

STRUCTURAL ORGANIZATION OF Na- AND K-MONTMORILLONITE SUSPENSIONS IN RESPONSE TO OSMOTIC AND THERMAL STRESSES

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Abstract—In order to understand the influence of salt concentration and temperature on the behavior and properties of clays used in drilling muds, we studied montmorillonite suspensions (4 g clay/100 g solution) in 0.1, 0.5 and 1 M NaCl and KCl solutions. A fraction of each sample was heated to 200 °C in a closed vessel for 7 d, then cooled at room temperature (RT, 25 °C). Small-angle X-ray scattering (SAXS) spectra were recorded, for all the samples, at RT. The structure of the clay particles was determined by comparing the experimental intensity with the theoretical intensity computed from a model that took into account the number of layers per particle, the hydration state of the layers (0, 1, 2, 3 or 4 water layers) and the order in the succession of these states. With this set of parameters, we can compute the mean statistical parameters \bar{M} (mean number of layers per particle), \bar{d} (mean interlayer distance) and $\bar{\delta}^2/\bar{d}^2$ (parameter describing the disorder of the distribution of interlayer distances). The evolution of these parameters shows that:

1) At low concentration (0.1 M NaCl or KCl), the samples do not consist of particles but of isolated layers ($M = 1$). The suspensions form gel-like structures. The difference between Na and K suspensions, or between heated and nonheated samples, is unnoticeable at the studied scale (5–500 Å).

2) An increase in salt concentration (from 0.1 to 0.5 M) brings the sample in a granular state: we notice the appearance of particles at 0.5 M ($\bar{M} \geq 25$). Differences appear between NaCl and KCl suspensions, and the temperature effect becomes visible. Thus, we noticed that in NaCl suspensions, particles are composed of hydrated layers (1, 2, 3 or 4 water layers) and internal porosity ($d > 30$ Å), whereas suspensions in KCl are characterized by the presence of interlayer distances of 10 Å, that is, of collapsed layers. Particles in the KCl suspensions are much thicker than in the NaCl corresponding ones, and also less hydrated at the interlayer level as well as at the internal porosity level. Further increase in salt concentration (0.5 to 1 M) amplifies this effect. As far as temperature is concerned, its effect is to promote the clay dispersion by breaking up the particles, dehydrating and disordering them. This effect is more important for low salt concentration, that is, when the system is less stressed.

Key Words—Montmorillonite, SAXS, Structure, Suspensions, Texture.

INTRODUCTION

Montmorillonite is used in drilling muds for its ability to form viscoelastic and thixotropic dispersions. The mechanism leading to the appearance of these properties is linked with the interlamellar swelling of clay in contact with an ionic solution (Méring 1946; Barshad 1953; Norrish 1954; Quirk 1968; Van Olphen 1977; Pons 1980; Saez-Aunon et al. 1983; Tessier 1984; Raussel-Colom et al. 1989). One problem occurring during drilling is to control the swollen states and their total or partial reversibility under the action of different physicochemical parameters and different stresses to which the clay can be subjected (charge-balancing cation, salt concentration of the solution, temperature).

Under stress, the uptake or loss of water by the clay occurs with a concomitant structural reorganization of the material at different scales (Millot 1964; Concaret 1967; Henin 1971; Monnier et al. 1973; Pedro 1976; Pons et al. 1981, 1982; Robertson et al. 1982; Tessier 1984; Ben Rhaïem 1983; Ben Rhaïem et al. 1986; Touret et al. 1990). In order to characterize the struc-

tural changes of these clays under different stresses, it was necessary to get a continuous picture of the organization levels from the structural ordering of the layer stacks up to the size of the first aggregates (Pons et al. 1981; Ben Rhaïem 1983; Tessier 1984; Touret et al. 1990). These studies proved that 3 structural scales must be considered: 1) parallel ordering of layers, creating more or less thick or more or less swollen particles, the limiting case being the 1-single-layer particle; 2) the mutual ordering of particles in aggregates; 3) the mutual ordering of aggregates (Figure 1) (Touret et al. 1990).

The technique used to describe these structural scales and to follow the structural evolution in relation to the different stresses is SAXS. It is a nondestructive technique, giving a continuous image of the structure and the microtexture (Pons 1980; Ben Rhaïem et al. 1987; Touret et al. 1990; Gaboriau 1991).

In this study, we will present the method of SAXS spectra interpretation in the particular case of heterogeneous systems. In a heterogeneous clay suspension, a swelling phase and a nonswelling phase are to be found inside the same particle. This method is valid

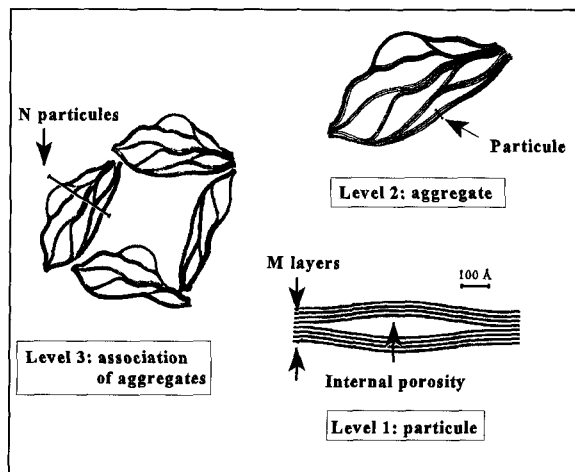


Figure 1. Schematic representation of the 3 structural levels in a clay-water system: the particle (level 1), the aggregates (level 2) and the association of aggregates (level 3).

for genuinely interstratified clay minerals (illite-smectite or kaolinite-smectite) but also in cases like the present one, where there exist collapsed clay layers because of the presence of K. Because, crystallographically, we cannot distinguish between exchangeable and nonexchangeable K, we will not speak in terms of “nonswelling phase” but of “collapsed phase”. We will also describe the structure, microtexture and structural changes of low-clay-concentration suspensions subjected to high salt concentration (NaCl and KCl) and to a temperature of 200 °C in an autoclave. In addition, we will quantify the interlayer and interparticulate water (Touret et al. 1990; Gaboriau 1991) in order to follow the distribution of these types of water at the different structural scales of the clay in suspension.

METHOD

Pons (1980) showed that, in the case of swelling clay systems, it is necessary to compare the experimental intensity X-ray scattering spectrum with a theoretical one simulated from a structural model. This model is based on the notion of particle and of particle internal structure (Pons et al. 1981; Ben Rhaïem et al. 1987; Touret et al. 1990). In the case of 2:1 phyllosilicates, the basic components of all structures are the layers. One particle consists of a stacking of *M* parallel layers; the limiting case $M = 1$ stands for isolated layers (Pons et al. 1981). The macroscopic edifice thus consists of the associations among particles (Figure 1).

Two types of systems are to be found: one, which we will call “homogeneous,” and the other, which we call “heterogeneous” by analogy with interstratified illite-smectite (Mac Ewan 1958; Reynolds and Hower 1970; Reynolds 1980; Gaboriau, 1991). The homogeneous system is composed of a unique swell-

ing phase. In the case of a homogeneous clay system with high water content, distances between layers can be different from one another inside the same particle (Pons et al. 1981; Ben Rhaïem et al. 1987). The sequence of spacings that separate the *M* layers is defined as a series of *r* different translations (d_i) that are influenced by the probabilities of occurrence (p_i) (Mering 1949; Mac Ewan 1958; Pons 1980; Reynolds 1980). The interlayer distance distribution function $p_i(d_i)$ characterizes the order within the particle (Saez-Aunon et al. 1983; Ben Rhaïem et al. 1986; Gaboriau 1991). In the case of a heterogeneous clay system with high water content, a particle consists of: 1) a swelling phase in which interlayer spaces can be different from one layer to another; 2) a nonhydrated phase in which, whatever the water content, there is only 1 distance between first neighbors. This distance of 10 Å corresponds to the thickness of a single, nonhydrated clay layer. Interstratified illite-smectite and kaolinite-smectite are the typical cases (Mac Ewan 1958; Reynolds and Hower 1970; Reynolds 1980). All these cases can be treated by the method we present here; in the case of the suspensions considered in this paper, we cannot tell whether the nonhydrated layers are permanently collapsed, or whether they can expand again. So, instead of “nonswelling phase”, we will speak of “collapsed phase”. In the general case, the method uses a stacking model that takes into account an interstratification between an homogeneous smectitic swelling phase and a collapsed phase (Gaboriau 1991).

Intensity Calculations

If we assume that (Pons et al. 1981; Gaboriau 1991): 1) layers have a great lateral extension and particles have all possible orientations in space, 2) the distance distribution inside the swelling phase is totally random, and 3) all the layers in the swelling phase have the same structure factor, that of the clay layer with 2 water layers, then the matrix expression of the scattered intensity is (Plançon 1981; Pons et al. 1981; de la Calle et al. 1993):

$$I(s) = \frac{1}{s^2} \sum_M \alpha(M) \text{Spur} \times \left\{ \text{Re} \left\{ [F][W] \left\{ [I] + 2 \sum_n \left(\frac{M-n}{M} \right) [Q]^n \right\} \right\} \right\} \quad [1]$$

where *s* is the modulus of the diffraction vector ($s = 2 \sin \theta / \lambda$, $\lambda =$ wavelength); $\alpha(M)$ the distribution of the number of layers per particle; Re means the real part of the final matrix; Spur, the sum of the diagonal terms of the real matrix; *M* the number of parallel layers per stack; *n*, an integer varying between 1 and (*M* - 1); [*F*] the structure factors matrix; [*I*] the unit matrix; [*W*] the diagonal matrix of the proportions of the 2 phases, and [*Q*] the matrix representing the in-

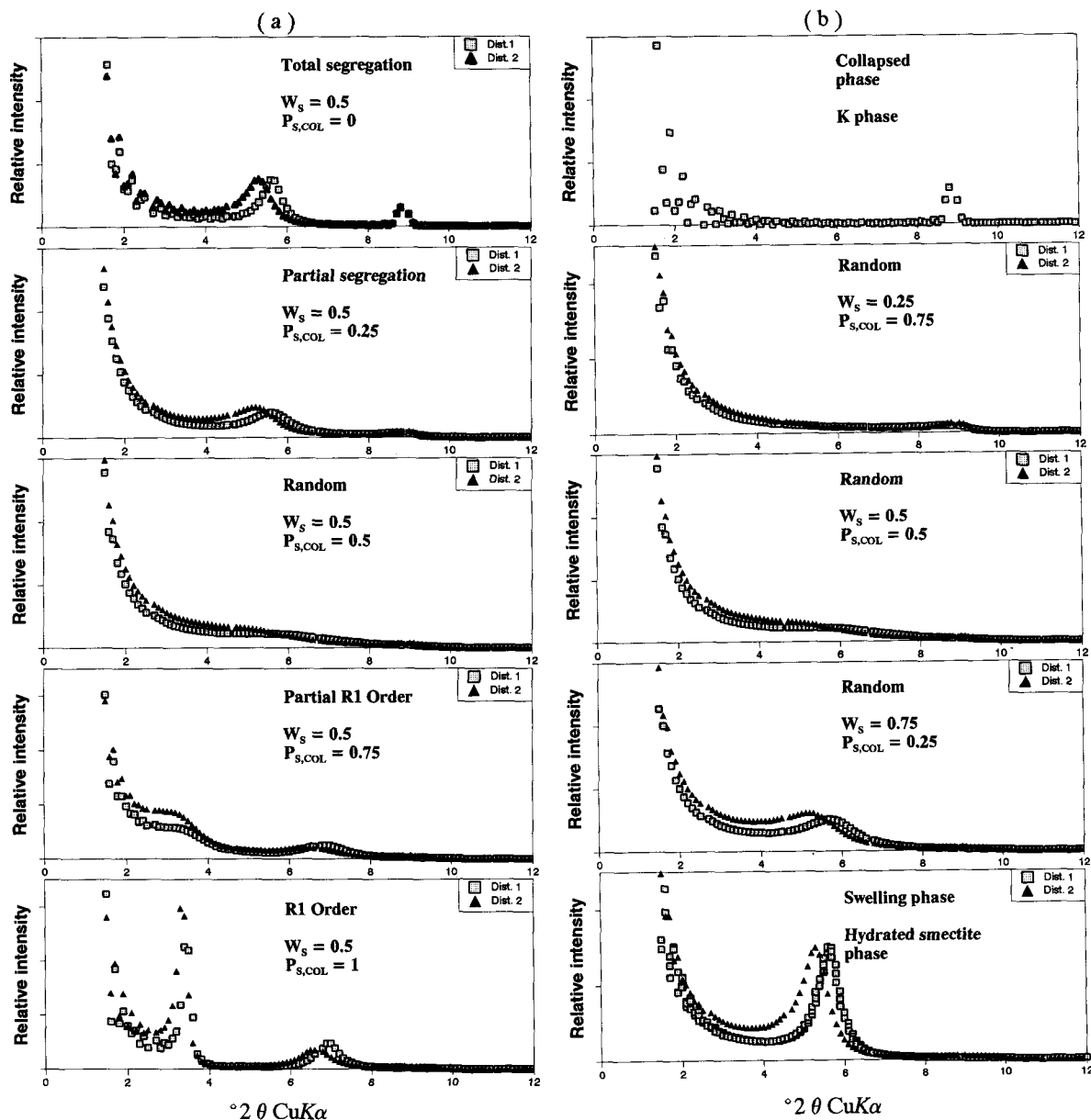


Figure 2. Theoretical intensity scattered by a set of identical particles. Each particle is composed of 25 layers, belonging to 2 different phases. W_s : abundance of swelling layers; W_{col} : abundance of non-swelling layers. Two types of interlayer distances distributions have been used: First distribution: symmetrical distribution around a 2-water-layer hydration state: $d_1 = 12.5 \text{ \AA}$, $p_1 = 0.2$; $d_2 = 15.5 \text{ \AA}$, $p_2 = 0.6$; $d_3 = 18.5 \text{ \AA}$, $p_3 = 0.2$. Second distribution: nonsymmetrical distribution: $d_1 = 12.5 \text{ \AA}$, $p_1 = 0.22$; $d_2 = 15.5 \text{ \AA}$, $p_2 = 0.33$; $d_3 = 18.5 \text{ \AA}$, $p_3 = 0.45$. Two cases are presented: a) at constant abundance $W_s = 0.5$, $W_{col} = 0.5$; b) for random interstratification of the 2 components. In this case, $W_{col} = P_{col,col} = P_{s,col}$ and $W_s = P_{s,s} = P_{col,s}$.

interference phenomena between adjacent layers. $[Q]$, $[F]$ and $[W]$ have the following forms:

$$[Q] = \begin{bmatrix} P_{s,s} \sum_i p_i \exp(2i\pi s d_i) & P_{s,col} \sum_i p_i \exp(2i\pi s d_i) \\ P_{col,s} \exp(2i\pi s d_{col}) & P_{col,col} \exp(2i\pi s d_{col}) \end{bmatrix} \quad [2]$$

$$[F] = \begin{bmatrix} F_s^* F_s & F_s^* F_{col} \\ F_{col}^* F_s & F_{col}^* F_{col} \end{bmatrix} \quad [3]$$

$$[W] = \begin{bmatrix} W_s & 0 \\ 0 & W_{col} \end{bmatrix} \quad [4]$$

where W_s and W_{col} are, respectively, the abundances of the swelling and collapsed phases; F_s^* and F_{col} the

structure factors related to the layers of the swelling and the collapsed phase; d_i the r possible distances between the layers of the swelling phase; p_i the probabilities of going from 1 layer of a thickness d_i in the swelling phase to another in the swelling phase; $P_{\text{col},s}$ the probability of going from 1 layer in the collapsed phase to another in the swelling phase ($P_{s,s}$, $P_{s,\text{col}}$ and $P_{\text{col},\text{col}}$ are defined in the same way).

The relationships between proportions of the swelling and collapsed phases and probabilities are given by:

$$\begin{aligned} W_s + W_{\text{col}} &= 1 \\ P_{s,s} + P_{s,\text{col}} &= 1 \\ P_{\text{col},s} + P_{\text{col},\text{col}} &= 1 \\ W_{\text{col}}P_{\text{col},s} &= W_sP_{s,\text{col}} \\ \sum_i p_i &= 1 \end{aligned} \quad [5]$$

For the swelling phase, it is possible to define the mean interlayer distance \bar{d} and the disorder parameter $\bar{\delta}^2/\bar{d}^2$ (Saez-Aunon et al. 1983):

$$\bar{d} = \sum_i p_i d_i \quad [6]$$

$$\frac{\bar{\delta}^2}{\bar{d}^2} = \frac{\sum_i [d_i - \bar{d}]^2}{\left(\sum_i p_i d_i\right)^2} \quad [7]$$

For a given p_i distribution, the different values of the independent parameters W_s and $P_{s,\text{col}}$ allow the calculation of all cases of interstratification ranging from systems containing randomly distributed swelling and collapsed phases to those with regular interstratification or with a total segregation between the 2 phases. All theoretical patterns were calculated using the "MANUEL₁" program (information available from C. H. Pons) for an IBM/PC or compatible. In Figure 2 are given different intensity profiles computed according to the particle model described above. For all cases given in the appendix, the mean number of layers per particle is 25. The spectra were computed using 2 different distances distributions: a symmetrical and a nonsymmetrical one. The distances correspond to clay layers hydrated with 1, 2, 3 or 4 water layers; such distributions were found in the studied samples. In Figure 2a we present the spectra obtained at constant abundance of the swelling phase ($W_s = 0.5$); in Figure 2b are presented the spectra obtained in the case of random systems (W_s and $P_{s,\text{col}}$ vary).

We notice that the shape and position of the reflection are influenced by each parameter. Complex combination of these factors results in the fact that 2 spectra of similar shape can correspond to 2 fundamentally different systems. It is then necessary to simulate the spectra to distinguish between them. An example is

Table 1. Studied samples.

Na-montmorillonite suspensions of 4 wt%†	
Salt concentration of the solution	Temperature‡
0.1 M NaCl	RT§
	200 °C
0.5 M NaCl	RT
	200 °C
1 M NaCl	RT
	200 °C
0.1 M KCl	RT
	200 °C
0.5 M KCl	RT
	200 °C
1 M KCl	RT
	200 °C

† 4 wt% = 4 g clay for 100 g solution.

‡ All the samples (heated or not) were studied at room temperature (RT).

§ RT = 25 °C.

given by the case "partial segregation $W_s = 0.5$, $P_{s,\text{col}} = 0.25$ " and "random $W_s = 0.75$, $P_{s,\text{col}} = 0.25$ ". It is also interesting to notice that, even when the abundance of the collapsed phase is high ($W_{\text{col}} = 0.5$), the 10-Å reflection is noticeable only in the segregation case. Thus, the absence of this reflection does not mean that there are no collapsed layers in the system. In all cases, the spectrum simulation is necessary to accurately describe the samples' structure and texture.

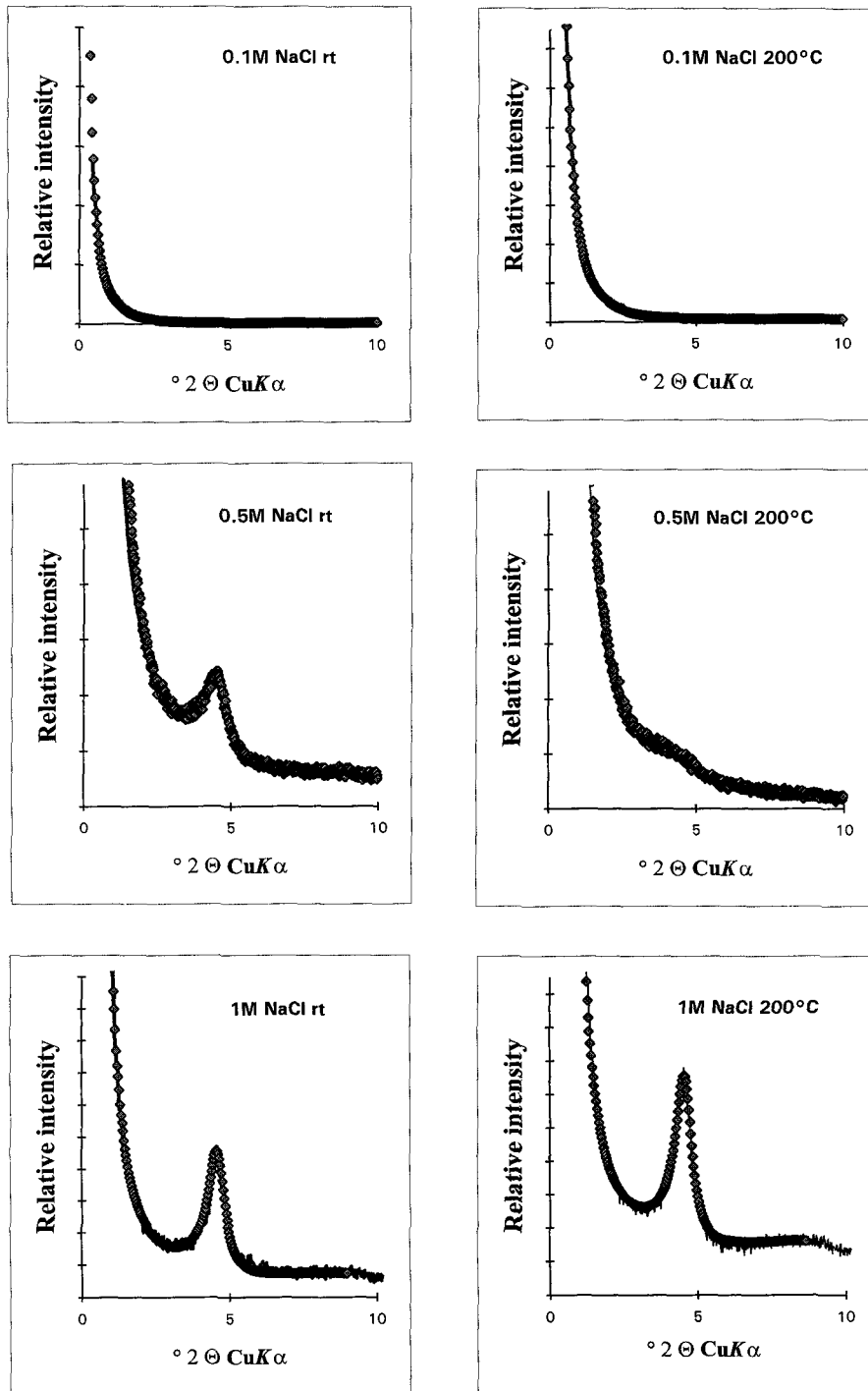
Water Content Calculations

Numerous works (Ben Rhaïem 1983; Tessier 1984; Ben Rhaïem et al. 1986; Touret et al. 1990; Gaboriau 1991) have shown that different types of water could be defined. We will call "total internal water" the water contained in the swelling phase of clay particles. It is the sum of the water contained in the interlayer spaces (1, 2, 3 or 4 water layers) and the water contained in the internal porosity, that is to say, the porosity inside the particle (Figure 1). The external water is all the remaining water, that is, outside the particle. The density of interlayer water depends upon whether the charge-balancing cation is Na or K, as well as upon the osmotic potential of the system (Farmer 1978; Pons et al. 1980; Newman 1987). However, Pons et al. (1981) have shown that the density of the water in the interlayer spaces and the internal porosity could be assumed, in a first approximation, to be similar to that of bulk water.

Under such conditions, the total internal water content, inside the particle, expressed in $g_{\text{water}}/g_{\text{clay}}$, is (Gaboriau 1991):

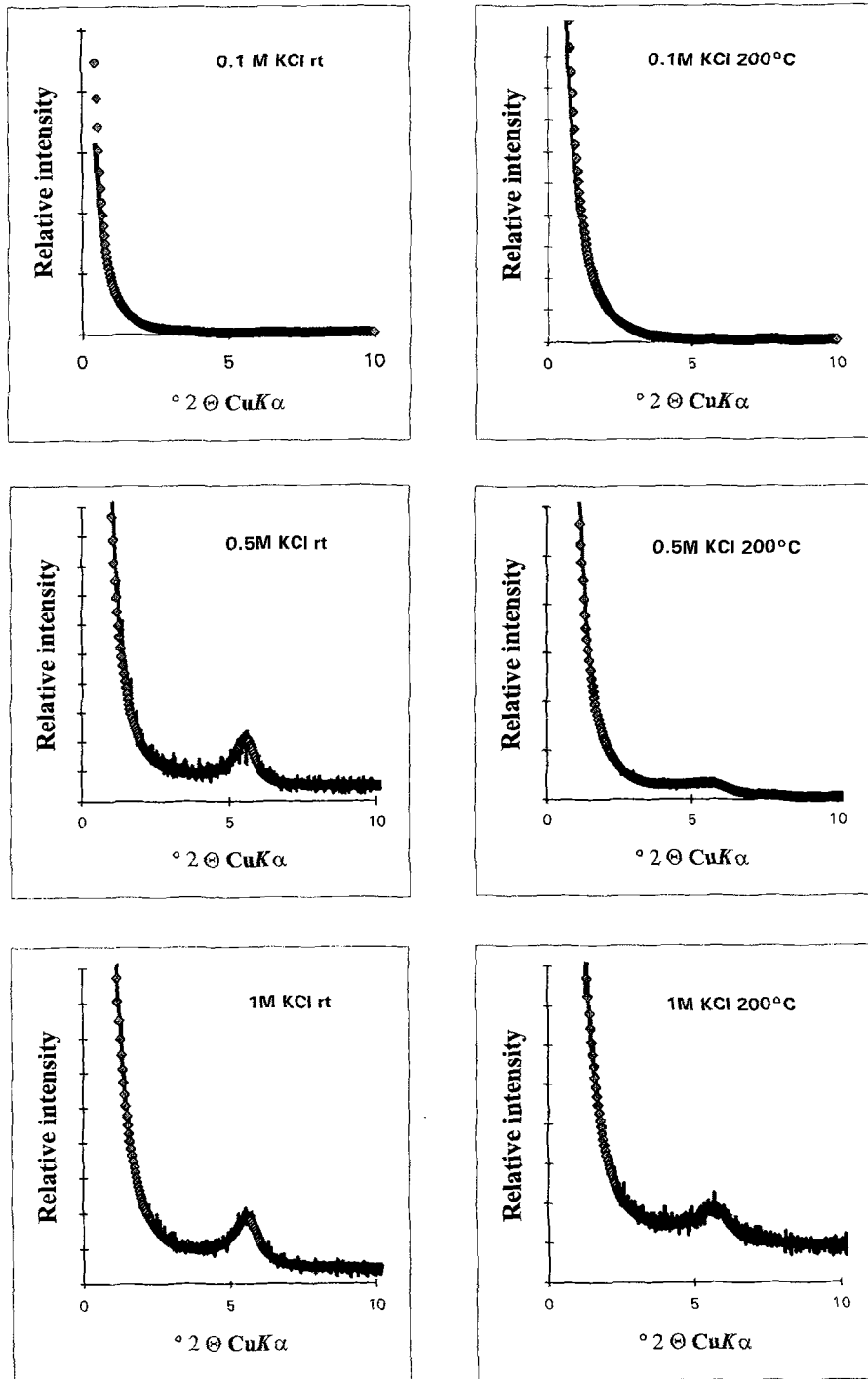
$$w_i = \frac{\text{Sp}(\text{tot}) \times (M - 1) \times (\text{Sm}/100) \times (\bar{d} - d_{\text{col}}) \times 10^{-4}}{2M} \quad [8]$$

where Sp(tot) is the total specific area; Sm, the percentage of swelling phase layers and d_{col} the distance



(a)

Figure 3. Comparison between experimental (continuous line) and theoretical (dots) spectra. a) samples in NaCl solutions; b) samples in KCl solutions. RT: room temperature.



(b)

Figure 3. Continued.

Table 2. Water contents, structural and textural parameters deduced from SAXS spectra analysis.

T °C	Collapsed phase $P_{col,coi}$	Swelling phase									
		Interlayer hydration				Internal porosity					
		p_{1c}	p_{2c}	p_{3c}	p_{4c}	$p_{30 \text{ \AA}}$	$p_{35 \text{ \AA}}$	$p_{40 \text{ \AA}}$	$p_{45 \text{ \AA}}$	$p_{50 \text{ \AA}}$	
NaCl	RT	—	0.032	0.261	0.199	0.381	0.037	0.054	0.037	—	—
0.5 M	200	—	0.205	0.215	0.215	0.250	0.100	0.005	0.004	0.004	0.002
NaCl	RT	—	0.033	0.279	0.295	0.367	—	0.008	0.009	0.008	—
1 M	200	—	0.031	0.265	0.280	0.399	—	0.008	0.009	0.008	—
KCl	RT	0.032	0.144	0.611	0.144	0.055	—	0.004	0.006	0.004	—
0.5 M	200	0.043	0.335	0.354	0.143	0.104	—	0.006	0.009	0.006	—
KCl	RT	0.029	0.197	0.554	0.131	0.073	—	0.004	0.008	0.004	—
1 M	200	0.093	0.232	0.461	0.130	0.064	—	0.005	0.009	0.005	—

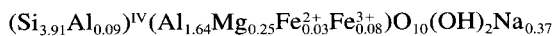
Key: p_{ic} : probability of finding i water layers between 2 adjacent clay layers; $p_{i \text{ \AA}}$: probability of occurrence of the $i \text{ \AA}$ distance between adjacent clay layers; $P_{col,coi}$: probability to go from 1 layer in the collapsed phase to another in the collapsed phase; M : mean number of layers per particle; d_c : mean interlayer distance; w_i : interlayer water (g_{water}/g_{clay}); w_l : lenticular water (g_{water}/g_{clay}); w_t : total internal water (g_{water}/g_{clay}).

between 2 layers in the collapsed phase. The water content in an interlayer space corresponding to a distance d_i is then given by:

$$w_i(d_i) = \frac{Sp(\text{tot}) \times (M - 1) \times (Sm/100) \times (d_i - d_{col}) \times 10^{-4}}{2M} \quad [9]$$

EXPERIMENTAL

The clay used in all experiments is a montmorillonite from Wyoming (USA), obtained from CECA Co. Samples have been prepared according to the following treatment (Jin 1994). After removal of impurities (mostly quartz and feldspar) by decantation, the clay was saturated with Na by 2 exchanges of 24 h in a 1 M NaCl solution, then washed free of salts. Washing was checked according to the $AgNO_3$ test. The clay was then lyophilized and powdered. The average structural formula of the Na-exchanged clay is (Jin 1994):



Samples consisted of 30-mL suspensions of 4 wt% (4 g clay for 100 g solution) of Na-montmorillonite in 0.1, 0.5 or 1 M NaCl or KCl solutions (Table 1) Ten mL of each sample were heated in a closed vessel at 200 °C during 7 d and then cooled at RT (25 °C). All samples (heated or not) were studied at RT.

X-ray Diffraction

Intensity data were recorded on a SAXS setup using a Rigaku rotating anode (12 kW) with a curved germanium monochromator ($CuK\alpha = 1.5405 \text{ \AA}$) (Tchoubar et al. 1978). The monochromatic beam is convergent in the horizontal plane and diverging in the vertical plane. It is possible to obtain a punctual collimation simply by limiting the height of the beam by

a pair of horizontal tantalum slits. Under such conditions, the direct beam dimensions at the focalization point are 300 μm by 500 μm . These experimental conditions make it possible to explore a domain of the reciprocal space corresponding to correlation distances ranging from 5 to 500 \AA . Alignment and calibration are performed using the 001 reflection of tetradecanol powder (Brindley 1981). The cell used is made of aluminium, with mica windows. The surface of the irradiated sample is 0.5 mm by 1 mm. As the autoclave used to heat the samples is not transparent to X-rays, all experiments had to be carried out at RT.

RESULTS

Qualitative Analysis of Experimental Patterns

An examination of the experimental patterns (Figures 3a and 3b) shows that they fall into 2 groups: 1) the 0.1 M NaCl and 0.1 M KCl patterns, showing a continuous decrease of the intensity; and 2) the 0.5 and 1 M NaCl or KCl spectra, showing some modulation of the intensity situated between 4 and 6 $^{\circ}2\theta$. These results indicate that: 1) the samples in the first group have a gel-like structure, and are composed of dispersed elementary layers (Pons 1980; Pons et al. 1981; Ben Rhaïem et al. 1987); 2) the samples corresponding to the second group have a structure of hydrated solids in which occur short-distance interactions between first neighbors (Pons et al. 1981; Ben Rhaïem et al. 1986; Ben Rhaïem et al. 1987; Gaboriau 1991). The sample then consists of a set of particles, connected or not, created by the more or less disordered stacking of hydrated layers with a limited number of interlayer water layers (0, 1, 2, 3 or 4) and internal porosity.

In Figures 3a and 3b we can compare the spectra at various NaCl and KCl concentrations and at the 2 different temperatures. The set of patterns shows that the change from a 0.1 M NaCl or 0.1 M KCl solution to

Table 2. Extended.

Structural parameters			Water contents		
<i>M</i>	<i>d</i>	Disorder	<i>w_i</i>	<i>w_p</i>	<i>w_t</i>
25	20.9	0.087	0.30	0.12	0.42
15	18.95	0.090	0.24	0.09	0.33
35	19.20	0.051	0.33	0.03	0.36
30	19.30	0.049	0.33	0.03	0.36
80	16.08	0.054	0.22	0.02	0.24
30	15.93	0.087	0.20	0.03	0.23
75	16.12	0.062	0.22	0.02	0.24
65	15.60	0.082	0.19	0.03	0.22

a more concentrated one (0.5 *M*) transforms the suspension from a gel structure to a hydrated solid structure. In the case of NaCl, this behavior is still more important when the concentration increases to 1 *M*. In this range of distances and at low concentration (0.1 *M*), the thermal stress does not significantly affect the shape of the spectra. However, in the case of 0.5 *M* KCl and 0.5 *M* NaCl suspensions, a strong influence of temperature on the clay structure can be noticed. This effect is far less important in the case of suspensions in 1 *M* NaCl or 1 *M* KCl.

Quantitative Analysis of Experimental Patterns

Table 2 presents the values of the different structural and textural parameters \bar{M} , \bar{d} and disorder, determined by adjusting the theoretical spectra (obtained from the structural model described above) to the experimental ones (Figures 3a and 3b). In the case of the 0.1 *M* NaCl and 0.1 *M* KCl samples, the absence of modulation means that the scattered intensity in the 5–500 Å domain corresponds to one scattered by a set of isolated layers, with no interaction between first neighbors. The intensity varies with the square of the structure factor of the layer (Pons et al. 1981). Thus, clay suspensions in 0.1 *M* NaCl and 0.1 *M* KCl have undergone an internal osmotic swelling and occur as ideal suspensions.

In the case of samples in more concentrated NaCl or KCl solutions (0.5 *M* and 1 *M*), the increase of the osmotic potential is responsible for the appearance, at a small distance of interaction, of a modulation reflecting the aggregation of layers into particles (Figures 3a and 3b). Figures 4a and 4b show the evolution of the distance distributions for the samples in 0.5 and 1 *M* NaCl and KCl solutions. Two groups of distances appear in these distributions. The first group, in which interlayer distances are <25 Å, reveals the existence of hydration states of 1, 2, 3 or 4 water layers. The second group of distances is characteristic of the internal porosity (Ben Rhaïem et al. 1987). In the case of suspensions in KCl, we notice the appearance of a probability ($P_{\text{col,col}}$) for the 10-Å interlayer distance characteristic of the collapsed phase, and that the in-

terstratification between the swelling phase and the collapsed phase was random (Figure 2).

Effect of The Osmotic Potential at RT

EVOLUTION OF PARTICLE SIZE. In the case of clay suspensions in NaCl, the increase in the osmotic potential from 0.1 to 0.5 *M* results in the aggregation of the isolated layers into particles of 25 layers (Figures 5a and 5b). Further increase to 1 *M* induces a face-to-face regrouping of these particles into thicker particles (35 layers at 1 *M*). In the case of KCl, the increase in the osmotic potential from 0.1 to 0.5 *M* induces a layer stacking into much thicker particles (80 layers) than in the case of NaCl. On the other hand, except for a slight tendency for \bar{M} to decrease (from 80 to 75), it seems that further increase in the concentration from 0.5 to 1 *M* does not significantly affect the particle size.

EVOLUTION OF THE INTERNAL STRUCTURE OF PARTICLES. In the range of the studied concentrations, there is no global change in the distance distributions when the concentration increases from 0.5 to 1 *M* (Figures 4a and 4b). However, the shape of the distributions, as far as distances <25 Å are concerned, is very different for the clay in NaCl and KCl solutions. We notice that the most probable number of interlayer water layers is indeed 2 in the case of K, whereas it is 4 in the case of Na. The nonsymmetrical distributions corresponding to suspensions in NaCl (Figure 4a) are typical of clays for which the charge-balancing cation allows unlimited swelling (Norrish 1954; Pons et al. 1981; Ben Rhaïem et al. 1987; Gaboriau 1991). Because of their symmetrical shape and the existence of 10-Å interlayer distances, distributions obtained in the case of KCl suspensions are typical of clays in which the charge-balancing cation does not favor unlimited swelling.

The analysis of the disorder parameter and the water contents (Table 2) enables clarification of the effect of concentration on the internal order of the particles. For NaCl suspensions at RT, the increase from 0.5 to 1 *M* is responsible for a perceptible diminution of the disorder parameter (Figure 5a), the mean interlayer distance (Figure 5a) and the total internal water content (Figure 6a). The diminution of these 3 parameters shows that in this concentration range, an increase in the osmotic potential produces an increase in order inside the particles, along with a dehydration of these, especially at the internal porosity level (Figure 6a). In the case of KCl suspensions, the increase from 0.5 to 1 *M* resulted mostly in an increase in the disorder parameter, the other parameters remaining unchanged. So, the water redistribution inside the particle is important in the case of NaCl, whereas it is almost unnoticeable in the case of KCl suspensions (the increase in the internal disorder can be related to a diminution of the number of layers per particle).

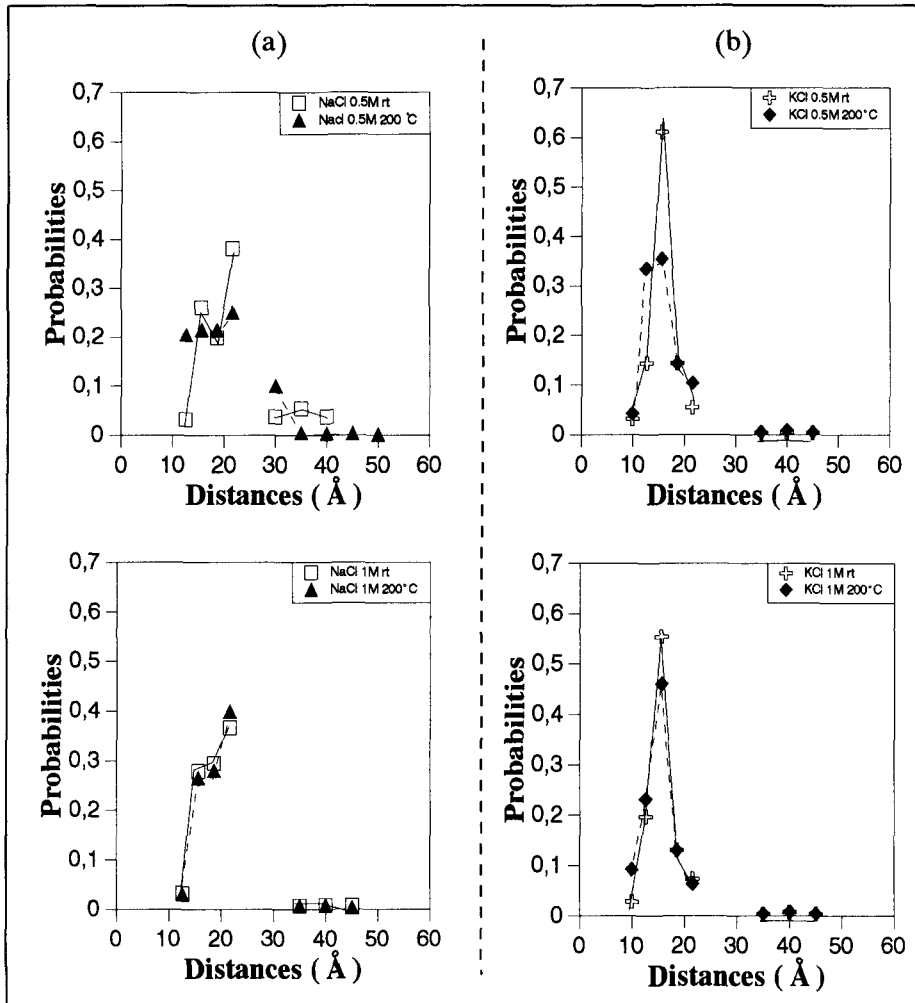


Figure 4. Distance distributions. a) samples in NaCl solutions; b) samples in KCl solutions. RT: room temperature.

Effect of Temperature at Given Salt Concentration

EVOLUTION OF THE PARTICLE SIZE. In all cases, an increase in temperature (RT 200 °C) is responsible for the diminution of the number of layers per particle (Figure 5). For a given cation, this decrease is always greater at 0.5 M than at 1 M. The KCl suspensions are the most sensitive to this particle-breaking effect. In the case of KCl samples, the ratio between \bar{M} at 200 °C and \bar{M} at RT is 0.375 at 0.5 M and 0.87 at 1 M, whereas it is only 0.06 for suspensions at 0.5 M NaCl and 0.086 for suspensions at 1 M NaCl.

EVOLUTION OF THE INTERNAL STRUCTURE OF THE PARTICLES. In the case of 0.5 M NaCl and KCl suspensions, the effect of temperature is strong, as shown in the evolution of the distribution of interlayer distances (Figures 4a and 4b). For the 0.5 M NaCl suspension heated to 200 °C, there is a nearly equal probability of the 1, 2, 3 and 4 water-layer hydration

states in the system (Figure 4a), and the internal porosity is less important than at RT (Figure 6a). On the other hand, the mean interlayer distance decreases, as does the total internal water content (Figures 5a and 6a). In this case, the increase in temperature probably leads to a liberation of the internal stresses at the scale of layers and connections among particle levels, allowing the system to fall into a state of lower entropy.

At 0.5 M KCl, the change in the distance distribution (Figure 4b) indicates an internal water redistribution to a more disorganized internal structure. This effect is confirmed by the large increase in the disorder parameter (Figure 5b). As the mean interlayer distance does not change, the slight loss in total internal water can be related to the diminution of the particle size (0.375). At this concentration, the effect of temperature stress is to make the system far less granular than

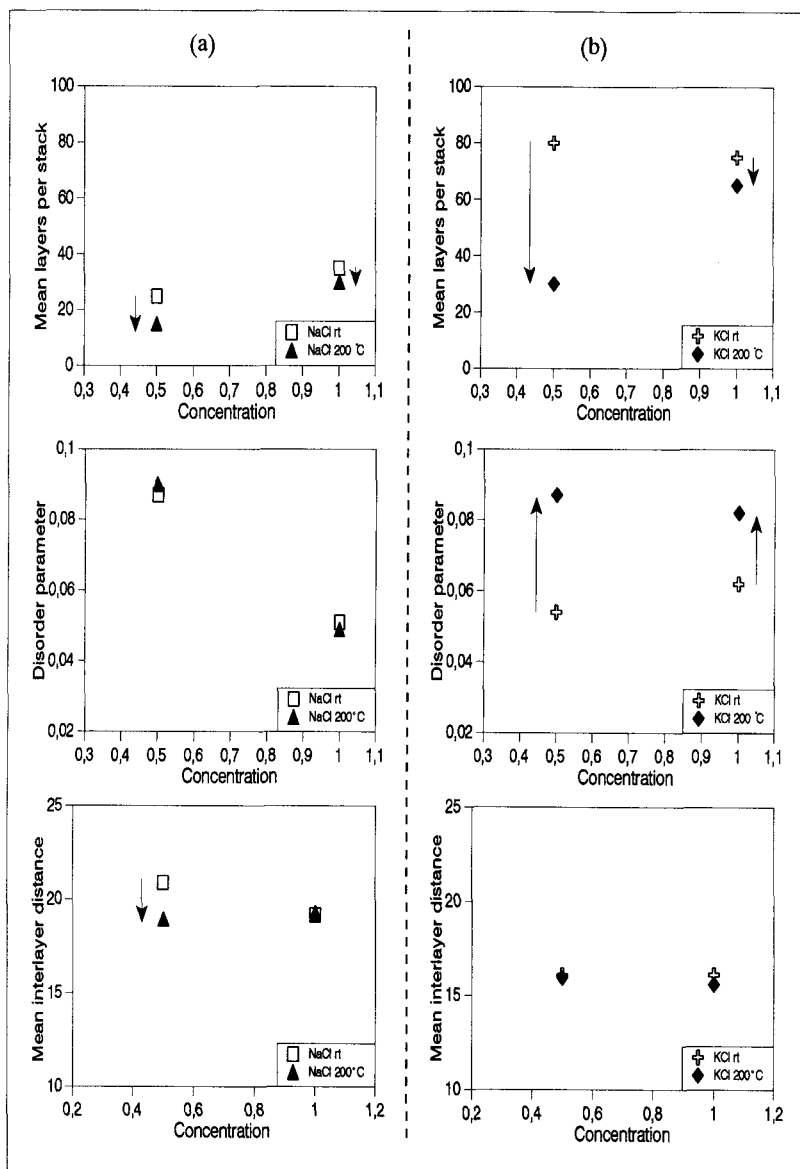


Figure 5. Evolution of the mean layers per stack, the mean interlayer distance and the disorder parameter with concentration. a) samples in NaCl solutions; b) samples in KCl solutions. RT: room temperature. The arrows underline the effect of temperature.

it was at the beginning, trending to a state situated between an ideal suspension and a granular one.

In the case of higher salt concentration (1 M NaCl or KCl), the effect of temperature is less important. As far as the 1 M NaCl solution is concerned, no effect of temperature can be noted on any parameters (mean interlayer distance, disorder and total internal water). This means that the osmotic stress sets the system in such a configuration that the stress related to temperature is too weak to induce changes at the level of the internal structure of the particle. At 1 M

KCl, the major change in the distance distribution is the great increase in the collapsed phase abundance (from 0.019 at RT to 0.093 at 200 °C) (Table 2). The probabilities of 1 water-layer distance also increase, balanced by the diminution of 2 and 4 water-layer probabilities (Figure 4). The internal porosity is not affected. Thus, the effect of temperature at 1 M KCl is a dehydration at the level of interlayer water. The internal structure of the particles in this case is much more disordered than it was at RT. Furthermore, we notice that this increase in the disorder parameter is

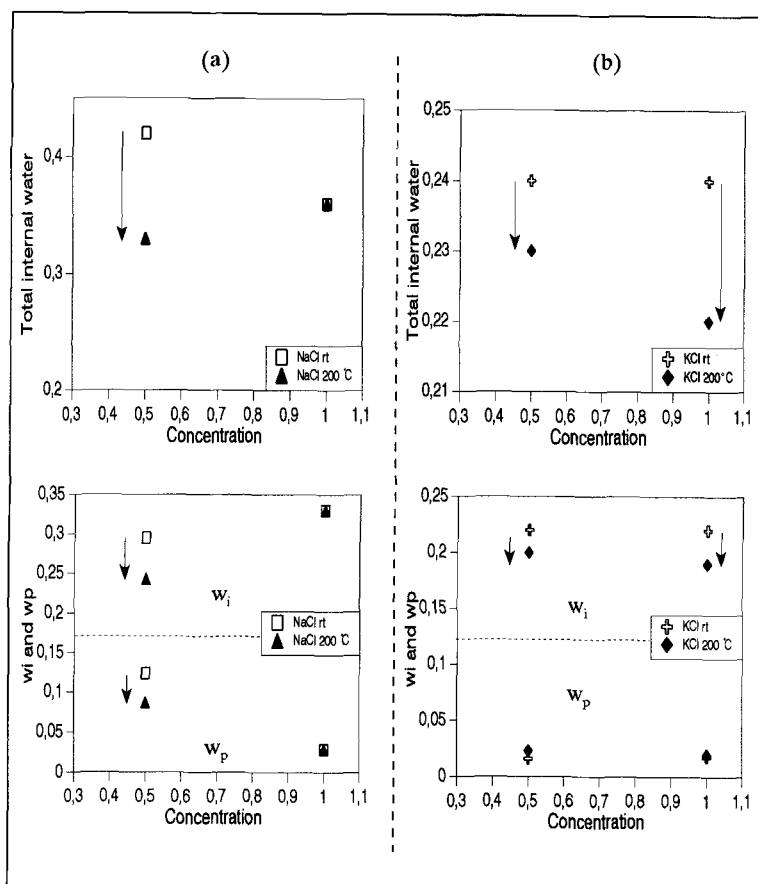


Figure 6. Total internal water content, interlayer water content and internal porosity water content evolution with concentration. a) samples in NaCl solutions; b) samples in KCl solutions. RT: room temperature. The arrows underline the effect of temperature. W_i : interlayer water ($g_{\text{water}}/g_{\text{clay}}$); W_p : internal porosity ($g_{\text{water}}/g_{\text{clay}}$).

less important at 1 M KCl than it was at 0.5 M KCl (Figure 5b).

DISCUSSION AND CONCLUSIONS

All these results suggest the following interpretations: at 0.1 M, the organizational differences between NaCl and KCl clay suspensions, along with their possible sensitivity to heating, cannot be seen in the 5–500 Å scale. Both are swelling systems. When the salt concentration increases, differences appear. The KCl suspensions are characterized by the presence of 10-Å interlayer distances which, at the same osmotic pressure, are never to be found in the NaCl samples. This can be explained by the fact that K size corresponds to the size of the hexagonal cavity, promoting the cation insertion in the clay layer. It must be noticed that we cannot crystallographically distinguish between exchangeable and nonexchangeable K, so that we cannot tell in our case whether the interlayer K is fixed or not by an increase in salt concentration. Another difference is that the NaCl suspensions are always more hydrated than the KCl corresponding ones. This spe-

cific behavior of K^+ , a monovalent cation like Na^+ , was previously noticed by Norrish (1954). An explanation for the fact that KCl layers are less hydrated than NaCl ones could be that the hydration sphere of K^+ is smaller than the one of Na^+ .

The global effect of an increase in salt concentration is to densify and dehydrate the particle, while modifying its internal order. The evolution of the disorder parameter we have established suggests that there exists a threshold of concentration corresponding to a maximum structural order which can be reached in suspensions such as those we consider here. In the case of Na, such a threshold would be at far higher concentration than in the K case.

As far as the temperature effect is concerned, it is interesting to note that we witness a hysteresis in the system: the heated samples do not recover their original structure after cooling at RT. What we describe here is the persistent effect of temperature after relaxation of the system. Heating of the suspensions promotes, in all cases, some degree of clay dispersion. However, the higher the osmotic potential, the less

marked this thermal effect. It seems then clear that there is a competition between ionic and thermal stresses, and that prolonged heating at 200 °C has less influence on suspensions subjected to high osmotic potential.

As far as the structure of the suspensions is concerned, the results enable us to get a more precise idea of their influence in drilling mud problems. When the mean number of layers is small (in the case of 0.5 *M* suspensions), the layers are associated edge-to-edge and form great membranes, that connect and create a porous network (Tessier 1984; Ben Rhaïem et al. 1987; Gaboriau 1991). When the layer number is high (0.5 *M* suspensions), thick particles probably associate in porous aggregates of finite size, not connected to one another (the concentration here is of 4% $w_{\text{clay}}/w_{\text{solution}}$). Their internal structure, determining their free water content, is the result of a fine balance between osmotic forces, tending to move particles apart, and stresses due to their criss-crossing that prevent it. These can be of 2 types: local electrostatic attractions, related to an inhomogeneous layer-charge distribution or to the presence of superficial charges (in the tetrahedral sheet) forming interparticle anchorage points, and criss-crossing of layers related to local conditions during sample preparation. The influence of the structure on a possible tamping in the drill (when the drilling mud becomes compact) is related to the particles' swelling state, and especially to swelling of the aggregates. It has thus been proved that tamping is more frequent when the mud is in a gel state than when it is in a granular state.

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