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# A CRITIQUE OF DIFFUSE DOUBLE LAYER MODELS APPLIED TO COLLOID AND SURFACE CHEMISTRY

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**Abstract**—The use of Derjaguin–Landau–Verwey–Overbeek (DLVO) theory in colloid science has continued to the present day in spite of the inability of this theory to explain, even qualitatively, numerous phenomena exhibited by clays and other colloidal materials. An alternative description of the fundamental forces involved in the formation of dispersions and gels was presented in 1938 by Langmuir, but was never widely accepted among colloid scientists. Recent experimental and theoretical work, particularly in Japan, has revived this alternative view, in which a long-range Coulombic attraction force appears to explain several phenomena, particularly transitions among ordered and disordered phases of colloidal particles in dilute salt solutions.

Examples are given from surface chemistry where rather complex models based on diffuse double layer theory are used to explain chemical adsorption behavior that often has a simpler explanation. It is argued that the rule of parsimony (Ockham's Razor) should be applied to complex models that appear to explain the data at hand before such models are taken to be generally valid. A satisfactory fit of model predictions to experimental data obtained under a very limited range of conditions does not prove the validity of the model. Thus, it is concluded that the DLVO theory and its modifications fail to meet the 2 criteria necessary to the acceptance of a theory: agreement with observations and simplicity.

**Key Words**—Clay Dispersion, Clay Swelling, Diffuse Double Layer, DLVO, Electrostatic Attraction Theory, Interparticle Forces, Ockham's Razor, Schiller Layers, Smectites.

## INTRODUCTION

The modern view of colloid science is based substantially on the long-existent diffuse double layer theory of repulsive interaction between charged particles, now termed the DLVO theory. Simple qualitative explanations of colloidal phenomena, as well as complex surface adsorption models, such as the triple layer model (Bolt and van Riemsdijk 1991), are extensions of this conception of long-range electrical repulsion and short-range van der Waals attraction in colloidal suspensions. In recent years, the complexity of these models has not in itself deterred their application because of the availability of computing power. The fact that such models often produce a satisfactory fit of experimental data does not, however, prove their general validity. In fact, Sposito (1995) has pointed out that any particular model does not generally produce an unambiguous description of data. If the goal is to mathematically fit a particular data set, these models may be interpreted as successful. However, if the goal is to find an accurate physical-chemical description of the surface and interparticle forces controlling colloidal behavior and adsorption reactions, then the underlying assumptions of these models must be tested for validity over a wider range of conditions. In this regard, the DLVO model has had very limited success in clay science, since it has only been shown to make reasonable predictions for freely swelling clay systems, notably Na and Li montmorillonites. Wider application has required additional complication of the theory by the addition of new parameters with values that cannot be tested experimentally.

There is a guiding criterion of the scientific method, referred to as Ockham's Razor (or the rule of parsimony), which states that, when choosing among rival hypotheses, all of which explain the observed facts, the simplest possible one is preferred (Feibleman 1972; Jefferys and Berger 1992). It has been argued that simpler hypotheses are more likely to be correct *a priori* and tend to make sharper, more testable predictions (Jefferys and Berger 1992). According to Ockham's Razor, an adequate explanation based upon, for example, the law of mass action must be preferred to one based on a less certain and more complex theory such as DLVO. The DLVO theory makes numerous assumptions about clay–ion–water systems, some of which have been challenged repeatedly (Williams et al. 1994). On the other hand, principles such as mass action and charge conservation are universally valid laws and apply to a system regardless of the model selected to describe it. If these principles are sufficient to account for observed data, the fact that the DLVO model is also consistent with the data is *not* evidence in support of the hypothesis that the model is correct. Unfortunately, the test of Ockham's Razor has rarely been applied to DLVO, and this theory has frequently been said to be "supported" by particular observations despite the failure to test alternate theories or simpler explanations based on accepted principles.

In this paper, I will outline some examples of colloid and surface adsorption phenomena that have simple explanations based on fundamental principles, and yet

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are commonly described in terms of the predictions of DLVO theory. In most cases, long-range forces do not need to be invoked to satisfactorily explain adsorption processes, but it will be shown that for processes where long-range forces are involved, such as colloidal dispersion, electrostatic attraction provides the most acceptable explanation, in contradiction to the DLVO model. Adsorption behavior of mineral surfaces can usually be understood in terms of simple mass action principles and coordination chemistry without invoking diffuse double layer models.

## A BRIEF HISTORY OF DLVO AND ALTERNATIVE (ELECTROSTATIC ATTRACTION) THEORIES

The DLVO version of the diffuse double layer theory, in which the electrical force in clay dispersions is assumed to be repulsive at all interparticle separations beyond the primary energy minimum, yet aggregation is considered the thermodynamically favored state, is presently accepted by most colloid scientists. This model was championed by Verwey and Overbeek (1946), although it is clear from the paper and the published general discussion following the paper that Overbeek considered the actual origin of the repulsion to be at least partly osmotic (generated by entropy associated with the counterions). In direct opposition, Langmuir and several others argued that the attractive force was of electrostatic origin (Langmuir 1938; Levine 1946; MacEwan 1948; Norrish 1954) and that the overall force could change from attractive to repulsive due to osmotic forces once the clay plates separated by more than some distance (suggested by MacEwan and Norrish, based upon their clay studies, to be on the order of 10–30 Å). Neither Langmuir nor MacEwan believed that the attractive van der Waals force was important in clay–water systems, arguing that it could not operate in water over the distances necessary to explain particle–particle attraction. Levine (1946) maintained that the Verwey–Overbeek model had not considered the rearrangement of counterions that would automatically result from double-layer overlap, and that the chemical potential, $\mu_i$, of the counterions would depend on $R$, the particle separation distance. In effect, a merging of double layers upon particle approach would cause redistribution of counterions into a single layer, and an attractive electrostatic force would result (Langmuir 1938; MacEwan 1948), with the repulsive force originating in the osmotic force of the counterions. The DLVO theory is unable to consider the counterions as mobile species that can adjust their positions to minimize free energy as interparticle distance is altered. Therefore, only at large particle separations, where diffuse double-layer overlap is small, could this model be expected to produce a good approximation of the potential energy. Modern simulation studies utilizing the Monte Carlo technique appear to support Langmuir's belief, predicting that the swelling pressure of clays always has an *attractive* electrostatic component (Guldbrand et al. 1984; Kjellander et al. 1988). Nevertheless, for clays with small layer charge and monovalent counterions, this attraction is overcome by the osmotic (entropic) contribution. In any event, the contribution of van der Waals dispersion forces to attraction between particles can only be estimated, and a recent study indicates that the accuracy with which the Hamaker constant for silicate-water systems is known may be quite low (Ackler et al. 1996).

Langmuir (1938) considered the electrostatic contribution to the force between particles as separate from the osmotic contribution, as do modern physical-chemical treatments of the system. He used the Debye–Huckel electrolyte theory to argue that cations would be free to distribute around the macro-anions (particles), and the electrostatic force would be attractive at all particle–particle distances. Verwey and Overbeek (1946) stated that this result was in error as a result of his "use of the linear Debye–Huckel approximation". (Note that the Debye–Huckel theory is derived assuming that the ionic interaction energies are weaker than the thermal energy, kT, and therefore can only be applied to quite dilute ionic solutions, equivalent to large average particle–particle separations). The Verwey–Overbeek model, on the other hand, calculated the force between the plates due to the electrical interaction of static double layers. It predicted a repulsive potential at intermediate separations, with a deep primary minimum of potential energy at close particle approach, and a shallow minimum at large distances which was a consequence of assuming the existence of a long-range van der Waals force. This potential energy function was used to explain the kinetic stability of colloidal dispersions, predicting a large potential barrier to coagulation in dilute electrolytes.

The Langmuir concept of long-range electrostatic attraction has been revitalized by the electrostatic interaction theory of Sogami (Sogami 1983; Sogami and Ise 1984; Smalley 1990). The attractive electrostatic model of dispersions is supported by observations that particles in stable dispersions do not necessarily occupy all of the volume of the solution as would be expected from the long-range repulsive force of the DLVO model, but rather tend to cluster at separations that are not space-filling (Ito et al. 1994; Dosho et al. 1993).

The concept of an attractive interaction can be illustrated in a simple way by comparing the electrostatic interaction between 2 clay plates for different simplified geometric arrangements of counterions. If the counterions are grouped along the midplane between plates (Figure 1a), an attractive interaction clearly results (van Olphen 1977), somewhat analogous to the net attraction resulting from the arrange-

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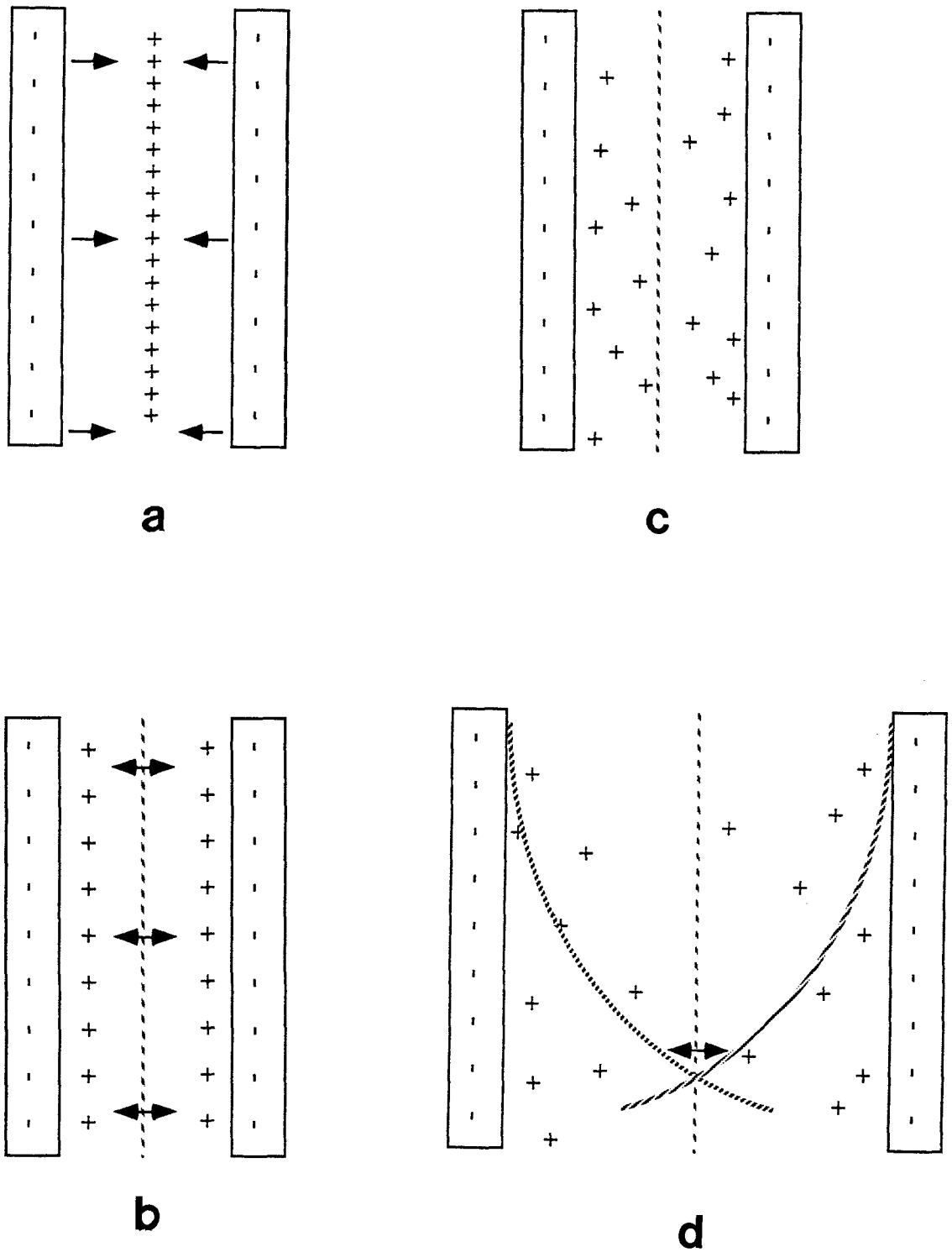



Figure 1. Diagrams of alternative simplified views of counterion distributions between like-charged plates.

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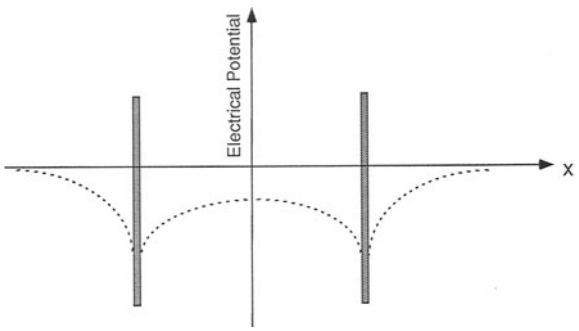



Figure 2. Electrostatic attraction (Sogami) model of electrical potential as a function of distance, $x$, between 2 clay plates.

ment of $Na^+$ and $Cl^-$ ions in a cubic array to form NaCl crystals. The lattice energy calculated from the Born–Lande equation is negative, indicating a net attractive electrostatic energy despite the greater ionic repulsion in the crystal. In other words, the electrostatic energy term favors the crystallization of NaCl from ions separated by large distances in solution. Similarly, the arrangement depicted in Figure 1a lowers its electrostatic energy as the 2 plates are brought closer together. Total collapse is prevented in real clay systems by hydration and osmotic forces.

If, in contrast, the counterions are depicted as associated with their respective layers (Figure 1b), the electrostatic energy of the system could be evaluated in terms of the interaction between 2 dipoles and would be repulsive (van Olphen 1977). However, this arrangement is not reasonable once diffuse double layers begin to interact, since individual cations are free to change to positions that lower the free energy of the system. Thus, the less-ordered counterion arrangement in Figure 1c may be more realistic. Calculating the electrostatic energy for the arrangement depicted in Figure 1c is more involved, but statistical mechanical calculations by Sogami and others show that the electrostatic component of the overall free energy is often attractive (Guldbrand et al. 1984; Engström et al. 1985; Ise 1986; Sogami et al. 1992). Because forces are balanced across the midplane, some have argued that "on the average, the electrical field generated by one half of the lamellar systems is zero at the position of the other half" (Guldbrand et al. 1984), and no electrostatic attraction between the plates can exist on average. Thus, attraction could only result from dynamic processes in which the counterions influence the positions of one another. In this way, Kjellander et al. (1988) have explained the restricted swelling of Ca(II)-smectites by a fluctuating electrostatic force whose time-averaged value is attractive. Although this force could be important, the lack of a *net* electrostatic interaction across the midplane is not evidence that the plates are not attracted or repelled. Thus, in Figure 1a, bringing the plates closer together lowers the electrostatic energy of the system because the cation–plate attractive energy term increases to a greater extent than the cation–cation repulsive energy term.

The traditional approach in DLVO is to consider each charged plate with its counterions as a single entity, which then possesses a negative electrical potential that decays with distance from the plate surface. Thus, if 2 plates approach (see Figure 1d), the potentials at the midplane are assumed to be additive as long as the interaction is weak, and the repulsive pressure is given by (van Olphen 1977):

$$p = 2nkT(\cosh \Psi_m - 1) \quad (1)$$

where $\Psi_m$ is the mid-plane potential, and $n$ is the ion concentration in the external solution (assuming a 1:1 electrolyte). This equation originates from the Debye–Hückel theory of osmotic pressures (Langmuir 1938), so that the swelling pressure in the DLVO theory is clearly a consequence of the osmotic force of interlayer cations. In this regard, there is no substantive disagreement between the electrostatic attraction theory of Sogami and the DLVO theory regarding the nature of the repulsive force. However, the Sogami theory differs from DLVO in that the situation depicted in Figure 1d would result in an electrostatic attraction (at least for highly charged particles), as the counterions are restricted to a reduced volume due to their interaction with the particles (Ise 1986). The model predicts that the electrical potential between clay plates is lower than that external to the plates, as shown diagrammatically in Figure 2, causing an electrical interparticle attraction.

## SWELLING AND SHORT-RANGE FORCES IN COLLOIDS

The DLVO theory fails to account, even qualitatively, for the short-range interactive behavior of hydrated clay particles. Smalley (1990) has argued this point persuasively, noting that DLVO theory, because it assumes the interparticle attractive force to be the short-range van der Waals force, predicts a primary energy minimum that is lower than the secondary minimum. If this were true, clays already in the aggregated state (such as dry clay powders) could not spontaneously disperse in water. The fact that many clays *do* spontaneously disperse in water is probably the consequence of the strong short-range hydration forces that are clearly non-DLVO in character (Christenson 1988). These forces extend beyond 10 Å at mica surfaces (Pashley 1981; Israelachvili 1985). In addition, osmotic forces contribute to swelling well beyond the 10-Å range.

Empirical evidence that the short-range interaction in layer silicate clays has an attractive electrostatic contribution is convincing. The fact that, when the negative layer charge of smectites is increased upon

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chemical reduction of structural Fe(III), there is a decreased tendency of the clay to swell in water (Lear and Stucki 1989), implies that the overall short-range electrostatic force of the clay particle–counterion system is attractive. It is well known that $Na^+$-smectites with relatively low layer charge tend to expand more freely in water or electrolyte solutions than those with higher layer charge, although location as well as magnitude of structural charge is important (Slade et al. 1991). Again, it is difficult to rationalize these observations unless the electrostatic force between clay plates in aqueous solutions is attractive, at least at relatively small separation distances. At spacings much below 50 Å, a repulsive force between hydrated mica plates has been measured, and attributed to short-range hydration effects (Pashley 1981; Israelachvili 1985; Christenson 1988). This force increases with increasing electrolyte concentration, a fact inconsistent with DLVO. Although these short-range interaction forces are clearly non-DLVO in origin, they are not definitive in testing continuum theories such as DLVO and Sogami because the assumptions inherent in these theories break down at short spacing.

Experimentally, it may be possible to provide some further insight into the nature of the forces causing and restricting clay swelling by observing effects of environmental factors such as temperature and pressure. Within the range of "crystalline" clay expansion, that is, $d(001)$ spacing $\leq$20 Å, it has generally been accepted that the opposing forces are hydration of interlayer cations and surfaces (repulsive) and electrostatic attraction across charged plates (Kittrick 1966). Both are strong forces, and neither is expected to be influenced by relatively small temperature or pressure changes. Thus, the observation that changing the temperature from 10 to 70 °C had no influence on the $d(001)$ spacing of either Ca(II)-montmorillonite (19.5 Å) in water or $Na^+$-montmorillonite in 0.3 *M* NaCl (20.4 Å) (unpublished data) was expected. Similarly, Zhang et al. (1993) found no evidence that temperature changes altered the stable interlayer spacing of $Na^+$-montmorillonite, even at spacing in excess of 60 Å. In marked contrast, a reversible collapse of macroscopically swollen *n*-butyl-ammonium vermiculite in water is induced by slight heating (Braganza et al. 1990), suggesting that higher temperatures either weaken the repulsive force or strengthen the attractive force relative to its opposing force in the highly expanded phase. If an attempt were made to explain this transition by DLVO theory, it would require that the repulsive electrostatic force diminish, or that the van der Waals force increase, at higher temperature. Neither of these requirements is physically reasonable. On the other hand, the Sogami model based on an electrostatic attractive force and an osmotic repulsive force (Sogami and Ise 1984) may account more easily for the temperature-dependence of phase transition between the highly-expanded (gel) state and the more collapsed (crystalline) state. Since higher temperature would increase osmotic pressure within both the clay and the external solution, there may be little overall influence of osmotic force on the temperature-dependence of the phase transition. However, higher temperature decreases the dielectric constant of water (from 80.1 at 20 °C to 69.9 at 50 °C), which could substantially increase the attractive force across plates, inducing collapse to the crystalline state. The measured thermal compression of charged latex particle suspensions has similarly been interpreted as a contradiction of DLVO theory, and evidence in favor of electrostatic interparticle attraction (Ise and Smalley 1994).

## LONG-RANGE FORCES IN COLLOIDS

The predictive ability of the DLVO model in clay studies has been tested largely by the effect of salt concentration on interlayer expansion of swelling clays, and has been moderately successful in this regard, at least for $Na^+$-saturated smectites. However, the model has generally not been compared with other models having different assumptions about the nature of the fundamental attractive and repulsive forces.

Recent developments, both theoretical and experimental, have undermined assumptions of the DLVO theory. The long-held assumption that the electrostatic (as opposed to osmotic) interaction between like-charged clay platelets is repulsive at all but close separation has been challenged on a theoretical basis by statistical mechanical models (Guldbrand et al. 1984; Engström et al. 1985; Kjellander et al. 1988) and mean field theory (Sogami et al. 1992). Furthermore, experimental observations, such as the appearance of voids in colloidal dispersions of uniform like-charged latex particles, attest to the existence of a long-range attractive force (Dosho et al. 1993; Ito et al. 1994) which prevents particles from assuming an even distribution due to random (Brownian) motion.

There is limited experimental evidence to resolve the nature of the electrostatic force at larger interparticle distances in layer silicate clays, but since electrostatic forces are relatively long-range compared to van der Waals and hydration forces, it is not unreasonable to expect that the electrostatic attraction would remain significant at interparticle separations of 100 Å or higher. For separations of 30 to more than 100 Å, the *c*-axis spacing in montmorillonite, $d$, varies inversely with the square root of electrolyte concentration, $c$, according to the equation:

$$d = 21 + \frac{11.4}{\sqrt{c}} \qquad [2]$$

and this behavior led to a non-DLVO model in which an osmotic repulsive force balances an attractive electrostatic force (Norrish 1954). The origin of the re-

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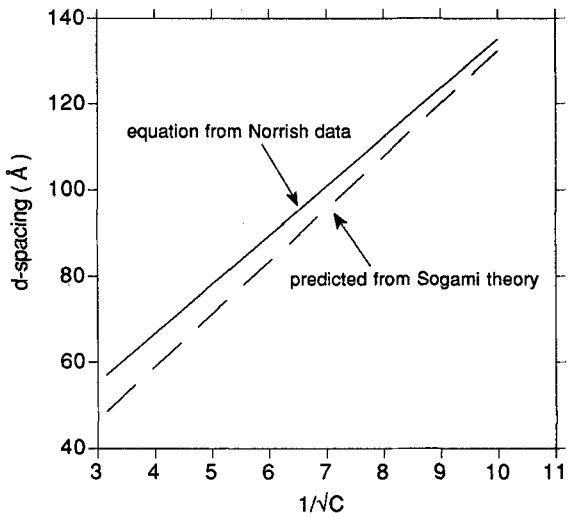



Figure 3. Comparison of Norrish and Sogami relationships of $d$-spacing to NaCl concentration within the concentration range of the Norrish experiments, based on Equations [3] and [4].

pulsive force is the thermal motion (entropy of mixing) of the counterions when diffuse double layers overlap (Engström et al. 1985), not electrostatic repulsion between overlapping double layers as commonly implied in references to DLVO. It is interesting that Norrish derived a simple equation from this model of clay swelling that establishes a constancy for the product of the inverse Debye screening length, $K$ (units of $Å^{-1}$), and the $d$-spacing, which at large spacing is:

$$K \cdot d \approx 3.8 \qquad [3]$$

More recently, the Coulombic attraction theory of Sogami has been shown to predict:

$$K \cdot d = 4.0 \qquad [4]$$

(Williams et al. 1994), in remarkably close agreement with Norrish's data, as Figure 3 illustrates clearly. The predicted Sogami spacings are calculated from the relationship of $K$ to molar concentration of electrolyte, $c$ (Smalley 1994), $K^2 = 0.107c$. Note that the predicted interparticle spacing from the Sogami theory has been adjusted for the thickness of the silicate plates (10 Å) in order to compare with Norrish's measured $d$-spacings.

## PHASE TRANSITIONS IN COLLOIDS

As pointed out by Smalley (1990), and much earlier by Langmuir (1938), the observed coexistence of separate phases (concentrated and dilute) at *reversible* equilibrium in colloidal dispersions is, in itself, evidence that particle–particle interaction is not repulsive at all separations, as required by DLVO. In other words, the dispersed state must be thermodynamically stable if it can be reversibly converted to the concentrated state. These 2 phases have been observed in suspensions of various anisodimensional particles (such as smectites, iron hydroxides, vanadium pentoxide and tungsten trioxide) as well as in suspensions of monodisperse latex particles (Coper and Freundlich 1937; Overbeek 1952; Dosho et al. 1993). The concentrated phase has a high degree of order, often leading to various optical effects such as birefringence and interference colors. The dilute phase consists of free, randomly oriented particles undergoing Brownian motion.

Free energy minima evidently exist in $Na^+$-smectites at silicate layer separations less than 100 Å, evidenced by the coexistence of phases with $c$-axis spacing of 20 Å and 40 Å (Norrish 1954; Viani et al. 1985). Phase transitions are also seen in $n$-butyl-ammonium vermiculite, which swells macroscopically in water (Braganza et al. 1990), and like the smectite, shows no coherent $c$-axis spacing in the transition from the crystalline to osmotic swelling state. The fact that these are *reversible* transitions indicates that the coexisting gel and crystalline phases represent equilibrium states, which are not possible within the framework of the DLVO theory (Smalley 1990).

The coexistence of Schiller layers or tactoids (platelets or rod-shaped particles aligned into ordered states) with an isotropic phase in various colloidal dispersions indicates that a balance of forces is also possible at large particle separations (>1000 Å) in clay-size materials. This balance of forces has usually been assumed to be the repulsive electrostatic force of DLVO theory with gravity, since Schiller layers and tactoids often form after a period of settling, and are destroyed reversibly by agitation. However, Onsager (1949) has pointed out that entropy-driven phase transitions are possible in suspensions of anisotropic particles as a consequence of Brownian motion, which produces an "osmotic" repulsion that stabilizes colloidal dispersions. This phenomenon is separate from (or in addition to) the osmotic pressure originating from the counterions, indicating that stable dispersions and phase transitions can, in principle, occur in *uncharged* colloidal particles. In fact, it is interesting that the remarkable 3-dimensional ordering of latex particles in suspension at separation distances of ≈1000 Å is evident only at very low ionic strength (Ise 1986), a condition that causes these charged polymers to unfold and occupy a larger volume. Thus, the repulsive force that maintains the large separation may be due to Brownian motion. When gravity is eliminated as a force by matching the density of the particles and solvent, long-range 3-dimensional order (≈1000 Å) of these charged latex particles still occurs, suggesting that an attractive long-range force is present (Dosho et al. 1993).

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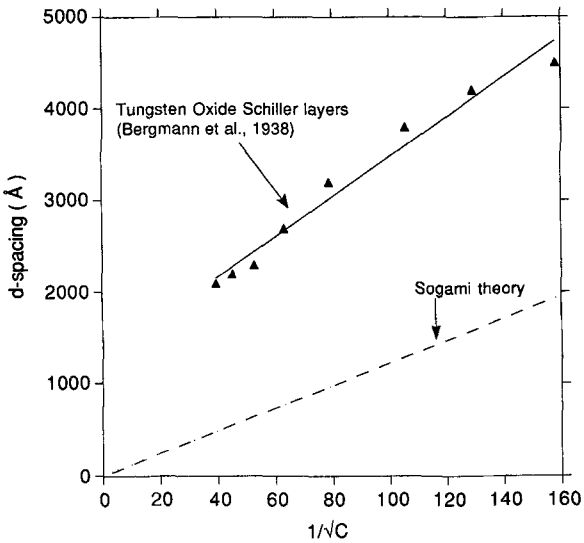



Figure 4. Schiller layer *d*-spacing for tungsten oxide platelets measured as a function of NaCl concentration. The broken line denotes the predicted *d*-spacing of the Sogami theory from Equation [4].

The dependence of *c*-axis spacing in Schiller layers on electrolyte concentration is qualitatively described by DLVO theory, but the theory often fails quantitatively. For example, it does not explain the resistance of lath-shaped tungsten oxide particles to approach closer than about 2000 Å at increasing ionic strength (Bergmann et al. 1938). In contrast, as shown in Figure 4, the spacings are fairly consistent with the $1/\sqrt{c}$ rule of swelling that follows from the Sogami theory. Although the actual *d*-spacings of the tungsten oxide plates are higher than the predicted spacings from Sogami theory, correction for the plate-thickness would bring the predicted and measured spacings into closer agreement.

In summary, there are a substantial number of experimental observations on clays and other colloidal systems to support the hypothesis of attractive electrostatic forces between like-charged particles, necessitating a reassessment of the basic assumptions of the DLVO theory.

## CHARGE AND ADSORPTION ON VARIABLE-CHARGE SURFACES

The DLVO theory appears to have been particularly misapplied to adsorption phenomena at oxide and other variable-charge surfaces, because most research on these systems has shown adsorbed ions to be in nondiffuse bonding associations with the surface (McBride 1989b). Nevertheless, the often-presented description of surface charge on variable-charge minerals such as oxides employs the Nernst equation to calculate a surface potential, which is then used in the diffuse double layer model to calculate surface charge (Gast 1977). The resulting predicted surface-charge dependence on pH is a function of ionic strength, with charge curves at all ionic strengths crossing over at the point of zero charge (PZC). These predicted surface charge curves are qualitatively consistent with measured surface charge of pure oxides, despite arguments that the Nernst equation is not appropriate for oxide minerals (McBride 1989a). They are, however, also consistent with a simpler Langmuir-based adsorption theory of $H^+$ and $OH^-$ on variable-charged surfaces (McBride 1994). Furthermore, the latter model, unlike the Nernst double layer model, predicts a limit on surface charge as pH is adjusted away from the PZC value. Experimental evidence, when corrected for mineral dissolution, is consistent with a surface charge maximum (Schulthess and Sparks 1986; Marcano-Martinez and McBride 1989). The Langmuir-based approach to oxide surface chemistry, relying only on the simple requirements of charge balance, mass action and coordination chemistry, adequately explains pH-dependent charge and adsorption behavior on oxides. Sposito (1995) has detailed the successes of this approach to oxides, much of it attributable to W. Stumm and coworkers.

Anions and cations adsorb on variable-charge mineral surfaces by both inner-sphere complexation (ligand exchange) and outer-sphere (electrostatic) association (McBride 1989b; Brown et al. 1989), behavior that is problematic for the application of diffuse double layer models to such surface reactions. Inner-sphere and outer-sphere mechanisms are distinguishable indirectly by the effect of ionic strength (that is, the presence of an indifferent electrolyte) on degree of adsorption (Hayes et al. 1988). Anions that adsorb by outer-sphere association (for example, selenate) are strongly sensitive to ionic strength; that is, adsorption of these anions is suppressed by competition with weakly adsorbing anions such as $Cl^-$ or $NO_3^-$. Conversely, anions that adsorb by ligand exchange either show little sensitivity to ionic strength (for example, selenite) or respond to higher ionic strength with *greater* adsorption (for example, borate). A lack of response to ionic strength is readily understood for such anions, since the bond that they form with the surface is strong. Consequently, anions that are weak Lewis bases (such as $NO_3^-$ and $ClO_4^-$) are unable to compete for coordination sites at surfaces (McBride 1994).

In contrast, the *increase* in adsorption in response to higher ionic strength, shown in Figures 5 and 6 for borate and phosphate (Barrow et al. 1980; Goldberg et al. 1993; Keren and Sparks 1994), does not have so straightforward an explanation. Obviously, the trend is opposite to that predicted by explanations based on anion–anion competition for sites. When it is observed, the explanation usually offered is the effect of ionic strength on the diffuse double layer thickness; that is, as ionic strength is increased, the double layer

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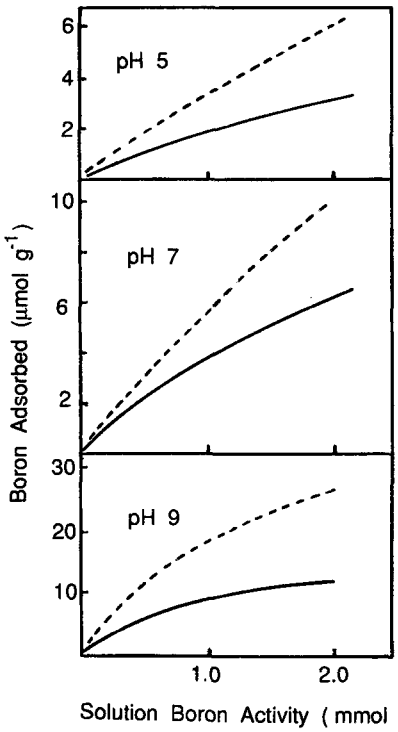



Figure 5. Boron adsorption isotherms for pyrophyllite at 3 pH values and 2 electrolyte concentrations, 0.01 *M* $NaNO_3$ (solid lines) and 0.1 *M* $NaNO_3$ (broken lines). Figure adapted from Keren and Sparks (1994).

contracts, allowing the anion of interest to approach negatively charged silicate clay or oxide surfaces and form an inner-sphere complex. In the case of layer silicate clays, although the anion bonding sites are believed to be at edges, it has been argued that high ionic strength diminishes the negative electrical field associated with both the planar surfaces (permanent charge) and the edges (pH-dependent charge) of layer silicate clays (Keren and O'Connor 1982; Keren and Sparks 1994). The influence of the electrical field of the planar surface on edge adsorption is attributed to "spillover" of the diffuse double layer at edges (Secor and Radke 1985). This explanation is only qualitative, although the phosphate adsorption data of Figure 6 have been fit quantitatively to a quadruple-layer adsorption model (Bowden et al. 1980). Such complex explanations for anion adsorption behavior are not generally subject to direct confirmation by experiment because they typically employ several fitting parameters that cannot be measured.

Since anion adsorption by ligand exchange involves direct coordination to a discrete surface metal cation, and is not prevented even when the adsorbing surface is negatively charged and expected to repel the anion, explanations based on electrical field theories rather than molecular descriptions of reasonably likely surface reactions may be inappropriate. This is suggested by the fact that borate adsorption on oxides and silicate clays is optimal around pH 8 to 10 (Goldberg et al. 1993); that is, borate adsorption is favored under conditions where the pH is higher than the PZC of the oxide and there is electrostatic repulsion between the anion and the surface. Furthermore, the positive effect of ionic strength on both borate and phosphate adsorption (Figures 5 and 6) is present even at pH as low as 5 (Barrow et al. 1980; Keren and Sparks 1994). At such low pH, it is doubtful that the DLVO-based electrostatic repulsion argument could explain the ionic strength effect on anion adsorption, particularly for minerals such as Fe and Al oxides that have points of zero charge above 7.

A simpler non-DLVO explanation for the ionic strength effect on anion adsorption by variable-charge surfaces follows directly from a reasonable reaction scheme for the surface ligand exchange reaction. This approach is similar to that of the constant capacitance model (Goldberg and Sposito 1984), but it ignores the surface electrical potential correction term, $\Psi$, while explicitly including in the reaction any inner- or outer-sphere counterions that must be adsorbed to balance surface charge created in the process. For boron, there is spectroscopic evidence that the adsorbed complex on oxides and kaolinite can have either trigonal or tetrahedral symmetry (Su and Suarez 1995). Although the exact chemical nature of the adsorbed boron complex is unknown, bonding is likely to involve the ligand exchange of surface $OH^-$ or $H_2O$, and coordination of $B(OH)_3^0$ or $B(OH)_4^-$ to surface metal ions (M) via a B-O-metal bond. Possibilities include:

$$\text{-M-OH} + Na^+ + B(OH)_4^- = \text{-M-O-B(OH)}_3^- \cdots Na^+ + H_2O \quad [5]$$

$$\text{-M-(OH)}_2^+ \cdots Cl^- + B(OH)_3^0 = \text{-M-O-B(OH)}_2 + H_2O + H^+ + Cl^- \quad [6]$$

The 1st reaction creates surface charge (cation exchange sites), whereas the 2nd reaction eliminates surface charge. It is evident from mass-action principles that any reaction that creates surface charge, like [5], is favored by higher concentrations of electrolytes (such as NaCl), since they enter into the reaction. Thus, the greater adsorption of boron at higher ionic strength (Figure 5) could be explained by the higher activity of cations in solution, which are available to compensate the surface negative charge generated by specific adsorption of borate.

In general, when the mass-action principle is applied to anion adsorption reactions that generate surface negative charge, it requires that higher background concentration of an indifferent electrolyte (that is, higher ionic strength) cause greater adsorption. Electrophoretic mobility and cation exchange capacity (CEC) measurements have confirmed that inner-sphere

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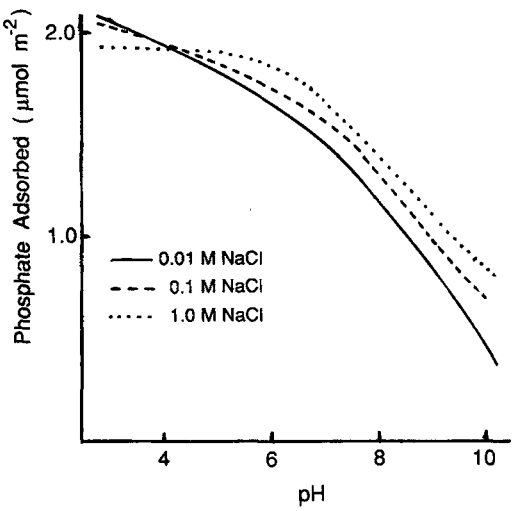



Figure 6. Phosphate adsorption on goethite as a function of pH at 3 background electrolyte (NaCl) concentrations. Figure adapted from Barrow et al. (1980).

complexation of anions actually does increase the net negative charge of variable-charge surfaces (Rajan 1978; Marcano-Martinez and McBride 1989; Su and Suarez 1995). Thus, this mass-action explanation is based on a well-documented fact: that excess surface negative charge is created by chemisorption of some oxyanions.

The ionic strength effect on anion adsorption may diminish or even reverse at lower pH (see Figure 6), a trend which may be due to greater involvement of protons in balancing the surface charge or associating with the anion. Thus at higher pH, phosphate adsorption generates surface negative charge that must be balanced by co-adsorbed cations from the electrolyte. At lower pH, however, adsorption is likely to diminish surface positive charge so that there is net release of anions such as $Cl^-$ from the surface, as shown on Figure 7. Also, because of the greater density of surface -M-$OH_2^+$ groups at lower pH, outer-sphere adsorption of anions may become more prevalent and allow for direct anion competition for these charge sites. The data of Barrow et al. (1980) suggest slight reduction of phosphate adsorption on goethite at higher ionic strength when the pH is below 4.5 (Figure 6), consistent with anion competition, although dissolution of the oxide becomes a complicating factor in interpreting adsorption data at very low pH.

The enhancement of anion adsorption by increased concentrations of indifferent electrolytes is relatively minor compared to that caused by salts of polyvalent cations. For example, Ca and Mg have an enhancing effect on the adsorption of $SO_4^{2-}$ and $PO_4^{3-}$ by oxides and soils (Helyar et al. 1976; Marcano-Martinez and McBride 1989; Bolan et al. 1993; Ajwa and Tabatabai 1995). It may be that $Ca^{2+}$ and other polyvalent cations

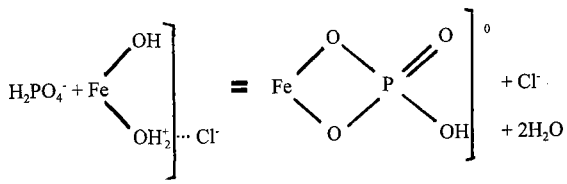



Figure 7. A possible bonding reaction of phosphate on iron oxide, showing the elimination of anion exchange sites.

are more effective than monovalent cations in compensating surface negative charge, or even that surface-catalyzed nucleation of metal $SO_4$ and metal phosphate occurs. The greater tendency of polyvalent cations to form inner-sphere ion pairs with surface-bound anions (ternary complexes) probably explains their effectiveness relative to monovalent cations in promoting anion adsorption. These effects, because they involve salts that are not indifferent electrolytes, are not explicable in terms of unmodified diffuse double layer models.

In summary, ionic strength effects on the adsorption of strongly bonding oxyanions at variable-charge surfaces are explicable on the basis of accepted chemical principles when all counterions adsorbed at the charge-balanced surfaces are taken into account. Experimental evidence for the inner-sphere bonding of numerous oxyanions (for example, phosphate, borate, sulfate and selenite) on variable-charge minerals, and the generation of surface negative charge by this adsorption reaction, is convincing. A necessary consequence of surface negative charge buildup is the co-adsorption of cations (such as $Na^+$, $K^+$ and $Ca^{2+}$) to maintain charge balance, and it follows from the mass-action principle that an increase in ionic strength increases the tendency for oxyanion adsorption. By a parallel argument, specific cation adsorption on variable-charge surfaces could be expected to increase with increasing ionic strength if the adsorption process generated surface positive charge. An alternative explanation for ionic strength effects based on contraction of the diffuse double layer at higher ionic strength is not consistent with all the chemical evidence, and furthermore fails the test of Ockham's Razor for choosing the simplest adequate hypothesis.

## CONCLUSIONS

Numerous phenomena observed in colloidal systems, including dispersion, osmotic swelling and phase transitions between ordered and gel states are demonstrated to be explained more satisfactorily by a diffuse double layer model incorporating an electrostatic attraction term (Sogami theory) than by the standard DLVO model. It appears that DLVO, which assumes no electrostatic attraction between charged colloidal particles, is only a reasonable approximation within a narrow range of conditions, applying to colloidal par-

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ticles with low surface charge density. Furthermore, the significance of van der Waals forces in attracting colloidal particles in aqueous suspension is doubtful.

The application of DLVO to adsorption phenomena, particularly those involving variable-charge minerals, is questioned on the basis of the rule of parsimony in selecting scientific hypotheses, since simpler explanations for the observed facts are available. It is argued that the parsimony rule (Ockham's Razor) should be applied systematically to all theories that purport to "explain" colloidal and adsorption behavior.

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