Surface energy of clay-synthetic humic acid complexes from contact angle measurement

Claire Jouany

SURFACE FREE ENERGY COMPONENTS OF CLAY-SYNTHETIC HUMIC ACID COMPLEXES FROM CONTACT-ANGLE MEASUREMENTS

Claire Jouany[1]

I.N.R.A., Science du Sol, 78026 Versailles, Cedex, France

Abstract—The surface free energy components of clay-organic complexes were determined to assess to what extent an organic adsorbate modified the surface properties of the mineral, insofar as the stability of soil aggregates is concerned. Adsorption isotherms for two synthetic, humic acid-like polymers were determined on a Ca-montmorillonite. From contact-angle measurements performed on dry surfaces, the surface free energy properties of the clay-organic complexes were determined using the two-liquid-phases method (water and hydrocarbons). This method allows both the dispersive and nondispersive components of the solid surface free energy, γ_S^p and γ_S^r, to be determined. The results show that a very small amount of polymer (1% by weight) adsorbed on the external surfaces of the montmorillonite decreased markedly the surface free energy components of the clay: γ_S^p decreased from 75 to 28 mJ/m² for polycondensate catechol (PC) and from 75 to 30 mJ/m² for polycondensate catechol triglycine (PCT), whereas γ_S^r ranged from 35 to 16 mJ/m² (PC) and from 35 to 17 mJ/m² (PCT). Although their chemical compositions were different, both polymers similarly modified γ_S^p and γ_S^r. Increasing the amount of polymer adsorbed (from 1% to 3.5% by weight) affected mostly γ_S^r, which became as low as 5 mJ/m²; meanwhile, γ_S^p decreased from 30 to 23 mJ/m². Possibly, the molecular orientation of the adsorbate changed in the process of dehydration. Following adsorption of synthetic humic acid-like polymers, dry Ca-montmorillonite complexes displayed γ_S values <50 mJ/m², which were consistent with the solid-water contact angles measured in air.

Key Words—Adsorption, Aggregate stability, Humic acid, Montmorillonite, Surface free energy, Wettability.

Résumé—Les composantes de l'énergie libre de surface sont mesurées pour des complexes organo-minéraux. Cette étude est menée dans le but de vérifier de quelle manière un revêtement organique modifie les propriétés de surface du minéral et peut jouer sur la stabilité structurale. On a déterminé les isothermes d'adsorption sur une montmorillonite calcique pour deux polymères synthétiques modèles d'acides humiques. L'énergie libre de surface des complexes organo-minéraux est calculée à partir de la mesure des angles de contact obtenus sur des surfaces déshydratées avec la méthode à deux phases liquides (eau et hydrocarbures). Cette méthode permet de déterminer à la fois γ_S^r et γ_S^p, qui sont respectivement la composante polaire et la composante dispersive de l'énergie de surface γ_S. Les résultats montrent qu'une quantité très faible de polymère (1% en poids) adsorbé sur les surfaces externes de la montmorillonite diminue de manière importante les composantes de l'énergie libre de surface du minéral: γ_S^p diminue de 75 à 28 mJ/m² pour le polycondensat catéchol (PC) et de 75 à 30 mJ/m² pour le polycondensat catéchol triglycine (PCT), alors que γ_S^r varie de 35 à 16 mJ/m² (PC) et de 35 à 17 mJ/m² (PCT). Bien que leurs compositions chimiques soient différentes, les deux polymères modifient pareillement γ_S^r et γ_S^p. Une augmentation sensible des quantités adsorbées (de 1% à 3,5% en poids) affecte principalement γ_S^r qui diminue jusqu'à une valeur de 5 mJ/m², alors que γ_S^p passe de 30 à 23 mJ/m². Ces modifications importantes sont attribuées à un changement d'orientation des polymères adsorbés, susceptible de s'être produit au cours de la déshydratation. Après adsorption de polymères synthétiques modèles d'acides humiques, la montmorillonite calcique à l'état sec présente des valeurs de γ_S inférieures à 50 mJ/m² qui sont en accord avec les angles de contact solide-eau-vapeur qui sont mesurés.

INTRODUCTION

Physical fertility of cultivated soils requires the organization of soil aggregates into water-stable units that promote a good transfer for gas and water and the proper conditions for seedling emergence. By immersing the aggregate in water, the pressure exerted by entrapped air and the swelling of the clay disrupt and breakdown aggregate units (Yoder, 1936; Concaret,

1967). High organic matter contents are frequently reported to be responsible for the high stability of soil aggregates (Hamblin and Greenland, 1977; Chaney and Swift, 1984). Organic matter generally increases aggregate stability on immersion by two mechanisms: (1) lowering the wettability and (2) increasing the cohesion of aggregate units (Monnier, 1965; Chassin, 1979; Giovannini *et al.*, 1983).

In addition to strongly hydrophobic molecules (e.g., lipids, waxes, chitins) which may cause severe reclamation problems, humic substances show little affinity for water and represent the organic fraction commonly associated with a high aggregate stability (Chaney and
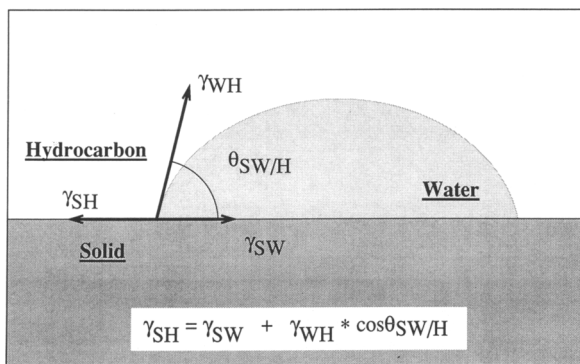
Figure 1. Equilibrium contact angle in a solid (S)-liquid 1 (W)-liquid 2 (H) system.

Swift, 1986; Tschapek *et al.*, 1973; Chassin, 1979; Giovannini and Lucchesi, 1984; Le Bissonnais, 1989). Thus, in soils, this organic fraction is capable of modifying the wetting properties of the high surface free energy hydrophilic minerals (Theng, 1982). The hydrophobic action of humic substances was suggested by Robinson and Page (1950) on the basis of contact-angle determinations on clay fractions extracted from high organic-matter content soils.

Chassin *et al.* (1986) determined γ_S for Ca-montmorillonite. In the present study, changes in γ_S were measured after adsorption of a synthetic humic acid on Ca-montmorillonite, and the extent by which the amount of adsorbate influenced the measured values was noted. For that purpose, the surface free energy components of the clay and clay complexes were determined from contact-angle measurements using the two-liquid-phases method.

METHOD

Two-liquid-phases method

Montmorillonite surfaces are extremely hygroscopic, and the adsorption of liquid or vapor on them severely decreases the surface free energy components of the solid (Chassin *et al.*, 1986; Chibowski and Staszczuk, 1988). Furthermore, because of the high surface free energy of montmorillonite, a finite contact angle for water on that mineral cannot be measured. To this author's knowledge, one of the few tensiometric methods that is suitable for surface characterization of such high energy solids is the two-liquids method, inasmuch as the hydration status for the clay mineral surface is controlled in this method (Tamai *et al.*, 1967; Schultz *et al.*, 1977). Thus, the bare surface can be probed and the manner by which the surface free energy components vary for increasing amounts of adsorbate on the mineral can be determined.

Generally, solid-liquid molecular interactions are thought to originate from London-dispersion forces and polar forces, which include dipole-dipole, dipole induced-dipole, hydrogen bond, and II bonding. As a consequence, the solid surface free energy can be expressed as the sum of the dispersive γ_S^D and the polar γ_S^P component of γ_S:

$$\gamma_S = \gamma_S^D + \gamma_S^P. \tag{1}$$

If a drop liquid is in equilibrium on the solid surface (S) in a two-liquid phases system (Figure 1) of water (W) and hydrocarbon (H), if the spreading pressure, Π_e, on the solid surface is assumed to be equal to zero, Young's general equation becomes:

$$\gamma_{SH} = \gamma_{SW} + \gamma_{HW} \cos \Theta_{SW/H}, \tag{2}$$

where γ_{SW} is the solid-water interfacial energy, γ_{SH} is the solid-hydrocarbon interfacial energy, γ_{HW} is the interfacial tension between water and hydrocarbon, and $\Theta_{SW/H}$ is the solid-water-hydrocarbon contact angle. This equation is valid only if water removes the hydrocarbon film at the solid surface. Hamilton (1972) and Schultz *et al.* (1977) considered this assumption to be verified in similar experimental conditions. Shanahan *et al.* (1982) confirmed the validity of this hypothesis from calculations of the energy of adhesion of the liquids to the surfaces.

Fowkes (1964) gave an empirical expression for the interfacial free energy (γ_{12}) between liquid 1 and liquid 2; he assumed that only London-dispersion interactions take place at the liquid-liquid interface, if one liquid is non-polar:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^D \gamma_2^D)^{1/2}, \tag{3}$$

where γ_1 and γ_2 are the liquid surface tension, and γ_1^D and γ_2^D are the dispersive components of the liquid surface tension.

Owens and Wendt (1969) extended Fowkes expression to solid-liquid systems, in which polar as well as dispersive interactions exist at the interface:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^D \gamma_2^D)^{1/2} - I_{12}^P, \tag{4}$$

where I_{12}^P represents the polar interaction energy term between phase 1 and phase 2.

The expression for γ_{SH}, the interfacial free energy between solid and hydrocarbons, results from Eq. (4):

$$\gamma_{SH} = \gamma_S + \gamma_H - 2(\gamma_S^D \gamma_H)^{1/2}. \tag{5}$$

Because hydrocarbons are non-polar, no polar interaction exists between the solid and the liquid; hence $I_{12}^P = 0$ and $\gamma_H^D = \gamma_H$.

From Eq. (4), the solid-water interfacial free energy can be obtained as well:

$$\gamma_{SW} = \gamma_S + \gamma_W - 2(\gamma_S^D \gamma_W^D)^{1/2} - I_{SW}^P. \tag{6}$$

Replacing γ_{SH} and γ_{SW} by their expressions, respectively Eq. (3) and (4), in Eq. (2), the general equation for a two-liquid-phases system results:

$$\gamma_W - \gamma_H + \gamma_{HW} \cos \Theta_{SW/H} = 2((\gamma_S^D)^{1/2}((\gamma_W^D)^{1/2} - (\gamma_H)^{1/2})) + I_{SW}^P, \tag{7}$$

Table 1. Surface and interfacial tensions for hydrocarbons and water (mJ/m²).[1]

Liquid	γ_L	γ_L^D	γ_L^P	γ_{LW}
Hexane	18.4	18.4	—	51.1
Heptane	20.3	20.3	—	51
Octane	21.3	21.3	—	51
Decane	23.4	23.4	—	51
Dodecane	25.35	25.35	—	51.15
Hexadecane	27.1	27.1	—	51.3
Water	72.6	21.6	51.0	—

γ_L = surface tension of the liquids. γ_L^D = dispersive component of the surface tension of the liquids. γ_L^P = polar component of the surface tension of the liquids. γ_{LW} = water-hydrocarbon interfacial tensions.

[1] From Schultz *et al.* (1977).

or:

$$Y = a\,X + b, \tag{8}$$

where γ_H, γ_{HW}, and γ_W^D are known and given in Table 1. The measurement of the contact angle of water under a series of alkanes, $\Theta_{SW/H}$, allows Eq. (7) to be calculated for each liquid and a straight line to be drawn whose slope equals 2 $(\gamma_S^D)^{\frac{1}{2}}$ and which has a y-intercept of I_{SW}^P (Figure 2).

Wu (1973) suggested that the harmonic-mean equation is more convenient than the geometric-mean equation to express I_{12}^P for high surface energy solids, because in a solid-water system:

$$I_{SW}^P = 4\,\gamma_S^P\gamma_W^P/(\gamma_W^P + \gamma_S^P), \tag{9}$$

or:

$$\gamma_S^P = \gamma_W^P I_{SW}^P/(4\gamma_W^P - I_{SW}^P), \tag{10}$$

where γ_W^P is known and given in Table 1.

This method was used to determine the dispersive and polar components of the surface free energy of solids equilibrated at 0% RH. For each solid, water contact angles were determined by using the same technique described by Chassin *et al.* (1986). Contact angles were measured with a Ramé-Hart telegoniometer equiped with a thermostatic chamber; samples were kept at 20°C. An average value of Θ corresponds to a minimum of 30 determinations. High-purity alkanes were used without further purifications.

MATERIALS

Ca-montmorillonite

SWy-1 Wyoming montmorillonite obtained from the Source Clays Repository of The Clay Minerals Society was used in this work. The <2.0-μm fraction of this Crook County, Wyoming, montmorillonite was purified according to the method given by Chassin *et al.* (1986) and washed three times with a 1.0 M CaCl₂ solution to transform the clay to a homoionic form. The suspension was then extensively washed with deionized water on a tangential ultrafiltration device
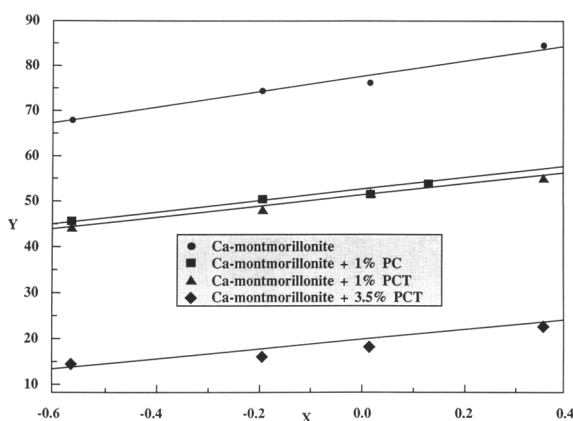

Figure 2. Plots of Eq. (5) for Ca-montmorillonite and its complexes with polycondensate catechol (PC) and polycondensate catechol-triglycine (PCT); $x = (\gamma_W^D)^{\frac{1}{2}} - (\gamma_H^D)^{\frac{1}{2}}$ and $y = \gamma_W - \gamma_H + \gamma_{WH}\cos\Theta_{SW/H}$.

until the solution was in equilibrium with a saline concentration $<10^{-4}$ M. The final suspension contained 25 g clay/liter.

Synthetic humic acid

Two synthetic humic acids were prepared according to the method of Andreux *et al.* (1980) by oxidation of catechol only, polycondensate catechol (PC), and of catechol in the presence of triglycine, polycondensate catechol-triglycine (PCT). These products differed mainly by their molecular weight and N content; their solubility in water was much higher for PCT because of incorporation of polypeptidic chains into the polycondensate; the pK_a of the main acidity was lower for PCT. These complexes have chemical compositions, functional groups, and molecular weights similar to those obtained for soil-extracted humic acids (Table 2). The PC polymer was used as a model for highly decomposed and stable aromatic compounds, whereas the PCT represented less humified and more aliphatic humic substances; these differences are evidenced from infrared spectra (Andreux *et al.*, 1980).

Clay-synthetic humic acid complexes

Adsorption isotherms were constructed at 20°C as follows: 125 mg of Ca-montmorillonite was reacted for 16 hr with 25 ml of organic solutions at concentrations ranging between 0 and 3.0 mg/ml. The organic solutions had a 0.05 ppm concentration in NaN₃ to prevent microorganisms growth; the NaN₃ did not appear to interfere with polymer adsorption. Adsorption took place in unbuffered media; the initial pH of the reacting solution ranged between 2.8 and 3.0.

The adsorption process progressed with a pH increase (equilibrium pH between 3.0 and 4.0) and dissolution of Ca, resulting from cation exchange between the Ca ions of the montmorillonite and H from the polycondensate. Afterwards, the suspension was cen-

Table 2. Characteristics of the polymers used.

	C content (%)	O content (%)	H content (%)	N content (%)	Molecular weight[1]	Total acidity (meq/g)
PC	51	35.3	2.9	—	10,000	4.2
PCT	47.8	36	4	11	30,000	5
Humic acid Theng (1979)	55–60	33–36	—	4	5000–100,000	6–10

PC = polycondensate catechol. PCT = polycondensate catechol-triglycine.
[1] Relative molecular weight, as determined on a dextran gel column calibrated using globular proteins.

trifuged at 20,000 rpm for 15 min; the resulting supernatant was decanted and analyzed for C and Ca.

The clay-polymer slurry was washed several times with deionized water until the supernatant was free of polymer; the resulting materials were termed the binding complexes (Andreux, 1981). The C contents of the supernatant solutions and binding complexes were determined by dry combustion, the evolved CO_2 being measured by coulometry; the C content values were converted into polymer content by using the polymer C content given in Table 2. Ca in solution was determined by atomic absorption.

The amount of polymer adsorbed on the clay was estimated by difference between the initial and the equilibrium polymer concentration. Isotherms were constructed by plotting the amount of polymer adsorbed and the amount of polymer bound (on the basis of 100 g of dry clay) against the equilibrium polymer concentration.

A 1% (by weight) clay-polycondensate complex was prepared for both polymers from the results obtained for binding isotherms (Figure 4), and a 3.5% complex was prepared for PCT only, because a maximum of 1% of the polycondensate PC could be fixed on the clay. The amount of Ca desorbed in the process of adsorption was 20% of the exchangeable cation on the clay. Unfortunately, smooth films from PC or PCT solutions were impossible to prepare: hence, the surface free energy components of the polymer itself could not be determined.

Oriented deposits on glass slides, prepared from a 25 g/liter suspension of the given complex, were al-

lowed to equilibrate for several weeks in desiccators at 0% RH (controlled with P_2O_5). X-ray powder diffraction (XRD) patterns obtained on oriented deposits equilibrated at 0% RH showed no polymer intercalation in the interlayer.

RESULTS

Adsorption isotherms

Adsorption isotherms were shown in Figure 3. Ca-montmorillonite adsorbed twice as much PCT as PC. These observations agree with the general behavior of polymer towards adsorption, the amounts adsorbed increasing with the size and molecular weight of the polymer (Theng, 1982). These results were similar to those reported by Evans and Russell (1959), Levy and Francis (1976), and Theng and Scharpenseel (1976), who obtained linear isotherms for similar equilibrium concentration ranges, the amounts adsorbed being of the same order of magnitude as those reported here for synthetic PC and PCT. Unlike Chassin *et al.* (1977), no adsorption plateau was noted. Previously, F. Andreux (CPB-CNRS, BP 5, 54501 Vandoeuvre-les-Nancy Cedex, France, personal communication) obtained linear isotherms for PCT adsorption on Ca-montmorillonite. Possibly, changes in the shape of the isotherm for concentrations >1.0 mg/ml originated from flocculation processes of the polymer on the mineral surface, taking place together with adsorption.

Binding isotherms

Binding isotherms are shown in Figure 4. For both polycondensates, extensive washing led to desorption of substantial amounts of polymer. Because no polymer intercalation was detected with XRD, this high retention on the mineral was probably not due to trapping in the interlayer.

Among several mechanisms reported by Theng (1979), water-bridging (outer-sphere complexes) interactions between the anionic or neutral functional groups of the polymer and the exchangeable cations on the clay through a water molecule seems to be the leading mechanism for adsorption of humic acid on divalent montmorillonite. Other bonding mechanisms, however, should still be considered, inasmuch as adsorption was conducted in unbuffered media (equilibrium pH ranged from 3.0 to 4.0).

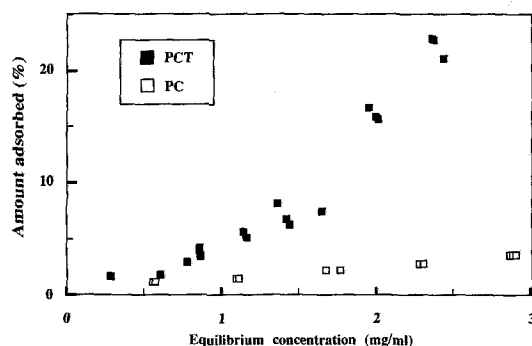A low pH can produce positive charges at crystal

Figure 3.   Adsorption isotherm for polycondensate catechol (PC) and polycondensate catechol-triglycine (PCT) on Ca-montmorillonite.
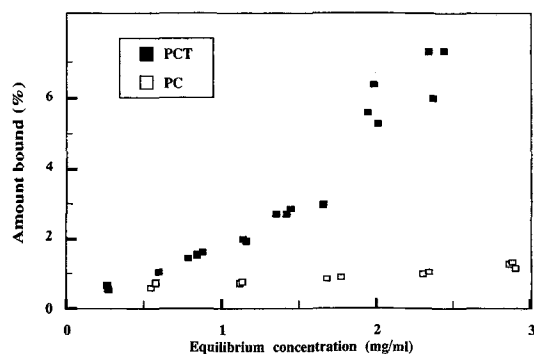
Figure 4.   Binding isotherm for polycondensate catechol (PC) and polycondensate catechol-triglycine (PCT) on Ca-montmorillonite.

Figure 5.   Polar γ_S^P and dispersive γ_S^D components of the surface free energy γ_S ($\gamma_S = \gamma_S^P + \gamma_S^D$) for Ca-montmorillonite and its complexes with polycondensate catechol (PC) and polycondensate catechol-triglycine (PCT); vertical bar on the column refers to standard error.

edges, and Al and Mg can be released by hydrolysis of the octahedral layer (readily exchangeable with the Ca ions on the clay). Mineral hydrolysis was confirmed by noting the clay's cation exchange capacity (CEC) and the exchangeable cations after adsorption of 1% PCT. (1) The clay's CEC changed from 92 to 84 meq/100 g; non-exchangeable Al possibly replaced initial Ca on the clay. (2) The resulting complex contained 6 meq/100 g of exchangeable Mg. Here, cation-bridging (inner-sphere complex) and anion-exchange interactions were likely as well (Sposito, 1984). Theng and Scharpenseel (1976) desorbed as much as 85% of the humic acid adsorbed on divalent montmorillonite; whereas only 70% was removed by adsorption on a trivalent clay (Al or Fe), if inner-sphere complexes were likely to be formed. Polymer segments adsorbed through inner-sphere complexes are less readily removed by water than those interacting through weak water-bridging complexes. This phenomenon must be considered in noting that an average of 40% of polymer adsorbed remains fixed on the montmorillonite after extensive
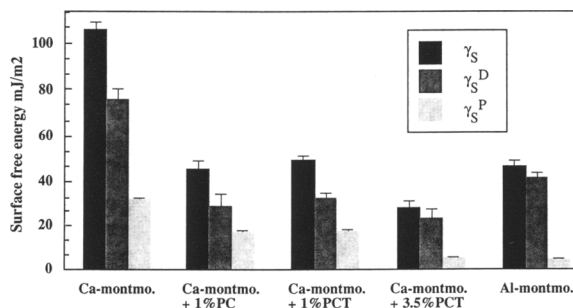
washings. This ratio tended to decrease, however, with the equilibrium concentration, suggesting an evolution of the interaction mechanisms between the polymer and the surface.

Surface free energy components of dry complexes

The surface free energy components for Ca-montmorillonite and the complexes were computed on the basis of the experimental data given in Table 3. The results reported in Figure 5 show that 1% (by weight) of the polymer bound to the mineral surface decreased γ_S significantly; both γ_S^P and γ_S^P were affected. γ_S^P decreased from 75 to 28 mJ/m² (PC) and from 75 to 30 mJ/m² (PCT), whereas γ_S^P changed from 31 to 16 mJ/m² (PC) and from 31 to 17 mJ/m² (PCT).

Increasing the amount of polymer adsorbed affected mostly the nondispersive term of γ_S, which was as low as 5.0 mJ/m², whereas γ_S^P was equal to 23 mJ/m². As a consequence, the surfaces of clay organic complexes had γ_S values <50 mJ/m².

Table 3.   Measured contact angles (degrees).

			Ca-montmorillonite		
	Liquid	Ca-montmorillonite	1.0% PC	1.0% PCT	3.5% PCT
$\Theta_{SW/H}$	Hexane	54.7 ± 1.6[1] 42[2]	—	90.0 ± 1.3 84	128.7 ± 2.2 27
	Heptane	—	90.6 ± 1.5 53	90.2 ± 1.5 33	—
	Octane	61.5 ± 1.7 38	92.4 ± 1.8 48	89.7 ± 1.5 61	129.2 ± 2.7 30
	Decane	61.3 ± 1.6 47	91.8 ± 1.5 43	91.9 ± 1.5 66	130.9 ± 2.4 27
	Dodecane	—	91.7 ± 1.6 38	—	—
	Hexadecane	64.8 ± 1.4 53	—	91.1 ± 1.4 77	128.3 ± 2.1 26
$\Theta_{SW/V}$	—	0	59.7 ± 2.7 32	51.5 ± 3.5 34	70.9 ± 2.3 47

$\Theta_{SW/H}$ = solid-water-hydrocarbon contact angle; $\Theta_{SW/V}$ = solid-water-air contact angle; PC = polycondensate catechol. PCT = polycondensate catechol-triglycine.
[1] ± Average standard deviation.
[2] Number of determinations.

DISCUSSION

In this study, Ca-montmorillonite showed large values for γ_S, which are characteristic for high surface-free-energy solids; these results are similar to those reported for similar surfaces by Giese *et al.* (1989) and by Chibowski and Staszczuk (1988) for smectites and kaolinites, respectively.

After a severe drying (0% RH), both organo-mineral complexes exhibited similar surface properties (Figure 5). The adsorption of synthetic humic acid on Ca-montmorillonite modified mainly the dispersive component of γ_S, which decreased by 60% and was as low as 30 mJ/m²; such low values have been frequently obtained, for example, for synthetic organic polymers: Nylon 6.6 or polymethyl metacrylate (Gerson, 1981). The low values obtained for γ_S are consistent with the chemical nature of the polymers PC and PCT, which contain mainly C and O. Absolom and Neumann (1988), reported similar γ_S values for dried protein layers, human serum albumin (HSA), and bovine serum albumin (BSA), all of which gave γ_S values between 28 and 52 mJ/m². Lee and Luner (1972) obtained γ_S values between 46 and 56 mJ/m² for lignins, the principal precursors of humus.

Because the molecular structure of PC and PCT and their hydrodynamic radii are not precisely known, the exact extent to which the mineral surfaces are covered is difficult to ascertain. Assuming a spherical structure for the polycondensates (Gosh and Schnitzer, 1980) and a hydrodynamic radius of a few tens of Ångstroms (as reported by Cornell *et al.,* 1986) and a BET specific surface of 30–40 m²/g for Ca-montmorillonite, the 1% organo-mineral complexes prepared for both polymers should not have presented surfaces fully covered by an adsorbate monolayer; at best, 50% of the surface should have been covered, whereas 100% of the surface should have been covered for the 3.5% complex, assuming no shrinkage of the adsorbate in the drying process.

Dispersive component of γ_S

According to Young (1958) and as was reported by Chassin *et al.* (1986), dispersive forces on Ca-montmorillonite originate from the silicate tetrahedra. Increasing the amount of adsorbate on the montmorillonite decreased the γ_S^D component of γ_S. Compared with results reported for alkylammonium-montmorillonite complexes by Jouany and Chassin (1987), the γ_S^D value obtained for the 1% complexes corresponds to that measured for an hexylammonium-montmorillonite, which showed a 68% coverage of the surface. If the amount of PCT was increased from 1% to 3.5%, γ_S^D decreased from 30 to 23 mJ/m². This difference is similar to that reported by Jouany and Chassin (1987), if the percentage of the mineral surface covered with alkylammonium chains increases from 68% to 100%. The changes in γ_S observed if the amount of adsorbate

increased correlate well with the calculated percentage of the surface covered by alkylammonium ions.

Polar component of γ_S

For Ca-montmorillonite equilibrated at 0% RH, γ_S^P originated mainly from the partially hydrated cations (Chassin *et al.,* 1986; Jańczuck and Białopiotrowicz, 1988); each organo-mineral surface displayed smaller values of γ_S^P compared with the untreated clay, because the initial Ca ions were complexed by the polymer or, in the process of adsorption, they were exchanged by Al, which presented hydration energies lower than Ca. Both situations are likely.

In Figure 5, unpublished results obtained on Al-treated Ca-montmorillonite, for which all of the Ca had been exchanged by Al, show a γ_S^P value (4.5 mJ/m²) very similar to that obtained for the 3.5% PCT complex (5.1 mJ/m²). The 1% complexes displayed an intermediate value (16 and 17 mJ/m²), meaning that Ca remained at the solid-air interface available for polar interactions with water.

Significant differences in γ_S^P were expected, however, between the different adsorbates, inasmuch as the PCT complexes contained hydrophilic nitrogeneous functional groups, quite able to interact strongly with water. This polymer is also much more soluble in water than the catechol polycondensate. Apparently, either the method used to probe the surface was not precise enough to detect the differences in the chemical composition of the adsorbates or, more likely, in the process of dehydration, the conformation of the molecules changed. This last scenario has already been proposed by several authors to explain the changes in wetting properties of soil organic matter after a severe drying (e.g., Farmer, 1978). Because of the flexibility of the organic molecules, hydrogen bonds occur between polar functional groups that are removed from the solid-air interface, the organo-mineral surface becoming hard to rewet.

Changes in the molecular orientation of the adsorbates are confirmed by the γ_S^P values for the two PCT complexes. Regardless of the amount of functional groups present on the surface and prone to interact strongly with water, drying removed them from the solid-air interface, and the surface displayed properties of a hydrophobic low surface free energy solid. Actually, solid-water-air ($\Theta_{sw/v}$) contact angles were measured on oriented deposits of the three complexes, previously equilibrated at 0% RH for several weeks. These measurements (Table 3) confirm that after drying the organo-mineral surfaces displayed a distinctly hydrophobic character; the largest angle was measured for the greatest amount of adsorbate.

In conclusion, the very small amount of synthetic humic acid adsorbed on Ca-Wyoming montmorillonite decreased its surface free energy, γ_S, and transformed the hydrophilic mineral into a hydrophobic

mineral. Furthermore, the chemical composition of the adsorbate had very little influence on the surface properties of organo-mineral complexes prepared in this investigation. The minimum amount of polymer necessary to transform the Ca-montmorillonite into a low energy and hydrophobic surface still remains to be estimated. After drying, no differences were apparent between PC and PCT, but whether the complexes would show the same trends when hydrated is not known.

ACKNOWLEDGMENTS

REFERENCES

Absolom, D. R. and Neumann, A. W. (1988) Modification of substrate properties through protein adsorption: *Colloids and Surfaces* **30**, 25–45.

Andreux, F. (1981) Utilisation de molécules modèles de synthèse dans l'étude des processus d'insolubilisation et de biodégradation des polycondensats humiques: *Bull. Ass. Fr. Etude Sol. Sci. Sol* **11**, 271–291.

Andreux, F., Golebiowska, D., and Metche, M. (1980) Polymérisation oxydative des O-diphénols en présence ou non d'amino-acides. Cas des systèmes (catéchol-glycocolle) et (catéchol-diglycylglycine): *C.R. Ass. Gén. Groupe Polyphenols. Logrono.* **9**, 178–188.

Chaney, K. and Swift, R. S. (1984) The influence of organic matter on aggregate stability in some British soils: *J. Soil Sci.* **35**, 223–230.

Chaney, K. and Swift, R. S. (1986) Studies on aggregate stability: *J. Soil Sci.* **37**, 337–343.

Chassin, P. (1979) Détermination de l'angle de contact acides humiques-solutions aqueuses de diols. Conséquences sur l'importance relative des mécanismes de destruction des agrégats: *Ann. Agron.* **30**, 481–491.

Chassin, P., Le Berre, B., and Nakaya, N. (1977) Influence des substances humiques sur les propriétés des argiles: *Clay Miner.* **12**, 261–271.

Chassin, P., Jouany, C., and Quiquampoix, H. (1986) Measurement of the surface free energy of Ca-montmorillonite: *Clay Miner.* **21**, 899–907.

Chibowski, E. and Staszczuk, P. (1988) Determination of surface free energy of kaolinite: *Clays & Clay Minerals* **36**, 455–461.

Concaret, J. (1967) Etude des mécanismes de la destruction des agrégats de terre au contact de solutions aqueuses: *Ann. Agron.* **18**, 65–144.

Cornell, P. K., Summers, R. S., and Robert, P. V. (1986) Diffusion of humic acid in dilute aqueous suspension: *J. Coll. Inter. Sci.* **114**, 149–164.

Evans, L. T. and Russell, E. W. (1959) The adsorption of humic and fulvic acids by clays: *J. Soil Sci.* **10**, 119–132.

Farmer, V. C. (1978) Water on particle surfaces: in *The Chemistry of Soil Constituents,* D. J. Greenland and M. H. B. Hayes, eds., Wiley, New York, 405 pp.

Fowkes, F. M. (1964) Dispersion force contributions to surface and interfacial tensions, contact angles, and heats of immersion: *Adv. Chem. Ser.* **43**, 99–111.

Gerson, D. F. (1981) *Methods in surface physics for immunology:* in *Immunological Methods* **2**, Academic Press, New York, 105–138.

Giese, R. S., van Oss, C., Norris, J., and Constanzo, P. M.

(1989) Surface energies of smectite clay minerals: in *Program Abstracts, Int. Clay Conf., Strasbourg, 1989,* p. 158.

Giovannini, G. and Lucchesi, S. (1984) Differential thermal analysis and infrared investigations on soil hydrophobic substances: *Soil Sci.* **137**, 457–463.

Giovannini, G., Lucchesi, S., and Cervelli, S. (1983) Water repellent substances and aggregate stability in hydrophobic soils: *Soil Sci.* **135**, 110–113.

Gosh, K. and Schnitzer, M. (1980) Macromolecular structures of humic substances: *Soil Sci.* **129**, 266–276.

Hamblin, A. P. and Greenland, D. J. (1977) Effect of organic constituents and complexed ions on aggregate stability of some East Anglian silt soils: *J. Soil Sci.* **28**, 410–416.

Hamilton, W. C. (1972) A technique for the characterization of hydrophilic solid surfaces: *J. Colloid Inter. Sci.* **40**, 219–222.

Jańczuck, E. and Białopiotrowicz, T. (1988) Components of surface free energy of some clay minerals: *Clays & Clay Minerals* **36**, 243–248.

Jouany, C. and Chassin, P. (1987) Determination of the surface energy of clay-organic complexes by contact-angle measurements: *Colloids and Surfaces* **27**, 289–303.

Le Bissonnais, Y. (1989) Analyse des processus de microfissuration des agrégats à l'humectation: *Bull. Ass. Fr. Etude Sol. Sci. Sol* **27**, 187–199.

Lee, S. B. and Luner, P. (1972) The wetting and interfacial properties of lignins: *Tappi* **55**, 116–121.

Levy, R. and Francis, C. W. (1976) Adsorption and desorption of cadmium by synthetic and natural organo-clay complexes: *Geoderma* **15**, 361–370.

Monnier, G. (1965) Action de la matière organique sur la stabilité structurale des sols: Thèse de Docteur Ingénieur, Université de Paris, Paris, 140 pp.

Owens, D. K. and Wendt, R. C. (1969) Estimation of the surface free energy of polymers: *J. Appl. Polymer Sci.* **13**, 1741–1747.

Robinson, D. O. and Page J. B. (1950) Soil aggregate stability: *Soil Sci. Soc. Amer. Proc.* **15**, 25–29.

Schultz, J., Tsutsumi, K., and Donnet, J. B. (1977) Surface properties of high-energy solids: *J. Coll. Inter. Sci.* **59**, 272–277.

Shanahan, M. E. R., Cazeneuve, C., Carre, A., and Schultz, J. (1982) Wetting criteria in three phases solid-liquid-liquid systems: *J. Chim. Phys.* **79**, 241–245.

Sposito, G. (1984) *The Surface Chemistry of Soils*: Oxford University Press, Oxford, 234 pp.

Tamai, Y., Makuuchi, K., and Suzuki, M. (1967) Experimental analysis of interfacial forces at the plane surface of solids: *J. Phys. Chem.* **71**, 4176–4179.

Theng, B. K. G. (1979) *Formation and Properties of Clay-Polymer Complexes*: Elsevier, Amsterdam, 262 pp.

Theng, B. K. G. (1982) Clay-polymer interactions summary and perspectives: *Clays & Clay Minerals* **30**, 1–10.

Theng, B. K. G. and Scharpenseel, H. W. (1976) The adsorption of ^{14}C-labelled humic acid by montmorillonite: in *Proc. Int. Clay Conf., Mexico City, 1975,* S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 643–653.

Tschapek, M., Pozzo Ardizzi, G., and De Busseti, S. G. (1973) Wettability of humic acid and its salts: *Z. Pflanzen. Bodenk.* **1**, 16–31.

Wu, S. (1973) Polar and nonpolar interactions in adhesion: *J. Adhes.* **5**, 39–55.

Yoder, R. E. (1936) A direct method for aggregate analysis of soils and a study of the physical nature of erosion losses: *J. Amer. Soc. Agron.* **28**, 337–351.

Young, C. J. (1958) Interaction of water vapor with silica surfaces: *J. Coll. Sci.* **13**, 67–85.