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BASELINE STUDIES OF THE CLAY MINERALS SOCIETY SOURCE CLAYS: COLLOID AND SURFACE PHENOMENA

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INTRODUCTION

The interface between the surfaces of clay minerals and other materials (aqueous solution, organic moieties, biomolecules, *etc.*) is of great importance to many geological, technological and biological processes. The examination of the structure and composition of mineral surfaces is advancing rapidly. However, the crystal structure of a mineral is only part of the information needed to understand the activity of the surface; we still do not fully understand the chemical and physical interactions at the surface or interface. One very powerful methodology for the study of surfaces and interfacial interactions is the determination of the thermodynamic properties of the surface. It became possible in the late 1980s to determine quantitatively the apolar and polar surface-tension components and parameters of liquids and solids (van Oss *et al.*, 1988; van Oss, 1994), and the experimental techniques necessary for obtaining surface free-energy components of minerals, and particularly of colloid-sized minerals, are also a recent development (Costanzo *et al.*, 1990; van Oss *et al.*, 1990, 1992; Giese *et al.*, 1991).

The theory underlying the thermodynamics of surfaces and interfaces is introduced here, illustrating the methodology of contact angle and ζ-potential measurements, and summarizing the results of these measurements on the Source Clays. Detailed studies of colloid and surface phenomena are found in Adamson (1990), van Oss (1994), and Hiemenz (1986).

SURFACE FREE ENERGY

Free energy of interfacial interaction

The free energy of adhesion between materials 1 and 2, *in vacuo*, is (after Dupré, 1869):

$$\Delta G_{12}^{\mathrm{adh}} = \gamma_{12} - \gamma_1 - \gamma_2 \quad (1)$$

where γ is the surface or interfacial tension and subscripts 1 and 2 refer to the materials under study. The free energy of interaction between materials 1 and 2, immersed in liquid 3, is:

$$\Delta G_{132} = \gamma_{12} - \gamma_{13} - \gamma_{23} \quad (2)$$

and the interaction between two particles or molecules of material 1, immersed in a liquid 3 then is

$$\Delta G_{131} = -2\gamma_{13} \quad (3)$$

In equations 1–3, the surface or interfacial tension, γ, is the sum of two components (van Oss *et al.*, 1988; van Oss 1994):

$$\gamma_i = \gamma_i^{\mathrm{LW}} + \gamma_i^{\mathrm{AB}} \quad (4)$$

where γ^{LW} is the Lifshitz-van der Waals component and γ^{AB} is the Lewis acid-base component.

Apolar or Lifshitz-van der Waals (LW) interactions

The apolar or Lifshitz-van der Waals electrodynamic forces (LW) comprise three distinct interactions: (1) randomly oriented permanent dipole–permanent dipole (orientation) interactions (described by Keesom, 1915, 1920, 1921a, b); (2) randomly oriented permanent dipole–induced dipole (induction) interactions (described by Debye, 1920, 1921); and (3) fluctuating dipole–induced dipole (dispersion forces as described by London, 1930; see also Overbeek, 1952). Each of these interactions decays rapidly with distance or length, ℓ, as ℓ^{-6} (see below). Of these three, the dispersion (or London) forces represent the main significant term in condensed media. Historically, the existence of these three apparently distinct effects complicated the treatment of the LW forces, but this impediment was removed by Lifshitz (1955) and Chaudhury (1984) who showed that, on a macroscopic scale, all three should be described with the same mathematical formalism, obviating the need to separate each contribution.

On a macroscopic scale, LW energies between plane parallel surfaces decay with distance as ℓ^{-2}. The apolar or LW component of the free energy of interaction for two spheres is:

$$\Delta G^{\mathrm{LW}} = -\frac{AR}{12\ell} \quad (5)$$

where ΔG^{LW} = apolar free energy component (LW), A = Hamaker's constant, ℓ = the surface to surface distance, and R is the particle radius.

Considering only LW forces, the Hamaker constant can be calculated by using:

$$2\gamma^{\mathrm{LW}} = -\Delta G = \frac{A}{12\pi\ell_0^2} \quad (6)$$

where the apolar surface tension component, γ^{LW}, of condensed materials can be determined by contact angle measurement with apolar liquids, ℓ_0 is the minimum equilibrium distance and was shown to be 0.157 nm (van Oss *et al.,* 1988). Although A applies to all three electrodynamic interactions (dispersion, orientation and induction), $A^{\text{dispersion}}$ is usually the significant term in condensed media (Chaudhury, 1984; van Oss *et al.,* 1988).

For two different apolar materials 1 and 2, the apolar or LW interfacial tension, γ_{12}^{LW}, is given by the Good-Girifalco-Fowkes combining rule (Fowkes, 1963; Good and Girifalco, 1960):

$$\gamma_{12}^{LW} = (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 \tag{7}$$

To derive values for the apolar or LW surface tension component of a solid, γ_S^{LW}, but only for those instances in which, besides electrostatic interactions (EL), no other energy components are active, the Young-Good-Girifalco-Fowkes equation (van Oss *et al.,* 1988) can be used:

$$1 + \cos\theta = 2\sqrt{\frac{\gamma_S^{LW}}{\gamma_L^{LW}}} \tag{8}$$

where θ is the contact angle formed between an apolar liquid and the surface of the solid, and the subscripts S and L are solid and liquid, respectively. See below for an example where there are both apolar and polar interactions.

Polar or Lewis acid-base (AB) interactions

The AB forces are always asymmetrical because they comprise the electron donating as well as the electron accepting properties of a surface. Thus, the AB surface free-energy component, γ^{AB}, consists of two non-additive parameters, one for the electron donor ($\gamma^{\ominus}$) and one for the electron acceptor ($\gamma^{\oplus}$). The relation between the AB component of the surface tension and these parameters for a single material, i, is (van Oss *et al.,* 1988; van Oss, 1994):

$$\gamma_{ii}^{AB} = 2\sqrt{\gamma_i^{\oplus}\gamma_i^{\ominus}} \tag{9}$$

and the AB interfacial free-energy component for the polar interaction between two different condensed-phase materials is expressed as:

$$\gamma_{12}^{AB} = 2(\sqrt{\gamma_1^{\oplus}\gamma_1^{\ominus}} + \sqrt{\gamma_2^{\oplus}\gamma_2^{\ominus}} - \sqrt{\gamma_1^{\ominus}\gamma_2^{\oplus}} - \sqrt{\gamma_1^{\oplus}\gamma_2^{\ominus}}). \tag{10}$$

The total interfacial tension can then be expressed as

$$\gamma_{12} = (\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}})^2 + 2(\sqrt{\gamma_1^{\oplus}\gamma_1^{\ominus}} + \sqrt{\gamma_2^{\oplus}\gamma_2^{\ominus}} - \sqrt{\gamma_1^{\ominus}\gamma_2^{\oplus}} - \sqrt{\gamma_1^{\oplus}\gamma_2^{\ominus}}). \tag{11}$$

Equation 11 shows that where $|\gamma_{12}^{AB}| > \gamma_{12}^{LW}$ and $\gamma_{12}^{AB} < 0$, the total interfacial tension is a negative value and gives rise to a repulsive interaction. Because the net interfacial tension (γ_{12} or, in aqueous systems, γ_{iw}) also comprises the apolar (LW) component, which is always positive, the total interfacial tension consists of contributions by apolar and polar forces simultaneously, so that the resultant γ_{12} may be either positive or negative.

The decay of the AB component of the interfacial surface free-energy with distance, for spherical particles of radius *R*, can be expressed as:

$$\Delta G_{\ell}^{AB} = \pi R \lambda \Delta G_{\ell_0}^{AB} e^{(\ell_0 - \ell)/\lambda} \tag{12}$$

where $\Delta G_{\ell_0}^{AB}$ is the free energy of interaction in the parallel flat-plate conformation, at the minimum equilibrium distance $\ell_0 \sim 0.157$ nm), as measured by contact angle determinations, where $\Delta G_{\ell_0}^{AB} = -2\gamma^{AB}$, and λ is the decay length of the liquid molecules taken here as λ = 1 nm for water (Claessòn, 1986).

Contact angle (θ) and Young's equation

Expressing the Young-Dupré equation for the contact angle (θ) of a liquid on a solid surface as:

$$(1 + \cos\theta)\gamma_L = -\Delta G_{SL}^{IF} \tag{13}$$

and taking into account that the total interfacial (IF) free energy as:

$$\Delta G_{SL}^{IF} = \Delta G_{SL}^{LW} + \Delta G_{SL}^{AB} \tag{14}$$

then, the relation between the contact angle and the surface-tension components and parameters is given by the extended form of the Young's equation (van Oss *et al.,* 1988; van Oss, 1994):

$$(1 + \cos\theta)\gamma_L = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{\oplus}\gamma_L^{\ominus}} + \sqrt{\gamma_S^{\ominus}\gamma_L^{\oplus}}). \tag{15}$$

The values of γ^{LW}, γ^{cq} and $\gamma^{\ominus}$ of a solid can be derived from measurements of the contact angle, θ, formed by a drop of liquid on a smooth surface of the solid, provided that the surface-tension properties of the liquid are known. Three or more liquids must be used, of which at least two must be polar. Contact angles obtained with apolar liquids (for which $\gamma^{\oplus}$ and $\gamma^{\ominus}$ are zero) so that $\gamma_L = \gamma_L^{LW}$ give directly the value of the LW surface tension component, γ_S^{LW} for the solid. Contact angles obtained with polar liquids yield values for $\gamma_S^{\oplus}$ and $\gamma_S^{\ominus}$ by the solution of a set of simultaneous Young's equations, with the number of equations equal to the number of polar liquids. With these techniques, contact angles may be measured with a standard deviation of 1°, which translates into errors for the γ values of ~2%.

Hydrophilicity vs. hydrophobicity of mineral surfaces

Water is often assumed to wet the surface of a hydrophilic solid and not wet the surface of a hydrophobic surface. In terms of thermodynamics, this criterion is unsatisfactory because all surfaces of condensed-phase materials attract H_2O molecules to a considerable degree, *i.e.* with a free energy of adhesion varying from a value of -40 mJ/m^2 for completely apolar surfaces, to -140 mJ/m^2 for strongly hydrophilic solids (van Oss, 1994). Recent developments in surface thermodynamic theory provide the basis for a quantitative definition of hydrophilicity and hydrophobicity, in terms of the free energy of interfacial interaction between two surfaces, in an aqueous environment (van Oss and Good, 1988; Good and van Oss, 1991; van Oss and Giese, 1995). The $\gamma^{\ominus}$ value is the value that is most closely connected to the hydrophilicity or hydrophobicity of the mineral surface. The free energy of interfacial interaction, ΔG^{IF}_{1w1}, between mineral surfaces 1 dispersed in water w, is the combination of equations 3 and 11. The Lifshitz-van der Waals or apolar part of this interaction (LW) is always negative (attractive) and is rarely the dominant factor for the solid surface. This value ranges from 0 to -5.5 mJ/m^2. The polar part of the interaction (AB) is most important in determining whether a particle is hydrophobic or hydrophilic. For a material to be neither hydrophilic nor hydrophobic, *i.e.* for ΔG^{IF}_{1w1}, ≈ 0, $\gamma_1^{\ominus}$ usually has to be of the order of 28 mJ/m^2 (taking the slight LW attraction into account). Hydrophobic surfaces, where ΔG^{IF}_{1w1}, < 0, *i.e.* those substances which tend to aggregate in water, have a $\gamma_1^{\ominus} < 28$ mJ/m^2 in general. Hydrophilic materials, for which ΔG^{IF}_{1w1}, > 0, repel each other when immersed in water; and tend to have values for $\gamma_1^{\ominus} > 28$ mJ/m^2 (van Oss, 1994; van Oss and Giese, 1995).

Electrostatic interactions (EL)

When a solid mineral comes into contact with water, its surface typically acquires an electrostatic charge, expressed as the surface potential, ψ_0. The origin of this charge is diverse and includes a differential dissolution of the surface, an ionization of the surface, a permanent structural imbalance in charge (*e.g.* the layer charge of clay minerals), a permanent electrostatic charge on the surface resulting from broken bonds, and a specific adsorption of charged species from liquid (Everett, 1988). The charges on the surface of the particle and the ions in solution create an electrical double layer. An extensive discussion of the role of double-layer theory in colloidal stability was given by Overbeek (1952). Whereas the exact arrangement of ions directly adjacent to the particle surface is not completely known, what is clear is that an anisotropic distribution of ions is associated with the surface and that the potential at the surface decreases with distance from the particle. The potential (ζ) at the slipping plane can be determined from measurements of electrokinetic mobilities. Such experiments involve, for example, the velocity of a particle as it moves through an electrolyte solution in response to an applied electric field. For the case where the particle size is much larger than the thickness of the diffuse ionic double layer, ζ potential can be related to the electrophoretic velocity, *U,* as follows (Overbeek, 1952):

$$U = \frac{\epsilon \zeta E}{4\pi\eta} \tag{16}$$

where ϵ is the dielectric constant of the medium, E is the electric field strength, and η is the viscosity of the medium.

For low to medium electrokinetic potentials (*i.e.* $\zeta < 50$ mV), the potential at the particle surface (ψ_0) is approximated from:

$$\psi_0 = \zeta\left(1 + \frac{z}{R}\right)\exp(\kappa z) \tag{17}$$

In this equation, z is the distance between the surface of the charged particle and the slipping plane (one usually may take this to be ~0.3–0.5 nm, taken here as 0.5 nm), R is the Stokes radius of the particles, and $1/\kappa$ is the thickness of the diffuse double layer (Debye length) (*e.g.* Overbeek, 1952). The value of κ may also be obtained by:

$$\kappa = \sqrt{4\pi e^2 \sum v_i^2 n_i^2 / \epsilon \mathrm{kT}} \tag{18}$$

where e is the charge of the electron (4.8×10^{-10} esu or 1.6×10^{-19} C), v_i is the valency of each ionic species, n_i is the number of ions of each species per cubic centimeter of bulk liquid, k is Boltzmann's constant (1.38×10^{-23} T/K), and T is the absolute temperature in degrees K.

Having determined ψ_0 and κ, the electrostatic interaction energy (ΔG^{EL}_{121}) for two spherical particles as a function of interparticle distance ℓ is given by:

$$\Delta G = \frac{1}{2}\epsilon R \psi_0^2 \ln(1 + e^{-\kappa\ell}) \tag{19}$$

where R is the radius of curvature of the spherical particle, and the other quantities are as described above.

The electrostatic interactions for materials whose ζ potentials are <~25–30 mV can usually be ignored because the electrostatic interaction energy (ΔG^{EL}_{1w1}) tends to be much smaller than the polar (ΔG^{AB}_{1w1}) or even the apolar (ΔG^{LW}_{1w1}) interaction energies. ΔG^{EL}_{1w1} is nearly always positive, *i.e.* repulsive. Note that the total interaction energy between particles 1 dispersed in water, is

$$\Delta G^{TOT}_{1w1} = \Delta G^{LW}_{1w1} + \Delta G^{AB}_{1w1} + \Delta G^{EL}_{1w1} \tag{20}$$

For small particles or molecules, add ΔG^{BR}_{1w1}, for a Brownian energy of ~1 kT.

METHODS

Preparation of clay films

The most accurate contact-angle measurements are obtained using a smooth, solid surface, although this

Table 1. Values of the surface-tension components and parameters (in mJ/m^2), and of the viscosities (in poise) of test liquids used for contact-angle measurements, at 20°C[1].

Liquid	γ_L	γ^{LW}	$\gamma^{\oplus}$	$\gamma^{\ominus}$	η
Hexane	18.40	18.40	0	0	0.00326
Octane	21.62	21.62	0	0	0.00542
Decane	23.83	23.83	0	0	0.00907
Dodecane	25.35	25.35	0	0	0
Tetradecane	26.56	26.56	0	0	0.02322
1-bromonaphthalene	44.4	44.4	0	0	0.0489
Diiodomethane	50.8	50.8	0	0	0.028
Ethylene glycol	48.0	29.0	1.92	47.0	0.199
Formamide	58.0	39.0	2.28	39.6	0.0455
Glycerol	64.0	34.0	3.92	57.4	14.90
Water	72.8	21.8	25.5	25.5	0.010

[1] From van Oss (1994).

is not possible for finely divided minerals such as non-swelling clay particles. A pseudo-crystal surface can be created by forming swelling clay minerals into a self-supporting, smooth film suitable for contact-angle measurement.

For this study, self-supporting smectite films were made by the evaporation of dilute (1–2%) clay mineral-water suspensions. The suspensions were deposited and dried on a variety of materials, including mica sheets, polystyrene, and sheets of various commercial polymer films. Smooth, thin films of the smectite and other clay minerals for contact-angle measurements can also be prepared on glass microscope slides or porous silver membrane filters (Hytrex Filter Division, Osmonics Inc., Minnetonka, Minnesota). The particles were kept in homogeneous suspension (1–2%) by continuous stirring on a magnetic stirrer, and aliquots of 5 mL were withdrawn with a pipette and distributed evenly on clean glass microscope slides (7.5 × 2.5 cm) or on the filters (diameter = 4.7 cm) which are kept strictly horizontal. The dried slides coated with the clay particles were extremely smooth.

Direct contact-angle measurements

After a film was removed from its substrate, it was placed upside down (*i.e.* with the smooth side up) on a glass microscope slide, which was positioned in front of a telemicroscope (Gaertner, Chicago, Illinois) with an eyepiece goniometer. Using Teflon/glass syringes equipped with stainless steel Luer-tipped hypodermic needles (Gilmont instruments, Chicago, Illinois), a drop (diameter of ~5 mm) of a liquid (α-bromonaphthaline, diiodomethane, formamide, glycerol or water; Table 1) was placed onto the smooth surfaces of the (smectite) clay films and the advancing contact angles (θ_{adv}) were measured directly on each side of the drop. No. 24 needles were used for water, formamide, 1-bromonaphthalene and diiodamethane, and no. 18 needles for glycerol because of its high viscosity. For each clay mineral, a total of 15 contact-angle measurements was made for each test liquid.

Thin-layer wicking

Kaolinites and attapulgites, however, in common with many other fine-grained minerals (*e.g.* all non-swelling clays) do not form suitable films; nor do they occur as large, perfect single crystals with well-developed faces. To determine the contact angle formed between a liquid (and air or vapor) and finely divided solid minerals, for which direct contact-angle measurements cannot be performed, the capillary rise method, or thin-layer wicking is applied. In this method, the rate of capillary rise (*i.e.* the capillary rise, h, in a time, t) of a liquid, L, is observed through a thin, uniform layer of powdered material deposited on a glass microscope slide, using Washburn's (1921) equation:

$$h^2 = \frac{tR_{eff}\gamma_L \cos\theta}{2\eta} \tag{21}$$

where R_{eff} is the effective interstitial pore radius, γ_L is the surface tension of the liquid, θ the contact angle between the liquid and the solid, and η the viscosity of the liquid. There are two unknowns in this equation, so that before $\cos\theta$ can be determined, the value of R_{eff} must be ascertained. This can be achieved by using low-energy apolar liquids, in this case heptane, octane, decane and dodecane, which spread over the solid surface without forming a finite contact angle. With spreading liquids, θ remains equal to zero, and $\cos\theta = 1$, because of the formation of a precursor film (van Oss *et al.*, 1992). With R_{eff} known, the contact angle between solid and the test liquids α-bromonaphthalene, diiodomethane, water, ethylene glycol and formamide can be determined (see Table 1).

To prepare the slides for wicking, the following procedure was used. Dry powders of the clay minerals were dispersed in distilled water as 2%, (w/v) suspensions. The particles were maintained in homogeneous suspension by continuous stirring. Aliquots of 5 mL were withdrawn with a pipette and distributed equally on clean glass microscope slides (2.5 × 7.5 cm) which

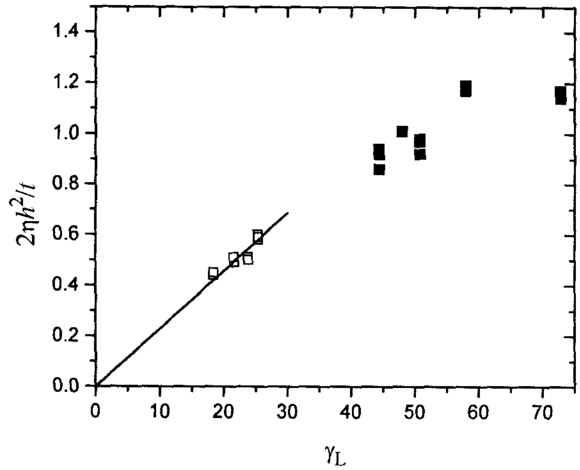

Figure 1. Plot of $2\eta h^2/t$ *vs.* γ_L (see equation 21) obtained by thin-layer wicking on KGa-1b plates with the test liquids: ordinate in 10^{-4} P cm^2 s^{-1}; abscissa in mJ/m^2. The open square symbols represent the low-energy spreading liquids and the solid square symbols represent the polar and apolar non-spreading liquids. The slope of the line yields $R_{eff} = (2.29 \pm 0.03) \times 10^{-6}$ cm.

were horizontal. After the water was allowed to evaporate for 12 h, the slides were dried for 12 h in an oven at 105°C and subsequently stored in a vacuum desiccator until needed.

The wicking occurs by placing the dried, coated glass slides in containers with a gas-tight ground-glass stopper. Glass containers are filled to a height of ~5 mm with one of the various liquids listed in Table 1. Before actual immersion, the coated slide is maintained inside the closed glass container for ~2 h, to allow the powder to become equilibrated with the vapor of the low-energy-spreading liquids whereas no equilibration is necessary with test liquids α-bromonaphthaline, diiodomethane, formamide, ethylene glycol or water. Then, the slide is immersed in the liquid (to a liquid height of ~5 mm), and the vertical movement of the liquid front through the layer of powder is observed. Using a stopwatch and with the help of small indentations which were applied to the glass slide at 2 or 3 mm intervals, several observations can be made of the times elapsed for the liquid front to reach different height intervals. About 35 slides were made for each clay sample, and each liquid was measured with at least three slides.

The best way to ascertain the value for R_{eff} (equation 21) in thin-layer wicking experiments is by plotting $2\eta h^2/t$ *vs.* γ_L for all spreading liquids used. A straight line should be obtained, going through the origin; the slope of this line yields R_{eff}. Figure 1 shows such a plot for the wicking of KGa-1 particles.

ζ potential

Electrophoretic mobilities were measured with a microelectrophoresis device described by van Oss *et al.* (1974), in which the capillaries used (100 μL "Drummond Microcaps", Drummond Scientific Co., Broomall, Pennsylvania) have an internal diameter of 1.0 mm and a length of 116 mm. They were coated on the inside with several layers of warm agarose, (5-A426, standard low electroendosmosis, J.T. Baker Chemical Co., Phillipsburg, New Jersey), in phosphate-buffered saline (PBS/10) solution, which was allowed to gel upon cooling. The PBS/10 solution of pH 7.3–7.5 and ionic strength (Γ/2) of 0.015 M consisted of 1 L of 0.880 g NaCl, 0.022 g KH_2PO_4, 0.119 g Na_2HPO_4, and distilled water. By using plastic tubing of appropriate internal diameter and length to draw the 2.5% warm (~55–60°C) agarose solution through the capillary and slowly blowing it out, a layer of agarose gel was deposited along the inner wall of the capillary. This procedure was repeated three or four times. Once a capillary was coated, a dilute particle suspension 0.05% (w/v) in PBS/10, of Γ/2 = 0.015 (ionic strength), could be drawn into the capillary. The particle suspensions were shaken lightly, and a few particles were aspirated into the capillary by suction; the capillary was then plugged at both ends with the same agarose gel.

After the capillary was placed into position and the potential applied, the particle velocities were measured immediately. Since individual clay crystals are too small to be observed using a microscope, aggregates were measured. Each sample was measured independently with at least three coated capillaries. The velocities of 6–12 aggregates in each capillary were taken in both directions and the average mobility was then calculated from these data and corrected for the true electrical length of the capillary and for the small electro-osmotic backflow caused by the slightly negatively charged agarose coating and plugs. The electric field strength was between 5.0 and 12.0 V/cm, from a DC power supply. In addition, the electrophoretic mobilities of standard glutaraldehyde-fixed human red blood cells in PBS/10 (Γ/2 = 0.015) were measured with this apparatus and found to be 2.07 μm s^{-1} v^{-1} cm which, within experimental error, was the same as published previously (van Oss *et al.*, 1974).

The ζ potential measurements can also be accomplished in a number of different ways such as with a Zetasizer (Malvern Instruments, Malvern, England) or an Automated Electrokinetics Analyzer (Pen Kem, Inc., Bedford Hills, New York).

RESULTS AND DISCUSSION

The observed contact angles of the various polar and apolar liquids on different clay particles of KGa-1b, KGa-2, PFl-1, SWy-2, STx-1, SAz-1 and SHCa-1 are listed in Table 2. The surface-tension components and the ζ potentials for these minerals are given in Table 3. The values of the apolar LW component of the surface tension of these clays are similar. However, the

Table 2. Contact angles (°) of test liquids from various clay minerals at 20°C.

Liquid	^{1}KGa-1b	^{1}KGa-2	^{1}PFl-1	^{2}SWy-2	^{2}STx-1	^{2}SHCa-1	^{2}SAz-1
1-bromonaphthalene	26.5	29.4	47.7	21.6 (2.4)	17.2 (1.8)	24.1 (1.0)	21.4 (3.1)
Diiodomethane	34.5	38.4	53.0	38.2 (1.7)	32.5 (1.4)	37.3 (2.7)	32.8 (4.1)
Ethylene glycol	23.3	25.6	43.6				
Formamide	27.2	31.5	51.8	27.3 (1.6)	7.4 (1.2)	13.8 (0.8)	13.1 (1.1)
Glycerol				44.8 (1.8)	34.1 (3.6)	25.6 (2.7)	26.8 (2.2)
Water	46.1	42.0	61.0	33.1 (1.4)	20.5 (2.8)	45.7 (1.5)	21.7 (2.6)
Pore size, $R \times 10^{-5}$ cm	2.29 (0.03)	1.15 (0.03)	2.62 (0.05)				

Number in parentheses is the standard deviation (°).
^{1} = Thin-layer wicking.
^{2} = Direct contact-angle measurements.

polar or Lewis acid-base parameters vary greatly depending on the mineral-surface properties.

Surface properties

Kaolinite (KGa-1b and KGa-2). The kaolinites are moderately hydrophilic ($\gamma^{\ominus}$ varies from 30 to 35 mJ/m^2) and have large negative ζ potentials.

Palygorskite (PFl-1). This mineral is mildly hydrophobic and has small negative ζ potential.

Smectites (SWy-2, STx-1, SAz-1 and SHCa-1). In general, smectites, in common with most materials, are primarily Lewis-base monopoles ($\gamma^{\oplus}$ is small), the value of the Lewis base parameter, $\gamma^{\ominus}$, varies from ~20 mJ/m^2 to ~50 mJ/m^2, depending on the specific clay, the magnitude of the layer charge, and the nature of the exchangeable cation. Most of these minerals are hydrophilic ($\gamma^{\ominus}$ >28 mJ/m^2; van Oss and Giese, 1995), except for SHca-1.

Electron-donicity of mineral surfaces

Table 3 shows that these clay minerals have typical values of γ^{LW} varying between 32 and 42 mJ/m^2 and small or zero values of $\gamma^{\oplus}$. The major variation lies in the $\gamma^{\ominus}$ values which range approximately from 20 to 50 mJ/m^2. The predominant electron-donicity can also be observed on other materials such as proteins, polysaccharides and other polymers (van Oss, 1994). Electron donicity is largely a consequence of the prevalence of oxygen in the Earth's lower atmosphere (≈20 vol.%) and in the Earth's surface (≈46.6 wt.%) (Klein and Hurlbut, 1993). The surface of an homogeneous dry polar solid is electron-donating only. Any electron-accepting capability occurs because the covalent and the electron-donor/electron-acceptor bonds between the atoms and/or molecules of the solid are completely coordinated inside the solid. Therefore, none of the covalent bonds is available for surface interactions, whereas either excess electron-donating or excess electron-accepting sites are available for surface interactions. On solid polar surfaces, these are most commonly excess electron-donating sites, thus making them monopolar electron-donors ($\gamma^{\oplus} \approx 0$) (van Oss *et al.*, 1997).

Colloidal stability

The particle potential ψ_0 and energies of interaction ΔG_{131} are model dependent. At present there are no reliable models for calculating the interaction energy and potential of particles having an irregular platy shape such as smectites. For a qualitative discussion of the behavior of the clays, a spherical shape and a radius of 1 µm are assumed. However, any errors made in the assumed radii do not significantly influence the results: errors only affect the scale of the free energies, but not the sign, or the relative values.

Colloidal stability, determined by the total free energy (ΔG_{131}^{TOT}) of interaction between two particles of the same material (1) immersed in a liquid (3), is favored when, at contact, $\Delta G_{131}^{TOT} > -1$ kT, especially when $\Delta G_{131}^{TOT} > 0$. Examination of the surface-tension components, the energies of interactions, and ζ poten-

Table 3. Surface-tension components and parameters (mJ/m^2), and ζ potentials (mV) of clay minerals in PBS/10 at 20°C.

Sample	γ_S^{LW}	$\gamma_S^{\oplus}$	$\gamma_S^{\ominus}$	ζ potential
KGa-1b	41.0	0.7	30.0	−49.2 (0.5)
KGa-2	39.6	0.5	34.9	−43.9 (1.5)
PFl-1	31.8	0.5	23.2	−24.2 (1.1)
SWy-2	40.9	0.4	44.6	−31.9 (1.6)
STx-1	42.8	0.9	48.6	−25.6 (1.8)
SHCa-1	40.8	3.2	20.7	−29.7 (1.2)
SAz-1	42.2	1.3	45.9	−21.0 (0.7)

Numbers in parentheses represent the standard deviation.

Table 4. Interaction energy, ΔG_{1w1}, (kT) of the clay particle immersed in aqueous solution at equilibrium distance ℓ_o = 0.157 nm, ionic strength $\Gamma/2$ = 0.015 and 20°C.

Particle	ΔG_{1w1}^{LW}	ΔG_{1w1}^{AB}	ΔG_{1w1}^{EL}	ΔG_{1w1}^{TOT}
KGa-1b	−730	5600	2640	7510
KGa-2	−640	11500	2100	13000
PFl-1	−230	−3100	640	−2690
SWy-2	−730	22400	1100	22800
STx-1	−860	24500	710	24400
SHCa-1	−730	−5070	960	−4800
SAz-1	−820	21000	480	20700

tials indicates that the stability of the stable suspensions is mostly related to the AB repulsive interaction, which is the direct result of the large surface electron donicity ($\gamma^{\ominus}$) of these clays (Table 4). Flocculation is largely caused by attractive AB (hydrophobic) interactions, and the van der Waals forces only make a secondary contribution (Table 4; see also van Oss *et al.*, 1990; Wu *et al.*, 1994).

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