EFFECT OF pH ON THE RHEOLOGICAL BEHAVIOR OF PURE AND INTERSTRATIFIED SMECTITE CLAYS

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Abstract—The effects of pH and ionic strength on the rheological behavior of aqueous suspensions of both crude and purified Wyoming bentonite and natural interstratified illite-smectite from Tunisia were investigated. Flow tests were performed on the four clay suspensions at a 10% clay concentration at different pH values. They showed that the rheological properties were highly sensitive to pH and the nature of the clay. The evolution of the yield stress as a function of pH is characterized by the presence of maxima and minima attributed to changes in the mode of association of the particles. The effect of pH on the behavior of clay suspended in NaCl solutions was also studied. The results show that the presence of NaCl has very little effect on the pH and yield stress values of the four materials.

Key Words—Aqueous Clay Suspensions, Flow Properties, Ionic Strength, pH, Yield Stress.

INTRODUCTION

Clay minerals are widely used in industrial applications, *e.g.* in the manufacture of ceramics, cosmetics, cement, drilling fluids, paints, *etc*. (Grim, 1968). These applications are mostly related to their specific physico-chemical and rheological properties such as gel formation, osmotic swelling, yield stress, and viscoelastic and thixotropic behavior (Sohm and Tadros, 1989; Abend and Lagaly, 2000). The minerals can either be used in their crude form or after various chemical treatments in order to bring out a particular quality to meet performance requirements.

Several models have been proposed in the literature to explain the mechanism of gel formation in clay aqueous suspensions. Van Olphen (1977) proposed a three dimensional 'cardhouse' resulting from the edge-to-face (E−F) interaction between the negatively charged faces and the positively charged edges of the clay particles. Norrish (1954) attributed the mechanism of gel formation to repulsive forces between the interacting diffuse double layers. Callaghan and Ottewill (1974) supported this idea and presented some evidence that the gel formation was due to long-range electrostatic double-layer edge-to-edge (E−E) and face-to-face (F−F) repulsions.

In the case of Na-montmorillonites, Pons *et al.* (1981), using small-angle X-ray diffraction, and Tessier (1984), using electron microscopy, opposed van Olphen's theory of the cardhouse suggesting that the gel structure was a consequence of a network of connected particles with lenticular pores, the walls of which are formed by an E−E association of several smectite layers. The same approach was developed by Coussot and van Damme (1997) and van Damme (2002) who analyzed the stability of the network from a mechanical point of view. They assumed that the size of the pores resulted from the competition between the repulsive osmotic forces and the elastic recoil forces due to the flexibility of the walls. Any parameter that can change the number of unit layers (*e.g.* nature of the cation, pH, ionic strength, *etc*.) will modify the flexibility of the walls and the rheological properties of the structure. Because of their very large lateral extension, some of the layers can locally overlap in a dense stacking while being separate elsewhere. The present authors have only worked under neutral pH conditions.

In a dilute clay suspension, the faces of the particles are always negatively charged due to the isomorphic substitutions in the octahedral sheets of the particles. On the other hand, the electronic charge on the edges of the particles depends on the pH of the solution. The edges behave as an oxide surface (Rand and Melton, 1977) and can be positively or negatively charged according to the pH of the solution. In fact, the kinetics of pH changes in the solution may lead to a heterogeneity of pH with some edges positively charged while others are negatively charged. Under these conditions, it is possible to have both positive and negative charges on the edges of particles at the same time. As the faces are always negatively charged, the isoelectric point for the edges (*i.e.* the pH for which the net charge of the edges is neutral) corresponds to a net negative overall charge.

Several authors have studied the effect of pH and salt on the rheological behavior of clays. Unfortunately, no general theory has been developed covering all these

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situations due to the large number of clays and the complexity of the interactions between clay particles. Schofield and Samson (1954), Street (1956), Flegmann *et al.* (1969), Nicol and Humter (1970) and Rand and Melton (1977) investigated the effect of pH on the yield stress of pure Na-kaolinites at low ionic strength. Their results show that the yield stress presents a maximum for pH values between 3 and 5. These researchers attribute this to the electrostatic E−F attractions between the negatively charged faces and the positively charged edges of the particles. Heath and Tadros (1983), Brandenburg and Lagaly (1988), Lagaly (1989), Sohm and Tadros (1989), Permien and Lagaly (1994a, 1994b) and Benna *et al.* (1999) considered the effect of pH and salt on the rheological behavior of bentonites. The conclusions from these studies vary and are sometimes contradictory. Heath and Tadros (1983) found a minimum value of the yield stress at pH 7 and they assumed that this value corresponded to the edges' isoelectric point. Brandenburg and Lagaly (1988) reached quite a different conclusion, showing that the yield stress presented a maximum at pH 4 and a minimum at pH 6.3. The maximum was considered to be the result of the strong interactions between the positively charged edges and the negatively charged faces in the acidic medium, forming a kind of cardhouse. Sohm and Tadros (1989) showed the presence of a first maximum at pH 7, which they attributed to the E−F associations. Lagaly (1989) and Permien and Lagaly (1994a, 1994b) supported the existence of the edge(+)/face(−) contacts (cardhouse) in an acidic medium and face(−)/face(−) contacts (band-like structures) in an alkaline medium. Benna *et al.* (1999) found maximum yield stress values at acidic pH values, ranging between 2.5 and 4.5, 3.5 and 6, 5 and 7, respectively, for the three studied clays. The authors explained the existence of the maxima by the E−F attractions and the formation of a cardhouse network. An explanation of these different interpretations could be the fact that the materials studied are very different from each other as the studies cover natural and purified smectites as well as activated commercial bentonites. In addition, the studies were carried out under different conditions of pH and NaCl concentrations making direct comparisons very difficult.

The objective of the present paper is to determine the influence of pH on the rheological behavior of two types of clay: (1) an interstratified illite-smectite from Tunisia; and (2) Wyoming bentonite from the USA. These two clays were studied in both their original and purified states.

EXPERIMENTAL

Materials

The research was carried out on two materials: (1) natural clay samples taken at a depth of 3 m in the Chouabine layer in the Jebel Om El Khecheb area, in southwestern Tunisia; (2) a natural Wyoming bentonite, used in the drilling fluids industry under the trade name MILGEL NT®. The Wyoming bentonite is an untreated material, chosen for comparison purposes, that is produced under specification 13A, Section 5 of the American Petroleum Institute (API, 1990).

Prior to its use, the Tunisian clay was crushed and only the dry powder passing through a 100 μm sieve was kept. The two clays were purified by the Na exchange method of Annabi-Bergaya (1978). The NaCl-exchange purification leads to the elimination of the impurities and the replacement of the exchangeable cations by Na ions. This exchange can be schematized by the following reaction:

$$n\text{NaCl} + \text{montmorillonite-}M^{n+} \rightleftharpoons$$
$$MCl^{n+} + \text{montmorillonite-}n\text{Na}^+$$
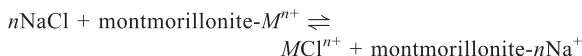
With an excess of Na$^+$ ions in the solution, the reaction is moved towards the right. The clay's exchangeable cations (M^{n+}) are thus replaced by nNa$^+$. To carry out this purification, 1 g of raw clay was mixed with 100 mL of a NaCl solution (1 M). After ~12 h of agitation of the prepared mixture, the suspension was centrifuged for 10 min at 3000 rpm. The supernatant liquid was then removed and the deposited solids resuspended in an additional 100 mL of 1 M NaCl solution. The agitation-centrifugation cycle is repeated several times in order to ensure that the possible exchange of cations by Na is completed. Once the clay is exchanged with Na it is characterized by a very high swelling capacity. Deionized water washing followed by a new centrifugation (5000 rpm for 30 min) makes it possible, on the one hand, to eliminate excess chloride ions and, on the other hand, to remove the remaining impurities. This washing is repeated until the clay forms a stable dispersion. At this stage, the excess chloride ions are eliminated by dialysis and a silver nitrate test was conducted to confirm the absence of Cl$^-$ ions. After dialysis, the resulting suspension is so diluted that it is likely that the basic intra-crystalline layers in each clay crystal are separated. The material is dried at 50ºC, crushed again and finally sieved to 63 μm in order to obtain a dry powder. As the material only contains a clay fraction of <2 μm, the total amount can be passed through a 63 μm sieve. The Jebel Om El Khecheb and Wyoming clays are referred to hereafter as CHa and W, respectively, with CHab and Wb indicating the clays in their original crude state, and CHap and Wp indicating the clays after purification.

Physicochemical methods

X-ray diffraction (XRD), chemical analysis, transmission electron microscopy (TEM), cation exchange capacity (CEC) and specific surface area (S_t) measurements were used to characterize the two clays.

XRD. The XRD patterns were obtained using a Philips PW1710 diffractometer with a Cu anticathode (λCuKα = 0.154040−0.154438 nm) at 40 kV and 20 mA. The

experiments were carried out on both raw and purified powders as well as on oriented samples for which the slides were prepared from wet purified clay. Some of the samples were then dried at room temperature, while others (CHa$_{(EG)}$ and W$_{(EG)}$) were immersed in glycol for 6 h and still others (CHa$_{(550°C)}$ and W$_{(550°C)}$) heated for 3 h at 550°C.

CEC. The CEC was determined using the methylene blue absorption technique (Taylor, 1985).

Specific surface area. The specific surface area (S_t) was measured using the ethylene glycol monoethyl ether method (Carter *et al.*, 1965).

TEM. The TEM observations were carried out by means of a Philips ultratwin CM 20 microscope. The sample preparation for TEM analysis followed the method of Tessier (1984) where porewater is first replaced by methanol, then propylene oxide and finally spur resin. The samples were then placed in an oven at 65°C for 24 h to polymerize the resin. This was done to prevent changes from occurring in the fabric of the samples due to dehydration while they were being observed in the microscope. After the resin had hardened, thin-sections ~40 nm thick were cut with a diamond knife using a Richert-Jung ultracut E microtome.

Rheological measurement techniques

Flow rheology measurements were carried out using a Haake RS 100 rheometer under controlled shear rate (CR) conditions. A cone plate geometry was chosen with a 35 mm cone diameter, an angle of 1°59′ and a 93 μm gap between the cone and the plate. In order to prevent water evaporation during the experiments, a cover was used to isolate the specimen (Magnin and Piau, 1990; Pignon *et al.*, 1996). Constant temperature was maintained at $T = 23°C$ with a controlled thermostatic bath. During the tests, the shear rate $\dot{\gamma}$ was increased step by step, and on each step the corresponding shear stress τ

was measured at equilibrium (*i.e.* after sufficient time to allow the shear stress to stabilize). The shear rate was changed by 30 s^{-1} every 180 s, corresponding to an average value of 0.17 s^{-2}.

Preparation of the suspensions

For all the rheological and pH measurements, the suspensions were prepared at a clay concentration of 10%. Previous shear tests showed that for CHap, this concentration corresponded to the transition from liquid to gel. Though the liquid gel transition occurs at a lower clay concentration in the case of Wp, the same concentration was used for all four clay suspensions (CHap, CHab, Wb and Wp) in order to facilitate the comparisons. Depending on pH and NaCl concentration, the aqueous solution was a mixture of distilled water or NaCl (0.1 M) solution and HCl (0.1 M) or NaOH (0.1 M). The HCl, NaCl and NaOH were purchased from PROLABO and were 99%, 99% and 98% pure, respectively.

As the mode of preparation has a great influence on the final state of the suspension and thus on its rheological behavior, all the samples were carefully prepared using the following procedure: the clay powder was mixed with water using an over-head mixer (Reax 2 HEIDOLPH shaking mixer ensuring a rotation of 360°) for 12 to 15 h. The samples were then allowed to rest undisturbed for 5 days before the rheological and pH measurements were conducted. As the pH changes with time, the pH values were measured in the suspensions themselves with the usual glass electrode immediately before the rheological measurements, *i.e.* after a long equilibrium time between the solution and the clay. Then the clay suspension was very carefully deposited on the measurement device by means of a spoon. Previous tests showed the reproducibility of results for strain rates >400 s^{-1} (Laribi *et al.*, 2005). To account for the fact that the measurements are sometimes perturbed at low strain rates, the analysis of the data was carried out only for strain rates >400 s^{-1}.
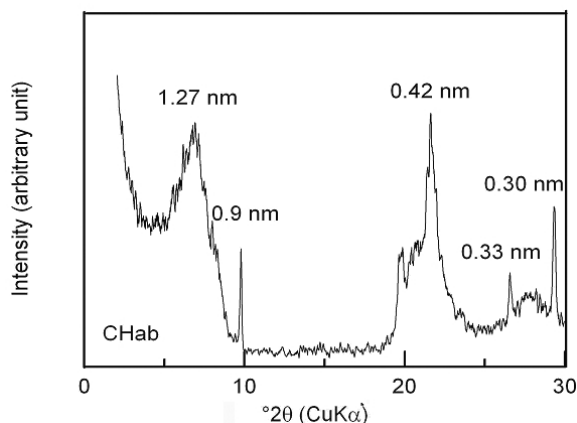

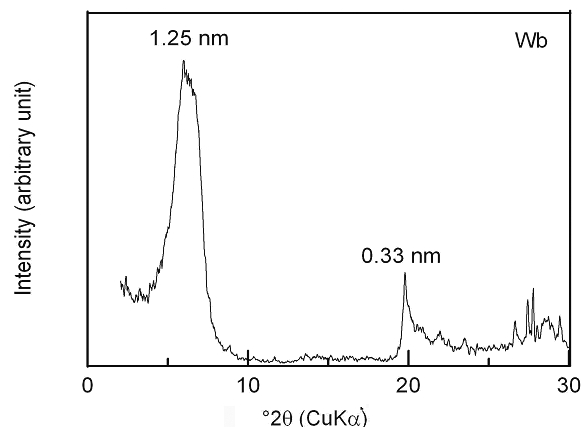Figure 1. XRD patterns for CHab.

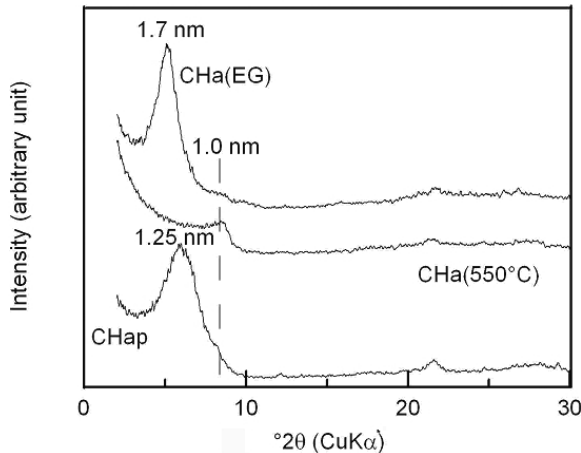Figure 2. XRD patterns for Wb.

Figure 3. XRD patterns for CHap.

RESULTS AND DISCUSSIONS

Physicochemical clay characterization

The two clays used in this study have been characterized in a previous study (Laribi, 2003). A brief summary of their properties is given below.

The XRD patterns shown in Figures 1 and 2 correspond to CHab and Wb raw clays, respectively. The reflections observed at 0.9 nm on the XRD pattern of CHab (Figure 1) can be attributed to the presence of a zeolite as an impurity. The peaks detected at 0.33 nm and 0.3 nm in Figures 1 and 2 indicate the presence of quartz and calcite.

The XRD patterns of CHap and Wp are represented in Figures 3 and 4, respectively. They show the presence of smectite in both clays (reflections at $d = 1.25$ nm for CHap and at 1.24 nm for Wp) and of illite in CHap (at $d = 1.0$ nm). After heating at 550ºC, these reflections move to 1.0 nm while the basal spacing (d_{001}) is expanded to 1.7 nm in ethylene glycol. The XRD results indicate that CHap is composed of smectite and illite mixed layers, whereas Wp is a smectite clay. Both clays contain quartz and calcite as impurities. A quantitative
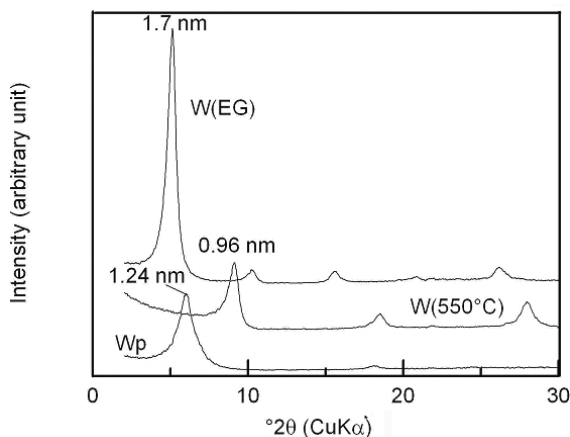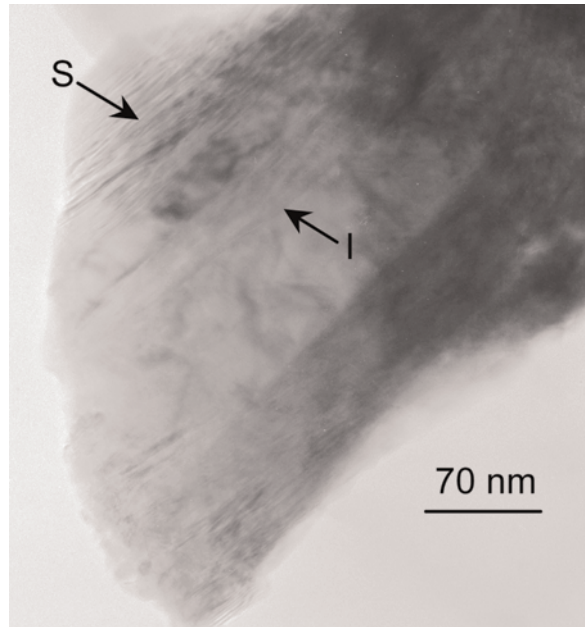

Figure 4. XRD patterns for Wp.

Figure 5. HRTEM image of CHap clay (S: smectite, $d = 1.3$ nm; I: illite, $d = 1.0$ nm).

analysis of the XRD results based on the diffracted intensity leads to approximate percentages of smectite and illite of 88% and 12%, respectively, in CHap.

The same conclusion can be drawn from TEM images of CHap and Wp. Figure 5 shows the presence of the two types of clay in CHap: smectite with 1.3 nm spacing and illite with 1.0 nm spacing. Local destructuration of the material can also be observed in this image. Figure 6 shows a 1.2 nm spacing for Wp which is characteristic of smectites. The CEC and S_t results are reported in Table 1.

Table 2 shows the chemical compositions of the two clays. According to Bailey (1980), the ideal formula of illite is: $\{K_{1.5}[Si_7Al][Al_{3.5}Mg_{0.5}]O_{22}\}$. The structural formula of CHap was derived from the chemical analysis, using the method of Mauguin (1928):
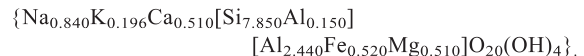
$$\{Na_{0.840}K_{0.196}Ca_{0.510}[Si_{7.850}Al_{0.150}]$$
$$[Al_{2.440}Fe_{0.520}Mg_{0.510}]O_{20}(OH)_4\}.$$

Table 1. Chemical analysis results.

	CHap (%)	Wp (%)	CHab (%)	Wb (%)
SiO$_2$	57	56	56	49
Al$_2$O$_3$	16	18	11	17
Fe$_2$O$_3$	5.0	4.1	4.4	4.5
MgO	2.6	1.5	3.3	3.7
TiO$_2$	0.51	0.58	0.59	0.030
Na$_2$O	3.2	3.2	2.7	2.7
CaO	3.6	1.8	5.7	3.1
K$_2$O	1.1	0.24	1.3	0.84
Total	89	86	84	81
Loss on ignition	11	11	15	19

Figure 6. HRTEM image of Wp clay.

Figure 7. Flow curves of CHab clay suspensions in water at different pH values.
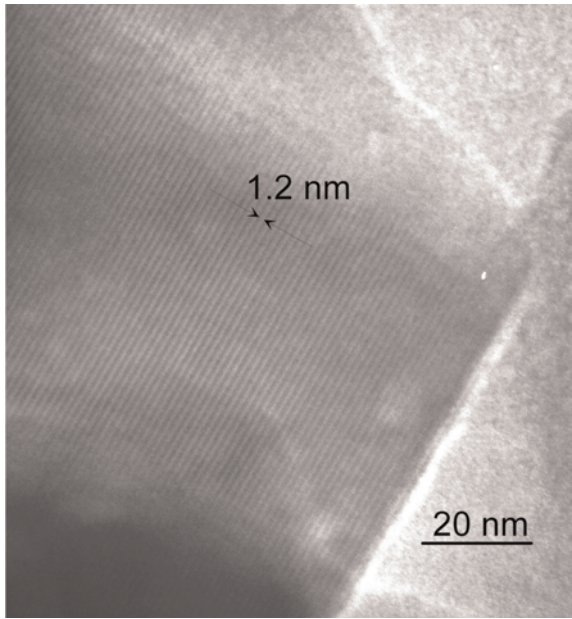
Based on the number of K atoms per clay mesh, the illite percentage in CHap was calculated as: 0.1968/1.5 ≈ 13%.

In the case of Wp, neither XRD patterns nor TEM images showed the presence of illite. Therefore, the presence of K can be attributed only to the exchangeable cations of the smectite fraction and not to the presence of illite in that clay.

Table 3 summarizes the physicochemical properties of the two clays in both raw and purified states. It shows that CHa is composed of mixed-layer illite-smectite. The illite fraction was estimated at 13%. The major impurities of the CHa clay are zeolite, calcite and quartz. The W clay is composed of smectite layers, with quartz and calcite-like impurities.

Effect of pH on aqueous clay suspensions

The flow curves of the 10% clay suspensions are shown in Figures 7−10, respectively, for CHab, CHap, Wb and Wp. Most of the suspensions feature a Bingham-type behavior. There is no clear classification of the curves with the pH. The two parameters of Bingham's model, the yield stress, τ_c, and the plastic viscosity, α, corresponding to the intersect of Bingham's line with the vertical axis and its slope, respectively, are plotted in

Figures 11 and 12 as a function of pH. The maximum yield stress and plastic viscosity increase from the Tunisian clay (CHa) to the Wyoming montmorillonite (W), and from the raw clays (subscript b) to the purified ones (subscript p). Except for the CHab curves, for which the values of the yield stress and plastic viscosity are very low and without any definite trend, all the other curves present a maximum for 'intermediate' pH values of 6.0, 8.5 and 7.2−9.2 for CHap, Wb and Wp, respectively. The maximum is very sharp in the case of the purified clays but, in the case of Wb, the number of experimental points is very limited, which could screen the real maximum. Generally, these results are similar to those obtained by Sohm and Tadros (1989).

The existence of the maxima may be explained by an E−E association between the positive and negative edges, due to high repulsive forces between the basal surfaces, resulting in the formation of cross-linked ribbons (M'Ewan and Pratt, 1957; Luckham and Rossi,
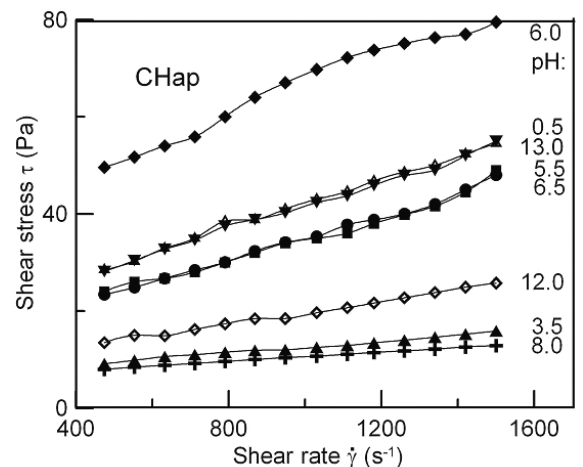
Table 2. CEC and SSA results.

	CHab	Wb	CHap	Wp
CEC (meq/100 g)	61.5	30.5	70	105
S_t (m^2/g)	406	523	590	673

Figure 8. Flow curves of CHap clay suspensions in water at different pH values.

Table 3. Physicochemical results.

	CHab	Wb	CHap	Wp
Mineral content derived from XRD	60% smectite 10% illite 10% zeolite 5% quartz 15% calcite	85% smectite 10% quartz 5% calcite	88% smectite 12% illite	Smectite
Chemical analysis			87% smectite 13% illite	100% smectite
TEM			Smectite (1.3 nm) Illite (1.0 nm)	Smectite (1.2 nm)
CEC (meq/100 g)	61.5	30.5	70	105
S_t (m^2/g)	406	523	590	673

1999). This association mode leads to a rigid network and gel. In fact, the area of the edges is small compared to the area of the faces, so that the electrostatic attraction between the edges and the faces is small compared to the repulsion between the faces of two close particles. For pH values below the maximum, where the pH becomes more and more acidic, the number of negative charges decreases, which leads to a progressive breakdown of the network. In this range of pH values, Tessier and Pedro (1982) and Lubetkin *et al.* (1984) showed the absence of E−F association in Na-montmorillonites and, therefore, the impossibility of a cardhouse structure under these conditions. Moreover, when the pH becomes very acidic, protons may attack the structure of the clay, which could result in the minima observed on some curves. For pH values larger than those of the maximum, the number of positive charges decreases and may cause the collapse of the structure (Benna *et al.*, 1999; Abend and Lagaly, 2000). The difference between the maxima of the raw and purified clays (CHab *vs.* CHap and Wb *vs.* Wp, respectively) can be explained by the fact that purification results in an increase in the concentration of

interlayer Na$^+$ ions and an increase in the swelling potential of the material causing it to becomes less deformable. Finally, the difference between the maxima of CHa and W clays is clearly the consequence of their mineralogy and particularly of the presence of illite in CHa. In fact, smectite particles have a large lateral extension, compared to their thickness, and a great flexibility. When suspended in water, smectite forms a 3-dimensional network, with a highly connected cellular fabric similar to that of a foam. One of the main differences between illites and smectites is the fact that the interlayer cations in illite are not hydratable, and non-exchangeable K$^+$ ions are located in the spaces between the tetrahedral sheets. The sheets are strongly bonded by the K$^+$ ions and form rigid platelets, like kaolinites, that orient parallel to each other. Their lateral extension is also much smaller than that of smectites (Coussot and van Damme, 1997; Blanc and van Damme, 1995; van Damme, 2002). As a consequence, when submitted to a shear stress, illites are much easier to deform than smectites, and they exhibit smaller shear strengths.
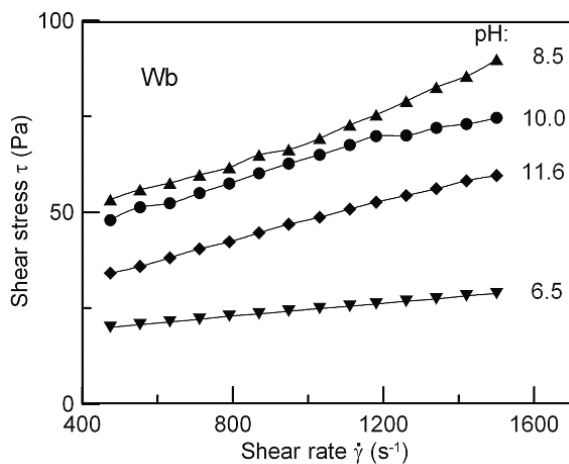
Figure 9. Flow curves of Wb clay suspensions in water at different pH values.
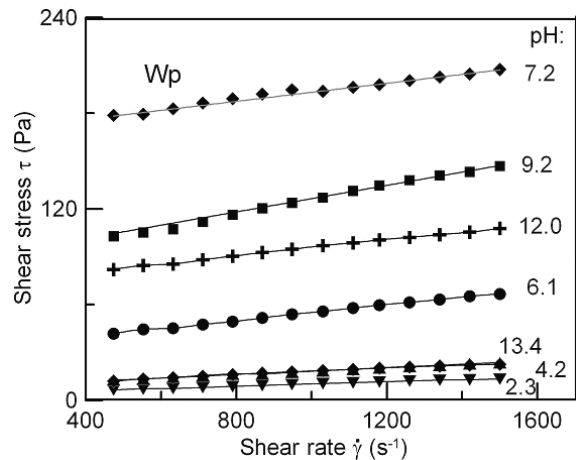
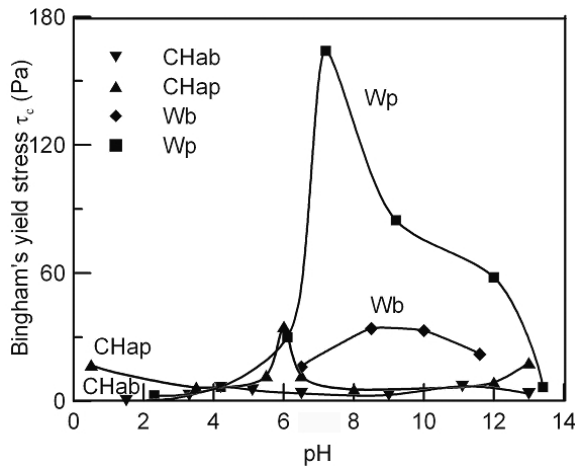Figure 10. Flow curves of Wp clay suspensions in water at different pH values.

Figure 11. Changes in Bingham's yield stress with pH for the four clays.

Figure 13. Flow curves of CHap clay suspensions in NaCl solutions at different pH values.

Effect of pH on clay suspensions in NaCl solutions

The flow curves of CHap and Wp suspensions in NaCl solutions are shown in Figures 13 and 14 and the changes in Bingham's yield stress and plastic viscosity, in Figures 15 and 16. In Figure 15, the presence of NaCl has very little affect on the pH values corresponding to the maxima of the yield stresses of the two clays, nor on the values of the maxima themselves. The shapes of the curves are very similar in both cases. The difference is more obvious when considering the plastic viscosity of the two clays and particularly that of Wp (Figure 16). Whereas the pH values for which the maxima occur are more or less the same, the plastic viscosities are higher for the suspensions in brine than for those in water. The large difference between the maximum plastic viscosity of Wp in NaCl solution (at pH 8.5) and in water may be due in the second case to the lack of an experimental point between 7.2 and 9.2, as these two pH values are very similar in the two suspensions. The effect of the
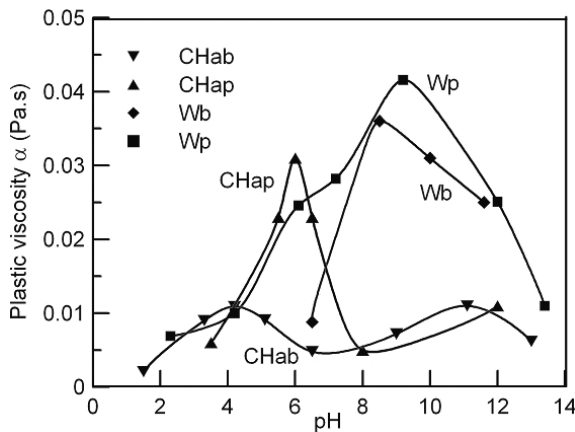
increase in the ionic strength of the solution should be to reduce the thickness of the diffuse double layers and increase the number of layers in clay particles, resulting in stiffer particle walls and larger elastic recall forces (van Damme, 2002), and to reduce the repulsive osmotic forces between the particles. However, the presence of NaCl at this concentration does not appear to modify the behavior of the suspensions noticeably, either qualitatively or quantitatively.

CONCLUSIONS

The study of the effect of pH on the rheological behavior of a pure smectite and of an interstratified clay, both in their raw and purified states, leads to the following conclusions: (1) there is no clear classification of the flow curves with pH; (2) qualitatively, the two purified clays exhibit similar rheological behaviors in that they present a maximum yield stress for pH values

Figure 12. Changes in Bingham's plastic viscosity with pH for the four clays.
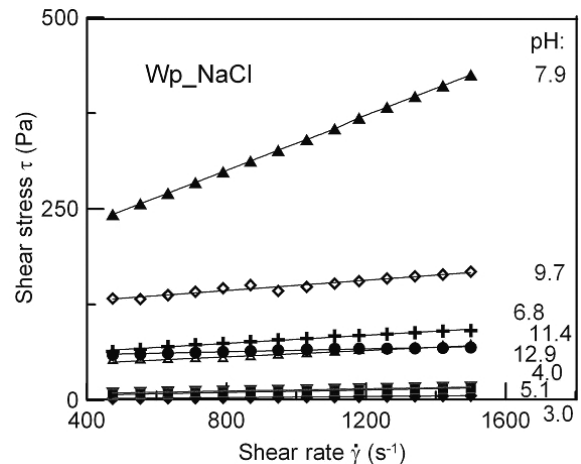

Figure 14. Flow curves of Wp clay suspensions in NaCl solutions at different pH values.
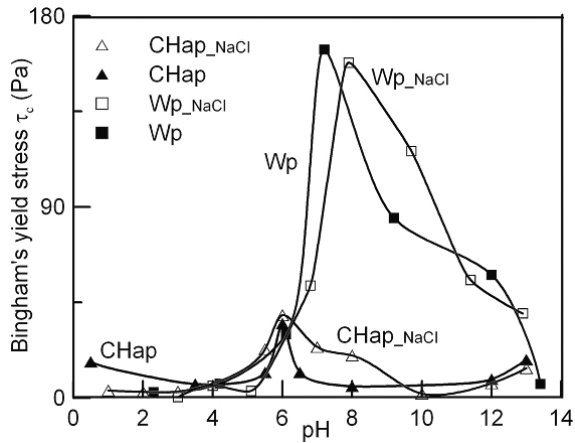
Figure 15. Comparison between the Bingham's yield stresses of the suspensions of the two purified clays in water and NaCl solutions at different pH values.

of 6 and 7.2 for CHap and Wp, respectively; (3) the observed differences are quantitative: at the same pH, the yield stress and the plastic viscosity of the pure smectite are distinctly higher than those of the interstratified one, which can be related to their mineralogical structure. The presence of 13% illite in the Tunisian clay leads to an important reduction in the affinity of the clay for water and results in local destruction of the material. (4) A noticeable increase in the yield stress and plastic viscosity between raw and purified clays is also observed. This difference can be attributed to the increase in the interlayer Na ions due to purification and the corresponding increase in the affinity of the material for water. (5) In the presence of dilute salt solutions, such as 0.1 M NaCl, the two clays behave in the same way as in water with little difference between their maximum yield stresses or the pH values at which the maxima occur.
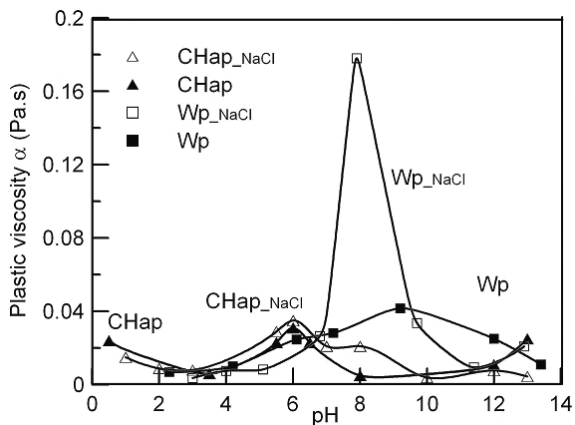

Figure 16. Comparison between the Bingham's plastic viscosities of the suspensions of the two purified clays in water and NaCl solutions at different pH values.

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