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Clay Swelling Inhibitors – Computer Design and Validation

Mike Hodder and Steve Cliffe, M-I SWACO; Chris Greenwell, University of Durham (UK); Pete Williams, Glyndŵr University (Wales, UK); and Peter Coveney, University College (London, UK).

Abstract

This paper explains how the combined use of computer simulation, high-end visualization and experimental studies can offer an improved insight into clay swelling inhibition and a greater understanding of the underlying mechanisms at the molecular level.

The latest generation of high-performance water-based drilling fluids based on polyetheramines offers significant improvements over previous best available technology such as glycol- and silicate-based fluids. Historically, the development of new shale inhibitors for water-based drilling fluids has relied to a great extent on empirical screening of products with limited understanding of the relationship between chemical structure and performance.

Computer simulations use a number of methods to determine the lowest energy state or the most stable conformational state of molecules when certain boundary conditions are applied. The results can be validated by comparing the swelling tendency of inhibitors predicted via simulation with that obtained from clay swelling inhibition and shale dispersion tests. Further validation is obtained by comparing x-ray diffraction patterns under the same conditions used in elemental (CHN) and thermogravimetric analysis (TGA), and by comparing vibrational frequencies with Fourier-Transformed Infrared (FTIR) spectroscopy.

Finally, visualization of the structures can be used to gain insight into why certain inhibitors effectively prevent clay swelling. This approach allows better predictions of inhibitor performance and offers the possibility of custom-designed products to further narrow the performance gap between water-based fluids and oil-based or synthetic-based systems.

Introduction

Historically, drilling fluid research has largely progressed by simple performance tests with different candidate products being compared for their effect on viscosity, fluid loss, lubricity, shale inhibition or other parameters as appropriate. There has been little emphasis on understanding the relationship between product structure and modes of interaction or performance mechanisms. There are several reasons for this. Suitable analytical equipment can be very expensive and in many cases chemical manufacturers have been reluctant to disclose precise compositional details, although this objection can be overcome in many cases by suitable legal agreements on confidentiality. Many commercial products are also mixtures with various distributions of molecular weight, degree of substitution, etc. Whilst this is a complication, it does not detract from the basic approach and indeed the modeling can easily determine the influence of these various molecular parameters.

In 2008, M-I SWACO decided on a different approach by joining several UK universities in a joint project, funded by the Technology Strategy Board R&D Collaborative Programme. The Technology Strategy Board is a business-led, non-departmental public body, established by the UK government to promote R&D and exploitation of technology. This project (TSB/CRD/100), is known by the acronym NIMES - New Improved Muds from Environmental Sources.[1] It encompasses a three-year work program with the main objective being the identification of new shale hydration suppressants by the use of molecular modeling techniques. The consortium consists of the Universities of Durham and Glyndŵr (Wrexham), University College, London and the Centre for Advanced Software Technology (CAST) which provides visualization software. Some earlier results from the project are presented in Reference 2. The literature is reviewed in Reference 3.

Molecular modeling is not an entirely new concept to the industry.[4-6] Previous attempts have led to many insights into the way in which various inhibitors function but the approach has not been fully exploited in the design of new products. It was hoped that increased computing power combined with a systematic validation of the modeling by various complementary chemical analysis techniques and with the more traditional performance tests, would be more successful.

Current best available technology for shale inhibition is believed to be based on polyetheramines of relatively low molecular weight that intercalate between the basal surfaces of clay minerals to inhibit swelling. By modeling this process, it is hoped that improved additives can be developed, the emphasis being on identifying more biodegradable materials derived from renewable resources.

Project Overview

The project is divided into three main work programs: (i) modeling and validation, (ii) visualization and (iii) development of a new generation drilling fluid. This paper will focus on the first of these.

Modeling and Validation Program

Three main objectives are set for this work program:

• To validate that the insight delivered from computer simulation is relevant, pertinent and comparable with the experimental methods employed.

• To illustrate the usefulness in using computer simulation to rationally design molecules.

• To show that the computer simulation provides a physical basis for understanding clay swelling inhibition rather than "chemical intuition".

Simulations

A typical simulation involves up to 10 million atoms over nanosecond intervals. To date, the modeling has been restricted to montmorillonite clay, but this will be expanded in the future to cover other clay types. The specific sodium-ion exchanged montmorillonite clay selected (Fig. 1) has a cation exchange capacity of 73.8 meq/100 g.

Periodic boundary conditions are used to define the unit cell size. It is assumed that all inhibitors and other ions are already intercalated between the platelets; the model then determines their equilibrium position. Ingress into the structure is not simulated. A variety of analyses can be carried out on the computed atom positions and forces acting on the atoms within the simulated models. These include:

- **d-Spacings** – the interlayer spacing of the clay systems as a function of water content and inhibitor molecule loading can be determined. Monte Carlo methods are used to establish the interlayer loading for a given d-spacing.
- **Radial Distribution Functions** – these give the coordination environment of an atom type over the time of the simulation and across a set distance. In essence, it divides space around an atom into layers, rather like an onion, and maps the atom density present within each layer. This will give data of hydrogen-bond networks and chelation.
- **Atom Density Plots** – These illustrate the density of any atom type across the interlayer environment and can give information on the arrangement and modes of interaction of inhibitor molecules.
- **Diffusion Constants** – Molecular dynamics allows monitoring of the system as it evolves over short time periods. This can be validated by NMR relaxation experiments.
- **Velocity Auto Correlation Function** – allows computation of power spectra, which can be compared to FTIR data.
- **Hydration Energetics** are used to evaluate changes in the potential energy of the system as a function of hydration, relative to a similarly expanded clay system without water. Comparison with the known potential energy of bulk water gives an indication of the tendency of the system to swell.

Experimental Validation

The various experimental techniques fall into the following basic groups – chemical analysis on dried samples, chemical analysis on hydrated samples, physicochemical techniques and performance tests.

Chemical Analysis of Dried Samples

- **Thermogravimetric Analysis (TGA).** Measures weight loss as a function of temperature. A sample is placed on a microbalance within a furnace under a flow of an inert gas. The sample is pyrolysed and the change in mass measured. TGA gives the relative amounts of water and organic material in the powder. In some cases, it is possible to discern different types of organic material, presumably related to the strength of interaction.
- **Elemental Analysis for C, H, and N** will give the amount of these elements in the solid sample. It is used to establish the amount of inhibitor in the clay matrix and can also give the degree of amine functionalisation.
- **X-Ray Diffraction (XRD)** on the powder establishes the interlayer spacing of the clay sheets under the same conditions used for CHN and TGA.
- **Fourier Transform Infrared Spectroscopy (FTIR)** is used to establish whether there is any protonation of inhibitors and also as a qualitative check to determine whether the inhibitor has been intercalated or not.
- **Solid State Nuclear Magnetic Resonance (NMR)** is being run at the Open University to establish if any information can be obtained regarding the relative diffusion constants of the various molecules in the clay matrix.
- **Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).** This technique determines concentrations of elements in the ppm-ppb range. It is used to measure exchangeable cations in solution or solid samples to give an indication of the relative amount of inhibitor uptake.

Chemical Analysis of Hydrated (Solution) Samples

- **Wet-Cell XRD**. This can be used to monitor the interlayer spacing of clays as a function of the hydration state and in the presence of inhibitors. A custom-designed cell has been built at Durham University and is awaiting trials.
- **Solution NMR** is used to establish the degree of functionalisation of macromolecule inhibitors.
- **Gel Permeation Chromatography (GPC)** is used to establish the range of molecular weights in various inhibitors tested.
- **React-IR**. This is a novel reflectance FTIR technique that can be used to monitor processes in real time in solution. Initial results have been obtained. Interpretation is not straight forward.

- **Small-Angle Neutron Scattering** will be used to examine polymer adsorption onto clay surfaces.

Physicochemical Techniques

- **Adsorption Isotherms**. These look at the adsorption of inhibitor onto clays as a function of concentration. The pH and salinity can be varied.
- **Dispersion Studies**. Clay is agitated in the presence of an inhibitor and the degree of dispersion assessed.
- **Flocculation Studies** - the flocculation behaviour of the mineral/inhibitor system can be studied in a particle size analyser, under flow conditions.

Performance Tests

Inhibitor performance is validated using traditional tests developed by the drilling fluids industry. For screening purposes, two tests have been used:

- **Hot-Roll Dispersion Test**. Sized (2-4 mm) samples of outcrop shale (e.g., Oxford clay) are exposed to water/inhibitor in hot-rolling cells for 16 hours, typically at 150°F. The samples are then passed through a 2-mm sieve to determine percentage dispersion and the recovered material analyzed for water content.
- **Rheological Measurements**. These can give insight into how well dispersed a clay is into its individual component sheets and the flocculated/aggregated state of a clay/inhibitor system.

Results

Polyetheramine

The results of a typical computer simulation using polyetheramine (PEA) under two different pH conditions are shown in Figure 2, with the corresponding atomic density plot in Figure 3. This illustrates the way in which this particular molecule attaches to the clay surfaces. This type of inhibitor represents current best-available technology and demonstrates four modes of interaction, which contribute to varying extent to determine performance:

- Cationic inhibitor species migrate to the clay surfaces where they screen the negative charges, reducing repulsion and hence swelling tendency.
- Uncharged species containing sufficient hydrophilic groups on the backbone can chelate (i.e., preferentially solvate) undisplaced cations, preventing hydration. Many glycols work in this way.
- At lower hydration states, molecules with more than one reactive group (such as diamines) can "pin" the clay layers together by adsorbing on top and bottom surfaces simultaneously.
- Cationic inhibitors can displace hydratable sodium ions from the cation exchange sites.

Polyethylene Glycol and Polypropylene Glycol

It is well known in the industry that a combination of polyethylene glycol (PEG) with potassium ions provides enhanced inhibition compared to PEG or potassium alone. Molecular modeling suggests that these materials form a molecular complex in solution, which is believed to be responsible for this effect. This is illustrated in Fig 4, which shows the modeled complex between PEG (molecular weight 600) and a potassium ion.

These conclusions suggested alternative routes to obtaining effective swelling inhibition. For example, a combination of simple diamines with polyethylene/-polypropylene glycols would combine all four mechanisms identified for the polyetheramines. Put another way, this combination should also produce synergistic benefits.

This hypothesis was evaluated in a cuttings recovery test, with results shown in Figure 5. Some synergistic effects between simple diamines and PEG 600 can be seen in the lower moisture content of the recovered outcrop clay material. While these results are promising, it is clear that the polyetheramine control sample still gives the best results. It would appear that combining all four inhibiting characteristics in one molecule leads to better performance. It should also be noted that many low molecular-weight diamines are quite toxic and have nasty odors that would make them unsuitable for general use.

Calculation of Hydration Energy

Calculating the hydration energy of a hydrated clay-inhibitor system and comparing it with the energy of a non-hydrated system and bulk water allows qualitative ranking of the effectiveness of each inhibitor. The hydration energy is the energetic driving force for water insertion and hence a good predictor of the relative swelling tendency. The theory is summarized in the Appendix.

Once the hydration energy of the clay, inhibitor system converges with that of bulk water, swelling will stop. An example is given in Figure 6. This shows the interlayer water potential energies as a function of increased water content for each inhibitor. The clay system used in this simulation is montmorillonite with sodium counter ions. The potential energy of bulk water is also shown (dotted line). In each case, the addition of water to the clay-inhibitor system lowers the potential energy of the water present relative to bulk water.

The least energetic gain seen is for polyetheramine inhibitors, while the greatest is for Polyethylene glycol (PEG 200). The relative swelling tendency can be easily compared to experimental data, for example unconfined linear swelling tests.

This approach has emphasized the importance of the cation especially with PEG/PPG and similar molecules used in cloud-point glycol systems, which are normally only effective in the presence of potassium ions.

This conclusion was reached in the earlier work[4]; however, this recent study suggests that the energetic gain of water insertion into clay with PEG and PPG is so great that swelling will be enhanced with these inhibitors in freshwater or under low-salinity (NaCl) conditions. This is confirmed by cuttings recovery tests.

Visualization

The visualization part of the research program involves the evaluation and selection of software tools to be linked with the simulation engine and incorporated into a high-speed grid computing environment. This allows users to have interactive visualization. This part of the project is carried out by the Centre for Advanced Software Technology (CAST) Limited, based in Bangor, North Wales.

The simulation engine is the LAMMPS software (Large-scale Atomic/Molecular Massively Parallel Simulator) developed at Sandia National Laboratories in the USA. This software simulates the molecular dynamics over a short period of time and provides various data parameters regarding energies and molecular movement.

The end user can run simulations on remote, high-speed grids such as HECToR, the UK's high-end computing resource available for use by academia and industry in the UK and Europe and funded by the UK Research Councils.

The software can provide visualization of the molecular structures as they develop by tracking the movement of molecules over the course of the simulation. These visualizations can take two primary forms: 3D visualization using a number of existing molecular visualization packages (including UCSF's Chimera and UIUC's Visual Molecular Dynamics); and 2D graphing of important data parameters. These visualizations can be produced to simultaneously display the 3D molecular lattice and associated 2D parameter graphs in an animated format. Additionally, parameter measurements taken from physical experimentation can be overlaid on the 2D results graphs to allow easy comparison.

The net benefit of the visualization package for the user is an end-to-end system for the study of new materials through use of high-performance computing simulations, molecular visualization and traditional 2D graphing, which enables rapid turnaround of new studies and comparison with experimental results.

Development of New Drilling Fluids

The ultimate project goal is the development and field trial of a new water-based drilling fluid system with improved performance. The preferred route is via modified polysaccharides. Synthesized materials with promising performance are analyzed to determine their chemical characteristics (molecular weight, degree of substitution, etc.) so that this data can be fed back into the modeling.

The performance to date has been encouraging with three modified cellulose derivatives nearly matching the polyetheramine control (Figure 7). The differences in moisture content, though small, are significant; the typical error in the test being ±0.3% in absolute terms. Similar performance has been seen with a modified starch derivative when used in conjunction with 2 lb/bbl of an encapsulating polymer (Figure 8). However, on a more dispersive Arne clay substrate, performance was clearly lacking (Figure 9).

Simple hot-roll dispersion tests do not provide the best method of discriminating between high-performance fluids, especially in the presence of encapsulating polymers, which invariably lead to high percentage recovery. It can be seen from Fig. 8 and Fig. 9 that a KCl/glycol system using a medium cloud-point glycol also gives good results. Better discrimination is seen in cuttings hardness and linear swelling tests, where the polyetheramines clearly out-perform the glycols, emphasizing the need to focus more on the moisture content measurements rather than the amount of recovered material.

Conclusions

The NIMES project represents the first systematic attempt to validate chemical modeling of shale swelling inhibitors by closing the loop between the modeling, chemical analysis and product performance.

The project has identified four mechanisms by which successful inhibitors function and shown that this can lead to the identification of synergistic performance by combining products that exhibit two or more of these mechanisms.

The calculation of hydration energetics clearly identifies why some polyalkalene glycols perform better than others and which require the presence of potassium ions. This allows better selection of materials in existing applications.

The ultimate goal of developing an improved clay hydration inhibitor has not yet been achieved. The project is still ongoing and it is hoped that the increased level of understanding will be invaluable in future drilling fluid research efforts.

Acknowledgments

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Nomenclature

PEA = Polyetheramine
PEG = Polyethylene glycol
PPG = Polypropylene glycol

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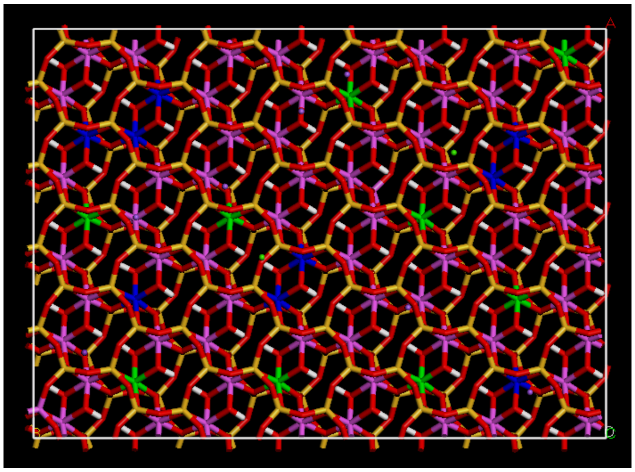

Figure 1. Model of montmorillonite with molecular formula $[Na_6Ca_2K][Si_{158}Al_2][Al_{62}Mg_9Fe_9]O_{400}(OH)_{80}.xH_2O$.

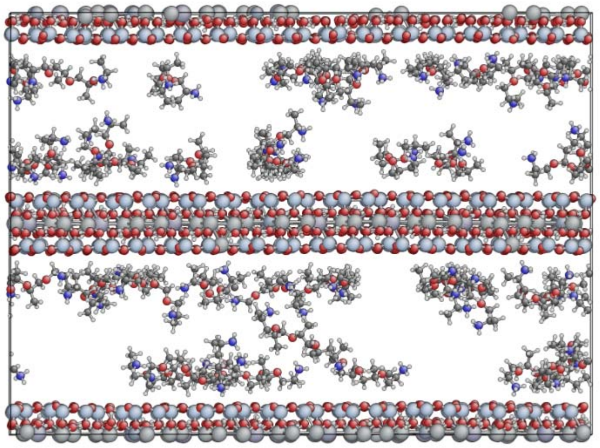

Figure 2. Polyetheramine adsorbed between montmorillonite platelets (water content 500-mg/g clay).

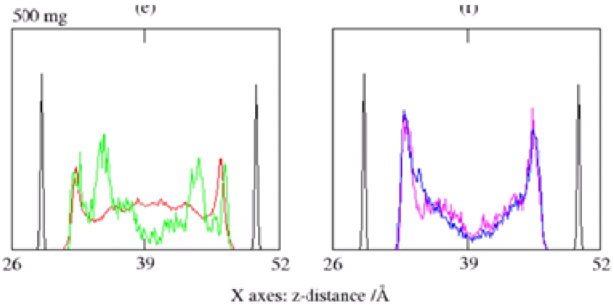

Figure 3. Atomic density plot of PEA. The left hand trace shows the distribution of nitrogen atoms in primary amine groups in green and oxygen atoms in water molecules in red. The right-hand traces plots carbon atoms in ether groups (green) vs. carbon in methyl groups (red).

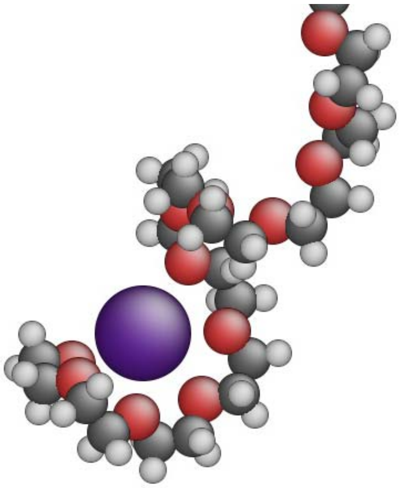

Figure 4. Chelation of a potassium ion by PEG 600.

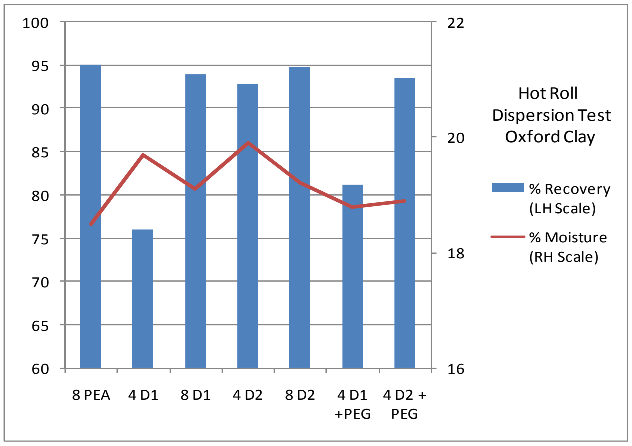

Figure 5. Results of hot-roll dispersion tests showing synergy between simple diamines (D1/D2) and PEG 600 with PEA control. Concentrations are in lb/bbl.

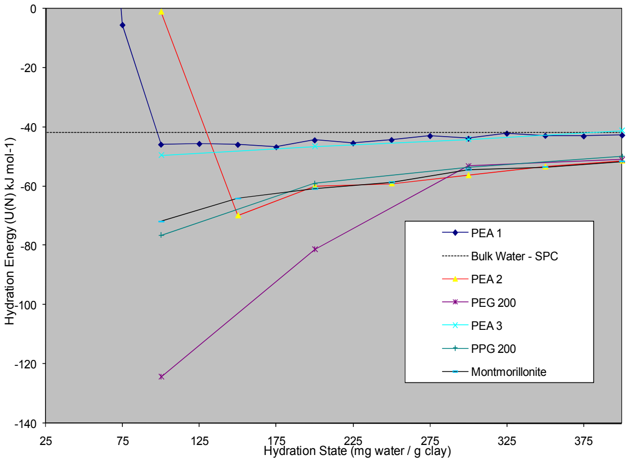

Figure 6. Hydration energy plot.

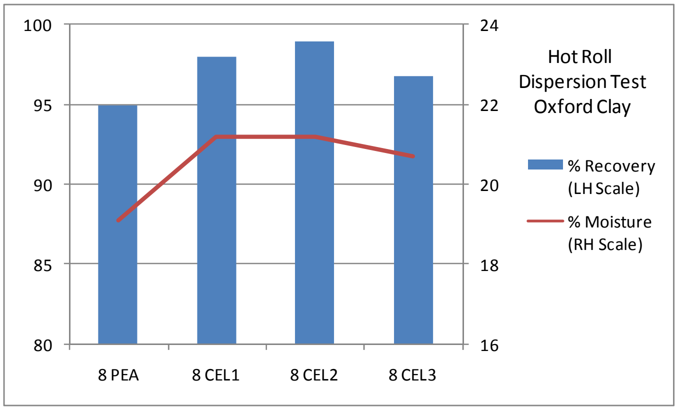

Figure 7. Results of hot roll dispersion tests showing performance of modified cellulose derivatives (CEL1, CEL2 and CEL3) compared to the polyetheramine (PEA) control. Concentrations are in lb/bbl.

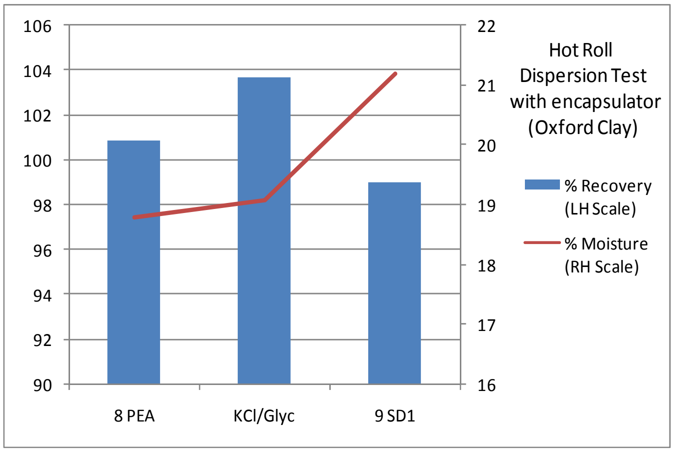

Figure 8. Results of hot roll dispersion tests with encapsulator showing performance of modified starch derivative (SD1) compared to the PEA and KCl/glycol controls. Concentrations are in lb/bbl.

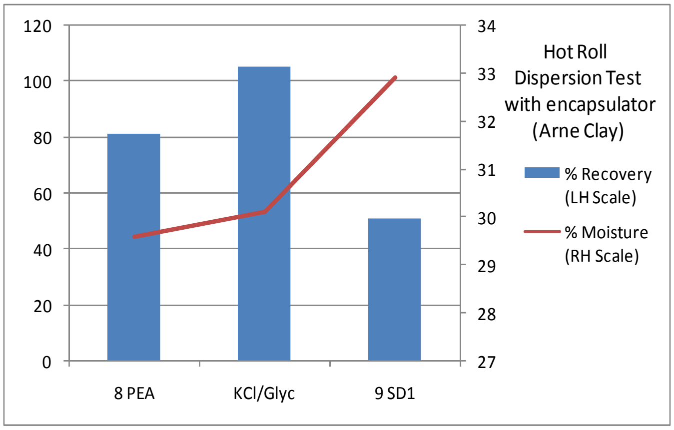

Figure 9. Results of hot roll dispersion tests with encapsulating polymer on the more dispersible Arne clay. Hydration suppressants tested are per Fig 8. Concentrations are in lb/bbl.

Appendix – Hydration Energy Theory

The energy of surface water adsorption (surface hydration), UH(N), is calculated as:

$$\Delta UH(N)=[U(N)-U(0)]/N \qquad \text{(Eq. 1)}$$

N is the number of water molecules, U(N) is the average potential energy of an equilibrium system with N water molecules on the surface, U(0) is the average potential energy of an equilibrated dry surface. The hydration energy calculated in this way is a convenient and useful parameter to describe the energetics of adsorbed water layers.

Whitley and Smith[7] recently demonstrated that entropic effects play only a relatively small, compensating role in the total balance of the hydration free energy for such layered mineral structures. Therefore, the hydration energy calculated according to Eq. 1 can be considered a good estimate of the free energy of water adsorption and the relative thermodynamic stability of the hydrated state.