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Interaction of cationic and anionic polyelectrolyte with SiO$_2$ and Al$_2$O$_3$ powders

Sami Boufi[a], Samir Baklouti[a,*], Cécile Pagnoux[b], Jean-Francois Baumard[b]

[a]*Laboratoire de Chimie Industrielle 2, équipe céramiques, ENIS, BP. W, 3038 Sfax, Tunisia*
[b]*SPCTS, ENSCI, 47 á73 Av. A. Thomas 87065 Limoges Cedex, France*

Abstract

The adsorption of anionic and cationic polyelectrolytes onto alumina and silica surfaces is studied. The results indicate that the polyelectrolyte-surface interaction is affected by various factors such as (i) polyelectrolyte nature, (ii) distribution and nature of the oxide surface sites, and (iii) medium properties. A strong interaction enhances the formation of a flat conformation of the adsorbed polyelectrolyte onto the surface, whereas a weak interaction leads to a loops conformation. The effect of the adsorbed polyelectrolyte on the electrokinetic behaviour of the two oxides was also investigated using an electrokinetic sonic amplitude analyser.
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1. Introduction

Polymer adsorption finds a widespread application in industrial processes such as, particle dispersion and stabilisation, flocculation and surface treatments. Numerous studies have been published concerning polymer-surface interactions.[1–6] Progress has been made due to both theoretical and experimental investigations,[7–9] but a lot still remains to be done, for instance concerning the configuration of adsorbed polymer onto solid surfaces and its impact on the dispersion properties.

The adsorption of polymer and its configuration onto a solid surface is a rather complex phenomenon, which is controlled by the competitive affinities of the polymer with the surface and the solvent. The driving force for adsorption is the polymer-surface interaction energy, which is counteracted by entropy effect that opposes adsorption. The configuration of adsorbed chain segments is a result of these two effects. Nevertheless this process is controlled by many other factors such as the nature of particle surface, polymer structure, pH, ionic strength etc., which are likely to interfere with and make it difficult to predict the behaviour of any polymer against any particle surface.

Colloidal processing of binary powder mixtures is widely encountered in many industrial applications, for instance in the elaboration of ceramic composites.[10,11] In order to get a good dispersion of the solid particles, a suitable polyelectrolyte has to be used.

The purpose of the present work is to improve our knowledge concerning polyelectrolyte interactions with two different ceramic powders (SiO$_2$ and Al$_2$O$_3$). Two organic polymeric compounds with different chemical structures were chosen, first PMA-M+, a commercial anionic dispersant and second, a cationic polymer which was synthetized in our laboratory. Interaction of polyelectrolyte with solid surfaces was analysed using electrokinetic and adsorption measurements. The effect of many factors such as polyelectrolyte nature and molecular weight, pH and ionic strength of the media, on the amount of the polymer adsorbed will be evaluated and correlated to the configuration of the adsorbed macromolecular chain. The resulting information should then contribute to the design of a dispersant adapted to such a binary mixture of different oxides.

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* Corresponding author.
E-mail address: samir.baklouti@fss.rnu.tn (S. Baklouti).

Table 1
Powder characteristics

Powder	Supplier	Specific surface area[a] ($m^2 g^{-1}$)	Average grain size d_{50}[b] (µm)	Zero point of charge (pH_{zpc})
Alumina Al_2O_3-α	P152SB Péchiney, France	3	1.35	8
Silica (quartz) SiO_2-α	C800 Sifraco Millicil, France	5	1.5	2

[a] Measured by the BET method.
[b] Measured using a Sedigraph.

2. Experimental procedure

2.1. Starting materials

The main features of the powders used in this study are summarised in Table 1.

Two polyelectrolytes are used in this work, the first one is a commercial anionic dispersant (Darvan C–Vanderbilt GB), which is essentially composed of a salt of polymethacrylic acid (PMA-M+) with carboxylate groups. Its dissociation degree depends on pH. In a weak ionic strength medium and above pH 7, the polyelectrolyte is fully dissociated. The second, synthesized in our laboratory, is a poly(*N-N-N* trimethyl ammonium ethylacrylate chloride) (PAD-Cl^{-1} Fig. 1). It is a cationic polyelectrolyte completely ionized in aqueous medium whatever the pH. Distilled water was used in all the experiments. pH was adjusted via addition of HCl and of NaOH, and ionic strength was adjusted via addition of NaCl.

2.2. Synthesis of PAD-Cl$^-$ polyelectrolyte

PAD-Cl$^-$ was prepared by radical polymerisation of *N-N-N* trimethyl ammonium ethylactylate chloride monomer (ADAMQUAT. MC80-ELF-AQUITAINE) with persulfate as initiator. The polymerisation was conducted in water at a temperature of 50 °C during 2 h.[12] The polymer was precipitated in a mixture of ethanol/acetone with a 70/30 (%) ratio. The precipitate was dried under nitrogen flow for 1 h, then dissolved in water to obtain a concentrated solution.

To vary the polymer molecular weight M_v, the ratio monomer/initiator was adapted. Molecular weight was evaluated from the intrinsic viscosity measurements using the Mark–Houwink equation.[12]
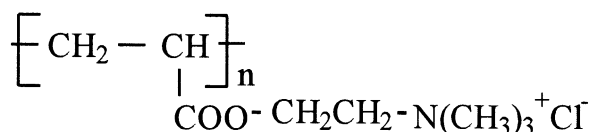
$$[\eta] = K M_v^a$$

Fig. 1. PAD-Cl$^-$ structure.

where $[\eta]$ is the intrinsic viscosity in dl g^{-1}. K and a are constants whose values depend on the nature of the polymer and of the solvent. The values adopted in this study are the same as those used for the polymethacrylic acid: $K = 3.75 \ 10^{-4}$ dl g^{-1}, $a = 0.7$.[14] Intrinsic viscosity was measured in KCl solution 1 M using a Ubbelhode viscosimeter. The results are summarized in Table 2.

2.3. Adsorption isotherm

Polyelectrolyte adsorption onto Al_2O_3 and SiO_2 surfaces was deduced from data obtained by a viscosimetric technique. Suspensions containing 2.5 vol.% solid were prepared with various amounts of polyelectrolyte. Ionic strength and pH were adjusted with NaCl, NaOH 0.1 M and HCl 0.1 M respectively. Suspensions were sonicated for 5 m at 50 W. Samples were then stirred for 24 h to reach chemical equilibrium. The suspensions were centrifugated at 2000 rpm for 1 h and the obtained supernatant was removed. The polyelectrolyte concentration was determined by measuring the relative viscosity of the supernatant with a capillary viscosimeter. This technique is based on the fact that, in an aqueous solution, the hydrodynamic volume of a polyelectrolyte coil is much greater compared to the uncharged polymer having the same molecular weight. This phenomenon occurs because the charged sites on the chain repel each other and cause coil expansion.[13] As a consequence the solution viscosity becomes sensitive to polyelectrolyte concentration down to very low values.

Table 2
Polyelectrolyte characteristics

Polyelectrolyte	Supplier	Intrinsic viscosity $[\eta]$ in (dl g^{-1})	Average molecular weight M_v
PAD$_0$-Cl$^-$	Synthesized	1.95	200,000[a]
PAD$_1$-Cl$^-$	Synthesized	1	80,000[a]
PAD$_2$-Cl$^-$	Synthesized	0.6	40,000[a]
PAD$_3$-Cl$^-$	Synthesized	0.1	8000[a]
PMA-M$^+$	Darvan C–Vanderbilt, GB	0.12	10,000[b]

[a] Determined by viscosimetric technique $[\eta] = 3.75 10^{-4} M^{0.7}$.
[b] Based on technical data.

Ubbelhode capillary viscosimeter was used in this study. It is operated by filling it with a suitable volume of liquid, drawing the liquid level to the upper mark above the bulb, and measuring the time required for the liquid meniscus to fall from the upper mark to the lower mark. The viscosity is proportional to the flow time.

Calibration curves have been first established for the polyelectrolytes (PAD-Cl$^-$ and PMA-M+) at pH 7.5–8.5, by plotting flow time versus polymer concentration. Fig. 2a and b reports curves related to PAD-C$^-$ with different molecular weights and PMA-Ml at the natural ionic strength (Fig. 2a) and PAD-C$^-$ at different ionic strengths (Fig. 2b). From the calibration curve, the concentration of the polymer in the supernatant could be deduced by measuring the corresponding flow time. If necessary and in order to obtain the same ionic strength as that of the corresponding calibration data, the supernatant ionic strength was adjusted. On the

other hand, the pH has a negligible effect on the PAD-C$^-$ dissociation degree, then to obtain the concentration of the polymer in the supernatant when the pH shifted, the same calibration curve was used. Indeed, in the 3–10 pH range, ionic strength did not exceed 10^{-3} mol l^{-1}, a value which does not greatly affect calibration curves (Fig. 2b). To minimise errors, the measurements were conducted at a fixed temperature ($T = 28$ °C) using a thermostatic bath and the diameter of the Ubbelhode capillary was chosen to have a flow time of more than 150 s.

The validity of the method was confirmed by the reproductibility of the results performed on blank solutions containing known amounts of polyelectrolyte. Adsorption isotherms of PMA-M$^+$ obtained by this technique and by the gravimetric method were very similar.[10] The viscosimetric method has the advantage of being rapid and precise, while not requiring large samples.
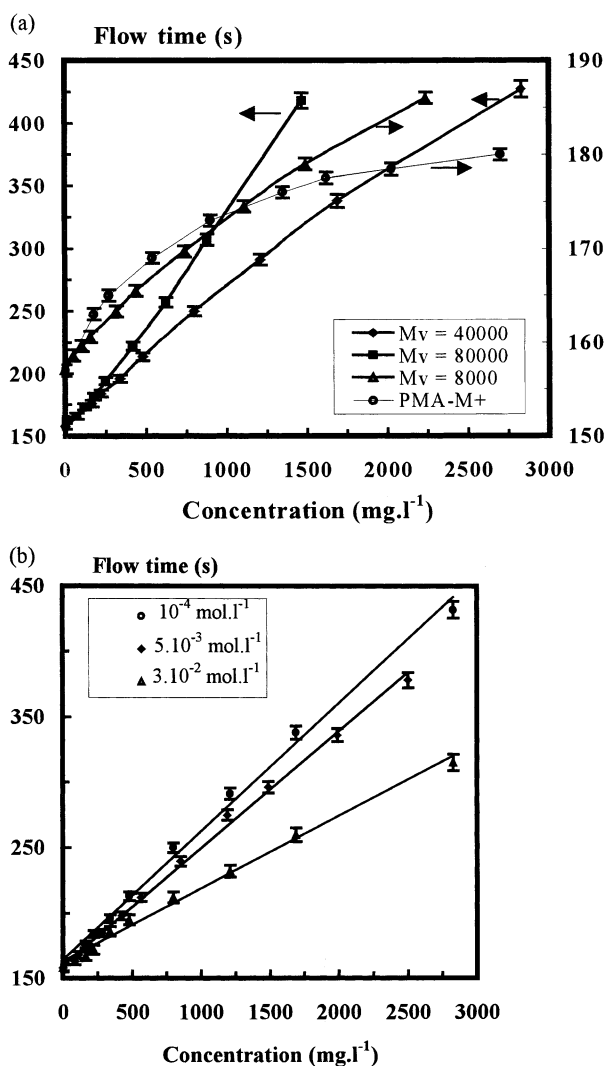
2.4. Electrokinetic measurements

The electrokinetic behaviour of the powder suspension was characterised by electrokinetic sonic amplitude (ESA) measurements (Model ESA-8000, Matec, Northborough, MA, USA).

This technique is based upon the acoustic wave that is generated by the respective motion of the diffuse electrical double layer of the charged particles submitted to a high-frequency electric field with an amplitude proportional to the electrostatic potential at the shear plane where the zeta potential is defined. The ultrasonic signal is detected and converted into a voltage (ESA) by a piezoelectric transducer. In the case of our suspensions, the ESA signal is directly proportional to the zeta potential: then the curves describing variations of the electrokinetic properties in terms of pH and/or polyelectrolyte amount will be presented with ESA values as the coordinates.

3. Results and discussion

3.1. Electrokinetic behaviour

Figs. 3 and 4 show the evolution of the ESA signal versus pH for alumina (Fig. 3) and silica (Fig. 4) suspensions prepared with and without polyelectrolytes.

The natural pH of a P152SB suspension is measured at a value of 8.5 and particles have a small negative surface charge, the value of the amplitude of the ESA signal is −0.54 mPa.m V^{-1}. This charge becomes equal to 0 at a pH of 8; at this pH, hydroxyl surface groups $=$Al–OH prevail. Above pH 8, the surface carries a negative charge, as a result of the formation of $=$Al–O$^-$ groups, which are generated from the dissociation of the

Fig. 2. Flow time data of polyelectrolyte solutions versus concentration at pH 7.5–8.5. (a) PAD-Cl$^-$ with different molecular weights and PMA-M$^+$ at the natural ionic strength, (b) PAD$_2$-Cl$^-$ at different ionic strengths.

hydroxyl groups of alumina. Below this pH, hydroxyl groups are protonated, and the surface charge will be dominated by $=Al-OH_2^+$ groups.

The addition of 0.2 wt.% PMA-M$^+$ increases slightly the natural pH to 8.8 and leads to a negative surface charge with a high amplitude (-2.9 mPa.m V^{-1}). As the pH becomes acid, the amplitude of the negative charge decreases to reach 0 mPa.m V^{-1} at a pH of 5; for pH < 5, the surface charge becomes positive and increases linearly to 2.5 mPa.m V^{-1} at a pH of 2 (Fig. 3a).

Addition of PAD-Cl$^-$ into alumina suspensions does not modify the natural pH further but the particles charge becomes positive and its density increases with the quantity of PAD-Cl$^-$ added (Table 3).

When the content of this polyelectrolyte is lower than 0.25 wt.% the ESA signal decreases again beyond pH≈8; for the smaller concentration of PAD-Cl$^-$ (0.05 wt.%), the surface charge becomes negative for a pH of 10.5 but above a content of 0.25 wt.%, a very small decrease occurred; at pH 12, the amplitude of the ESA signal remains high at a positive value of 2.2 mPa.m V^{-1}. For a pH lower than pH≈8, the positive charge decreases whatever the concentration of polymer, and

from pH 6.5 addition of PAD-Cl$^-$ leads to no modification of the ESA values of pure alumina suspensions; the curves are superimposed.

Concerning SiO$_2$ suspensions (Fig. 4), at the natural pH of 7, a negative surface charge with an amplitude of -1.7 mPa.m V^{-1} is measured and the amplitude decreases in acidic media to reach a value of -0.6 mPa.m V^{-1} at pH 2. Addition of PMA-M$^+$ does not bring any modification to the electrokinetic properties; the curve versus pH is superimposed to that obtained without additive and is not shown in Fig. 4. On the other hand, small addition (i.e. 0.075 wt.%) of PAD-Cl$^-$ leads to rapid sign reversal of the ESA values which remained constant at a value of 1.7 mPa.m V^{-1} in the large pH range studied (i.e. 2.5–11); further addition of cationic polyelectrolyte up to 2 wt.% do not bring any modification of the electrokinetic properties; the curves are superimposed.

The electrokinetic study has allowed to assess the nature of the binding sites on the particle surface accountable for the interaction with polyelectrolyte. To determine accurately the parameters which influence the interaction between the surface and the additives and to investigate the adsorbed polyelectrolyte configuration at the solid/liquid interface, adsorption isotherms had been performed at different conditions.
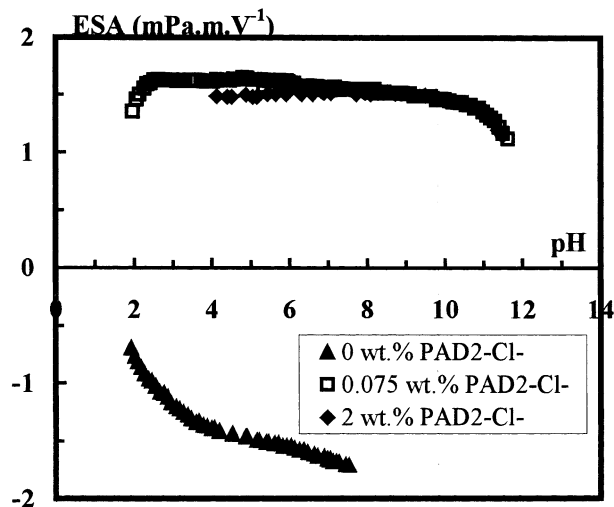
Fig. 3. ESA signal data versus pH for alumina suspension without and with: (a) PMA-M$^+$, (b) PAD$_2$-Cl$^-$.

Fig. 4. ESA signal data versus pH for silica suspension without and with PAD$_2$-Cl$^-$.

Table 3
Electrokinetic properties of alumina suspensions without and with additives

Additive	None	0.05 wt.% PAD$_2$-Cl$^-$	0.1 wt.% PAD$_2$-Cl$^-$	0.25 wt.% PAD$_2$-Cl$^-$	0.2 wt.% PMA-M$^+$
pH	8.5	8.8	8.7	8.4	8.8
ESA (mPa.m V^{-1})	-0.5	1.3	2.6	2.8	-2.7

3.2. Adsorption measurements

3.2.1. At natural pH of suspensions

Figs. 5 and 6 report adsorption isotherms for PMA-M^+ and PAD$_3$-Cl$^-$ on Al$_2$O$_3$ and SiO$_2$, respectively, at the natural suspension pH value, without any addition of NaCl. These plots represent the amount of polymer adsorbed per unit surface area versus the initial concentration (wt.% of polymer with respect of ceramic powder). In all cases, the amount adsorbed increases as the polymer concentration increases, until a plateau is reached. The shape of these isotherms suggests a monolayer adsorption of polyelectrolyte, whatever the substrate or the polymer nature.[15]

3.2.1.1. Adsorption of PMA-M+ onto Al$_2$O$_3$ and SiO$_2$ particles.
The adsorption isotherm of PMA-M^+ onto alumina particles clearly exhibits the characteristics of a high affinity adsorption, the adsorption plateau is close to 0.5 mg m^{-2} (4.85 µmol of polyelectrolyte m^{-2}). These results are consistent with the previous studies done by Baklouti et al.[10] This confirms the reliability of the method used to measure adsorption.

Adsorption of PMA-M^+ onto Al$_2$O$_3$ results from different modes of interaction. Over the 5–8 pH range, the adsorption of the anionic polyelectrolyte results essentially from electrostatic interaction between negatively charged carboxylic groups and the positively charged surface. Below pH 5, hydrogen bonding and ligand exchange process between =Al–OH$_2^+$ and –COOH groups become the relevant mode of interaction.[16]

Around the ZPC (8) of alumina powder, most hydroxyl surface groups are neutral and the polymer is fully ionised, so a high amplitude of negative surface charge is measured (Fig. 3a). As the pH becomes acid, carboxylate and free hydroxyl groups are respectively protonated (–COOH and =AlOH$_2^+$) leading on the one hand to a decrease of the negative contribution to the surface charge and on the other hand to a positive contribution which compensates the negative one at pH = 5; for pH < 5, =AlOH$_2^+$ groups prevail.

The very small quantity of PMA-M^+ (Fig. 6) absorbed onto silica particles confirms the absence of modification of electrokinetic properties of the suspension when this polyelectrolyte is added revealing a weak affinity of PMA-M^+ onto a negative surface. The weak adsorption of PMA-M^+ over the entire pH range suggests that no adsorption can take place between the different form of carboxyl groups (–COOH or –COO$^-$) and particle surface, in particular in basic media, probably because of the mutual repulsion between –COO$^-$ groups and the negatively charged SiO$_2$ surface, which impedes the accumulation of polymer segment chains.

3.2.1.2. Adsorption of PAD-Cl$^-$ onto Al$_2$O$_3$ and SiO$_2$ particles.
In the case of the PAD-Cl$^-$ adsorption onto an alumina surface (Fig. 6), the isotherm plateau is close to 1.5 mg m^{-2} (7.77 µmol monomer of polyelectrolyte m^{-2}) which is a higher value than for PMA-M^+. This value in the case of PAD-Cl$^-$ has been attributed to a difference in the configuration of the adsorbed polyelectrolyte chain. Indeed, in the case of PMA-M^+, segmental chains are adsorbed in a relatively flat conformation,[4] with each macromolecular chain apparently covering a relatively large amount of surface area.
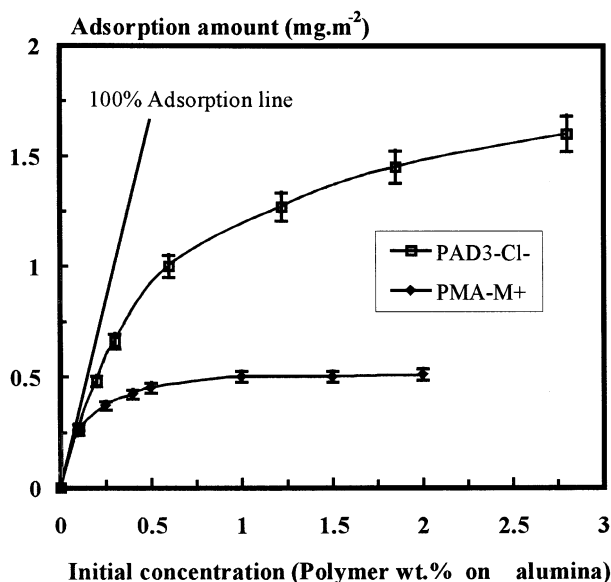

Fig. 5. Adsorption isotherms for PAD$_3$-Cl$^-$ and PMA-M^+ onto alumina versus initial concentration at the natural ionic strength and the natural pH ~ 8.5.
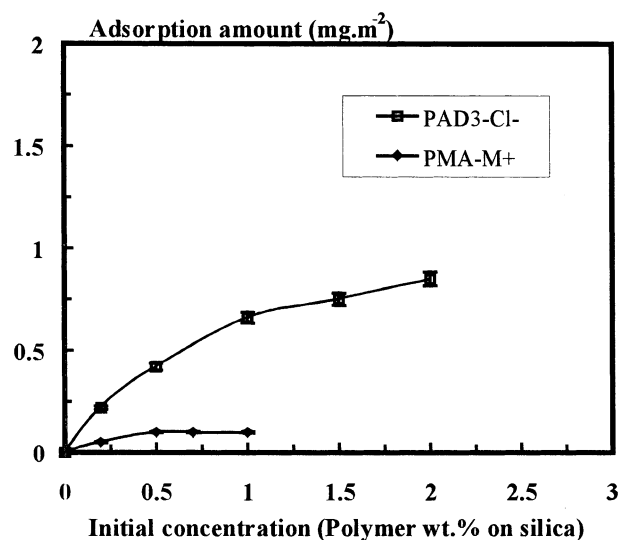

Fig. 6. Adsorption isotherms for PAD$_3$-Cl$^-$ and PMA-M^+ onto silica versus initial concentration at the natural ionic strength and pH 7–8.
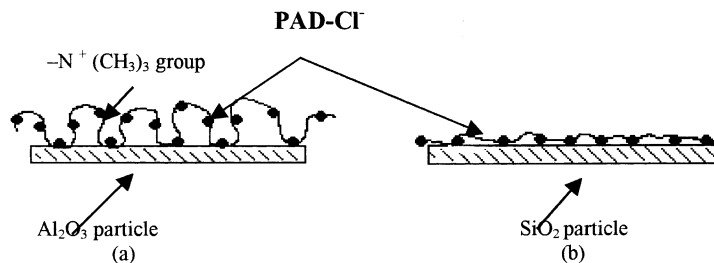
PAD-Cl⁻

Fig. 7. Schematic illustration of the PAD-Cl⁻ conformation adsorbed on: (a) alumina, (b) silica.

On the other hand the greater amount of adsorbed PAD-Cl⁻ results from the formation of loops in the adsorbed conformation. The projected surface area of adsorbed chain is relatively small, and more adsorbed chains are required to establish a saturated monolayer. A schematic illustration of the conformation of PAD-Cl⁻ adsorbed at a solid/liquid interface of Al_2O_3 and SiO_2 is proposed in Fig. 7.

PMA-M⁺ is not adsorbed onto SiO_2 powder (~ 0.1 mg m⁻² or ~ 0.97 µmol monomer m⁻²), whereas PAD-Cl⁻ is well adsorbed (~ 0.75 mg m⁻² or ~ 3.88 µmol monomer m⁻²). It is well known that the driving force for polymer adsorption is the polymer-surface interaction, which is counteracted by the loss of configurational entropy for chain segments that opposes adsorption.[17,18] The higher the interaction energy, the flatter the adsorbed polymer coils. In the 7.5–8.5 pH range, the Al_2O_3 surface is dominated by =Al–OH groups with some minority of =Al–OH$_2^+$ groups. Such sites promote strong interactions with –COO⁻ and –COOH groups of PMA-M⁺ in different manners; (i) by electrostatic interaction with =Al–OH$_2^+$ (ii) hydrogen bonding between =Al–OH and –COOH groups and (iii) chemical adsorption resulting from a ligand exchange process between surface hydroxyl groups and –COO⁻, which leads to the formation of =Al–OOC-complex.[16] All these interaction modes promote the adsorption of PMA-M⁺ polyelectrolyte in a relatively flat conformation onto the Al_2O_3 surface. However, in the same pH range, PAD-Cl⁻ adsorption is driven essentially by a non electrostatic mechanism as pointed out from electrokinetic studies. The main interaction modes are (i) hydrophobic interaction which would have the tendency to drive the polymer onto the particle surface to reduce the free energy associated with the structuring of water molecules around the hydrophobic moieties of PAD-Cl⁻ and (ii) acid-base interaction between =Al–OH and –(NCH$_3$)$_3^+$ groups. Nevertheless, these two interaction modes are too weak to counteract the loss of configurational entropy resulting from the flattening of the polymer chains, so that PAD-Cl⁻ is weakly anchored onto alumina particles and protrudes in the bulk solution as loops and tails.

3.2.2. Influence of pH onto PAD-Cl⁻ adsorption

The effect of the suspension pH on the PAD-Cl⁻ adsorption onto an alumina surface is presented in Fig. 8.

The adsorption capacity is strongly enhanced by a pH increase. The maximum adsorbed reaches a value of 5.5 mg m⁻² at pH$\sim$10 and only 2.5 mg m⁻² at pH$\sim$8. This effect may be ascribed to the increase of negative charge density on the alumina surface because of a rising pH, providing thus more interaction sites on which polyelectrolyte chains can anchor.

PAD-Cl⁻ is a fully ionised polyelectrolyte whatever the pH values. Below pH 6.5, the mutual repulsion between the positive surface charges of Al_2O_3 and ammonium polymer groups impedes its adsorption onto the particle surface. In the 6.5–9 pH range, the steep rise in the magnitude of the ESA values denotes the beginning of PAD-Cl⁻ adsorption. The adsorption of this polymer first balances the negative charge due to the deprotonated OH groups and the excess of ionised groups develops a positive charge onto alumina particles. As basic media enhance adsorption because of electrostatic attraction
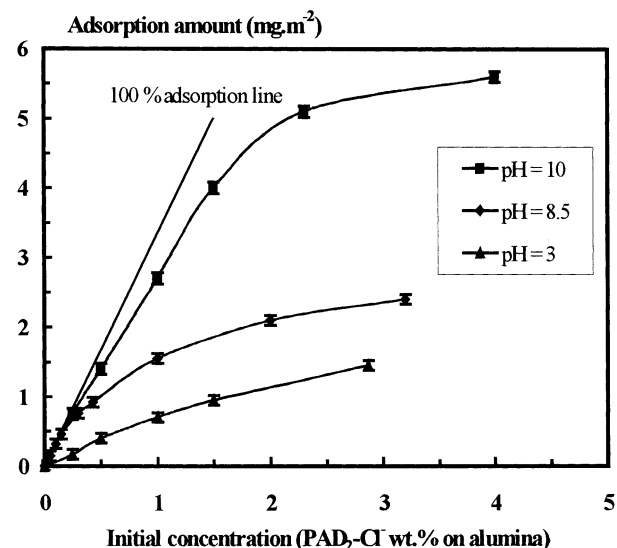

Fig. 8. Adsorption isotherms for PAD$_2$-Cl⁻ on alumina as a function of suspension pH.

between the molecule and the surface, the positive charge remains high and nearly constant for a sufficient amount of polyelectrolyte added (i.e. 0.25 wt.%) denoting that surface saturation has occurred.

In this pH range, the predominance of =Al–OH group underlines the prominent role of hydroxyl surface groups in the interaction with cationic polyelectrolyte, presumably via hydrophobic interaction and acid-base interaction. The latter results from the amphoteric character of =Al–OH and from the acidic character of $-N(CH_3)_3^+$ group of PAD-Cl$^-$. Under acidic pH, PAD-Cl$^-$ seems to be adsorbed to some extent. This weak adsorption was not high enough to change the electrokinetic properties.

The adsorption capacity for SiO$_2$ seems to be slightly dependent on pH in the range 3–7 (Fig. 9). The maximum of adsorption remains the same. These results confirm the electrokinetic properties of silica suspensions prepared with PAD-Cl$^-$. This phenomenon may be explained by the fact that in this pH range, the negative charge density does not vary significantly. A small addition of PAD-Cl$^-$ leads to a rapid signal reversal of the ESA values (Fig. 5) which results in positively charged particles. The electrokinetic properties are essentially no longer dependent on pH or on polymer concentration. The zero point of charge (pH$_{zpc}$) of SiO$_2$ is close to 2, and above this pH, particles surface is dominated by –Si–O$^-$ groups. Electrostatic forces become favourable to strong interactions between the cationic PAD-Cl$^-$ and the negatively charged surface, which leads to rapid saturation. It is clear that polyelectrolyte adsorption onto SiO$_2$ surfaces is driven primarily by electrostatic interactions.
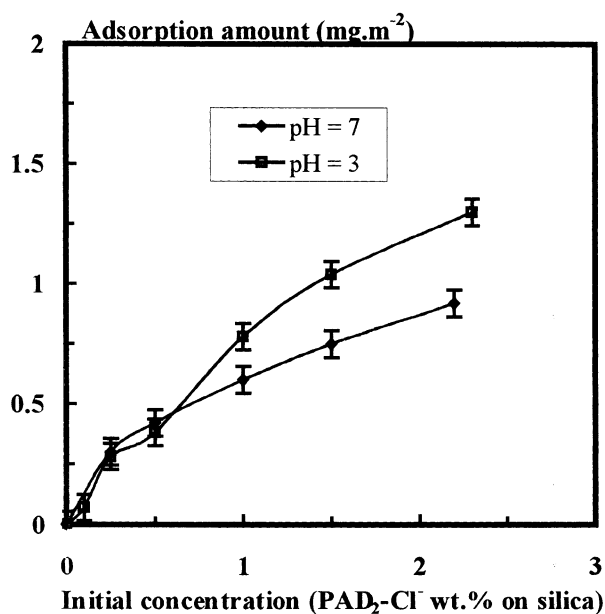
3.2.3. Influence of molecular weight onto PAD-Cl$^-$ adsorption

Analysing the molecular weight dependence of PAD-Cl$^-$ on isotherm adsorption revealed different behaviours for SiO$_2$ and Al$_2$O$_3$. In the first case (Fig. 10) there is no molecular weight dependence, the isotherms are superimposed; such a result is quite foreseeable if we assume a flat conformation of the adsorbed polymer onto SiO$_2$ surface. On the other hand, increased adsorption capacity is observed in the case of Al$_2$O$_3$ as indicated in Fig. 11. This fact may be ascribed to the increase in gyration radius as the molecular weight of the polymer increases. Hence, when the polymer is adsorbed, the loss of configurational entropy will be more important, and the macromolecular chains prefer
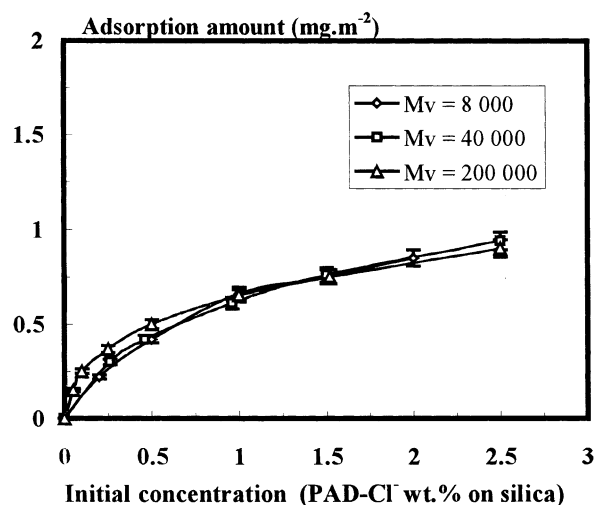

Fig. 10. Adsorption isotherms for PAD-Cl$^-$ on silica as a function of its molecular weight at the natural ionic strength and pH 7–8.

Fig. 9. Adsorption isotherms for PAD$_2$-Cl$^-$ on silica as a function of suspension pH.
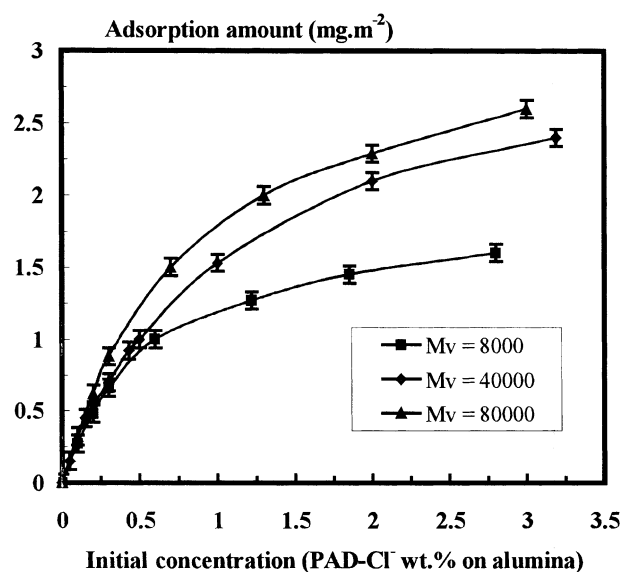

Fig. 11. Adsorption isotherms for PAD-Cl$^-$ on alumina as a function of its molecular weight at the natural ionic strength and the natural pH∼8.5.

to adopt a coiled conformation onto the particles surface. Nevertheless, it seems that the gap between adsorption isotherms is reduced as the molecular weight increases, which suggests that beyond certain molecular weight values, a limiting adsorption capacity is attained, this result is in agreement with other reported studies.[19]

4. Conclusions

Interaction of an anionic and cationic polyelectrolyte with Al_2O_3 and SiO_2 surfaces in aqueous media was investigated using a combination of adsorption and electrokinetic measurements. The nature of the binding sites that determine the interaction modes of the surface with polyelectrolyte have been identified.

In the case of PAD-Cl^- the adsorption onto Al_2O_3 takes place notably up to pH 6.5. In the 6.5–9 pH range, the polymer is adsorbed in a coiled conformation as a result of weak interactions between $=Al–OH$ groups and $-N(CH_3)_3^+$ polyelectrolyte groups. On the other hand, the strong electrostatic interactions between the mutual opposite groups of the SiO_2 surface and the cationic polyelectrolyte allow a flat adsorption of PAD-Cl^- on SiO_2.

Electrokinetic measurements revealed that a monolayer adsorption of PAD-Cl^- onto Al_2O_3 and SiO_2 brings about a positively charged surface whatever the pH of the medium. Such effect is a reliable mean to stabilise aqueous suspensions of colloidal mixtures based on electrostatic repulsion. The influence of polyelectrolyte structure on rheological behaviour and particle dispersion is under investigation.

References

1. Pugh, R. J. and Bergstrom, L., *Surface and Colloidal Chemistry in Advanced Ceramics Processing. Surfactant Sciences Series*, 51. Marcel Dekker, New York, 1994

2. Parfitt, G. D. and Rochester, C. H., *Adsorption from Solution at the Solid/Liquid Interface*. Academic Press, New York, 1983.

3. Paik, U., Hackley, V. A. and Lee, H. W., Dispersant-binder interaction in aqueous silicon nitride suspensions. *J. Am. Ceram. Soc.*, 1999, **82**, 833.

4. Cesarano III, J., Aksay, I. A. and Bleir, A., Stability of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, 1988, **71**(4), 250–255.

5. Hackley, A. V., Colloidal processing of silicon nitride with poly(acrylic acid): I, adsorption and electrostatic interactions. *J. Am. Ceram. Soc.*, 1997, **80**(9), 2315–2325.

6. Hackley, V. A., Paik, U., Kim, B. and Malghan, S. G., Aqueous processing of sintered reaction-bonded silicon nitride: I. Dispersion properties of silicon powder. *J. Am. Ceram. Soc.*, 1997, **80**(7), 1781–1788.

7. Evers, A. A., Fleer, G. J., Scheutjens, J. M. H. M. and Lyklema, J., Adsorption of weak polyelectrolytes from aqueous solutions. *J. Colloid Interface. Sci.*, 1986, **111**(2), 446–454.

8. Bohmer, Evers, V. A. and Schentjens, J. M. H. D., Weak polyelectrolytes between two surfaces: adsorption and stabilization. *Macromolecules*, 1990, **23**, 2288–2301.

9. Lyklema, J., *Fundamentals of Interface and Colloid Science: Solid-Liquid Interfaces*. Academic Press, London, 1995.

10. Baklouti, S., Pagnoux, C., Chartier, T. and Baumard, J. F., Processing of aqueous α-Al_2O_3, α-SiO_2 and α-SiC suspensions with polyelectrolytes. *J. Eur. Ceram. Soc.*, 1997, **17**, 1387–1392.

11. Stearns, L. C., Zhao, J. and Harmer, M. P., Processing and microstructure development in Al_2O_3–SiC 'nanocomposites'. *J. Eur. Ceram. Soc.*, 1992, **10**, 473.

12. Eastmand, C., Ledurth, A., Russo, S. and Sigwalt, P., Polyelectrolyte. In *Comprehensive Polymer Science*, Vol. 6. Pergamon Press, Oxford, 1988.

13. Champetier, G., In *Chimie Macromoléculaire,* Vol. 1, ed. Herman. 1972, pp. 150–200.

14. Van-Krevelen, D. W., *Properties of Polymers*, 2nd edn. Elsevier, 1991.

15. Gebhardt, J. E. and Fuerstenn, D. W., Adsorption of polyacrylic acid at oxide/water interfaces. *Colloids Surface*, 1983, **7**, 221–231.

16. Hidber, P., Graule, T. and Gauckler, L., Influence of the dispersant structure on properties of electrostatically stabilized aqueous alumina suspensions. *J. Eur. Ceram. Soc.*, 1996, **17**, 239–249.

17. Lindman, B., Jonsson, B. and Kronberg., B., *Surfactants and Polymers in Aqueous Solution*. John Wiley & Sons, 1998, pp. 295–318.

18. Fowkes, F. M. and Mostafa, M. A., Acid-base interaction in polymer adsorption. *Ind. Eng. Chem. Prod. Ress. Dev.*, 1978, **1**(17), 3.

19. Van der Schee, H. A. and Lyklema, J., A lattice theory of polyelectrolyte adsorption. *J. Phys. Chem.*, 1984, **88**, 6661–6667.