

## BOOK REVIEW

**Clay-Water Interface and its Rheological Applications**, edited by N. Güven and R.M. Pollastro. Published by The Clay Minerals Society.<sup>1</sup>

This book is the fourth in the CMS series of paperbacks which are essentially proceedings of the Workshops held in conjunction with the annual meetings. It differs from its previous companion volumes in being subject-oriented rather than devoted to a single technique and its applications. Moreover the subject is of crucial importance. The nature and properties of the vicinal water in clays, extending into areas such as interparticle forces, colloidal stability and flocculation, and swelling, and the consequences of these phenomena for the macroscopic flow properties of clay dispersions. Each chapter is written by a well-known expert in his area. While the six chapters exhibit some overlap, this is acceptable and inevitable in a multi-author work spanning such a range of inter-dependent topics.

The first chapter, by Necip Güven, deals with the structure and dynamics of water, electrolytes and smectite-electrolyte systems, and fills about one third of the book, extending on to a discussion of interlayer forces at the molecular level. In part, the chapter nicely updates and extends the seminal review article by Sposito and Prost which appeared in *Chemical Reviews* in 1982. He discusses recent key advances made by Des McConnell's team at Oxford, who have done some impressive Monte Carlo and molecular dynamics simulations on smectite-water systems. They find evidence for three kinds of water in these systems, which may be termed "bound water", "free water" and "cavity water", the first referring to water in the inner hydration shells of the exchangeable cations and the last to water embedded in the ditrigonal cavities of the siloxane surfaces. In addition, they established that Na<sup>+</sup> and Mg<sup>2+</sup> cations are differently located, the bivalent ions preferring a central location, co-ordinated to 6 water molecules, while sodium ions tend to remain near one of the siloxane surfaces, forming an inner sphere complex with a triangle of surface oxygen atoms and three intralamellar water molecules. The "free water" not directly co-ordinated to exchanged cations diffuses at a rate much faster than the co-ordinated water or the cations.

The Oxford team's work is in remarkable good agreement with previous spectroscopic data, particularly from quasi-elastic neutron scattering measurements. Unfortunately, even with today's computational resources it is a major challenge to go to interlayer separations larger than three or four molecular water sheets to test Stern-Gouy-Chapman and DLVO-type theories. Güven covers such theories and their limitations. It seems to me that at least two of these are crucial. The assumption of uniform surface electrical potential is certainly invalid, even for pyrophyllite, and certainly for octahedrally charged smectites. Secondly, it is clear that there must be additional short-range repulsive interactions between clay surfaces, of neither double-layer nor Born hard-sphere type. These appear to be associated with specific surface or ion hydration effects, and have been directly measured for a number of systems by the techniques pioneered by Israelachvili and others. These are probably dipolar in origin, as proposed by Van Oss and colleagues.

Güven contributed a second chapter (ca. 40 pages, split approximately evenly between theory and applications) dealing with the macroscopic rheological behaviour of smectite dispersions. Here the author appears to be standing on rather less firm ground as an expert. Certainly this subject is outside of my own domain, so I asked two rheologist friends (one experimentalist and one theoretician) to comment on this chapter. Both expressed some concerns about the theoretical part of the chapter, in the sense that some of the definitions and equations were a little non-standard or potentially misleading. In particular, this applied to the definition of plastic viscosity given. It is suggested that readers seeking an overview of the theory of the subject should consult one of the books, such as "An Introduction to Rheology" by Barnes, Hutton and Walters, published by Elsevier in 1989. The applications section of Güven's chapter is focused mainly on dilute dispersions of smectite in the compositional range of drilling fluids, including some high pressure and high temperature rheometry from the author's own group. This is not, however, compared with other people's measurements, and the chapter as written shows no evidence of a thorough search through the recent petroleum engineering literature.

The third chapter, by Garrison Sposito, is a concise and narrowly focused chapter. He begins by reviewing different pieces of experimental evidence (viscosity, light scattering and small-angle neutron scattering) for the existence of quasi-crystals, containing several elementary 10 angstrom smectite units plus up to three intracrystalline water layers, even in dilute dispersions. Using this fact, plus the assumption that some of the remaining counterions external to such quasi-crystals may be condensed near the siloxane surface in a Stern-like layer, Sposito shows that modified Gouy-Chapman (MGC) theory can account quantitatively for the swelling of monovalent ion-exchanged smectites (M-smectites) in electrolytes up to 0.1 molal.

The fourth chapter, by Philip Low, is entitled "Interparticle Forces in Clay Suspensions: Flocculation, Viscous Flow and Swelling". The first two of the three subtopics are dealt with concisely and clearly. As might be expected, most space is devoted to the topic of swelling, and presents again the author's well-known position on the subject based on more than 40 years of research. This may be summarized as follows:

- (i) DLVO theory cannot explain measured force-interlayer separation curves for M-smectites, especially at separations of less than ca. 4 nm.
- (ii) Zeta potentials derived from electrokinetic measurements are typically 3 to 5 times lower than the surface electrostatic potentials of smectites calculated from charge densities derived from cation exchange capacities. This implies that most of the cations in smectites are bound near particle surfaces in Stern layers, and cannot therefore contribute to long-range repulsive interactions.
- (iii) Smectite swelling must therefore be attributable to a long-range modification of the water structure caused by the presence of the surfaces and their hydration.

No attempt is made to reconcile the clear difference of views represented by the last two chapters. Perhaps I will throw caution to the wind and attempt some kind of judgment here. In my view, admittedly based on many fewer years' experience than Professor Low's, but backed up by many years of experiments by other people, including Warkentin, Bolt, Otewill and others, is that DLVO or Stern-Gouy-Chapman

<sup>1</sup> This review will also appear in *Clay Minerals*.

models, while far from quantitative accuracy, especially in the presence of more concentrated electrolyte solutions, do approximately describe the swelling behaviour of M-smectites. Sposito shows, in my view convincingly, that even Low's own data are well described by an MGC model. I am concerned about Low's calculation of the relative counterion populations in the Stern and diffuse layers based on the zeta potential measurements. It is true that zeta potentials are several times lower than the surface potentials of smectites, but Low appears to assume that there is complete coincidence between the Outer Helmholtz plane and the plane of shear, which is not necessarily the case. In any case, the highly non-uniform surface charge densities for smectites computed by Bleam (and reviewed in Güven's first chapter) implies that such planes will be far from flat with respect to the smectite surface. Where the surface charge density is highest, clusters of ions may lie relatively close to the surface but may retain their mobility, as suggested by Sposito. Most people would agree that DLVO theory fails at lower separations, in the domain of the hydration forces. While some perturbations of water structure may propagate to larger distances than appear to be indicated by the dynamical spectroscopic measurements, it is not yet clear how this would provide a mechanism for long-range osmotic swelling. About 40 years ago, Norrish showed that sodium montmorillonite in brines of various ionic strengths swelled to a spacing which varied inversely as the square root of the ionic concentration, entirely in accordance with the prediction for overlapping diffuse dou-

ble layers. Perhaps the Monte Carlo studies may eventually put this matter to rest.

The final two chapters in the book are entitled "Particle Associations in Clay Suspensions and their Rheological Implications" by Van Olphen and "Characteristics and Mechanisms of Clay Creep and Creep Rupture" by J. K. Mitchell. Van Olphen's chapter gives a brief overview of the factors controlling the stability of clay colloids and the flow behaviour of suspensions. He retains the notions of edge-to-face flocculation and cardhouse structures which, while perhaps important in kaolinite suspensions, seem not to be significant for smectites according to recent SEM images taken using flash-freezing techniques. These show ribbon and honeycomb structures, with extensive face-to-face association of flexible, highly curved particles. Mitchell's contribution focuses on the civil engineer's domain between the Atterberg limits. In these denser, drier systems, motion is associated with the breaking of interparticle bonds, an activated process following Eyring rate theory. Mitchell also introduces a more recent model which accounts for the time dependence of creep rates.

Overall, the book is a very useful contribution to the subject, and anyone involved in any way with clay-water systems would find this a worthwhile addition to their shelves. The CMS are to be congratulated, not least for the highly user-friendly price.

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