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Sol−Gel Transitions in Aqueous Suspensions of Synthetic Takovites. The Role of Hydration Properties and Anisotropy

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To reach a better understanding of the behavior of suspensions of charged colloidal platelets, takovite samples with a general formula Ni_{1-x}, $Al_x(OH)_2$, $An^{z-}_{x/z}$, yH_2O, where An is an interlayer anion, were synthesized. These materials belong to the family of layered double hydroxides (also referred to as anionic clays). They can be easily prepared in the laboratory by coprecipitating mixed nickel and aluminum salts by NaOH. Their charge can be adjusted by changing the synthesis conditions, while the hydration properties can be modified by using various interlayer anions. On the basis of oscillatory measurements, rheological phase diagrams were obtained by plotting the sol−gel transition as a function of solid content and ionic strength for three monovalent anions: F^-, Cl^-, and NO_3^-. In all cases, the phase diagrams exhibit a negative slope, i.e., the sol−gel transition shifts toward lower solid contents for increasing ionic strength. The nature of the interlayer anion has a strong influence, the sol−gel line moving toward higher solid content in the order takovite F^- < takovite Cl^- < takovite NO_3^-. These differences cannot be assigned to changes in the surface charge of the samples as zeta potential measurements reveal a constant charge for the three anions. Postsynthesis hydrothermal treatments were then performed in order to modify the size and anisotropy of takovite NO_3^-. The aspect ratio of the particles appears as a key parameter controlling gel formation as it has a very pronounced effect on the rheological phase diagrams. Particles with higher aspect ratio exhibit a sol/gel transition at lower solid contents and with a reduced dependence on ionic strength.

Introduction

Suspensions of natural colloidal clay platelets exhibit a wide variety of structural and mechanical properties (spontaneous ordering, gelling, thixotropy, ...) and are then frequently used as thickeners, fillers and antisettling agents. The physical properties of clay suspensions have therefore been extensively studied, and various gelation mechanisms have been hypothesized. They are based either on electrostatic repulsions between individual platelets or on the formation of a three-dimensional aggregated network.[1−6] The nature of the interlayer cation has a strong influence on the sol−gel transition and, depending on the ionic strength, two types of gels referred to as repulsive and attractive gels were proposed to exist in the rheological phase diagram of montmorillonites.[6] Unfortunately, natural clay samples are usually very polydisperse in both shape and size. In that context, most recent studies on the structure of clay suspensions have

been carried out using synthetic laponite samples[7−17] that can be considered as monodisperse charged disks of 25 nm in diameter and 1 nm in height. The "phase diagram" solid concentration/ionic strength observed for laponite suspensions exhibits, above an ionic strength of 10^{-4} M/L, a transition line from a liquid to a soft solid, which presents a negative slope as a function of ionic strength. The origin of this line remains debated. Some authors[9,12] believe that the mechanism for gel formation is the same all along this line and always corresponds to a repulsive gelation for particles with varying anisotropy resulting from changes in the Debye screening length with increasing ionic strength. On the contrary some other authors[8,15] believe that two different regimes must be distinguished in this

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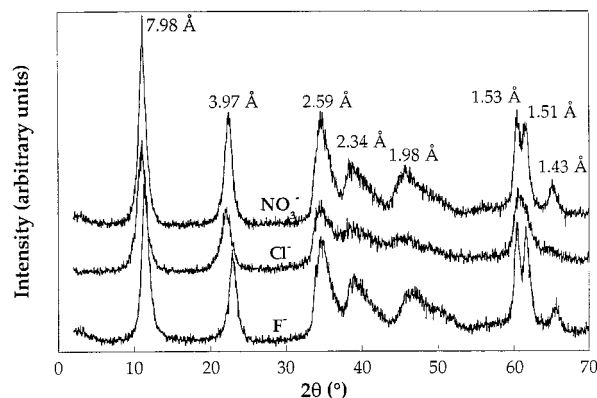(16) Bonn, D.; Kellay, H.; Tanaka, H.; Wegdam, G.; Meunier, J. *Langmuir* **1999**, *15*, 7534.
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region. For lower ionic strengths ($\leq 10^{-4}$ M/L), when the Debye screening length is of the same order of magnitude as the particle diameter, there is clear evidence of a re-entrant line[14,17] in the phase diagram where the liquid−soft solid transition is mainly driven by electrostatic repulsions. However, due to its narrow chemical stability window (pH 9−10) and to its small nonadjustable particle size, the use of laponite does not enable exploration of the whole range of parameters required for understanding the status of the solid−liquid transition in suspensions of charged colloidal disks.

This clearly shows that much information could be obtained from a model synthetic system of charged colloidal platelets where both charge and particle anisotropy could be adjusted. The first option would be to use synthetic clay minerals other than laponite. Such an approach has recently been used for both dioctahedral[18,19] and trioctahedral clays.[15] However, synthesizing reasonable amounts of well-characterized clay samples with controlled characteristics is not a straightforward task[20] as long hydrothermal treatments are generally required. An alternative approach consists of focusing on other inorganic systems whose synthesis can be more easily controlled. Such strategy was recently applied to the study of the colloidal properties of uncharged aluminum hydroxide[21,22] or nickel hydroxide[23] platelets.

As far as charged colloidal platelets are concerned, the family of layered double hydroxides (LDHs) could represent a very valuable candidate as a model system. LDHs, also referred to as anionic clays, are layered minerals bearing a positive permanent structural charge compensated by exchangeable interlayer anions.[24−27] Their general formula can be written as $M^{II}_{1-x}, M^{III}_x(OH)_2, An^{z-}_{x/z}, yH_2O$, where M^{II} is a divalent metal, M^{III} a trivalent metal, and An an anion. These materials can easily be synthesized in the laboratory, and their compositional variability makes them potentially attractive for various uses, such as, catalysts or catalyst supports[24,28,29] wastewater treatment,[30−32] selective ion exchange,[33] electrochemistry,[34] or rheology modifiers.[35,36] In the present paper, we report preliminary studies on the rheological behavior and sol−gel transitions in aqueous dispersions of takovite samples (Ni-Al LDH) with various interlayer monovalent anions of different hydration properties and for hydro-

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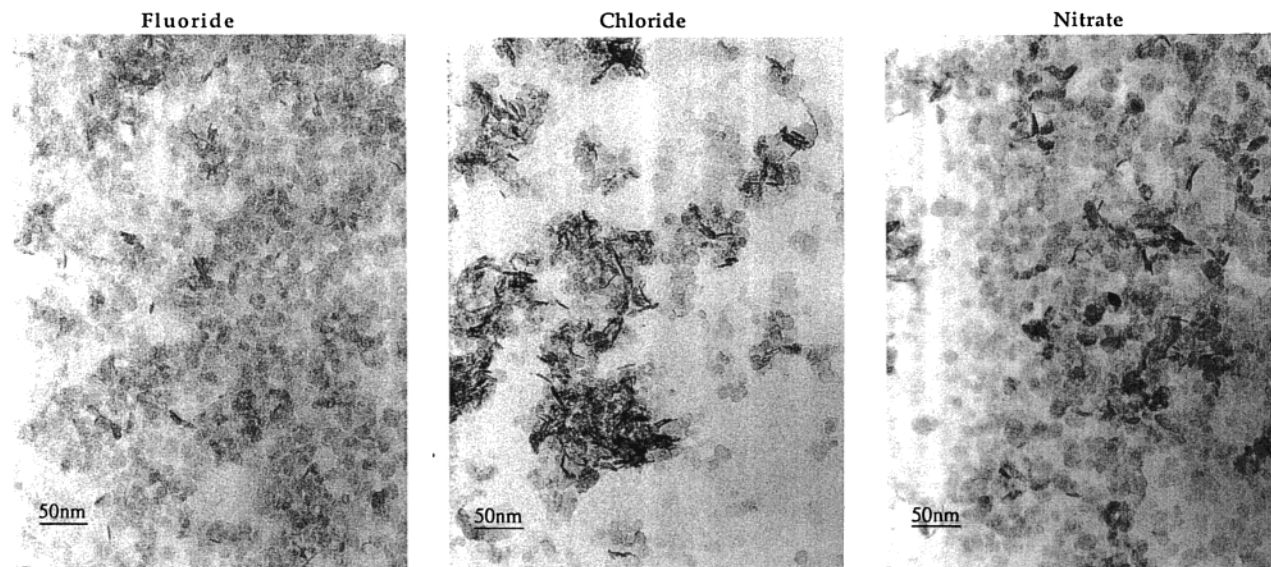
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Figure 1. X-ray diffraction patterns of takovite samples with various interlayer anions.

thermally treated particles with increasing aspect ratio. The nickel−aluminum sample was chosen because of its stability at neutral pH, which has three valuable consequences: (i) such a system should be very suitable for low ionic strength studies; (ii) the faces and edges of the particles should both be positively charged at neutral pH; (iii) undesirable exchange by divalent carbonate anions should be minimized.

Materials and Methods

Synthesis. The synthesis of takovite samples was carried out using the classical constant pH coprecipitation procedure. In this method the pH of a 300-mL quantity of H_2O was adjusted to pH 7.1 by using dilute sodium hydroxide. A mixed nickel and aluminum salts solution (1.5 L, total metal concentration 1.0 M, Ni/Al = 7) and a 2.0 M NaOH solution were then added dropwise to the reaction vessel at rates that maintained the pH constant at 7.1 ± 0.1 under vigorous stirring. After consumption of all the metal chloride solution, the obtained suspension was aged under stirring for 18 h. The resulting green slurry was then washed free of excess ions by successive centrifugation and redispersion in MilliQ water. Part of the sample was air-dried for subsequent analysis whereas the rest was kept in suspension in closed flasks.

The first experimental batch, referred to as Tak-1, was obtained using nickel and aluminum chloride. The final suspension was split into three parts for anion exchange. Anion exchange was carried out by resuspending the slurry three times overnight in 1.0 M NaF or NaNO₃ solutions. The resulting suspensions were then washed of excess ions by centrifugation. Three products kept in suspension were then obtained: Tak-1-Cl, Tak-1-F, and Tak-1-NO₃.

The second experimental batch referred to as Tak-2 was obtained using nitrate salts. The final slurry was split into four parts. The first one was kept in suspension (sample Tak-2-25) whereas the three others were treated hydrothermally at 100 °C for 24 h (Tak-2-100), 140 °C for 24 h (Tak-2-140), and 180 °C for 72 h (Tak-2-180). The hydrothermal treatment was carried out using a Parr stainless steel autoclave under stirring.

All samples were kept in suspension as preliminary tests showed that after drying, full resuspension was very difficult to achieve. The suspensions at various solid contents were then prepared by rotoevaporation of the initial suspension after addition of some known amounts of electrolyte. The final solid content and resulting ionic strength of the concentrated suspension were then determined by drying. Suspensions at lower solid contents were subsequently obtained by dilution in a solution at the appropriate ionic strength.

Characterization Techniques. Elemental analyses for cation content were carried out by atomic absorption spectrometry at the University of Melbourne Chemical Engineering Analytical Laboratory using solutions prepared by dissolving approximately 100 mg of solid samples in concentrated HNO₃. The chlorine content was obtained by a colorimetric technique, and the fluoride content was obtained using a specific electrode.

Figure 2. Transmission electron microscopy micrographs of takovite samples with various interlayer anions.

X-ray diffraction patterns of takovite powders were recorded at the University of Melbourne Chemical Engineering Analytical Laboratory on a Phillips PW 1800 diffractometer using the Cu Kα radiation (1.5406 nm).

Infrared spectra were obtained in transmission on a Bruker IFS 55 IR interferometer on pressed KBr pellets (1 mg of sample and 170 mg of KBr).

Electrophoretic mobility measurements were performed on a Coulter Delsa 440 Doppler electrophoresis apparatus. Approximately 20 mL of takovite suspension was dispersed in 500 mL of NaX solution where X is the same anion as the interlayer anion of the takovite. Ionic strengths of 10^{-3} and 10^{-2} M L^{-1} were used. The pH values were adjusted using dilute HX and NaOH. To avoid problems related with the exact definition of the stationary layer in the electrophoretic cell,[37] measurements were taken at four different positions in the cell to recalculate the complete mobility profile. The mobility at the stationary layer was then deduced using Komagata's equation.[38,39]
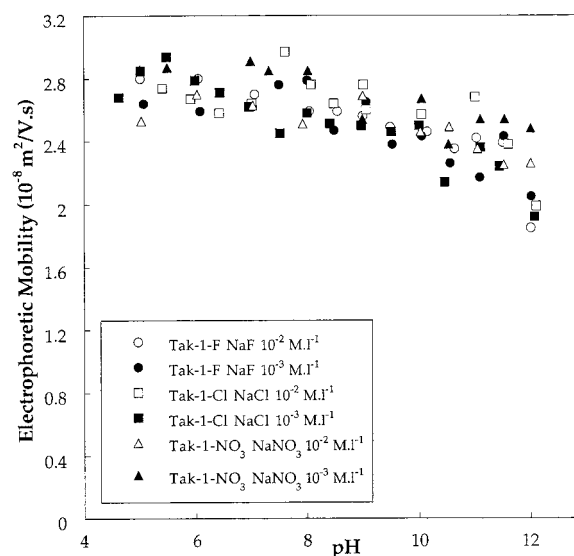
Transmission electron microscopy (TEM) investigations were performed with a Phillips CM20 electron microscope running at 200 kV. Samples for TEM were prepared by depositing a small drop of takovite suspension onto a copper grid with thin film carbon deposited on one side. After evaporation of the solvent, particles remain on the carbon grid as a thin film.

Critical coagulation concentrations were evaluated from simple visual observations after adding known amounts of electrolyte in ≈1 wt % takovite suspensions.

Rheology Measurements. Frequency strain response of the suspensions to oscillatory shear stress was performed using an imposed stress rheometer (CarriMed) with a cone and plate geometry. The amplitude of the applied stress was chosen in the linear viscoelastic regime. For each sample, the data were recorded in the range of frequency between 0.2 and 10 Hz after a standing period of 10 min. The samples were held at constant temperature (20 °C), and the interface exposed to the atmosphere was coated with a thin layer of silicone oil to minimize evaporation.

Results and Discussion

Influence of the Interlayer Anion. *Sample Characterization.* On the basis of chemical analysis results, the structural formula of samples Tak-1 can be written as $Ni_{0.823}Al_{0.177}(OH)_2(An)_{0.177} \cdot 0.9H_2O$. The exchange is complete as no chloride was detected in either Tak1-F or Tak1-NO$_3$. Diffuse reflectance infrared spectra exhibit a very small shoulder around 1450 cm^{-1}, which can be

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Figure 3. Evolution versus pH of the electrophoretic mobility of takovite samples with various interlayer anions for ionic strengths of 10^{-3} and 10^{-2} M L^{-1}.

assigned to a weak contamination by carbonate anions, that can be estimated as no more than 2% of the total anionic exchange capacity.
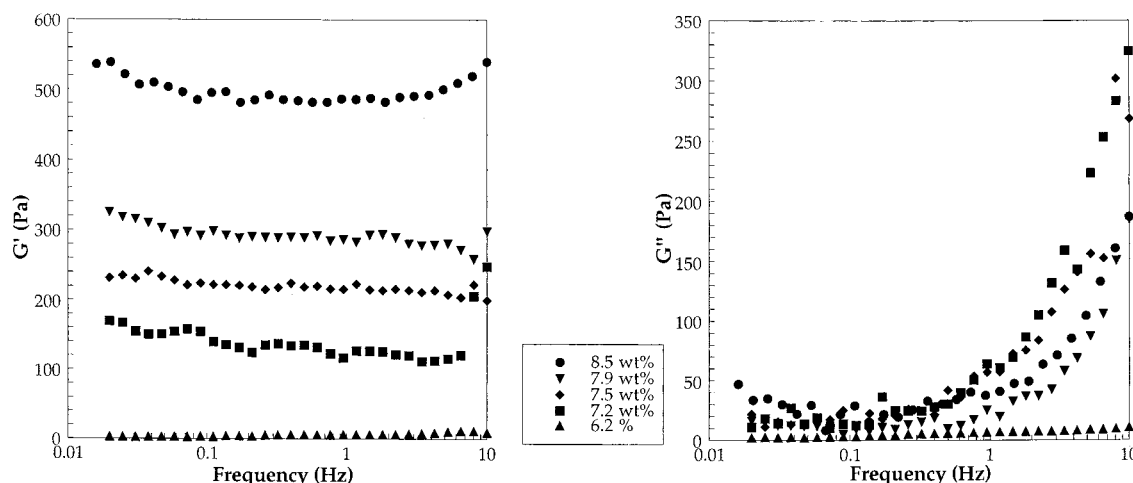
The X-ray diffraction spectra of Tak-1 samples are presented in Figure 1. Whatever the interlayer anion, the obtained patterns are typical of layered takovite-like samples. The diffraction lines corresponding to the interlayer distance are located at 7.98 Å for the chloride and nitrate sample and at 7.86 Å for the fluoride sample, which could be related to the smaller size of this anion.

TEM micrographs of the three samples are presented in Figure 2. They reveal roughly monodisperse platelets hexagonal in shape with diameters ranging between 10 and 20 nm with an average diameter around 15 nm. The nature of the interlayer anion does not seem to affect particle morphology, but the nitrate sample exhibits more particles on the edge that appear thicker than in the two other cases.

Figure 3 displays the evolution of the electrophoretic mobility of these three samples as a function of pH. The curves present a similar pattern independent of the interlayer anion, ionic strength, and background elec-
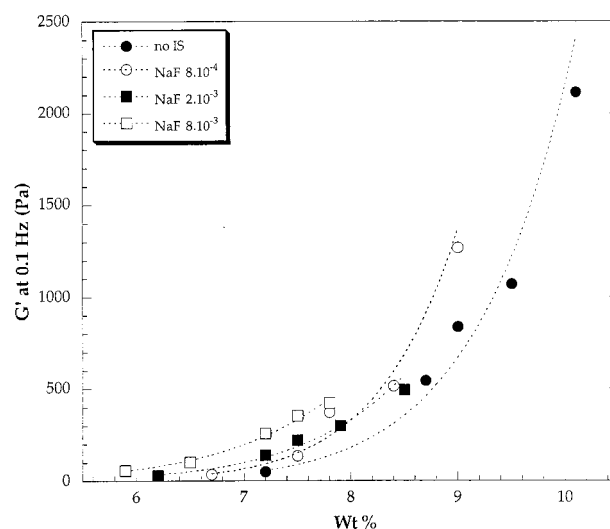
Figure 4. Evolution as a function of frequency of the storage modulus (G') and the loss modulus (G'') for sample Tak-1-F at various solid concentrations.

trolyte. The electrophoretic mobility is constant around 2.7×10^{-8} m^2/(V s) for $4 \leq pH \leq 8$ and decreases slightly above pH 8. Such behavior is inverse of what is observed for clay minerals which display a decrease at low pH followed by a negative plateau at neutral and alkaline pH.[40] The same interpretation can then apply to takovites. The plateau corresponds to the permanent positive charge of the layers whereas the decrease at alkaline pH corresponds to the dissociation of amphoteric −Al−OH (IEP around 8−9[41]) and −Ni−OH groups (IEP around 11−12[41]) located at the edge of the platelets. This confirms that at neutral pH both the faces and edges of the platelets are positively charged.

Rheology Measurements. Figure 4 presents the frequency dependence of both the storage modulus (G′) and loss modulus (G″) for various suspensions of Tak-1-F for an ionic strength of 3×10^{-3} M L^{-1}. For a solid content of 6.2%, $G'(\omega)$ and $G''(\omega)$ are both weak and have roughly similar magnitudes indicating a slightly viscous suspension. In contrast, for solid contents >7%, $G'(\omega)$ is significantly higher than $G''(\omega)$ and does not vary much with frequency in the dynamical range between 10^{-2} and 10 Hz. These two features indicate a gel-type behavior.

Figure 5 displays the evolution of G' at an arbitrarily chosen frequency of 0.1 Hz for various solid contents and ionic strengths. The curves obtained display a power law behavior as observed for various clay systems such as laponite[12,14] or montmorillonite.[42,43] For a given solid concentration G' increases with increasing ionic strength. If one makes the assumption that the gelation mechanism is the same whatever the ionic strength, then all the data obtained could be placed on a master curve according to a power law behavior $G'(0.1) = A(C - C_0)^\beta$, where C_0 is the solid concentration for the sol−gel transition. In the case of Tak-1-F, this appears to be indeed the case with $A = 55$ and $\beta = 2.35$, a value equal to that obtained for laponite.[12,14] With such treatment, the concentration corresponding to the sol−gel transition can be determined for each ionic strength, which allows a drawing of the rheological phase diagram displayed in Figure 6. As observed in the case of laponite,[12,14,17] this phase diagram

Figure 5. Evolution of the storage modulus (G') at a frequency of 0.1 Hz as a function of solid concentration for sample Tak-1-F at various ionic strengths.
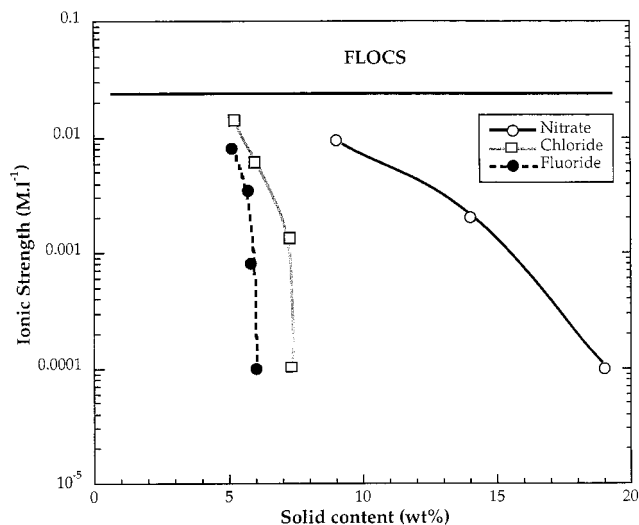
Figure 6. Rheological phase diagrams of sample Tak-1. Influence of the nature of the interlayer anion.

exhibits a transition line with a negative slope in opposition with what would be observed for spherical colloids.

When the interlayer anion is chloride (Tak-1-Cl), the rheological properties are very similar to those of the

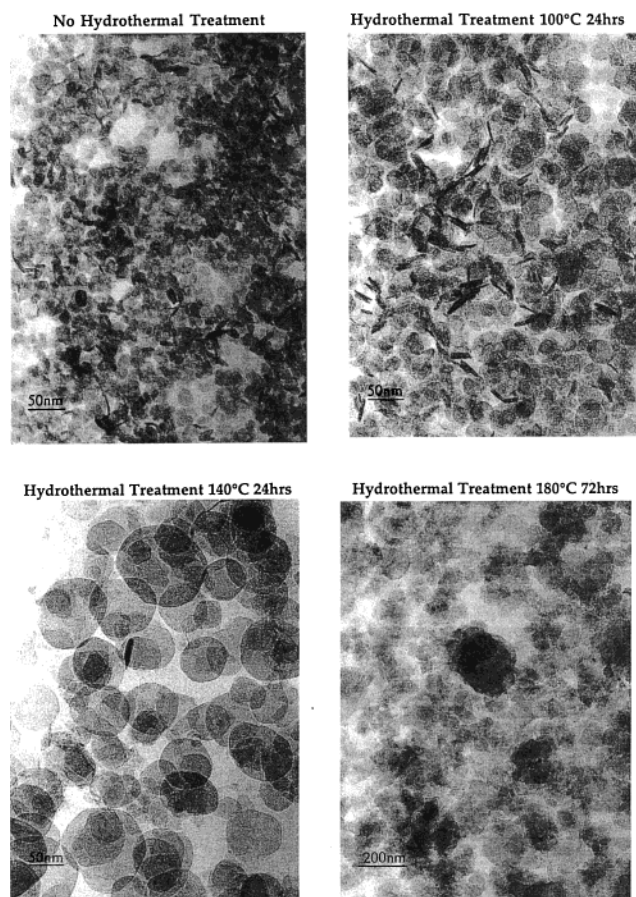(39) Pelton, R.; Miller, P.; McPhee, W.; Rajaram, S. *Colloids Surf.* **1993**, *80*, 181.

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Figure 7. Transmission electron microscopy micrographs of sample Tak-2-NO$_3$ subjected to different hydrothermal treatments.

fluoride sample ($A = 28$ and $\beta = 2.28$), the transition line being slightly shifted toward higher solid contents (Figure 6). In the case of nitrate (Tak-1-NO$_3$), the evolution of G' at 0.1 Hz as a function of solid content exhibits a different behavior as the transition between an elastic gel and a viscous solids is very abrupt for low ionic strengths whereas data at higher ionic strength display a pattern more similar to the two other interlayer anions.

The influence of the nature of the interlayer anion on the rheological phase diagrams of takovite is highlighted in Figure 6. The fluoride and chloride samples exhibit very similar behavior, whereas the nitrate case is markedly distinct. As these differences cannot be assigned to changes in surface charge, they may well be linked to differences in the anisotropy of the particles resulting from changes in the hydration properties of the interlayer anions. This interpretation is somewhat confirmed by TEM results (Figure 2) as the edges of Tak-1-NO$_3$ particles appear clearly thicker than those of the other two.

Influence of Particle Anisotropy. Figure 7 presents the TEM micrographs of samples Tak-2 after hydrothermal treatments at increasing temperatures. Chemical analysis results yield an average formula of Ni$_{0.837}$Al$_{0.163}$(OH)$_2$(NO$_3$)$_{0.163}$·1.1H$_2$O, whereas X-ray diffractograms show that these samples are pure takovite. The size of the initial particles (Figure 7a) is very similar to what was observed for Tak-1 samples, i.e., roughly monodisperse hexagonal platelets with an average diameter of 15 nm. After hydrothermal treatment at 100 °C during 24 h (Figure 7b), the particles are larger, still reasonably monodisperse, and exhibit a hexagonal shape. Their diameter varies between 25 and 50 nm with an average
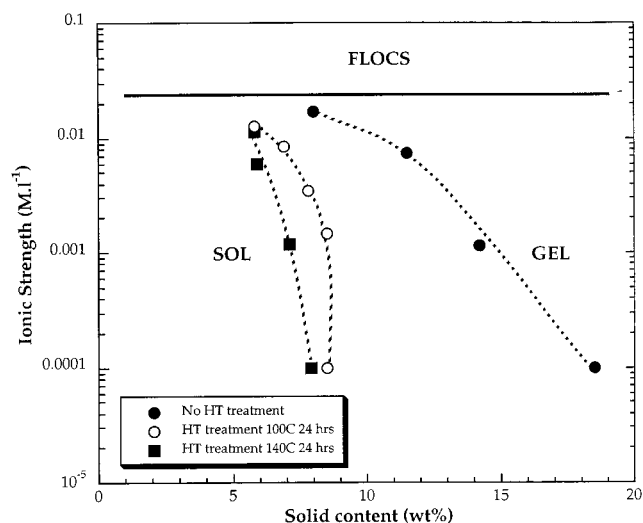
Figure 8. Changes in the rheological phase diagrams of sample Tak-2-NO$_3$ as a function of the hydrothermal treatment.

diameter around 35 nm. After hydrothermal treatment at 140 °C during 24 h (Figure 7c), the takovite particles exhibit a more discoidal aspect. Polydispersity increases with particle diameters ranging between 40 and 130 nm. After hydrothermal treatment at 180 °C during 72 h (Figure 7d), the particles are much more polydisperse between 40 and 250 nm and have lost their hexagonal or discoid shape.

The rheological phase diagrams corresponding to these samples are presented in Figure 8. Sample Tak-2-180 is not presented in this graph as it does not really exhibit a gel-type behavior and tends to phase separate upon concentration. With no hydrothermal treatment, the transition line has the same shape and position as what was observed for samples Tak-1-NO$_3$ (Figure 6) in agreement with the similar composition and size of these two samples. With increasing aspect ratio, the sol–gel transition line shifts toward lower solid contents which definitely shows that anisotropy plays a major role in controlling the properties of suspensions of charged colloidal platelets. The influence of ionic strength decreases with increasing aspect ratio. This would tend to confirm the mechanism in which particle anisotropy is partially controlled by the decrease of the Debye length with increasing ionic strength.[9,12,14] Indeed, according to such a mechanism, particles with a low aspect ratio should be more sensitive to ionic strength, as observed in our experiments.

Conclusion

This study clearly reveals the potential of layered double hydroxides as model-charged colloidal platelets for fundamental studies of sol–gel behavior. Gel formation in aqueous suspensions of takovite where both edge and faces are positively charged at neutral pH cannot be related to the presence of a house of cards structure, sometimes proposed to explain the gel structure of clay minerals. Platelet anisotropy is a key parameter controlling the sol–gel transition. The patterns observed for increasing aspect ratio seem to support a single gelation mechanism controlled by the shape and extension of the ionic cloud around the platelets.

Our study should certainly develop along two main lines. On one hand synthesis procedures and hydrothermal treatments have to be refined in order to obtain more monodisperse particles. On the other hand, structural information about the mutual arrangement of particles in the gel state should be obtained through optical

measurements, microscopy images (freeze fracture and X-ray microscopy), and scattering experiments. The status of the sol−gel transition line would be better defined from measurements of the osmotic pressure developed by the gels for various ionic strengths. Finally, the influence of the structural charge of takovite platelets should be investigated by reproducing similar studies with particles having a constant aspect ratio and a variable charge.

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