

# Osmotic Equilibrium and Depletion Induced by Polyelectrolytes in Clay Dispersions

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Pseudoternary systems of negatively charged clay (montmorillonite), anionic polyelectrolyte (sodium polyacrylate), counterions, and water exhibit a local segregation of two distinct phases on a colloidal scale. The microscopic osmotic equilibrium condition in the diphasic dispersion sets the spacing observed between the sodium montmorillonite platelets: the effect of polyelectrolyte is equivalence to an external depletion force equilibrating electrostatic repulsion. In the case of calcium montmorillonite clay, the osmotic stress effect is only observed when sufficient polyelectrolyte is added to saturate the ion condensation of all calcium clay counterions on the polyelectrolyte chain.

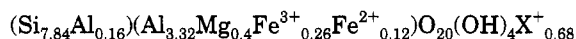
## 1. Introduction

Small molecular weight anionic polyelectrolytes are extensively used for their dispersing effect on smectite clays such as, for example, additives to drilling fluids.<sup>1</sup> Although polymer-clay systems may involve a large number of microscopic configurations,<sup>2</sup> until now most models of fluidification mechanisms involved "specific" effects based on polyelectrolyte adsorption at the clay surfaces.<sup>3-5</sup> Our aim is to show that such a dispersing effect is ruled by another mechanism. In that sense, we have investigated through small-angle X-ray scattering<sup>6</sup> the effect of an anionic polyelectrolyte on a model clay system.

## 2. Experimental Section

**2.1. Materials. 2.1.1. Samples.** The reference montmorillonite clay (SWy-1, Na-montmorillonite, Crook County, Wyoming) provided by the Clay Mineral Society was purified and converted to a single-ion form (sodium or calcium). The clay was first dispersed in pure water and the resulting suspension centrifuged. Then the ionic exchange was completed by repeated cycles of dispersion in a molar salt solution (NaCl or CaCl<sub>2</sub>) and centrifugation. Finally, the suspension was washed with pure water and centrifuged until the excess chloride was eliminated. A test with silver nitrate indicated the absence of residual chloride. Completion of the ion exchange was checked by chemical analysis of the montmorillonite counterions. The ion-exchanged clay was then dried at 35 °C. The montmorillonite obtained as a cohesive material was then macroscopically ground again into powder for easier manipulation.

According to chemical analysis by X-ray fluorescence and atomic absorption, the unit cell formula of the purified sample was<sup>7</sup>



This formula shows that there is 0.68 charge per unit cell, representing a cation exchange capacity of 80 mequiv/100 g of dry clay.<sup>8,9</sup> The montmorillonite density was equal to 2.7 g cm<sup>-3</sup>.

Sodium polyacrylate was obtained from Cyanamid, with an average molecular weight measured by gel permeation chromatography of ~5000. The as-received solution was ultrafiltrated against pure water, using a dialysis bag with a mass cutoff of 1000 Da. The final polyacrylate concentration was determined using total carbon analysis (Dohrmann DC 80).

**2.1.2. Sample Preparation.** The montmorillonite powder was first dispersed in pure water (Milli-Q filtering system, resistivity of approximately 20 × 10<sup>6</sup> Ω·cm), producing clay swelling. An equivalent mass of polyelectrolyte solution was added in a second step to the montmorillonite suspension.

Without added salt, the sodium montmorillonite swells in water. At a solid concentration above 40 g L<sup>-1</sup>, a thick paste is obtained. To avoid this, the solid concentration investigated was limited to 4, 10, and 17 g L<sup>-1</sup> and the polyacrylate concentration was constant and equal to 10 g L<sup>-1</sup>.

In a second series of experiments, the clay concentration was fixed at 10 g L<sup>-1</sup>, with four polyelectrolyte concentrations equal to 0.5, 1.0, 7.1, and 10 g L<sup>-1</sup>.

All samples were metastable as a uniform yellow translucent solution, similar to the one obtained with the simple sodium montmorillonite-water dispersion. After two weeks of aging, polyelectrolyte clay suspensions exhibited a macroscopic phase separation.

At any concentration of solids, limited swelling occurs with calcium montmorillonite; this includes a rapid sedimentation of the aqueous clay suspension without added polyelectrolyte. In the mixed systems investigated, the clay concentration was equal to 17 g L<sup>-1</sup> and two polyacrylate concentrations were investigated (0.5 and 5 g L<sup>-1</sup>). The presence of polyelectrolyte modifies the macroscopic behavior of the samples: at low polyelectrolyte concentration the sediment volume decreases, whereas a complete dispersion of the calcium montmorillonite occurs with the highest polyelectrolyte concentration. As in the previous ternary system, a slow, macroscopic phase separation was observed after two weeks of aging.

**2.2. Structural Analysis.** The microstructure of the samples was investigated by combining a Holmes-type camera for small-angle X-ray scattering (SAXS) and a high-resolution Bonse and Hart camera designed for ultra-small-angle X-ray scattering<sup>10</sup>

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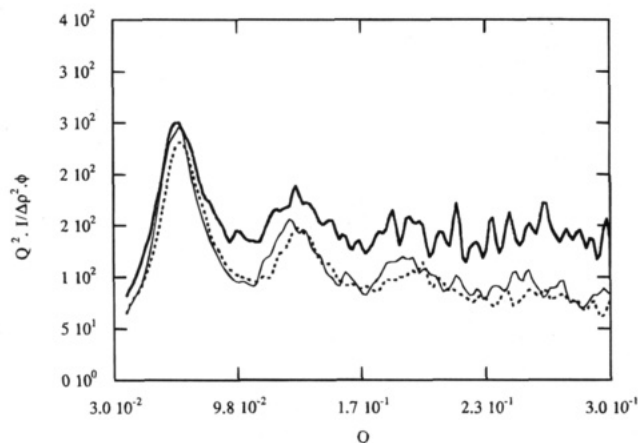
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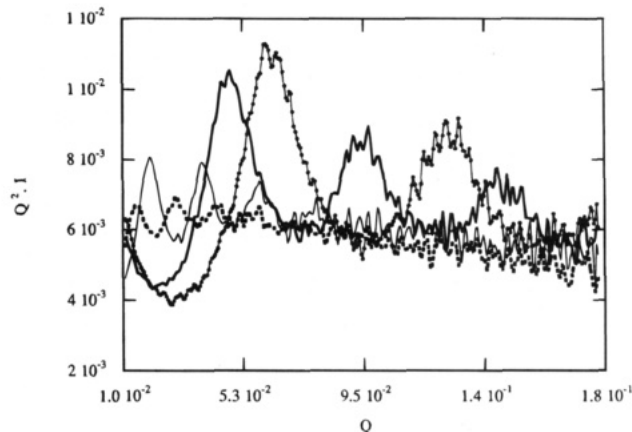
**Figure 1.** Scattering spectra recorded from ternary systems of sodium montmorillonite, sodium polyacrylate, and water. Considering a fixed polyelectrolyte concentration of  $10 \text{ g}\cdot\text{L}^{-1}$ , we show the evolution of the structure factor under variation of the montmorillonite clay concentration: (light line)  $4 \text{ g}\cdot\text{L}^{-1}$ , (dashed line)  $10 \text{ g}\cdot\text{L}^{-1}$ , and (dark line)  $17 \text{ g}\cdot\text{L}^{-1}$ .

(USAXS). As in previous studies of clay dispersions,<sup>11</sup> the experimental data were converted to scattering cross-sections on an absolute scale expressed in inverse centimeters. A desmearing procedure was also applied, according to Lake's iterative method.<sup>12</sup> The electronic density contrast term,  $(\rho_{\text{clay}} - \rho_{\text{solvent}})^2$ , calculated from the chemical content and density, was equal to  $1.85 \times 10^{22} \text{ cm}^{-4}$ .

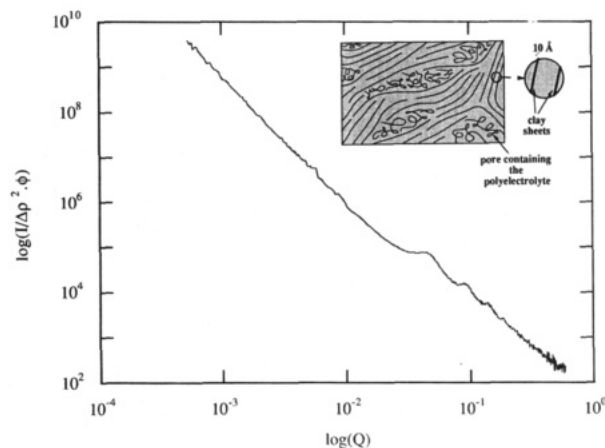
### 3. Results and Discussion

**3.1. Sodium Montmorillonite in the Presence of Polyacrylate.** The effect of clay concentration on the microstructure of a ternary system of sodium montmorillonite, polyacrylate, and water is shown in Figure 1. The corresponding SAXS curves are compared after normalization by the volume fraction of the clay particles and the electronic contrast term. The contribution of the form factor of the clay platelets ( $P(Q) = kQ^{-2}$ ) was removed by division. Three maxima (spacings 1, 2, and 3) appear on the scattering diagram and indicate a strong correlation between the clay platelet positions. The position of the first peak is the most probable distance between adjacent platelets. In Figure 1, it is shown that the clay concentration does not affect the observed periodicity: osmotic pressure, the key intensive variable in the dispersion, is not fixed by the clay concentration.

On the other hand, an increase of the polyelectrolyte concentration produces a decrease of the distance between clay platelets, as shown in Figure 2: the polyelectrolyte concentration sets the osmotic pressure in the sample and allows us to describe this intensive variable. The Bragg peak position allows determination of the interlamellar spacing. The observed values for polyelectrolyte concentrations of 0.5, 1.0, 7.1, and  $10 \text{ g}\cdot\text{L}^{-1}$  were, respectively, equal to 410, 300, 120, and  $90 \text{ \AA}$ . If we assume an ideal distribution of the montmorillonite platelets in water, involving a smectic structure between parallel plates on a perfect 1D lattice, a simple calculation<sup>13</sup> indicates that, for a  $10 \text{ g}\cdot\text{L}^{-1}$  montmorillonite suspension, the equilibrium interparticle distance if all water present induces swelling is  $2600 \text{ \AA}$ . The sample is necessarily biphasic on a microscopic scale. This conclusion is confirmed by the strong increase of the scattering intensity observed in the USAXS region (Figure 3). Such a strong increase in the



**Figure 2.** Scattering spectra recorded from ternary systems of sodium montmorillonite, sodium polyacrylate, and water. Considering a fixed montmorillonite concentration of  $10 \text{ g}\cdot\text{L}^{-1}$ , we show the evolution of the structure factor under variation of the polyelectrolyte concentration: (dashed line)  $0.5 \text{ g}\cdot\text{L}^{-1}$ , (light line)  $1 \text{ g}\cdot\text{L}^{-1}$ , (dark line)  $7.1 \text{ g}\cdot\text{L}^{-1}$ , and (circles)  $10 \text{ g}\cdot\text{L}^{-1}$ .



**Figure 3.** Scattering spectra presented on a log-log plot from an aqueous sodium montmorillonite suspension at  $10 \text{ g}\cdot\text{L}^{-1}$  containing sodium polyacrylate at  $7.1 \text{ g}\cdot\text{L}^{-1}$ . The inset provides a schematic representation of the equilibrium phases.

USAXS scattering has been shown elsewhere as the signature of a biphasic inhomogeneity.<sup>11,14,15</sup>

The coexistence of low periodicity values within the clay platelets with large regions of low electronic density can only be explained with the schematic microstructure of the two phases in equilibrium, as shown in the inset of Figure 3. Because they are seen in the USAXS range, the typical sizes of polyelectrolyte and clay domains are in the micrometer range, but USAXS data alone cannot determine the average shape of the domains in equilibrium. However, we know that equilibrium of water volumes between clay and polyelectrolyte domains implies equality of osmotic pressure between the two phases. Our next goal is then to measure this pressure and to check that it is really the driving mechanism to limited local clay swelling.

Low molecular weight polyacrylate is expected to induce relatively high osmotic pressure; thus, a standard membrane osmometer cannot be used to measure this pressure. To overcome this limitation, we have employed a vapor pressure osmometer (Knauer A0280). After calibration with sodium chloride solutions, the osmotic pressure of the polyacrylate solutions was measured for pure poly-

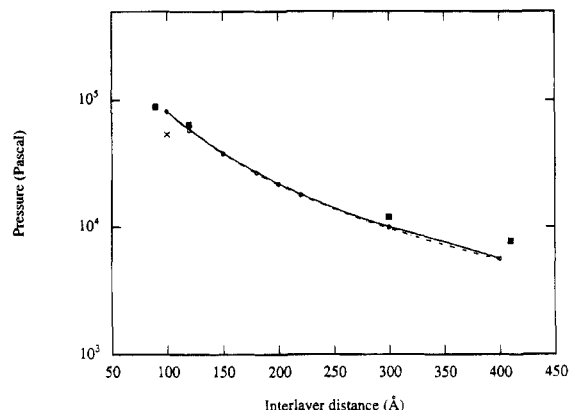
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**Figure 4.** Osmotic pressure versus interlamellar distance, obtained with a ternary system of sodium montmorillonite, sodium polyacrylate, and water (■). These experimental data are compared to the calculated electrostatic repulsive pressure arising between two planar charged surfaces ( $\sigma = -0.12 \text{ C}\cdot\text{m}^{-2}$ ) in pure water (○). The effect of a theoretical  $10^{-6} \text{ M}$  ionic strength is also included (---). We finally report the interlamellar distance deduced from a classic osmotic stress experiment, involving equilibrium between a sodium montmorillonite suspension and a 16% w/w dextran solution (×).

acrylate.<sup>16</sup> The osmotic pressure of pure polyelectrolyte as a function of observed swelling periodicity is shown as black filled squares in Figure 4.

Within the Poisson–Boltzmann approximation, the electrostatic repulsive pressure arising in the “counterion only” case, between two planar charged surfaces in pure water, is given by<sup>17</sup>

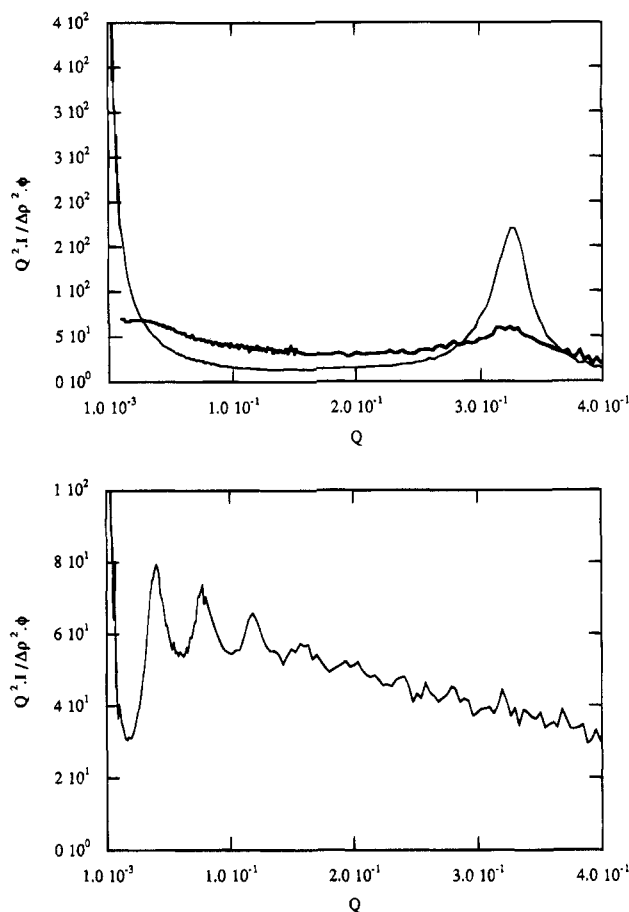
$$P = 2\epsilon\epsilon_0(kT/ze)^2K^2$$

where  $K$  is a constant determined in terms of the surface charge density  $\sigma$  and interlamellar distance  $D$  by the implicit relation

$$-\left(\frac{2kTK}{ze}\right) \tan\left(\frac{KD}{2}\right) = \frac{\sigma}{\epsilon\epsilon_0}$$

Using an indicative structural surface charge density equivalent to the montmorillonite ionized surface sites ( $\sigma = -0.12 \text{ C}\cdot\text{m}^{-2}$ ), we have then estimated a theoretical profile for the purely electrostatic repulsive pressure. As expected, it can be seen in Figure 4 that the only measurable interaction between clay platelets is of electrostatic origin. The effect of the presence of  $10^{-6} \text{ M}$  uncontrollable ionic strength, indicated by a dashed line in figure 4, also confirms this result. The exact numerical value of the surface charge of the clay is not relevant for this conclusion. The overall pressure in the sample is thus set by the polyelectrolyte.

We now come to a counterexperiment which cannot be explained by any “specific interaction” model used in the literature.<sup>3–5</sup> We now impose the osmotic pressure externally from the outside of a dialysis tubing. To avoid any specific effect of a polyelectrolyte, we chose the hydrophilic neutral polymer largely used in DNA, proteins, and other colloidal systems by Parsegian and co-workers.<sup>18</sup> This neutral macromolecule (Dextran T500, Pharmacia) was dissolved in pure water (16% w/w), thus imposing a



**Figure 5.** Scattering spectra recorded from various calcium montmorillonite suspensions: (a, top) A comparison between a  $17 \text{ g}\cdot\text{L}^{-1}$  aqueous calcium montmorillonite suspension without polyelectrolyte (light line) and a three-component system involving the same clay concentration and  $0.5 \text{ g}\cdot\text{L}^{-1}$  sodium polyacrylate (dark line). (b, bottom) Effect of an increase of the polyacrylate concentration ( $5 \text{ g}\cdot\text{L}^{-1}$ ) in the previous systems.

known osmotic stress on the order of  $10^5 \text{ Pa}$ ,<sup>19</sup> analogous to a  $10 \text{ g}\cdot\text{L}^{-1}$  polyacrylate concentration. An aqueous montmorillonite suspension ( $10 \text{ g}\cdot\text{L}^{-1}$ ) was placed in the dialysis tubing. After osmotic stress equilibration, the equilibrium interlamellar distance measured by SAXS is shown as an × in Figure 4. The observed pressure is in the same range, whatever the molecular origin of the osmotic stress. The only “specificity” of the polyelectrolyte is to set high osmotic pressures at low polymeric mass content.

An Onsager transition of the clay platelets is therefore induced by the polyelectrolyte dispersed in the excess water phase, as shown in the inset of Figure 3. The situation without added electrolyte has already been discussed by Marcelja et al.<sup>20</sup> The diphasic system, with locally parallel platelets, is more fluid than without external stress: this osmotic effect can be seen as a depletion process, while the polyelectrolyte acts as an effective attraction between clay platelets.

**3.2. Calcium Montmorillonite in the Presence of Polyacrylate.** Spontaneous swelling of montmorillonite in the presence of divalent ions does not occur, as is shown in Figure 5a: an intense diffraction peak related to a  $d(001)$  spacing of  $1.9 \text{ nm}$  is observed for a  $17 \text{ g}\cdot\text{L}^{-1}$  calcium montmorillonite suspension. Addition of a small quantity of polyelectrolyte ( $0.5 \text{ g}\cdot\text{L}^{-1}$ ) strongly decreases the in-

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**Table 1. Supernatant Cation Composition of a 17 g·L<sup>-1</sup> Aqueous Calcium Montmorillonite Suspension Containing 5 g·L<sup>-1</sup> Sodium Polyacrylate**

sodium		calcium	
calcd content (ppm)	measd content (ppm)	calcd content (ppm)	measd content (ppm)
900 <sup>a</sup> ≤ c ≤ 1225	780	0 ≤ c ≤ 270 <sup>a</sup>	280

<sup>a</sup> These values correspond to a complete exchange of the calcium clay counterions by sodium counterions provided by the polyelectrolyte.

tensity of the diffraction peak. For the same clay concentration, but with a higher polyelectrolyte content (5 g·L<sup>-1</sup>), the diffraction peak has completely disappeared and now at least three Bragg peaks are measured in the low *Q* region (Figure 5b).

A recent series of theoretical and experimental studies<sup>21–22</sup> has shown that the limited swelling of the calcium clays was due to the ion–ion correlation effect for divalent ions; this gives rise to a strong attractive component in the electrostatic interaction between charged planes. Structural changes observed under polyelectrolyte addition may then be related to a calcium ion exchange between the sodium polyacrylate and the calcium montmorillonite. According to Manning's theory,<sup>23</sup> counterions condense onto the polyelectrolyte chain to reduce its charge density. To observe a stable system, the reduced linear charge density  $\xi$  must be limited to a level to give  $\xi \approx 1$ , where  $\xi$  is given by

$$\xi = \frac{e^2}{\epsilon_1 k T b z_i}$$

where  $z_i$  is the counterion valence and  $b$  the average distance between the charges. When divalent cations are added to a polyelectrolyte solution, they will condense and replace the original monovalent counterions. Such a phenomenon has been shown in several experimental studies of polyelectrolytes.<sup>24–27</sup>

To demonstrate this ion exchange mechanism directly, we analyzed the polymer concentration in the supernatant after phase separation for the 17 g·L<sup>-1</sup> calcium montmorillonite aqueous suspension containing 5 g·L<sup>-1</sup> polyelectrolyte. Then using an inductively coupled plasma spectrometer, we determined the cation content (sodium and calcium) in that supernatant. In Table 1, results are compared to the calculated values by taking into account clay and polyelectrolyte concentrations as well as the montmorillonite cation exchange capacity. The conclusion is that all the divalent counterions have been extracted from the clay platelets and are now bound to the polyelectrolyte. The problem reduces to the equilibrium between sodium clay with polyelectrolyte partially neutralized with divalent ions. The main effect of condensed ions is to reduce the osmotic pressure in the sample. The charge content of the montmorillonite clay  $C_{zi}$  was estimated by the following relation:

$$C_{zi} = C_{\text{clay}}(E/z_i)A_i$$

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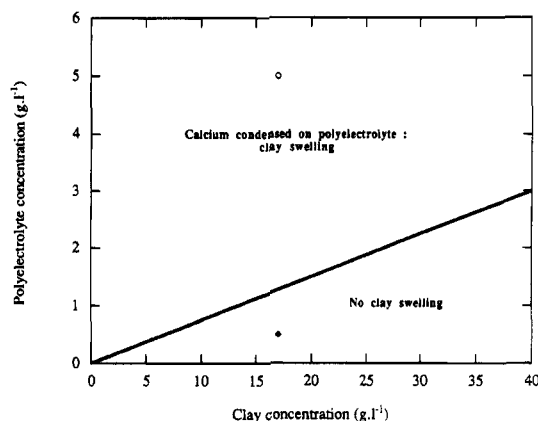
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**Figure 6.** Diagram illustrating the ionic exchange between clay and polyelectrolyte counterions. Complete exchange occurs above the stoichiometric conditions (straight line), giving rise to a sodium montmorillonite clay. Experimental data reported in that diagram represent a complete exchange case (O), occurring with a 17 g·L<sup>-1</sup> aqueous calcium montmorillonite suspension and 5 g·L<sup>-1</sup> sodium polyacrylate, and a partial exchange case (●), occurring with a 17 g·L<sup>-1</sup> aqueous calcium montmorillonite suspension and 0.5 g·L<sup>-1</sup> sodium polyacrylate.

where  $z_i$  and  $A_i$  are, respectively, the counterion valence and atomic weight,  $E$  is the exchange capacity of clay expressed as a mole of charge per gram of clay ( $0.8 \times 10^{-3}$  mol·g<sup>-1</sup>), and  $C_{\text{clay}}$  is the clay concentration (g·L<sup>-1</sup>). According to the chemical composition, the polyelectrolyte sodium charge content  $C_{zi}$  was equal to

$$C_{zi} = 0.245C_{\text{pol}}$$

where  $C_{\text{pol}}$  represents the polyelectrolyte concentration (g·L<sup>-1</sup>). The ionic exchange between the polyelectrolyte and the montmorillonite can thus be illustrated by a diagram (Figure 6) reporting polyelectrolyte versus clay concentrations. A straight line corresponding to the stoichiometry separates two regions, with the sodium montmorillonite in the upper part and a mixed sodium–calcium type in the lower part. Experimental data when reported in that diagram show the distinct cases: a complete and a partial exchange.

The absence of Bragg peaks associated with a local layer stacking of 1.9 nm is also consistent with a complete exchange of the calcium clay counterions by sodium. As far as basal spacing of smectite powders can be related to the clay counterion composition,<sup>28</sup> the previous result was also confirmed by wide-angle X-ray scattering patterns produced from a dry film of the polyelectrolyte clay aqueous suspension. Whereas a calcium montmorillonite clay exhibits a  $d(001)$  spacing value equal to 1.5 nm, we found for the polyelectrolyte–calcium clay mixture a  $d(001)$  value of 1.25 nm: this corresponds to  $d(001)$  for sodium montmorillonite.

As in the sodium montmorillonite case, the scattering pattern derived from the USAXS apparatus indicates a biphasic dispersion. Therefore, we still observed an osmotic equilibrium between a smectic phase resulting from oriented clay platelets and the polyelectrolyte regions.

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