



Full paper/Mémoire

## Kaolin–poly(methacrylic) acid interaction: Polymer conformation and rheological behavior

Afef Jmal Ayadi<sup>a,\*</sup>, Cécile Pagnoux<sup>b</sup>, Samir Baklouti<sup>a</sup><sup>a</sup>Laboratoire de chimie industrielle, École nationale des ingénieurs de Sfax, BP 3038, Sfax, Tunisia<sup>b</sup>SPCTS, ENSCI, CNRS, 47-73, avenue Albert-Thomas, 87065 Limoges, France

## ARTICLE INFO

## Article history:

Received 8 March 2010

Accepted after revision 27 September 2010

Available online 3 December 2010

## Keywords:

Clay (kaolin)  
Dispersion  
Polymer  
Polyelectrolyte  
Adsorption  
Rheology

## Mots clés :

Argile (kaolin)  
Dispersion  
Polymère  
Polyélectrolyte  
Adsorption  
Rhéologie

## ABSTRACT

The interaction between an ammonium salt of polymethacrylic acid (PMA) and kaolin and its effect on the suspension rheology behavior have been investigated. Adsorption measurements showed significant affinity between PMA and kaolin particles. This adsorption takes place only on the edges of the surface of the particles. The shape of the adsorption isotherm suggests the formation of a monolayer according to the Langmuir model. The amount of PMA adsorbed on kaolin at the equilibrium depends on the pH and the ionic strength of suspensions. According to the adsorption results and the shape of kaolinite particle, the dispersant takes probably a plate conformation on the edges of the surface of the kaolin particle at natural pH (7.7–8) and low ionic strength but a loop conformation at acidic pH (5.5–6) and low ionic strength, and also at natural pH and high ionic strength (0.1 M). Good agreements were observed between adsorption results and rheological properties. The PMA has an efficacious dispersing power for kaolin suspension at natural pH (7.7–8) and low ionic strength.

© 2010 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## R É S U M É

L'objectif de cette étude est de comprendre les interactions entre le PMA et le kaolin et de montrer la conformation du polymère adsorbé à la surface des particules et aussi de montrer son effet sur la rhéologie des suspensions. L'étude de l'adsorption du polymère (PMA) sur le kaolin a montré qu'il y a une affinité significative entre les particules et le dispersant. Cette adsorption a lieu seulement sur la surface des bords des particules. La forme des isothermes d'adsorption prouve qu'il y a formation d'une monocouche selon le modèle de Langmuir. La quantité de PMA adsorbée sur les particules de kaolin dépend essentiellement des impuretés, du pH et de la force ionique des suspensions. En se basant sur la quantité adsorbée de PMA à l'équilibre et sur la forme des particules de kaolin, nous avons constaté que le polymère prend une conformation plane sur la surface des bords des particules à pH naturel (7,7–8) et à faible force ionique mais une conformation en boucle à pH acide (5,5–6) et faible force ionique et aussi à forte force ionique (0,1 M) et pH naturel. Les résultats ont montré aussi une bonne concordance entre l'adsorption du polymère et la rhéologie des suspensions. Le PMA est un dispersant efficace pour les suspensions de kaolin à pH naturel et à faible force ionique.

© 2010 Académie des sciences. Publié par Elsevier Masson SAS. Tous droits réservés.

\* Corresponding author.

E-mail address: afefjmal@yahoo.fr (A.J. Ayadi).

## 1. Introduction

The dispersion behavior of clay suspensions is very important in environmental sciences, ceramic processes, the petroleum and paper industries. In this case many studies have been conducted on pure reference clays and clay mixtures [1–4]. Clay–polymer interactions are involved in a large variety of technical areas such as soil stabilization, water treatment and mud formulations for drilling oil wells [5,6].

To disperse clays in aqueous suspensions with polyelectrolyte addition, several important factors such as pH, surface chemistry of powder, and nature and amount of the polyelectrolyte used must be understood and controlled [7–9]. The adsorption of anionic or cationic polymers on ceramic powders has been studied as a function of pH [10–12] and ionic strength [4]. Adsorption of uncharged polymers on kaolin has also been investigated [3]. This adsorption affects strongly the rheological behavior of kaolin suspensions. Fundamental properties of kaolin particles, such as their size, morphology, surface charge, mineralogical composition and chemical impurities in the clay affect also significantly this rheological behavior of kaolin suspensions [13–18].

Kaolinite, the main mineral of kaolin material, has a complicated surface chemistry because of heterogeneity of charged edges and faces [18,19]. It is a 1:1 dioctahedral aluminosilicate that has two different basal cleavage faces [20,21]. One basal face consists of a tetrahedral siloxane surface of very inert Si–O–Si links. The other basal surface consists of an octahedral  $\text{Al}(\text{OH})_3$  sheet [22]. Both of these surfaces are theoretically neutral [10]. At the edges of the 1:1 layer, the structure is disrupted and broken bonds occur, which are accommodated as OH groups [23]. These edges are estimated to occupy approximately 20% of the whole kaolinite surface [22,24].

Polar sites, mainly octahedral Al–OH and tetrahedral Si–OH groups, are situated at the broken edges and exposed hydroxyl terminated planes of clay lamellae [18]. The amphoteric sites Al–OH are conditionally charged, and have either positive or negative charges, depending on the pH solution [20,25] due to protonation/deprotonation of exposed hydroxyl groups in aqueous solutions [23]. Although, this phenomena seems to be difficult for Al–OH sites of basal surface, most studies affirm that the silica faces of kaolin [2,18] have usually negative charges independently of pH value.

Several studies on kaolin suspensions with many kinds of dispersants such as the ammonium salt of polymethacrylic acid (PMA) and the sodium salt of polymethacrylic acid (PAANA), sodium hexametaphosphate, sodium tripolyphosphate were investigated in which they focus on rheological behavior, adsorption isotherms, zeta potential [2–4,9,10,26–30], but there are few indications or demonstrations concerning the conformation of the adsorbed polymer especially PMA on the kaolin's particles and its effect on rheological behavior.

The aim of the present work was to study PMA adsorption on kaolin in aqueous suspension as a function of pH, ionic strength and dissolved impurities, in order to understand the mechanism and conformation of polymer

adsorption on kaolinite particles. The effect of this adsorption on the rheological behavior of suspensions was also investigated.

## 2. Experimental procedure

### 2.1. Raw materials

Natural kaolin (kaolin codex) supplied by the central pharmacy (Tunisia) was selected as the raw material for the present investigation. The powder has a specific area of  $8.9 \text{ m}^2/\text{g}$  determined by nitrogen adsorption (BET). Major mineral impurities, which this kaolin contains, are quartz, illite and  $\text{Fe}_2\text{O}_3$  as determined by X-ray diffraction. The kaolin contains also dissolved impurities. The isoelectric point IEP is about 7.7 measured by zetasizer. The kaolin particles are typically thin and plate-like with a pseudo-hexagonal shape as determined by SEM. In order to quantify the nature and the amount of dissolved impurities in aqueous suspensions of natural kaolin, the supernatant of centrifuged suspensions was analyzed by the ICP method. The result of the analysis shows that the amount of total multivalent and coagulant cations must not be neglected in this study.

An ammonium salt of polymethacrylic acid (PMA) provided by the R.T. Vanderbilt Company, Inc was used as a dispersing agent for kaolin suspensions. It is an aqueous solution with a pH 7.5. The average molecular weight of this anionic polyelectrolyte was  $15\,000 \text{ g/mol}$  (monomer unit of PMA  $-\text{CH}_2-\text{C}(\text{CH}_3)-\text{COO}^- \text{NH}_4^+$  weight =  $103 \text{ g}$ ). A cationic Polymer PDMAC (polydiallyldimethylammonium chloride,  $M_n = 150\,000 \text{ g/mol}$ ) and orthotoluidine blue (indicator) were used for the titration of free PMA polyelectrolyte in solution. On the other hand, sodium tripolyphosphate (STPP) was used as a reference dispersant for rheological behaviors of kaolin suspensions.

The pH was adjusted via the addition of HCl and ionic strength conditions were found by using an aqueous solution of  $\text{NaNO}_3$  at a concentration of  $10^{-1} \text{ M}$ .

### 2.2. Experimental methods

This work aims to study the PMA interaction with the kaolin mineral powder as received and without soluble impurities in suspension. For this reason, the supplied kaolin powder was washed. It was introduced in an aqueous solution and then centrifuged and the supernatant was discarded; this operation was repeated many times. Washed kaolin was recuperated then dried and finely pounded.

#### 2.2.1. Adsorption isotherms

Aqueous suspensions of 30 wt % of natural and washed kaolin with different concentrations of PMA were prepared at different pH (natural  $\text{pH} \approx 7.7$ –8 and acidic  $\text{pH} \approx 5.5$ –6) and ionic strengths  $I$  (natural  $I$ ,  $I = 10^{-1} \text{ M NaNO}_3$ ). Each slurry was ultrasonicated for desagglomeration, and the mixing was carried out by magnetic agitation during 24 hours in order to reach adsorption equilibrium. The suspensions were then centrifuged at a speed of 8500 rpm for 25 min and the supernatants were removed

and were stored at 4–5 °C for one night before analysis. The amount of free polyelectrolyte in the supernatant was determined by a colloid titration technique using the cationic PDMAC and orthotoluidine as an indicator. The details of the method are described in many references [31–33]. All titrations were carried out under conditions of low ionic strength, obtained by dilution of the supernatant sample with distilled water. The limit of efficiency of this method was given in a previous study [31]. Each titration was repeated three times.

Preliminary tests conducted on PMA have confirmed the validity of the method. Tests, conducted on solutions with known concentrations, have indicated that the amount of ionized PMA is a function of pH solution and ionic strength as it is shown in a previous study [7].

### 2.2.2. Rheological tests

Slurries of natural and washed kaolin were prepared by mixing an appropriate amount of kaolin with distilled water in which the dispersant was dissolved, followed by ultrasonication and 24 hours shaking. The final solid content was 50 wt %. Rheological tests were carried out at 25 °C by using the rate controlled coaxial cylinder viscosimeter HAAKE ROTO VISCO 1, Thermo Electron Corporation. The rheological test consists of a preshear step at 200 s<sup>-1</sup>, in order to homogenize suspension rheology history, and then a linear increasing of the shear rate from 0 to 600 s<sup>-1</sup> for 5 min.

## 3. Results and discussions

### 3.1. Dissociation of PMA

PMA contains ionizable carboxylic acid groups, which are capable of dissociation depending on the pH of the solution [2,7]. The dissociation results of used PMA at different pH values are presented in Fig. 1. These results are obtained, after repeating the same experiment many times, by colloid titration technique using cationic polyelectrolyte (PDMAC).

The dissociated fraction ( $\alpha$ ) decreases from 100% at pH 12 to 35% at pH 4. Under this pH value the experimental method is not efficient. PMA becomes a negatively charged polymer when it is dissociated, the number of negative

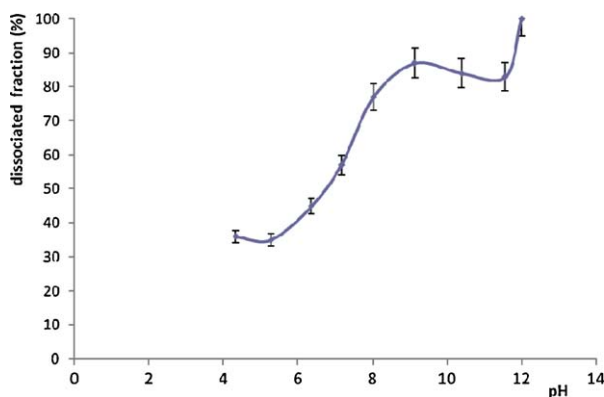


Fig. 1. Dissociated fraction of PMA as a function of pH.

charges on each polyelectrolyte increases as its extent of dissociation increases [7]. In fact, the PMA changes from a partially neutral polymer at low pH to a totally negatively charged polyelectrolyte at pH = 12. In these cases the PMA conformation changes in solution from a small volume at acidic pH and low dissociated fraction to a bigger volume at basic pH and high dissociation fraction.

### 3.2. Adsorption of PMA on kaolin

The adsorption isotherms of PMA onto the kaolin sample (natural and washed kaolin) are presented in Fig. 2 at different pH and ionic strengths.

The measurements were conducted at the natural pH (7.7–8) and acidic pH (5.5–6) with or without ionic strength effect (NaNO<sub>3</sub> 10<sup>-1</sup> M). The shape of all adsorption isotherms of natural and washed kaolin shows a monolayer adsorption of the dispersant on kaolin particle surface, in fact the amount of PMA adsorbed increases as the polymer concentration increases until a plateau is reached. The maximum amounts of adsorbed PMA ( $C_{max}$ ) on washed kaolin at natural and acidic pH (low ionic strength) and at natural pH and high ionic strength were respectively 0.13 mg/m<sup>2</sup>, 0.15 mg/m<sup>2</sup> and 0.08 mg/m<sup>2</sup>. This amount was 0.24 mg/m<sup>2</sup> for natural kaolin at natural pH and low ionic strength.

At natural pH and low ionic strength, adsorption results show a good affinity between PMA polyelectrolyte and natural kaolin. This affinity is lower with washed kaolin, as the slope of the curve is lower. On the other hand, the maximum amount of the adsorbed polymer was 0.13 mg/m<sup>2</sup> and 0.24 mg/m<sup>2</sup> on respectively the washed and the natural kaolin surface. The difference can be explained by a complexation mechanism between soluble cations impurities and the polyelectrolyte (PMA), which phenomena reduces the free PMA molecules concentration in the supernatant.

The amount of PMA adsorbed on the washed kaolin surface is higher than that obtained in another study [2] (0.085 mg/m<sup>2</sup>) for the adsorption of 3400 MW sodium polyacrylate (NaPAA) on the surface of kaolin at a pH 7. The shifty difference may be attributed mainly to the difference in the molecular weight of each dispersant. In fact, the amount of adsorbed polymer at saturation increases when its molecular weight increases as was demonstrated in last studies [34,35].

The pH value of solution is one of the main parameters that control the nature and the density of the charges on the kaolin particle surface [26]. The pH controls also the dissociated fraction of PMA. The maximum adsorbed amount of PMA increases when the suspension's pH decreases to 5.5 and reaches a maximum of 0.15 mg/m<sup>2</sup> for washed kaolin. The raising of the adsorption density at the plateau is not very high and may be explained by an increase in the density of positive sites on the edge surface of kaolin particles, which represents only 20% of the total surface. Therefore, the adsorption amount of the polymer increases as a result of interaction between COO<sup>-</sup> groups of PMA and Al-OH<sub>2</sub><sup>+</sup> sites of particles.

At high ionic strength and natural pH and according to the adsorption results, the affinity of kaolin into the PMA

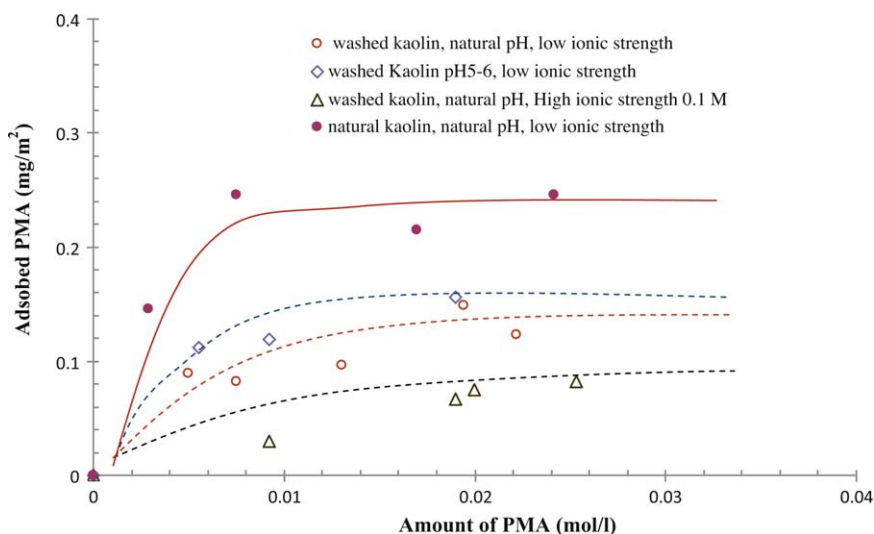


Fig. 2. Adsorption isotherms of the PMA onto natural and washed kaolin as a function of amounts of polyelectrolyte at the equilibrium at different pH and different ionic strengths.

decreases as the slope of the curve is lower and the maximum amount of PMA adsorbed decreases ( $0.08 \text{ mg/m}^2$  for washed kaolin). This behavior is the result of a screening effect of the  $\text{Na}^+$  counter ions on  $\text{COO}^-$  groups, which stabilizes  $\text{COO}^-$  function and then decreases the adsorption kinetic by electrostatic interactions and of the compression of the electric double layers, which causes coagulation phenomenon by face-edge interactions.

Comparison of the adsorbed amount of PMA at saturation onto the surface of kaolin particles and that onto the surface of alumina powder with almost the same specific area studied in a previous works [36] indicates that the adsorption density of the polymer on the surface of alumina is larger (almost  $0.4 \text{ mg/m}^2$ ) than that on kaolin particles (almost  $0.13 \text{ mg/m}^2$ ). Moreover, most researches [18,20,25] affirm that kaolin particles faces are usually negatively charged or with stable Al-OH groups and its edges have positive and/or negative charges depending on the pH value of suspensions. Then PMA, with 75% carboxylate groups fraction at pH 8 (Fig. 1), is adsorbed mainly on the edges of the particle by both electrostatic and hydrogen interactions as it was indicated by others studies [2]. The PMA interaction with basal planes is possible via hydrogen bond but seems to be low at pH 8, it could increase when suspension pH decreases and the  $-\text{COOH}$  groups increase.

In addition, the edges represent approximately 20% of the total surface.

Kaolin powder used in this study has a surface area of  $8.9 \text{ m}^2/\text{g}$ . Within the hypotheses that PMA is adsorbed only

on the edges of the kaolin particle (which is calculated and is approximately equal to  $1.78 \text{ m}^2/\text{g}$ ) and that the adsorption density of PMA on the surface of kaolin at saturation is equal to  $0.13 \text{ mg/m}^2$  at natural pH (7.7–8). So the amount of adsorbed polymer on edges is calculated to be  $0.65 \text{ mg/m}^2$  which is higher than that observed on alumina surface.

On the other hand, at natural pH (7.7–8) PMA is partially dissociated with a fraction ( $\alpha$ ) value of 75% (Fig. 1). So that the amount of dissociated groups  $\text{COO}^-$  of PMA adsorbed on the edges is calculated (on the basis of monomer unit weight of PMA  $103 \text{ g}: -\text{CH}_2-\text{C}(\text{CH}_3)-\text{COO}^- \text{NH}_4^+$ ) to be  $0.0047 \text{ mmol/m}^2$  (Table 1). Besides, the concentration of Al-OH site on kaolin surface is about  $0.035 \text{ mmol/g}$ , according to other work [19], which corresponds to  $0.004 \text{ mmol/m}^2$  for studied kaolin at our conditions (Table 1).

According to these results, at natural pH, the concentration of maximum Al-OH<sub>2</sub><sup>+</sup> groups on the surface is slightly lower than that of free  $\text{COO}^-$  groups on PMA, we can predict that the conformation of PMA chains in the adsorption layer has a plate shape.

Whereas at acidic pH, the amount of Al-OH<sub>2</sub><sup>+</sup> groups on the surface is higher than that of free  $\text{COO}^-$  groups on PMA, which leads that the adsorption of PMA on the edges of kaolin has a loop conformation.

At natural pH and high ionic strength ( $10^{-1} \text{ M NaNO}_3$ ) the amount of adsorbed polymer is smaller than that of totally ionized Al-OH<sub>2</sub><sup>+</sup> on the edges surface of particles, so that the PMA conformation on the edges of kaolin has, in these conditions, probably also a loop shape.

Table 1

Adsorbed amounts of PMA on washed kaolin particles edges at different pH and ionic strengths.

Experimental conditions	$C_{\text{max}}$ ( $\text{mg/m}^2$ ) on total particle	$C_{\text{max}}$ ( $\text{mg/m}^2$ ) on edges	$C_{\text{max}}$ ( $10^{-6} \text{ mol/m}^2$ ) on edges	$\alpha$ (%) dissociation factor	Free ( $\text{COO}^-$ ) ( $\text{mmol/m}^2$ )	[Al-OH] ( $\text{mmol/m}^2$ )
Natural pH (7.7–8)	0.13	0.65	6.31	75	0.0047	0.004
Acidic pH (5.5–6)	0.15	0.75	7.28	40	0.0029	0.004
Ionic strength $10^{-3} \text{ NaNO}_3$	0.08	0.4	3.88	75	0.0029	0.004

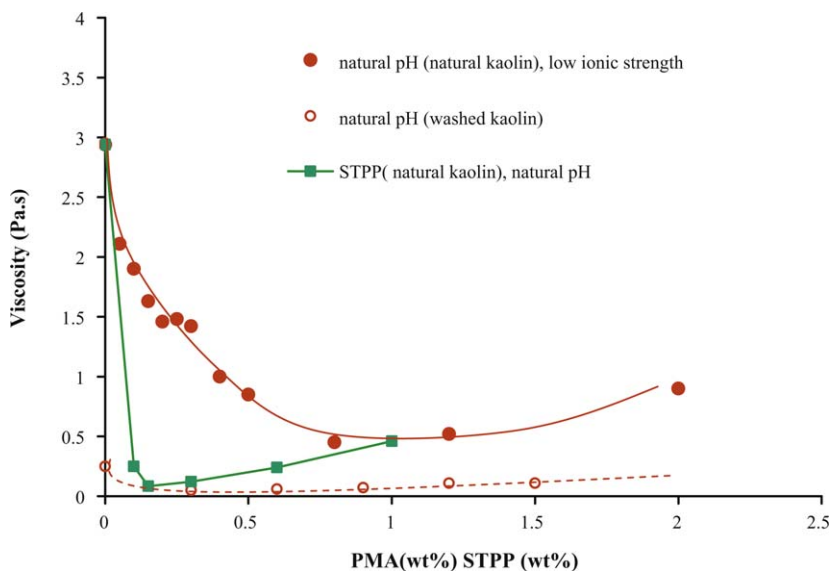


Fig. 3. Evolution of the viscosity of natural and washed kaolin suspensions as a function of the amount of added PMA at  $100 \text{ s}^{-1}$ , natural pH = 7.7–8 and natural ionic strength.

### 3.3. Rheological properties

The rheological properties of the kaolin dispersion depend on different factors, including the shape and size distribution of the suspended particles, the volume fraction of particles and the amount, the type and the conformation of polymers added to the dispersion [14,16]. Viscosity and shear stress measurements realized in this study were investigated in order to analyze the effect of PMA on the rheological behavior of kaolin at each condition (natural pH (7.7–8), acidic pH (5.5–6) and

different ionic strengths). All suspensions prepared with PMA present a pseudo-plastic rheological behavior over all the range of dispersant concentration investigated. The effect of the PMA on the viscosity of natural and washed kaolin suspensions at a constant shear rate  $100 \text{ s}^{-1}$  is shown in Figs. 3 and 4. These figures contain also the effect of STPP dispersant used as a reference.

According to these results and in all cases at shear rate  $100 \text{ s}^{-1}$ , viscosity decreases with additive to reach a minimum at an optimal concentration, and then increases when an excess of dispersant is introduced. This behavior

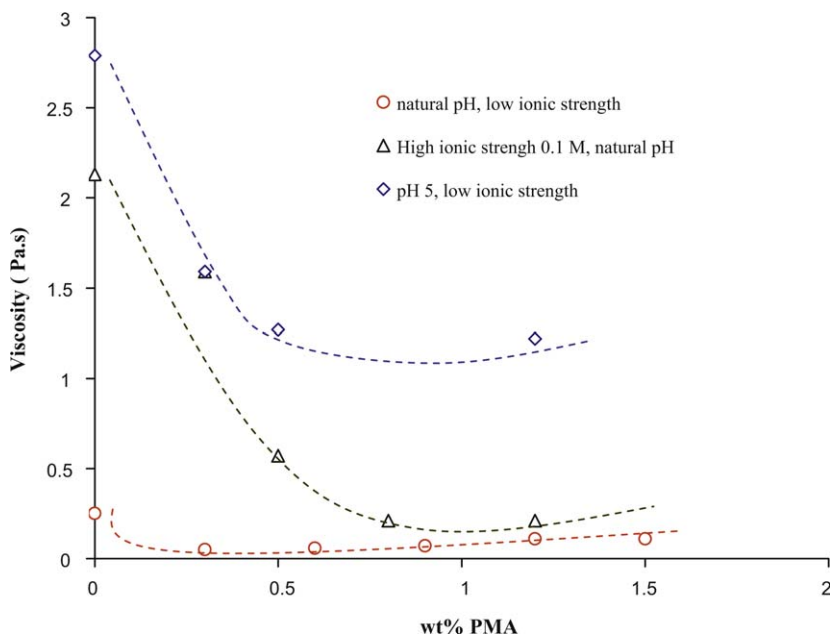


Fig. 4. Evolution of the viscosity of washed kaolin suspensions as a function of the amount of added PMA at  $100 \text{ s}^{-1}$  for different pH and different ionic strengths.



was well described in the literature [26]. Above the adsorption saturation the excess of dispersant is not adsorbed on particles and causes flocculation and coagulation of the suspension.

As can be observed in Fig. 3, STPP, used as a reference in our study, presents an efficacious dispersant power giving lower viscosity at low concentration (only 0.15 wt %). This effect is due to an electrostatic mechanism of dispersion and to the small molecule size of STPP.

For washed kaolin and at natural pH and low ionic strength (Fig. 3), PMA presents similar dispersing power as STPP with almost 0.3 wt % (0.008 mol/l). This value agrees with the adsorption results where the plateau is reached at 0.3 wt %. Adsorbed PMA onto positive sites of the particle surfaces enhances electrosteric repulsion between particles and causes a deflocculation of suspensions characterized by a low viscosity. This viscosity is shown to be slightly lower than that obtained with STPP. This difference can be explained by the steric dispersing effect of this polymer besides of its electrostatic effect. On the other hand, the presence of dissolved multivalent cations as coagulant impurities increases probably the suspension viscosity as it is shown in Fig. 3 for natural kaolin suspension.

At high ionic strength and natural pH (Fig. 4), because of the lowest amount of adsorbed PMA on kaolin according to adsorption isotherms, the viscosity of suspensions is higher than that of suspensions at low ionic strength. This phenomenon may be explained by coagulation of particles in suspension due to the compression of electric double layers in presence of high indifferent electrolyte and to the loop conformation effect of adsorbed PMA.

At acidic pH = 5.5–6 suspensions present higher viscosity than those prepared in all other conditions this fact is due to the steric effect of PMA adsorbed on kaolin particles according to its big size (loop conformation) and also to the possible interaction face–edge (heterocoagulation) since the positive charges density on the particle surface was increased when the pH value of suspensions was reduced.

#### 4. Conclusion

The interaction between PMA and kaolin was investigated to demonstrate its adsorption conformation on particles and to show its effect on the suspension rheology behavior. PMA-kaolin suspension was studied as a function of PMA amount at different pH and ionic strength.

From this investigation, it was shown that the adsorption of PMA takes place only on the edges surface of kaolin particle and it is mainly the result of electrostatic interaction between  $\text{Al-OH}_2^+$  sites and  $\text{COO}^-$  groups.

According to the adsorption results, at natural pH and low ionic strength, the adsorbed PMA has probably a plane conformation on the particle edges. Whereas, at natural pH with high ionic strength (0.1 M  $\text{NaNO}_3$ ) and at acidic pH, the conformation of PMA chains in the adsorption layer seems to have a loop shape.

It was shown also that, at natural pH and low ionic strength, PMA has an efficacious dispersing power equivalent as that of STPP.

Good agreements were seen between adsorption conformation and its effect on rheological behavior. At acidic pH and low ionic strength, suspensions present higher viscosities due to the steric effect of PMA conformation and also to the possible face–edge interaction (heterocoagulation) caused by the increase of positive charges on kaolin's particles.

At high ionic strength and natural pH, viscosity of suspensions is higher than that of suspensions at low ionic strength. This phenomenon may be explained by coagulation of particles in suspension due to the compression of electric double layers in presence of high indifferent electrolyte, and to the loop conformation effect of adsorbed PMA.

#### Conflict of interest statement

We have no conflict of interest.

#### References

- [1] F.O. Cunha, M.L. Torem, J.C. D'Abreu, *Miner. Eng* 19 (2006) 1462.
- [2] A.A. Zaman, R. Tsuchiya, B.M. Moudjil, *J. Colloid Interface Sci* 256 (2002) 73.
- [3] K.A. Backfolk, J.B. Rosenholm, J.C. Husband, D.E. Eklund, *Colloids Surf* 195 (2001) 151.
- [4] D. Penner, G. Lagaly, *Appl. Clay Sci* 19 (2001) 131.
- [5] M.J. Sanchez-Martin, M.C. Dorado, J. Hazard. Mater 150 (2008) 115.
- [6] Peng Liu, *Appl. Clay Sci* 38 (2007) 64.
- [7] J. Jau-Ho, W. Hong-Ren, *J. Am. Ceram. Soc* 81 (1998) 1589.
- [8] D. Santhiya, S. Subramanian, K.A. Natarajan, S.G. Malghan, *Colloids Surf* 16 (2000) 143.
- [9] M. Sjöberg, L. Bergström, A. Larsson, E. Sjöström, *Colloids Surf* 159 (1999) 197.
- [10] N. Tekin, E. Kadinci, O. Demirbas, M. Alkan, A. Kara, *J. Colloid Interface Sci* 296 (2006) 472.
- [11] B.P. Singh, S. Bhattacharjee, L. Bersa, D.K. Sengupta, *Ceram. Int* 30 (2004) 939.
- [12] N. Tekin, O. Demirbas, M. Alkan, *Microporous Mesoporous Mater* 85 (2005) 340.
- [13] F. Andreola, E. Castellini, T. Manfredini, M. Romgnoli, *J. Eur. Ceram. Soc* 24 (2004) 2113.
- [14] S. Jogun, C. Zukoski, *J. Rheol* 40 (1996) 1211.
- [15] J. Labanda, P. Marco, L. Lorens, *Colloids Surf* 249 (2004) 123.
- [16] R.G. de Kretser, P.J. Scales, D.V. Boger, *Colloids Surf* 137 (1998) 307.
- [17] G. Lagaly, *Appl. Clay Sci* 4 (1989) 105.
- [18] E. Tombacz, M. Szekeres, *Appl. Clay Sci* 34 (2006) 105.
- [19] P.V. Brady, R.T. Cygan, K.L. Nagy, *J. Colloid Interface Sci* 183 (1996) 356.
- [20] T.M. Herrington, A.Q. Clarke, J.C. Watts, *Colloids Surf* 68 (1992) 161.
- [21] E. Pefferkorn, L. Nabzar, A. Carroy, *J. Colloid Interface Sci* 106 (1985) 94.
- [22] W.M. Carty, *Am. Ceram. Soc. Bull* 77 (1999) 72.
- [23] M. Alkan, O. Demirbas, M. Dogan, *Microporous Mesoporous Mater* 83 (2005) 51.
- [24] K.L. Konan, C. Peyratout, J.P. Bonnet, A. Smith, A. Jacquet, P. Magnoux, P. Ayrault, *J. Colloid Interface Sci* 307 (2007) 101.
- [25] M.J. Avena, M.M. Mariscal, C.P. De Pauli, *Appl. Clay Sci* 24 (2003) 3.
- [26] A. Papo, L. Piani, R. Ricceri, *Colloids Surf* 201 (2002) 219.
- [27] P. Marco, J. Labanda, J. Lorens, *Powder Technol* 48 (2004) 43.
- [28] E. Castellini, G. Lusvardi, G. Malavasi, L. Menabue, *J. Colloid Interface Sci* 292 (2005) 322.
- [29] S. Baklouti, M.R. Ben Romdhane, S. Boufi, C. Pagnoux, T. Chartier, J.F. Baumard, *J. Eur. Ceram. Soc* 2 (2003) 905.
- [30] F. Andreola, E. Castellini, J.M.F. Ferreira, S. Olhero, M. Romagnoli, *Appl. Clay Sci* 31 (2006) 56.
- [31] H. Bouhamed, S. Boufi, A. Magnin, *J. Colloid Interface Sci* 312 (2007) 279.
- [32] H. Bouhamed, A. Magnin, S. Boufi, *J. Colloid Interface Sci* 298 (2006) 238.
- [33] M.R. Ben Romdhane, T. Chartier, S. Baklouti, J. Bouaziz, C. Pagnoux, J.F. Baumard, *J. Eur. Ceram. Soc* 27 (2007) 2687.
- [34] Y.K. Leong, P.J. Scales, T.W. Healy, D.V. Boger, *Colloids Surf* 95 (1995) 43.
- [35] D. Santhiya, G. Nandini, S. Subramanian, K.A. Natarajan, S.G. Malghan, *Colloids Surf* 133 (1998) 157.
- [36] M.R. Ben Romdhane, S. Boufi, S. Baklouti, T. Chartier, J.F. Baumard, *Colloids Surf* 212 (2003) 271.