

BOOK REVIEW

Clay Swelling and Colloid Stability. Martin Smalley. CRC Press, Taylor and Francis Group, 2006, 272 pp. [ISBN 0-8493-8079-0] Price \$139.95.

The DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, formulated by Derjaguin and Landau (1941) and later independently by Verwey and Overbeek (1948), laid the foundations for our understanding of particle interactions in colloidal lyophobic dispersions and their kinetic stabilities. The configuration of the electrical double layers had been described previously by the Gouy-Chapman model with refinements later by many other investigators. In this model the counterions were reduced to point charges, liquid media were represented by a uniform dielectric constant, and colloidal particles by flat and uniformly charged large surfaces. The particle interactions in DLVO theory were assumed to be essentially controlled by two opposing forces, the screened Coulombic repulsion and by the London-van der Waals attraction. These oversimplifications have caused several problems in the application of the DLVO theory since its inception. For the last 50 years, various refinements and corrections were proposed to explain these discrepancies or to reconcile the theory with the observed data. This monograph calls an end to these corrections for the DLVO theory both on experimental and theoretical grounds. It is, therefore, a very important publication. It will be beneficial to the reader if I present this review in two parts:

Part 1 presents the author's own experimental data collected over the years that led him down the path for the formulation of a new theory for the stability of hydrophobic colloids. Chapters 1–7 are devoted to this section which is the essence of the monograph.

Part 2 discusses the configurations of counterions and water molecules in the interfaces between macroions *i.e.* charged platy colloidal particles in Chapters 8–10. The effects of a special polymer, PEO, on the stability of $n\text{-C}_4\text{H}_9\text{NH}_3^+$ -vermiculite dispersion, on its interlamellar separation, and the stacking order and crystallinity of the vermiculite layers are examined in Chapters 11–13.

Part 1. The author first explains how and why he selects an aqueous dispersion with vermiculite as platy macroions and $n\text{-butylammonium}$ ($n\text{-C}_4\text{H}_9\text{NH}_3^+$) as counterions for testing the swelling and stability of this system. The selection of the components of the system are really well thought out considering the morphological and structural characteristics, and particle associations of this mineral in an electrolyte solution. For the reader to understand the importance of this selection, a few

comments may be in order, though, given the advanced level of this monograph, the reader is expected to be familiar with these topics. The crystal structure of vermiculite is well established, unlike those of the other clay minerals. The silicate layers form well defined hydration complexes in their interlayer spaces; hydrated vermiculite can maintain its crystallinity with a 1.94 nm basal spacing. The charges on the basal surfaces of vermiculite layers are constant and localized over a periodic pattern due to Al^{3+} -for- Si^{4+} substitutions (Bleam, 1990). These charges generate a strong electric field. Because of the large lateral dimensions of the individual vermiculite layers, face-to-face associations of layers are strongly favored in aqueous dispersions. $n\text{-C}_4\text{H}_9\text{NH}_3^+$ ions, on the other hand, appear to be ideal counterions with both polar and hydrophobic non-polar ends. In an aqueous medium, hydrated vermiculite layers readily form well-defined stacks with one-dimensional order having interlayer spacings up to several tens of nm. Smalley was able to measure the thicknesses of these electrical double layers up to 62 nm. The actual thicknesses of the electrical double layers were measured precisely to this extent probably for the first time. For this purpose, experiments were designed with exceptional sophistication along with use of the most advanced diffraction systems with small angle neutron scattering (SANS). Long-wavelength neutron diffractometers were used to study the swelling states of the vermiculite. Smalley was able to determine precisely the one-dimensional long-range orders in $n\text{-butyl NH}_3^+$ -vermiculite dispersions with salt concentrations ranging from 0.001 M to 0.1 M in ten-fold step increases in concentration. He established that d spacings varied systematically from the initial 19.4 Å for the crystalline swelling to 122 Å at 0.1 M, to 330 Å at 0.01 M, and to 620 Å at 0.001 M salt concentrations. Smalley was now confronted with glaring discrepancies between his experimental data and predictions from DLVO. Smalley's careful correlations between the interparticle distances with the Debye screening constant ($1/k$) were completely beyond the realm of DLVO. Moreover, Smalley was surprised to realize that DLVO recourses to long-range van der Waals forces for the secondary minimum in the interparticle potential curve. Smalley, disappointed with the prominent DLVO theory, looked elsewhere for an explanation, instead of introducing real or imaginary correction factors for the purpose of reconciliation with the theory. He found a promising approach in Sogami and Ise's treatments of 'electrostatic interactions in macro-ionic solutions' of spherical macro-ions (Ise and Sogami, 2005). Smalley adopted this approach

to the platy particles of *n*-butyl NH_3^+ -vermiculite and formulated the 'Exact Mean Field Theory Solution' for platy hydrophobic colloids. These formulations reveal the long-range electrical attraction between platy charged colloids, which he names as 'Coulombic Attraction Theory' or simply 'CAT'. The author shows that the magnitude of the secondary minimum of the interparticle potential curve reflects the balance between the osmotic repulsion and long-range Coulombic attraction. His calculations of Gibbs free energies as a function of interparticle distances indicate that the observed swelling states with a one-dimensional order represent reversible phase transitions in the above system.

Coulombic attraction theory was further elaborated by statistical thermodynamics to secure its theoretical grounds. These calculations theoretically confirm the existence of long-range weak-attraction electrical forces. The long-range Coulombic attraction between macro-ionic platelets was visualized as if they were being held together by a ribbon of counterions midway between the platelets. Ise and Sogami (2005) depict the long-range electrical attraction between the platelets as more like a metallic bond. Thus, both theoretically and conceptually the Coulombic Attraction Theory effectively accounts for long-range electrostatic attraction between macro-ions in colloidal dispersions.

The author also gives a comprehensive account of the effects of uniaxial compression on the one-dimensional vermiculite gel at varying salt concentrations in Chapter 3. The results show that the effective surface potential remains fairly constant over a large range of salt concentrations, again in disagreement with DLVO. The author also deals with the discrepancies related to the application of the Nernst equation to the dispersions of platy macro-ions. He points out that the Nernst equation applies to the surface potentials created by the potential determining ions. The vermiculite's layer surfaces on the other hand, expose inherent constant charges. Chapter 4 deals with the problem about Donnan membrane equilibrium in the aqueous dispersions of platy macro-ions. Donnan equilibrium treats the partition of ions across membranes without any interactions with ions unlike a clay membrane.

Smalley's monograph on the stability of colloids with platy macro-ions and that by Ise and Sogami (2005) on the dispersions of spherical macro-ions open together a new era in Colloid Science. They represent a remarkable breakthrough in our understanding of particle interactions in colloidal systems.

Part 2. The author then attempted to determine the structure and distribution of the counterions and water molecules in vermiculite-electrolyte interfaces in the region adjacent to the surfaces of vermiculite layers. Diffuse neutron scattering measurements with substitution of hydrogen with its deuterium isotope show that

the 'naked' silicate layers (10 \AA) are coated with bilayers of water molecules 6 \AA thick on both sides. There was no Stern layer of counterions which was expected from the DLVO model. The counterions were found as segregated layers $\sim 4 \text{ \AA}$ thick beyond the bilayers of water molecules. These measurements were then confirmed with inverse Monte Carlo simulations.

For some reason, the short-range effects of hydration forces on the vermiculite surfaces were not considered at all. Highly charged surfaces of vermiculite layers may have higher hydration energies than those of the counterions in the system. It is feasible that strong electrostatic field of the vermiculite surface can even attract a second layer of water molecules. The special counterions like *n*-butyl NH_3^+ or *n*-propyl NH_3^+ have polar heads with NH_3^+ and non-polar tails. They may develop a hydration complex on one side consisting of a monolayer of water but a diffuse one on the tail side. Thus the structured segment of water bilayer may develop between clay surfaces and the heads of the counterions. The single layer of unstructured water molecules may preferably appear on the tail sides of the *n*-butyl NH_3^+ ions. Hydration complexes of counterions and those of the colloid surfaces are expected to be specific for each system. Counterions may have a variety of hydration energies, hydration numbers and hydration shells. Quadrupole structure of the water molecules and their H bonds may have significant effects on the short-range structure of the clay-water interface. For instance Cs^+ as a counter ion may appear in the Stern layer by forming an 'inner-sphere' complex with the silicate layer. Similarly Mg^{2+} may form an 'outer-sphere' complex sharing one layer of water molecules with the same surface of the clay mineral. Interestingly enough, an organic ion like *n*-butyl NH_3^+ finds itself even further away from the surface of the vermiculite layer. The variations in the nature of the hydration shells of counterions and features of the charged particle surfaces, may deserve some consideration before drawing general conclusions on the structure of the region adjacent to the clay surface.

The effects of a special non-ionic polymer PEO (polyethylene oxide) on the stability of a vermiculite-salt-water system, and on the interlamellar configurations and stacking order of vermiculate layers are examined in Chapters 11–13. Isotope substitutions of hydrogen with deuterium were carried on both counterions and on polymer chains of the system. The structural states of the gels were then studied with neutron scattering. Most of the data were collected with PEO by varying temperature and *M* (molecular weight of the polymer) and keeping other factors constant such as solid fraction at 0.01%, salt concentration at 0.1 M, and pressure at 1 atm without applying uniaxial stress. A detailed picture of the interlayer region was then drawn. The PEO segments were found to have replaced the water molecules on the surfaces of vermiculite layers

while the counterions were moved further away into the interlayer region. This polymer was assumed to establish large number of bonds (of van der Waals type) to the vermiculite surfaces; each bond as a bridge is shown to provide a drawing force of 0.6 pN. The PEO polymers were found to draw the successive layers closer when their molar weights were greater than a certain critical level. This is the concept of bridging flocculation proposed by the author, instead of a 'depletion' flocculation. The latter is related to osmotic pressure that is caused by the uneven concentrations of counterions in the interlayer space and in the outside medium. The intercalation of PEO polymers was also found to significantly improve the stacking order of the vermiculite layers and thus enhance their crystallinity.

The investigations in the monograph were designed with great care. They gave invaluable experimental data, collected with the most sophisticated methods and interpreted in terms of highly advanced theories. This special aqueous system with PEO, vermiculite macroions, and *n*-butyl NH₃⁺ counterions will certainly serve

as guiding models for future studies on the structure and stability of the colloidal systems. This monograph deserves, therefore, to be praised as a paradigm for future studies in Colloid Science.

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