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SHORT COMMUNICATION

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Polydisperse fractal aggregate formation in clay mineral and iron oxide suspensions, pH and ionic strength dependence

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Abstract pH- and ionic-strength-dependent aggregation of permanently and conditionally charged clay mineral (montmorillonite) and iron oxide (magnetite) particles was investigated by means of dynamic light scattering and rheology. An indifferent electrolyte (NaCl) was used. The surface charging of solids was determined by acid–base titration. The point of zero charge (PZC) of magnetite seemed to be at pH 8.0 ± 0.1. The permanent negative charges on the basal plane of montmorillonite influence the interfacial distribution of H^+ and Na^+ ions. The pH dependence of the electrophoretic mobility showed directly the dominance of negative charges on montmorillonite lamellae independently of pH, while for magnetite the sign of the mobility reversed at pH $\sim$ 8.0. Montmorillonite particles formed stable suspensions; coagulation did not take place below 35 mM 1:1 electrolyte independently of pH. The aggregation of magnetite sol becomes significant near the pH of the PZC even at low ionic strength. Colloidal stability in composite systems was investigated at pH $\sim$ 4, where oxide and clay mineral particles are oppositely charged. At the lowest NaCl concentrations (1, 5 mM) the mixed systems remained stable and aggregation of oppositely charged particles could not be observed at all. Heterocoagulation of dissimilar particles needed a definite amount of dissolved electrolytes (about 8 mM). Mixed clay mineral and oxide systems are more sensitive to electrolyte under acidic conditions than those separately. Rheological investigation of the mixed clay mineral–oxide suspensions at pH $\sim$ 4 provided proof for the absence of attractive particle interaction at low ionic strength (2 mM). A physical network of oppositely charged particles could form only at higher salt concentration, for example, in the presence of 10 mM NaCl. The yield value of plastic systems showed a significant maximum at 1:15 magnetite/montmorillonite mass ratio.

Key words Montmorillonite · Magnetite · Surface charging · Homocoagulation · Heterocoagulation

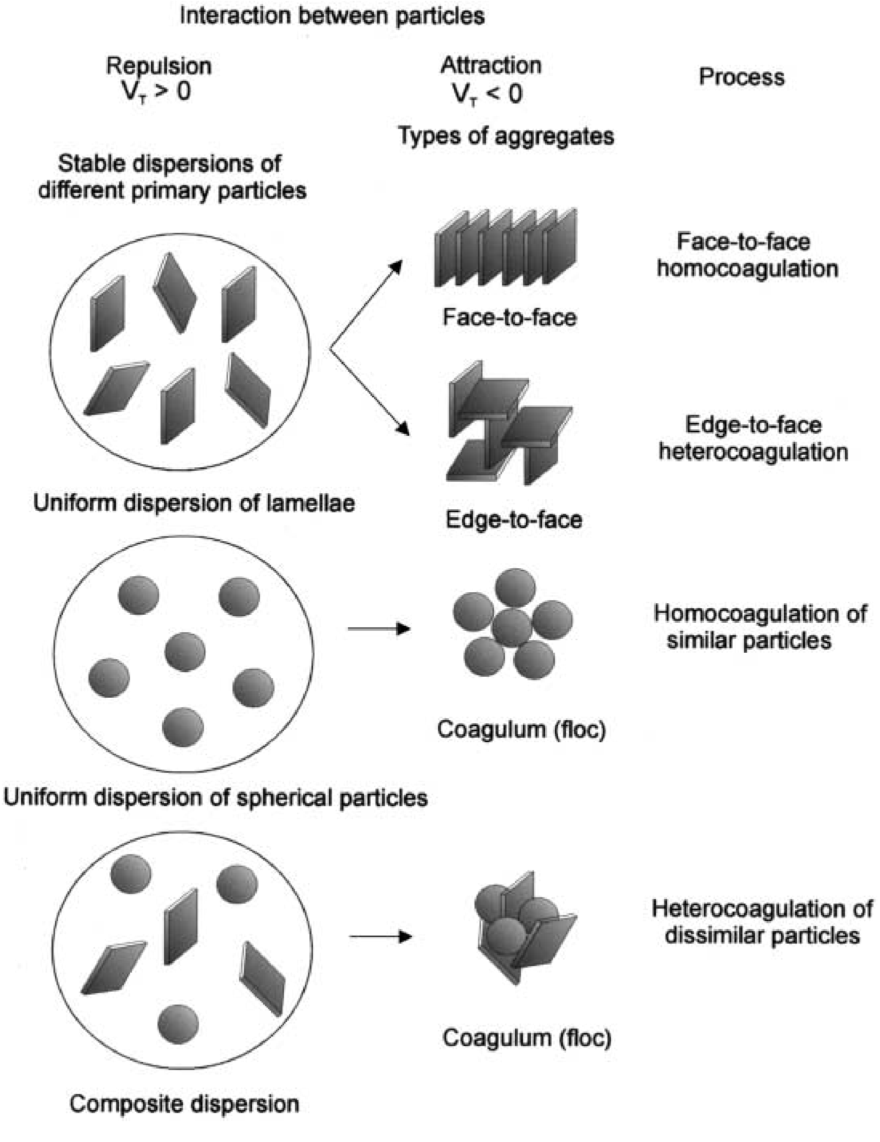
Introduction

Clay mineral and metal oxide particles are the most abundant inorganic colloid particles in aqueous systems. Aggregation of these particles under changing solution conditions takes place spontaneously in a natural environment [1, 2]. The colloidal stability of aqueous dispersions is mainly determined by the pH and the ionic strength of solution as well as the presence of specifically adsorbed multivalent ions. These parameters can be considered as master variables determining the composition of the solid/liquid interfacial layer.

In aqueous systems particle surfaces develop electrical charges in two principal ways: either permanently, from isomorphic substitution of ions in the crystal lattice of solid particles (e.g. permanent negative charges on montmorillonite plates), or conditionally, from the reactions of surface functional groups with dissolved ions in the aqueous phase (e.g. Al–OH on the edges of clay mineral plates or Fe–OH on the iron oxide surface with H^+/OH^-) [3]. Clay lamellae constituted from silica tetrahedral and alumina octahedral sheets have negatively charged sites on the basal planes owing to the substitution of the central Si and Al ions in the crystal lattice. However, the amphoteric sites, mainly Al–OH groups, situated at the broken edges of clay lamellae are conditionally charged, i.e. either positive or negative charges can be developed depending on the pH. This surface charge heterogeneity presented originally by van Olphen [4] then supported and elaborated further in many subsequent and recent investigations [5–12] governs the particle interactions in clay mineral 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. The attraction between the oppositely charged parts results in aggregates with edge-to-face heterocoagulated structures below pH ~ 7, while face-to-face homocoagulated structures can form in the interaction of the charge-screened basal planes of clay lamellae as shown schematically in Fig. 1.

In metal oxide suspensions charge development occurs by direct proton transfer to surface hydroxyl groups. Surface charging is controlled by the pH and the

Fig. 1 Schematic representation of particle–particle interactions in colloidal dispersions



ionic strength of the aqueous medium. The formation of electric charges can be explained by the acid–base properties of surface hydroxyl groups. H^+ and OH^- ions are considered as the potential-determining ions according to the IUPAC recommendation [13]. The surface charge of pure metal oxide is positive below the pH of the point of zero charge (PZC), while it is negative above that. pH-dependent surface charging of magnetite and the solubility of iron oxide particles in aqueous suspensions have been studied [14]. Acid–base titration and zeta-potential measurement showed charge reversal at about pH 6 with increasing pH in the absence of multivalent cations. The solubility of magnetite over the acidic region becomes appreciable below pH ~ 4, where the concentration of dissolved iron ions rises above 10^{-4} M.

In oxide suspensions coagulation occurs around the PZC. even at low ionic strength [15–17]. Suspensions are stable far from the PZC, but an increase in salt concentration induces homocoagulation of particles [16–19]. Heterocoagulation of positively charged oxides with negatively charged clay mineral particles may take place at pH values below about 7, depending on the mineral composition and the solution conditions. A schematic presentation of homo- and heterocoagulation processes can be seen in Fig. 1. It is well known in soil science that iron oxides contribute significantly to aggregate stability of clay soils. A Coulombic attraction is supposed between the positively charged oxide and the negatively charged clay mineral particles. Charge characteristics of iron oxides and their interaction with different clay minerals (kaolinite and illite) have been studied [20, 21] over a broad range of pH without paying attention to ionic strength. An unusual trend in the electrolyte concentration dependence of the heterocoagulation kinetics of oppositely charged latex particles was published recently [22].

In this work pH-dependent particle aggregation of permanently and/or conditionally charged clay mineral and iron oxide samples (montmorillonite and magnetite) was studied as characteristic examples for mineral particles in natural aqueous systems. We show ionic strength dependence of colloidal aggregation, homo- and heterocoagulation of similar and dissimilar mineral particles under acidic condition (at pH ~ 4) in dilute and dense systems.

Experimental

Materials

Montmorillonite was obtained from Wyoming bentonite (USA). A clay mineral fraction smaller than 1 μm was prepared by allowing the larger particles to settle in a dilute (10 g/l) suspension and then decanting. About 10% of bentonite was discarded. To obtain the monocationic sodium montmorillonite, the suspension was treated with 1 M NaCl. After centrifugation of the suspensions at 3600 rpm the supernatant solution was discarded and replaced with fresh solutions. The procedure was repeated three times. The ionic strength of the 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 smaller electrolyte concentration of the medium was reached by dilution. The exchange capacity of montmorillonite was 56 mEq/100 g (by NH_4^+ exchange).

Synthetic magnetite was prepared by alkalizing concentrated aqueous solutions of $FeCl_2$ and $FeCl_3$ [14]. The suspension was centrifuged at 3600 rpm, the supernatant solution was discarded and the sediment washed with Millipore water, then rinsed three times with 0.01 M NaCl solutions and finally dialyzed against 0.01 M NaCl. Magnetite sol was stored in a closed vessel.

All measurements were performed at constant ionic strength in indifferent 1:1 electrolyte (NaCl) solutions. Solutions and suspensions were prepared, stored and measured in carefully cleaned vessels. Chromium sulfuric acid was used to oxidize organic impurities. The water was obtained directly from a Millipore apparatus. All chemicals used were analytical reagent grade products (Reanal, Hungary).

Methods

Potentiometric acid–base titration

The pH-dependent surface charge was determined by acid–base titration under a CO_2-free atmosphere using NaCl electrolyte to maintain a constant ionic strength of 0.01 M. Before titration the suspensions were stirred and bubbled with purified nitrogen for 1 h. Equilibrium titration was performed by means of a self-developed titration system (GIMET1) with 665 Dosimat (Metrohm) burettes, nitrogen bubbling, a magnetic stirrer and a high-performance potentiometer at 25 ± 1 °C. The whole system (millivolt measure, stirring, bubbling, amount and frequency of titrant) was controlled using an IBM PS/1 computer using AUTOTITR software. A Radelkis OP-0808P (Hungary) combination pH electrode was calibrated for three buffer solutions to check the Nernstian response. The hydrogen ion activity versus concentration relationship was determined from reference electrolyte solution titration, so the electrode output could be converted directly to hydrogen ion concentration instead of activity. In the first cycle, suspensions were titrated by standard HCl solution down to pH 4, then by standard base solution (NaOH) up to pH 9–9.5, then again by acid solution in the second cycle. The titration was reversible within the reproducibility of this method except for the first down curve of the montmorillonite titration.

The net proton surface excess amount (Δq, mol/g) is defined as a difference of $H^+(n^\sigma_{H^+})$ and $OH^-(n^\sigma_{OH^-})$ surface excess amounts related to unit mass of solid, $\Delta q = n^\sigma_{H^+} - n^\sigma_{OH^-}$. The surface excess amount of any solute, like H^+ and OH^- here, can be determined directly from the initial and equilibrium concentration of solute for adsorption from dilute solution [23]. The values $n^\sigma_{H^+}$ and $n^\sigma_{OH^-}$ were calculated at each point of the titration from the electrode output using the actual activity coefficient from the slope of H^+/OH^- activity versus concentration straight lines for background electrolyte titration.

Electrophoretic mobility measurement

The electrophoretic mobilities of clay mineral and magnetite particles were measured at 25 ± 0.1 °C in a capillary cell (ZET 5104) with ZetaSizer 4 (Malvern, UK) apparatus. Stock dispersions of montmorillonite and magnetite containing 0.01 M NaCl were diluted to 0.05 g/l solid content and the salt concentration of dilute systems was adjusted to 0.002 M NaCl. The pH of dilute dispersions (magnetite, montmorillonite and their mixture) was adjusted from about 4 to about 9 by HCl or NaOH solutions and was measured directly before introducing the sample into the capillary cell.

Particle size determination

Dynamic light scattering (DLS) measurements were performed using a ZetaSizer 4 apparatus operating at $\lambda = 633$ nm produced by a He–Ne laser at a scattering angle of 90° at 25 ± 0.1 °C. Particles from the stock dispersions were dispersed in electrolyte solutions with different concentration. The pH of the dilute systems was adjusted in the range 4–10 and measured directly before a sample was placed in the quartz cell. pH-dependent particle aggregation was measured at constant ionic strength, while coagulation kinetics measurements were performed at different salt concentration, but constant pH ~ 4 for magnetite, montmorillonite and their mixture.

The correlation functions were evaluated by cumulant analysis [24]. The first-order autocorrelation function, $g^1(t)$, can be given as $g^1(t) = \exp(-\Gamma t + (\mu_2/2!)t^2 + (\mu_3/3!)t^3 + \ldots)$, where Γ is an average decay rate; Γ characterizes the mean, μ_2 the width and μ_3 the skewness of the distribution. If $qR \ll 1$, the translational diffusion is the dominant dynamics. The diffusion coefficient (D_t) can be calculated, $\Gamma = D_t q^2$, where the scattering vector, q, is $q = (4\pi n/\lambda)\sin(\theta/2)$, and from the Stokes–Einstein equation, $D_t = kT/6\pi\eta R_H$, the hydrodynamic radius (R_H) can be obtained. (In the equations:k is the Boltzmann constant, T is the temperature, η is the viscosity of the medium, n is the refractive index of the solution, λ is the laser wavelength and θ is the scattering angle.)

Rhological measurement

The flow curves were determined in a shear rate range (0–100 1/s) of a Haake RV20 CV100 viscometer using a Money–Ewart ME15 sensor system type at constant (25 ± 0.1 °C) temperature. The shear rate was increased for 3 min to measure up curves, then decreased to get down curves. Montmorillonite suspensions (3 g/100 g) containing different amounts of magnetite from 0 to 0.6 g/100 g were measured. The effect of ionic strength on the formation of a coherent network of oppositely charged particles at pH ~ 4 was investigated in parallel at 0.002 and 0.01 M NaCl.

Results and discussion

Surface charge state

To characterize the pH dependence of surface charging, the apparent net proton surface excess was determined by acid–base titration. The net proton surface excess amount is shown in Fig. 2 versus pH functions for montmorillonite and magnetite at a constant ionic strength of 0.01 M NaCl, which is an indifferent electrolyte for clay minerals [6, 11, 16]. The curves for the montmorillonite and iron oxide reflect the essential differences between these solid materials. The 2:1 layer-type montmorillonite has a high permanent layer charge and negligible variable charge [6, 11], while magnetite particles develop only variable charges [14].

The positive values of the net proton surface excess show the accumulation of protons on the montmorillonite surface (upper curve in Fig. 2). The permanent negative charges are compensated by the exchangeable cations, which are Na^+ in the suspension initially present owing to the salt treatment and exhaustive dialysis against 0.01 M NaCl solution. Na^+ ions are exchanged by H^+ ions in the following ion-exchange process during the acidic titration cycle

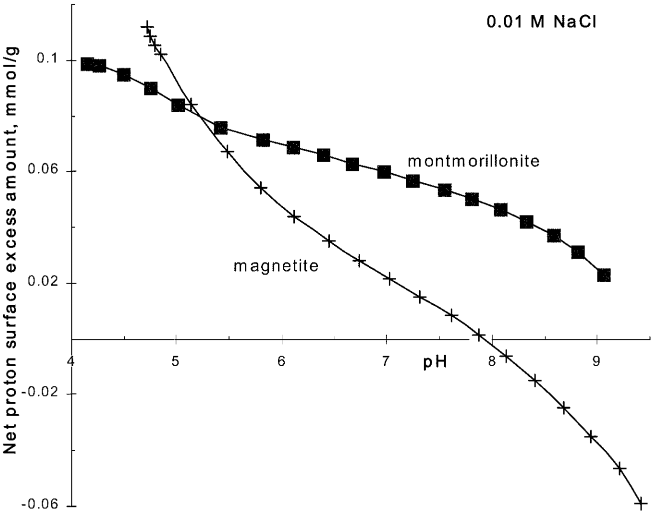


Fig. 2 pH dependence of net proton surface excess amount determined by acid–base titration for montmorillonite and magnetite at 0.01 M ionic strength

$$\text{Na clay} + (H^+)_{aq} \rightleftharpoons \text{H clay} + (Na^+)_{aq} \qquad (1)$$

and they remain specifically adsorbed [6] during the alkaline cycle, since the affinity of H^+ ions to the exchange sites is much higher than that of Na^+ ions. The ion-exchange equilibrium shifts slightly with decreasing activity of H^+ ions at roughly constant concentration of Na^+ ions. The net proton excess amount (Δq) calculated as the difference between the surface excess amount of protons ($n^{\sigma}_{H^+}$) and that of hydroxide ions ($n^{\sigma}_{OH^-}$) will therefore be positive even at high pHs, since the contribution of the amphoteric edge sites to the total charge of smectites is not significant [10].

The other curve of Fig. 2 demonstrates the pH dependence of the net proton surface excess amount for magnetite, which is proportional to the surface charge (σ_o) of iron oxide, since this solid can develop charges only conditionally [14], and the present electrolyte (NaCl) seems to be indifferent. The PZC value was determined as the intersection points of σ_o versus pH curves belonging to the different ionic strength, not shown here, and its value was at pH = 8.0 ± 0.1, which is significantly higher than the pH of the isoelectric point (IEP) of about 6 determined from zeta-potential measurement using electrolyte $NaClO_4$ [14]. The oxide particles are negatively charged above the PZC and positively below it because of the surface reaction of H^+ and OH^- ions.

$$\underline{Fe}\text{- }OH + H^+ \rightleftharpoons \underline{Fe}\text{ - }OH_2^+ \qquad (2)$$

$$\underline{\mathrm{Fe}}\text{ - OH} + \mathrm{OH} \rightleftharpoons \underline{\mathrm{Fe}}\text{- O}^- + \mathrm{H_2O} \qquad (3)$$

The farther the pH of solution from the pH of the PZC, the higher the charge density of the magnetite particles over the pH range from about 4 to 10. Below this roughly defined limit of acidic pH the dissolution of iron oxide becomes perceptible [14] and the dissolved iron species strongly influence the surface charge of particles and the interparticle interactions.

Charge state of particles

The pH dependence of the electrophoretic mobility for specimen mineral particles is characteristically different for magnetite, montmorillonite and their mixture (Fig. 3). The dominance of permanent negative charges on clay mineral particles becomes obvious from the negative mobility values observed over the whole range of pH. The conditionally charged magnetite particles have an IEP at pH ~ 8, estimated from the electrophoretic mobility versus pH curve, where the sign of measured values reverses. This point is called the zeta-potential reversal [13]. The pH of the PZC and the IEP seems to be the same. This fact also suggests that the electrolyte used is indifferent, so the distribution of Na^+ and Cl^- ions at the interface is only determined by the local electrostatic field developed in the protonation/deprotonation reactions of Fe–OH surface sites (Eqs. 2, 3). The pH dependence of the electrophoretic mobility measured in the 1:1 mixture of 0.05 g/l magnetite and 0.05 g/l montmorillonite sols is similar to the curve of magnetite, but the apparent pH of the zeta-potential reversal (pH ~ 5) is much lower than the IEP of magnetite (pH ~ 8) presumably owing to electrostatic interaction between oppositely charged clay mineral and oxide particles. The number of positive charges on magnetite and the negative basal plane charges on montmorillonite under the given solution conditions ($I = 0.002$ M, pH ~ 5) estimated from the charge potential curves of magnetite and the cation-exchange capacity of montmorillonite are about 35 and about −560 μmol/g, respectively. Comparing these data, it is obvious that an assumption of simple neutralization between the opposite charges of dissimilar particles cannot be an acceptable explanation.

Particle aggregation in dilute systems

The specimen clay mineral and oxide particles in aqueous medium are electrostatically stabilized from a colloidal stability point of view. Aggregation–dispersion processes can take place depending on the structure of the electric double layer formed on the surface of the particles. The particle aggregation in dilute suspensions can be characterized by particle size determination. DLS can provide reliable size data even when the system is undergoing coagulation [25, 26].

The pH dependence of the hydrodynamic radius calculated from the cumulant analysis of first-order correlation functions can be seen in Fig. 4. Comparing the measured curves for montmorillonite and magnetite sols with only 0.01 M of electrolyte, it is obvious that the pH-induced particle aggregation is characteristically different for these solids. The colloidal stability of permanently or conditionally charged particles is actually determined by their surface charge state. The highly charged montmorillonite particles form stable suspensions; the average particle size is constant above pH 4

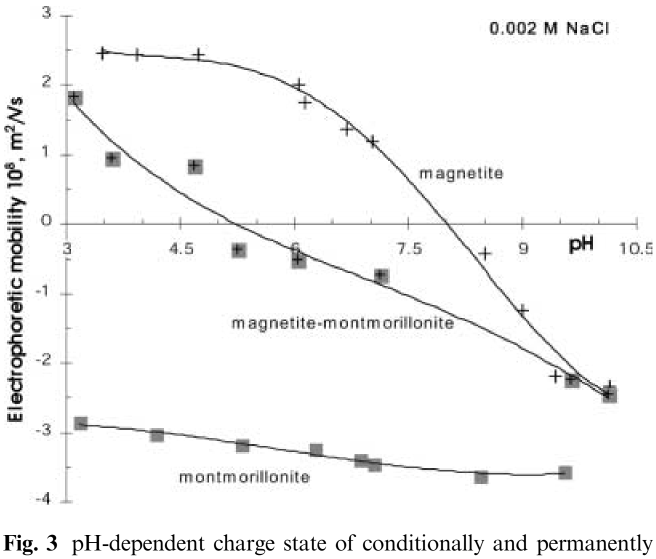


Fig. 3 pH-dependent charge state of conditionally and permanently charged particles and their 1:1 mixture

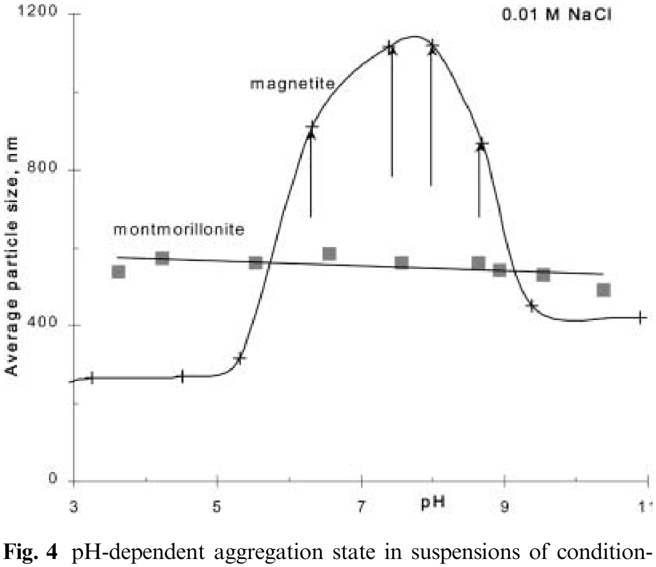


Fig. 4 pH-dependent aggregation state in suspensions of conditionally and permanently charged particles at low ionic strength

as explained elsewhere [10, 16]. In principle, the positively charged edges can interact with the negative basal plates below pH ~ 7; however, edge-to-face heterocoagulation does not take place at such a low ionic strength because of the spillover of the dominant electric double layer on the basal plane of montmorillonite [27]. A significant increase in the average particle size of magnetite around pH 8 shows a pronounced aggregation near the pH of the PZC, where electrostatic repulsion between particles is negligible, in accordance with amphoteric oxide reported in the literature [15, 17]. It should be mentioned that the reproducibility of measured size data for colloidally stable systems was very good within ±5%, and though the relation $qR \ll 1$ was not obviously fulfilled, the size data measured at different scattering angles did not show systematic differences. However, the particle size measured for the destabilized magnetite sols increased with time, showing the progress of coagulation. The range of size data measured in coagulating sols is marked with arrows in Fig. 4.

Some examples for coagulation kinetics taking place in magnetite and montmorillonite sols and their mixture are shown in Fig. 5. It can be seen that both simple sols are stable, i.e. the average particle sizes are low and constant, below 20 mM NaCl at pH ~ 4. Only higher salt content can induce coagulation. Diffusion-limited aggregation is observed at 150 mM magnetite and at 35 mM montmorillonite sol. This latter value is in good agreement with the critical coagulation concentration of sodium-rich Wyoming montmorillonite dispersion (critical coagulation concentration of 15–30 mM for coagulating electrolyte NaCl [28]). It correlates well with the theoretical prediction of Secor and Radke [27] for spillover of the diffuse double layer on montmorillonite particles. The exact solution of the Poisson–Boltzmann equation for a thin disc with positive edge and negative face charges revealed that for a salt content below about 10 mM the negative electrostatic field emanating from the particle face spills over into the edge region; therefore, the positively charged edge exhibits a negative electrostatic field. This results in a repulsive electrostatic potential for interparticle edge-to-face interaction. At 100 mM, where the diffuse layer is highly compressed and so the edge already exhibits a positive electrostatic field, an edge-to-face electrostatic attraction is expected. Therefore the theoretically predicted region of edge-to-face aggregation falls into 10–100 mM of 1:1 salt concentration. It is probable that in our coagulation kinetics experiment the positively charged edges of montmorillonite lamellae interact with the negative basal plates, forming edge-to-face loose fractal aggregates at 35 mM NaCl. Coagulation kinetics measurements for magnetite sols have not been published yet. Our results are in accordance with the kinetics data for the coagulation of hematite sol, where diffusion-limited aggregation resulting in loose fractal aggregates with a fractal dimension 1.7 ± 0.1 was induced by counterion screening at a KCl concentration higher than 80 mM at pH 6 [18].

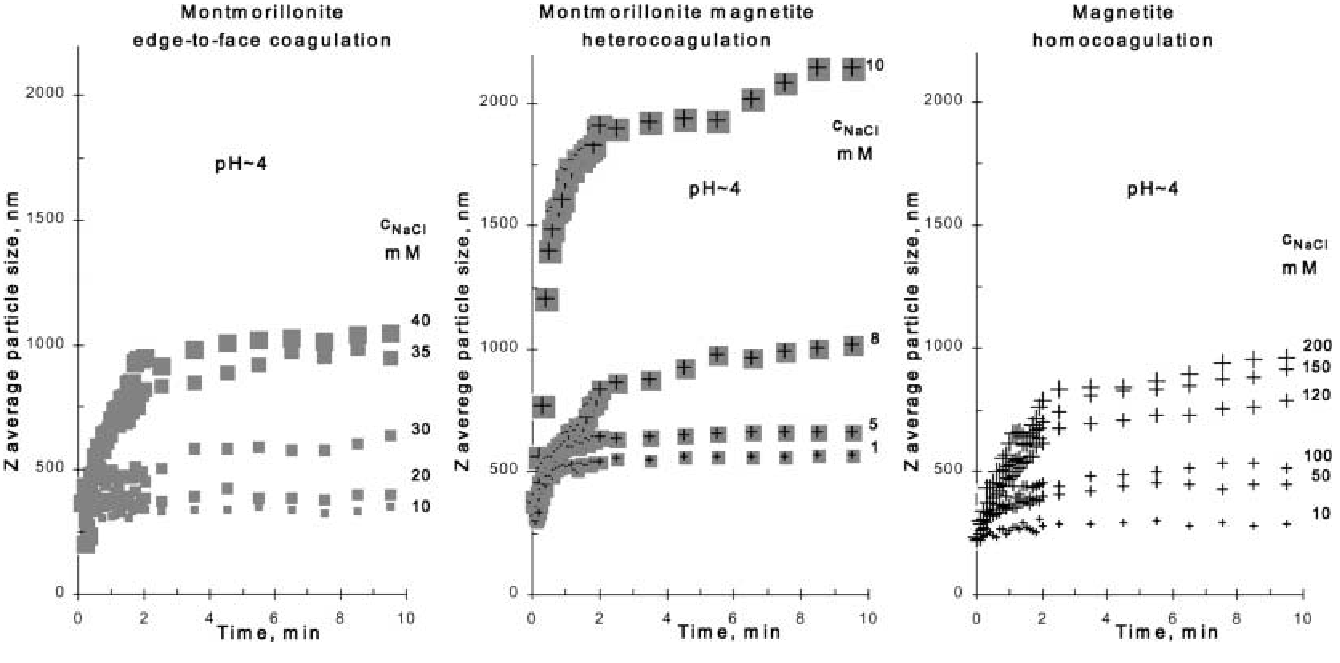


Fig. 5 Size evolution of aggregates in montmorillonite and magnetite sols and their mixture at different electrolyte concentrations. Coagulation kinetics measured by dynamic light scattering at 25 °C

The results for the composite systems, however, are somewhat surprising, since particle aggregation could not be observed at the lowest NaCl concentrations (1, 5 mM), though the mixed systems contain positively charged magnetite and negatively charged montmorillonite particles at the given pH (about 4). Heterocoagulation of oppositely charged particles could take place only above a certain concentration of NaCl (about 8 mM) and diffusion-limited aggregation was induced by 10 mM NaCl. The experimental fact that adhesion between the freely colliding oppositely charged particles cannot be reached at low electrolyte concentration is just the opposite of any intuitive expectation. Exact solution of the Poisson–Boltzmann equation for constant charge, however, resulted in repulsion at close approach between particles of opposite charges [29]. In heterocoagulation studies expressions [30] for the constant potential case, such as the well-known Hogg–Healy–Fuerstenau approach [31], always give attraction between the oppositely charged particles, in good agreement with experimental results in general, especially for fairly low potentials. Gregory [32] stated that in practical systems neither a constant potential nor a constant charge assumption is likely to be correct, the "true" situation lying somewhere between them. Gregory proved theoretically that interaction of unequal constant-charge double layers may be repulsive over the low κd region (κ is the reciprocal Debye length, proportional to the salt concentration, d is the distance from the surface) even for particles with opposite potential. However, there is no convincing experimental evidence for these "counterintuitive" effects, since most results on heteroaggregation indicate attraction for oppositely charged surfaces. In our case montmorillonite is considered a typical example for a constant-charge flat particle, while the potential is constant for the spherical magnetite particles at constant pH, since H^+ ions are potential-determining ions for metal oxides in aqueous media [13]. Interparticle interaction of dissimilar particles of this kind seems to be a fairly unusual case from a colloid stability point of view. It may say that montmorillonite–iron oxide mixed systems at a low salt concentration give the first experimental evidence for repulsion between oppositely charged surfaces, which is interpreted only on the basis of Derjaguin–Landau–Verwey–Overbeek (DLVO) forces considering the electrostatic and van der Waals interactions. However, additional short-range repulsions also have to be supposed, which arise from the so-called non-DLVO forces [29]. A formula for the sphere–plate Born repulsion has been published and applied mainly to particle deposition on collector surfaces [29]. An assumption of a relatively strong additional repulsion due to the overlap of hydration layers emanating chiefly from the alkali and chloride ions adsorbed onto the silica and oxide surfaces, called hydration repulsion [29, 33], is highly probable in our systems.

Summarizing the coagulation kinetics study, it has to be stated that the mixed clay mineral–oxide systems are more sensitive to electrolyte under acidic conditions (pH $\sim$ 4), where heterocoagulation of oppositely charged dissimilar particles is induced by much lower salt concentration (about 10 mM) than that for homocoagulation of either montmorillonite (35 mM) or magnetite (150 mM) particles.

Particle aggregation in dense systems

In any colloidally stable dispersions the overall particle interaction is repulsive; therefore, particles repel each other and the freely moving primary particles endeavor to place themselves as far from each other as they can. Particles of colloidally unstable dispersions collide and stick closely together, and so a more or less loose physical network of adhered particles forms in dense systems, since a large amount of dispersion medium is entrapped in the network of particles. This structure shows a certain resistance against mechanical forces. The formation and the mechanical properties of a particle network in coagulated colloidal dispersions can be investigated by means of rheology [34]. In general, stable suspensions show ideal liquidlike, Newtonian flow behavior, while the appearance of plastic character refers to the network formation of aggregated particles. Flow curves of plastic, pseudoplastic systems always show a linear part over the higher range of shear rate. According to the Bingham model [34] the gradient of this line is the plastic viscosity (η_{pl}) of a plastic body and the value obtained when the line is extrapolated to zero shear rate is the Bingham yield value (τ_{B}).

The effect of electrolytes on the flow behavior of sodium montmorillonite dispersions has been investigated [35–37]. At salt concentrations below the coagulation value, the influence of the electric double layer on the mobility of particles (secondary electroviscous effect) [36, 37] or a combination of random coagulation and particle orientation effects [35] determines the flow behavior of montmorillonite suspensions. Dispersions with solid content above about 3% became gel-like with the appearance of a yield value and viscoelastic properties [36] and tixotropy [35]. In this low ionic strength region the yield value and the viscosity of 2% sodium montmorillonite suspensions decreased to a minimum at about 2–20 mM NaCl with increasing salt concentration owing to the narrowing of diffuse ionic layers [36]. The formation of a stronger particle network with a significant yield value in 3% sodium montmorillonite suspensions containing 2 and 10 mM NaCl cannot be expected even at low pHs.

The formation of a heterocoagulated particle network in mixed montmorillonite and magnetite suspensions, however, is highly probable at pH $\sim$ 4, where magnetite particles are positively charged. It was supposed that small oxide particles act as adhesives between clay lamellae, increasing significantly the number of bondages between clay mineral plates. Therefore, a magnetite-concentration-dependent increase in the yield value of composite suspensions can be expected. This assumption proved to be valid only up to a certain limit of magnetite content in the mixed systems containing 0.01 M NaCl as shown in Figs. 6 and 7. Above this limit, however, the heterocoagulated structure formed becomes significantly weaker. All the suspension contained 3 g/100 g montmorillonite and the strongest particle network in the composite systems formed at 0.2 g/100 g magnetite content (Fig. 7). The mass ratio of oxide to clay mineral is 1:15 at the maximum of the yield value. The variation in the Bingham yield value (τ_B) with pH for illite iron oxide complexes with different iron oxide contents has been published [20]. Taking the data from Ref. [20] at pH ~ 4, the function τ_B versus iron oxide content with a maximum at 1:20 oxide to clay mineral ratio can be plotted. The trend of these data is exactly the same as that in the present work for montmorillonite magnetite systems (Fig. 7). Accounting for the charge balance of permanent negative montmorillonite (0.56 mmol/g) and variable positive magnetite (about 0.15 mmol/g as seen Fig. 1.) charges at pH ~ 4 at that particular composition where the strongest particle network forms, it seems that the number of negative basal plane charges is about 50 times larger than that of positive charges on the oxide surface. It is obvious that a large charge excess of clay mineral platelets exists in the strongest heterocoagulated network, in which the number of oxide particles adhered to clay mineral lamellae is optimal. This structure cannot be assigned to a simple balance between opposite charges. The coverage of montmorillonite plates with magnetite particles increases with increasing magnetite-to-montmorillonite ratio, resulting in a significant stabilization of mixed systems at the given electrolyte concentration (10 mM NaCl) which is only a heterocoagulation threshold, but is significantly lower than the salt concentration required for homocoagulation of magnetite particles ($c_{coag} = 150$ mM).

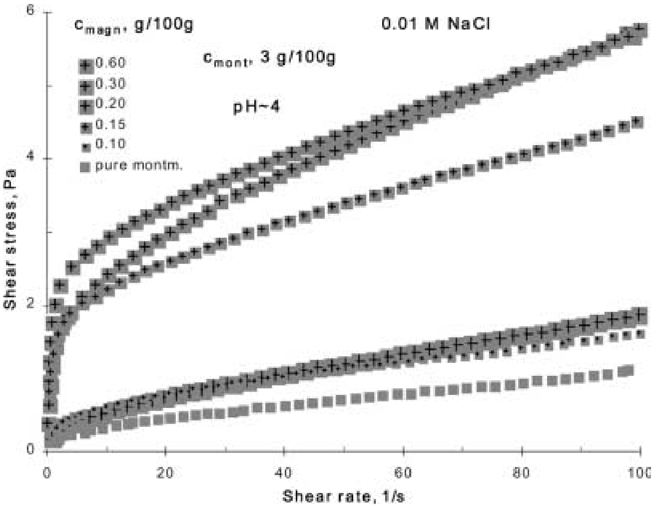


Fig. 6 Flow curves of mixed montmorillonite magnetite suspensions containing 0.01 M NaCl at pH ~ 4

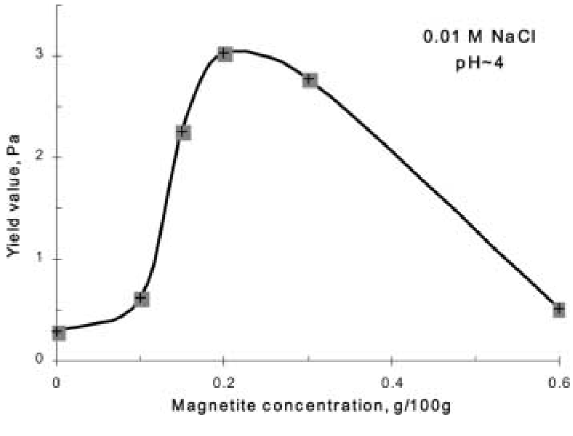


Fig. 7 Dependence of yield value on magnetite content in mixed montmorillonite–magnetite systems

The most interesting experimental fact of the rheological investigation of composite systems was that at low ionic strength, below the heterocoagulation threshold, there was no sign of particle network formation in mixed suspensions of oppositely charged particles. Flow curves of mixed montmorillonite–magnetite suspensions at 0.002 M NaCl (Fig. 8), independently of the presence of oppositely charged particles, display rather Newtonian flow character, which occurs only in colloidally

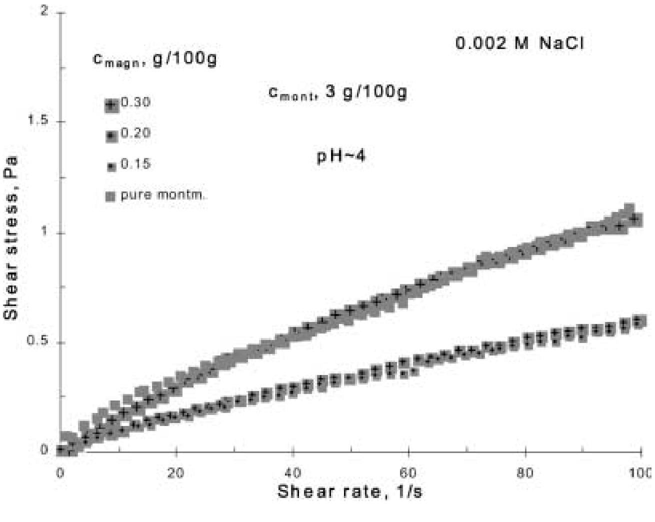


Fig. 8 Flow curves of mixed montmorillonite–magnetite suspensions containing 0.002 M NaCl at pH ~ 4

stable systems. This experimental fact provides indirect proof for the interaction between oppositely charged particles, which has to be repulsive under the given condition. This unique finding is in good harmony with the results of coagulation kinetics measured in the mixed systems at a NaCl concentration below 5 mM by means of DLS (Fig. 5, center).

Conclusion

In accordance with any intuitive expectation, we can conclude that the formation of fractal aggregates owing to the Coulombic interaction between either the oppositely charged parts of montmorillonite lamellae or the oppositely charged particles of mixed montmorillonite–magnetite suspensions occurs only if the pH of the aqueous medium is acidic, where the amphoteric surface sites are protonated, i.e. positively charged surfaces develop. The ionic strength dependence of the particle–particle interaction of this kind is not simple from a theoretical point of view. It is an experimental fact that the edge-to-face heterocoagulation of montmorillonite lamellae occurs above a threshold salt concentration; its interpretation, for example, by means of the spillover of a diffuse double layer on the basal plane [27], is not widely accepted.

Our noteworthy experimental finding is that the random collision of oppositely charged clay mineral and iron oxide particles in both dilute and dense aqueous suspensions does not necessarily result in particle adhesion and that the oppositely charged surfaces can attract each other only above a heterocoagulation threshold of electrolyte concentration. It seems to be inconsistent with any intuitive expectation. Coagulation kinetics and rheological investigation of mixed clay mineral and magnetite suspensions at pH ~ 4 proved the presence of stable mixed sols at 2 mM NaCl and the existence of a heterocoagulation threshold of about 10 mM NaCl. It is possible that montmorillonite–iron oxide mixed systems at low salt concentration give the first experimental evidence for repulsion between oppositely charged surfaces as predicted theoretically by Gregory on the basis of DLVO forces. However, additional short-range (Born and hydration) repulsions, so-called non-DLVO forces, are also probable in the iron oxide and clay mineral systems in the presence of alkali halides.

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