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DLVO AND NON-DLVO INTERACTIONS IN HECTORITE

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Abstract—The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory sums the attractive van der Waals and repulsive electrostatic forces as a function of separation distance to predict the interaction between charged particles immersed in a liquid. In aqueous media, however, non-electrostatic *polar* (electron acceptor/electron donor or Lewis acid/base) forces between particles with high energy surfaces often are comparable to, or greater than, the components of DLVO theory. By means of contact angle measurements on smooth self-supporting clay films, the values of the polar surface forces (AB) and the van der Waals forces (LW) of hectorite were measured. Determinations of ζ were used to derive the electrostatic forces (EL). Calculations based on the values obtained for the EL, LW, and AB forces show that for smooth spheres with a radius of 1 μm in a $\geq$0.1 M NaCl solution a net attraction exists leading to flocculation. At NaCl concentrations of $\leq$0.01 M, a repulsion energy of about +500 to +1300 kT exists at separation distances $\leq$50 Å, preventing contact between particles, thus ensuring stability of the colloidal suspension. At these concentrations, theory predicts that small clay particles or edges of clay crystals having an effective radius of curvature $\leq$10 Å should be energetic enough to overcome the repulsion barrier which prevents flocculation. Experimentally, for NaCl solution concentrations of $\geq$0.1 M, suspensions of hectorite particles flocculated, whereas at concentrations of $\geq$0.01 M, the suspensions remained stable. These experimental results agree with the predictions made by summing all three forces, but contradict the calculations based on classical DLVO theory.

Key Words—Colloid, Contact angle, DLVO theory, Electrostatic forces, Hectorite, Polar forces.

INTRODUCTION

The forces between colloidal particles of clay minerals in aqueous suspensions are of great importance to many geological and industrial processes. For example, the rheologic properties of phyllosilicate minerals, neglecting impurities, are controlled by the relative magnitudes of their surface energy components. Until recently, these forces have been described in the context of the classical DLVO theory, named after its originators Derjaguin and Landau (1941) and Verwey and Overbeek (1948). This model, however, takes into consideration only the electrostatic (EL) and the Lifshitz-van der Waals electrodynamic (LW) forces; it does not take into account the polar forces that are often the dominant forces between particles in polar media (van Oss *et al.*, 1987a, 1987b, 1988a).

For some time, the presence of physical forces in colloidal systems other than the EL and LW was surmised, particularly for the interaction energies of particles separated by short distances ($\leq$50 Å). For example, Israelachvili and McGuiggan (1988), in their review of forces between surfaces in liquids, discussed several systems in which the presence of unaccountable attractive and repulsive forces were observed. They suggested that these deviations from classical DLVO theory were due to the existence of additional forces rather than to a complete breakdown in the DLVO theory. For clay particle interactions in particular, the additional repulsive forces could, in part, be attributed to hydration forces, but the origin of these forces was not clear. Low (1987) also concluded that at small interparticle distances an additional interaction force, which he ascribed to the hydration of the (001) surfaces, must be taken into account.

The additional forces, as mentioned above, are often referred to as "hydrophobic interactions" if particle-particle attraction exists, and as "hydration pressure" if particle-particle repulsion exists. The origin of these forces lies in electron acceptor-electron donor interactions (in the Lewis acid-base sense). The term polar (AB) forces is used to refer to all such interactions (van Oss *et al.*, 1987a, 1987b, 1988a, 1988c). The AB forces (which include hydrogen bonding), if strongly asymmetrical or monopolar, are responsible for the orientation of water molecules adsorbed on the surfaces of a clay mineral, and, as expected, water molecules oriented on the surface of one particle will repel water molecules oriented in the same manner on the surface of an adjacent particle (Parsegian *et al.*, 1985). If the orientation of the water molecules by the surface of the clay mineral is sufficiently strong, the two particles will not be able to approach each other, or, if particles are close together, they will be forced apart as additional oriented water molecules are adsorbed on the two surfaces. On the other hand, if the clay mineral's surface is more weakly monopolar, its capacity for orienting the most closely adsorbed water molecules is less pro-

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nounced, and the clay particles will approach each other under the influence of their net van der Waals (LW) attraction. Thus, the "solvation" (or "hydration") effects are, in the final analysis, caused by the orientation of adsorbed water molecules due to the monopolar AB forces, and these "hydration" effects are, in their turn, responsible for the medium-range to long-range influence of the underlying AB forces. Thus, the AB forces are capable of explaining the phenomena generally described as "solvation" effects. These solvation effects also explain why AB interactions are not as short-range as might be supposed.

In 1984, Chaudhury made a clear distinction between the AB forces occurring in colloidal systems and all three types of LW forces (Chaudhury, 1984; van Oss *et al.*, 1987a, 1987b, 1988a, 1988b; see also Fowkes, 1963). The omission of the AB forces, which may be one or two orders of magnitude greater than the EL and LW forces (van Oss *et al.*, 1988a), is the origin of most of the anomalies that were observed if the DLVO theory was used to interpret interfacial interactions in polar media (Girifalco and Good, 1957; Good and Girifalco, 1960; Fowkes, 1963).

The addition of AB forces to the EL and LW forces yields a new and potentially powerful theory capable of predicting many aspects of clay behavior and, particularly, the behavior of colloidal clay mineral suspensions. The purpose of the present study is to describe and explain the stability of hectorite suspensions and to illustrate the methodology behind the measurement of the individual components of the forces. As a test of the predictions of the classical and extended DLVO theories, hectorite suspensions in aqueous solutions of different NaCl molarities were prepared.

THEORY OF SURFACE ENERGY COMPONENTS

DLVO theory arrives at a free energy (Gibbs energy) of interaction between particles by summing the repulsive EL interactions and the attractive LW interactions as a function of particle separation (l) to arrive at a total free energy of interaction for a given separation. The problem is that the calculated curves of energy vs. particle separation often do not match experimental results, thus putting predictive values into a rather precarious position.

Classically, energy vs. distance diagrams only consider the sum of EL and apolar LW forces; but in polar and especially in aqueous media AB energies, whether repulsive or attractive, commonly are as much as 100 times greater than LW energies, and 10 or more times greater than EL energies at close range (10–50 Å). Thus, in aqueous solutions, the inclusion of AB forces is not a novel and supplementary refinement of the DLVO theory, but a drastic correction, which for the first time allows aqueous interactions to be calculated on a reasonably accurate scale.

Electrostatic forces (EL)

Repulsive electrostatic interactions between particles arise from unsatisfied electronic charges on the surfaces of the particles. In clay minerals, these charges are generally (but not always) negative and arise from structural cation substitutions. Because the layer charge of clay minerals is determined by the amount and kind of cationic substitution, the surface charge density is independent of salt concentration in the suspension solution. As explained below, however, the salt concentration is very important in the flocculation-deflocculation behavior of clay minerals.

In terms of the chemical formula, clay crystals are electrostatically neutral, but this is not true if the clay is added to water to form a suspension. As the clay particles become dispersed in water, some of the charge-balancing cations are desorbed and go into solution; very quickly, an equilibrium between the desorbing and adsorbing cations is reached. This fluctuating cation loss and gain means that as long as the clay is kept submersed it has a small, net negative charge. This negative charge, plus the (apparently unsatisfied) charge due to the unequal distribution of surface charge and charge-balancing cations, constitutes the electric potential of the clay particles, as manifested by their electrokinetic surface potential. It is this surface potential that is responsible for the clay's ability to remain in suspension, seemingly forever, in a polar solvent such as water. Although, as stated above, the charge density is an inherent property of a clay crystal and cannot be changed by the presence of cations in solution, the presence of cations can decrease the effect of the charge potential.

Double layer theory has been extensively used to evaluate the interaction of charged clay particles in salt solutions of various strengths. An extensive discussion of the role of double layer theory in clay colloid chemistry was given by van Olphen (1977); see also Overbeek (1952a).

Briefly, the Stern model of the double layer theory says that on the surface of a charged particle within a colloidal suspension are strongly bound counter-ions and water molecules. This static layer is referred to as either the Stern layer or the inner-Helmholtz plane. The next layer out from the particle surface and its associated Stern layer is the more diffuse outer-Helmholtz plane containing hydrated counter-ions along with water molecules that can orient more freely. Although the potential at the particle surface is known to decrease with distance from the particle, it cannot be measured because of the interference of the counter-ions and the water molecules in the inner- and outer-Helmholtz planes. What can be determined is the electrokinetic, or zeta potential (ζ). This is the potential at the plane that separates the particle and its bound water molecules from the freely moving water molecules of the

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solution. This plane is referred to as the slipping plane. Using electrophoresis to measure the velocity U of a particle through a liquid medium in an applied electric field and the Helmholtz-Smoluchowski equation, ζ can be obtained (assuming that the particle size is much larger than the thickness of the double layer and that ζ is fairly small, see, e.g., Overbeek and Wiersema, 1967; van Oss, 1975), as follows:

$$U_{EL} = \epsilon\zeta E/4\pi\eta, \quad (1)$$

where ϵ = the dielectric constant of the medium, ζ = the electric potential at the slipping plane, E = the applied field strength, and η = viscosity of the medium.

This equation assumes that $\kappa a > 100$ and $\zeta \leq 50$ mV. For particles with a = 10,000 Å, $\kappa a \approx 180$. For the very smallest particles, as an example, a = 1000 Å and the ionic strength, $\Gamma/2 = 0.01$, $1/\kappa = 56$ Å, giving $\kappa a = 18$. Thus, the value of ζ calculated with the von Smoluchowski equation is really more dependable than the Hückel equation. The very smallest particles might have a ζ that is 20% higher than the one assumed here, but, in any event, the ζ used was the median of the Gaussian distribution of all the ζ values measured.

From ζ, the potential at the particle surface (ψ_0) can be determined. For relatively small ζ values the two are related by:

$$\psi_0 = \zeta(1 + z/\alpha)e^{\kappa z}, \quad (2)$$

where z is the distance between the surface of the charged particle and the slipping plane (usually z is taken to be about 5 Å), α is the Stokes radius of the particles, and κ is the inverse Debye length (the Debye length is the thickness of the double layer) and is given by:

$$\kappa = \sqrt{4\pi e^2 \sum v_i^2\eta_i^2/\epsilon kT}, \quad (3)$$

where e is the charge of the electron (4.8×10^{-10} e.s.u. or 1.6×10^{-19} C), v_i = the valency of each ionic species, η_i = the number of ions of each species per cubic centimeter of bulk liquid, k = Boltzmann's constant (1.38×10^{-23} J/K), and T = the absolute temperature in degrees K. Values of the Debye length $1/\kappa$ for several aqueous 1-1, 1-2, and 2-2 electrolyte solutions can be found in van Oss (1975).

The electrostatic, or double-layer potential is always repulsive and is roughly exponential in distance dependence. As long as the value for ζ is between about 10 and 60 mV, the electrostatic interaction energy, or the free energy (ΔG_l^{EL}), between two spheres of radius R as a function of distance l can be calculated using:

$$\Delta G_l^{EL} = 0.5\epsilon R\psi_0^2 \ln[1 + \exp(-\kappa l)] \quad (4)$$

where ΔG_l^{EL} = electrostatic free energy component, at distance l from surface, ϵ = dielectric constant of the medium; for water $\epsilon \sim 80$, R = radius of curvature of the particle, and ψ_0 = potential at the particle surface, in electrostatic volts.

Lifshitz-van der Waals apolar forces (LW)

Lifshitz-van der Waals apolar electrodynamic forces (LW) consist of: (1) randomly oriented permanent dipole-permanent dipole (orientation) interactions (described by Keesom and reported by van Oss *et al.*, 1988a), (2) randomly oriented permanent dipole-induced dipole (induction) interactions (described by Debye and reported by Chaudhury, 1984; van Oss *et al.*, 1988a), and (3) fluctuating dipole-induced dipole (dispersion forces) (described by London and reported by Overbeek, 1952b; Mahanty and Ninham, 1976). Each of these interactions decays rapidly with distance as l^{-6}.

Given that l_0 is the equilibrium distance and R (the radius of a sphere) $\gg l$, the apolar component of the free energy of interaction for two spheres is:

$$\Delta G_l^{LW} = -AR/12l = \Delta G_{l_0}^{LW}(Rl_0)/12l, \quad (5)$$

where ΔG^{LW} = apolar free energy component (LW), A = Hamaker constant, and l = distance from surface.

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

$$2\gamma^{LW} = -\Delta G_{l_0}^{LW} = A/12\pi l_0^2, \quad (6)$$

provided the apolar surface tension component, γ^{LW}, of the condensed material is known. Although A applies to all three electrodynamic interactions (dispersion, orientation, and induction; see Chaudhury, 1984), $A_{dispersion}$ is usually the main significant term in condensed media (van Oss *et al.*, 1988a).

LW forces normally are attractive, but may be repulsive in interactions between two *different* materials suspended in a liquid, depending on the properties of the materials and the liquid in which they are immersed; for the conditions described in the present paper, the LW forces are attractive.

In general, the free energy change of a solid (S) or liquid (L) can be expressed as a function of its surface tension or surface energy, (γ):

$$\Delta G = -2\gamma, \quad (7)$$

and more specifically for the LW interactions:

$$\Delta G^{LW} = -2\gamma^{LW}. \quad (8)$$

For Lifshitz-van der Waals interactions between any materials 1 and 2, the Good-Girifalco-Fowkes combining rule (Good and Girifalco, 1960; Fowkes, 1963) is applicable:

$$\gamma_{12}^{LW} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2, \quad (9)$$

which may also be written as:

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$$\gamma_{12}^{LW} = \gamma_1^{LW} + \gamma_2^{LW} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}\,. \quad (10)$$

The free energy of interaction between materials 1 and 2 can be written according to the Dupré equation (Dupré, 1869):

$$\Delta G_{12}^{LW} = \gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW}. \quad (11)$$

To derive values for the non-polar surface energy γ_S^{LW}, but only for those instances in which, besides EL forces, no other energy components are present, the Young-Good-Girifalco Fowkes equation (van Oss *et al.*, 1988a) can be used:

$$1 + \cos\theta = 2\sqrt{\gamma_S^{LW}/\gamma_L}, \quad (12)$$

where θ is the contact angle measured for a drop of an apolar liquid placed on the surface of the solid.

Polar (AB) surface tension parameters of a solid

The polar (AB) surface-energy parameters include all Lewis electron-acceptor-electron-donor, or Lewis acid-base (AB) interactions. Because Lewis acid-base interactions include hydrogen-donor and hydrogen-acceptor interactions, the hydrogen-bonding interactions are always included in AB interactions. The total surface energy can be broken down into two main (additive) components (Fowkes, 1963; Chaudhury, 1984; van Oss *et al.*, 1987a, 1987b, 1988a, 1988b):

$$\gamma = \gamma^{LW} + \gamma^{AB}. \quad (13)$$

Because the asymmetry of AB forces must always be taken into account, the (non-additive) electron-acceptor (γ^+) and electron-donor (γ^-) parameters of the polar component (γ_i^{AB}) of the surface energy of compound i are expressed as:

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+\gamma_i^-}, \quad (14)$$

(van Oss *et al.*, 1987, 1988), and the polar components of the free energy of interaction between materials 1 and 2 are expressed as:

$$\Delta G_{12}^{AB} = -2\left(\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right). \quad (15)$$

From the Dupré equation (Eq. (11)), which is also valid for AB interactions, and from Eqs. (9), (13), (14), and (15):

$$\gamma_{12} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 + 2\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}\right). \quad (16)$$

Expressing the Young-Dupré equation as:

$$(1 + \cos\theta)\gamma_L = -\Delta G_{SL}^{tot}, \quad (17)$$

where S and L = solid and liquid, respectively, and taking into account that

$$\Delta G^{tot} = \Delta G^{LW} + \Delta G^{AB}, \quad (18)$$

the relation

$$(1 + \cos\theta)\gamma_L = -\Delta G_{SL}^{LW} - \Delta G_{SL}^{AB} \quad (19)$$

is obtained, which upon combination with Eq. (10), (11), and (14), becomes

$$(1 + \cos\theta)\gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right). \quad (20)$$

Thus, to obtain all these parameters (γ_S^{LW}, γ_S^+, and γ_S^-) of the solid, contact angles must be determined with at least three liquids, of which two must be polar (van Oss *et al.*, 1987a, 1988a).

The equation describing the decay with distance of the AB free energy (ΔG_l^{AB}) for two spheres is:

$$\Delta G_l^{AB} = \pi R\lambda\Delta G_{l_0}^{AB} e^{(l_0 - l)/\lambda}, \quad (21)$$

where R = radius of curvature of the particle, λ = the decay length of the liquid molecules here taken as $\lambda \approx 10$ Å for water, $\Delta G_{l_0}^{AB}$ is the free energy of interaction in the parallel flat plate conformation, at the minimum equilibrium distance l_0, as measured by contact angle determinations, where $\Delta G_{l_0}^{AB} = -2\gamma^{AB}$.

Theoretically, if liquid water were not hydrogen bonded, the value for λ would be close to 2 Å (Chan *et al.*, 1979), but about 10% of the water molecules engage in hydrogen bonding so that $\lambda \approx 10$ Å seems a more reasonable estimate. Recent experiments have reported values of λ as high as 130 Å (Christenson, 1988; Rabinovich and Derjaguin, 1988), but various artifacts, due to minute surface irregularities on the coated surface of the force balances used, were probably responsible for these large values. Using

$$\Delta G = \Delta G^{EL} + \Delta G^{LW} + \Delta G^{AB}, \quad (22)$$

a total free energy vs. distance curve can be constructed taking into account the polar AB, the apolar LW, and the electrostatic EL forces and, by varying κ (see Eqs. (2)–(4)), separate curves can be constructed for specific salt concentrations.

MATERIALS AND METHODS

Materials

The hectorite clay used in this study was from Hector, California (sample SHCa-1, from the Clay Mineral Repository of the Clay Minerals Society) and has the

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composition $(Na_{0.28}K_{0.01}Ca_{0.01})(Mg_{2.65}Li_{0.33}Al_{0.02})Si_4O_{10}(OH)_{1.35}F_{0.65}$ (Ames *et al.*, 1958). Hectorite was chosen for several reasons. It is an important mineral both industrially and scientifically. Because the clay is thixotropic, smooth self-supporting films can be easily fabricated. Hectorite, however, commonly has fine-grained calcite as an impurity. The SHCa-1 sample used in the present study contained both calcite and a small amount of dolomite. The clay was purified by repeated dispersal in distilled water, followed by centrifugation. The <2-μm fraction was used for the contact angle measurements. This fraction contained neither calcite nor dolomite as indicated by X-ray powder diffraction, and no reaction to HCl treatment was noted. In the infrared spectrum, a small amount of carbonate was visible; this impurity had no effect on the contact angle experiments. The average particle size present in aqueous suspensions was 2.8 μm as determined by analysis with a Malvern Particle Sizer model 3000 E.

The α-bromonaphthaline, diiodomethane, formamide, and glycerol were all analytical grade, and the water was triply distilled.

Fabrication of films

Self-supporting hectorite films were made by the evaporation of dilute (1 to 4%) hectorite-water suspensions. Only the fine fraction, collected by 6 min of centrifugation at 600 rpm, of a 4 wt. % hectorite suspension was used. The suspensions were deposited and dried on a variety of materials, including mica sheets, polystyrene, and sheets of various commercial polymer films.

Güven (1988) described the morphology of hectorite as that of extremely thin ribbons or laths, having lengths ranging from 0.1 and 2 μm, widths ranging from 0.05 and 0.2 μm, and being just a few layers thick (one layer is about 10 Å thick).

Contact angle measurements

The surface tension of the liquids used in the contact angle measurements is easily determined or can, for many, be found in published tables (see Jasper, 1972, for example). After a film had been 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 telescope equipped with a goniometer (Gaertner, Chicago). Using Teflon syringes (Gilmont), a drop of liquid was placed on the surface of the clay film and the advancing contact angle was measured on both sides of the drop. For a complete discussion on methods of measuring contact angles, see Neumann and Good (1979).

The contact angles measured on smooth hectorite films using drops of α-bromonaphthaline and diiodomethane were used to determine the value of γ_S^{LW} of the hectorite film using Eq. (12). The contact angles measured with the polar liquids (water, formamide, and glycerol) were used to determine the contributions of the two parameters γ^+ and γ^- of the polar surface tension γ_S^{AB} of hectorite, using Eq. (20).

The contact angles were measured at 20°C. Given the conditions of relative humidity under which the contact angles were measured, the surface of the hectorite film was undoubtedly covered by a monolayer of water. The adsorbed water could not be completely removed from the hectorite films; this was not a problem, because the aim of this study was to examine a clay mineral under conditions reasonably similar to those in a geological environment.

Electrophoresis

The initial electrophoretic measurements were made with a microelectrophoresis device described by van Oss *et al.* (1974), in which a microscope was used to observe the mobility of particles moving through a capillary tube coated with agarose under the influence of an applied potential. Because individual clay crystals cannot be seen using a binocular microscope, aggregates were observed. A very small amount of untreated hectorite was dispersed in a 0.01 M NaCl solution in the capillary tube. The clay-salt solution mixture was shaken, the capillary placed into position, and the particle velocities were immediately noted. Even though the hectorite used was not purified, the effect of Ca ions in the suspension solution was negligible because the calcium occurs in the form of calcite, and the mobility measurement was made too quickly to allow significant numbers of Ca ions to go into solution.

The second set of measurements were made with a 0.04% suspension of the fine fraction of hectorite dispersed in a 0.01 M NaCl solution, using a Malvern Zetasizer 2C instrument. Field reversals were used in both sets of measurements. Determinations of ζ from this set of electrophoretic measurements (Overbeek and Wiersema, 1967; van Oss, 1975) were used to calculate the potential at the surface of the particle.

RESULTS AND DISCUSSION

The initial electrophoresis measurements gave a ζ value of -44 mV; the second set yielded an average value of -38 mV (the two values are within experimental error). All calculations reported here were based on the second set of measurements. The surface tension parameters for the apolar and polar liquids used are given in Table 1. The contact angles of the various polar and apolar liquids on hectorite films are listed in Table 2; the values for γ_S^{LW} and the γ_S^+ and γ_S^- parameters of γ_S^{AB} are given in Table 3. The much larger value measured for the contribution of the polar electron-donor parameter, γ_S^-, relative to the polar electron-acceptor parameter, γ_S^+, to the surface energy of the hectorite clay reflects the oxygen-rich outer surfaces (001) of hectorite.

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Table 1. Surface tension parameters for apolar and polar liquids used to measure contact angles.

Liquid	γ_L	γ_L^{LW}	γ_L^{+}[3]	γ_L^{-}[3]
α-Bromonaphthaline[1]	44.4	44.4	—	—
Diiodomethane[1]	50.8	50.8	—	—
Water[2]	72.8	21.8	25.5[4]	25.5[4]
Glycerol[2]	64	34	3.92	57.4
Formamide[2]	58	39	2.28	39.6

Surface tension components and parameters are reported in mJ/m².

[1] Apolar liquids: $\gamma_L = \gamma_L^{LW}$; $\gamma_L^{+} + \gamma_L^{-} = 0$.

[2] Polar liquids: $\gamma_L = \gamma_L^{LW} + \gamma_L^{AB}$.

[3] γ_L^{-} and γ_S^{+} are the non-additive parameters of the γ_L^{AB} contribution to the total free energy.

[4] These are taken to be equal by convention (van Oss *et al.*, 1987a, 1988a).

Table 2. Advancing contact angles of the various polar and apolar liquids on hectorite films.

Liquids	Observed contact angles	Calculated contact angles
α-Bromonaphthaline	20.0°	26.4°
Diiodomethane	43.0°	39.4°
Water	63.0°	60.9°
Glycerol	67.5°	63.1°
Formamide	57.3°	52.1°

The calculated contact angles were determined using Young's equation and the parameters listed in Table 3.

Table 3. Values for components of the surface energy of hectorite as deterined from contact angle measurements (reported in mJ/m²).

Component	Value
γ_S^{LW}	39.9
γ_S^{-}	23.7
γ_S^{+}	0.

γ_S^{+} and γ_S^{-} are the non-additive parameters of the γ_S^{AB} contribution to the total free energy as described in the text.

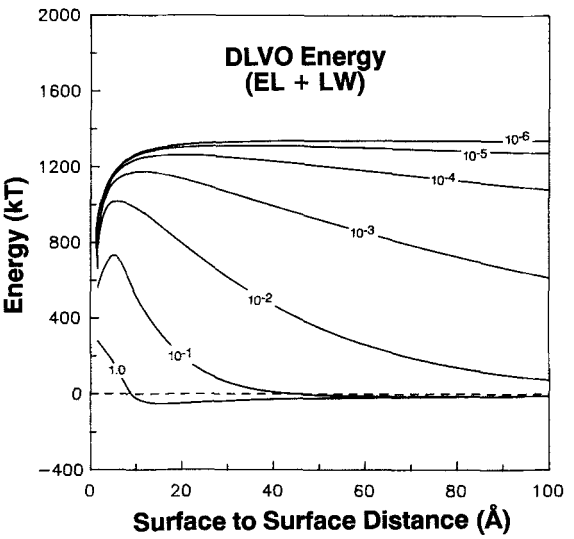


Figure 1. Free energy curves obtained using classical DLVO theory for 1 μm hectorite particles in various concentrations of NaCl solution, showing that no flocculation should occur because of energy maximum at small inter-particle distances.

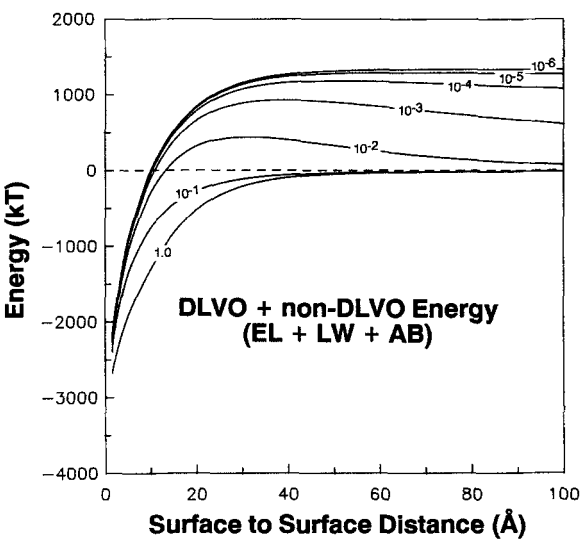


Figure 2. Free energy curves obtained if polar AB forces are included in total free energy of interaction curves, for hectorite particles with radius of 1 μm in various concentrations of NaCl solution. These curves show that flocculation should occur in all hectorite-NaCl solution suspensions if NaCl concentration is equal to or greater than 0.1 M.

Role of electrolyte concentration

In classical DLVO theory EL and LW forces are the only contributors to the free energy of particle interaction. The total DLVO energy was calculated for hectorite-NaCl suspensions as a function of the distance between the surfaces of two spherical particles, using various concentrations of NaCl (Figure 1). The Born repulsion energy was not calculated; the minimum contact distance between the surfaces of two particles was taken to be 1.5 Å (van Oss *et al.*, 1988a). DLVO theory predicts that hectorite-NaCl solution suspensions should be stable, i.e., no flocculation should occur, for all the salt concentrations included in the calculations, because a substantial repulsive barrier exists which prevents the particles from approaching each other. The extended DLVO theory, which includes the polar AB forces, predicts that flocculation should occur in all hectorite-NaCl solution suspensions if the NaCl concentration is equal to or greater than 0.1 M (Figure 2).

To test the predictions of the classical DLVO and the extended DLVO theories, two sets of four hectorite-water suspensions (1% and 4% suspensions) were pre-

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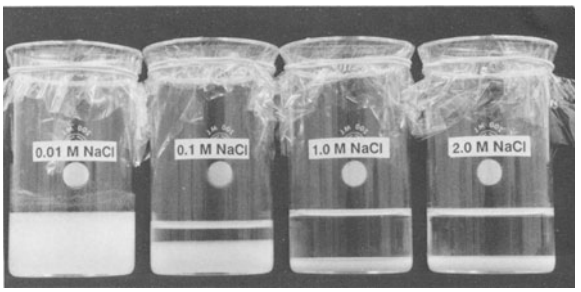


Figure 3. Suspensions of hectorite (1 wt. %) in NaCl aqueous solutions of different molarities. The flocculation behavior closely follows the predictions of the extended DLVO theory as shown in Figure 2.

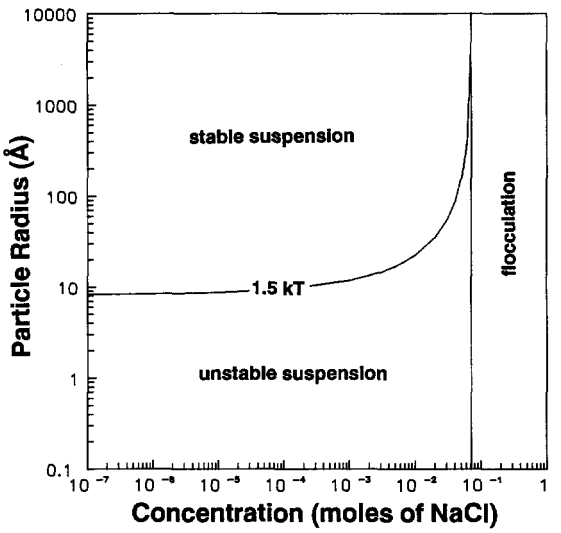


Figure 4. Fields of stability and flocculation for suspensions of hectorite as function of particle radius and NaCl concentration.

pared. Each set included 2.0, 1.0, 0.1, and 0.01 M NaCl concentrations. Although the potential at the surface of a particle is independent of the ionic strength of the aqueous solution, it is dependent on the pH of the solution; the pH may be changed by varying the ionic strength. The pH of the hectorite suspensions encountered in the flocculation experiment ranged between 6.9 and 8.4. A separate set of ζ potential measurements was made covering this range of pH, and the resulting values indicated that the observed change in ζ was within experimental error. Gelling was not a problem in monitoring flocculation behavior, because it did not occur for hectorite suspensions of $\leq 3\%$ solids. A thixotropic gel can form in a 4% hectorite suspension in either pure or dilute salt solutions, as was observed in the 4% hectorite-0.01 M NaCl solution mixture.

For both sets, the suspensions in 1.0 and 2.0 M NaCl flocculated and settled out, the suspensions in 0.1 M NaCl partially flocculated, although much more so for the 1% suspension (Figure 3) than for the 4% suspension (not shown in Figure), and the suspensions in 0.01 M NaCl remained stable. The flocculation occurred within 24 hr (overnight), and the stable suspensions remained so for several months. These results are in close agreement with the extended DLVO calculations and indicate that the classical DLVO theory is inapplicable for hectorite (and perhaps for all smectites) dispersed in aqueous electrolyte solutions.

The lack of agreement between theory and experiment using only the classical DLVO theory, compared with the good agreement between theory and experiment using DLVO plus non-DLVO forces, is not surprising. Theoretical prediction and experimental observations of non-DLVO forces are as old or older than the theory itself (Christenson, 1988).

Role of effective particle radius

As the radius of a macro-ion or particle decreases, its repulsive interaction energy ΔG^{EL} decreases for a given electrostatic potential (see Eq. (4)). This effect was investigated to see if it influenced the flocculation behavior of hectorite particles. Calculations of ΔG suggest that reducing R, for a fixed salt concentration, can lower the energy barrier to ~ 1.5 kT (the energy of Brownian motion), which is sufficiently small to allow flocculation. Figure 4 shows that for a given concentration of NaCl solution, a critical hectorite particle size exists above which the suspension should remain stable due to the dominance of repulsive EL interaction forces, and below which the repulsive interaction forces are ~ 1.5 kT. As an example, hectorite dispersed in an aqueous solution having a concentration of 0.01 M NaCl will be stable for particles having an effective radius ≥ 20 Å. The illustration shows that flocculation should occur if the effective radius of a significant proportion of the hectorite particles is smaller than this value. The extended DLVO theory predicts (Figure 2) that hectorite dispersed in a 0.01 M NaCl solution should not flocculate. The experiment described earlier is in agreement (Figure 3), as expected, inasmuch as few hectorite particles probably had an effective radius of ≤ 20 Å.

Eqs. (4), (5), and (21) show that R is directly related to ΔG, which indicates that as R decreases the energy barrier decreases along with the depth of the energy well. This means that even though particles having a sufficiently small R, at a given salt concentration, can approach each other to the contact point, their mutual attraction is weak and this may inhibit flocculation. Overbeek (1988) stated, however, that if two particles of the same sign but of different potential approach each other nearly to the contact distance, the particle having the greater potential can induce a sign change in the particle having the smaller potential, causing attraction. In 1954, Derjaguin showed (see his Eq. (18)) that this behavior should occur for particles having the

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same sign of charge dispersed in a relatively dilute electrolyte with potentials differing by as much as about 60%. Thus, reducing R to the critical value allows clay particles to approach each other, and, if the potentials of the particles are sufficiently different, the change of sign will increase the electrostatic attraction between them, thereby promoting attraction and flocculation. A somewhat analogous behavior was observed for the adhesion of erythrocyte cells in dilute dextran solutions (van Oss and Coakley, 1988).

Role of induced charges

Under appropriate pH conditions, edge-to-face attraction between clay particles may possibly result from the basal surfaces of clay crystals having a negatively charged double layer, whereas a positively charged double layer exists at the edges of the crystals. The lack of structural continuity at the crystal edges leaves some cations incompletely compensated, resulting in a charge imbalance. This supposition appears to be supported by electron micrographs that show the preferential edge adsorption of negatively charged gold particles on the edges of kaolinite crystals (Thiessen, 1942, 1947) and by the fact that clays exhibit a certain degree of anion exchange capacity (van Olphen, 1977).

The phenomenon of induced change of sign of charge and the role that the radius of curvature (R) plays in reducing repulsive energy barriers suggest that positive charges on edge sites of clay particles need not always be invoked to explain the attraction of negatively charged species; if the size of the anionic particles is small enough, as for the gold particles mentioned above, they may easily be attracted to crystal edges of small effective radius.

CONCLUSIONS

Although the rheological properties of clay minerals depend in large part on the values of the components of their surface energies, which in turn determine how a clay mineral will behave in any given process, very little is known about the absolute values of these surface energy components. For example, classical DLVO theory does not accurately predict flocculation behavior of hectorite suspensions in saline solutions. Adding the AB forces to the DLVO forces, however, allows a much more accurate prediction of the ionic strength at which flocculation occurs.

Knowing the values of all the surface tension parameters of clay minerals, leading to the quantitative expression of their AB interactions, has tremendous potential. Some of the areas in which these measurements could find application include separation science (see also van Oss *et al.,* 1987b) and its converse, the ability to mix select quantities of different clays to obtain desired properties; clay catalysis especially in the pillared clays; and in the design of clay minerals having required surface characteristics.

In the present paper only the results of the DLVO and non-DLVO free energy curves as applied to the clay mineral hectorite have been discussed. For this mineral a self-supporting film can be used to make the required contact angle measurements. For other clays, however, such as talc and kaolinite, other methods of contact angle measurement must be used.

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REFERENCES

Ames, L. L., Jr., Sand, L. B., and Goldrich, S. S. (1958) A contribution on the Hector, California bentonite deposit: *Geochem. Cosmochim. Acta* **47,** 363–375.

Chan, D. Y. C., Mitchell, D. J., Ninham, B. W., and Pailthorpe, B. A. (1979) in *Water, Vol. 6,* F. Franks, ed., Plenum, New York, 239–278.

Chaudhury, M. K. (1984) Short range and long range forces in colloidal and macroscopic systems: Ph.D. thesis, SUNY at Buffalo, Buffalo, New York, 215 pp.

Christenson, H. K. (1988) Non-DLVO forces between surfaces—Solvation, hydration and capillary effects: *J. Dispersion Sci. Technol.* **9,** 171–206.

Derjaguin, B. V. and Landau, L. (1941) *Acta Physicochim. U.S.S.R. 14,* p. 633 (see also Derjaguin, 1954).

Derjaguin, B. V. (1954) A theory of the heterocoagulation, interaction and adhesion of dissimilar particles in solutions of electrolytes: *Discuss. Faraday Soc.* **18,** 85–98.

Dupré, A. (1869) *Théorie Mécanique de la Chaleur:* Gauthier-Villars, Paris, 484 pp.

Fowkes, F. M. J. (1963) Addition of intermolecular forces at interfaces: *J. Phys. Chem.* **67,** 2538–2541.

Girifalco, L. A. and Good, R. J. (1957) A theory for the estimation of surface and interfacial energies. I. Derivation and application to interfacial tension: *J. Phys. Chem.* **61,** 904–909.

Good, R. J. and Girifalco, L. A. (1960) A theory for the estimation of surface and interfacial energies. III, Estimation of surface energies of solids from contact angle data: *J. Phys. Chem.* **64,** 561–565.

Güven, N. (1988) Smectites: in *Hydrous phyllosilicates other than micas,* S. W. Bailey, ed., *Reviews in Mineralogy, 19,* Mineralogical Society of America, Washington, D.C., 497–560.

Israelachvili, J. N. and McGuiggan, P. M. (1988) Forces between surfaces in liquids: *Science* **241,**795–800.

Jasper, J. J. (1972) The surface tension of pure liquid compounds: *J. Phys. Chem. Ref. Data* **1,** 841–1010.

Low, P. F. (1987) Structural component of the swelling pressure of clays: *Langmuir* **3,** 18–25.

Mahanty, J. and Ninham, B. W. (1976) *Dispersion Forces:* Academic Press, New York, 236 pp.

Neumann, A. W. and Good, R. J. (1979) Techniques of measuring contact angles: in *Surface and Colloid Science, Vol. 2,* R. J. Good and R. R. Stromberg, eds., Plenum Press, New York, 348 pp.

Overbeek, J. Th. G. (1988) Double-layer interaction between spheres with unequal surface potentials: *J. Chem. Soc. Faraday Trans. 1,* **84,** 3079–3091.

Overbeek, J. Th. G. (1952a) Electrokinetics: in *Colloid Science, Vol. 1,* H. R. Kruyt, ed., Elsevier, Amsterdam,194–244.

https://doi.org/10.1346/CCMN.1990.0380206 Published online by Cambridge University Press

Overbeek, J. Th. G. (1952b) The interaction between colloidal particles: in *Colloid Science, Vol. 1,* H. R. Kruyt, ed., Elsevier, Amsterdam, 245–277.

Overbeek, J. Th. G. and Wiersema, P. H. (1967) Interpretation of electrophoretic mobilities: in *Electrophoresis, Vol. 2,* M. Bier, ed., Academic Press, New York, 1–52.

Parsegian, V. A., Rand, R. P., and Rau, D. C. (1985) Hydration forces: What next?: *Chemica Scripta* **25,** 28–31.

Rabinovich, Y. I. and Derjaguin, B. V. (1988) Interaction of hydrophobized filaments in aqueous electrolyte solutions: *Colloids Surfaces* **30,** 243–251.

Thiessen, P. A. (1942) Wechselseitige Adsorption von Kolloiden: *Z. Elektrochem.* **48,** 675–681.

Thiessen, P. A. (1947) Kennzeichnung submikroskopischer Grenzflächenbereiche verschiedener Wirksamkeit: *Z. Anorg. Chem.* **253,** 161–169.

van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry:* 2nd ed., Wiley, New York, 318 pp.

van Oss, C. J. (1975) The influence of the size and shape of molecules and particles on their electrophoretic mobility: *Separ. Purif. Meth.* **4,** 167–188.

van Oss, C. J., Chaudhury, M. K., and Good, R. J. (1987a) Monopolar surfaces: *Advances Colloid and Interface Sci.* **28,** 35–64.

van Oss, C. J., Chaudhury, M. K., and Good, R. J. (1988a) Interfacial Lifshitz-van der Waals and polar interactions in macroscopic systems: *Chem. Rev.* **88,** 927–941.

van Oss, C. J. and Coakley, W. T. (1988) Mechanisms of successive modes of erythrocyte stability and instability in the presence of various polymers: *Cell Biophys.* **13,** 141–150.

van Oss, C. J., Fike, R. M., Good, R. J., and Reinig, J. M. (1974) Cell microelectrophoresis simplified by the reduction and uniformization of the electro-osmotic backflow: *Anal. Biochem.* **60,** 242–251.

van Oss, C. J., Good, R. J., and Chaudhury, M. K. (1987b) Determination of the hydrophobic interaction energy—Application to separation processes: *Sep. Sci. Tech.* **22,** 1–24.

van Oss, C. J., Good, R. J., and Chaudhury, M. K. (1988b) Additive and nonadditive surface tension components and the interpretation of contact angles: *Langmuir* **4,** 884–891.

van Oss, C. J., Good, R. J., and Chaudhury, M. K. (1988c) Estimation of the polar parameters of the surface tensions of liquids or contact angle measurements of gels: in *Membrane Fusion,* S. Ohki, D. Doyle, T. D. Flanagan, S. W. Hui, E. Mayhew, eds., Plenum, New York, 113–122.

Verwey, E. J. W. and Overbeek, J. Th. G. (1948) *Theory of the Stability of Lyophobic Colloids:* Elsevier, Amsterdam, 205 pp.

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