



Elastic network of lamellar particles: formation and rheological characterization

Andrea Majzik, Etelka Tombácz

University of Szeged, Department of Colloid Chemistry
H-6720 Szeged, Aradi Vt. 1. Hungary
e-mail: maja@chem.u-szeged.hu

ABSTRACT

Montmorillonite is the most often studied swelling clay mineral. The layers have permanent negative charges due to isomorphous substitutions, and pH-dependent charges develop on the surface hydroxyls at the edges. Wyoming montmorillonite sample (Swy-2) was studied. A specific patch-wise charge heterogeneity of montmorillonite lamellae, i.e. oppositely charged surface parts of layers, exists only under acidic conditions. Edge-to-face heterocoagulated structure forms below pH of PZC of edges ($\text{pH}_{\text{PZC, edge}} \sim 6.5$) and above a threshold salt concentration, where the hidden electric double layer (edl) of positively charged edge region has emerged. Characteristic changes in gel formation and in rheological properties induced by decreasing pH in dense suspensions containing 0.01 M NaCl provided experimental evidence for the structure of particle network. A significant increase in thixotropy and yield values, and also the formation of viscoelastic gels only below $\text{pH} \sim 6.5$ verify that attractive interaction exists between oppositely charged parts of lamellar particles in the less concentrated systems. However, solid-like feature with pronounced viscoelasticity, more or less strong network of lamellar particles with large yield values can form in more concentrated montmorillonite suspensions even at higher pHs.

Key words: montmorillonite, rheology, pH-dependent properties, elastic gel formation

INTRODUCTION

Although the pH-dependent colloidal behavior and several properties of montmorillonite suspensions are well-known for decades, the unique charge heterogeneity of montmorillonite platelets, the different modes of association between asymmetric particles, i.e. edge-to-face, face-to-face, edge-to-edge, which result in particular properties and applications of suspensions, are still in the focus of clay research and the subject of even recent papers (Ramos-Tejada et al., 2001; 2003; Janek and Lagaly, 2001; Penner and Lagaly, 2000; 2001; Bergaya and Lagaly, 2001; Abend and Lagaly, 2000; Durán et al., 2000; Benna et al., 1999; Yildiz et al., 1999; Altin et al., 1999; de Kretser et al., 1998).

The effect of pH and indifferent electrolytes is mutual; none of them can be interpreted alone. The material characteristics of montmorillonite govern the formation of local electrostatic field around the highly asymmetric clay platelet (in respect of both the aspect ratio and surface charge density of edge and face) in aqueous medium containing indifferent electrolytes. The main contribution to the surface charge of montmorillonite layers is the permanent negative charge on the basal planes due to the isomorphous substitutions (Van Olphen, 1963). A negative charge

associated with cation replacement in the tetrahedral sheet (e.g., Al^{3+} for Si^{4+}) results in localized charge distribution, whereas much more diffuse negative charge comes from cation replacement in the octahedral sheet (e.g., Mg^{2+} for Al^{3+}) (Johnston and Tombácz, 2002). This excess of negative lattice charge is compensated by the exchangeable cations in the diffuse part of the dominant electric double layer (edl) on faces (Tombácz and Szekeres, 2004). Additional polar sites, mainly octahedral Al-OH and tetrahedral Si-OH groups, are situated at the broken edges (Johnston and Tombácz, 2002). These amphoteric sites are conditionally charged, and so variable (either positive or negative) charges can develop at the edges by direct H^+ or OH^- transfer from aqueous phase depending on the pH. To give a characteristic pH of point of zero charge (PZC) belonging to the amphoteric edge sites ($\text{pH}_{\text{PZC,edge}}$) is useful. The variable edge charges are compensated by a cloud of counter ions in a hidden edl, into which the dominant edl extending from the particle faces probable spills over at low concentration of indifferent electrolytes (Tombácz and Szekeres, 2004). This last is probable, if the thickness of edl (Debye length, e.g. ~ 3 nm at 0.01 M) is larger than that of the thin of lamella (less than 1 nm as estimated from crystallographic data (van Olphen, 1963).

The surface charge heterogeneity of clay minerals presented originally by van Olphen (1963), then supported and elaborated further in many subsequent and recent investigations (Tombácz et al., 1990; Zhao et al., 1991; Thompson and Butterworth, 1992; Zhou and Gunter, 1992; Heil and Sposito, 1993; Keren and Sparks, 1995; Sondi et al., 1997; Schroth and Sposito, 1997; Tombácz, 2002), dictates the particle interactions in aqueous montmorillonite suspensions. Although the overall particle charge is always negative, both negatively and positively charged parts on the surface of clay mineral particles exist simultaneously under acidic conditions ($\text{pH} < \text{pH}_{\text{PZC,edge}}$). However, the positive double layer near the edge of plates is hidden at low concentration of indifferent electrolytes, and so a second approaching particle cannot perceive it. The attraction between the oppositely charged parts results in aggregates with edge-to-face heterocoagulated structure below the pH of edge PZC (~ 7), only if the positive edge region is emerged above a threshold of electrolyte concentration (Tombácz and Szekeres, 2004). An extended DLVO model was used to calculate the pH-dependence of face-to-face, edge-to-face and edge-to-edge interactions, which includes a repulsive short range interaction due to structural or hydration forces, the so-called polar acid-base contribution besides the electrostatic and van der Waals contributions (Durán et al., 2000). The theoretical prediction correlated well with the experimental results.

In any colloidal stable suspensions the overall particle interaction is repulsive, while more or less loose physical network of adhered particles forms in the unstable suspensions. Whatever the reason, the formation of particle networks strongly affects the mechanical, flow properties of clay suspensions. In general, stable suspensions show liquid-like (viscous) Newtonian flow behavior with shear thinning or thickening character, while the appearance of plastic character frequently together with thixotropy refers to the network formation of aggregated particles. The rheology of clay suspensions is the subject of tremendous works for several decades, especially because of the wide-ranging practical application. The effects of several variables, i.e. suspension concentration, the quality and quantity of added salts, as well as the effect of thinning agents on the flow properties have been investigated as seen e.g. in the excellent recent papers (Abend and Lagaly 2000; Ramos-Tejeda et al., 2001; 2003) and that for pH-dependence (Janek and Lagaly, 2001; Penner and Lagaly, 2001; Durán et al., 2000; Yildiz et al., 1999; Benna et al., 1999; Heath and Tadros, 1983).

The objective of present work is to determine the pH-dependent rheological properties of montmorillonite suspensions by means of steady-state flow curves, creep tests and forced oscillation measurements, and to characterize the viscoelastic network built from the thin lamellae of montmorillonite.

METHODS

Preparation of montmorillonite suspensions

Montmorillonite was obtained from Wyoming bentonite (Swy-2 sample). Cation exchange capacity (CEC) value is 105 meq/100 g (Grim and Güven, 1978). Clay mineral fraction smaller than 1 μm was prepared by allowing the larger particles to settle down in a dilute (10 g/l) suspension and then decanting. About 10% of bentonite was discarded. To obtain the

monocationic Na-montmorillonite, a calculated amount of NaCl was added to the remaining suspension to adjust salt concentration 1 M. After centrifugation of the suspensions at 3600 RPM, the supernatant solution was discarded and replaced with fresh 1 M NaCl solution. The procedure was repeated three times. The ionic strength of suspension was progressively lowered, first by washing with Millipore water and then by dialysis against 0.01 M NaCl, to that used in the experiments. The progress of dialysis was controlled by measuring conductivities of inner and outer phases daily. Na-montmorillonite suspensions (~65 g/L) in dialysis tubes reach equilibrium state at 0.01 M within two weeks. This procedure provides a definite initial state with constant ionic strength at self-pH of suspensions for further work. The stock suspensions were stored in refrigerator at 4-5 °C. The water was obtained directly from a Millipore apparatus. All the used chemicals were analytical reagent grade product (Reanal, Hungary).

3 and 4 g/100 g montmorillonite suspensions containing 0.01 M NaCl were prepared at three particular pH values, pH >8, ~6 and ~5, where edges of lamellae hold negative, zero and positive charges, respectively. The pHs of dense suspensions were adjusted with adding estimated amounts of 1 M NaOH or HCl solutions. The pHs of well-homogenized suspensions were measured, then all were stored in sealed vials for three days. The equilibrium pH values of suspensions were measured after rheological measurements. The pH shift during 3-day-standing was about 0.2-0.3 pH unit.

Rheological measurements

The rheological measurements were performed with a shear stress controlled rheometer HAAKE RS 150 and a cone-plate sensor (DC60/2° Ti) at temperature 25±0.1°C controlled by a HAAKE DC 30/K20 thermostat. The portions of suspensions were carefully placed on the measuring plate of rheometer, and the measuring position was reached at low speed (0.6 cm/min). Three types of measurements were performed:

Flow curve (upward) was measured with a shear rate ramp over one minute from 0 to 50 1/s, then the ramp was reversed to measure downward flow curve. The downward curves were evaluated according to the Bingham-model using data analysis option of RheoWin software.

Creep test was performed to determine the viscoelastic behavior under static condition. A constant stress was applied for one minute and the resulting strain was measured (creep), then stress was released and strain was measured for one minute (recovery). Various constant stresses were applied to the different samples. The 3 g/100 g suspensions were measured over the lower range (2, 3, 5 and 10 Pa), while the 4 g/100 g samples at higher stresses (5, 10 and 13 Pa). The shear creep compliance (J, 1/Pa) was calculated dividing the measured shear strain (γ) values by the applied stress (τ , Pa).

The viscoelastic properties of suspensions were tested in **oscillation mode** under dynamic condition, too. In these measurements, a sinusoidal oscillating strain is applied with an assigned frequency and amplitude. First the frequency sweep was measured from 0.1 to 10 Hz, then the stress sweep from 0.1 to 30 Pa at constant frequency (1 or 2 Hz depending on the linear viscoelasticity regions of samples). The magnitude of the elastic (G' storage modulus) and viscous (G'' loss modulus) components of the tested samples can be evaluated from the time dependent stress signal. The phase shift angle (δ) which is 90° for purely viscous and zero for purely elastic substances, can be also calculated using RheoWin software.

RESULTS AND DISCUSSION

The pH-dependent structures forming in the different suspensions of the lamellar particles were investigated. We focused on especially that conditions under which elastic network can be built in the montmorillonite suspensions.

Relatively dense suspensions (3 and 4 g/100 g montmorillonite) were chosen for measurements, because these concentrations seemed to be appropriate to study the pH-dependent behaviour (Tombacz and Szekeres, 2004). First the results of the most frequently used rheological measurements, the steady-state flow curves of montmorillonite suspensions at different pHs are shown in Fig.1.

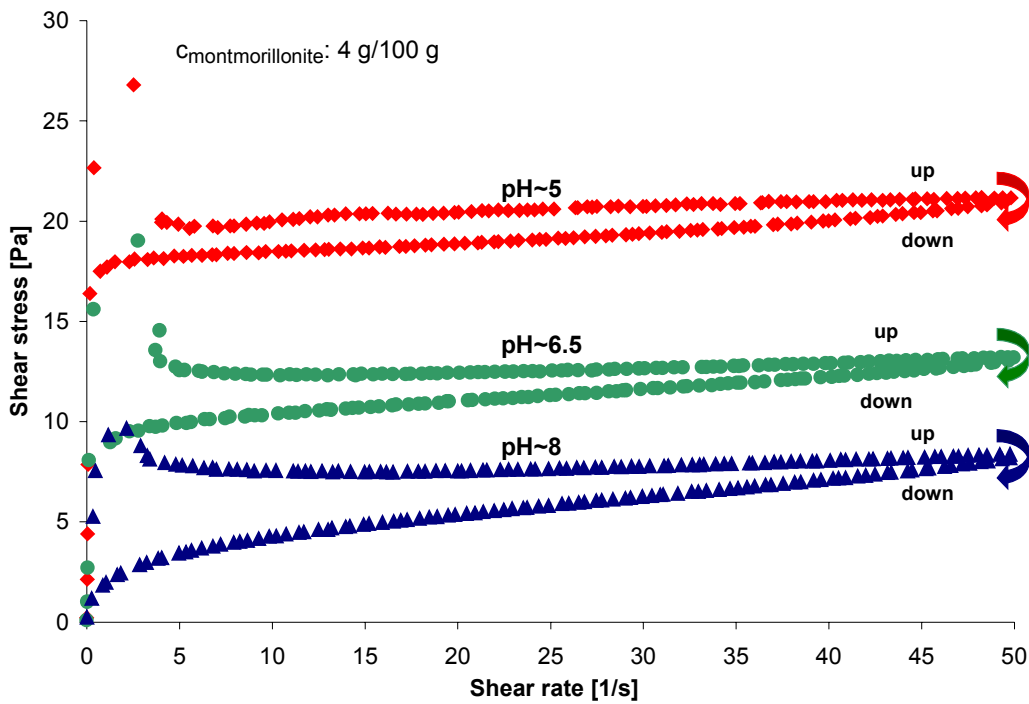
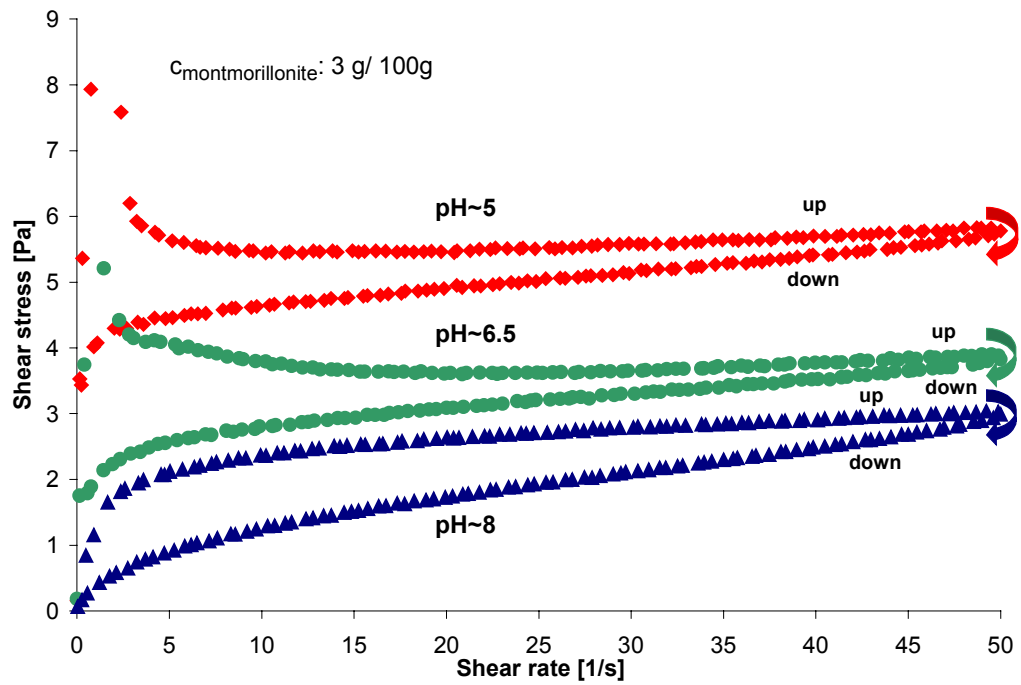


Fig. 1. Flow curves measured with an increasing (upward) then decreasing (downward) shear rate ramp for 3 g/100 g (up and down) and 4 g/100 g (up and down) montmorillonite suspensions containing 10.5-12.5 mM NaCl at different pHs above (\blacktriangle : 8) and below (\bullet : 6.5 and \blacklozenge : 5) the pH of PZC of edges (~ 6.5) at $25 \pm 0.1^\circ\text{C}$.

The significant change in flow character with decreasing pH is obvious, and it can be seen that the upward and downward curves are not identical, hysteresis loops appear in the figures, which are characteristic of thixotropic systems. The pseudoplastic character is more pronounced in the more concentrated suspensions, and this character is increased with decreasing pH. At and below the pH of edge PZC (~6.5) edge to face heterocoagulated network of montmorillonite particles can form, because the edges and faces of lamellae are oppositely charged. However, the edges of lamellae become negatively charged in alkaline suspension, therefore the whole surface of lamellae bears similar charges. The uniformly charged particles repel each other, strong gel structure cannot form, and so the stable montmorillonite sol shows rather shear thinning flow character, especially in the less concentrated systems (bottom curve in the Figure of the 3 g/100 g montmorillonite). The evaluation of downward curves over the plastic flow range (above ~10 1/s) according to the Bingham model results in extrapolated yield values and plastic viscosities of each suspension. The values calculated by the analysis option of Rheo Win software are summarized in Table 1.

Table 1. The evaluation of downward curves over the plastic flow range (above shear rate ~10 1/s) according to the Bingham model ($\tau = \tau_B + \eta_{pl} \, d\gamma/dt$, where τ is the shear stress, τ_B [Pa] is the Bingham yield value, η_{pl} [Pas] is the plastic viscosity and $d\gamma/dt$ [1/s] is the shear rate).

Montmorillonite suspensions			
pH	τ_B [Pa]	η_{pl} [Pas]	regression
3 g/100 g			
5	4.37	0.026	0.9983
6.5	2.57	0.024	0.9955
8	0.90	0.040	0.9975
4 g/100 g			
5	17.67	0.061	0.9881
6.5	9.71	0.064	0.9983
8	3.51	0.091	0.9991

The extrapolated yield values increase significantly with decreasing pH of suspensions similarly to the effect of increasing salt concentration (Abend and Lagaly, 2000), whereas the plastic viscosity values do not show systematic change with pH apart from their definitely larger values in both alkaline suspensions. A decrease in pH slightly below the PZC of amphoteric edges (pH~6.5) causes a significant change in the flow behavior. In acidic suspension (uppermost curves at pH~5) a strong attractive gel (Abend and Lagaly, 2000), here the edge-to-face heterocoagulated network, can form because of the attraction of oppositely charged edges and faces of montmorillonite platelets. The yield value is proportional to the mechanical strength of physical network and depends on the number and the strength of bondages between particles in unit volume of suspensions (Firth and Hunter, 1976). The lower the pH the larger the amount of positive charges on the edges of montmorillonite plates, therefore the attraction between the positively charged edges and negative basal plates becomes stronger with decreasing pH.

It was supposed that the solid-like gels formed spontaneously from the thin lamellae due to Coulombic attraction between oppositely charged parts of montmorillonite plates have elastic character within a limited range of applied stress, which is presumably comparable with the characteristic yield values of particle networks. Static and dynamic methods were used to study the viscoelastic properties of montmorillonite gels formed under different conditions. Several series of creep tests and forced oscillation measurements were performed. Only some results will be presented here to demonstrate the trends of changes in structure.

A series of creep and recovery curves measured at different pH are shown in Fig. 2.

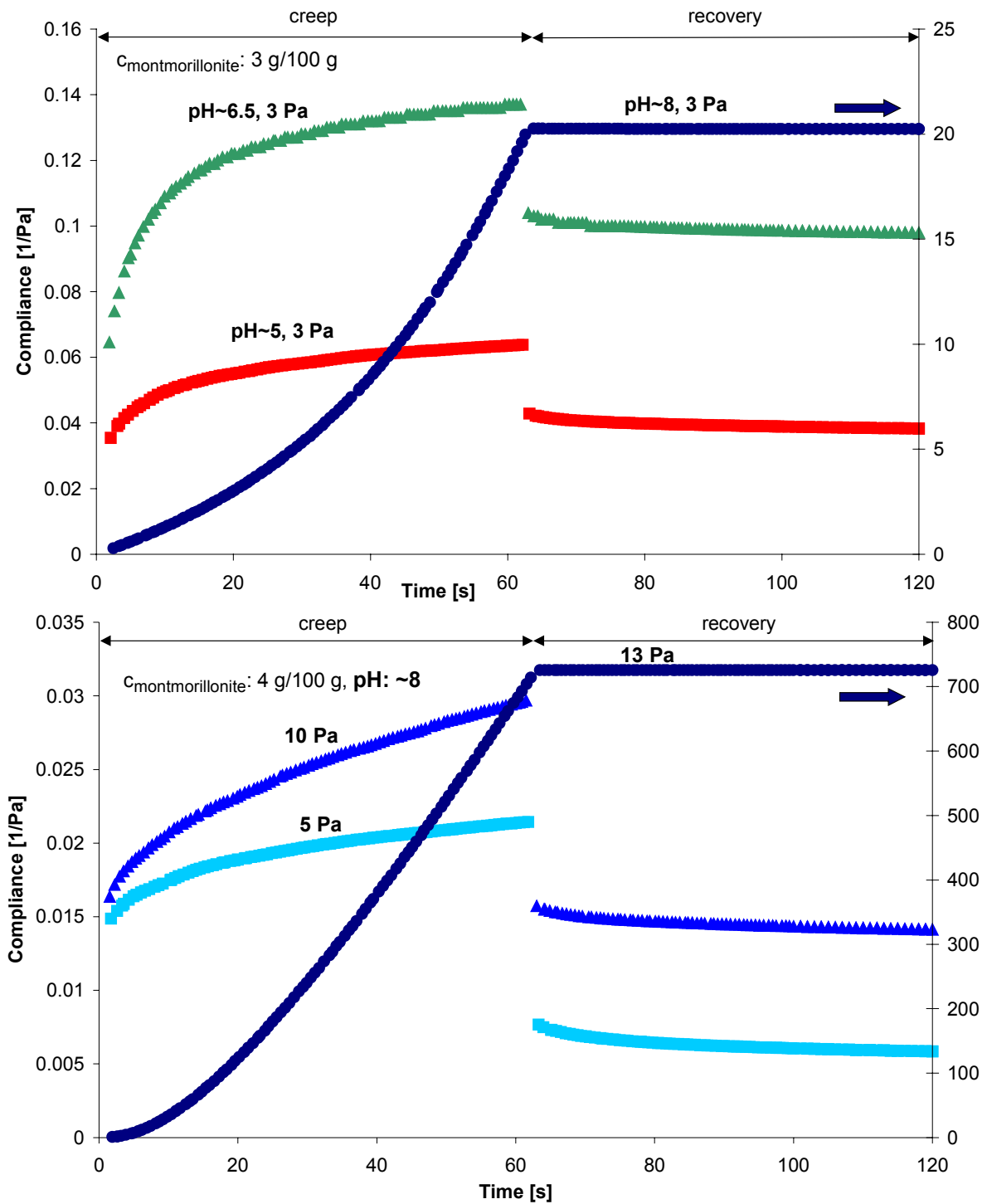


Fig. 2. Creep and recovery results for 3 and 4 g/100 g (top and bottom, respectively) montmorillonite suspensions containing 10.5-12.5 mM NaCl at different pHs at $25 \pm 0.1^\circ\text{C}$ (●: pH:~8, 3 Pa, 13 Pa) and below (▲:pH:6.5, 10 Pa and ■:5, 5 Pa) the pH of PZC of edges (~6.5).

The behavior of alkaline suspension (Fig. 2 top) is essentially different from that of acidic ones in good harmony with the feature of flow curves, if the applied stress is in the range of yield values (Table 1.). While almost ideal Newtonian (liquid-like) behavior was detected for suspension containing uniformly charged particles at pH~8, since deformation continually increased in a linear manner as long as the stress was applied, and there was no any restoration at all in the absence of attraction between particles. However, suspensions below pH~6.5, where particle network can build in dense suspensions due to attractive forces between the oppositely charged parts of lamellae, an elastic response in the jelly-like suspensions definitely appears besides viscous deformation at the given shear stress, since a significant part of deformation was reversible (elastic). The contribution of elastic component to the viscoelastic deformation of sample is obvious, since the applied stress results in an instantaneous strain jump, which restores after releasing. However, a significant non-recoverable deformation remained due to the presence of viscous component. This creep test proved that attractive gel forms below the pH of edge PZC due to the electrostatic attraction between positively charged edges and negatively charged plates of montmorillonite lamellae, which has considerable elasticity besides viscous properties. It has to be mentioned that elasticity of thixotropic montmorillonite gels can be observed, if only the applied stress is below their yield values (Fig. 1). The elastic behaviour of montmorillonite gels can be detected only up to a limited values of applied stress (~10 Pa in Fig. 2 bottom), which is in good harmony with the initial yield value on flow curve (~9 Pa in Fig. 1 bottom), however, above it the viscous character of suspension becomes dominant.

Forced oscillation with an assigned frequency and amplitude was applied to measure the viscoelasticity of montmorillonite gels. The same 3 and 4 g/100 g montmorillonite suspensions with different pHs (~5, 6.5 and 8) were measured. Since the frequency sweep measurements from 0.1 to 10 Hz showed linear viscoelasticity regions of samples in low frequency region, the stress sweep was measured at either 1 or 2 Hz frequencies. Some among the several measurements are showed in Figs. 3 and 4. It can be seen that the elastic (G' storage) modulus is larger than the viscous (G'' loss) modulus at low stresses showing the dominance of elastic character. However, when an increasing stress is applied this relation is reversed at stress ~7 and ~10 Pa for pH ~6.5 and ~5 suspensions (Fig. 3.) and ~22 and ~27 Pa for pH ~6.5 and ~5 (Fig. 4.), respectively, which indicate the break down of elastic particle network and the appearance of viscous flow at stronger shear forces. A similar trend with increasing stress is obvious from the change in phase shift angle (δ) from 10-20° characteristic of more elastic body to ~80° close to the purely viscous substances. The magnitude of storage modulus measured here is comparable with the values published recently for different montmorillonite suspensions, in which the effect of coagulating electrolytes (Grim and Güven, 1978) and liquefying humic acid (Ramos-Tejeda et al., 2001) was investigated. A sharp decay of storage modulus at shear stress ~1 Pa applied in the oscillatory experiment at 1 Hz frequency was measured in 5% w/w Na-montmorillonite suspension (pH~7, 0.01 M NaCl) (Ramos-Tejeda et al., 2001) in accordance with our results at lower pHs.

As regards the pH-dependent viscoelasticity of montmorillonite suspensions, it is worth comparing the curves of phase shift angle as a function of the applied shear stress (Fig. 5). An inflection of curves at about 45° with decreasing pH of suspensions appears at ~10, ~20 and ~30 Pa, respectively, showing that gradually stronger shear forces are necessary to break down the elastic particle network formed with decreasing pH in the suspensions. These characteristic shear stress values are in the same region as the initial yield values of the identical suspensions (Fig. 1 bottom). Aggregation by NaCl was accompanied by an increase in yield value and storage modulus (Grim and Güven, 1978) similarly to the effect of decreasing pH here.

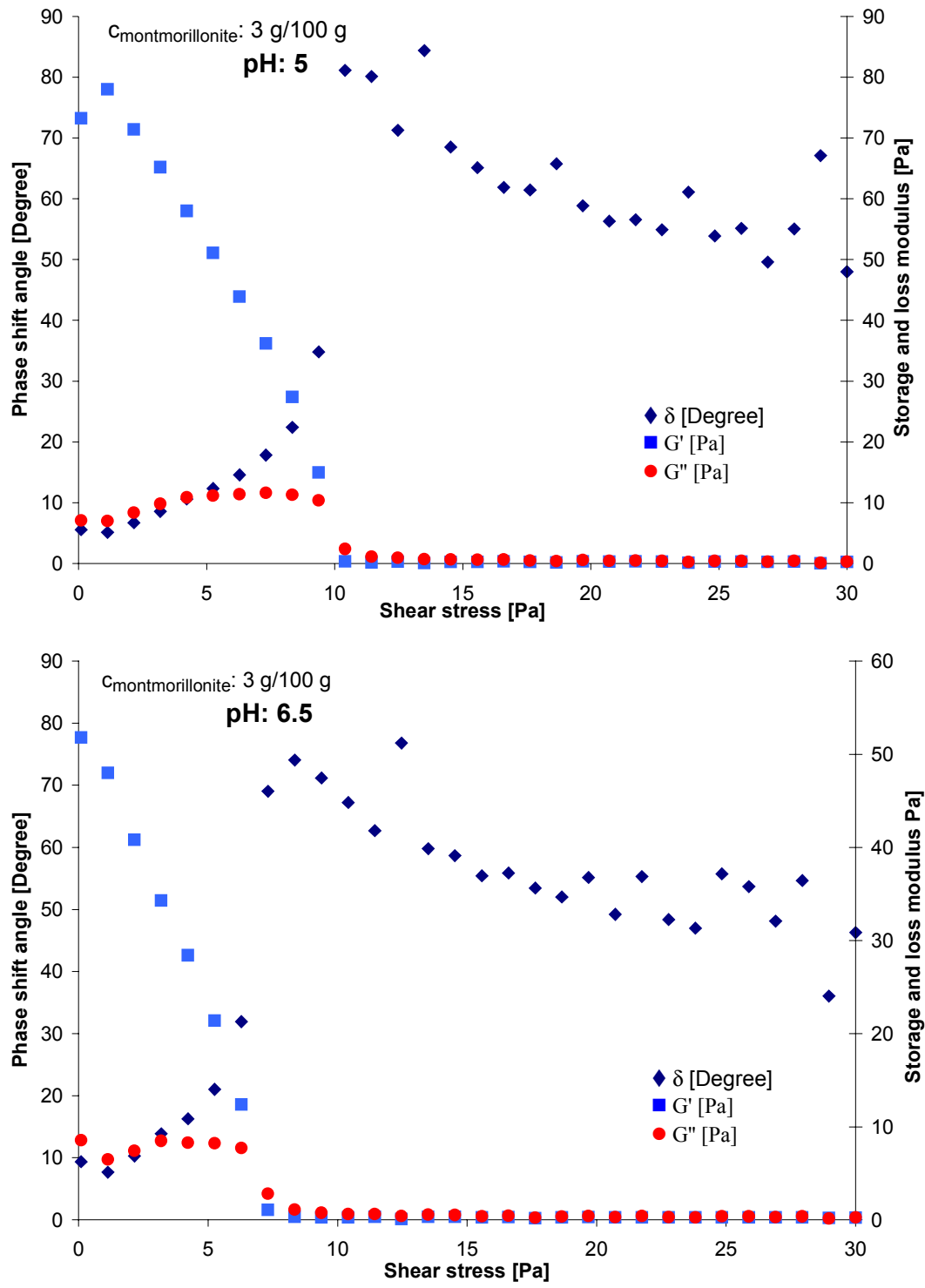


Fig. 3. Storage (G' : ■) and loss (G'' : ●) modulus, and phase shift angle (δ° : ◆) of 3 g/100 g montmorillonite suspensions at pH ~5 and ~6.3 (top and bottom, respectively) as a function of the applied shear stress at $25 \pm 0.1^\circ\text{C}$.

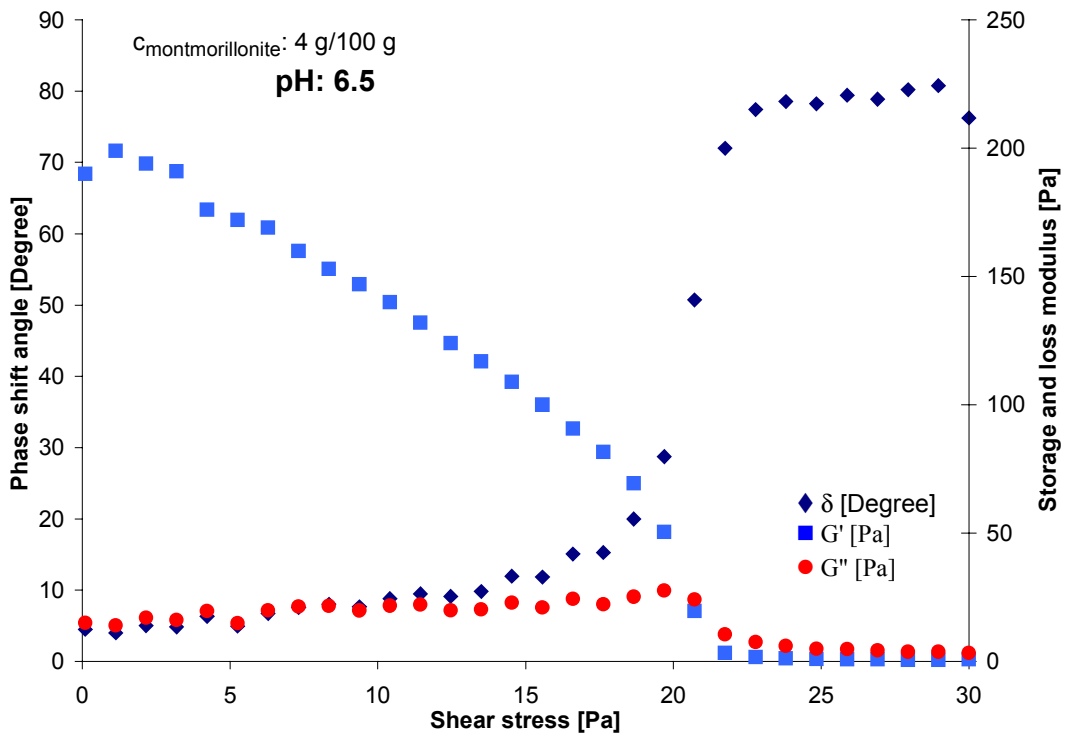
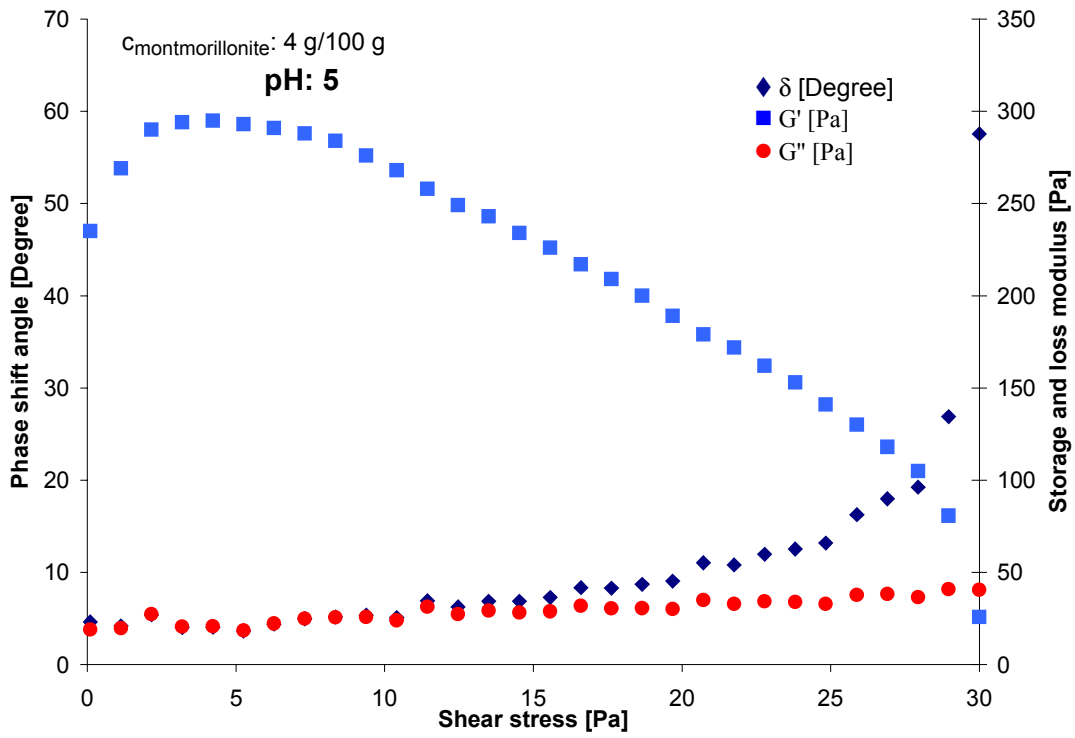


Fig. 4. Storage (G' : ■) and loss (G'' : ●) modulus, and phase shift angle (δ° : ◆) of 4 g/100 g montmorillonite suspensions at pH ~5 and ~6.3 (top and bottom, respectively) as a function of the applied shear stress at $25 \pm 0.1^\circ\text{C}$.

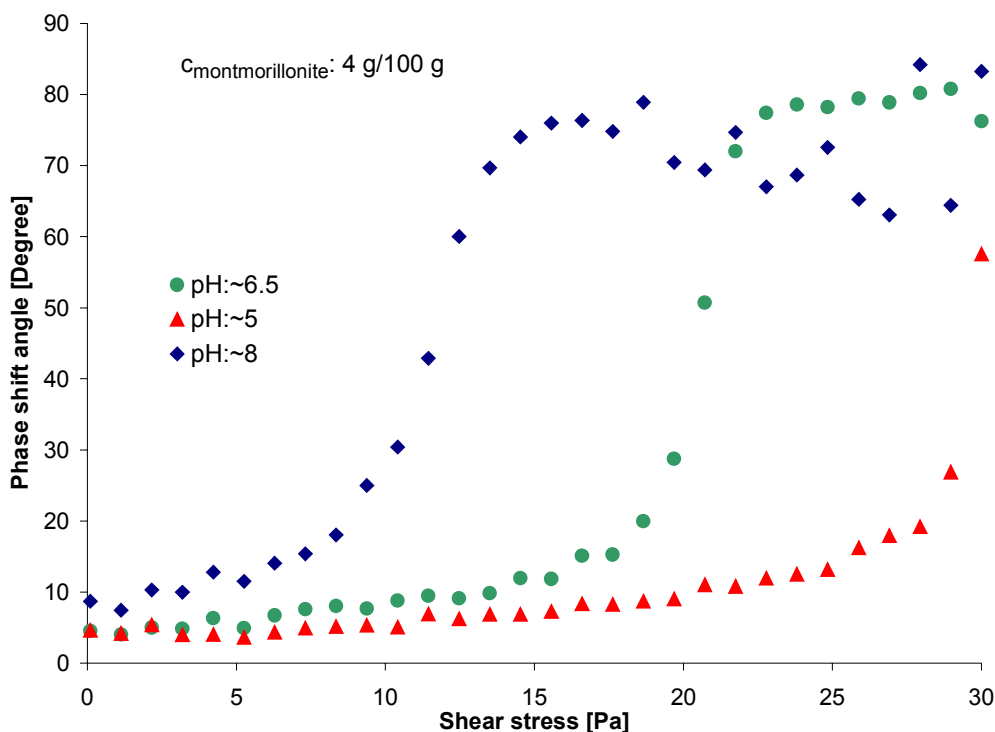


Fig. 5. Phase shift angle (δ°) of 4 g/100 g montmorillonite suspensions at pH ~8(\blacklozenge), ~6.5(\bullet) and ~5 (\blacktriangle) as a function of the applied shear stress at $25 \pm 0.1^\circ\text{C}$.

CONCLUSION

In aqueous systems, the colloidal interactions between clay mineral particles are generally governed by local electrostatic field developing around particles due to the neutralization of surface charges. The composition of aqueous solution influences both the surface charging and the charge neutralization. Among clay minerals montmorillonite (2:1 layer silicate) as the most often studied swelling clay was chosen for a comprehensive study to show how the pH dependent surface charge heterogeneity of clay lamellae influences the particle interactions in suspensions, the ordering of lamellae and the structure of particle network formed in montmorillonite gels. Montmorillonite particles hold both permanent negative charges on faces and pH-dependent charges mainly on Al-OH sites at the broken edges. These clay lamellae have patch-wise charge heterogeneity below the pH of PZC of edges (~ 6.5), where positively charged, protonated Al-OH_2^+ sites exist besides the negatively charged faces of lamellae. Edge-to-face heterocoagulation between the oppositely and poorly charged parts of platelets is induced by relatively low salt concentration (typically between 10 and 50 mM 1:1 electrolyte) at and below the pH of PZC of edge sites. While well-ordered lamellae packages cannot form in montmorillonite films under these conditions, the gelation of montmorillonite sols is advanced, an easy formation of semi-solid attractive gels with significant thixotropy and viscoelasticity is obvious below pH~6.5. At higher pHs, however, the repulsion is the overall interaction between the uniformly charged lamellae, and so rather liquid-like, colloiddally stable montmorillonite sols exist in dilute salt solutions. However, solid-like feature with pronounced viscoelasticity, more or less strong network of lamellar particles with significant yield values can form in more concentrated montmorillonite suspensions even at higher pHs.

ACKNOWLEDGEMENT

This work was supported by the grant OTKA T034755. The authors are grateful to FLORIN Rt. providing Rheometer HAAKE RS150 for our services.

REFERENCES

- Abend, S., Lagaly, G., 2000.** Sol-gel transition of sodium montmorillonite dispersions. *Appl. Clay Sci.*, 16, 201-227.
- Altin, O., Özbelge, Ö., Dogu, T., 1999.** Effect of pH in an aqueous medium on the surface area, pore size distribution, density, and porosity of montmorillonite. *J. Colloid Interface Sci.* 217, 19-27.
- Barnes, H.A., Hutton, J.F., Walters, K., 1989.** *An Introduction to Rheology*, Elsevier, Amsterdam.
- Benna, M., Khir-Arigoib, N., Magnin, A., Bergaya, F., 1999.** Effect of pH on rheological properties of purified sodium bentonite suspensions. *J. Colloid Interface Sci.* 218, 442-455.
- Bergaya, F., Lagaly, G., 2001.** Surface modification of clay minerals. *Appl. Clay Sci.*, 19, 1-3.
- Durán, J.D.G., Ramos-Tejada, M.M., Arroyo, F.J., González-Caballero, F., 2000.** Rheological and electrokinetic properties of sodium montmorillonite suspensions – I. Rheological properties and interparticle energy of interaction. *J. Colloid Interface Sci.* 229, 107-117.
- Firth, B.A., Hunter, R.J., 1976.** Flow properties of coagulated colloidal suspensions I., II. and III. *J. Colloid Interface Sci.* 57, 248-275.
- Grim, R.E., Güven, N., 1978.** *Bentonites, Geology, Mineralogy, Properties and Uses, Developments in Sedimentology 24.* Elsevier, Amsterdam.
- Heath, D., Tadros, Th.F., 1983.** Influence of pH, electrolyte, and poly(vinyl alcohol) addition on the rheological characteristics of aqueous dispersions of sodium montmorillonite. *J. Colloid Interface Sci.* 93, 307-315.
- Heil, D., Sposito, G., 1993.** Organic-matter role in illitic soil colloids flocculation 1. Counter ions and pH and 2. Surface charge. *Soil Sci. Soc. Am. J.* 57, 1241-1246 and 1246-1253.
- Janek, M., Lagaly, G., 2001.** Proton saturation and rheological properties of smectite dispersions. *Appl. Clay Sci.* 19, 121-130.
- Johnston, C.T., Tombácz, E., 2002.** *Surface Chemistry of Soil Minerals.* In: J.B. Dixon, D.G. Schulze (Eds.), *Soil mineralogy with environmental applications.* Soil Science Society of America, Madison, Wisconsin, pp. 37-67.
- Keren, R., Sparks, D.L., 1995.** The role of edge surfaces in flocculation of 2:1 clay minerals. *Soil Sci. Soc. Am. J.* 59, 430-435.
- de Kretser, R.G., Scales, P.J., Boger, D.V., 1998.** Surface chemistry-rheology inter-relationships in clay suspensions. *Colloids Surfaces A.* 137, 307-318.
- Penner, D., Lagaly, G., 2000.** Influence of organic and inorganic salts on the coagulation of montmorillonite dispersions. *Clays Clay Min.* 48, 246-255.
- Penner, D., Lagaly, G., 2001.** Influence of anions on the rheological properties of clay mineral dispersions. *Appl. Clay Sci.* 19, 131-142.
- Ramos-Tejada, M.M., de Vicente, J., Ontiveros, A., Duran, J.D.G., 2001.** Effect of humic acid adsorption on the rheological properties of sodium montmorillonite suspensions. *J. Rheology*, 45, 1159-1172.
- Ramos-Tejada, M.M., Ontiveros, A., Plaza, R.C., Delgado, A.V., Duran, J.D.G., 2003.** A rheological approach to the stability of humic acid/clay colloidal suspensions. *Rheol. Acta* 42, 148-157.
- Schroth, B.K., Sposito, G., 1997.** Surface charge properties of kaolinite. *Clays Clay Minerals*, 45, 85-91.
- Sondi, I., Milat, O., Pravidic, V., 1997.** Electrokinetic potential of clay surfaces modified by polymers. *J. Colloid Interface Sci.* 189, 66-73.
- Thompson, D.W., Butterworth, J.T., 1992.** The nature of laponite and its aqueous dispersions. *J. Colloid Interface Sci.* 154, 236-243.
- Tombácz, E., Ábrahám, I., Gilde, M., Szántó, F., 1990.** The pH-dependent colloidal stability of aqueous montmorillonite suspensions. *Colloids Surfaces*, 49, 71-78.

- Tombacz, E., Szekeres, M., 2004.** Colloidal behavior of aqueous montmorillonite suspensions: the specific role of pH in the presence of indifferent electrolytes. *Applied Clay Science*, in press.
- Tombacz, E., 2002.** Adsorption from Electrolyte Solutions. In: J. Tóth (Ed.), *Adsorption: Theory, Modeling, and Analysis*. Marcel Dekker, New York, pp. 711-742.
- Tombacz, E., Nyilas, T., Libor, Zs., Csanaki, Cs., 2003.** Surface charge heterogeneity and aggregation of clay lamellae in aqueous suspensions. *Progr. Colloid Polymer Sci.* (in press)
- Van Olphen, H., 1963.** *An Introduction to Clay Colloid Chemistry*. Interscience, New York.
- Zhao, H., Low, P.F., Bradford, J.M., 1991.** Effects of pH and electrolyte concentration on particle interaction in 3 homoionic sodium soil clay suspensions. *Soil Sci.* 151, 196-207.
- Zhou, Z., Gunter, W.D., 1992.** The nature of the surface charge of kaolinite. *Clays Clay Min.* 40, 356-368.
- Yildiz, N., Sarikaya, Y., Calimli, A., 1999.** The effect of the electrolyte concentration and pH on the rheological properties of the original and the Na₂CO₃-activated Kütahya bentonite. *Appl. Clay Sci.* 14, 319-327.