



Review

A review of non-DLVO interactions in environmental colloidal systems

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Abstract

The interaction and behavior of surfaces or colloids is of quantitative significance in understanding the transport and fate of compounds and microorganisms in environmental systems. Historically, the DLVO model of colloid stability has described these interactions. This model finds its basis in a force (energy) balance that comprises attractive van der Waals and repulsive electrostatic interactions. Recently, the DLVO model has been found unable to fully describe biotic and abiotic colloidal behavior in aqueous media. The suspending phase (commonly water) is often treated as a force (energy) transmitting or propagating medium. It is reasonable to believe that the structure of water may participate in a more significant fashion. Moreover, other moieties (sorbed and dissolved) may also have non-DLVO effects. Significant work has been focused on extending the precepts of the traditional DLVO model to accommodate these non-DLVO forces (energies). This paper reviews many of the interactions that play a role in environmental systems and are not commonly subsumed by the traditional DLVO model: e.g., hydrogen bonding and the hydrophobic effect, hydration pressure, non-charge transfer Lewis acid base interactions, and steric interactions.

1. Introduction

Environmental systems by their nature are comprised of interfaces. These interfaces may exist in a variety of forms (e.g., solid-solid, solid-liquid, liquid-liquid, liquid-gas, solid-gas) and impact the fate and transport of contaminants and microorganisms. The scientific and engineering community has devoted significant effort to exploring the nature of these interfaces and developing mathematical models to describe interacting force and energy fields. Although significant advances have been made in our understanding of these interactions, major portions of the environmental engineering and science community have ignored the larger body of knowledge addressing these advances. For example, recent (as late as 2001) textbooks

on environmental engineering continue to espouse unqualified classical DLVO theory to describe colloid stability in aqueous media, even when many cases have been documented where this approach does not suffice (*inter alia*, Chedda & Grasso 1994; Grasso et al. 1995). Indeed, in 1999, the journal *Colloids and Surfaces B: Biointerfaces* (Volume 14) dedicated a special issue commemorating the 50th anniversary of DLVO theory. A significant portion of the issue was devoted to extending the model by exploring non-DLVO interactions. Figure 1 presents a summary scheme of the various interactions discussed in this paper, which may be influential in governing colloidal processes and stability in environmental systems. After a brief review of the classical DLVO approach, an overview of various interactions not typically

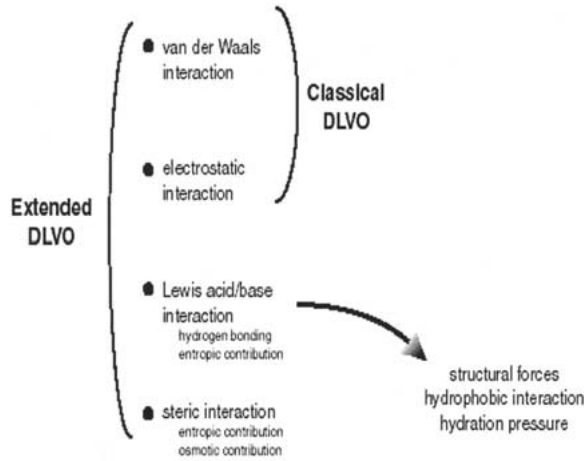


Figure 1. General scheme of interactions influential in governing environmental colloidal processes and stability.

subsumed by traditional approaches and that may be influential in governing environmental colloidal processes and stability is presented. Since most environmentally related colloidal processes occur in the nanometer spatial domain, near field interactions, such as Born repulsion, are not addressed here.

2. A brief review of the classical DLVO approach

The first successful attempts to quantitatively describe colloidal stability interactions were conducted in Russia (Derjaguin & Landau 1941) and the Netherlands (Verwey & Overbeek 1948) and resulted in the now famous DLVO (Derjaguin-Landau-Verwey-Overbeek) model. The development of classical DLVO theory for colloidal stability had been traditionally accepted to be inclusive of all primary interfacial forces of significance. DLVO theory was developed by balancing attractive dispersion (London-van der Waals) and repulsive electrostatic coulombic forces. Both van der Waals (vdW; now expanded to include dispersion, induction and orientation Lifshitz-van der Waals interactions) and Coulombic forces can be either repulsive or attractive depending on chemical structure, suspending medium properties, and surface potential. More recently, other primary forces have been implicated in surface interactions. Furthermore, of the original two primary forces (vdW and electrostatic forces), it was recently argued that these two interaction energies cannot be considered separately (Ninham et al. 1997; Ninham & Yaminsky 1997; Ninham 1999). However, since this remains a point of

controversy and since present and accepted models of molecular forces as applied to natural and engineered systems treat these interaction energies separately, we will follow standard practice in the brief discussion of traditional DLVO interactions presented here.

2.1 Electrostatic interactions

The mathematics that describe the electrostatic force find their origin in the Poisson–Boltzmann distribution (see Israelachvili 1992). Numerous models have been developed from this fundamental relationship. Simplified models are based on assumptions about particle surface charge and potential, and particle geometry (see Elimelech et al. 1995). An electrostatic interaction energy model used to describe the commonly encountered geometry of a sphere, 1, and a flat plate, 2, in water, w , is given by (Gregory, 1975; see also Elimelech et al. 1995):

$$\Delta G_{1w2}^{EL} = 64\pi\alpha\epsilon\epsilon_o \left[\frac{kT}{ze} \right]^2 \beta_1\beta_2 \exp(-\kappa h) \quad (1)$$

where

$$\beta_i = \tanh \left[\frac{ze\psi_o}{4kT} \right] \quad (2)$$

where

- α = particle radius, m
- ϵ = dielectric constant of the medium
- ϵ_o = permittivity in a vacuum, $\frac{C^2}{J \cdot m}$
- k = Boltzman's constant, $1.381E-23 \frac{J}{\sigma K}$
- T = temperature, °K
- z = valence of electrolyte
- e = electron charge, $1.602 \times 10^{-19} C$
- ψ_o = surface potential, V
- d = separation distance, m
- κ = reciprocal of the Debye length, m^{-1}

The reciprocal of the Debye length, κ , is given by:

$$\kappa = \sqrt{\frac{1000e^2N_A}{\epsilon kT} \sum_i z_i M_i} \quad (3)$$

where

- N_A = Avagadro's Number, 6.02×10^{23} molecules/mol
- M_i = molar concentration of electrolyte, mol/L

According to relationships [1] to [3], an increase in electrolyte concentration results in a decrease in the Debye length and concomitant reduction in electrostatic interaction energy, ΔG_{1w2}^{EL} . The strength of this Coulombic energy dissipates exponentially away from the surface. The reciprocal of the Debye length (κ) represents the center of mass of the diffuse counter ion cloud. At a specific salt concentration, known as the critical coagulation concentration, the electrostatic interaction force can be virtually neutralized. Changes in pH can also influence the range and magnitude of electrostatic forces. Reactions between protons and charged surface functional groups can change the net surface potential on a particle. At a surface specific pH, reactions between protons and surface functional groups can result in a net surface potential that approaches zero; the pH at which this occurs is called the isoelectric point (see Parks 1977).

2.2 Van der Waals interactions

The vdW interaction energy for the geometry described in §2.1 can be modeled as (Hunter 1986):

$$\Delta G_{1w2}^{vdW} = \frac{-A_{1w2}r}{6d} \left\{ 1 + \frac{d}{2r+d} + \frac{d}{r} \ln \left(\frac{d}{2r+d} \right) \right\} \quad (4)$$

where

$$A_{1w2} = \text{unretarded Hamaker constant (Hamaker 1934) for a sphere of radius, } r, \text{ and a flat plate suspended in water, } \approx (A_{11}^{1/2} - A_{ww}^{1/2})(A_{22}^{1/2} - A_{ww}^{1/2}), \text{ J}$$

The unretarded Hamaker constant is composed of nondispersion ($A_{v=0}$) and dispersion ($A_{v>0}$) components, such that (Mahanty & Ninham 1976; see also Israelachvili 1992):

$$A = A_{v=0} + A_{v>0} \quad (5)$$

For the simplified case of identical particles, 1, suspended in air, 3, Lifshitz continuum theory can be used to estimate the constitutive parts (Israelachvili 1992):

$$A_{v=0} = \frac{3}{4}kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 \quad (6)$$

$$A_{v>0} = \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \quad (7)$$

where

$$\begin{aligned} h &= \text{Planck's constant} = 6.626\text{E-}34 \text{ J s} \\ \nu_e &= \text{dominant electronic absorption frequency in the UV range, s}^{-1} \\ n &= \text{refractive index of material} \end{aligned}$$

Israelachvili (1992) reported that, in many cases, the approximations given by equations [6] and [7] yield similar results to those of the more rigorous relationships developed by Hough and White (1980). It should be noted here that London-van der Waals forces may be retarded because electrodynamic interactions that give rise to dispersion forces are propagated at the finite speed of electromagnetic radiation. Starting at distances of about 10 to 100 nm, in the time it takes for the electric field of one atom to reach a second atom and for the field caused by the induced dipole to return to the first atom, the trajectories of individual electrons change direction and the dipoles experience considerably weaker attraction (Israelachvili 1992; van Oss 1994). Retardation effects at various separation distances have been confirmed experimentally by Israelachvili and coworkers (1978, 1992). The effects of retardation vary with wavelength as well as with distance (van Oss 1994). Consequently, no single closed-form equation is available for calculating the influence of retardation as a function of separation distance.

3. Hydrogen bonding

Colloidal interactions in environmental systems most often take place in the presence of water molecules. Water has many unique characteristics that can be attributed to the propensity of molecules to hydrogen bond with itself or other moieties in solution or on surfaces. Although hydrogen bonds were not named as such until the early 20th century, the effect of hydrogen "bridges" and weak bonds on certain properties of substances had been observed by many early investigators (Pauling 1960). Measurements of the melting and boiling points of similar substances illustrate a decrease in the melting and boiling points with decreasing molecular weights, with the exception of H₂O as shown in Figure 2. Water possesses much higher melting and boiling points than expected from the trend of the series. This effect is now known to derive from the existence of hydrogen bonds between water molecules.

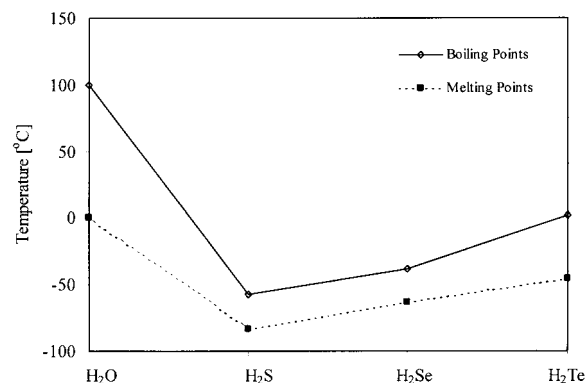
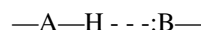


Figure 2. Melting and boiling points of a hydride series illustrating the relative importance of hydrogen bonding (adapted from Pauling 1960).

The hydrogen atom has only a single electron orbital ($1s$) and therefore cannot form more than one covalent bond (Pauling 1960). Hydrogen bonds occur when electronegative atoms bonded to hydrogen atoms draw electrons closer. This results in an “unshielded” proton, a Lewis acid, having an affinity for a group with a pair of available electrons, a Lewis base. A hydrogen bond between a group “B” functioning as a Lewis base, and a hydrogen atom bonded to atom “A”, may be conceptualized as:



where \cdots denotes a hydrogen bond, and $:$ is a lone electron pair.

The degree of electronegativity of the atom bonded to the hydrogen affects the nature of the hydrogen bond. Pauling (1960) presented the concept of partial ionic character of chemical bonds. Chemical bonds may not be completely ionic or covalent, but intermediate between the two extremes depending on the degree of electronegativity of the bonding atoms. Similarly, hydrogen bonds cover a continuum of properties due to the variability of the electronegativity of the atoms involved. Hydrogen bonds range from strong to weak; strong bonds have a predominately covalent nature, whereas weak bonds are mainly electrostatic (Table 1).

Hydrogen bonds are ubiquitous in environmental systems, where there is a predominance of polar entities in an aqueous medium. Gutowski (1991) reported energies between 1.9 and $6.0 \text{ kcal}\cdot\text{mol}^{-1}$ for hydrogen bonds involving chlorine, nitrogen, and oxygen. These values fall in the range of moderate and weak strength (Table 1). More specifically, C-

Table 1. Properties of hydrogen bonds (Jeffrey 1997)

Strength	Interaction	Bond lengths		Bond energy [kcal mol ⁻¹]
		H—:B [Å]	A—:B [Å]	
Strong	Mostly covalent	~1.2–1.5	2.2–2.5	14–40
Moderate	Mostly electrostatic	~1.5–2.2	2.5–3.2	4–15
Weak	Electrostatic	2.2–3.2	3.2–4.0	<4

H—O_w hydrogen bonds, and hydrogen bonds with π electrons tend to form weak hydrogen bonds (Jeffrey 1997). Moderate-strength hydrogen bonds can form with acids, alcohols, and biological molecules, while strong hydrogen bonds are possible with acid salts and HF complexes (Jeffrey 1997).

In water molecules, the oxygen atom with an electronegativity of 3.5 (Pauling 1960) draws electrons from hydrogen atoms that have electronegativities of 2.1. Thus, the oxygen atom has a high electron density as shown in Figure 3. This creates both electron acceptor (or proton donor) hydrogen atoms, and an electron donor (or proton acceptor) oxygen atom. The result is an attractive hydrogen bond between individual water molecules. Of the eight electrons that encircle the nucleus of the oxygen atom in a water molecule, two are close to the nucleus and unable to bond, two are involved with chemical bonds with hydrogen atoms, and two pairs are adjacent to the oxygen nucleus and available to hydrogen bond. While these two electron pairs may not be constrained to specific locations on the nucleus, they are available to hydrogen bond with two electron acceptors (or proton donors). Thus, each water molecule has two proton donor sites (the hydrogen atoms) and two proton acceptor sites (the two lone electron pairs).

These four hydrogen-bonding locations on water molecules provide an opportunity for water to form a tetrahedral coordinated structure (Narten & Levy 1972; Jeffrey & Saenger 1991). Pauling (1960) pointed out that water “. . . has a structure that involves a great deal of randomness, and yet it is likely that there are certain configurations of groups of water molecules that occur with high frequency . . .”. From X-ray diffraction patterns in liquid water, Narten and Levy (1972) determined the average coordination number of water to be slightly greater than four, supporting the tetrahedral structure for liquid water.

Solid/liquid interfaces in environmental systems comprise various functional groups. If water exists

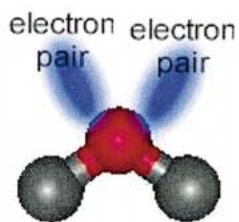


Figure 3. Schematic of a H_2O molecule showing configuration of atoms and electrons available for hydrogen bonds.

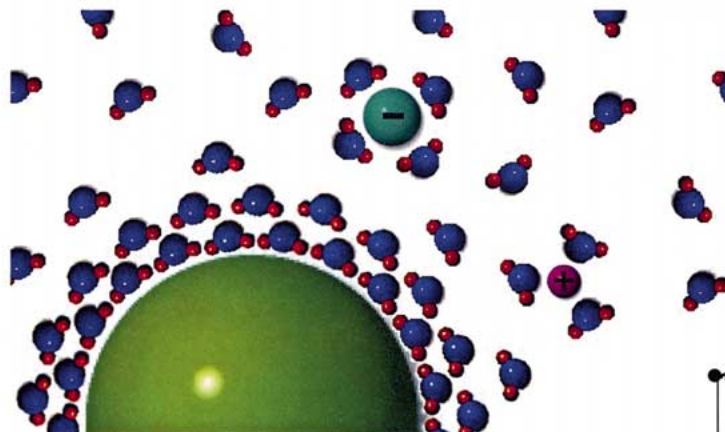


Figure 4. Orientation of water molecules in hydration shells.

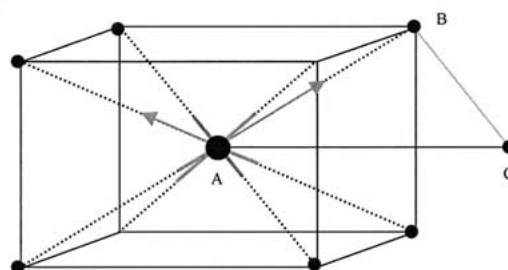


Figure 5. Lattice Fluid Theory for water surfaces is sectioned into body-centered cubic lattice. Site A and B are occupied by water molecules. Empty lattice sites that surround A are referred to as vacancies. Site A has eight nearest neighbors (primary shell, site B) and six next-nearest neighbors (secondary shell, site C). Arrows indicate proton donation, gray sticks indicate either acceptors or indifferences. (adapted from Besseling 1997).

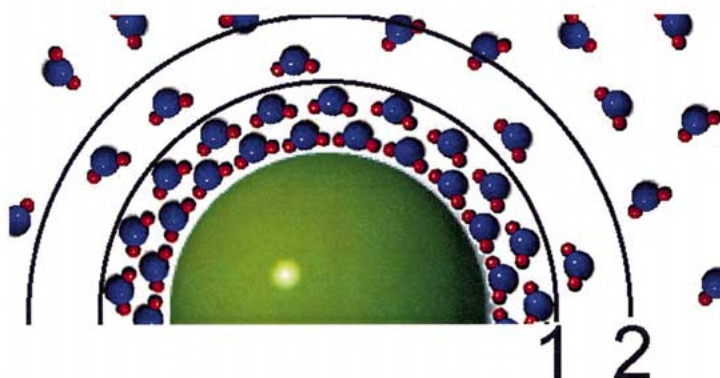


Figure 6. Layers of hydration around a surface. The density of water molecules around a surface is highest in the proximity of the surface and decays with distance to the density observed for water molecules in the bulk solution. This results in several layers of hydration (1, 2, ..., n).

at the interface, these surface functional groups may interact via hydrogen bonding with the water molecules or through a water bridge with other adjacent surfaces. Since water molecules have both proton acceptor and donor sites, they may interact with either proton donor or acceptor groups on surfaces. Just as hydrogen bonding may determine bulk properties such as melting and boiling points (Figure 2), it may affect surface properties and colloidal behavior in aqueous media.

Inorganic environmental colloids such as minerals typically possess hydroxy- and oxy-surface moieties. For example, silica has silanol groups (—Si—OH) that may hydrogen bond with water. The oxygen of the water molecule serves as a proton acceptor interacting with the hydrogen of the silanol groups (Lasaga, 1990). Hydrogen bonds may also form between polar water molecules and —O sites on hematite surfaces (Parks 1990). Water adjacent to such a colloidal surface is hydrogen bonded to the surface groups, and therefore rendered immobile. Liquid water further from this immobile layer has increasing water-water hydrogen bonds (Parks 1990). Surface groups on hydrophilic clays can also hydrogen bond with water molecules (Forslind & Jacobsson 1975; Schindler 1990).

Hydrogen bonding can also occur between water molecules and organically coated solid material. Natural organic matter, including fulvic and humic acids, has carboxyl and phenolic groups at a concentration of 1 to 10 mM/g (Schwarzenbach et al. 1993). These groups can hydrogen bond with water and other species in solution. Non-polar surfaces without hydrogen bonding sites can participate in what are known as hydrophobic or exclusion interactions. The interaction between water and surfaces may be quantified through contact angle measurements. Generally, water contact angles greater than 90° are considered indicative of hydrophobic surfaces (Zettlemoyer et al. 1975).

Environmental colloids that are hydrophobic in nature have a tendency to aggregate in water. A hydrophobic colloid suspended in water results in a discontinuity in the hydrogen-bonded structure of water such that adjacent water molecules become oriented to maximize the number hydrogen bonds. The water molecules adjacent to the surface thereby become ordered due to the presence of this non-polar surface. This ordering results in a decrease in entropy when compared to bulk conditions. The spatial extent of

structured water near an interface is a debated topic. Values range from a few to thousands of angstroms (Drost-Hansen 1965; Horn 1972; Israelachvili & Wennerström 1996). As mentioned before, the ordering of water is typically assumed to be affected by interface polarity (Du et al. 1994; Kitano et al. 2001) and to decay exponentially away from the interface (Churaev & Derjaguin 1985; Belaya et al. 1987; Marrink et al. 1993; van Oss 1994). It has been presumed that this ordering results in “hydration” or “structural” forces, which have been measured with atomic force microscope (AFM; Gruen & Marcelja 1983; Cevc 1991) (see section 4 on structural forces). Hydrophobic interactions are discussed in greater detail in section 5.

4. Structural forces

Hydrogen bonding commonly serves as the mechanistic basis of structural forces; proton-donor and proton-acceptor parameters are used in describing structural forces. Generally, for a solvated surface, solvent molecules highly restricted in their motion experience structural forces (Israelachvili 1992). When the solvent is water, this orientation restriction is referred to as hydration pressure. Israelachvili (1992) further explains that this effect is not limited to a *primary hydration shell*, but rather it propagates radially (assuming a spherical particle) outward towards the bulk solution in to a *secondary hydration shell*.

Figure 4 represents an idealized depiction of the orientation of water molecules in hydration shells. When an ion moves close to a particle surface, the charge on the ion may change the structure of the hydrogen-bonding network. The water molecule will re-orient its polarized charge with oppositely charged ions or surfaces. Water molecules in the hydration shell around a particle can rotate and subsequently break the hydrogen bond with its nearest neighbor. Molecules that orient around a surface, collectively form the hydration shell. The resulting net charge on the outside of this shell has the same sign (i.e., positive or negative) as the surface. This charge on the outside of the shell will orient the next layer of water molecules, which is called the second hydration shell. The hydrogen-bonding network decays as one moves from the polar or charged surface toward the bulk of the suspending medium.

In this second hydration shell, the hydration pressure still exists, but there is less restriction to the rotation of water molecules. With a reduction in rotational restriction, these shells can extend further. As hydration pressure decays with distance, an empirical exponential function for repulsive hydration can be developed (Molia-Bolivar & Ortega-Vinusea 1999):

$$\Delta G_h = \int_d^\infty \pi \alpha P_o \lambda e^{-(d/\lambda)} dH = \pi \alpha P_o \lambda^2 e^{-(d/\lambda)} \quad (8)$$

where

ΔG_h = hydration interaction energy, J

d = distance between the surfaces of two particles,

α = particle radius, m

λ = decay length, m

P_o = hydration pressure constant

Pashley (1981a, b) and Israelachvili and Pashley (1984) have suggested an additional primary structural force. Butt (1991) noted that Pashley (1981a, b) had measured a primary short-range repulsive force in addition to the repulsive electrostatic force and opposing attractive van der Waals force. Pashley (1981a, b) describes this additional repulsive force as a function of divalent cations dissolved in solution. An electrolyte in solution can convert the entropically unfavorable orientation of water molecules in bulk solution to a more favorable orientation along the colloid surface-liquid interface. Therefore, structural forces become stronger with increasing hydration energy of the background electrolyte (Pashley 1981a, b).

The development of a theoretical framework to accommodate these structural forces is attributed to the pioneering work of Marcelja and Radic (1976). Marcelja and Radic (1976) developed a mathematical description for the observations of Le Neveu et al. (1976), which showed an exponentially decaying repulsive (hydration) force between lipid bilayers. Marcelja and Radic (1976) showed mathematically that the free energy change, considered initially as chemical potential, was induced by the changes in adjoining layers of liquid. Broadly, they considered that any structural difference from the bulk liquid would give rise to this force. The free energy of interaction between the fluid and the particle surface was assumed to be a function of an order parameter:

$$\eta(d) = C_1 e^{d/\zeta} + C_2 e^{-d/\zeta} \quad (9)$$

where

$\eta(d)$ = a measure of the order of an arbitrary parameter in excess ordering within a homogenous bulk fluid

d = surface location

C_1, C_2 = coefficients determined by boundary conditions

ζ = $(C_1/C_2)^{1/2}$ = coherence length of the order parameter η , m

This phenomenological approach was only considered a mathematical representation. A physical interpretation was developed later by Israelachvili (1992).

4.1 Attractive structural forces

To model the structure of water, the body-centered cubic lattice, which has a coordination number of eight (with each lattice site surrounded by eight nearest neighbors, see Figure 5), is often used in describing hydration interactions. Lattice sites can be either vacant or occupied by a molecule, which accounts for density variations. The water molecule is modeled as a monomer (i.e., an object that occupies a single site). To account for orientation dependent interactions between two water molecules, as well as those between water molecules and surfaces, energetically different faces are attributed to this monomer. Two faces represent protons (hydrogen-donor faces), two faces represent the lone pair of electrons (hydrogen-acceptor faces), and the remaining four faces are indifferent. Hydrogen-donor and hydrogen-acceptor faces are arranged tetrahedrally with respect to the center of the molecule, as are the indifferent faces. A hydrogen bond is present when a hydrogen-donor face is directed to a hydrogen-acceptor face. At the solid/water interface, distribution of water molecules will be impacted by the hydrogen-donor and hydrogen-acceptor potentials of the surface. When the density of water molecules in the boundary layer is lower than that in the bulk liquid, a negative surface excess of water occurs and the density of water gradually increases with distance towards its bulk value. This negative surface excess of water leads to a mechanism of surfaces being pushed together by the bulk water. In other words, interactions between the surfaces are attractive and the strength of the attraction appears to be more or less proportional to the absolute value of the negative surface excess.

Electron-donor and electron-acceptor parameter values for a surface are relative values compared to a baseline value. If only structural forces are considered, one can define a surface as being either *hydrophilic* or *hydrophobic* based on the electron-donor and electron-acceptor values. For surfaces having both the electron-donor and electron-acceptor values greater than that of water, the surface is termed hydrophobic. Attractive structural forces (viz. hydrogen-bonding forces) result in hydrophobic interactions (van Oss 1994), while repulsive structural forces (viz. hydration pressure) result in hydrophilic interactions.

4.2 Repulsive structural forces

Solvation layers form around particles suspended in an aqueous medium (position 1 in Figure 6). This structured hydrogen-bonded network decays away from the surface (position 2 in Figure 6). The pressure of the water in the boundary layer increases as surfaces approach one another resulting in a repulsive interaction. The strength of the repulsive interactions appears to be more or less proportional to the absolute value of the positive surface excess. Repulsive structural forces are only significant at surface separations less than ~ 20 nm (Forsman et al. 1997).

A common misconception in current literature is that hydration pressure is the forcing function for the repulsive interaction between two surfaces with predominating electron-donor values at the distance of closest approach. However, van Oss (1991) described this repulsive interaction as manifested via the interaction between the two hydration shells on each surface. Thus, the forcing function is actually the result of hydrogen-bonding repulsion from the opposing layers of orientated water molecules.

Israelachvili and Wennerström (1996) suggested that structured water might not be responsible for the stabilizing effect traditionally attributed to hydration pressure. They propose that repulsion of hydrophilic surfaces in aqueous media may derive from decreases in entropy associated with confinement of thermally mobile surface groups and that hydration pressure may be attractive or oscillatory based on the geometry of approach of the two surfaces and the interaction of their electric fields (Israelachvili & Wennerström 1996). They further suggest that organization of water as a result of surface-water interactions is restricted to the first layer of molecules and may not be propagated away from the surface as originally thought.

5. Hydrophobic interactions

As discussed in sections 3 and 4 on hydrogen bonding, aqueous colloidal systems have generally been characterized as either hydrophobic or hydrophilic based on their relative affinity for water. The origin of hydrophobic and hydrophilic interactions is not entirely understood. Indeed, particle-particle interactions that cannot be explained via traditional electrostatic and van der Waals interactions are commonly grouped together into generic categories referred to as either *hydrophobic interaction*, if attractive in nature, or *hydration pressure*, if repulsive in nature. The *hydrophobic* effect has been given a great deal of attention in the physical organic chemistry literature and has been explained through arguments that center on the decrease in entropy of water molecules associated with cavity formation for the dissolution of hydrophobic moieties. Alternatively, when the cause of hydrophilic surfaces remaining separated in aqueous media cannot be explained through classical arguments of colloid stability (i.e., DLVO theory), hydration pressure has been credited for this phenomenon (Israelachvili & Wennerström 1996).

Ninham and co-workers (1997) proposed that the shortcoming of traditional DLVO theory in predicting particle stability arise from the *ab initio* decomposition of forces into non-interacting van der Waals and Coulombic components. More specifically, they suggest that not accounting for dispersive interactions between colloidal surfaces and dissolved ions is primarily responsible for the reported discrepancies of the traditional colloidal stability modeling approach.

An operationally expedient approach to addressing non-DLVO interactions has been proposed by van Oss and co-workers (1988). They have proposed that non-DLVO interactions can be attributed to Lewis acid/base interactions in the framework of non-charge transfer complexes that are thought to account for hydrogen-bonding and structural effects. These interactions are asymmetric; consisting of an electron accepting component (γ^+) and an electron donating component (γ^-), and can be either attractive or repulsive. Values of γ^+ and γ^- can be quantified through surface tension measurements with polar liquids such as glycerol, water, or formamide. Together with van der Waals interactions, these Lewis acid/base interactions comprise the total surface tension

$$\gamma_i = \gamma_i^{vdW} + \gamma_i^{AB} \quad (10)$$

where

$$\begin{aligned}\gamma_i^{vdW} &= \text{van der Waals component of surface} \\ &\text{tension, N/m} \\ \gamma_i^{AB} &= 2\sqrt{\gamma_i^+ \gamma_i^-} \text{ Lewis acid/base component} \\ &\text{of surface tension, N/m}\end{aligned}$$

Although Fowkes (1964) suggested a similar degeneration of surface tension some years ago, his approach resulted in dispersive and monopolar components that were always attractive. These Lewis acid/base interactions have also been linked to electrostatic forces (van Oss 1994). This linkage is somewhat consistent with Ninham theory of non-DLVO forces (1997), in that DLVO inconsistencies derive from an incomplete accounting of system interactions. For clay surfaces, the Lewis acid parameter, γ^+ , is typically very small and does not vary significantly among clay types ($\gamma^+ = 1.0 \text{ mJ m}^{-2}$). On the other hand, the Lewis base component, γ^- , ranges from ca. 5 mJ m^{-2} for pyrophyllite to 60 mJ m^{-2} for mica. van Oss and Giese (1995) have proposed delineating hydrophobicity and hydrophilicity for clays through the use of the Lewis base parameter. They suggest that clays with γ^- values greater than 27.9 mJ m^{-2} are hydrophilic and those with γ^- values less than 27.9 mJ m^{-2} are hydrophobic.

The surface Lewis acid/base properties deriving from a dynamic interaction between a sphere (1) and a flat plate (2) in water (w) can be measured in order to further understand and predict the net interaction (Wu et al. 1995; van Oss 1994). The Lewis acid-base (AB) free energy of adhesion, ΔG_{1w2}^{AB} , is given by

$$\Delta G_{1w2}^{AB} = -2(\gamma_{1w}^{AB} + \gamma_{2w}^{AB} - \gamma_{12}^{AB}) \quad (11)$$

where

$$\begin{aligned}\gamma_i^+ &= \text{electron-acceptor parameter of the polar} \\ &\gamma_i^{AB} \text{ surface tension component of} \\ &\text{material (i)} \\ \gamma_i^- &= \text{electron-donor parameter of the polar } \gamma_i^{AB} \\ &\text{surface tension component of material (i)}\end{aligned}$$

The AB component of the interfacial tension between materials (i) and (j) is written as:

$$\gamma_{ij}^{AB} = 2 \left(\sqrt{\gamma_i^+ \gamma_i^-} + \sqrt{\gamma_j^+ \gamma_j^-} - \sqrt{\gamma_i^- \gamma_j^+} - \sqrt{\gamma_i^+ \gamma_j^-} \right) \quad (12)$$

The γ_i^{LW} , γ_i^+ , and γ_i^- components are determined simultaneously, by means of contact angle (θ)

measurements. The value of γ_{ij}^{LW} can only be positive value or zero, while γ_{ij}^{AB} can be either positive, zero or negative. The total interaction energy is given by:

$$\Delta G_{1w2}^{TOT} = \Delta G_{1w2}^{AB} + \Delta G_{1w2}^{vdW} + \Delta G_{1w2}^{EL} \quad (13)$$

One may also include the Brownian motion interaction energy, but the value of this is typically on the order of $1 kT$. Since this energy is often one or two orders of magnitude smaller than those associated with AB or LW energies, it is commonly neglected.

All three forces (vdW , AB , and EL) can act at non-negligible distances in aqueous media. Because each force decays with distance between the colloid and surface with different spatial dependencies, energy versus distance plots (taking LW , AB , and EL forces into account) must be defined to predict adhesion (van Oss et al. 1992; van Oss 1994). Figure 7 presents magnitudes of and spatial behavior of interaction energies for the example of polystyrene microspheres (with carboxylated surface groups) and glass suspended in an aqueous solution (ionic strength of 0.1 M NaCl and a pH of 3.5). For spherical geometries, ΔG^{AB} decays exponentially: as $\exp(-d/\lambda)$ where λ is the decay length of water ($\lambda \approx 1.0 \text{ nm}$) and d is the separation distance. Thus, colloids with spiculations, sharp edges, or other protrusions with a small effective radius, can more easily overcome a net macroscopic repulsion than completely smooth particles, and can, therefore, engage in adhesion via microscopic sites located at the distal ends of such protrusions.

Grasso and Smets (1998) reported on the bacterium, *Pseudomonas aeruginosa*, partitioning in a ternary system (microbe/water/dolomite). They observed a five-fold increase in partitioning to dolomite in the stationary growth phase when compared to the logarithmic and decay growth phases. Figure 8 depicts the potential energy plots for this ternary system. The changes in the Lewis base characteristics of the microbe surface were reported to be primarily responsible for the difference in behavior and concomitant potential energy profiles among the three growth phases. The electrostatic potentials did not vary significantly among growth phases and were determined to play a rather inconsequential role in partitioning behavior. Similarly, the changes in van der Waals energies among the various growth phases were found to be small. It was concluded that Lewis acid-base interactions governed partitioning behavior in the systems studied.

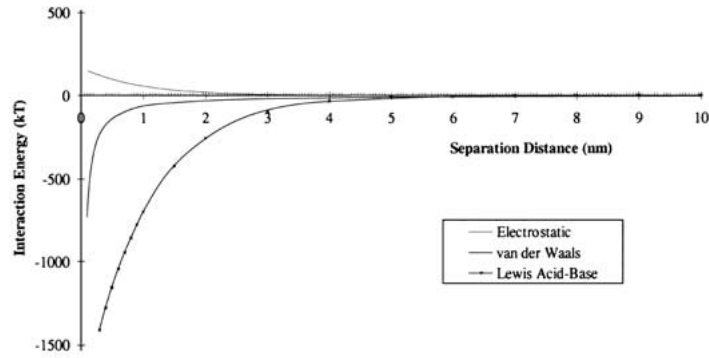


Figure 7. Potential interaction energy profiles interaction between polystyrene microspheres (with carboxylated surface groups) and glass suspended in water; Ionic strength = 0.1 M NaCl, pH = 3.5.

6. Solution chemistry

Suspending solution chemistry can significantly influence a range of interfacial forces between particles altering particle interactions and stability. Indeed, well-known mechanisms of coagulation are created and controlled by changes in solution chemistry (e.g., Amiratharajah & O'Melia 1990). Modifications in solution chemistry can alter both solution properties such as surface tension and particle surface properties such as charge and potential.

6.1 Indifferent electrolytes

The effects of ionic strength on the vdW interaction energy have been studied extensively (Davis & Ninham 1972; Mahanty & Ninham 1976; Marra 1985; Bowen & Jenner 1995; Mishchuk 1995; Bowen & Williams 1996; Yaminsky et al. 1996). Changes in the vdW interaction energy, as a function of electrolyte concentration, can be attributed to screening of the non-dispersion portion of the Hamaker constant. The dispersion component has been assumed to remain unaltered by the presence of electrolytes because the electrolyte cannot respond to high frequencies (Mahanty & Ninham 1976; see also Israelachvili 1992). Mahanty and Ninham (1976) have developed a model that accounts for this phenomenon. For the limit where $\kappa d_o \ll 1$, the effect of electrolyte on the Hamaker constant is given by:

$$A = A_{v>0} + A_{v=0} \{1 - (2\kappa d_o)^2 [-\ln(2\kappa d_o) + 0.5722] \frac{2\varepsilon_1^2}{\varepsilon_1^2 - \varepsilon_2^2} + O[(\kappa d_o)^2 \ln(\kappa d_o)]\} \quad (14)$$

This model indicates that vdW forces are reduced in salt solutions. However, as discussed in section 2 on

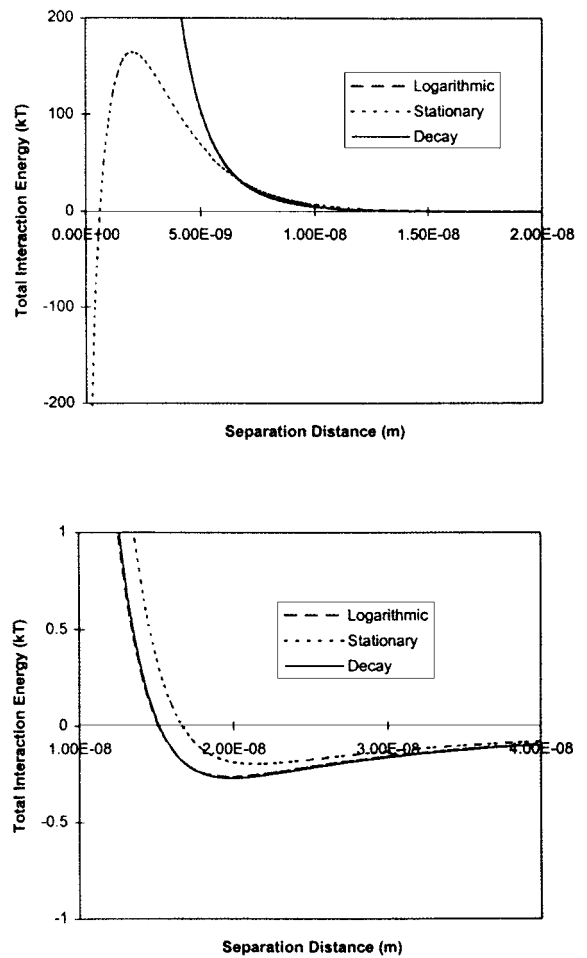


Figure 8. Dolomite-*P.aeruginosa* potential interaction energy profiles. Bottom panel is an expanded view of the secondary minimum *ca.* 20 nm (adapted from Grasso & Smets 1998).

the classical DLVO approach, within the framework of the conventional DLVO colloid stability model, an increase in electrolyte concentration typically has more influence on the electrostatic interaction energy than on the vdW interaction energies, and results in increased attraction between two similar surfaces (see Hiemenz 1986; Elimelech et al. 1995).

Butkus and Grasso (1998) recently reported that screening of the non-dispersion portion of the Hamaker constant does not appear to be the sole contributor to the total change in vdW energy, as predicted by the model illustrated in equation [14] and that indifferent electrolytes may affect interfacial energy in other ways. In fact, much evidence suggests that the conventional DLVO model fails to completely explain the effects of aqueous electrolytes on interfacial forces. Several studies that do not conform to the framework of the conventional DLVO model have been reported in the literature. The presence of indifferent electrolytes has been reported to increase the energy available for coagulation beyond that predicted by the conventional DLVO model (Chheda and Grasso 1994; Wu et al. 1994, 1994b; Grasso et al. 1995; Craig et al. 1998). Further, Chou (2001) recently reported that long range electrostatic interactions in electrolytes modify contact angles on charged substrates in a scale and geometry dependent manner. Consequently, it is likely that indifferent electrolytes also influence non-DLVO force components.

Non-DLVO interactions have been attributed to the free energy of cohesion of the suspending liquid, which can be quantified from its surface tension (see van Oss 1994). An increase in the total surface tension of a solvent, with all other factors held constant, generally results in a decrease in particle stability (see equation [11]). It is well known that electrolytes increase the surface tension of water (Heydweiller 1910; Onsager & Samaras 1934; Drost-Hansen 1965; Horvath 1985; Stairs 1995; Weissenborn & Pugh 1996). Accordingly, the presence of electrolytes should decrease particle stability. In addition, multi-valent ions have a greater effect on surface tension than monovalent ions (Weissenborn & Pugh 1996). This effect of electrolytes on the surface tension of water has been described by image forces (Onsager & Samaras 1934) and changes in the structure of water (Drost-Hansen 1965).

The effects of strong acids and strong bases on the surface tension of water have also been investigated. Addition of inorganic acids to water appears to have a small effect on the total surface tension

of water. Hård and Johansson (1977) suggested that the conjugate base of strong acids and not the proton might be responsible for decreases in surface tension. Addition of strong bases has been reported to have an effect that is similar to that of electrolytes (Craig et al. 1993; Hård & Johansson 1977). Weissenborn and Pugh (1996) reported that the conjugate acid of a strong base is responsible for increases in the surface tension of water. In addition, data presented by Hård and Johansson (1977) suggest that the increase in water surface tension caused by the conjugate acid of a strong base are much more pronounced than the decrease in surface tension caused the conjugate base of a strong acid. Consequently, it appears that the cation is responsible for the electrolyte effect on the surface tension of water and possibly non-DLVO interactions (see Pashley 1981a). It has also been proposed that aqueous electrolytes may disrupt the interfacial structure of water (Sposito & Prost 1982; Pashley & Quirk 1984; Franks et al. 1999) and thereby, affect non-DLVO forces (Derjaguin & Churaev 1987; Baygents & Saville 1991).

Butkus and Grasso (1998) reported that ionic strength appears to influence the electron donor capacity for water. They also reported that the hydrophilicity of a surface impacted the nature of ionic strength effects on the van Oss AB parameters; given a specific electrolyte concentration, an increase in surface hydrophilicity resulted in greater changes in γ^+ and γ^- . Salt may change the ordering of water dipoles at (or near) the surface, which may result in a decrease in interfacial entropy (Leberman & Soper 1995). A decrease in entropy, which is not compensated by a decrease in enthalpy will result in an increase in the interfacial free energy, thereby adding stability to particle systems. Colic et al. (1997) also reported on an observed short-range repulsion, between surfaces in electrolyte solutions, which they attributed to counterions located near the surface. They noted that the repulsive interaction was a function of the bare ion radius. Using neutron diffraction, Leberman and Soper (1995) reported that salt effects on water of hydration were also ion specific. On the other hand, Israelachvili and Wennerström (1996) noted that the changes in solvent structure resulting from the presence of aqueous electrolytes in the interfacial region did not influence interfacial forces.

Some of the disparities between experimental studies and conventional DLVO theory have been attributed to ion correlation effects (Guldbrand et

al. 1984; Kjellander & Marcelja 1988). Ion correlation forces are considered attractive vdW forces between polarizable ions located at an interface. As two particles approach one another, the “conducting” layers of ions at each interface become attractive at (small) distances <4 nm (see Israelachvili 1992). This phenomenon is not subsumed in the Poisson – Boltzmann equation and Lifshitz theory that form the underpinnings of the conventional DLVO theory. Unfortunately, no colloid stability models presently address ion correlation effects. Additional research is, clearly, needed in this area (see Ninham & Yaminsky 1997; Ninham 1999).

6.2 Surface complexation

It was noted in the section above that indifferent electrolytes *decreased* particle stability. Electrolytes have also been reported to *increase* particle stability. For example, colloids have been observed to restabilize as a function of electrolyte concentration (Yotsumoto & Yoon 1993; Butkus & Grasso 1999; Stenkamp et al. 2001; Subramaniam et al. 2001). Similarly, Craig et al. (1993) observed an increase in the stability of nitrogen gas bubbles with increases in aqueous electrolyte concentration. These observations may be explained by considering the influence of surface complexation on interfacial forces.

Many surfaces can react with water to form surface functional groups whose charge varies with pH. Reactions between surface functional groups and ions in solution are well known (Harrison & Berkheiser 1982; Davis & Kent 1990; Sposito 1990; Dzombak & Morel 1990; Stumm & Morgan 1996). Surface complexation of these groups with ions in bulk solution has been widely reported to result in a change in colloid stability (Lyklema 1978; Pashley 1981a, b; Liang & Morgan 1990; Boisvert et al. 1997; Butkus & Grasso 1999; Subramaniam et al. 2001). These changes in colloid stability can result from alterations in both conventional DLVO and non-DLVO forces.

As noted before, surface charge and surface potential are primary variables that influence electrostatic interactions. For surfaces that are capable of reacting with hydronium ions, changes in solution pH can lead to changes in surface charge and a concomitant change in the electrostatic interaction energy (see Lyklema 1978). The change in surface charge caused by changes in pH has been known to influence the polarity of surfaces. For example, Holmes-Farley et al. (1985) reported that lowering the pH of water

placed on a polyethylene carboxylic acid (PE-CO₂H) surface increased the hydrophobicity of the surface (due to protonation of the surface groups) and resulted in increased water contact angles. Further, surface complexation of other potential determining ions can also lead to changes in the net surface charge at a given pH (Breeuwsma & Lyklema 1973) and alter the polarity of a surface (van Oss 1994).

Surface functional groups form adsorption complexes upon reaction with adsorptive species in solution. Adsorption complexes are typically classified into inner-sphere and outer-sphere complexes (Sposito 1981). An *inner-sphere complex* has no water molecule interposed between the surface functional group and the ion or molecule that binds, whereas an *outer-sphere complex* has at least one such interposed water molecule. Outer-sphere surface complexes always contain solvated adsorbate ions or molecules. Ions adsorbed in surface complexes can be distinguished from those in the *diffuse layer* (Sposito 1984) because the former species remain immobilized on surfaces over long time scales. These three types of surface species – inner-sphere complex, outer-sphere complex, and diffuse layer ions – represent three modes of adsorption of small aqueous ions that contribute to the formation of the electrochemical double layer on surfaces (Sposito & Grasso 1998).

Figure 9 illustrates the three kinds of surface species observed for hydrated Cu²⁺-doped smectites bearing bivalent adsorbed cations. Also shown in Figure 9 are the characteristic residence time scales for a water molecule diffusing in a bulk liquid (L); for an ion in the diffuse swarm (DI) for an outer-sphere surface complex (OSC); and for an inner-sphere surface complex (ISC; Sposito & Grasso 1998). These time scales ranging from picosecond to nanosecond (Ohtaki & Radnai 1993) can be compared with the molecular time scales that are probed by conventional optical magnetic resonance, and neutron scattering spectroscopies. For example, all three surface species remain immobile while being probed by optical spectroscopy, whereas only the surface complexes may remain immobile while being probed by electron spin resonance (ESR) spectroscopy (Sposito 1984; Johnston et al. 1993).

Complexation of electrolytes with surface functional groups may influence interfacial forces in a manner that is not consistent with quantification by conventional DLVO models. It has been reported that even so called “indifferent electrolytes” can adsorb onto particle surfaces (Parks 1984; Elimelech &

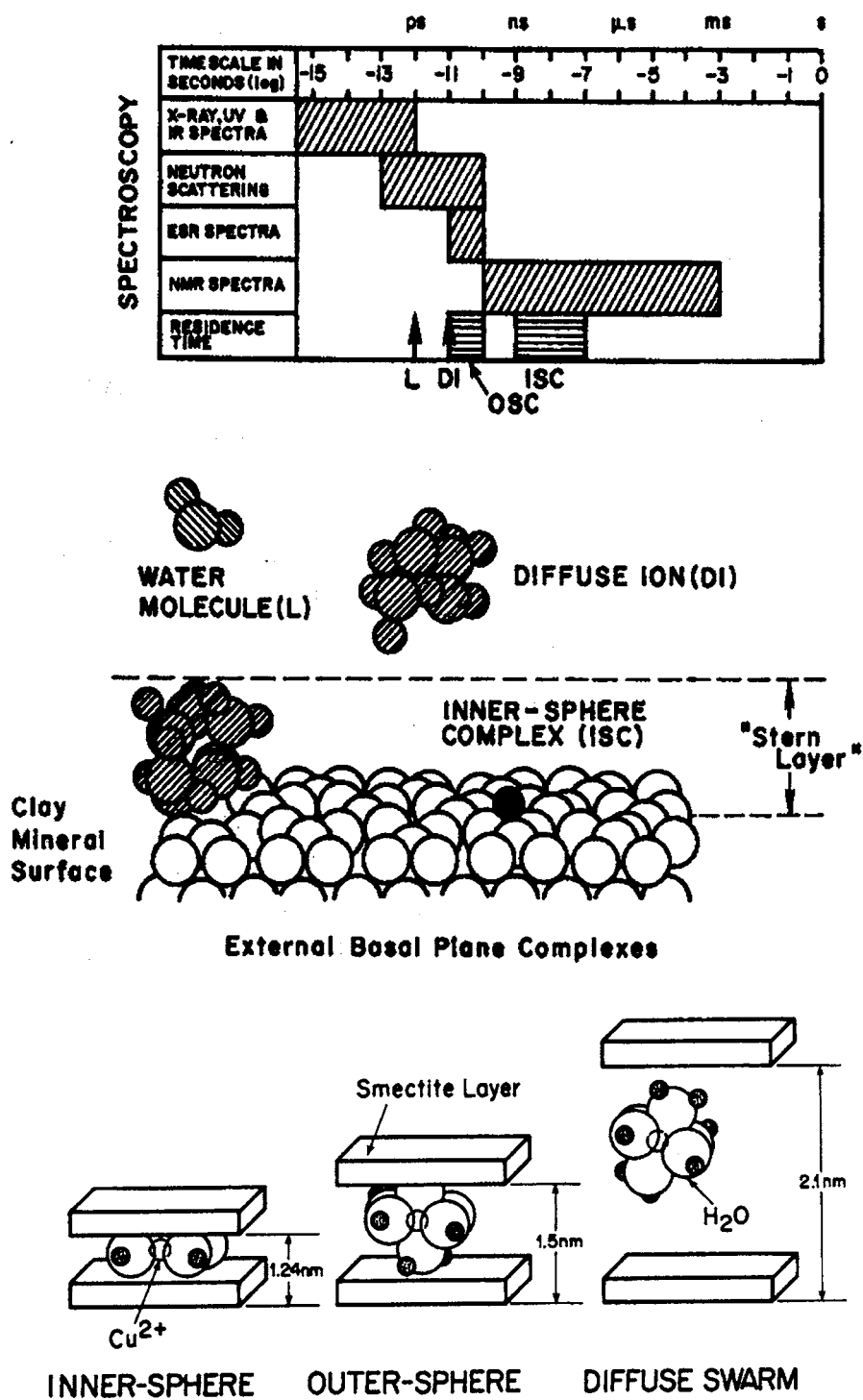


Figure 9. Cationic surface species on the basal planes of 2:1 layer type clay minerals. Inset indicates the spectroscopic methods used to quantify counterion surface species, their intrinsic time scales over which molecular structure is probed, and the residence time of surface species. Also shown are the three kinds of surface species (inner sphere, outer sphere, diffuse swarm ions) observed for hydrated Cu^{2+} -doped smectites bearing bivalent adsorbed cations (adapted from Sposito & Grasso 1998).

O'Melia 1990a). For example, using a surface force apparatus, Pashley (1981a,b) measured the force between two mica surfaces in electrolyte solutions and reported that deviations from the conventional DLVO theory were observed and noted to be a function of electrolyte type and concentration. These observations were related to the ion exchange properties of the mica surface and the waters of hydration surrounding the ion. The salt was reported to adsorb onto the mica surface, which resulted in a repulsive hydration force. Pashley (1981a, b) noted that hydration forces appeared to approach an asymptotic value above a salt specific concentration. The etiology of this observation was attributed to saturation of the charged mica surface sites. Experimental findings below the salt specific concentration were reported to be consistent with conventional DLVO concepts (Pashley, 1981a, b). Pashley and Quirk (1984) reported that the net hydration force, measured between mica surfaces in high concentrations of NaCl, was significantly lower than the hydration force measured in NaCl solutions that contained just sufficient electrolytes to fully cover the mica surfaces. Pashley (1981b) reported that pH indirectly affected the hydration force by changing the surface charge, thereby affecting the magnitude of salt adsorption. Pashley (1981a) also noted that sorption of the H_3O^+ ion did not result in a repulsive hydration force between mica surfaces in acidic solutions, which is similar to the findings of Craig et al. (1993) for nitrogen gas bubbles in acidic solution.

Change in the composition of surface-associated functional groups, resulting from ligand exchange reactions and/or changes in pH, can result in a change in interfacial polarity (Holmes-Farley et al. 1985; Parks 1990; Israelachvili 1992; Wu et al. 1994; Adamson and Gast, 1997; Veeramasuneni et al. 1997). Contact angle data can be used, as a first approximation, to estimate the influence of surface complexation on interfacial polarity. Figure 10 illustrates changes in contact angles of deionized water and diiodomethane on hydrous ferric oxide colloids as a function of phosphate adsorption at pH 6, up to monolayer coverage of phosphate (Butkus & Grasso 2001). The trendlines through the data illustrate that the contact angle of water decreased as a function of increased phosphate adsorption, while the contact angle of diiodomethane remained relatively constant. The lack of change in diiodomethane contact angle was interpreted to suggest that the apolar component of surface tension remains relatively unchanged as a function of bound phosphate. Therefore, the changes in deionized

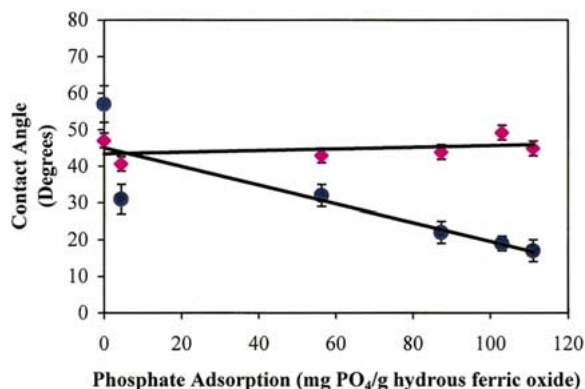


Figure 10. Changes in contact angle at the probe liquid-hydrous ferric oxide interface as a function of phosphate adsorption. Traces have been superimposed on the figure to illustrate trends in the data. Error bars on the figure represent one standard deviation. Deionized water (●), diiodomethane (◆), 0.01 M NaCl, pH 6 (adapted from Butkus & Grasso 2001).

water contact angle, as a function of phosphate adsorption, was thought to derive from changes in the polar component of free energy.

Changes in surface charge may also increase association of surfaces with solvents (van Oss 1994; Israelachvili 1992). Additionally, binding of an ion, which increases the number of surface-associated hydroxyl groups, can lead to additional hydrogen bonding at the solid-liquid interface (Butkus & Grasso 2001). Changes in the association between solvents and a colloid surface can induce a concomitant change in non-DLVO forces that derive from solvent-surface interactions. Butkus and Grasso (1999) observed an increase in the stability of ferric hydroxide colloids as a function of surface complexation of phosphate. They reported that the increase in stability appeared to be independent of net surface charge in the pH range investigated. They also reported that the increase in stability was caused by changes in the polar component of free energy, as a function of phosphate complexation, and that this change in interfacial energy was consistent with predictions of an extended DLVO (EDLVO) model.

7. Physical interactions

7.1 Osmotic pressure and depletion attraction

Osmotic pressure has been used to model forces between colloids forming a basis for some EDLVO models (see van Oss 1994; Bowen & Williams 1996).

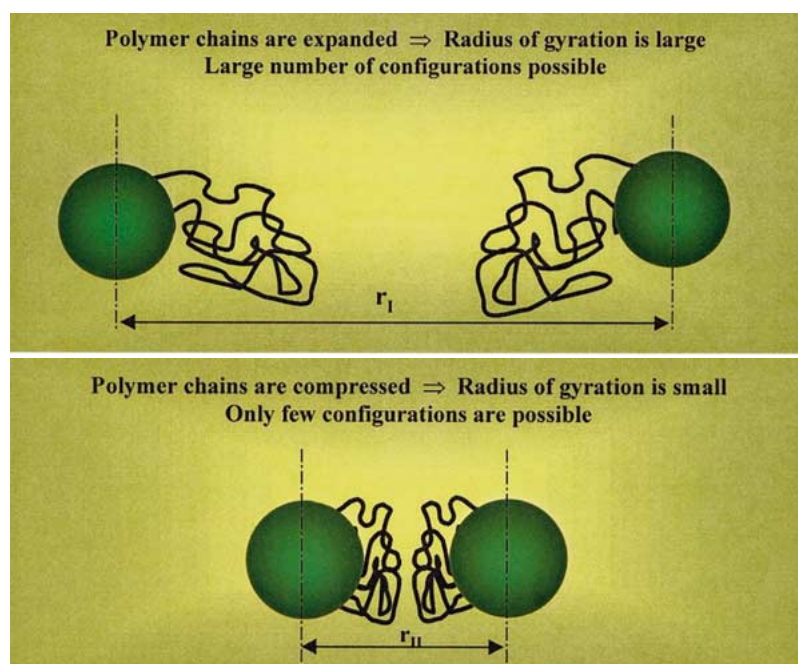


Figure 11. Schematic of entropic contribution to steric interactions.

Osmotic pressure is more commonly used when modeling depletion interactions in colloidal systems. Depletion interactions can occur in systems that have particles with disparate sizes. For example, consider a system that contains two large spheres; say one μm in diameter, in a dispersion comprised of relatively small colloids on the order of say 10 nm in diameter. As the two spheres approach one another, the smaller colloids will be excluded from the gap between them, which results in a decrease in osmotic pressure between the spheres. This reduction in osmotic pressure results in an attractive force called a *depletion attraction*.

Using total internal reflection microscopy, Odiachi and Prieve (1999) measured depletion forces between a polystyrene sphere and a glass slide caused by laponite colloids in electrolyte solutions. They modeled the depletion attraction between the sphere and the glass slide by calculating changes in osmotic pressure as the laponite was forced from the gap between them. Odiachi and Prieve (1999) reported that electrolytes reduced the magnitude and range of depletion forces by reducing the effective size of the laponite particles via double layer compression.

7.2 Surface roughness

The DLVO and EDLVO theories assume that particle surfaces are smooth. In reality, colloidal surfaces

can be quite heterogeneous (Walz 1998). Indeed, AFM has provided numerous examples of particle surface heterogeneity (see Maurice 1996). Surface roughness can lead to significant disparities between experimental findings and model predictions (Hull & Kitchener 1969). Refinement of DLVO and EDLVO models to include the effects of surface roughness has led to model predictions that are more congruent to measured results (Elimelech & O'Melia 1990; Bhattacharjee et al. 1998; Walz 1998).

7.3 Microbubble cavitation

Bunkin and coworkers (1997; see also Ninham et al. 1997) have suggested that the presence of dissolved gases can influence interfacial energies, especially near hydrophobic surfaces. They proposed that cavitation of microbubble clusters near hydrophobic walls can lead to long range interactions. Bunkin and coworkers (1997) also reported that cavitation of microbubble clusters was influenced by electrolyte type, electrolyte concentration, the presence of dissolved gas and the hydrophobicity of the surface. Colloid stability models have yet to incorporate the role of microbubble cavitation in particle-particle interactions (see Ninham 1999).

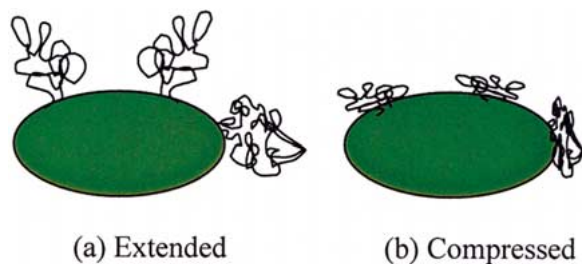


Figure 12. Structure of adsorbed polymers.

7.4 Steric interactions

Polymers have been used for several decades to prevent colloidal particles from aggregating and to control the stability of colloidal suspensions in natural and engineered environmental systems. This mode of stabilization, termed steric stabilization (Heller & Pugh 1954) also has important applications in food technology and in the paint industry. Surfactants and polymeric macromolecules have a tendency to adsorb on suspended particles in solution, forming layers 10 to 20 nm in thickness. The adsorbed polymers are thermally mobile and extend out from the surface into solution, and may rearrange their positions and orientations in response to temperature, interactions with solvent molecules, rearrangements of neighboring surface molecules and proximity to another surface (Hiemenz & Rajagopalan 1997).

As two polymer coated surfaces approach each other at distances of separation of less than twice the thickness of the adsorbed layer, interaction between the two layers takes place (Sato & Ruch 1980). Steric interactions are those forces that result from interactions between such adsorbed chains and/or chain elements (Rijnaarts et al. 1999) and can be defined quantitatively in terms of the energy change occurring upon interaction of the adsorbed layers. Steric interactions can be attractive or repulsive.

The physical basis of the steric repulsion is a combination of (i) a volume restriction effect arising from the decrease in possible configurations in the region between the two surfaces and (ii) an osmotic effect due to the relatively high concentration of adsorbed polymers in the region between the two surfaces as they approach one another.

7.4.1 Entropic contribution

As two particles with adsorbed polymer layers approach one another, the thermal movement of the polymer chains is restricted, and the entropy of the

individual polymer chains decreases. Mackor (1951) and Mackor and van der Waals (1952) originally proposed this entropic contribution to steric interactions. Hesselink et al. (1971a, b) described this phenomenon as a volume restriction effect. It is assumed here that the particles themselves are impenetrable. Therefore, the adsorbed layer is compressed and the polymer segments contained in the interaction region lose configurational entropy. This interaction, which occurs due to the reduced configurational entropy of polymer chains at a surface, is the most important type of steric interaction and is repulsive in nature. It is commonly referred to as *steric or overlap repulsion*. This is schematically illustrated in Figure 11. Small amounts of attractive forces may operate between particles until some separation distance where the entropic overlap effects take over and repulsion occurs. The interaction energy, $G_{entropic}$, is given by (Hesselink et al. 1971a, b):

$$\frac{G_{entropic}}{kT} = 2\nu \ln \frac{\Omega(d)}{\Omega(\infty)} \quad (15)$$

where

- ν = number of polymer chains per unit area
- $\Omega(d)$ = number of configurations of the polymer chain at a separation distance d
- $\Omega(\infty)$ = number of configurations of the polymer chain at infinite separation

$G_{entropic}$ is always positive and hence, repulsive.

7.4.2 Osmotic contribution

A second interaction that contributes to steric interactions is the mixing or osmotic interaction, which results from the free energy obtained in mixing two surfactant or polymer layers. It was assumed that the adsorbed layers of the two particles can overlap each other when the two particles collide. It was also assumed that no desorption of the adsorbed layers occurs on collision (Sato & Ruch 1980). In this model, the polymer segments are in contact with solvent molecules, and this contact with the solvent is reduced as a result of the contact between the polymer segments in the interaction region. Further, as a result of this increase in the segment concentration in the interaction region, there is also a reduction in the configuration entropy of the adsorbed molecules. The mixing interaction energy, G_{mixing} , can be quantified

by using Flory-Krigbaum theory (1950):

$$\frac{G_{mixing}}{kT} = \frac{4\pi V_p^2}{V_s} v \left(\frac{1}{2} - \chi \right) \left(\delta - \frac{d}{2} \right)^2 \left(3R + 2\delta + \frac{d}{2} \right) \quad (16)$$

where

- V_p = molar volume of the polymer, m³/mol
- V_s = molar volume of the solvent, m³/mol
- δ = thickness of the adsorbed polymer layer, m
- d = separation distance between the two approaching particles, m
- R = radius of gyration of the polymer, m
- χ = Flory-Huggins interaction parameter

Steric interactions between surfaces coated with polymers depend on several factors. One important factor is the quality of the solvent. An “ideal” solvent (also referred to as a *theta* solvent) is one in which the individual segments in the polymer chain do not interact with each other. This is the case when the interaction of a polymer segment with the solvent is as strong as the interaction between two segments. In a “good” solvent, polymer segments favor contact with the solvent. Since the compression of the polymer layer by an approaching surface tends to squeeze out the solvent in the intermediate region and cause segment-segment interactions to take place, the net result is repulsion. In a “poor” solvent, the opposite effect takes place and the monomer segments attract each other (Hiemenz & Rajagopalan 1997). From equation (16), it is evident that if $\chi < 0.5$ (chains are in good solvent condition), G_{mixing} is positive and the interaction is repulsive. If $\chi > 0.5$ (chains are in poor solvent condition), then G_{mixing} is negative and the interaction is attractive. In the absence of specific interactions such as hydrogen bonding, a poor solvent may become a good solvent if the temperature increases because temperature may change the nature of the solvent-polymer segment interactions.

Other important factors that affect forces between polymer coated surfaces are the mode of attachment of the polymer to the surface (grafted or physically adsorbed), as well as the density of the polymers at the surface. The structure of the polymer when it is physically adsorbed on a surface in which it protrudes far from the surface is usually referred to as extended

(cf. Figure 12(a)). This occurs when the interactions between the polymer and surface is minimal compared to that between the polymer and solvent. On the other hand when the polymer is strongly adsorbed on the surface (driven in part by poor compatibility with the solvent), a compressed structure (Figure 12(b)) usually results.

With very close packing, steric forces can be operative over large distances. Steric attractive forces arise when polymers protrude far from the surface to which they are attached and can bind to both particles. This binding leads to a bridging force, which are usually attractive at large separations. Intersegment forces caused by the direct interaction between polymer segments of the two approaching surfaces can be attractive as well; however, this interaction depends strongly on the nature of the solvent.

Walker and Grant (1996) found that polymer chain length and flexibility are also important factors governing forces between polymer coated surfaces. They reported that a critical polymer length was required for stabilizing inorganic colloids suspended in an aqueous solution at high salt concentration. This critical polymer length was found to depend on background electrolyte concentration, implying that polymer molecules stabilize particles through a combination of steric and electrostatic – or electro-steric forces.

Klein (1980, 1983) carried out the first systematic study of the interaction between polymer-coated particles in a poor solvent (cyclohexane) using a surface force apparatus (Israelachvili & Adams 1978). An attraction between the surfaces was observed in this study. When the interaction between poly(ethylene oxide) adsorbed to mica was studied in a good solvent (Klein & Luckham 1982, 1984), the interaction was found to be repulsive at all separations at full coverage of the polymer, and was in good agreement with the scaling theory of De Gennes (1982, 1987). The interaction between adsorbed polymer layers at the onset was explained by the increase in osmotic pressure with increased polymer concentration in the gap between the surfaces. For very high molecular weight polymers, and at partial coverages of the particle surfaces by the polymers, an attraction was observed. This attraction has been attributed to a bridging interaction due to the polymer simultaneously adsorbing to both the approaching surfaces.

More recently, AFM has been employed to probe steric interactions between adsorbed polyelectrolytes (Biggs & Healy 1994; Biggs 1995; Braithwaite et

al. 1996). Pedersen and Bergstrom (1999) measured the forces between a sphere and a plane surface of zirconia immersed in a low molecular weight poly(acrylic acid) using AFM. Measurements were carried out at high pH where the adsorbed, highly charged anionic polyelectrolyte extended far into the solution, resulting in a combination of steric and electrostatic interactions. Steric interactions were found to predominate and the electrostatic contribution was small at an ionic strength of 0.01 M. The measured steric forces were found to be highly dependent on time and on the interaction history of the adsorbed polymer layer.

There are conflicting opinions in the literature as to whether steric interactions and other extended DLVO forces are additive. While several studies have considered these contributions to be additive (van Oss 1994; Jucker et al. 1998; Giasson et al. 1998; Freitas et al. 2001); others disagree with this approach (e.g. Rijnaarts et al. 1999). These authors contend that charging of the macromolecules affects the segment density distributions and the χ values (Fleer et al. 1993), and therefore, the various contributions are not independent of one another. Nevertheless, the more common approach to quantifying steric interactions is to assume that the total interaction energy is the summation of the various contributions presented in this paper. Steric forces are then quantified from the deviation of experimental data from extended-DLVO predictions. These experimentally inferred polymer interaction energies have also been favorably compared with independent calculations based on equations [15] and [16].

8. Comparing two particle stability models

Van Oss et al. (1990) reported on the use of the classical DLVO model (with *unretarded* van der Waals forces) to study the stability of a thixotropic suspension of hectorite. Jar tests involving a suspension of hectorite at various concentrations (10, 100, 1000, 2000 mol_c/m³) of NaCl solution demonstrated that the critical coagulation concentration (CCC) was approximately equal to 100 mol_c/m³. Figure 13 depicts the results of both DLVO and EDLVO (using the van Oss approach) modeling of an aqueous suspension of hectorite particles with an average size of 2 μm. Using the data reported by van Oss et al. (1990) and a modified Levenberg-Marquardt algorithm, Sposito and Grasso (1998) predicted a value of ccc = 140

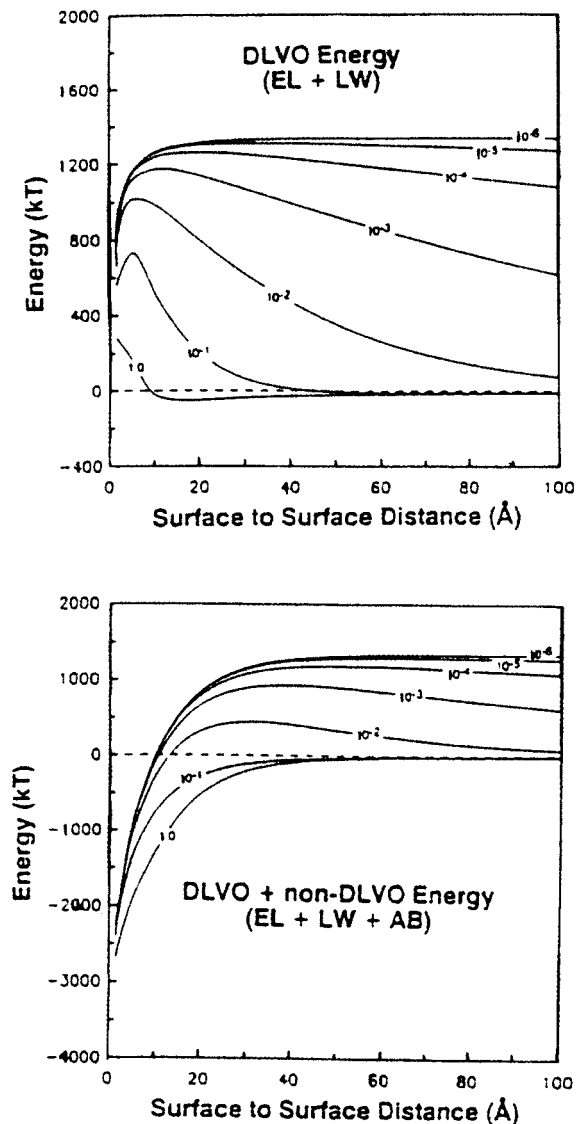


Figure 13. Potential energy curves for the hectorite-water-hectorite system. The top panel represents the traditional DLVO approach (electrostatic + van der Waals (unretarded) interactions). The bottom panel represents an extended DLVO approach (electrostatic + van der Waals (unretarded) + Lewis acid-base interactions) (adapted from Sposito & Grasso 1998).

mol_c/m³ and a critical distance, $d_c = 4.8$ nm. These results are consistent with the findings of van Oss et al. (1990). Moreover, the critical distance was determined to be less than 10 nm, thus supporting the use of an *unretarded* van der Waals model. Clearly, the traditional DLVO approach was unable to capture the dynamics of the system. The EDLVO model was found to be consistent with experimental results,

suggesting that Lewis acid-base interactions play a significant role in the coagulation of hectorite suspensions (Sposito & Grasso 1998).

9. Summary

Understanding the interaction and behavior of surfaces or colloids in environmental systems is of critical importance in our ability to model these systems accurately. The classical model of colloid stability, DLVO, has historically described these interactions. This model derives from an energy balance composed of attractive and repulsive interactions. The original model focused exclusively on attractive van der Waals and repulsive coulombic interactions. In the last several years, traditional models have been unable to describe environmental colloidal behavior. The structure of water *inter alia* has been implicated. This paper reviewed many of the interactions that play a role in environmental systems not commonly subsumed by traditional particle stability models: e.g., hydrogen bonding and the hydrophobic effect, hydration pressure, non-charge transfer Lewis acid base interactions, and steric interactions. Whatever approach is used to model particle stability, the initial assumptions, boundary conditions and parameter estimations techniques used as part of the model must temper the results. The complexity of environmental systems will most likely preclude the development of a singular approach that will be extensible to all scenarios. Although significant advances in our understanding of systems behavior have been made, there is still much fertile ground for continued research.

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