September 2010 *ISSN : 0974 - 7486* *Volume 6 Issue 3*

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 6(3), 2010 [160-166]

Rheology of clay-water and clay-water-salt systems: Sol-gel transition and flocculation

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Received: 16th March, 2010 ; Accepted: 26th March, 2010

ABSTRACT

The effect of clay percentage and NaCl addition on the rheological behavior of aqueous suspensions of a purified bentonite was investigated. The sol-gel transition (SGT) was detected using three methods: (i) the grump of viscosity with clay percentage, (ii) the steady flow curves and (iii) the detection of hysteresis buckle by increasing-decreasing shear stress cycles. Results showed a SGT (at 6.5% (w/w)) of clay. The effect of NaCl addition was studied on sol suspensions (1.5%, 3.25% and 4.5% (w/w) of clay) and on gels (6.5% and 7.5% (w/w) of clay). For diluted sols the electrovisquous effect was detected at about 0.01% (w/w) of NaCl by a slight minimum of viscosity. The critical flocculation concentration (CFC) corresponded to 0.04% (w/w) of NaCl and suspensions stayed stable until 0.1% (w/w) of NaCl (maximum of viscosity) after which, sedimentation was observed. The CFC value of the semi diluted sol was 0.05% (w/w) of NaCl and since the flocculation; the suspension became a stable gel until (0.1% (w/w)) of NaCl (max of viscosity) where a thin film of water surmounted it. For gels, the flocculation seemed to occur by stages; it started at 0.02% and continued until (0.2% (w/w)) of NaCl where a thin layer of water appeared.

KEYWORDS

Microporous materials;
Sol gel transition (SGT);
Suspension stability;
Critical flocculation concentration (CFC).

INTRODUCTION

The bentonite clays have very interesting properties and are industrially appreciated. Particularly, clay suspensions can improve the rheological properties of many industrial formulations.

Many factors such as pH, ionic strength have a great influence on the rheology and stability of aqueous clay suspensions. A stable colloidal suspension flocculates when a critical quantity of salt is added. The corresponding concentration of salt is called critical flocculated concentration (CFC).

Since the amount of clay in the suspension remains constant, the flocculation is explained by a variation in the nature of interparticular interactions. When a clay suspension flocculate, three different interactions may happen: Face-Face (F-F), Edge-Edge (E-E) and/or Edge-Face (E-F). The electric interaction energy for these three associations is governed by three different double layer combinations. The van der Waals energy is not the same for these three associations as different geometry have to be considered in the summation of interactions between all atoms of the two interacted sheets and then the curves of total potential interaction energy were not the same for the different associations. However, these associations can not be done necessary with the same importance when a clay suspension flocculates. F-F associations conduct essentially to large and thick particles, while B-B and B-F give voluminous tri dimensional system.

The investigation of the influence of electrolyte addition on the rheological behavior of swelling clays diluted and semi-diluted suspensions was the aim of many studies[1-11].

The influence of NaCl on the viscosity of Na-montmorillonite suspensions has been studied by[1,12]. A minimum of viscosity was detected for very small concentration of electrolyte then the viscosity increased as the electrolyte's concentration rose. Hence, the sudden increase of viscosity has been attributed to the flocculation that was explained by the predominance of B-F and F-F interparticular interactions. It was noted also that the pure gels have been obtained from positive edge-to-negative face linking by Coulomb forces. The electrolyte-containing gels resulted from van der Waals attraction becoming predominant when the energy barrier due to the double layer repulsion was reduced.

Other authors[7] quoted that the changes in the rheological behavior of sodium-montmorillonite suspensions after NaCl addition could be adequately explained without resorting to the traditional Edge-Face, heterocoagulation model. The onset of thixotropy at low to moderate NaCl concentrations (0.05–0.1M) could be explained by a combination of random coagulation and particle orientation effects. At higher NaCl concentrations (0.2M) Face to Face aggregation reduced the number of interacting flow units and both the overall rheological parameters and the degree of thixotropy decreased.

The investigation of coagulation phenomena of aqueous montmorillonite sols under various pH and NaCl concentrations has been studied[13]. The authors noticed that Edge-to-Face heterocoagulation occurred above NaCl concentration 25-26 mmol L^{-1} at acidic pH (~4). the Edge-to-Face attraction between the poorly charged edges and negatively charged faces of platelets was probably around the pH of point of zero charge of edges (6.5) and with concentration of NaCl typically around 50 mmol L^{-1}. The homocoagulation at pH 8-8.5 with the formation of face-to-face aggregates required much higher salt concentration (typically around 100 mmol L^{-1} NaCl) to compress the dominant electric double layer on the highly charged faces of particles.

Other authors have studied the effect of pH and salt concentrations on the aqueous Wyoming bentonite dispersions[14]. They observed that, for the studied pH values, there was monotonous decrease of the yield stress, flow consistency index and apparent viscosity with increasing salt concentration.

However, only few studies were undertaken on the phenomenon of flocculation in gels[15]. The authors tested gel suspensions but unfortunately, they investigated neither clay dilute suspensions nor small NaCl concentrations.

The aim of this work is to study the influence of NaCl addition on sols and gels clay suspensions and then to try to explain the mechanism by which flocculation occurs. To reach this goal, the influence of the clay fraction on the rheological properties was initially studied with an aim of detecting the sol gel transition. Thereafter, the influence of the variation of the ionic force (by addition of NaCl) on the stability of clay suspensions was then studied.

MATERIALS AND METHODS

Materials

The clay used was from Jbel Stah, near the town of Gafsa in the south east of Tunisia. The crude sample contains 60% of clay and 40% of impurities essentially quartz, calcite and dolomite. A soft purification was done; it consisted on NaCl exchanges followed by water washing and then dialysis to eliminate the excess chloride ions[16].

The clay fraction (noticed as "JSp") is a dioctahedral interstratified smectite-illite containing 71% of smectite and 11% of illite; the 18% remaining are kaolin. The tetrahedral deficit contribution charge is about 61.3% of the total deficit charge which indicates that the smectite fraction has a beidellitic character.

The cation exchange capacity (CEC), measured by adsorption of copper ethylene diamine is 63meq/100g of calcined clay and its specific surface area is 762.59 m^2g^{-1}. This later propriety is very important since it indicates the ability of the clay to swell. The sodium chloride NaCl (99.8%) was provided by Prolabo.

Preparation of suspensions

To determine the sol-gel transition aqueous clay suspensions have been prepared with clay percentages ranging from 1 to 10% w/w: the required amount of JSp clay was dispersed in water; the mixture was shacked during 24 hours and then left at rest.

Concerning the NaCl effect, five clay percentages were investigated; three of them correspond to sol suspensions (1.5%, 3.25% and 4.5% (w/w)) and two gels (6.5% and 7.5% (w/w)). The percentages of NaCl investigated are listed in TABLE 1.

Suspensions were prepared on two stages. The purified clay was previously mixed with distilled water, mechanically shacked (160rpm) for 5 hours and left at rest for 14hours. Then the electrolyte (NaCl) solution (50% by weight of the final suspension) was added to the clay aqueous suspension. The mixture was finally mechanically shacked (160rpm) for 5 hours and left at rest for 24 hours before experiments.

Rheometry

The shear stress and the viscosity were measured by a rheometer type Tech Stress Rheometer connected to a computer equipped with a Soft Ware Tech Stress. Measurements were made at an imposed shear rate. Two geometries were used; coaxial cylinders for sol dispersions and flat cones for gels. During the rheometrical measurements, viscosity and shear stress were read in the range of speed [0.1, 300s^{-1}]. The hysteresis buckles of the variation of the shear stress as a function of the shear rate were obtained by cycles of increasing-decreasing stress in the range of (0-300s^{-1}).

All the rheometrical measurements were carried out on the purified clay fraction (JSp).

RESULTS AND DISCUSSION

Effect of the clay fraction on the shear stress and viscosity

The variation of the shear stress and the apparent viscosity as a function of shear rate at different clay percentages were shown respectively in figure 1 and 2. The hysteresis buckles were plotted on figure 3.

From these curves, the rheological behavior of clay suspensions could be described. Figure 1 showed that, for clay percentages varying from 1% to 6 % (w/w), a Newtonian behavior was exhibited; this was revealed by a constant viscosity value when the shear rate varied. When the clay percentage increased the rheological behavior changes and becomes rheofluidifiant. The transition between the two behaviors occurred at 6.25% (w/w) of JSp: it is the sol-gel transition (SGT). The variation of the viscosity as a function of the clay percentage (Figure 2) showed a sudden increase of viscosity from 6.25% (w/w) of clay corresponding to the SGT. The SGT was confirmed also by figure 3 where the hysteresis buckle was observed at this value. The three methods converge and confirm the percentage of clay corresponding to the SGT (6.25% (w/w)). Indeed this value is considered relatively high with comparison to a smectite and this could be attributed to the presence of kaolin with considerable quantities.

The different observed phenomena could be explained according to the particles arrangement. In diluted suspensions (1% and 3% of clay), the particles were separated and the interactions were very low. The electrical double layers were so developed to ensure the particle repulsion. It results well dispersed and separated clay particles explaining the Newtonian behavior. Nevertheless, when the clay percentage increased (4% and 5%), before the SGT, the particles became more voluminous but remained dispersed in the suspension. At this stage, the increase in the viscosity might be due to the excluded volumes of particles which began to touch each other. As the clay percentages increased, the density of the suspensions increased and links between clay particles became to appear leading to interparticular interactions which explain the rheofluidifiant behavior. At the SGT, a three dimensional network was established between connected particles, and then the interparticular interactions were so important. Consequently, the suspension was more rigid and a gel appeared confirming the sudden rise of viscosity after the SGT.

Influence of NaCl addition on the rheological behavior

Sol suspensions

The variation of the apparent viscosity as a function of NaCl concentrations was reported in figure 4, 5 and 6. For 1.5% of clay, all the curves showed the same particularities: a slight minimum of viscosity at 0.01% of NaCl (1.73 mmol L^{-1}); a sudden rise of viscosity since 0.04% of NaCl (6.94 mmol L^{-1}) and a maximum at 0.1% of NaCl (17.37 mmol L^{-1}). These results were in accordance with those obtained by[8,9] who supposed that a Na-montmorillonite suspension had a typical CFC in the interval of 5-10 mmol L^{-1}.

These results were also found for 3.25% of clay for

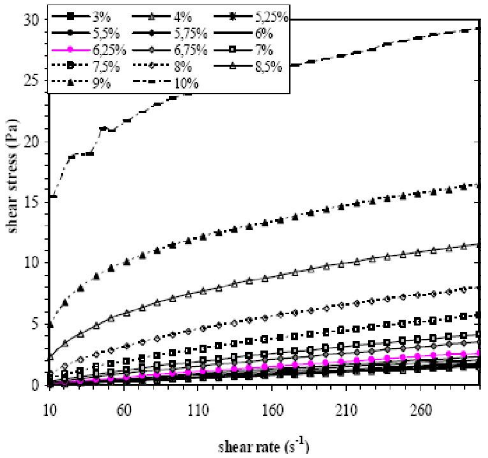

Figure 1 : Variation of the shear stress as a function increasing of the shear rate: Steady state flow curves

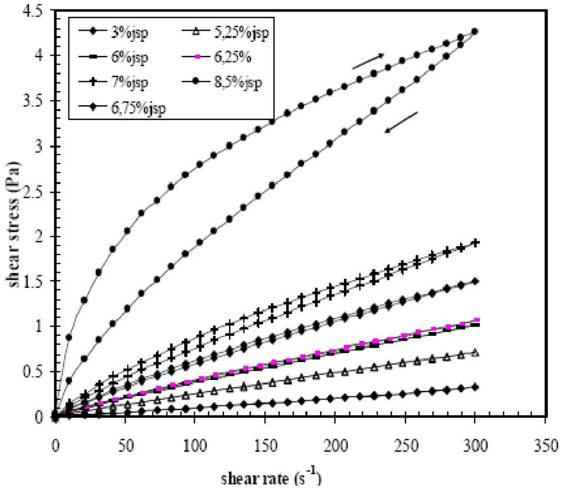

Figure 2 : Flow curves obtained by decreasing shear stress

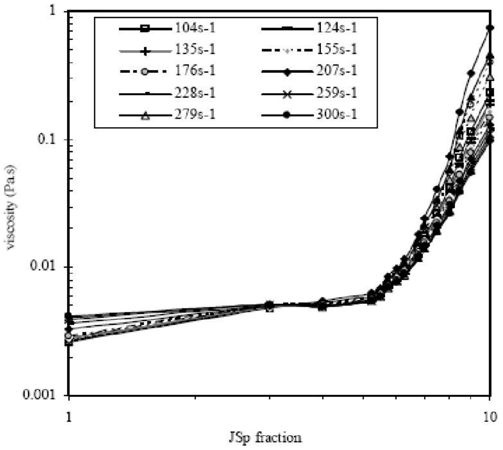

Figure 3 : Variation of the viscosity as a function of the clay percentage (w/w)

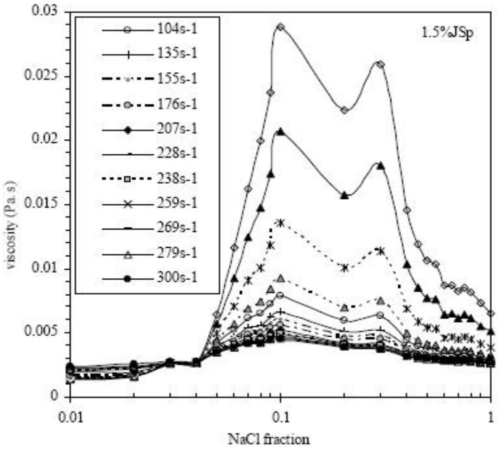

Figure 4 : Variation of the viscosity as a function of NaCl percentage (w/w). 1.5% JSp

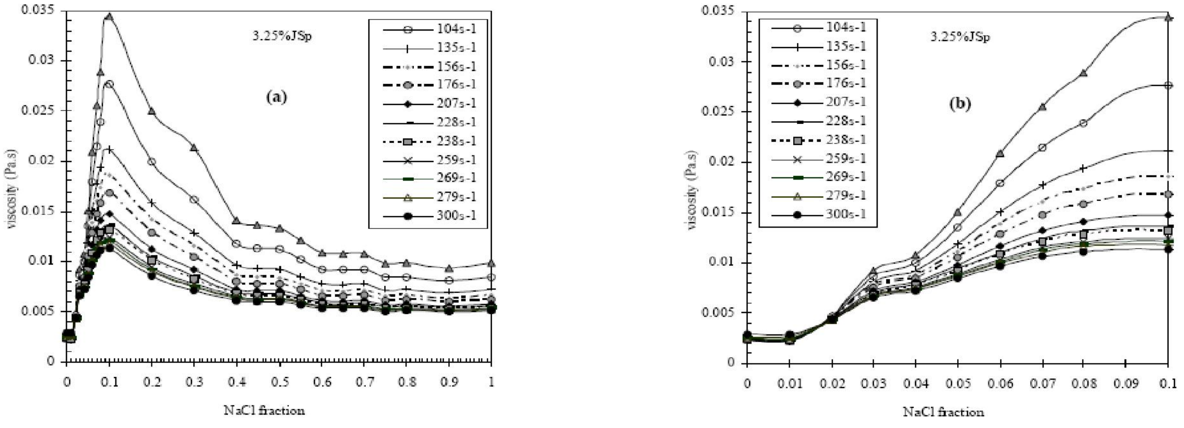

Figure 5 : Variation of the viscosity as a function of NaCl percentage (w/w). 3.25% JSp, (a): % NaCl from 0 to 1 and (b): NaCl from 0 to 0.1

which the minimum of viscosity was also at 0.01% of NaCl (1.77mmol L^{-1}) and the CFC at 0.04% of NaCl (7.07mmol. L^{-1}). However, at 4.5% of clay (Figure 6), the variation of the viscosity did not show any minimum for low NaCl percentages, the rise of viscosity appeared at 0.05% of NaCl (8.954 mmol L^{-1}) and the maximum remained at 0.1% of NaCl (17.82 mmol L^{-1}).

These results were also found for 3.25% of clay for which the minimum of viscosity was also at 0.01% of NaCl (1.77mmol L^{-1}) and the CFC at 0.04% of NaCl

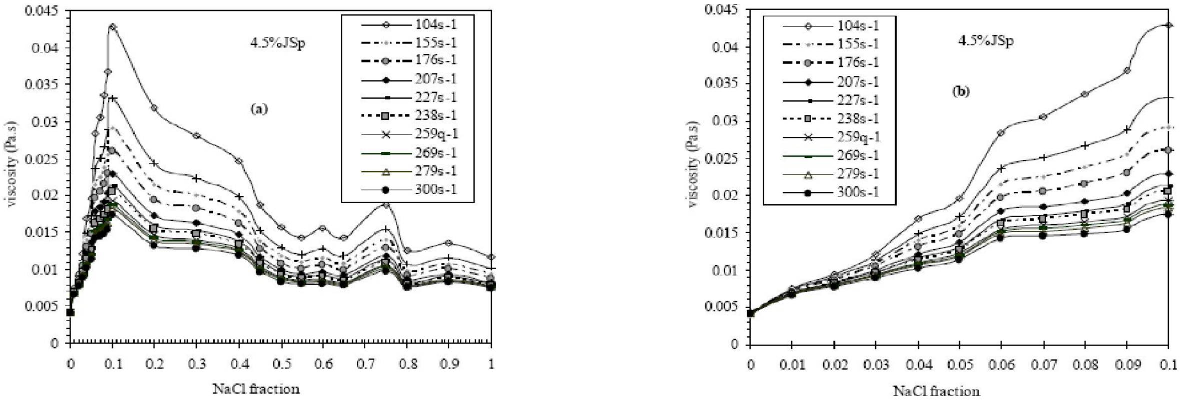

Figure 6 : Variation of the viscosity as a function of NaCl percentage (w/w). 4.5% (a): % NaCl from 0 to 1 and (b): %NaCl from 0 to 0.1

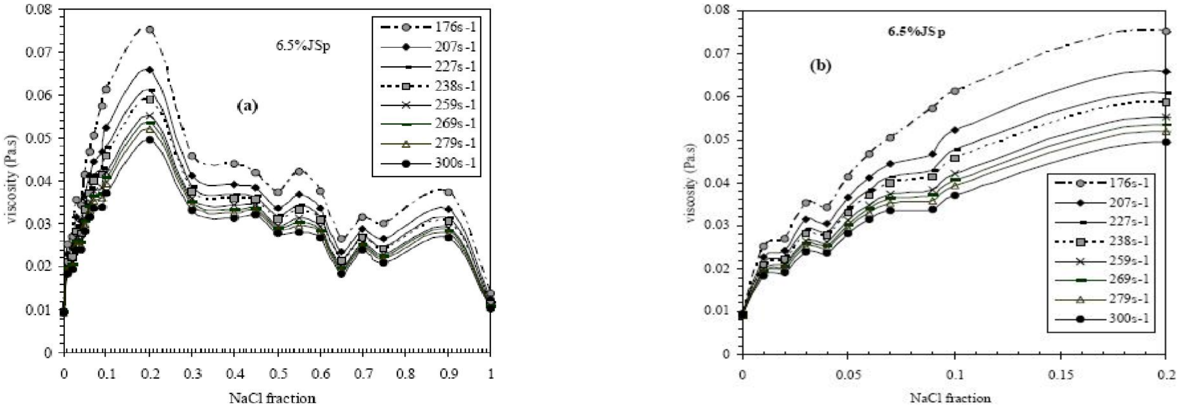

Figure 7 : Variation of the viscosity as a function of NaCl percentage (w/w). 6.5% JSp. (a): %NaCl from 0 to 1 and (b): % NaCl from 0 to 0.2

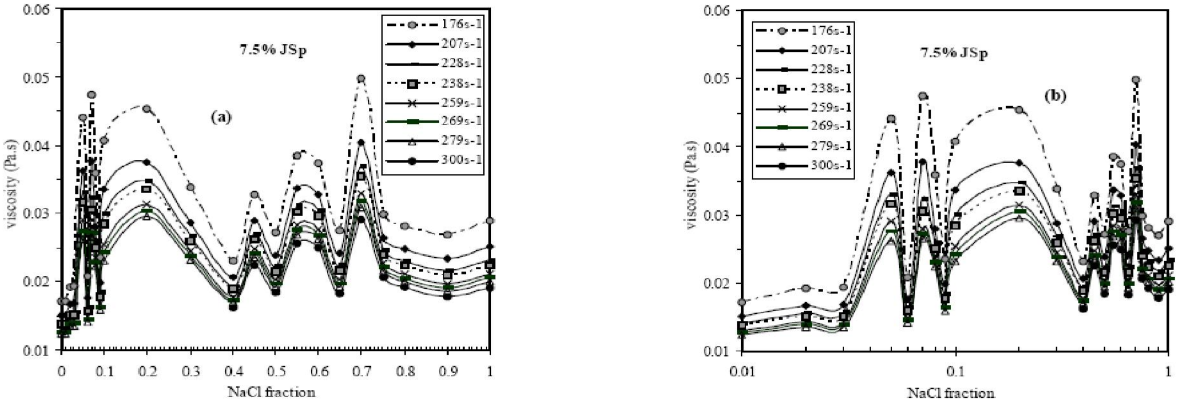

Figure 8 : Variation of the viscosity as a function of NaCl percentage (w/w). 7.5% JSp. (a): linear scale (b): logarithmic scale

(7.07mmol. L^{-1}). However, at 4.5% of clay (Figure 6), the variation of the viscosity did not show any minimum for low NaCl percentages, the rise of viscosity appeared at 0.05% of NaCl (8.954 mmol L^{-1}) and the maximum remained at 0.1% of NaCl (17.82 mmol L^{-1}).

In absence of NaCl, diluted suspensions had a Newtonian behavior, the particles were dispersed and the forces between their electrical double layers were repulsive (F-F). When NaCl was added with very slight amounts, the sodium cations Na^{+} disturbed the double layer without compressing it. It results a slight decrease in the intensities of repulsive forces and then a decrease in the viscosity: it is the electrovisquous effect. This effect was observed for diluted sol suspensions (1.5% and 3.25% JSp) and not for the semi diluted sol 4.5% JSp. In the latest, there was no contact between particles but the excluded volumes overlap and this probably persisted even when the double layers were dis-

TABLE 1 : The investigated percentages of NaCl

%NaCl	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1	0.2
(w/w)	0.3	0.4	0.45	0.5	0.55	0.6	0.65	0.7	0.75	0.8	0.9	1

turbed preventing the detection of the electrovisquous effect. A new addition of NaCl causes the compression of the double layers and the intensities of electrostatic repulsion forces decreased again. But at this stage, the attractive Van der Waals forces between clay particles (predominantly type Face-to-Face (F-F), but also Face-to-Edge (F-E) and Edge -to-Edge (E-E)) began to increase and then to contribute in the total interparticular interactions. The increase in these intensities against those of the repulsive forces generates the flocculation when F-F, E-F and E-E interactions become probable. This phenomenon of flocculation was detected by a considerable increase in the rheological parameters.

For higher amount of NaCl, double layers were so compressed that the voluminous clay particles were so contracted and therefore some of the interparticular links were broken causing sedimentation which was visually easy to detect. Indeed, during experiments, sedimentation began at 0.2% and at 0.1% of NaCl for respectively 1.5% and 3.25% of JSp. It was important to note that the layer of water surmounting the sediment increased with NaCl concentration. For other authors[1], a decrease of the threshold value of shear stress at high electrolyte concentration was observed for sol suspension (3.25% of clay). This result was explained by the predominance of F-F interactions. Hence, these associations gave voluminous aggregates that destabilize the suspension and then finish by to sediment.

Nevertheless, for 4.5% of JSp a gel was obtained after flocculation and no sedimentation was observed.

Gel suspensions

Two clay percentages higher than that corresponding to the SGT were tested (6.5% and 7.5%). The first corresponds to a soft gel (6.5% of JSp) and the second to a rigid gel (7.5% of JSp). The obtained results were shown on figure 7 and 8.

For very small amounts of added NaCl, no minimum of viscosity was observed for the two gels. The electrovisquous effect seemed to be observable only in diluted sols when the small amount added can disturb the clay-water system.

For the soft gel, the flocculation seemed to occur by stage because the rise of the viscosity presented successive leaps. The first leap began at 0.02%, the second one at 0.04% and the third at 0.09% of NaCl. A maximum of viscosity was observed at 0.2% of NaCl, it corresponded to the beginning of the visual appearance of a thin layer of water surmounting the gel. Above this maximum, the decrease of viscosity did not occur progressively but presented some particular points like the semi dilute sol (4.5% JSp). This last result let one think that, like the flocculation, the destabilization of a gel by increasing the ionic strength occurred by stages or by zones.

In the curves corresponding to the rigid gel (Figure 8), the sudden rise of viscosity was absent. These curves showed many maxima on both sides of a maximum at 0.2% of NaCl. Moreover, some visual observations showed that from 0.03% of NaCl the gel became more rigid until 0.2% of NaCl and after this value a thin layer of water surmounting the gel was observed. Thus flocculation started from 0.03% and continued up to 0.2% of NaCl after which sedimentation appeared.

However the presence of many maxima suggested that the flocculation phenomenon occurred in the three-dimensional network of clay particles by domains, and that the breakdown of the interparticular links for high ionic strength occurred also by domains.

This suggestion was founded on the results of former studies cited in the literature (based on X-ray scattering, X-ray diffraction, SEM, TEM, ESEM and NMR) which showed that a gel suspension of smectite clay consisted of the interconnection of clay particles forming a three-dimensional network with zones of different densities of clay particles and in which water was imprisoned[17-20]. Moreover, other authors[21] found that montmorillonite gels were in two phases, one anisotropic and one isotropic with more water content. This segregation in gel structure was attributed to the heterogeneous distribution of the clay surface charge[22]. TEM observations have shown that the cakes obtained from a static filtration of gels showed some regions that are denser than others[23].

The addition of an electrolyte to such heterogeneous system caused probably multiple reactions: when the dilute zones flocculate, the concentrated ones didn't flocculate and when the dense zones flocculate the dilute one were not stable and this explained the multitude of maxima observed either for gel suspensions or for semi dilute sol after flocculation.

More recently, some authors noticed this type of segregation from environmental scanning electron microscopy (ESEM) observation[24]. They found that at high particle and salt concentrations, a montmorillonite suspension texture on the micrometer length scale was constituted by a large clay-poor regions and a network of clay-rich areas.

CONCLUSIONS

The sol-gel transition (SGT) was located at 6.25% (w/w) of clay by three methods: the grump observed in the variation of the viscosity as a function of clay percentage, the steady flow curves and the detection of hysteresis buckle by increasing-decreasing shear stress cycles.

The phenomenon of flocculation happened differently in diluted sols, semi diluted sols and gels. It appeared that a very small quantity of added NaCl disturbed only the diluted sols.

The CFC of sol suspensions was detected by a sudden increase of the viscosity which happened at 0.04% of NaCl for diluted sol and at 0.05% of NaCl for the semi diluted one. From 0.1% of NaCl the clay suspension lost its stability and sediments.

For gels, it was seemed that flocculation occurred by stages. Indeed, as these heterogeneous systems were constituted by diluted and concentrated zones, the most diluted domains would probably flocculate in first followed progressively by the more concentrated ones. The destabilization of gels in presence of NaCl showed the same mechanism as flocculation.

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