WETTABILITY OF MONTMORILLONITE CLAYS IN HUMIC ACID SOLUTIONS

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Abstract—The effect of humic acid (HA) adsorption on the hydrophilicity of two different montmorillonite samples (Na-montmorillonite, NaMt, and a Na-fluorinated Na-montmorillonite, FNaMt, or 'Rassoul') was investigated. The changes in the wettability of clays were discussed in terms of the non-electrostatic free energy of interaction between the clay particles immersed in aqueous humic acid solutions (ΔG_{121}), using the van Oss-Chaudhury-Good (vOCG) model. The surface free energy components (both non-polar or Lifshitz-van der Waals, and polar or acid-base) of clays were obtained from contact angle measurements, after adsorption of humic acid, at acid or basic pH, in 10^{-2} M NaCl solutions. It was found that: (1) at acid pH, a progressive decrease in the hydrophilic character of both clays was observed when the humic acid concentration was increased; (2) at basic pH, the hydrophilic character of both samples studied increased with HA concentration; (3) the effect of humic acid adsorption on the wettability of model edge surfaces of the laminar montmorillonite particles was estimated from a parallel study on silica and alumina surfaces, and only a slight decrease in the hydrophilicity was observed, whatever the pH of the liquid media. The ζ potentials of both clays in the absence and presence of humic acid were determined and the linkage between ζ potential and the electron-donor character of the materials is discussed.

Key Words—Humic Acid, 'Rassoul', Sodium-montmorillonite, Surface Free Energy, Wettability.

INTRODUCTION

Clay minerals are known to have very variable wetting behavior. Thus, the enthalpy of wetting (ΔH_w) of clays can reach the highest values among natural inorganic materials (ranging from ~ -55 mJ/m^2 for smectites up to ~ -500 mJ/m^2 for kaolinites) (Lyklema, 1995). Moreover, in the particular case of smectites, the wettability can change from moderately hydrophobic to strongly hydrophilic (Giese *et al.*, 1996). Assessing the degree of hydrophilicity of clays is an important task as it significantly affects their stability when dispersed in aqueous media. Hydrophilic smectites will tend to remain stable in suspension because the affinity of the particles for the solvent is higher than the mutual affinity between the particles. On the contrary, stable sols of hydrophobic smectites do not form spontaneously and special tricks are required to prepare and stabilize them. Furthermore their aggregation will be more likely. This is true because, as in many other colloidal systems, the aggregation between particles is not ruled by van der Waals and electrostatic interactions alone. We believe that a full account and prediction of the stability of clay particles would be incomplete if hydrophobic/hydrophilic interactions were not considered. Generally speaking, according to the so-called extended DLVO theory of colloidal stability (Israelachvili, 1992; van Oss, 1994), hydrophilic (hydro-

phobic) surfaces can display a strong, short-ranged repulsion (attraction) that may dominate the role of the above-mentioned classical interactions. As a consequence, the quantitative determination of the wetting behavior of any particular smectite mineral appears to be an essential step in its characterization, since it may be determinant of its colloidal stability.

This subject is specially relevant in environmental and soil sciences. It is well known (Tarchitzky *et al.*, 2000) that the structural units of soil aggregates are strongly dependent on the formation of primary soil particles assembled by colloidal forces between particles of, mainly, clays and metal oxides. The intensity of these colloidal interactions is modified by the adsorption of natural organic matter (NOM), especially humic substances, the most abundant organic substances in nature, and metallic cations on the particles. As a consequence, the stability, permeability, flow properties and pollutant transport capacity of clay colloidal suspensions in soils and natural waters seem to be controlled by adsorption of NOM (Sondi and Pravdić, 2002; Tarchitzky *et al.*, 2000; Tiller and O'Melia, 1993). Such adsorption usually implies a stabilizing effect attributed to an increase in electrostatic or steric repulsion between the particles (Kretzschmar *et al.*, 1997; Sondi and Pravdić, 1998; Tiller and O'Melia, 1993; Tombácz *et al.*, 1999). Nevertheless, less attention has been paid to the effect of NOM adsorption on the wettability of clay minerals, neglecting the possible modification of the particle-particle interactions of interfacial origin, which can be very intense in the case of clay minerals.

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To our knowledge, in the last decade only four papers (Bantignies *et al.*, 1997; Giese *et al.*, 1996; Grattoni *et al.*, 1995; Jouany, 1991) have dealt with the quantification of the effect of organic compounds adsorption on the hydrophilic character, and consequently on the wettability, of clay minerals. In particular, Jouany (1991) investigated the effect of synthetic humic acid-like polymers on the wettability of Ca-montmorillonite, which was quantified through the estimation of the dispersive and polar components (Fowkes, 1964; Owens and Wendt, 1969) of the clay surface free energy.

In a recent work (Ramos-Tejada *et al.*, 2001) we studied the effect of humic acid (HA) adsorption on the electrokinetic and rheological properties of aqueous Na-montmorillonite (NaMt) suspensions. We came to the conclusion that quantities such as apparent viscosity, rigidity modulus and compliance modulus of these suspensions in the presence of HA seem to be controlled essentially by the changes provoked in the electrostatic interactions between the particle surfaces (faces and edges) of the laminar NaMt particles. In the present work, we focus on the effect that humic acid adsorption provokes on the interfacial interactions (van der Waals attraction, and hydrophilic repulsion) between particles of two different kinds of montmorillonite clays: Na-montmorillonite (NaMt) and a fluorinated Na-montmorillonite (FNaMt).

The estimate of the non-electrostatic interactions was made by determination of the surface free energy of the solids obtained from contact-angle measurements using the van Oss-Chaudhury-Good (vOCG) model (van Oss, 1994; Giese *et al.*, 1996).

EXPERIMENTAL

Materials

Samples of NaMt and FNaMt were investigated. The NaMt was obtained from a natural bentonite from Almeria (Spain), and the FNaMt from a natural bentonite named 'Rassoul', from the High Atlas Mountains in Morocco. The chemical composition of the original mineral samples was determined by X-ray fluorescence (XRF) (Table 1). The crystal structure of both bentonites was investigated by X-ray difraction (XRD) using the powder method in a Philips PW1710 diffractometer (Netherlands). The <2 µm fraction was used for these determinations. The chemical analysis indicates that the original Spanish bentonite was a montmorillonite with high Na^+ content as exchangeable cation. 'Rassoul' consists of a montmorillonite with a high Ca^{2+} content.

The surface chemical composition of the original 'Rassoul' was determined by XPS (X-ray photoelectron spectroscopy) (Perkin-Elmer, USA), and a considerable percentage (3.53%) of fluorine atoms was found, so that F^- anions partially substitute for OH^- in the montmorillonite structure (van Olphen, 1977). It is the presence of different exchangeable cations (Ca^{2+}, Na^+, K^+), and its great capacity to adsorb and absorb organic matter, that explains the traditional use of 'Rassoul' for cosmetic purposes (washing and cleaning of hair and skin) in the region of north Morocco (Cabrerizo *et al.*, 1989).

The bentonite and 'Rassoul' samples were homo-ionized using the following procedure: (1) the <2 µm size-fraction was separated by sedimentation from a water suspension of ground mineral; (2) 30 g of the particles thus obtained were stirred for 1 h in 250 mL of 1 M NaCl solution; (3) the samples were centrifuged and the supernatant solution discarded (steps 2 and 3 were repeated four times); (4) the resulting solids were centrifuged and redispersed in Milli-Q water until the conductivity of the supernatant solution was <10 µS/cm; (5) the clay particles were finally dried at 100ºC and kept in polyethylene flasks. The specific surface areas of dry NaMt and FNaMt were measured by means of N_2 adsorption using the BET multipoint method in a Quantasorb Jr. (Quantachrome, USA) apparatus. The values obtained were 54.1 m^2/g (NaMt) and 165.9 m^2/g (FNaMt).

Al_2O_3 and SiO_2 powders (Riedel de Haën, Germany; purity >98%) were used for indirect estimation of the effect of humic acid adsorption on the (model) edges of clay particles, because the surface groups (silanol and aluminol) present in the edge surfaces are similar to those in alumina and silica sols.

Solutions of humic acid were prepared by dissolving its Na salt (Sigma-Aldrich, Germany), without further purification, in a 10^{-2} M NaCl aqueous solution. Ochs *et al.* (1994) reported an elementary analysis and ash content of this chemical, and found that its molecular weight distribution shows two peaks at 1000 and 5000 g/mol. Milli-Q water was used in the preparation of the suspensions.

Methods

ζ potential. The ζ potential values were calculated using the Smoluchowski formula (Arroyo and Delgado, 2002), from electrophoretic mobility data obtained with a Malvern Zetasizer 2000 (Malvern, England) at 25.0±0.5ºC, using suspensions containing 0.5 g/L solids.

Table 1. Bulk chemical composition (wt.%) of original bentonite (taken from Linares, 1993) and 'Rassoul' clay particles obtained by XRF analysis.

Compound	SiO₂	Al₂O₃	Fe₂O₃	MnO₂	MgO	CaO	Na₂O	K₂O	TiO₂	P₂O₅	H₂O	Others
'Rassoul'	56.6	1.68	0.78	0.01	25.8	2.14	0.27	0.50	0.18	0.02	–	11.0
Bentonite	58.5	20.2	2.70	–	6.70	1.08	1.35	0.61	–	–	9.00	5.80

Measurements were performed 24 h after the preparation of the suspensions, and the pH was readjusted immediately before measuring the mobility.

Surface free energy determination. Surface free energy of clays was determined from measurements of advancing contact angles of three probe liquids (diiodomethane, water and formamide) of known surface tension components, on dry clay layers. The clay solid surface was prepared by drying a concentrated (4% w/v) NaMt (or FNaMt) suspension uniformly spread on a dry, clean microscope glass slide. The powder was previously dispersed in a 10^{-2} M NaCl solution with the desired pH and sodium humate concentration (between 0 and 300 mg/L) for 24 h. The solids were separated by centrifugation and redispersed in water. It was found that spreading a volume of 2.5 mL of these aqueous suspensions on the slides was enough to ensure a thickness of the clay-humic complex providing contact angles significantly different to those corresponding to the bare glass support. After placing the suspensions, the clay-covered slides were first dried at room temperature and finally at 80ºC on a hot plate. A similar procedure was followed with silica and alumina powders. The contact angles formed by the three probe liquids were measured with a Ramé-Hart 100-07-00 (USA) telegoniometer. The images of drops placed on the clay layers were captured using a video camera adapted to the goniometer, immediately after their deposition with a Gilmont (USA) micrometer syringe. Only stable drops (in the case of water, before swelling of clay) were used to compute the surface free energy components of the solids.

According to vOCG theory (van Oss, 1994), the surface free energy, γ_i, of a material i can be expressed as the sum of two components, non-polar or Lifshitz-van der Waals (LW) and polar or acid-base (AB), as:

$$\gamma_i = \gamma_i^{\mathrm{LW}} + \gamma_i \mathrm{AB} \tag{1}$$

the latter term (γ_i^{AB}) being the result of the electron-donor (γ_i^-) and electron-acceptor (γ_i^+) characteristics of the material:

$$\gamma_i^{\mathrm{AB}} = 2\sqrt{\gamma_i^+ \gamma_i^-} \tag{2}$$

Because all compounds in a condensed state attract water molecules to a considerable degree, and consequently the free energy of solid-water adhesion is always negative, in the vOCG approach it is proposed that the best quantitative expression of the hydrophobicity or hydrophilicity of a material is related to the non-electrostatic interaction between the solid particles (phase 1) immersed in aqueous solution (phase 2) given by:

$$\begin{aligned}\Delta G_{121}^{\mathrm{TOT}} &= \Delta G_{121}^{\mathrm{LW}} + \Delta G_{121}^{\mathrm{AB}} \\ \Delta G_{121}^{\mathrm{LW}} &= -2(\gamma_1^{\mathrm{LW}} - \gamma_2^{\mathrm{LW}})^2 \\ \Delta G_{121}^{\mathrm{AB}} &= -4\left(\sqrt{\gamma_1^-\gamma_1^+} + \sqrt{\gamma_2^-\gamma_2^+} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}\right)\end{aligned} \tag{3}$$

A material should be considered hydrophilic when $\Delta G_{121}^{\mathrm{TOT}} > 0$ (hydrophilic repulsion), and hydrophobic if $\Delta G_{121}^{\mathrm{TOT}} < 0$ (hydrophobic attraction).

The surface free energy components of the solid material (1) can be obtained from the contact angles (θ) formed by the three above-mentioned liquids on the solid surface, by solving the system of Young's equations of the type (van Oss, 1994):
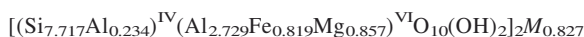
$$2\sqrt{\gamma_1^{\mathrm{LW}}\gamma_2^{\mathrm{LW}}} + 2\sqrt{\gamma_1^+\gamma_2^-} + 2\sqrt{\gamma_1^-\gamma_2^+} = \gamma_2(1+\cos\theta) \tag{4}$$

where the surface tension components ($\gamma_2^{\mathrm{LW},+,-}$) of the three liquids (water, formamide and diiodomethane) are known (van Oss, 1994).

RESULTS AND DISCUSSION

Mineralogical analysis

The mineralogical composition of both clays was obtained from XRD patterns and in Figure 1 we show the XRD patterns for the <2 μm clay samples. It is apparent that the bentonite (NaMt) sample is an almost pure montmorillonite, although previous work on the same sample (Caballero *et al.*, 1983; Linares, 1993) suggested the presence of cristobalite (1%), and quartz and calcite (traces). Thus it is possible to calculate the structural formula of this material, given that it is practically monomineralic. The corresponding structural formula is (Caballero *et al.*, 1983; Linares, 1993):

$$[(\mathrm{Si}_{7.717}\mathrm{Al}_{0.234})^{\mathrm{IV}}(\mathrm{Al}_{2.729}\mathrm{Fe}_{0.819}\mathrm{Mg}_{0.857})^{\mathrm{VI}}\mathrm{O}_{10}(\mathrm{OH})_2]_2 M_{0.827}$$

However, for the 'Rassoul' sample (Figure 1), significant amounts of different minerals can be detected. The estimated mineralogical composition obtained from Figure 1 is: montmorillonite (83%); quartz (3%); dolomite (8%); and calcite (6%).

ζ potential

The effect of HA adsorption on the surface electrical properties of the clay particles was investigated by measuring the electrophoretic mobility of clay suspensions both in presence and absence of humic acid. Figure 2 shows the ζ potential of the particles as a function of pH, at constant ionic strength (10^{-2} M NaCl) without addition of HA. It can be observed that ζ is negative for the whole pH range investigated. Furthermore, changing pH between 3 and 10 only provokes a ζ potential variation around 10 mV. This is in agreement with previous findings by other authors (Heath and Tadros, 1983; Sondi *et al.*, 1997; Benna *et al.*, 1999; Durán *et al.*, 2000), who suggested that the measured ζ potential corresponds essentially to face surfaces of the laminar clay particles, as expected from the well-known fact that the relative amount of such surfaces is much larger than that of edges. Since the electric charge on the former is due to isomorphous substitution of the structural cations (van Olphen, 1977),
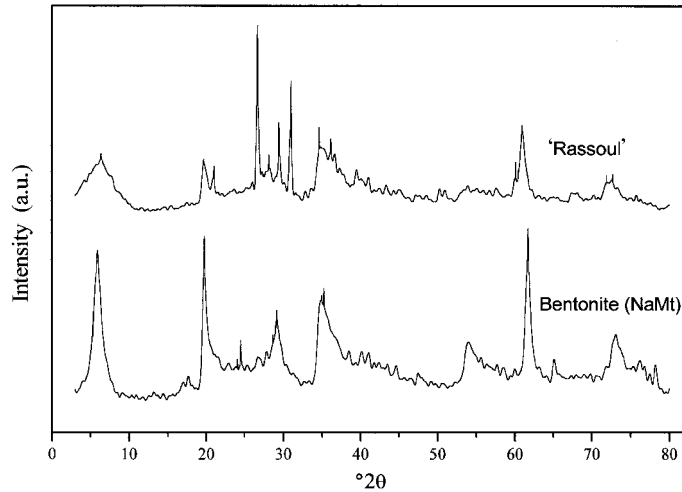
Figure 1. XRD pattern of the <2 μm fraction of the bentonite (NaMt) and 'Rassoul' clays. Debye-Scherrer method; CuKα radiation.

it is reasonable that ζ is little affected by the pH of the medium. It is also worth mentioning that the ζ potential of montmorillonite is systematically 5 mV larger in absolute value than that of 'Rassoul'.

The effect of HA adsorption on the ζ potential of both clays is plotted in Figure 3 for pH 3 and pH 9. The concentration range studied extends from 0.1 to 100 mg/L. This interval was chosen considering that the maximum concentration of humic substances in natural waters can be as high as 50 mg/L, as reported by Jones and Bryan (1998). The effect of HA addition on the ζ potential of NaMt is rather small, no more than 3 mV at either pH. The surface electrical properties of

'Rassoul' appears to be more sensitive to humic substances, since ζ can increase by up to −10 mV for this clay. In order to explain the different effects of HA adsorption at different pH values on the ζ potential of the two clays (Figure 3), the chemical composition of humic acid must be considered. As reported by Tipping (1993), humic substances typically contain $5-10$ meq g^{-1} ionizable groups, mainly phenolic and carboxylic ones (Jones
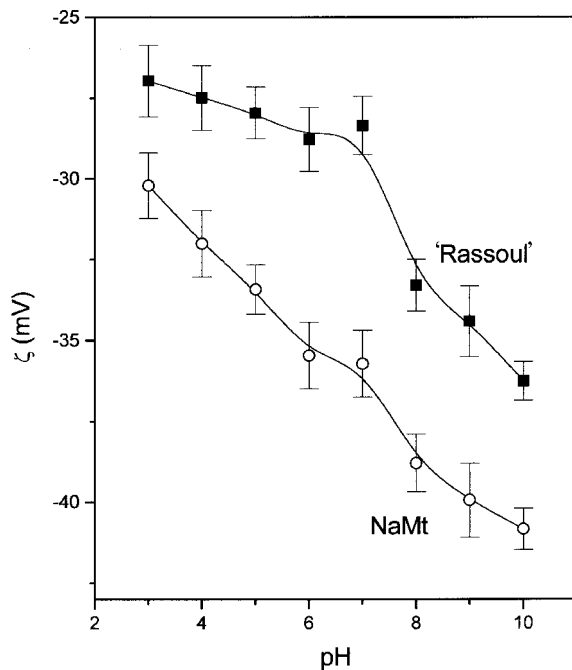

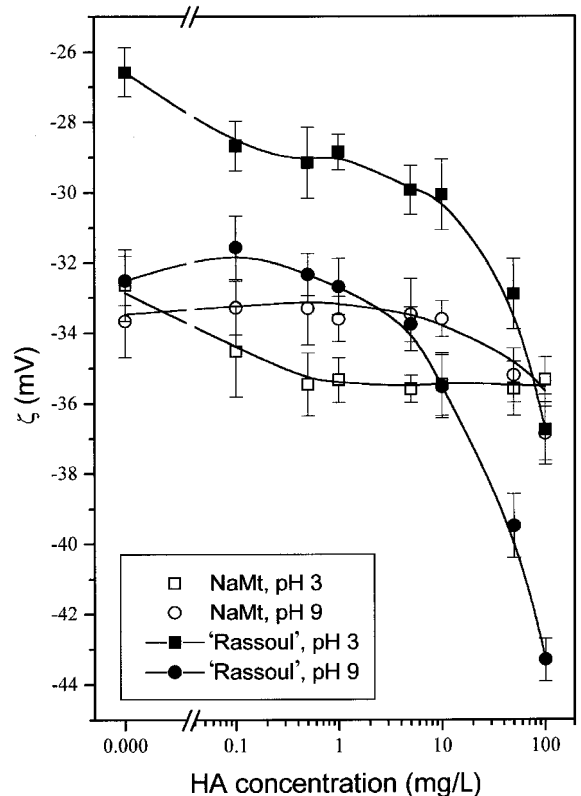Figure 2. ζ potential of NaMt and FNaMt ('Rassoul') as a function of pH. Ionic strength 10^{-2} M NaCl.

Figure 3. ζ potential of NaMt and FNaMt ('Rassoul') as a function of humic acid concentration in solution, at different pH values, and constant ionic strength, 10^{-2} M NaCl.

and Bryan, 1998; Liu and González, 1999), which confer metal binding properties on them. So, we can expect that at acid pH the carboxylic groups will largely be in non-ionic form (R-COOH), whereas at basic pH they will predominantly be as carboxylic R-COO$^-$ groups. On the other hand, as mentioned above, the excess charge on the faces of clay minerals (~99% of the total surface area of laminar smectite particles: Sondi and Pravdić, 1998, 2002; Sposito, 1984) is negative and produced by the isomorphous substitution of structural ions. Therefore, the adsorption of neutral or negative HA molecules on the negative faces of NaMt or 'Rassoul' cannot originate from electrostatic interactions only, but mainly through coordinative interactions, *i.e.* the formation of surface mono- or bidentate metal ion-HA complexes as proposed by Ochs *et al.* (1994). This assumption was corroborated in our previous work on the rheological behavior of HA-NaMt suspensions (Ramos-Tejada *et al.*, 2001, 2002).

Surface free energy and HA adsorption

Following the procedure mentioned in the experimental section, the contact angles of water, formamide and diiodomethane were measured on NaMt and 'Rassoul plates'. In Table 2 we summarize the results obtained for different pH values (3 and 9) and variable HA concentrations. The gradual increase in the contact angle of water at pH 3, when the clay has been precontacted with increasingly concentrated HA solutions, provides a first insight into the progressive hydrophobization of the materials at this pH. A similar trend was observed with 'Rassoul', but not with NaMt at pH 9. Similarly, the contact angles of the other two

liquids do not follow a definite trend of variation. This proves that the simple analysis of contact angle data can lead to erroneous conclusions. We will show below that it is just the exact calculation of ΔG_{121} (equation 3) which allows a rigorous estimate of the wettability of clays.

From the data in Table 2 the surface free energy components of NaMt and 'Rassoul' were calculated using equation 4. The results are shown in Figures 4 and 5, respectively. The electron-acceptor (γ^+) values are not presented because in all cases they were very close to zero. The two clays show the typical monopolar character ($\gamma^+ \approx 0$; $\gamma^- > 0$) of smectites, previously reported by Giese *et al.* (1996). On the other hand, the non-polar component (γ^{LW}) of NaMt was always close to 45 mJ/m^2, and no significant effect was observed after HA adsorption or pH changes. In the case of 'Rassoul' (Figure 5), only a slight increase (ranging between 42 and 49 mJ/m^2) of γ^{LW} was observed after HA adsorption, whatever the pH. However, this change should have little effect on the whole hydrophilic character which is dominated essentially by changes in the electron-donor character that has a strong effect on ΔG_{121}^{AB} (see equation 3).

In fact, the electron-donor parameter (γ^-) shows a significant dependence on HA adsorption (Figures 4, 5). At pH 3, a decrease was observed in both samples, and the opposite effect (an increase in γ^- with HA adsorption) occurs at pH 9. Another important fact is the lower electron-donor character of 'Rassoul' as compared to NaMt. Interestingly, this difference has its counterpart in the ζ potential of both clays (Figure 2):

Table 2. Contact angles (°) of water, formamide and diiodomethane on Na-montmorillonite and fluorinated Na-monmorillonite ('Rassoul') surfaces for the different pH and humic acid concentrations indicated.

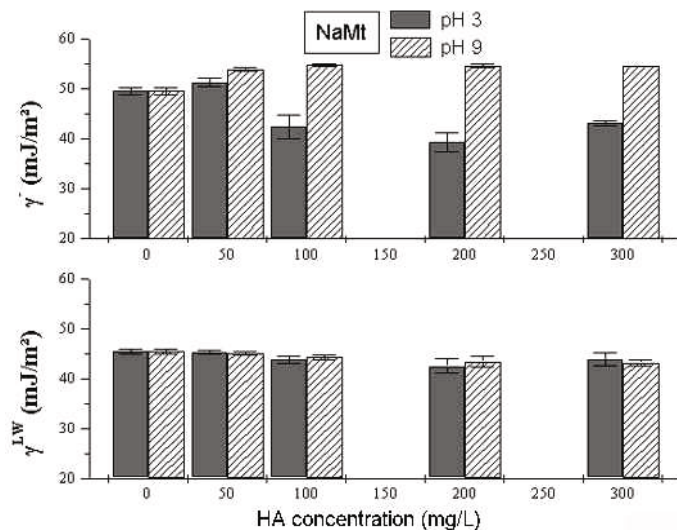| Material	pH	Humic acid concentration (mg/L)	θ (water)	θ (formamide)	θ (diiodomethane)
NaMt	3	0	17	6.5	30
		50	15	7	27.5
		100	28	14.5	31
		200	30	10	34
		300	25	7	31
	9	0	17	6.5	30
		50	9.5	6.1	28
		100	7.5	6	30
		200	6	4	32
		300	7.5	5	32
'Rassoul' (FNaMt)	3	0	33	7	34
		50	40	24	24
		100	45	33	19
		200	48	39	13
	9	0	33	7	34
		50	34	13	25
		100	35	24	16
		200	41	34	17

Figure 4. Surface free energy components (γ^-: electron-donor parameter; γ^{LW}: Lifshitz-van der Waals component) of Na-montmorillonite particles as a function of humic acid concentration of the aqueous medium, at 10^{-2} M NaCl ionic strength, and pH = 3 or 9. The error bars represent the standard deviation.

NaMt particles are clearly more negative than 'Rassoul' ones for the whole pH range. On the other hand, it has been proven repeatedly (Wu *et al.*, 1994a, 1994b; Durán *et al.*, 1995, 1999) that more negatively charged inorganic particles display a stronger electron-donor character when in the presence of solutions of simple cations.

In order to explain the opposite effects of HA adsorption at different pH values on the electron-donor parameter of the clay particles, the mechanisms described above for the adsorption of humic acid on them can be recalled. The adsorption of HA on clays at acid pH would provoke a decrease in the electron-donor character of the surface through the adsorption of non-ionic, and mainly hydrophobic, organic HA molecules. On the contrary, the adsorption at basic pH implies the coverage of the clay surface by anionic HA molecules

with the consequent increase in γ^-. We can thus state that the effect of HA adsorption on the surface thermodynamic properties of NaMt and 'Rassoul' cannot be established unequivocally, without taking the pH of the aqueous media into consideration, because of the different ionization degree of HA molecules at acid and basic pH. A similar conclusion was obtained by Tarchitzky *et al.* (2000) on the basis of stabilization studies of soils by humic substances. Nevertheless, the effect of pH was not mentioned by Jouany (1991) in her work on surface free energy of clay-HA systems.

In order to confirm this in a more quantitative way, an estimate of the non-electrostatic free energy of interaction between clay particles (ΔG_{121}^{TOT}; equation 3) was carried out. Figure 6 shows the calculated values of ΔG_{121}^{TOT} of NaMt and 'Rassoul' at different pH values (3 and 9) and variable HA concentration (the Figure also
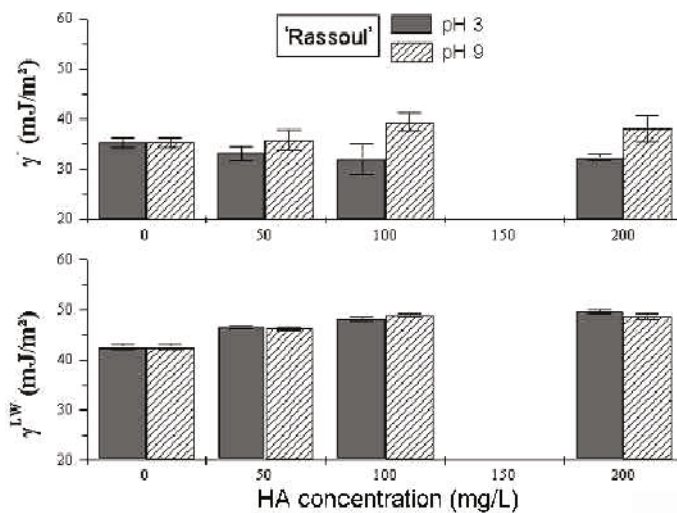

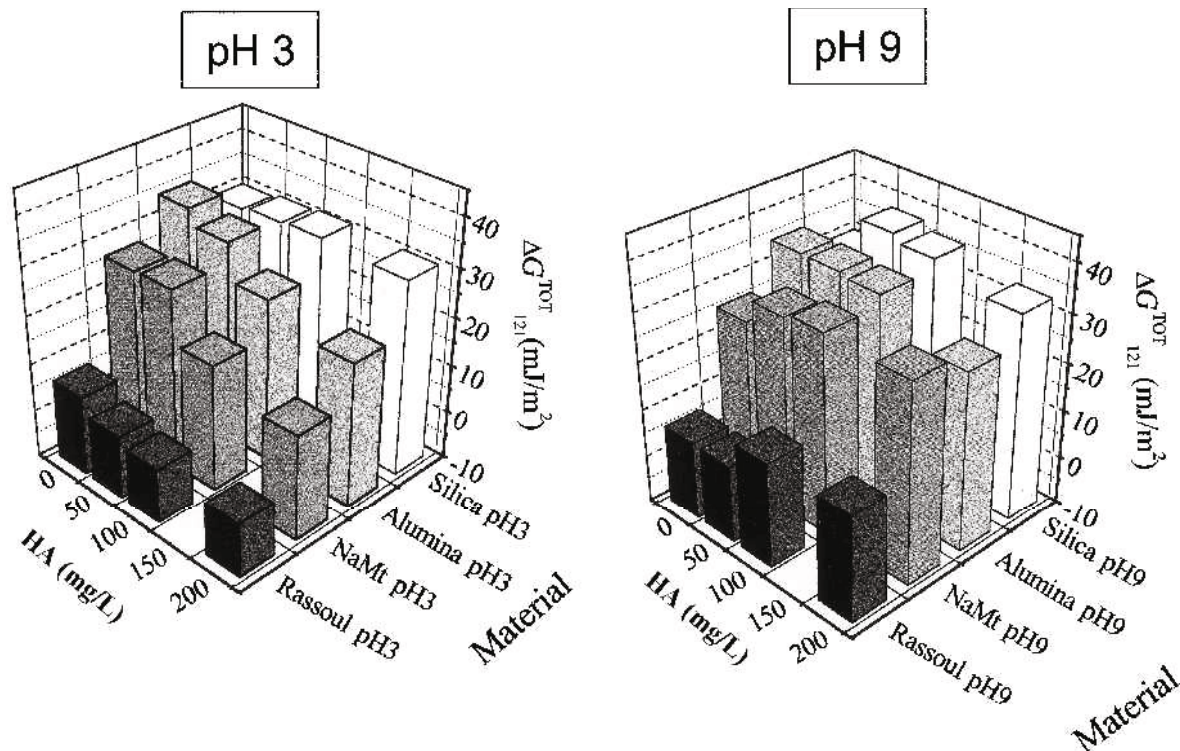Figure 5. Similar to Figure 4, but for 'Rassoul' clay.

Figure 6. Free energy of interaction (ΔG_{121}) between solid particles of the materials indicated (phase 1) immersed in aqueous media (phase 2) at the pH values indicated, as a function of humic acid concentration.

contains data for alumina and silica for reasons that will be made clear below). According to equation 3, ΔG_{121}^{TOT} is the sum of two terms, ΔG_{121}^{LW} and ΔG_{121}^{AB}, and they both contribute in our system in opposite directions: ΔG_{121}^{LW} is negative, ranging between 6 and 10 mJ/m^2, while ΔG_{121}^{AB} is positive and larger than ΔG_{121}^{LW}. So, the final balance is dominated by the acid-base contribution. As observed in Figure 6 (pH = 3), the increase in HA concentration implies a decrease in the hydrophilic character of both NaMt and 'Rassoul'. As a consequence of the lower values of γ^- ('Rassoul') with respect to γ^-(NaMt), the values of ΔG_{121}^{TOT}('Rassoul') are lower than those of ΔG_{121}^{TOT}(NaMt). In addition, at HA concentration >100 mg/L, the values of ΔG_{121}^{TOT}('Rassoul') are close to zero (~1 mJ/m^2), at the limit of hydrophobic behavior.

A completely different behavior was found at pH 9 (Figure 6). The addition of humic acid makes both clays more hydrophilic. The reason seems to be the different degree of ionization of HA molecules. At pH 3 the adsorbed molecules are mainly neutral, with the subsequent progressive screening of the hydrophilic character of the clays caused by adsorption of non-ionized organic (hydrophobic) molecules. On the contrary, the adsorption of ionized HA molecules at pH = 9 enhances the hydrophilicity of both samples. We can conclude that the adsorption of HA at basic pH improves the wettability of these montmorillonite clays, and the opposite effect is produced at acid pH.

The degree of correlation between the variations of ζ and γ^- is of interest. Such a correlation can be established for solutions of simple ions. We will consider the presence of complex molecules such as the polyelectrolyte HA. Figure 3 (ζ *vs.* HA concentration) and Figures 4 and 5 (γ^- *vs.* HA concentration) indicate the existence of that linkage in basic solutions, *i.e.* when the carboxylic groups of HA molecules will be mostly ionized. This is not true at acid pH: although ζ increases slightly upon addition of humic acid (Figure 3), γ^- displays the opposite behavior, *i.e.* a small but significant decrease in the electron-donor component of the surface free energy of the particles. The adsorption of non-ionized organic molecules (hence, essentially hydrophobic) dominates the modification of the thermodynamic quantities.

Role of faces and edges

An additional consideration arises if we keep in mind the heterogeneous nature of the montmorillonite particles. In previous paragraphs we have considered the overall effect of HA adsorption on clay particles, reflecting essentially the behavior of the face surfaces (the major part of total surface area). But in order to complete the analysis, we will try to separate the possible effect of HA adsorption on the edge surfaces. We note that, as demonstrated in many works (*e.g.* Luckam and Rossi, 1999), the colloidal stability of

Table 3. Contact angles (º) of water, formamide and diiodomethane on alumina and silica surfaces for the different pH and humic acid concentrations indicated.

Material	pH	Humic acid concentration (mg/L)	θ (water)	θ (formamide)	θ (diiodomethane)
Al_2O_3	3	0	9	12.5	15.5
		100	20	10	13
		200	23	10	16
		300	22	10.5	10
	9	0	9	12.5	15.5
		100	11	16	18
		200	21	16.5	19
		300	19	10.5	19
SiO_2	3	0	12	7	19.5
		50	12.5	10	20
		100	9	5	20
		200	14	11	20
	9	0	12	7	19.5
		50	6	15	18
		100	7	15	18.5
		200	5	5	18

bentonite suspensions is strongly determined by edge-to-face interactions. However, the wetting behavior of edges is not experimentally accessible. An estimate is possible, however, if we consider (Durán *et al.*, 2000; Luckam and Rossi, 1999; Ramos-Tejada *et al.*, 2001, 2002; Sondi and Pravdić, 1998, 2002) that the surface chemical behavior of edges is determined by the presence of silanol and aluminol groups, similar to those of alumina and silica in aqueous media. With this assumption in mind, we studied the wettability of alumina and silica in HA solutions in an entirely parallel way as previously described for clays. Table 3 and Figures 6 and 7 show the necessary data for contact angles, electron-donor component, and free energy of interaction, for both silica and alumina. Both materials

have electron-donor character ($\gamma^+ \approx 0$), with γ^{LW} values ($\approx 45-50$ mJ/m^2) similar to those reported by Chibowski (1993) and somewhat larger than those obtained by Giese *et al.* (1996) using the techniques of measuring contact angles on silica and alumina plates and thin-layer wicking, respectively. As observed in Figure 7, the parameter γ^- of both pure materials is between 50 and 60 mJ/m^2, again comparable with results obtained by other authors. Furthermore, little effects of either HA addition or pH changes on γ^- are observed.

A better picture of the hydrophilicity changes provoked by HA addition can be obtained from the total free energy of interaction summarized in Figure 6. A significant effect of HA adsorption can be observed only for Al_2O_3, whereas no clear tendency appears for
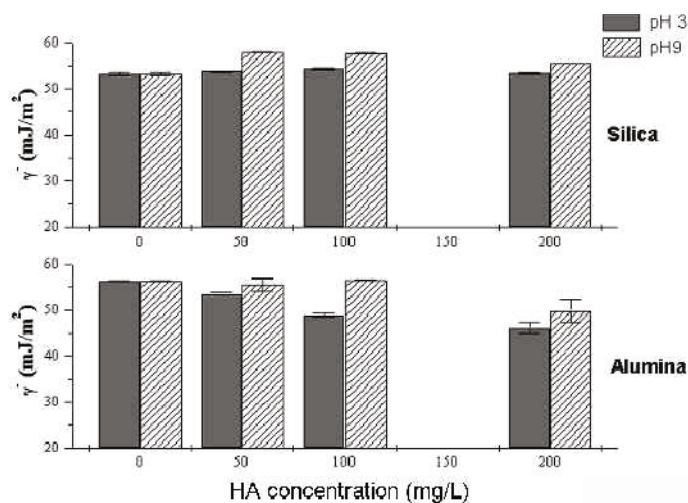

Figure 7. Electron-donor parameter (γ^-) of the surface free energy of silica and alumina as a function of humic acid concentration (pH 3 or 9, and 10^{-2} M NaCl).

SiO$_2$. A similar conclusion was reached in previous works (Ramos-Tejada *et al.*, 2001; Sondi and Pravdić, 1998, 2002) from ζ potential measurements of alumina and silica in humic or fulvic acid solutions. These results demonstrate the higher surface activity of aluminol groups, as compared to silanol, in the adsorption of humic substances (see also Buleva and Petkanchin. 1999; Elfarissi and Pefferkorn, 2000). We could conclude, in view of the results in Figure 6, that only a slight decrease of the hydrophilic character of the edges is expected as a consequence of HA adsorption on the aluminol sites presents in the edge surfaces.

In previous works (Ramos-Tejada *et al.*, 2001, 2002) the adsorption isotherms of HA on NaMt at pH 3, 7 and 9 were obtained. We found an adsorption density ranging from 6 mg/m^2 (pH = 9) to 17 mg/m^2 (pH 3) for 200 mg/L of HA equilibrium concentration. A Langmuir-shaped isotherm was obtained, and, contrary to pH 3, adsorption saturation was apparently reached at pH 9. We concluded, in the above referenced works, that at pH 3, clay particles must have surfaces very favorable to adsorption of neutral or negatively charged HA molecules. We demonstrated that such surfaces are precisely the particle's edges due to essentially electrostatic interactions, and that such favorable circumstances disappear when the pH is 9 because of the change of sign of the surface charge of edges. From those data we can infer that at an acid pH the surface coverage is more pronounced than at a basic one, but any quantification of actual surface coverage is difficult to provide. We have no information about the geometrical conformation of HA molecules on the surface, and the shape of the isotherms does not provide any clues as to changes in molecular orientation and configuration on clay surfaces. Nevertheless, we can infer from adsorption isotherms and the wettability study presented in this work that the progressive adsorption of HA on clay surfaces, and the subsequent increase in surface coverage, confer a more hydrophobic (hydrophilic) character to clay surfaces at acid (base) pH of the solution.

CONCLUSIONS

The wettability of montmorillonite clays (two types, NaMt and FNaMt, were considered in this work) can be established quantitatively by determining the free energy of interaction between the particles in aqueous solution. The hydrophilic character of the clays can be modified by humic acid adsorption in different ways:

(1) At acid pH: the adsorption of humic acid progressively decreases the hydrophilicity of both clays. As a consequence, the wettability of these materials becomes reduced when this organic polyelectrolyte is adsorbed, because HA molecules are predominantly in its non-ionic form.

(2) At basic pH: it is expected that HA molecules mainly adsorb in anionic form. Consequently, an increasingly electron-donor character of both clays is found, which implies an increment of the hydrophilic repulsion between clay particles as HA adsorption progresses. Hence, an improvement of the wettability of both samples (NaMt and 'Rassoul') is produced at basic pH. In this case, a clear linkage is observed between the evolution of ζ potential and of the electron-donor character of both clays, because of the ionization of the carboxylic groups present in the adsorbed molecules of HA.

(3) The above points concern the directly determined hydrophilicity of clay particles which can be ascribed to the behavior of face surfaces of the laminar clay particles. However, an indirect estimate of the wetting behavior of edges is possible, from surface free energy measurements on silica and alumina particles, that bears similar surface groups (silanol and aluminol) as edges of montmorillonite platelets. With this assumption, we estimated that only a slight decrease in the hydrophilicity of edges is predictable, whatever the pH, mainly through adsorption on the more active aluminol sites.

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