from a practical point of view it is well known that steric stabilization of suspensions at intermediate volume fraction (referred to later as semi dilute suspensions) is difficult to obtain both with neutral polymers and polyelectrolytes. The use of high molecular weight charged polymers improves the flocculation efficiency in industrial processing as compared to lower weight ones while no effect of molecular weight is expected in flocculation by charge neutralization mechanism.

Up to now , only a few results are available concerning the coupling between particle aggregation and polymer adsorption. In this paper we attempt to study this coupling via the mechanisms involved in aggregation: equilibrium bridging and non-equilibrium bridging. The influence of the concentration of particles (in the range from dilute to semi dilute suspensions) and of the polymer dose on bridging flocculation has been systematically investigated under quiescent conditions. The relative contribution of these two mechanisms has also been determined. We also studied the consequence of this aggregation on further polymer adsorption.

Silica particles and sulfonated polystyrene latex were chosen as model suspensions. We used high molecular weight neutral and cationic polymers: i) standard polyethylene oxide (PEO) used for gel permeation chromatography (GPC) with a narrow molecular weight distribution as well as polymolecular samples and ii) low charge density cationic copolymers which were expected to enhance bridging flocculation.

We have compared the results of electrophoretic measurements with isotherm curves in order to characterise the amount of polymer adsorbed on the particles. The electrophoretic technique was used to study the adsorption/aggregation coupling.

Materials and methods

Colloidal particles

Non-porous silica particles PST1, purchased from Nissan Chemical Industries, were used. Particles were washed by H_2O_2 into an ultrafiltration cell, then rinsed for two weeks with deionized water from a Millipore milli Q system, containing small amounts of NaOH, until the conductivity of a suspension of 250 g/l ranged between 5 and 10 μS/cm. The pH of these concentrated suspensions in water was around 7.5. Monodisperse polystyrene sulfonate latex PSS4 has been prepared in two steps. In the first step a polystyrene seed was obtained by emulsion, polymerization of styrene carried out at 60 °C using the following recipe (deionized water: 900 g, styrene 90 g, sodium dodecylsulfate 1 g, $NaHCO_3$ (buffer) 0.75 g with an initiator redox system containing 0.75 g of $K_2S_2O_8$ and 0.1 g of $Na_2S_2O_5$). The second step was carried out after 24 h with a continuous addition at 10 ml/h of a mixture containing 10 ml of deionized water, 8 g of styrene and 2.1 g of potassium styrene sulfonate. The final overall conversion was 96%. Concentrated latex suspensions were extensively washed prior to use by successive centrifugation steps and dispersion in pure water by ultrasonication (US). The hydrodynamic radius measured by QELS was 60 nm for PST1 and 100 nm for the latex. The specific surface areas were respectively 22 and 28 m^2/g. All the suspensions were prepared by dilution of cleaned concentrated suspensions in maleic acid buffer at pH 6. The ionic strength was imposed by the buffer and was fixed at $5 \cdot 10^{-3}$ M to prevent the particle aggregation. At pH 6, 0.1 charge/nm^2 were measured on silica by potentiometric titration with NaOH 10^{-2} M [9]. The latex carried 0.94 charge/nm^2 (i.e. 43 μeq/g, 15 $\mu C/cm^2$) corresponding to strong acid groups. The pH of the most concentrated ($C = 50$ g/l) silica suspension used in this study was 6.5. No specific adsorption of the buffer has been detected.

Polymer solutions

Commercial PEO (Aldrich) of nominal molecular weight 10^6 and 2.10^6 designated as PEO 1M and PEO 2M, were used. The average molecular weight and the polydispersity index M_w/M_n measured by gel permeation chromatography (GPC) for the PEO 1M (PEO 2M) were respectively $6.8 \cdot 10^5$ ($9.8 \cdot 10^5$) and 3.5 (2.3) reflecting broad distributions. Standard PEO used for GPC of molecular weight of 860000 (STD 860) was also used for its narrow molecular mass distribution ($M_w/M_n = 1.03$). Statistical polyelectrolytes were prepared by a radical copolymerization of acrylamide, AM, and 3 methacrylamido-propyl-trimethyl ammonium chloride, MAPTAC. The cationicity (molar ratio of cationic monomers, in %) was equal to 5%. It was determined by a potentiometric titration of the chlorine counterions using $AgNO_3$ 10^{-2} M and also from the Cl elemental analysis. The average molecular mass $M_w = 1.1 \cdot 10^6$ was derived from the Mark–Houvink law using intrinsic viscosity measurements. Required parameters were previously determined [10]. The polydispersity index was 6.3 according to gel permeation chromatography measurements. The polymer solutions were also prepared in maleic buffer at pH 6 and ionic strength $5 \cdot 10^{-3}$ M imposed by the buffer. The solutions were gently stirred for 24 h and passed through a 0.22 μm filter. For higher precision, the initial concentrations *Ci* were then measured using an organic carbon analyser (Dohrman DC 80).

Mixing of the suspensions and the polymer solutions

Particle aggregation by polymers is known to be sensitive to the mixing and stirring conditions. Equal volumes of silica suspensions and polymer solutions were mixed together, the particles being added into tubes containing the polymer solutions. Tubes were then softly turned over two or three times, without shaking, in order to obtain homogeneous mixtures, which could then be left at rest or rotated according to the experiments.

Adsorption isotherms

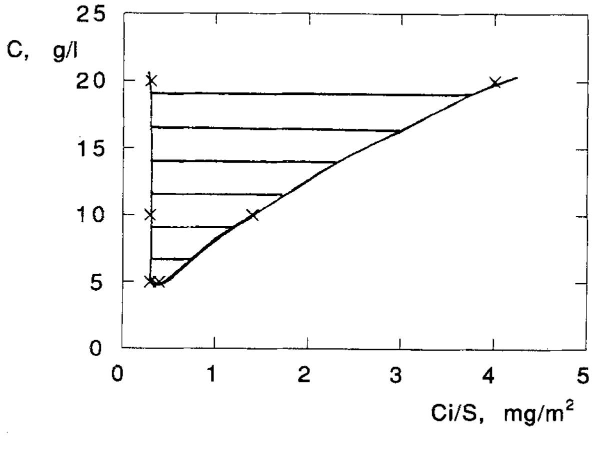
The polymer/suspension mixtures 1:1 (v/v) were stirred for 15 h. After centrifugation, the residual polymer concentration was determined by using an organic carbon analyser. PEO adsorbed on silica through hydrogen bonds while polyelectrolyte adsorbed on silica and latex through the cationic monomers. Neutral acrylamide segment did not adsorb on particles.

Electrophoresis

The electrophoretic mobility of bare and covered particles was measured using two zetameters Laser Zee, Model 501 and Model 3000 (Pen Kem Inc.). More automated than the former, the latter gave the distributions of the electrophoretic mobilities of a particle sample. These distributions were characterized by the mobility corresponding to the highest peak and by the width at half-height. The values of ζ-potential were derived from the Smoluchowski relationship. With latex, reproducible values of ζ-potentials were only obtained with freshly washed suspensions. Indeed high quantities of organic carbon could be found in the supernatant phase during the washing step of concentrated suspensions by successive centrifugation steps. The ζ-potential of bare silica particles was stable.

The silica particle concentration, C, used for these devices were 0.4 g/l (0.01 g/l for PSS4) for the zetameter model 3000 and 0.04–0.004 g/l (0.001–0.0002 g/l for PSS4) for the model 501. Polymer adsorption must be carried out in more concentrated suspensions so that adsorption on the bottle can be neglected. The appropriate concentrations were obtained by dilution with maleic buffer just prior to use. In the first experiments, the values of the ζ-potential of particles covered by cationic polymers greatly varied with the dilution. Various hypotheses were tested. This variation could not be attributed to polymer desorption upon dilution nor to the excess of polymer in solution which decreased with dilution. In those very dilute suspensions, measurements were critically sensitive to negatively charged substances such as silicates for instance. Good results were only obtained when deionized water, used in the preparation of samples, was passed through an additional cationic filter (Pall Industries) which retained unknown negative impurities. Experimental agreement was then achieved between the two pieces of apparatus, the 3000 device giving higher precision.

Fig. 1 Schematic phase diagram of the flocculation range of silica particles (PST1) by high molecular weight neutral PEO 2M under quiescent conditions (pH = 6, the ionic strength is $5 \cdot 10^{-3}$ M). C is the particle concentration and Ci/S the polymer dose (Ci is the initial polymer concentration and S the total surface of particles per unit volume). The completed area indicates flocculated suspensions



Adsorption/aggregation coupling

When the polymer/particles mixture flocculated, we measured the polymer concentration Ce, in the supernatant phase and examined how the polymer was distributed between aggregated and isolated particles by using the electrophoretic technique. The ζ-potential of isolated particles belonging to the supernatant phase was measured after dilution in maleic buffer if necessary. Aggregated particles were dispersed by ultrasonication (US) after dilution to avoid further polymer adsorption. Preliminary tests with and without US performed on silica particles with various amounts of adsorbed polymer (neutral and cationic) confirmed that US did not modify the ζ-potential of covered particles.

Results and discussion

Neutral polymers

Influence of the particle concentration on bridging flocculation

The silica suspensions in maleic buffer ($5 \cdot 10^{-3}$ M, pH 6) were stable owing to electrostatic repulsion between the particles. The silica suspensions were prepared with various concentrations ranging from 1 to 50 g/l. The polymer dose ranged from 0.1 to 10 mg/m^2 for each concentration. The silica/polymer mixtures were left to stand at room temperature for 15 h, flocs were then simply detected by visual observations. Small aggregates were not detected. The flocculation by the highest molecular weight polymer (PEO 2M) is sensitive to the particle concentration. At low particle concentration ($C = 5$ g/l), the suspensions are stable whatever the polymer dose is. When the volume fraction of particles is slightly increased (10 g/l), particle bridging is observed at low particle coverage. Mixtures are heterogeneous, and a flocculated phase can clearly be distinguished. The o.f.c. occurs at $C_i/S = 0.3$–0.4 mg/m^2 but many isolated particles still belong to the supernatant phase. When the aggregates are dispersed by US, they do not form again. This aggregation corresponds to non-equilibrium bridging. In an excess of polymer, suspensions are sterically stabilized. The aggregation occurs over a larger range of polymer dose with increasing particle concentration. In such concentrated suspensions, the number of particles, which are not flocculated by polymers, or the total volume of the flocs are very sensitive to the mixing conditions. However using our standard experimental procedure we can give a schematic phase diagram, depicted in Fig. 1, reflecting the flocculation area of silica PST1 by PEO 2M.

As expected, flocculation also depends on the molecular weight of the polymers. With PEO 1M and STD 860, the suspensions are stable after 12 h of contact under quiescent conditions whatever the polymer dose and the particle concentration below 100 g/l. However instantaneous flocculation can be observed during the mixing step in semi-dilute suspensions (20 g/l), in excess of PEO 1M. But the instantaneous aggregates are broken by the gentle turn over of the tube after mixing. At the end the suspensions do not settle and appear stable.

Adsorption of PEO on particles not showing aggregation

Provided the molecular weight of polymer was low enough, aggregation did not occur. As a sensitive technique, we used electrophoretic measurements to follow polymer adsorption. The ionic strength was fixed at 10^{-3} M in order to ensure the complete stability of the suspensions. The polydispersity effect theoretically predicted by Cohen-Stuart et al. and since observed on various suspensions [11–13], can clearly be evidenced, as seen in Fig. 2. In the case of PEO 1M, the curves referring to the electrophoretic mobility versus the equilibrium polymer concentration C_e obtained at various concentrations (Fig. 2a) can be merged into a master curve when expressed as a function of the polymer dose (Fig. 2b). The ζ-potential continuously increases even at low coverage and all over the range of C_i/S to get its maximal value $\zeta_{\max}$ in excess of polymer. On the contrary, the ζ-potential of particles covered by standard PEO reaches its maximum value $\zeta_{\max}$ when the polymer dose is equal to $\Gamma_{\max}$ reflecting the very high affinity of PEO for silica particles. A contact time of 30 min is usually sufficient to reach constant potentials, except at low particle coverage ($C_i/S < 0.4$ mg/m^2), where several hours are required with polydisperse samples (PEO 1M and 2M). This slow kinetic effect is attributed to the progressive exchange of small adsorbed chains by larger ones. This slow variation of the ζ-potential is not observed at higher coverage.

Influence of the particle aggregation on polymer adsorption

As described by the phase diagram in Fig. 1, a suspension of $c = 20$ g/l and a dose of PEO 2M varying from 0.2 to 4 mg/m^2 flocculates under quiescent conditions. The ζ-potential of isolated particles always corresponds to the saturation coverage. On the contrary, the values of ζ-potential of particles belonging to the floc correspond to low coverage. The polymer concentration Ce in the supernatant phase can exceed the initial polymer concentration indicating that the volume occupied by the floc cannot be neglected. This concentration Ce then slowly decreases with time. From these observations we can confirm that low amounts of polymer are needed to form aggregates by polymer bridging. Aggregation seems to limit the polymer adsorption and sedimentation of the flocs to exclude the polymer outside the aggregates. Particle aggregation induces both an excluded volume effect and an excluded surface effect. Particles located inside the aggregates are not accessible to the polymer in solution. Non-equilibrium bridging between particles lead to a heterogeneous distribution of the polymer throughout the particles. Both isolated particles and particles located outside the aggregates can be completely covered by the polymer while particles trapped inside the aggregates were less covered.

High affinity type isotherms are expected with standard STD 860 adsorbed on silica. The curves should not depend on the particle concentration as they do with

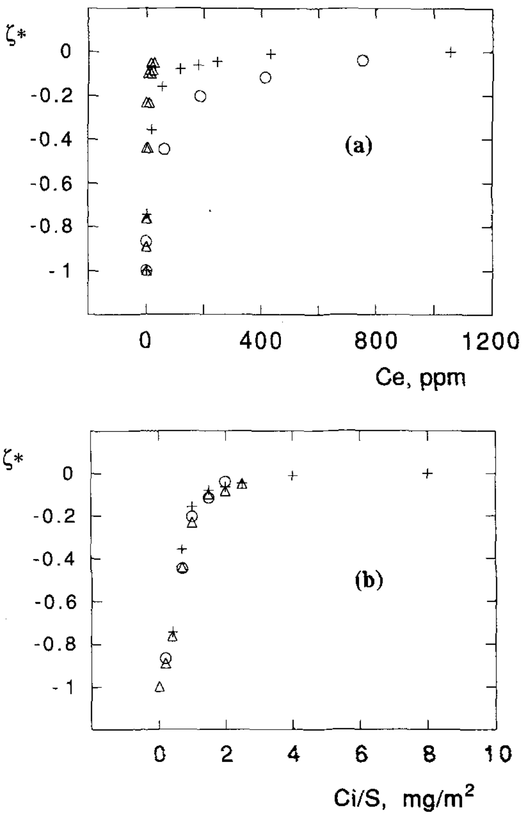
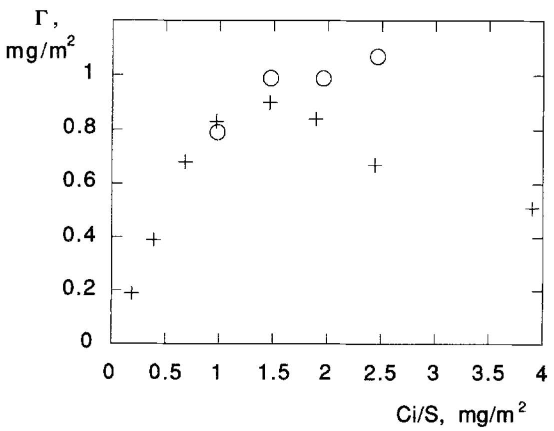


Fig. 2 Change in the adimensional zeta-potential ζ^* of silica particles ($\zeta^* = (\zeta - \zeta_{\max})/(\zeta_{\max} - \zeta_0)$, where ζ_0 is the potential of the bare particles and $\zeta_{\max}$ the potential of saturated particles) as a function of the equilibrium concentration, Ce, of the polymer PEO 1M (Fig. 2a) and as a function of the polymer dose Ci/S (Fig. 2b). The particle concentration is (○) 20 g/l, (+) 5 g/l and (△) 0.4 g/l. pH = 6, the ionic strength I was fixed to 10^{-3} M to completely prevent particle aggregation during the polymer adsorption

polydisperse samples. Experimental isotherms are shown in Fig. 3 for two particle concentrations 5 and 20 g/l. The curve obtained with the more concentrated suspension exhibits a maximum in the amount of adsorbed polymer and a decrease with increasing C_i. The volume of the floc can be neglected after centrifugation with this particle concentration. The decrease of the maximal amount Γ_{max} is explained rather by the occurrence of particle aggregation enhanced by stirring and by the excluded surface effect previously observed with PEO 2M in quiescent conditions. The recorded decrease would imply that 15% of the particle surface is located inside the aggregates and is not accessible to the polymer.

Fig. 3 Adsorption isotherm of the standard PEO STD 860 on silica particles PST1. The particle concentrations were (o) 5 g/l and (+) 20 g/l. The adsorbed amount, Γ, is expressed as a function of the polymer dose Ci/S (pH = 6, the ionic strength is $5 \cdot 10^{-3}$ M)



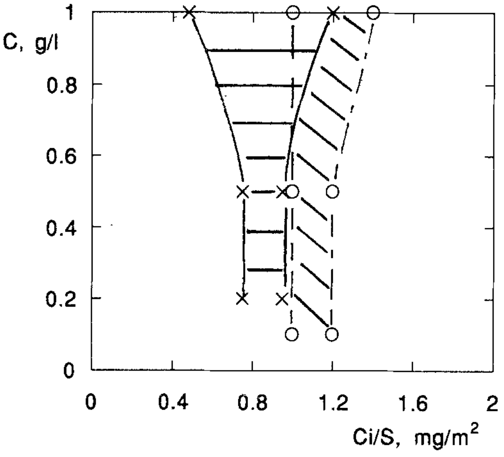


Fig. 4 Schematic phase diagram of the flocculation range of silica PST1 (X) and latex PSS4 (o) by the cationic copolymer PAM/MAPTAC in dilute suspensions under quiescent conditions. C is the particle concentration and Ci/S the polymer dose. Completed areas correspond to flocculated suspensions (pH = 6, the ionic strength is $5 \cdot 10^{-3}$ M)

Cationic polymers

Influence of particle concentration on bridging flocculation

Mixtures of silica or latex suspensions with polyelectrolyte were prepared as previously. For each particle concentration, the polymer dose Ci/S usually ranged from 0.1 to 3 mg/m^2. The macroscopic behavior of the suspensions depends on the particle concentration. In very dilute systems ($C < 0.4$ g/l), see Fig. 4, both suspensions show a net optimal polymer dose (1–1.2 mg/m^2 for latex and 0.75–0.95 mg/m^2 for silica) at which aggregation is completely efficient, with no particles in suspensions. If the floc is dispersed by US, particles aggregated again with the same efficiency, indicating that adsorbed chains reached their equilibrium conformation before bridging. At this optimum flocculation, there is a net attractive force between covered particles. The ratios n_+/n_- are summarised in Table 1 at the o.f.c. and for the maximum amount Γ_{max}. Those ratios are very different according to the nature of the particles. For silica, the cationic charges are in large excess while negative charges are still predominant for latices even at saturation. As expected with low charged polymers, aggregation can be described by a bridging mechanism resulting from the neutralisation of negative charges by the cationic monomers. Outside this flocculation range, the suspensions are stable.

Increasing the particle concentration above 1 g/l, flocculation occurs over a larger range of the polymer dose as shown in Fig. 5 for silica particles. The efficiency of flocculation changes with the polymer dose and is very sensitive to the mixing step. Below the o.f.c., small finite size aggregates can be seen in the supernatant phase but they do not form again after dispersion by US. In an excess of polymer, more and more isolated particles can be distinguished from the flocculated phase when the polymer dose increases. The suspensions flocculate again after applying US.

Under quiescent conditions, both bridging mechanisms occurred in semi-dilute suspensions, non-equilibrium bridging being predominant in default of polymer and equilibrium being present in excess. Similar behavior is observed with more concentrated silica suspensions ($C > 20$ g/l) when the polymer dose is varied. But below the o.f.c., a part of the aggregates flocculates again after US probably indicating the simultaneous occurrence of the two bridging mechanisms.

Table 1 Ratio between the number n_+ of cationic charges on the adsorbed copolymer and the number n_- of negative charges carried by the particles for two coverages corresponding to the flocculation range and to particle saturation

Particles	Number of charges/nm^2	(n_+/n_-) at the o.f.c.	(n_+/n_-) at the saturation
Silica PST1	0.1	2.4–3.2	3.5–4
Latex PSS4	0.9	0.4–0.5	0.6–0.7

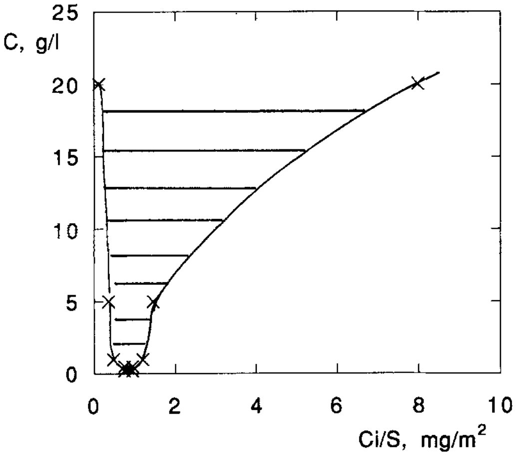


Fig. 5 Schematic view of the broadening of the flocculation range of the silica PST1 by the cationic copolymer in semi-dilute suspensions. C is the particle concentration and Ci/S the polymer dose. Completed area corresponds to flocculated suspensions (pH = 6, the ionic strength is $5 \cdot 10^{-3}$ M)

Adsorption of polyelectrolytes on particles not showing aggregation

Aggregation of dilute suspensions induced by the polyelectrolyte occurs over a narrow range of polymer dose. The polymer adsorption on latices and silica is followed outside this flocculation range by using the electrophoretic technique. Linear variations of the ζ-potential with the polymer dose are obtained for the two kinds of suspension as represented in Fig. 6. Below the o.f.c. thin polymer layers are expected, the neutralization of negative groups by cationic monomers represented the major contribution to the change in ζ-potential. This linear variation agrees with the experimental observation that the fraction p of adsorbed monomers is constant during the progressive adsorption of a similar copolymer on Na montmorillonite [14].

Silica particles saturated with the copolymer reached a positive value of the ζ-potential ($\zeta_{max} = +15$ mV) while latex particles did not ($\zeta_{max} = -4$ mV). This discrepancy can be explained by the excess of cationic charges brought about by the polymer in the case of silica.

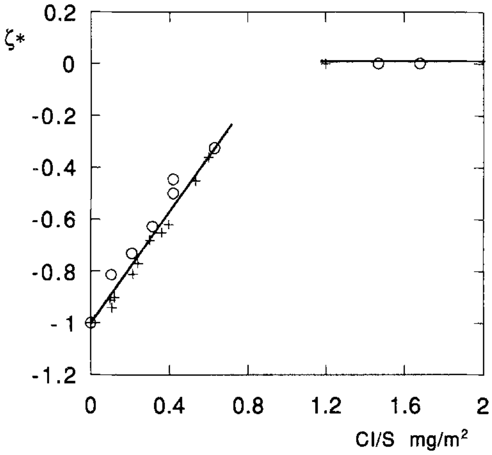


Fig. 6 Variation of the adimensional zeta-potential ζ^* of silica (+) and latex (○) with the dose Ci/S of the cationic copolymer. $\zeta^* = (\zeta - \zeta_{max})/(\zeta_{max} - \zeta_0)$, where ζ_0 is the potential of the bare particles and ζ_{max} the potential of saturated particles. No measurements were performed in the flocculation range. pH = 6, the ionic strength is $5 \cdot 10^{-3}$ M

The maximum values ζ_{max} are reached when the polymer dose Ci/S is equal to the maximum amount Γ_{max} of adsorbed polymer in spite of the polydispersity of the copolymer. The exchange of small chains by the larger ones, observed with neutral polymers, does not occur with this low charged polyelectrolyte. It is attributed to the high adsorption energy of the cationic monomers on the negative sites of silica or latex. Microcalorimetric studies of analogous polyelectrolytes on clay particles indicated 4 kT of adsorption energy instead of 0.1 kT for neutral polymers [14].

These experimental results show that the amount of polymer adsorbed by homogeneous suspensions is governed by the ratio Ci/S because of the very high affinity of the copolymer for the particle surfaces.

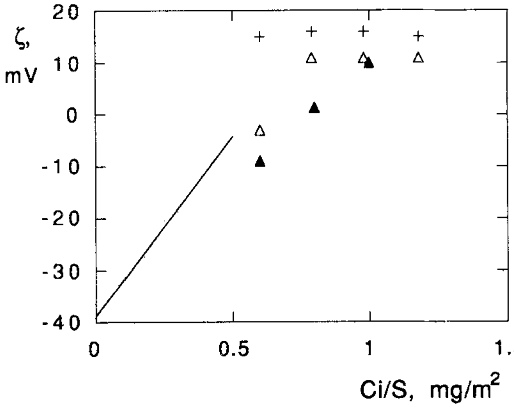
Influence of the particle aggregation on polymer adsorption

In semi-dilute systems ($C \geq 5$ g/l), polymer/silica mixtures, left at rest, are clearly heterogeneous in a wide range of polymer doses.

Above $Ci/S = 0.6$ mg/m^2 significant concentrations of unadsorbed polymer, Ce, are detected for all studied particle concentrations. In a large excess of polymer, Ce, measured after decantation of the aggregates, can exceed the initial polymer concentration following the exclusion of the polymer from the flocculated phase, as previously seen with neutral polymers. The ζ-potential of isolated particles always corresponds to the saturation if $Ce \neq 0$. In this case, the ζ-potential of flocculated particles is always lower than $\zeta_{\max}$. It ranges from -3 and $+11$ mV for the different mixtures, corresponding to flocculation by equilibrium bridging determined in dilute suspensions. In Fig. 7, the ζ-potentials of isolated and flocculated particles are compared, for two particle concentrations (5 and 20 g/l), to the reference curve, a straight line obtained without aggregation. As for neutral polymers, aggregation prevents further polymer adsorption. In these heterogeneous suspensions, the effective amount of polymer adsorbed on flocculated particles depends both on the particle concentration and polymer dose. For a given mixture, the effective coverage results from the competition between the kinetics of particle aggregation by equilibrium bridging and the kinetics of polymer adsorption near particle saturation. The spectra of mobility recorded after US are always narrow, indicating that polymer is rather homogeneously distributed throughout the flocculated particles, see Fig. 8a, even it is difficult to predict the effective coverage.

Below the o.f.c., ($Ci/S < 0.6$ mg/m^2), all polymer chains are adsorbed. There are very few isolated particles and many finite size aggregates. The mobility spectra obtained after US (see Fig. 8b) are very broad compared to those obtained in excess of polymer (Fig. 8a). The width of these spectra revealed the dynamic feature of the aggregation. The coverage of aggregated particles deduced from ζ-potential measurements (-20 to -10 mV) ranges between 0.3–0.43 mg/m^2. Similar coverages were previously obtained in the dilute regime without leading to aggregation. These results support the suggestion that non-equilibrium bridging is the major mechanism involved in the flocculation below the o.f.c. In more concentrated suspensions ($C = 20$ g/l), both bridging mechanisms could contribute to flocculation even below the o.f.c. Some particles flocculated by non-equilibrium bridging with a small amount of polymer; as a consequence of the excluded effect, the polymer concentration in the solution increased, allowing the irreversible flocculation of other particles by equilibrium bridging.

Fig. 7 Variation of the zeta potential, ζ, of flocculated (△) and isolated (X) silica particles covered with the cationic copolymer as a function of the polymer dose Ci/S and for two particle concentrations filled symbols $C = 5$ g/l empty $C = 20$ g/l. The values of the ζ-potential were compared to the reference straight line, obtained in dilute silica suspensions not showing aggregation



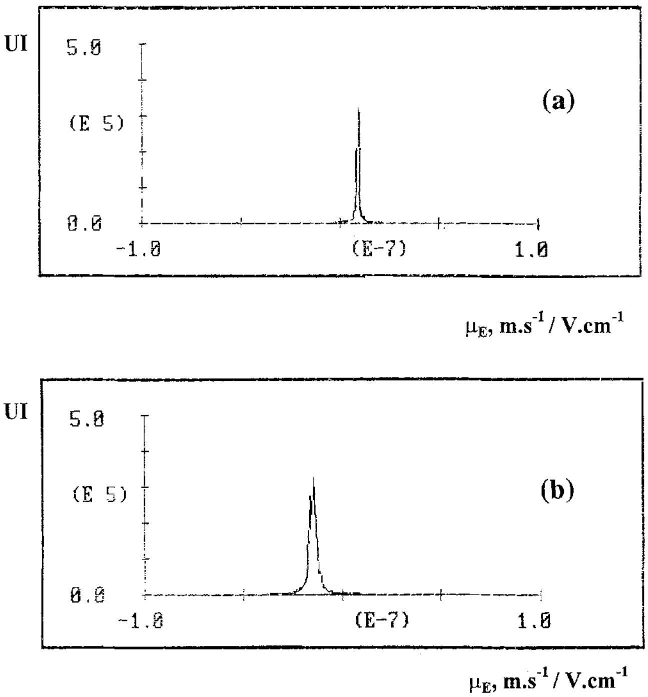


Fig. 8 Spectra of the electrophoretic mobility μ_E obtained with the 3000 laser Zee meter device. Silica particles were flocculated by equilibrium bridging (Fig. 8a) and non-equilibrium bridging (8b) with the cationic copolymer and dispersed after dilution in maleic buffer by ultrasonication just before measurements

A similar behavior is observed with latex. Under minimal stirring conditions, non-equilibrium bridging is predominant at low amounts of polymer. The transition from this mechanism to the other one is observed by increasing the polymer concentration above the o.f.c.

What are the consequences of the particle bridging by polyelectrolytes on the shape of the isotherm curves? Electrophoretic measurements have shown in dilute suspensions the very high affinity of the copolymer for the latex, but the stirring of the semi dilute suspensions is found to enhance particle aggregation over the range of polymer dose studied (0–8 mg/m^2). The isotherm obtained, under stirring conditions, is shown in Fig. 9 with a particle concentration $C = 20$ g/l and compared to the theoretically expected straight line. Three areas can be considered.

i) Below $Ci/S = 0.8$ mg/m^2, non-equilibrium bridging is expected to be the major contribution to the flocculation. Significant equilibrium polymer concentration Ce is found indicating that there are not enough isolated par-

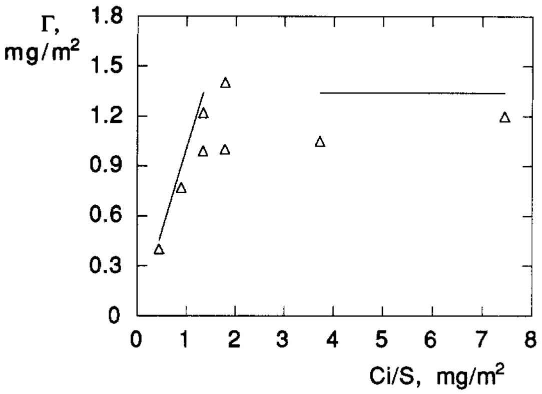


Fig. 9 Adsorption isotherm of the cationic copolymer on the polystyrene sulfonate latex PSS4. The adsorbed amount, Γ, is expressed as a function of the polymer dose Ci/S and compared to the expected value (straight line) which should be obtained in dilute suspensions not showing aggregation. The particle concentration C was equal to 20 g/l, pH = 6, the ionic strength is $5 \cdot 10^{-3}$ M

ticles to adsorb the polymer excess, resulting from the excluded effect. At low polymer dose, aggregation decreases the initial slope of the isotherm curve.

ii) In the intermediate range of the polymer dose, ($1 < Ci/S < 4$ mg/m^2) strong aggregation is observed and equilibrium bridging is expected to be predominant. Experimental results for adsorption are not reproducible. It can be thought that both bridging mechanisms contribute to the flocculation in this intermediate range of the polymer dosage. These mechanisms occur at different particle coverages and thus do not have the same consequences on the polymer adsorption. Their relative contribution is determined by the mixing step, which appears to be difficult to control in spite of the standard experimental procedure used in this study and explains the difficulty of obtaining reproducible data.

iii) In an excess of polymer ($Ci/S > 7$ mg/m^2), the fast kinetics of polymer adsorption decrease the occurrence of the non-equilibrium bridging. Mixtures were still flocculated but there are more and more saturated particles in suspension and the coverage of flocculated particles by equilibrium bridging can be very close to saturation. The experimental amount of adsorbed polymer Γ asymptotically tends to Γ_{max}.

Conclusion

Our study has shown a strong coupling between polymer adsorption and particle aggregation by bridging. In the case of non-equilibrium bridging, small amounts of polymer are involved in aggregation. The flocculation results from the competition between the kinetics of the adsorption/reconformation of polymer chains and the probability of two particles to be in close proximity. As a consequence, this mechanism is enhanced and occurs over a large range of the polymer dose when the particle concentration is increased and when the polymer/particles mixtures are stirred. Such aggregation is expected, even with low molecular weight polymers, provided the particle concentration is large enough. In the case of equilibrium bridging, large amounts of adsorbed polymer, often close to the saturation are involved in aggregation. In an excess of polymer, flocculation results depend on the competition between the kinetics of polymer adsorption at high surface coverage and the kinetics of particle aggregation. The occurrence of equilibrium bridging is governed by the thickness of the polymer layer and the particle coverage. For a given ionic strength, it can only take place with polymers of high enough molecular weight and then occurs whatever the particle concentration.

With both equilibrium and non-equilibrium bridging, particle aggregation prevents further polymer adsorption and leads to a heterogeneous distribution of the polymer throughout the suspension. The consequences on the shape of the isotherm curves differ according to the aggregation mechanism. Significant decrease of Γ, resulting from aggregation, is found with non-equilibrium bridging because of the small amounts of polymer involved. When both mechanisms contribute to the flocculation, the value of Γ depends on their relative extent. In the intermediate range of copolymer dose, their respective contribution is critically sensitive to the mixing step leading to non-reproducible experimental results.

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