

**Structure and forces
in bentonite MX-80**

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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Summary

Wyoming bentonite (MX-80) and its ion exchanged forms, Na and Ca montmorillonite, have been studied experimentally and theoretically. A variety of experimental techniques have been used in order to gain insight into the structural conditions in dry clay as well as clay in equilibrium with a bulk solution of given ionic composition. The main objective has been the swelling behaviour and osmotic pressure of montmorillonite clay when the bulk solution contains a mix of monovalent sodium and divalent calcium ions. For a clay system in equilibrium with pure water, Monte Carlo simulations predict a large swelling when the clay counterions are monovalent, while in presence of divalent counterions a limited swelling is predicted with an aqueous layer between the clay lamellae of about 1 nm. This latter result is in excellent agreement with small angle x-ray scattering data, but in disagreement with dialysis experiments, which gives a significantly larger swelling for Ca montmorillonite in pure water. Obviously, there is one lamellar swelling and a second “extra-lamellar” swelling, which could be the result of a phase separation in the clay. Montmorillonite in contact with a salt reservoir with both Na^+ and Ca^{2+} counterions will only show a modest swelling unless the sodium concentration in the bulk is several orders of magnitude larger than the calcium concentration.

The limited swelling of clay in presence of divalent counterions is a consequence of ion-ion correlations, which reduce the entropic repulsion as well as give rise to an attractive component in the total osmotic pressure. Ion-ion correlations also favour divalent counterions in a situation where we have a competition with monovalent ones. A more fundamental result of ion-ion correlations is that the osmotic pressure as a function of clay sheet separation becomes non-monotonic, which indicates the possibility of a phase separation into a concentrated and a dilute clay phase. This phenomenon could explain the “extralamellar” swelling found in the dialysis experiments.

Sammanfattning

Vi har undersökt såväl naturlig Wyoming-bentonit (MX-80) som de jonbytta formerna med endast Na^+ - eller Ca^{2+} -motjoner. Olika experimentella metoder har använts för att belysa strukturen hos både den torra leran och en lera i jämvikt med en bulklösning med en given saltsammansättning. Målsättningen har varit att studera svällningen och det osmotiska trycket för leran då den står i jämvikt med en vattenfas som innehåller en blandning av mono- och divalenta motjoner. För en lera som står i jämvikt med rent vatten, förutsäger våra Monte Carlo-simuleringar en kraftig svällning med monovalenta motjoner, medan i närvaro av divalenta motjoner blir svällningen begränsad med ett ungefär 1 nm tjockt vattenlager mellan lerskikten. Resultaten från simuleringar av ett lamellärt lersystem är i perfekt överensstämmelse med lågvinkelröntgenmätningarna (SAXS) men i konflikt med dialyseexperiment. Uppenbarligen finns det en lamellär svällning och en "extralamellär" svällning. En konsekvens av de olika svällningsförloppen för mono- och divalenta joner är att en lera, som står i kontakt med en saltlösning innehållande både natrium- och kalciumjoner endast kommer att uppvisa en begränsad svällning. För att leran ska uppvisa en kraftig svällning krävs att halten av monovalenta motjoner i bulkfasen är flera storleksordningar större än halten av divalenta motjoner.

Den begränsade lersvällningen i närvaro av divalenta motjoner är ett resultat av jon-jon-korrelationer, vilka kraftigt reducerar den entropiska repulsionen samtidigt som de ger upphov till en attraktiv komponent i det osmotiska trycket. Dessa båda effekter finns inte med i Poisson-Boltzmann-ekvationen som ofta används för att beräkna osmotiska tryck i kolloidala system. Det är således inte tillrådligt att tillämpa Poisson-Boltzmann-ekvationen i lersystem med divalenta motjoner, eftersom den ger kvalitativt felaktiga osmotiska tryck. Jon-jon-korrelationer gör också att kompetitionen mellan monovalenta och divalenta joner väger över till de senares fördel. Ett mer fundamentalt resultat av jon-jon-korrelationerna är att det osmotiska trycket blir en icke-monoton funktion av lerskiktsseparationen, vilket indikerar en möjlig fassetparation i en koncentrerad och en utspädd lersfas. Detta kan vara förklaringen till den "extralamellära svällningen".

Contents

1	Introduction	7
2	Theoretical section	9
2.1	Model system	9
2.2	Interactions	9
2.3	Osmotic pressure	10
3	Experimental Section	11
3.1	Materials and chemicals	11
3.2	Wyoming MX-80 bentonite	11
3.3	Cleaning of MX-80 bentonite	11
3.4	Na and Ca montmorillonite	12
4	Instruments and Methods	13
4.1	Osmotic swelling in dialysis pocket	13
4.2	Swelling in glass tubes	13
4.3	Swelling in desiccator	13
4.4	Transmission Electron Microscopy	14
4.5	Small angle x-ray scattering	14
4.6	NMR spectroscopy	14
5	Results	17
5.1	Monte Carlo simulations	17
5.2	Free swelling clay	20
5.3	Dialysis experiments	22
5.4	TEM results	23
5.5	SAXS results	25
5.6	NMR results	27
6	Discussion	29
7	Conclusions	31
8	References	33

1 Introduction

This work was initialized by SKB, as a part of their program for long term isolation of nuclear waste. When storing nuclear waste it is essential that no radioactivity leaks into the environment and considerable efforts have been invested in an attempt to find a safe and stable way of storing the waste. In the present scheme the waste is to be kept in copper containers embedded in clay. A natural clay, bentonite MX-80, is to be used as sealing material /1, 2, 3/. The success for such a containment depends of course on a stable structure of the clay. In this context stable means that the clay should be able to sustain considerable changes in the surrounding ground water including a salinity of glacial melt water as well as ordinary sea water, while still being an effective hydraulic barrier.

Dry bentonite, or more correctly its main component montmorillonite, is built up by layers approximately 1 nm thick, each consisting of two tetrahedral and one octahedral unit. The latter consists of Al(III), coordinated with oxygen, and is surrounded by the two tetrahedral sheets consisting of oxygen coordinating Si(IV). In bentonite one aluminum atom shares oxygen atoms with the two silica sheets, which gives the unit cell formula, $[Al_2(OH)_2(Si_2O_5)_2]$ /4/. The bentonite layers are charged due to exchange of Al(III) with for example Mg(II) and/or Fe(II) yielding an excess of negative charges. To obtain electroneutrality bentonite clay holds, most commonly, sodium or calcium ions as counterions.

This lamellar structure should make bentonite clay a perfect model system for an electrical double layer where the swelling and stability in saline solution depend strongly on counterion valency and surface charge density /5/. The situation is, however, from a structural point slightly less ideal. Clay is normally not a homogeneous lamellar material. It might be better described as a disordered structure of collections of platelets, sometimes called tactoids. This complicates the theoretical analysis, which always has been limited to the swelling/deswelling of the tactoids themselves (*intra-lamellar swelling*). Various hypotheses have been put forward for the arrangement of the tactoids, but none are really convincing and none of them are based on possibly existing forces between the tactoids. Additional complications come from the fact that the platelets may not be uniform in neither size nor surface charge density.

A negatively charged surface with its affinity for cations is itself a reason why bentonite is used for containing and cleaning up nuclear waste – highly positively charged heavy metal ions produced by nuclear disintegration are adsorbed by the clay surface.

The first part of this report deals with the results from MC simulations of a clay model system. The importance of ion-ion correlations in the presence of divalent counterions is demonstrated and the resulting attractive double layer forces lead to the prediction of a non-swelling clay provided that the ratio between calcium and sodium ions is sufficiently high. These results are based on the assumption that the clay platelets build lamellar structures of the sort depicted in Figure 2-1. Free swelling clay experiments (see below) as well as NMR experiments /6/ indicate that Ca montmorillonite swells more than the simulations predict and we have taken this as an indication of that the clay structure is not a microscopically homogeneous lamellar structure. In order to verify these indications, we have initiated an extensive set of experimental studies, including osmotic swelling, NMR, transmission electron microscopy (TEM), and small angle x-ray techniques (SAXS). The results of these are described below.

The report is organized as follows: First we discuss the clay model used in the calculations and the different experimental techniques used. The following starts with a presentation of the results from the Monte Carlo simulations. Then follows a description of the osmotic studies and the results from the various spectroscopic techniques used. Finally, we discuss the possible structural scenarios and draw some conclusions.

2 Theoretical section

2.1 Model system

A simplified model of montmorillonite would be to treat it as two planar negatively charged surfaces neutralized by sodium and/or calcium counterions – see Figure 2-1. The lamellae is assumed to be in equilibrium with an infinite salt reservoir of known salt concentration (bulk solution). This has for a long time been the generally accepted model system /7, 8/ and the statistical mechanical problem has been solved using the Poisson-Boltzmann (PB) equation /9, 10/. The latter is an excellent approximation in the presence of monovalent counterions, but it fails completely when the bulk solution also contains divalent counterions /11, 12, 13/. In order to obtain reliable results we have to go beyond the mean-field approximation inherent in the PB equation and use e.g. Monte Carlo (MC) simulation techniques or more advanced liquid state theories /14, 15/.

2.2 Interactions

We attempt to model the interaction between two clay platelets in a salt solution containing both monovalent and divalent cations (i.e. Na^+ and Ca^{2+}). The platelets are approximated as two infinite parallel charged sheets with a uniform surface charge density, σ . The separation is denoted h and the intervening solution containing co- and counterions is in equilibrium with an infinite bulk solution with known salt concentrations of relevant species. The water molecules are treated as a dielectric continuum with a relative dielectric permittivity, $\epsilon_r = 78$. In this *Primitive Model* we treat all charged species as charged hard spheres and the interaction, between two charges i and j separated a distance r , can be formally described as,

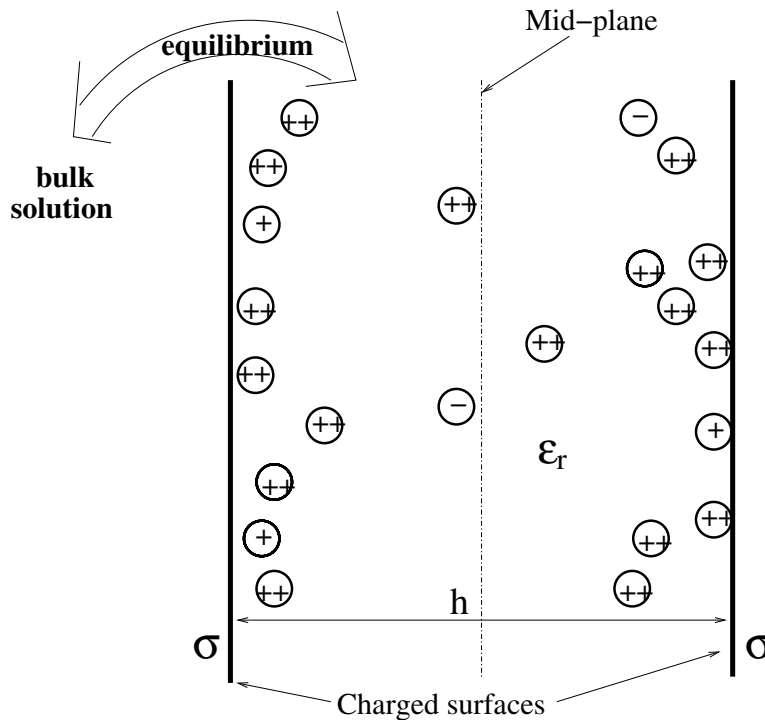


Figure 2-1. Schematic picture of two clay platelets with neutralizing counterions.

$$u(r) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 \epsilon_r r} \quad r > d_{hc} \quad (\text{Eq. 1})$$

$$u(r) = \infty \quad r > d_{hc} \quad (\text{Eq. 2})$$

where Z_i is the ion valency, e the elementary charge, ϵ_0 the permittivity of vacuum and $d_{hc} = 4 \text{ \AA}$ is the hard sphere diameter of the ion. The ions also interact with the charged wall and an external potential is included in order to take care of the interactions ranging outside the simulation box /16, 17/. Figure 2-1 shows a schematic picture of the system.

2.3 Osmotic pressure

The osmotic pressure of the confined solution, p_{osm}^{conf} , may be calculated according to either of the following expressions /11, 12/:

$$\begin{aligned} p_{osm}^{conf} &= k_B T \sum_i c_i(\text{wall}) - \frac{\sigma^2}{2\epsilon_r \epsilon_0} \\ p_{osm}^{conf} &= k_B T \sum_i c_i(\text{mp}) + p^{corr} + p^{hc} \end{aligned} \quad (\text{Eqs. 3})$$

where c_i is the concentration of species i and mp stands for mid-plane. These relations are exact within the primitive model. The term p^{corr} comes from the fact that ions on either side of the mid-plane correlate and give an attractive contribution to the pressure. In the mean-field description this term disappears, since the theory neglects correlations across the mid-plane. Here we have used the second relation for the evaluation of the pressure, since it tends to give the best accuracy. If the ions have a finite size d_{hc} , one also gets a hard core term, p^{hc} , which describes the additional pressure due to the finite volume of the ions.

The hard core radius has a clear physical origin, that is, ions can not overlap due to the quantum mechanical exchange repulsion. In simulations, or other theories of electrolyte solutions, it tends, however, to achieve a character of fitting parameter. There is no clearcut choice of d_{hc} – should it be the bare ion diameter or that of a hydrated ion? Fortunately for the present study of not too highly charged clay particles there is a relatively broad range for d_{hc} where it has only a weak effect on the interparticle forces. An interesting discussion of the importance of the ionic size can be found in a combined experimental and theoretical study by Kekicheff et al. /18/.

Eqs. 3 give the osmotic pressure in the confined region, but the experimentally interesting quantity is the net osmotic pressure,

$$p_{osm} = p_{osm}^{conf} - p_{osm}^{bulk} \quad (\text{Eq. 4})$$

where the bulk pressure is calculated for a bulk with the same chemical potential(s) as the double layer. This means that the concentration in the bulk and in the double layer can differ quite a lot and it is only the chemical potentials that are the same. This is the proper condition for equilibrium. A consequence of this, is that there exists a strong competition for different valency counterions. That is, it is enough with a relatively small concentration of divalent counterions in the bulk in order to have a double layer that is completely dominated by the divalent ions. For example, the concentration ratio c_{Ca}/c_{Na} in the double layer and in the bulk can easily differ by a factor of 100. In addition to the electrostatic pressure there is also a contribution from the so-called van der Waals interaction /9, 10, 19/,

$$p_{osm}^{tot} = p_{osm} - \frac{A}{6\pi} \left[\frac{1}{\hat{h}^3} - \frac{2}{(\hat{h} + d)^3} + \frac{1}{(\hat{h} + 2d)^3} \right] \quad (\text{Eq. 5})$$

where $\hat{h} = h + d_{hc}$, d is the thickness of a clay platelet and A is the Hamaker constant, for which we have used the value of $2 \cdot 10^{-20} \text{ J /20/}$.

3 Experimental Section

3.1 Materials and chemicals

Sodium chloride (NaCl, $M_w = 58.44$ g/mol) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $M_w = 147.02$ g/mol) were purchased from MERCK. Milli-Q water was used to prepare the NaCl and CaCl_2 solutions with salt concentrations in the range of 10 mM to 1 M. Hydrochloric acid (37% HCl) obtained from MERCK was prepared as 0.5 M for adjusting pH. Deuterium oxide (D_2O 99.8% D) was from ARMAR Chemicals, Switzerland and snake skin dialysis tubing (3.5 K MWCO, 1 mils) for the dialysis experiments was bought from PIERCE, US.

3.2 Wyoming MX-80 bentonite

It exists a number of bentonites differing in mineral and ion content. The important aspect for this study is the amount of divalent counterions and the surface charge density. The Wyoming bentonite (MX-80) used in this study has been characterized by Karnland et al. /3/ and in particular the amount of cationic counterions is accurately known, while the surface charge density is sometimes a more illusive quantity. Cadene et al. /21/ give a stoichiometric value of -0.13 C/m² for sodium montmorillonite, but at the same time they claim that the “apparent sheet charge” is only 8% of this value. Spitzer has modelled experimental osmotic pressures from a series of Wyoming bentonites with various monovalent counterions and based on PB calculations he finds an effective surface charge density of -0.11 C/m² and similar values have been reported elsewhere /22/. These numbers are of course average values and it has been suggested that both size and charge polydispersity can be of importance for the swelling behaviour of bentonite. One indication that this is *not* the case can be found in the experiments of Michot et al. /23/. They size fractionated Na montmorillonite and found that all three size distributions had the same cation exchange capacity. The osmotic behaviour of the three fractions was also almost identical. Table 3-1 summarizes the major components present in MX-80 bentonite supplied by the American Colloid Company.

3.3 Cleaning of MX-80 bentonite

This part describes the procedure how Wyoming MX-80 bentonite as received from the supplier was cleaned. 20 gram of MX-80 bentonite was shaken and washed with 250 ml Milli-Q water for 24 h in order to remove the larger impurities. Different size fractions of the clay were separated by filtration using filter paper. The clay fractions were then collected and dried in an oven for 3 h at 110°C in order to remove preabsorbed water /24, 25/. The final dry clay was then grinded and used in the experiments. Figure 3-1 shows the clay before and after the cleaning procedure.

Table 3-1. Major mineral and cation components in Wyoming MX-80 bentonite /3/.

Component	wt-%
Montmorillonite	87
Mica	4
Albite	3
Quartz	3
Cristobalite	2
Na ⁺	72
Ca ²⁺	18
Mg ²⁺	8
K ⁺	2

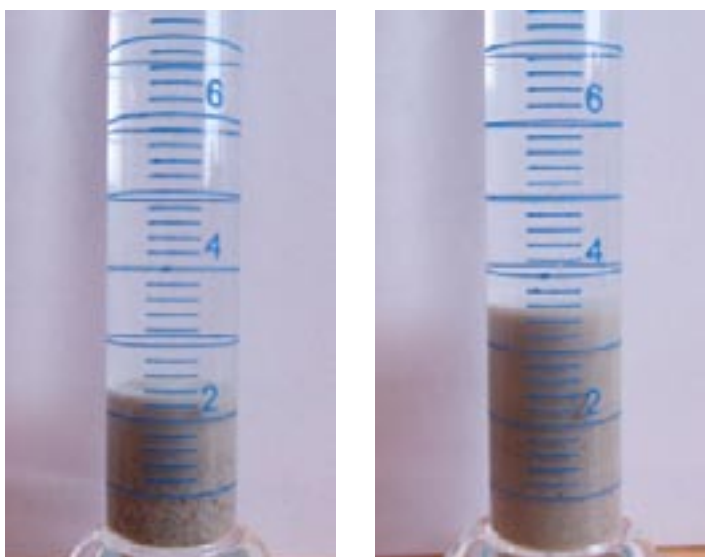
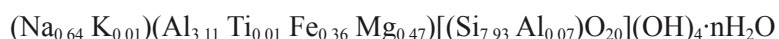


Figure 3-1. Wyoming bentonite MX-80 before (left) and after (right) the cleaning procedure. The clay (1.5 g) is in contact with a 1 M NaCl solution.

3.4 Na and Ca montmorillonite

The Na and Ca montmorillonites used in this study were obtained after purifying Wyoming bentonite MX-80 at the laboratory of Clay Technology AB. The purification procedure was as follows: A 10 g portion of MX-80 bentonite was dispersed in 1 l of 1 M analytical grade chloride solution of the desired cation and left to settle. The supernatant was removed and the procedure repeated three times. The material was washed three times with de-ionized water and the supernatant was removed after centrifugation. The suspension was separated from the accessory minerals by decanting. In order to remove excess electrolytes, the clay suspension was transferred to dialysis membranes (Spectrapore 3, 3500 MWCO) and placed in plastic containers with deionized water. The water was changed daily until the electrical conductivity was below 10 $\mu\text{S}/\text{cm}$. The material was redispersed in 1 l of 1 M analytical grade chloride, and the process was repeated. The final montmorillonite was dried at 60°C and milled to an aggregate grain size similar to that of MX-80. The structural formula of the Na-exchanged montmorillonite was determined by ICP-AES elementary analysis /3/:



and that of the Ca-exchanged form as:



4 Instruments and Methods

4.1 Osmotic swelling in dialysis pocket

Two different procedures were used for the swelling. One series of experiment used Snake-Skin dialysis tubing, which were cut to appropriate length and put into Milli-Q water for 24 h. One end of the tubing was folded over twice and attached. Then 1 g of clay was added and the Snake-Skin tubing was rolled up in the open end and pressed slightly to remove the air inside the pocket, and then folded over twice and attached to make a clay pocket.

The tubings were placed in 500 ml of Milli-Q water and stirred at room temperature (25°C) for four days – see Figure 4-1 for a picture of the setup. The clay pockets were transferred into 500 ml of 100 mM NaCl for a week changing the salt solution every other day. Thereafter the NaCl concentration was increased to 200 mM and the samples were treated as described for another week.

4.2 Swelling in glass tubes

For this series of experiments, 1 g of clay was dispersed in glass tubes or measuring cylinders with Milli-Q water. Clay suspensions were shaken until complete dispersion and left to settle for some days. The amount of clay was measured by the suspension height in the cylinders and the samples were photographed at different intervals in order monitor the swelling. This set of experiments was carried out in order to obtain a qualitative picture of how the different clay systems swell under varying salt conditions.

4.3 Swelling in desiccator

Approximately one gram of either Na or Ca montmorillonite was placed in a beaker, which was placed in a desiccator. The desiccator also contained an additional beaker with millipore water of various NaCl concentrations. Prior to use the clay was dried in an oven at 95°C, in order to remove all preabsorbed water. By changing the salt concentration in the solution (from zero to saturated) the chemical potential of water was regulated and thereby the swelling of the clay could be controlled. The weight increase of the samples were monitored in order to follow the swelling over time. These dry experiments were conducted at room temperature, 25°C.

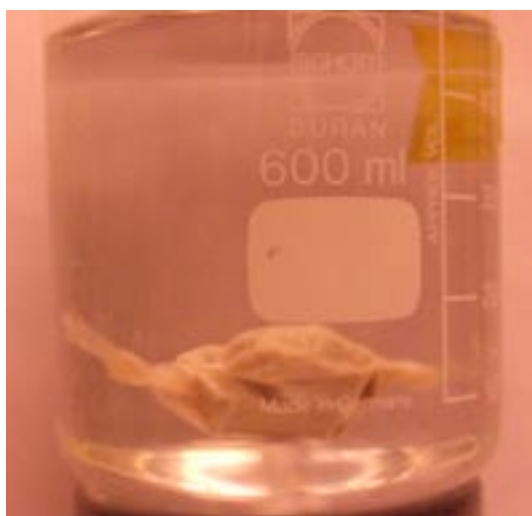


Figure 4-1. Dialysis pocket with clay in a beaker placed on a magnetic stirrer.

4.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) techniques allow the following properties of clay minerals to be determined in a non-destructive way /26, 2, 27/: (i) morphology; (ii) structure (by selected area electron diffraction, SAED); (iii) lattice imaging (by high-resolution transmission electron microscopy, HRTEM); and (iv) chemical composition (by energy dispersive X-ray fluorescence, EDXRF). The TEM study was carried out using a JEOL 3000F high-resolution transmission electron with a field-emission electron source. The microscope is equipped with video rate camera, and a 2 x 2 k CCD camera for HR image recording. The structural resolution is 0.17 nm in conventional mode, and 0.13 nm in STEM mode with high-angle annular detector. The microscope has an Oxford XEDS system and a Gatan Imaging Filter (2 x 2 k) for analysis of chemical composition with a spatial precision below 1 nm. Specialised holders for specimen transfer at liquid nitrogen temperature, in situ heating, scanning tunnelling microscopy with simultaneous TEM viewing. Small amounts of the dry powder from the four types of clays, MX-80 bentonite, clean MX-80 bentonite, Na and Ca montmorillonite were dispersed with some drops of ethanol with purity 99.5%. The samples were placed on thin carbon films and put into the Be holder and inserted into a special TEM, which allows the specimens to be studied at 25°C.

4.5 Small angle x-ray scattering

Small angle x-ray scattering (SAXS) /28, 29, 30/ has been used to study the structure of the clay platelets of various forms of MX-80 bentonite. The instrument was a Kratky compact camera with a linear position sensitive detector (MBraun, Graz), and a Seifert ID 3000 (3.5 kW) generator – see Figure 4-3. Equipped with two separate detectors, the instrument may record, simultaneously, the scattered intensity at both low and wide angles.

MX-80, Na and Ca montmorillonite have been studied at varying water content. The water content has been varied from very high values, corresponding to dilute clay solutions and full swelling to very small values. The salt free samples were prepared by dispersing 0.1 g of clay in Milli-Q water. The full swelling samples of the clay-salt system were prepared by adding the same amount of different clays in powder form to 10 ml of salt solution of varying composition. The samples were then shaken and placed to equilibrate at 25°C for a week. Two types of holders were used: one made from aluminum sheets and the other was a quartz capillary.

4.6 NMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy provides information on both the structural and dynamic aspects of solids, including clay minerals /31, 32, 33/. Our instrumental setup was a Bruker DMX100 spectrometer and a Bruker MSL 100 spectrometer interfaced to a variable field electromagnet.

Samples of various forms of MX-80 bentonite were used. All samples were fully swollen and prepared by adding large amounts of D₂O (Armar Chemicals, Switzerland) to the clay powders. The clay was put into an NMR tube and the water content was reduced upon heating to 75°C in time intervals from 10 to 60 min.

The intention was to use ²H-NMR to detect the extra-lamellar swelling in clays at high water contents. With extra-lamellar swelling we mean the uptake of water between large suspended clay particles (“tactoids”) – see Figure 5-1 (left). Each clay particle can also take up water internally between the planar montmorillonite layers, which build the solid part of the clay particle. We refer to this swelling as intra-lamellar swelling, see also Figure 5-1 (right). Similar cartoons have been put forward as possible structures for natural clays in the past, see e.g. references /24, 34/ and references therein.



Figure 4-2. Transmission electron microscopy (TEM) apparatus.

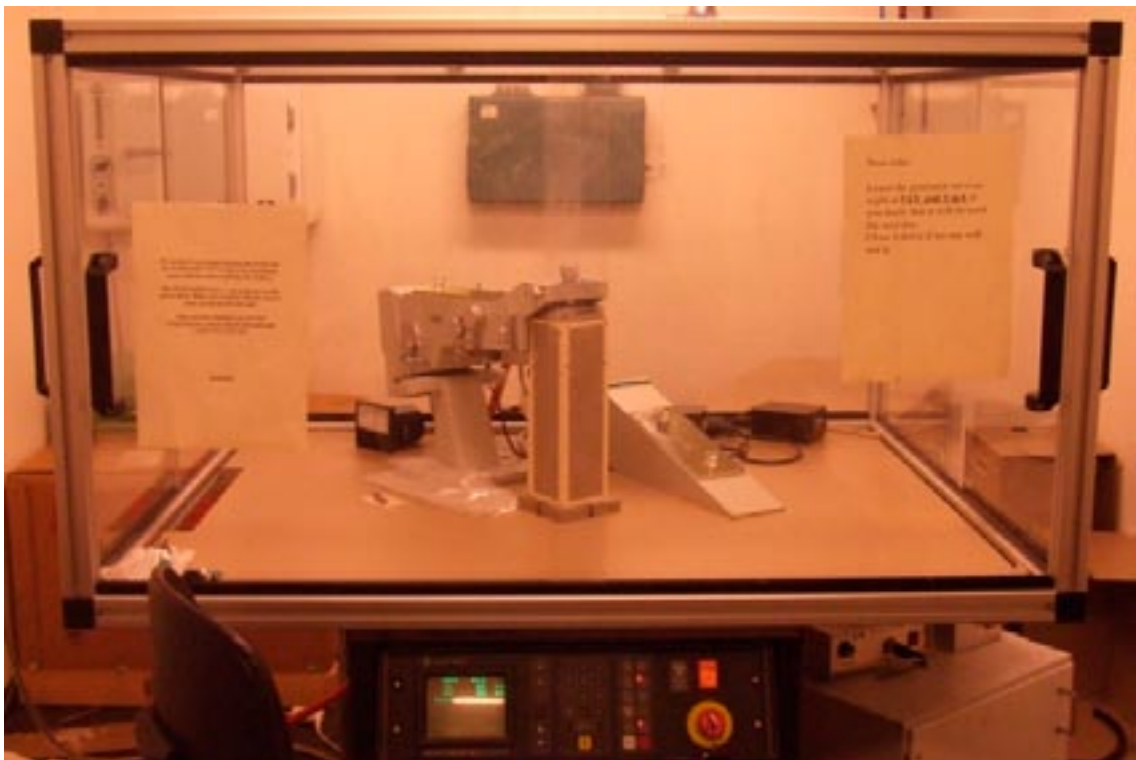


Figure 4-3. Kratky camera for small angle x-ray scattering.

5 Results

5.1 Monte Carlo simulations

The simulations were carried out with the Metropolis algorithm /35/ in the grand canonical ensemble /36, 37/. The number of ions varied between 100 and 1,000, depending on salt conditions. Initially we studied two salt free system with the surface charge densities -0.07 and -0.14 C/m^2 . In one case monovalent counterions were used and in the second case divalent and the results are shown in Figure 5-2. Monovalent counterions always lead to a monotonic repulsion between the clay particles, while with divalent counterions and the higher surface charge density we see an attraction due to ion-ion correlations. An interesting feature is that an increase in surface charge density leads to an increased repulsion with monovalent counterions, while the opposite is seen with divalent counterions. Figure 5-2b covers a range in surface charge density from -0.05 to -0.13 C/m^2 and it shows that electrostatic interactions alone is enough to give an attractive osmotic pressure if $|\sigma| > 0.07$ C/m^2 . Note that the non-monotonic curve in Figure 5-2b has a weak maximum indicating the possibility of two phases in co-existence. Experimental studies on Ca hectorite indicates that this can actually happen in clay systems /33/. The pressure curves in Figure 5-2 are lacking the attractive van der Waals component included in Eq. 5.

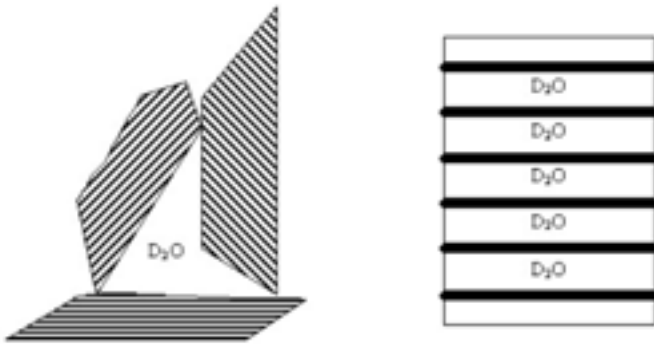


Figure 5-1. Schematic picture of the extra-lamellar swelling between the tactoids (left) and the intra-lamellar swelling between the clay platelets (right). The thick lines represent single clay platelets swelling of a model clay system.

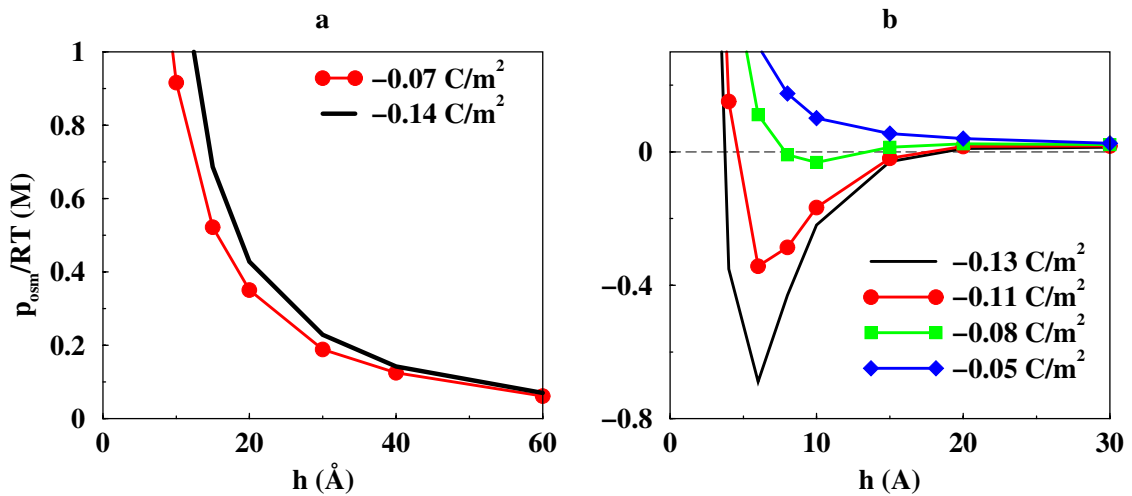


Figure 5-2. The electrostatic component of the osmotic pressure as a function of separation. The bulk solution consists of pure water; i.e. $\mu = 0$ and the surface charge density is indicated in figure. a) Monovalent counterions and b) divalent counterions.

Addition of the van der Waals attraction introduces a small decrease of the pressures as can be seen in Figure 5-3 – with monovalent counterions the pressure is still repulsive, while the pressure with divalent counterions becomes slightly more attractive. The corresponding pressure calculated with the PB equation is also added for comparison. Obviously the latter gives a qualitatively incorrect result with divalent counterions!

The van der Waals interaction becomes important with monovalent counterions when the double layer repulsion has been screened out by a high salt content. Under these conditions the van der Waals attraction can dominate and even a clay with exclusively monovalent counterions shows a very limited swelling – the water layer reaches a maximum of about 1 nm similar to systems with divalent counterions and in excellent agreement with the SAXS measurements – see below. Figure 5-4 shows how the addition of salt eventually leads to a non-swelling state.

Figure 5-5a shows the rather trivial result of adding an 1:1 salt to a system with only monovalent counterions. Adding salt leads to a screening of the repulsion as predicted by mean-field theory. Figure 5-5b shows that a system with divalent counterions is less sensitive to salt addition than a system with monovalent counterions, which has also been seen experimentally /18/.

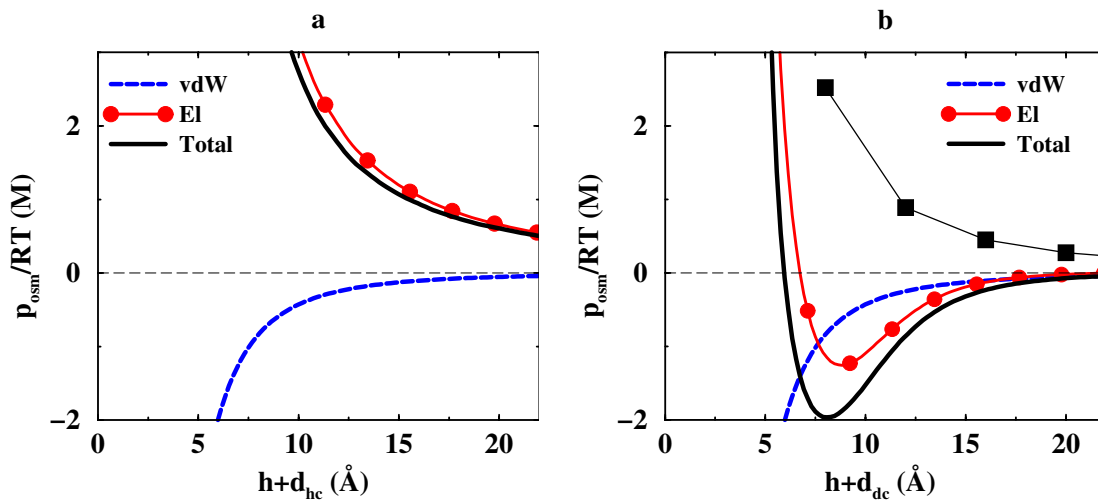


Figure 5-3. The total osmotic pressure as a function of separation for a surface charge density of -0.16 C/m^2 . a) Monovalent counterions and b) divalent counterions. The thin line with squares is obtained from the PB equation.

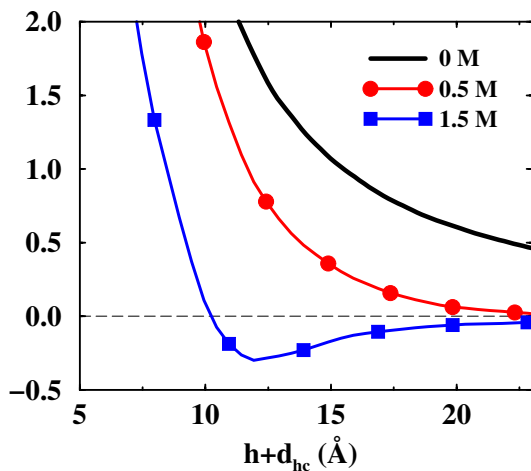


Figure 5-4. Salt effect on the total osmotic pressure in a system with only monovalent counterions and $\sigma = -0.14 \text{ C/m}^2$. Note that the van der Waals interaction is included.

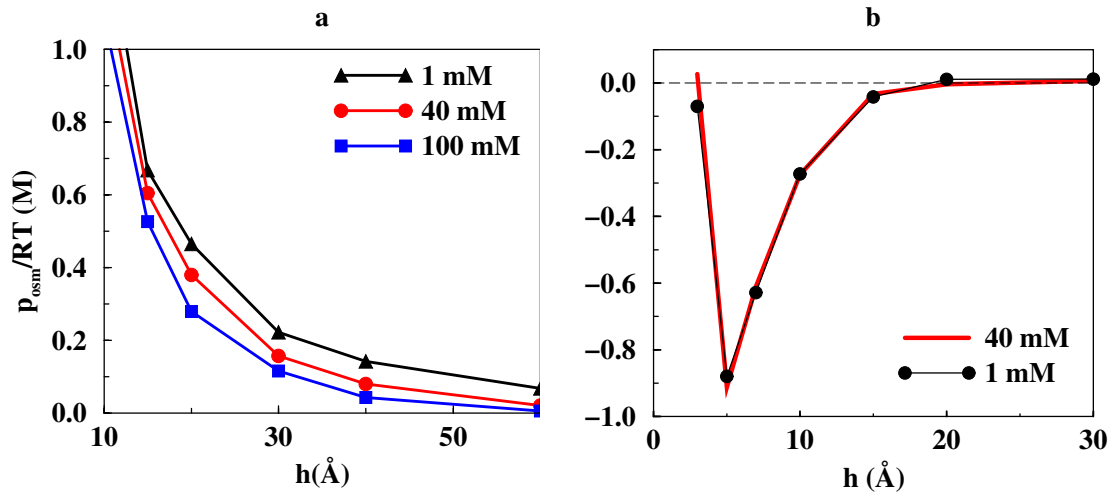


Figure 5-5. Salt effect on the net osmotic pressure with $\sigma = -0.14 \text{ C/m}^2$. a) 1:1 salt and b) 2:1 salt.

We have also simulated a clay system in equilibrium with a salt solution containing both mono- and divalent counterions, for example, a mixture of sodium and calcium ions. The valency of the coion is of less importance and we have for simplicity taken it to be monovalent. With both mono- and divalent counterions in the bulk there will be a competition for the charged surfaces. Divalent counterions will dominate in the double layer in general, but the detailed outcome will depend mainly on two factors, the surface charge density and the concentration ratio between mono- and divalent counterions in the bulk. Figure 5-7 shows that a system with $\sigma = -0.14 \text{ C/m}^2$ can sustain a ratio of almost 100 and still maintain a net attractive double layer force between the clay particles. If the surface charge density is increased then an even higher ratio is possible. In the opposite situation, with a lower surface charge density, ion-ion correlations become less important and calcium ions will not dominate the double layer interaction.

Note that the amount of monovalent counterions between the surfaces is very low and typically only a few per cent of the particle charge is neutralized by monovalent counterions. This means that if we prepare the system such that the amount of monovalent counterions in the slit is fixed, then it suffices to increase the relative amount of sodium ions to approximately 10% in order to extinguish the attractive component in the double layer interaction – see Figure 5-6. A possible consequence of this phenomenon is that even a small non-electrostatic effect, e.g. a weak specific adsorption of to the clay surface, that favours the monovalent counterions can change the interaction from attraction to repulsion.

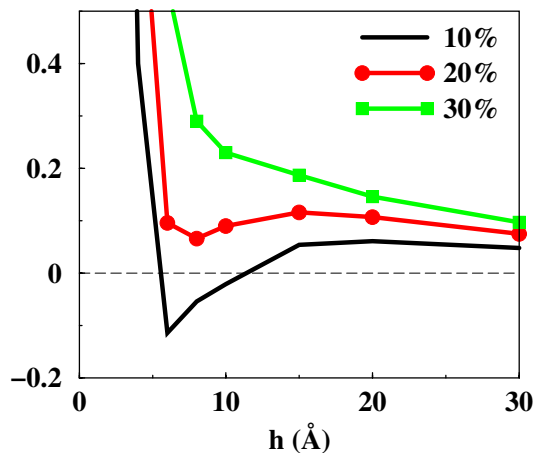


Figure 5-6. The net osmotic pressure as a function of separation. The system is equilibrium with pure water and the amount of monovalent/divalent counterions has been varied. The fraction of surface charge neutralized by monovalent counterions is indicated in figure and surface charge density is $\sigma = -0.11 \text{ C/m}^2$.

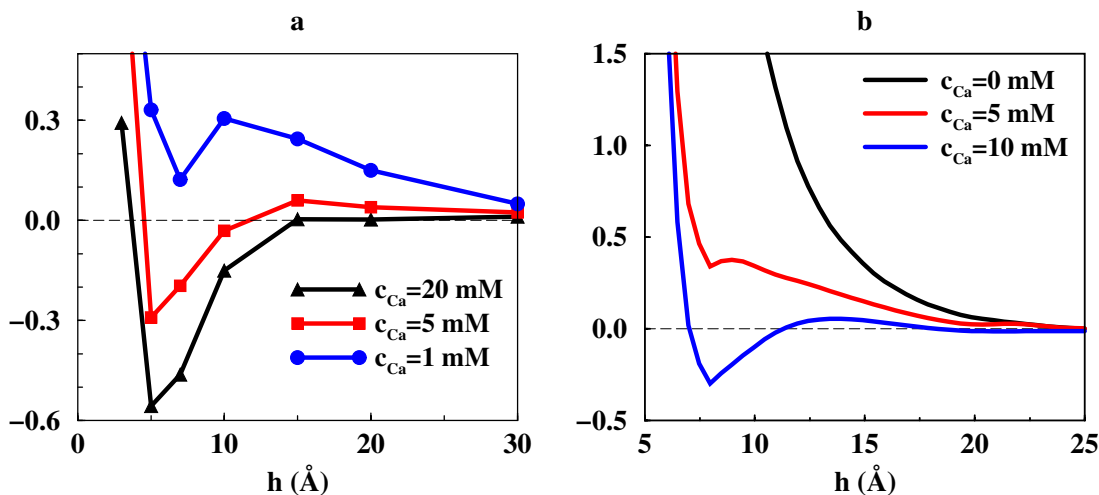


Figure 5-7. The net osmotic pressure as a function of separation. The bulk contains a mixture of NaCl and CaCl₂. The former is kept constant at a) 100 and b) 500 mM, while the CaCl₂ concentration is varied as indicated in the graphs.

The curve in Figure 5-7b with an attractive minimum corresponds approximately to the salt conditions in ocean water (500 mM monovalent cations and 10 mM divalent cations).

5.2 Free swelling clay

In an attempt to study the osmotic swelling of clay, we prepared solutions of Na and Ca montmorillonite in tubes. A small amount of clay (approximately 0.2 g) was put on the bottom of the tubes and solutions of varying salinity were added. The samples were photographed at different time intervals and the swelling could be followed.

The swelling of Na montmorillonite in NaCl solutions is quite rapid and equilibrium is reached after a few days – see Figure 5-8. Visual inspection shows the clay to swell at least one order of magnitude in volume for the lowest NaCl concentration of 0.2 M. With increased salt concentration one can observe a reduced swelling and with 2 M there is a very fast and limited swelling.

Ca montmorillonite shows a more modest swelling in contact with 0.2 M NaCl solution – see Figure 5-9. The initial swelling is most likely due to an exchange of calcium ions with monovalent sodium ions. At sufficiently high NaCl concentration all calcium ions will be exchanged and effectively the conditions will be the same as in Figure 5-8. Figure 5-10 displays a reduced swelling compared to Figure 5-8, which is due to the replacement of sodium ions in the double layer by divalent calcium ions.

Calcium montmorillonite in contact with a calcium chloride solution swells less than its Na counterpart as demonstrated in Figure 5-11. The limited swelling at low salt content is due to the absence of double layer repulsion in the present of divalent counterions. That is, the swelling behaviour seen in Figures 5-8–5-11 is in qualitative agreement with Monte Carlo simulations of the model system in Figure 2-1. The quantitative agreement, however, is poor and the final swelling in Figure 5-11 is much larger than *both* simulations and scattering experiments predict, since it includes both intra- and extra-lamellar swelling. We will return to this problem in the discussion section.

In the “dry” experiments in desiccator the clay absorbs water through the atmosphere in the closed vessel. Different salt content in the salt solution at the bottom of the desiccator determines the amount of water uptake. When looking at experiments conducted at 25°C, see Figure 5-12, one clearly sees that the sodium clay swells more than the calcium clay, at least when $c_{NaCl} \leq 1$ M. The difference in swelling between Na and Ca montmorillonite is less than expected. One can also note that the initial process seems to be the same in all the experiments. Calcium

montmorillonite swells slightly more initially and at high electrolyte concentrations it actually swells more than Na montmorillonite. The systems behave qualitatively the same at a higher temperature, 48°C (data not shown).

The swelling in desiccator is, however much smaller than the swelling seen in the (wet) dialysis experiments below – see e.g. Figure 5-13. The difference in swelling behaviour between the wet and dry experiments is well known, but has not been properly explained. There are a few possible explanations. One possibility is that it is a transport problem (affecting the rate of the swelling not the equilibrium). Another explanation could be that the van der Waals force is different at the clay-vapour-clay interface compared to the clay-water-clay interface. A larger van der Waals force would of course decrease the swelling.

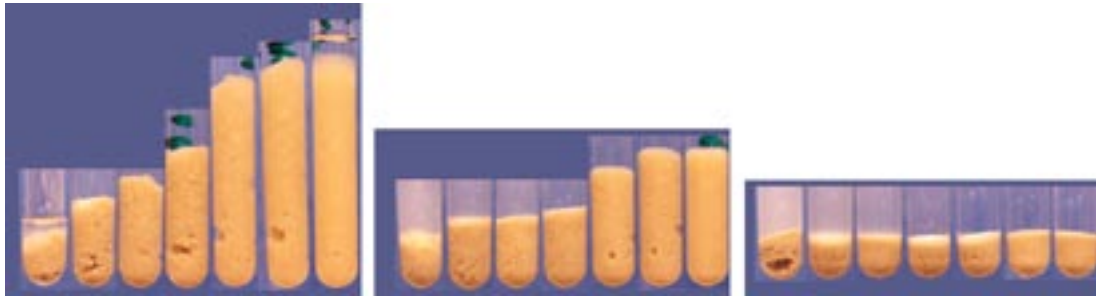


Figure 5-8. Na montmorillonite in contact with NaCl solutions of varying concentrations; from left to right the concentrations are 0.2, 0.5 and 2 M, respectively. The tube photos in each figure has been taken after 1min, 5min, 10min, 1h, 1 day, 4 days and 20 days, respectively.



Figure 5-9. Ca montmorillonite in contact with NaCl solutions of varying concentrations; from left to right the concentrations are 0.2, 0.5 and 2 M, respectively. The tube photos in each figure has been taken after 1min, 5min, 10min, 1h, 1 day, 4 days and 20 days, respectively.



Figure 5-10. Na montmorillonite in contact with CaCl₂ solutions of varying concentrations; from left to right the concentrations are 0.01, 0.05 and 0.1 M, respectively. The tube photos in each figure has been taken after 1min, 5min, 10min, 1h, 1 day, 4 days and 20 days, respectively.



Figure 5-11. Ca montmorillonite in contact with CaCl₂ solutions of varying concentrations; from left to right the concentrations are 0.01 and 0.05, respectively. The tube photos in each figure has been taken after 1min, 5min, 10min, 1h, 1 day, 4 days and 20 days, respectively.

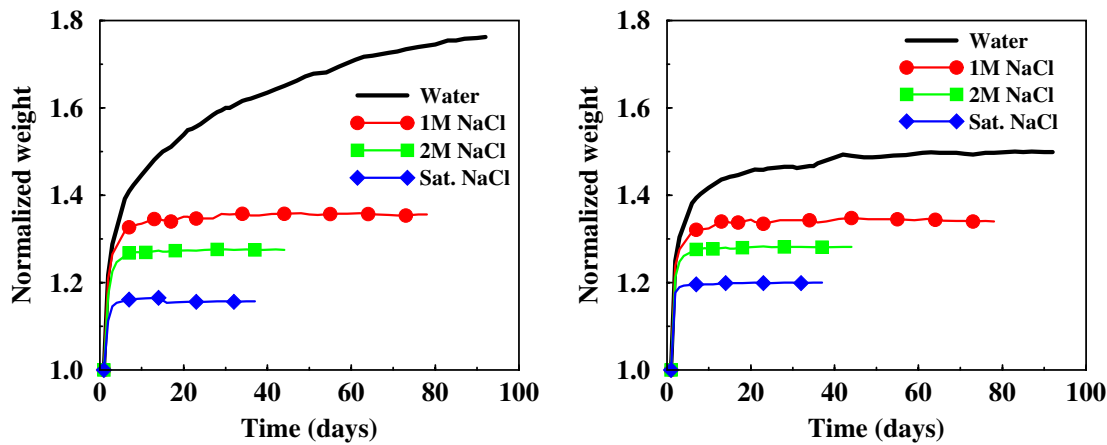


Figure 5-12. Swelling in desiccator at 25°C in equilibrium with various salt solutions as indicated in the graphs. left: Na montmorillonite and right: Ca montmorillonite.

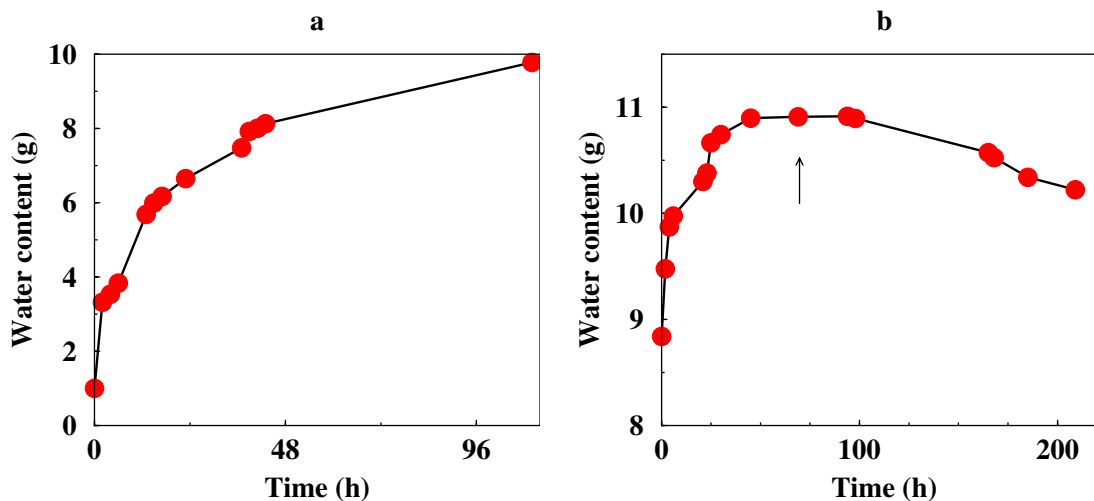


Figure 5-13. Dialysis result with MX-80 bentonite. Originally one gram of clay was placed in the dialysis pocket and the solution was replaced at intervals and the pocket with clay and water was weighed. a) Swelling against pure water and b) swelling against a 100 mM salt solution. This experiment was started from the clay swollen in pure water. The arrow indicates the time at which the NaCl concentration was increased to 200 mM. Both curves are average from two independent experiments.

5.3 Dialysis experiments

We have also analysed the swelling of MX-80 bentonite in a dialysis pocket. Approximately 1 g of clay was placed in a pocket made from a semi-permeable membrane and was allowed to equilibrate in different salt solutions. In the first experiment MX-80 was placed in pure water and during a period of four days it swelled continuously as shown in Figure 5-13a. Obviously, the swelling has not reached an equilibrium and the final swelling should be more than a factor of ten in weight. This is in agreement with the simulation results in Figure 5-6, which shows that it is enough with 10–20% monovalent counterions in order to create a repulsive double layer pressure when the clay is swelling in equilibrium with pure water. In MX-80 more than 50% of the surface charge is neutralized by sodium ions – see Table 3-1.

After a swelling period of four and a half day, water was exchanged with a salt solution containing 100 mM NaCl. The swelling continued, but seems to have reached a plateau after 2–3 days – see Figure 5-13b. At this point the concentration of NaCl was increased to 200 mM and a deswelling could be observed.

MX-80 contains large portion of Ca^{2+} as counterions, but the system is still dominated by Na^+ ions and when allowed to swell against pure water as in Figure 5-13a the net osmotic pressure is strongly repulsive in agreement with the simulation results presented in Figure 5-6. Replacing the sodium ions with divalent counterions should, according to the MC simulations significantly reduce the swelling, see e.g. Figure 5-2b. Figure 5-14 shows a smaller swelling for Ca montmorillonite than for MX-80, but still much larger than predicted by the simulations. This discrepancy between experiment and theory will, however, be resolved by the SAXS experiments reported below.

5.4 TEM results

To obtain information about the structure we have carried out high resolution TEM microscopy on dry MX-80, sodium and calcium montmorillonite. We have found no significant structural differences between the clay types.

With the TEM-technique we are able to identify individual clay particles and estimate their extension in the lateral direction as well as the thickness of the particles. Figure 5-15 (left), obtained for Na montmorillonite, illustrates a typical result and the crystal particles can be described as rather thin flakes build up of 5–20 layers, say, close to 1 nm thick each. Similar observations have been made by Hicher et al. /27/. As discussed in the introduction each layer consists of two structural units, one octahedral aluminum sheet in between two tetrahedral silica sheets. Interestingly, the resolution of the instrument is high enough to obtain some information on the structure of these sheets; note the lines in the upper part of Figure 5-16.

The flakes may locally be rather irregularly distributed. In the lower part of Figure 5-15 (right) we see how three clay particles are roughly perpendicularly oriented relative to each other. One thicker flake is edge standing and two very thin flakes are sticking out from the clay sample, one standing on edge and one lying flat. The lateral dimension of the latter can be estimated to about 50 x 100 nm. In Figure 5-17 (left) we have another example of an individual, flat lying particle. The lateral dimensions in this case is larger and correspond to ~ 100 x 200 nm. Several flakes can also be arranged in ordered aggregates, which is illustrated in Figure 5-17 (right).

The fact that clay particles have rather limited extension in all dimension is an important observation in order to interpret the swelling behaviour. Will will return to this question below.

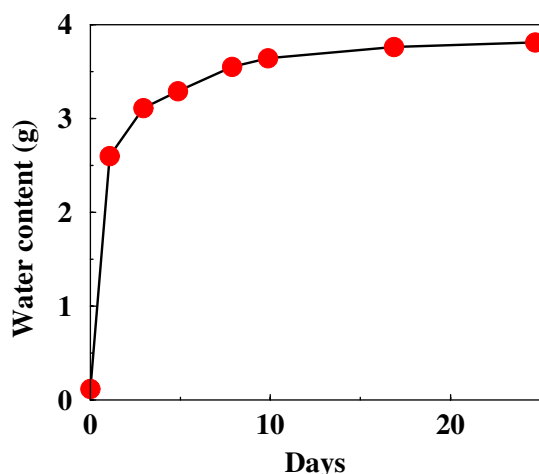


Figure 5-14. Dialysis result of Ca montmorillonite. One gram montmorillonite was placed in the dialysis pocket, which was placed in pure water. The weight increase of the pocket was followed over time.

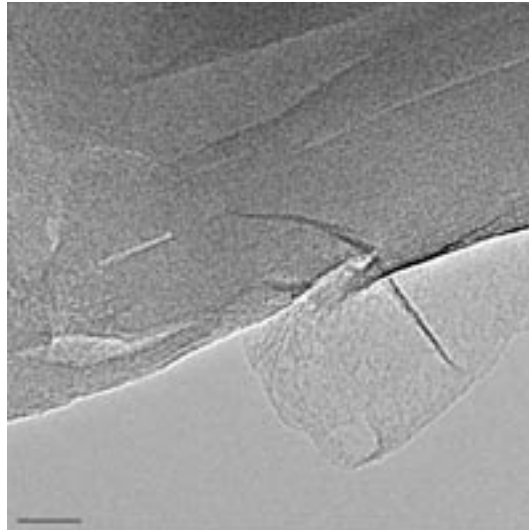
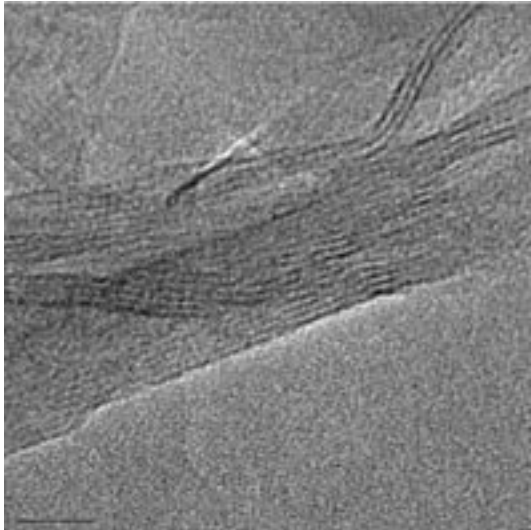


Figure 5-15. Left: TEM image of sodium montmorillonite showing the lamellar structure built of individual clay platelets. In some areas of the picture the resolution is high enough to reveal the individual atomic layers. The bar in the lower left corner corresponds to 10 nm. Right: Image of cleaned MX-80. The bar corresponds to 20 nm.



Figure 5-16. This is a magnification of the TEM image of sodium montmorillonite in Figure 5-15a showing the lamellar structure built of individual clay platelets. In some areas of the picture the resolution is high enough to reveal the individual atomic layers.

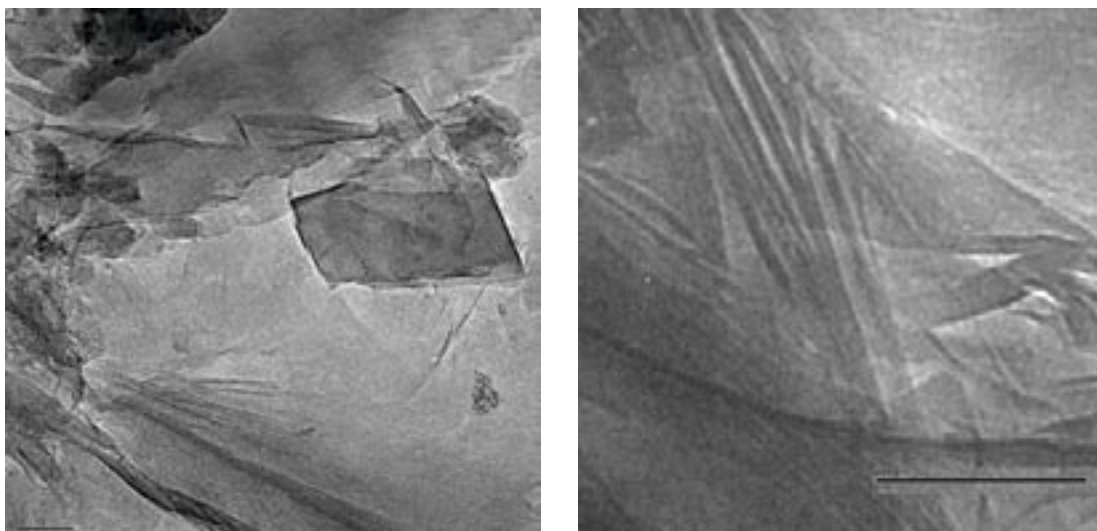


Figure 5-17. Left: Calcium montmorillonite. The bar corresponds to 50 nm. Right: TEM image of natural MX-80. The bar corresponds to 200 nm.

5.5 SAXS results

The results of the above simulations and free swelling experiments do not seem to agree. Simulations predict a very limited swelling for calcium montmorillonite and that is true even if the system is in equilibrium with a bulk solution that is dominated by sodium ions. Simulations still predict that ion-ion correlations dominate and that the net electrostatic pressure is attractive. Thus, the question arises if the swollen clays in, for example, Figures 5-9 and 5-10 are homogeneous systems of stacked montmorillonite layers with a uniform spacing or the structure is better characterized as a dispersion of small lamellar aggregates each with a limited number of clay layers.

In order to obtain some insight into this question we have performed a few diffraction studies using x-ray. Details of the experimental procedure can be found elsewhere and here we concentrate on the analysis of the spectra. The instrumental limitations are such that repeat distances above approximately 100 Å are difficult to detect. It would of course be desirable to go beyond this limitation, something that can be achieved with a more advanced instrument, but for our discussion it suffices with the present accuracy.

Figure 5-18a shows a strong swelling of Na montmorillonite when put into contact with a salt solution containing 100 mM of NaCl and the swelling is larger than the instrumental limitation of 100 Å. Increasing the salt concentration further up to 1 M of NaCl extinguishes the double layer repulsion to an extent that van der Waals forces dominate the interaction. Under these conditions the clay only incorporates a small amount of water; the thickness of the aqueous layer is only about 10 Å as deduced from the x-ray data in Figure 5-18b and in agreement with the simulation results in Figure 5-4.

Calcium montmorillonite shows a completely different swelling behaviour. Successive addition of pure water to Na montmorillonite leads to increasing separation between the clay platelets, but in Ca montmorillonite the maximal thickness of the water layer is approximately 10 Å corresponding to a repeat distance of 20 Å. Figure 5-19a shows a single peak at the same q-value independent of the water content. A free swelling Ca montmorillonite, Figure 5-19b, shows the same behaviour with an x-ray peak at a q-value corresponding to a repeat distance in real space of 20.5 Å. This result is in agreement with the simulated force curve in Figure 5-2b, but it is in conflict with DLVO theory. This competition is further demonstrated in MX-80 bentonite with a mix of Na and Ca counterions. Initially one can observe a scattering peak at around 20 Å, while in excess water MX-80 swells beyond the limits that can be detected (> 100 Å) with the present equipment – see Figure 5-20. Again, these results are in agreement with Monte Carlo simulations (Figure 5-6) as well as the dialysis experiments in Figure 5-13a.

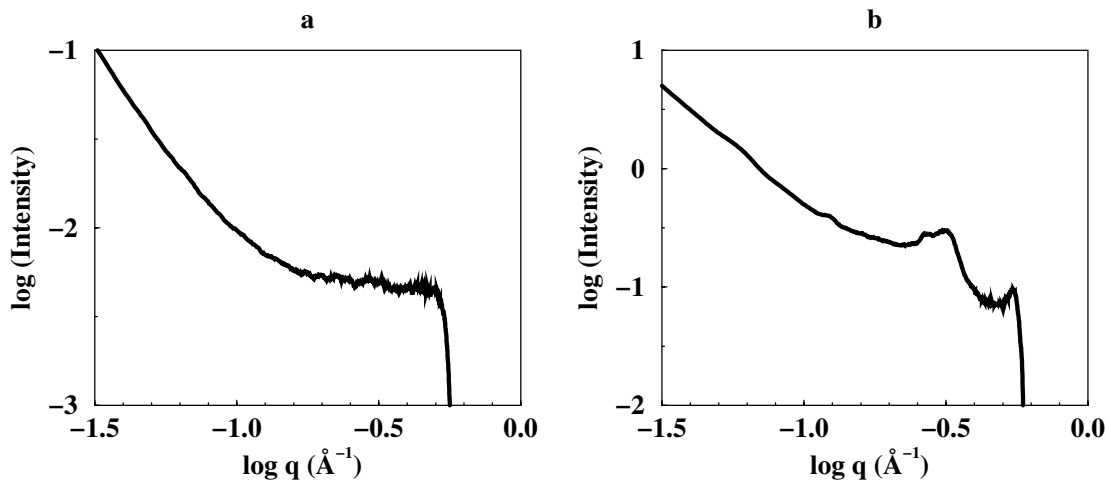


Figure 5-18. X-ray scattering intensity as a function of wave vector for Na montmorillonite in contact with a NaCl solution. a) 100 mM and b) 1 M. The peak in b) corresponds to a repeat distance of 20 Å.

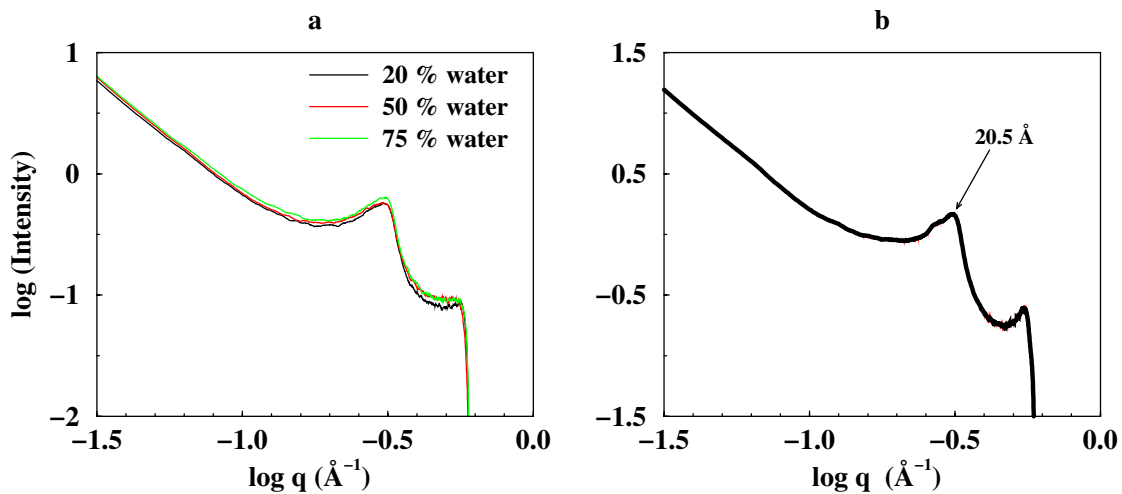


Figure 5-19. X-ray scattering intensity as a function of wave vector for Ca montmorillonite: a) with limited amount of water; the weight % of water is given in the graph and b) in excess water. The repeat distance is indicated in the graph.

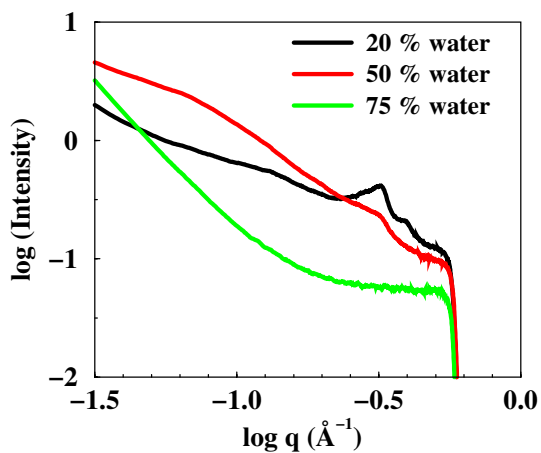


Figure 5-20. X-ray scattering intensity as a function of wave vector for MX-80 bentonite in contact with limited amount of water; the weight % of water is given in the graph.

The addition of a small amount (10 mM) CaCl₂ together with 100 mM NaCl restores the attraction and a peak at around 20 Å reappears in the scattering curve – see Figure 5-21. One can also note that the cleaning procedure has an effect on the structure. This is possibly due to a reduction of salt content in the clean MX-80.

5.6 NMR results

From the obtained ²H-NMR spectra it is clear that there are always some D₂O-molecules in the clay samples that, during the time of a single NMR-fid, experience an anisotropic environment. Molecules in an isotropic environment will give only a single peak in the NMR spectrum. On the other hand, if the mean environment to the studied D₂O molecules in an NMR experiment is anisotropic during the time of a single NMR-fid a very characteristic NMR spectrum with a double peak is obtained – see Figure 5-22a. When more water is added the distance between the two peaks in the spectrum, the so called quadrupolar splitting, is reduced, as can be seen in Figure 5-22b. The quadrupole splitting, Δ, in the ²H-NMR spectra in Figure 5-22, can for a non-oriented (powder) spectrum of large planar water layers be written as:

$$\Delta = \left| \sum p_i \frac{3}{4} \chi_i S_i \right| \quad (\text{Eq. 6})$$

where p_i is the fraction of deuterons in site i , χ_i the quadrupole coupling constant and S_i the order parameter in site i . Since it is only the D₂O-molecules that are near the solid surfaces in a clay particle that give a significant value to the quadrupole splitting Δ will depend on the ratio between these molecules and all D₂O-molecules in the sample. Many water molecules per surface area will give a small splitting and vice versa. Another possible interpretation is that one half of the quadrupole doublet in Figure 5-22a is broadened out and that the right peak in Figure 5-22b is caused by isotropic D₂O-molecules. Further investigations are needed in order to distinguish between these possibilities.

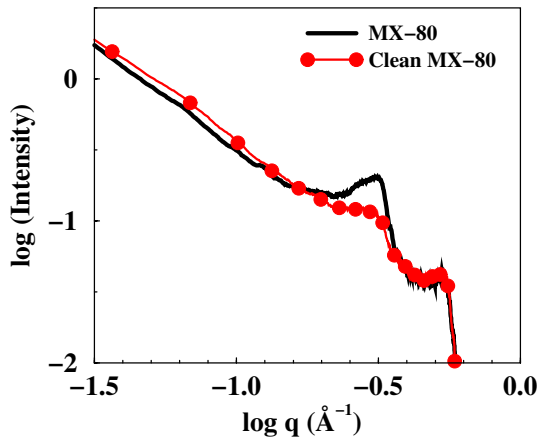


Figure 5-21. X-ray scattering intensity as a function of wave vector for MX-80 in contact with a salt solution containing 100 mM NaCl and 10 mM CaCl₂. The black solid curve is for natural MX-80, while the red curve with symbols represents clean MX-80.

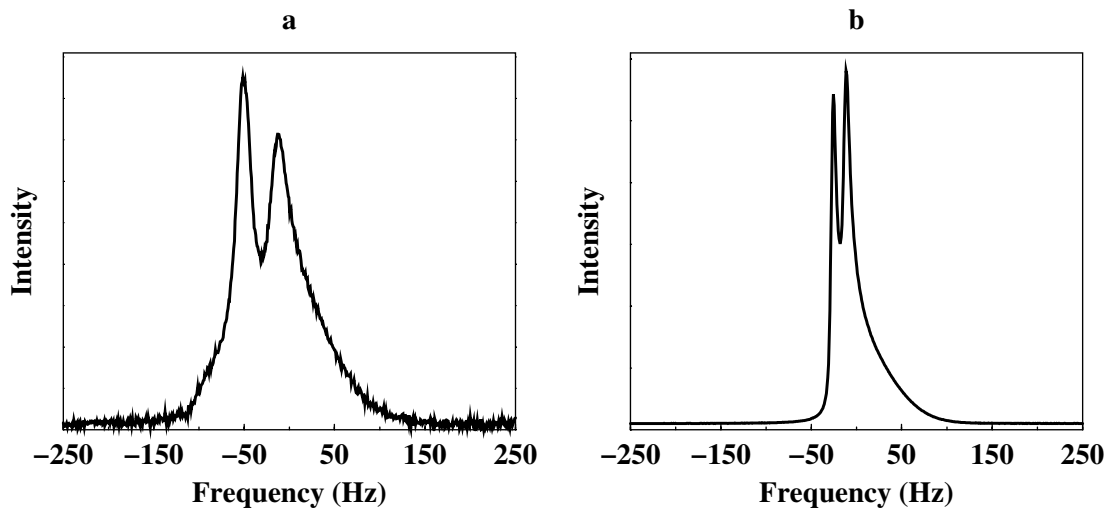


Figure 5-22. The ^2H -NMR spectrum from a sodium montmorillonite sample with a) 30% D_2O . b) 60% D_2O .

If the clay aggregates are large enough and if there are external D_2O -molecules, due to an extra-lamellar swelling, that do not mix with the internal D_2O -molecules during the time of a single NMR-fid, then a different ^2H -NMR spectrum is obtained, as demonstrated for a peat sample in Figure 5-23. This type of spectrum was, however, never observed in our experiments. The most probable reason is that the multilamellar clay aggregates in bentonite are not large enough to prevent diffusion of D_2O -molecules between intra- and extra-lamellar regions during the time of a single NMR-fid. The mean displacement of a D_2O -molecule in the x-direction in a time interval t can be estimated as:

$$\langle x \rangle \approx \sqrt{2Dt} \quad (\text{Eq. 7})$$

where the diffusion coefficient $D \approx 2 \cdot 10^{-9} \text{ m}^2/\text{s}$ for D_2O and the time t for a single NMR-fid is around 0.05 s. This means that $\langle x \rangle$ for D_2O is around $10 \mu\text{m}$ during an NMR-fid. If the aggregates are smaller than $10 \mu\text{m}$, then the intra- and extra-lamellar D_2O -molecules will mix and a double peak is observed instead of a triplet. We will in coming experiments reduce the temperature to near 0°C and/or investigate other clay minerals to see if the reduced diffusion will give a spectrum like in Figure 5-23. If so, there is a possibility to estimate the average size of the clay platelets and to gain further structural information. We note, however, that the platelets seen in the TEM experiments are sub-micron size and the NMR experiments may require a different approach.

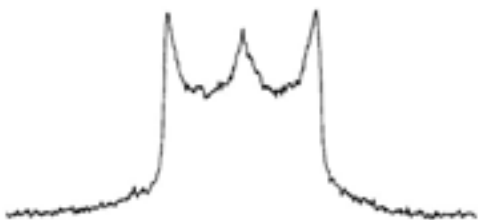


Figure 5-23. The ^2H -NMR spectrum from a peat sample (unpublished data).

6 Discussion

One objective of this investigation was to use Monte Carlo simulations in order to study the swelling of bentonite in saline water. The traditional double layer theory, the so called DLVO theory, contains two ingredients: i) a repulsive interaction due to the direct electrostatic interactions between the charged surfaces, counterions and added salt and ii) an attractive term due to van der Waals forces. The direct electrostatic term is in the DLVO theory derived from the Poisson-Boltzmann equation, which is a mean-field approximation and as a consequence this term is always repulsive. The approximation underlying the Poisson-Boltzmann equation means that ion-ion correlations are neglected. It turns out to be a valid approximation in the presence of monovalent (counter)ions, but it fails completely with divalent or multivalent counterions. When ion-ion correlations are taken into account, as is done in Monte Carlo simulations, then the presence of divalent counterions usually leads to an attractive interaction between two charged objects. A higher charge on the particles gives, counterintuitively, a stronger attraction! This can be understood as a competition between repulsive *entropic* forces on one hand and attractive *energetic* terms on the other. The change from, for example, Na to Ca counterions means that the entropic term is strongly reduced and the attractive forces due to ion-ion correlations are allowed to dominate. This means that the Poisson-Boltzmann equation can NOT be used to describe the stability of clay systems, where divalent calcium or magnesium ions or any other multivalent cation are present.

The importance of ion-ion correlations depends on the valency of the counterions, the surface charge density of the clay platelets and of the solvent used. For clay in a natural setting, the solvent will exclusively be water and we can concentrate on the counterion valency and the surface charge density. In a system with mixed counterions, e.g. Na⁺ and Ca²⁺, there will be a competition and if Na⁺ dominates then the clay will swell, while in the opposite situation we will have a non-swelling system. That is, the clay will incorporate a water layer of approximately 1 nm but not more. This competition will depend on the surface charge density and a higher surface charge density will favour calcium counterions and a non-swelling behaviour. In a clay with only calcium counterions, the transition between swelling and non-swelling happens at a surface charge density around -0.07 C/m^2 (not taking the van der Waals interaction into account).

In our original “free swelling” experiments, Figures 5-8–5-11, we found that Ca montmorillonite was incorporating much more water than predicted by simulations. Similar findings were reported by the Stockholm group using a sophisticated NMR technique /6/. This made us question the simple picture of clay consisting of well organized platelets in a perfect lamellar structure. Using x-ray scattering we have been able to show that there is a lamellar component in calcium montmorillonite that swells to about 1 nm water layer. This means that there is a second structural component that shows much larger swelling. The structure of this component is unknown and x-ray scattering has not been helpful to unravel this. Thus, we might describe the swelling in terms of a “traditional” intra-lamellar swelling, well described by simulations, combined with an extra-lamellar swelling, of which we have no experimental structural information.

We can, however, speculate of the origin for the unexpected swelling of calcium montmorillonite. An enlargement of the simulated osmotic pressures in Figure 5-2b shows that the pressure curves are non-monotonic – Figure 6-1. For such a situation, there exists in principle two stable separations as indicated in the figure (cf. van der Waals loop). Thus, the swelling we see in the dialysis experiments with Ca montmorillonite could be a result of this effect. The concentrated phase is seen by SAXS, but the dilute phase could be outside the range of the instrument. In principle, one should observe a macroscopic phase separation /38/, but its absence could be due to kinetic barriers.

An important parameter is the surface charge density of the clay, which for bentonite is often quoted to be of the order of -0.10 to -0.15 C/m². A consequence is that in a mixed salt environment, with both mono- and divalent cations, bentonite clay will only swell in a limited region. At low sodium concentrations, ion-ion correlations will ensure a net attractive pressure and at high sodium levels van der Waals forces will do the same. A similar conclusion was reached by Karnland et al. /39/ based on sedimentation experiments.

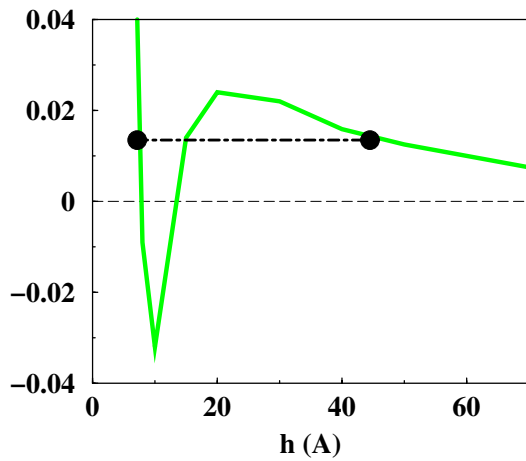


Figure 6-1. Simulated osmotic pressure as a function of separation with divalent counterions and a $\sigma = -0.08$ C/m². The two stable separations are shown as black spheres and connected with a dot-dashed line. The PB pressure is shown for comparison – black line with symbols.

7 Conclusions

- The Poisson-Boltzmann equation can not be used for predicting the swelling behaviour of natural clays.
- The swelling behaviour is mainly governed by counterion valency and surface charge density. Divalent counterions and high surface charge density prevent swelling, while monovalent counterions favour a large swelling.
- There exist two structural components in bentonite clay with different swelling behaviour.
- The intra-lamellar component swells in accordance with simulations meaning that it shows a large swelling if dominated by monovalent counterions but only a limited swelling (1 nm) if divalent counterions prevail.
- The “extra-lamellar” swelling is larger and poorly understood and ought to be studied in more detail both experimentally and theoretically.

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