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ORIGINAL CONTRIBUTION

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Novel features of smectite settling

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Abstract Aqueous suspensions of Ca or Mn montmorillonite were left to settle in cylinders ranging in diameter, D, from 1.0 to 7.7 cm after magnetic stirring and/or manual tumbling. Changes in height, H, of the interface between the turbid suspension and the clear supernatant were recorded visually as a function of time, T. In the absence of added electrolytes the H/T plots were approximately linear, but after addition of electrolytes they assumed an inverse S shape. An initial latency period was followed by a time of rapid settling and, finally, by slow compaction of the sediment until no further changes occurred. Within a limited range of concentration the latency period increased exponentially with decreasing D. It increased with increasing height of the settling columns, H_i, and with increasing concentration of the suspensions. With Mn montmorillonite the rate of fast settling also depended on D. The parameters of the H/T plots depended on the prehistory of the samples. Fairly reproducible results were obtained in duplicates within any one series of experiments, but changes in the pretreatment altered the parameters. Treatment of the suspensions with an ultrasonic tip changed the settling process drastically. Sedimentation became very slow, the effects of D and H_i on the latency period were reversed and the final sediment volume increased. The effects of vessel diameter on sedimentation observed are much greater than any wall effects described in the literature. The changes observed after ultrasonication of the suspensions, particularly the reversal of the effects of D and H_i on the settling process, are novel features.

Keywords Settling · Smectite · Vessel parameters · Ultrasonication

Introduction

The process of sedimentation of dispersions of fine particles is of considerable theoretical and practical interest and has therefore been extensively researched for many years. New developments in equipment and the possibilities offered by computer modeling have provided a new impetus, as evidenced by many recent publications and various review articles [1, 2, 3, 4].

Sedimentation of colloidal suspensions can occur in different ways:

1. The particles settle individually under gravity, without flocculation. Particles of different size and density settle at different rates.
2. Two or more particles interact on collision to form floccules. These grow in the course of settling, generally by fractal growth, and the floccules settle individually.
3. The particles join to form a volume-filling transient network. These transient arrangements are stable for a period of time (the latency or induction period), but subsequently collapse spontaneously. A well-defined

interface develops, which separates a clear supernatant from a subsiding suspension.
4. At higher concentrations, some suspensions form stable gels and no sedimentation occurs.

Model experiments with colloidal suspensions reported in the literature were most frequently performed with uncharged, spherical particles of uniform size, such as latex spheres. It is still unclear which of the many mathematical models can be applied to nonideal systems such as those containing either nonisometric or multiple particles [4]. We studied settling of the clay mineral montmorillonite. Clay minerals are nonspherical, polydisperse and carry permanent as well as pH-dependent variable charges. It seems improbable that a valid mathematical model can be developed at present for systems as complex as clay suspensions. Indeed, despite the abundance and importance of clays, in general, and smectites, in particular, their settling mechanism is very incompletely understood. It is therefore important to observe the details of the settling process experimentally, as a possible basis for future modeling. The present study is geared to that end.

Montmorillonite saturated with the divalent ions Ca^{2+} or Mn^{2+} was selected for the investigation. Ca montmorillonite was chosen because of its natural abundance and its industrial applications. The choice of Mn montmorillonite was fortuitous, but it proved to be a convenient model substance. Various factors affecting the settling process in aqueous suspension were studied, including the addition of electrolytes, the parameters of the containing vessels, the concentration and pH of the suspensions and the effects of different pretreatments, in particular ultrasonication.

Experimental

Materials

To prepare monoionic montmorillonite samples of the fine fraction of Clay Mineral Standard, Upton, Wyoming, no. 25 were saturated with manganese or calcium by repeated saturation with 1 N $MnCl_2$ or $CaCl_2$ solution, respectively. Coarse particles were discarded. The fine fractions were washed with deionized water until no reaction with $AgNO_3$ occurred. No impurities were detected in the X-ray diffraction patterns. Electron microprobe analysis established that the samples were, indeed, monoionic Mn and Ca montmorillonite, respectively.

Particle size analysis, performed with a GALAI-CIS1 instrument, showed that the particles were not of uniform size. The equivalent diameter of all the particles was less than 2 μm, and about 90% had a diameter of less than 1 μm.

Method

Mn and Ca montmorillonite suspensions of different concentrations were prepared. Portions of these suspensions, similarly pretreated, were allowed to settle in a series of glass cylinders of different diameter under ambient conditions. Experiments were performed without and with addition of known amounts of $MnCl_2$ or $CaCl_2$. Pretreatment ranged from brief tumbling to protracted magnetic stirring and/or exposure to a 50 W standard laboratory ultrasonic bath. Because the kind of pretreatment strongly affected the parameters of the settling process, great care was taken to ensure that the suspensions in any one set of experiments experienced the same pretreatment.

The settling curves show the changes in the height, H, of the supernatant with time, T. Unless otherwise stated, the initial height of the columns, H_i, was 9 cm.

Treatment with an ultrasonic tip: portions (500 ml) of the suspensions were ultrasonicated, using a 1.2-cm ultrasonic tip with vibrations of 20 kHz. The samples were exposed to different doses of vibration energy, as specified in the text.

Results

Sedimentation of montmorillonite suspensions

Sedimentation of Ca or Mn montmorillonite in the absence of added electrolyte was very slow. Particles or floccules settled individually under gravity with a concentration gradient increasing towards the bottom of the cylinders. Plots of H versus T were approximately linear and independent of the diameter, D.

Addition of small amounts of salt to the system not only accelerated sedimentation, but changed the pattern completely. Plots showing changes of H with T assumed an inverse S shape of the type shown in Fig. 1. In the first stage, the latency period (also termed induction period or period of delayed settling), the suspension occupied the entire volume of the column and little settling was observed. This was followed by a time of rapid sedimentation and finally by a stage of slow settling, until no further changes were detected in the voluminous sediments. The surfaces of the final sediments frequently resembled the crater of an extinct volcano, which introduced a small error in the accuracy of the measurements of the final height, H_f.

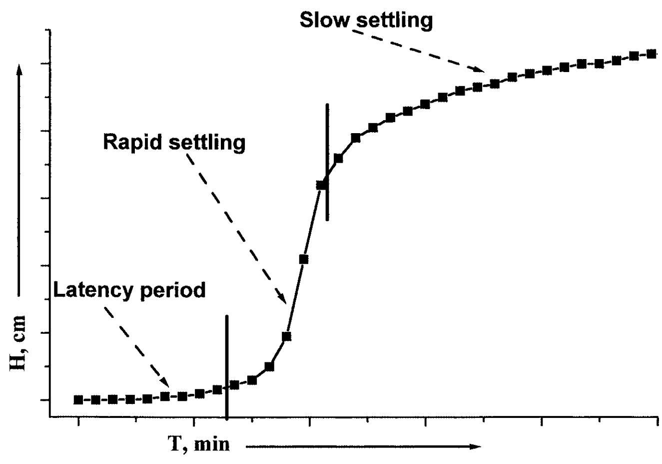

Fig. 1 Schematic plot of the height of the supernatant, H, against time, T

After the initial period of delayed sedimentation a well-defined boundary separated the clear supernatant liquid from the turbid suspension. During the settling process horizontal stratification developed throughout the lengths of the columns (Fig. 2). The lenticular strata with higher concentrations of suspended clay did not extend throughout the entire cross-section of the settling columns. The regions of lower concentration were interconnected by tortuous channels. Stratification frequently persisted even in the final sediments. The serrations observed along the edges of the cylinders are pockets of water or very dilute suspension.

Within a limited range of concentration (see later) these features were common to all the suspensions studied, but, as in most processes involving colloids, the various parameters of the settling plots are very sensitive to elusive factors affecting the system. Settling plots obtained in different series with similar pretreatment were not entirely reproducible and only general trends could be compared; however, these trends were consistent and reproducible, although within any particular set of about ten cylinders one or two occasionally diverted from the general pattern and were disregarded. Replacement of a glass cylinder by a plastic one of the same diameter did not affect the parameters of the settling curves.

The parameters of the settling plots are sensitive to various factors. Some of these are detailed in the following.

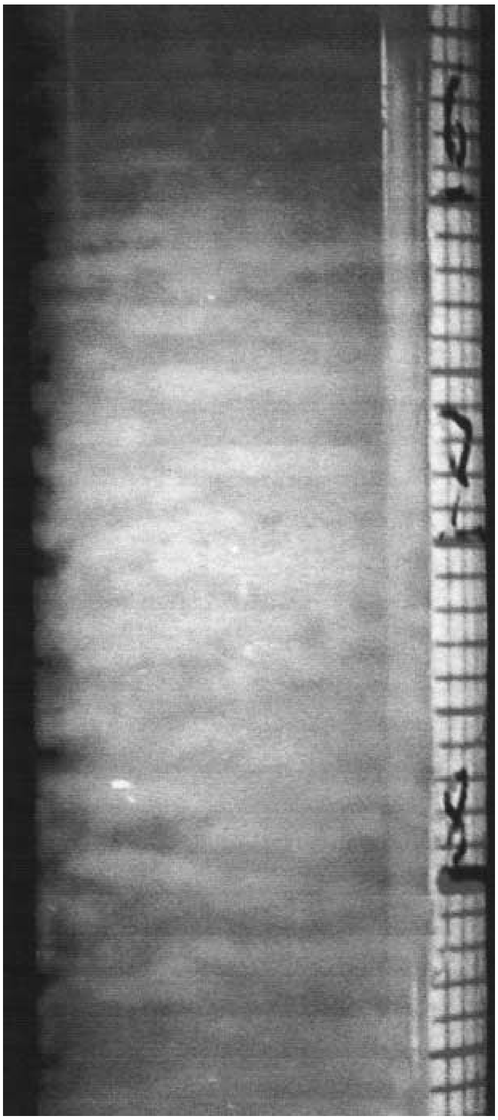

Fig. 2 Horizontal lenticular stratification of subsiding 2.68 g/l suspension of Mn montmorillonite (+0.4 g/l $MnCl_2$)

Effect of the diameter of the cylinder

H/*T* plots for the settling process of a suspension of Mn montmorillonite with added electrolyte are shown in Fig. 3. The suspension was stirred magnetically for 2 h before transfer to the cylinders, which ranged in

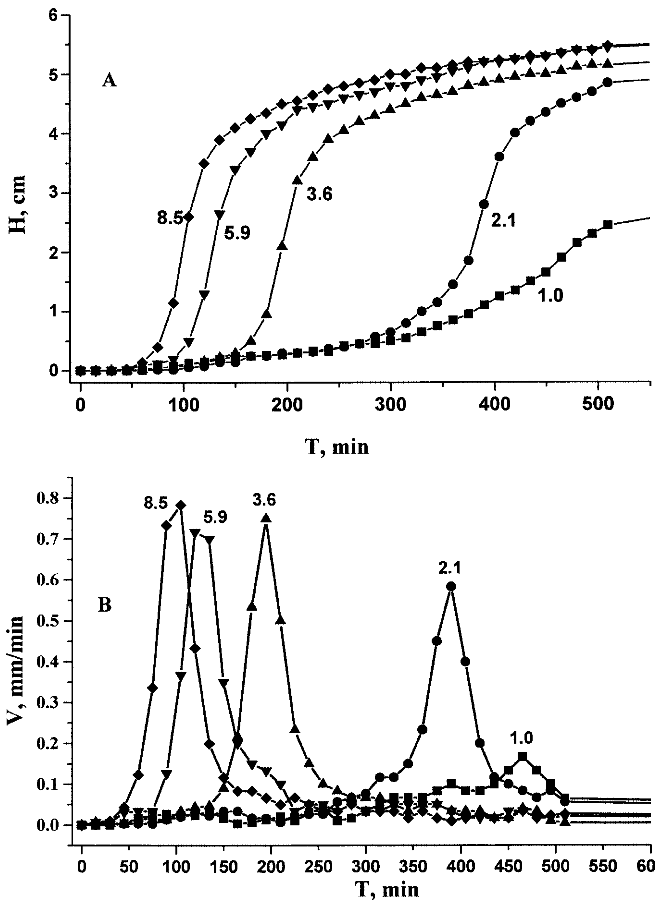

Fig. 3A,B 3.76 g/l suspension of Mn montmorillonite (+0.4 g/l $MnCl_2$) in cylinders with *D* (cm) as shown, $H_i = 9$ cm. **A** *H*/*T* plots; **B** plots of rate of settling, *V*, versus *T* derived from **A**

diameter from 1.0–8.5 cm. The changes in the rate of settling, V, with T derived from these plots are presented in Fig. 3B.

The effect of the diameters of the columns on the settling process is striking. In each set of experiments, after different pretreatments of the suspension, the latency period increased exponentially with decreasing D. The rate of settling during the rapid stage decreased with D, but this effect was restricted to cylinders with small D and was more pronounced with Mn than with Ca montmorillonite. The final, slow stage of settling was similar in all the cylinders of any given series and the sediments tended towards the same final concentration.

Effect of the column height

In the experiments described so far all the cylinders were filled to a height of 9.0 cm. In another set of experiments, cylinders of the same diameter were filled to different heights. The corresponding H/T and V/T plots are shown in Fig. 4. It is evident that the latency period was more protracted for the taller columns, but the maximum rate of fast settling ultimately attained was greater. Stratification was observed throughout the entire columns, whatever the initial height. In the final steady state the volume of sediment per weight of solid was similar in all the columns.

Effect of the initial concentration of the suspension

Experiments were carried out with suspensions of Mn montmorillonite of three different concentrations, 6.74, 3.76 and 2.68 g/l respectively. The H/T plots obtained with the most concentrated suspension had the same inverse S shape as those observed with more dilute suspensions, but did not show similar systematic changes with D. Reducing the concentration from 3.76 to 2.68 g/l accelerated the settling process, both by reducing the latency period and by increasing the rate of rapid settling (compare Fig. 5A, B with Fig. 3A, B). Very dilute suspensions did not settle at a measurable rate and did not give rise to a well-defined interface.

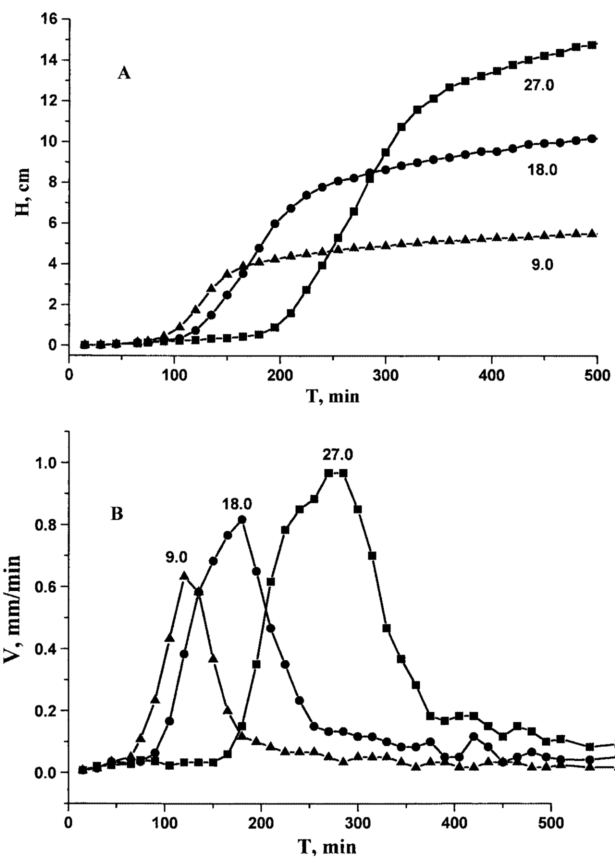

Fig. 4A,B 3.76 g/l suspension of Mn montmorillonite (+0.4 g/l $MnCl_2$) in cylinders with $D=3.6$ cm and H_i as shown. **A** H/T plots; **B** V/T plots derived from **A**

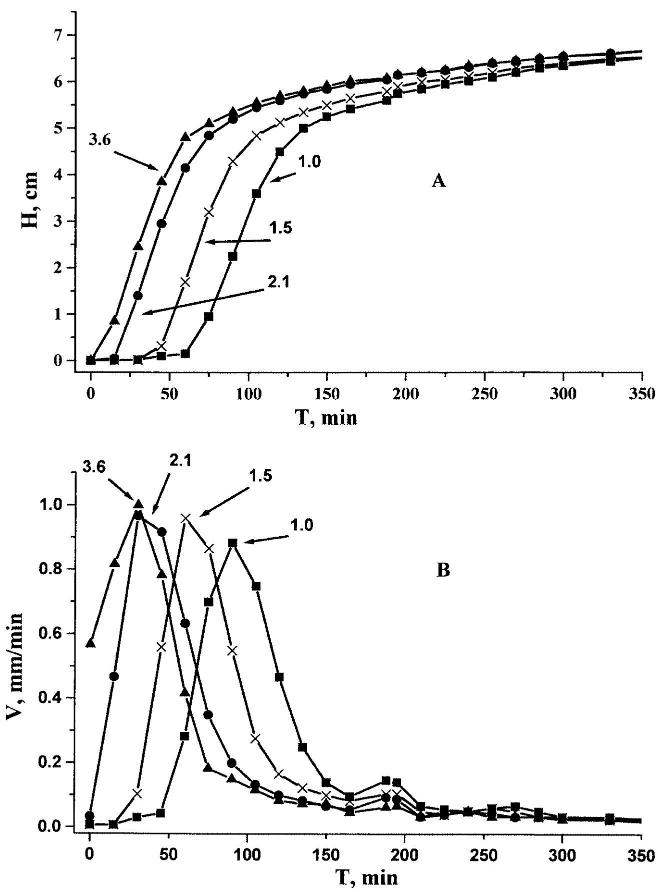

Fig. 5A,B 2.68 g/l suspension of Mn montmorillonite (+0.4 g/l $MnCl_2$) in cylinders with D (cm) as shown, $H_i=9$ cm. **A** H/T plots; **B** V/T plots derived from **A**

The H/T plots obtained with a 3.0 g/l suspension of Ca montmorillonite were somewhat erratic, but the settling curves of suspensions of lower concentration (1.8 and 1.5 g/l) showed systematic changes with D, similar to those observed with Mn montmorillonite at higher concentrations.

Effect of pretreatment

The problem of obtaining reproducible results in experiments with colloidal suspensions is well known. None of the pretreatments attempted, which comprise more or less protracted magnetic stirring and/or manual tumbling and/or immersion in an ultrasonic bath, led to a homogeneous suspension, on the one hand, and to entirely reproducible results, on the other. The best reproducibility was obtained with samples that were stirred and subsequently gently tumbled, as was also observed by previous investigators in studies of other colloidal systems [5]. However, although the parameters of the H/T plots, and in particular the duration of the latency period, varied with the pretreatment, the shapes of the curves were similar and the trends observed were consistent.

Effect of pH

H/T plots for suspensions of Ca montmorillonite at three different pH values are presented in Fig. 6. The H/T plots preserved their inverse S shape throughout. Lowering the pH caused a significant increase in the latency period. At any given pH, the latency period increased with decreasing D, much more at lower than at higher pH. The maximum rate of settling decreased from about 7.0 mm/min at pH 8 to 5.0 and 2.6 mm/min at pH 5.0 and 1.5, respectively. The final sediment volume increased with decreasing pH (see later).

The effects of changing the pH values were reversible. After reverting to a pH of 5 from either the low or the high pH, the settling process returned to its original form. Whatever chemical changes may have occurred in the system, these did not permanently affect the settling behavior of the suspensions.

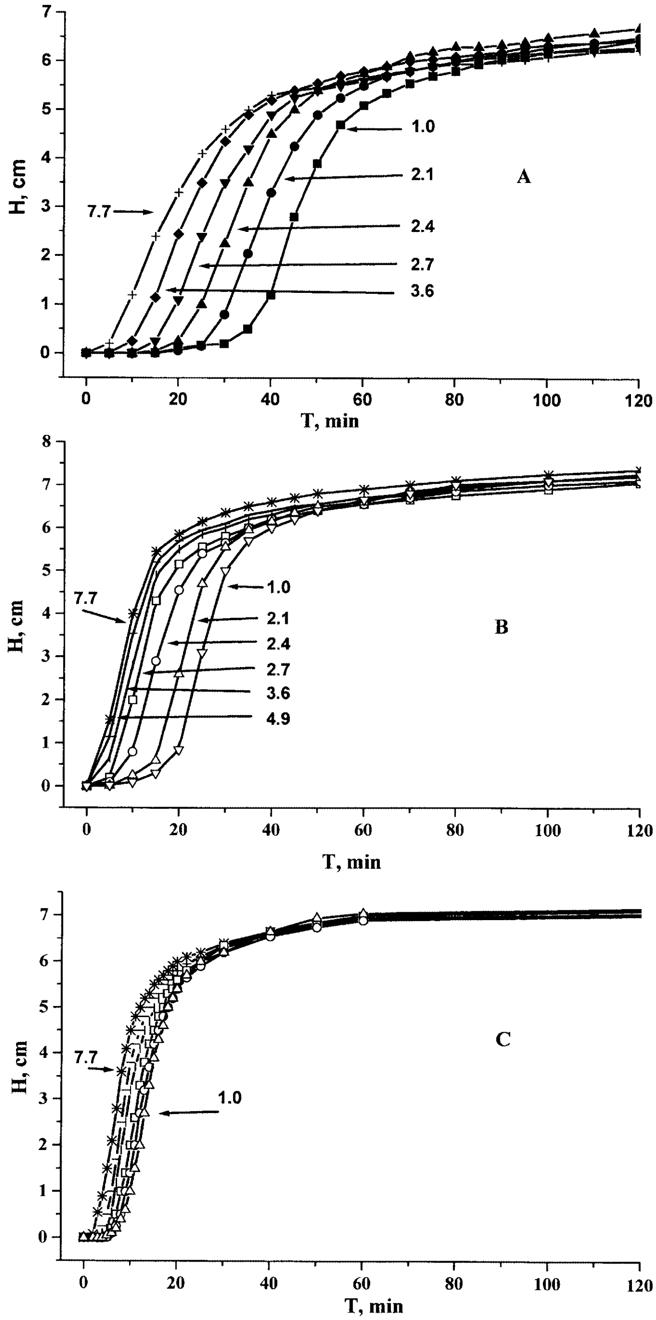

Fig. 6A–C H/T plots for a 1.5 g/l suspension of Ca montmorillonite (+0.8 g/l $CaCl_2$) in cylinders with D (cm) as shown, $H_i = 9$ cm. **A** pH 1.5; **B** pH 5.0; **C** pH 8.0

Sediment volume

The final concentration, c_f, of the sediments varied considerably in different series. After stirring or tumbling of the suspensions the values ranged from 18 to 9 g/l and from 14.1 to 8.7 g/l for Mn and Ca montmorillonite, respectively. No correlation was obtained between the final sediment volume and D, H or the pretreatment of these suspensions. An inverse correlation was, however, observed between the initial concentration, c_i, of the suspensions and the normalized final concentration, c_f/c_i. Plots of c_f/c_i versus c_i for all the stirred or tumbled suspensions of either Mn or Ca montmorillonite at pH 5–5.5 can be fitted by linear curves of the type $y = a + bx$. The average values for Mn montmorillonite, based on 21 independent series of measurements comprising a total of 126 individual settling experiments, are $a = 5.1 \pm 0.5$ and $b = 0.3 \pm 0.1$. The corresponding values for Ca montmorillonite, derived from 11 independent series of measurements comprising 127 individual experiments, are $a = 7.6 \pm 0.6$ and $b = 1.1 \pm 0.2$. The experimental variables include the diameters and heights of the cylinders, the concentration of the suspensions and different pretreatments.

The average values of c_f/c_i for a suspension of Ca montmorillonite of initial concentration 1.5 g/l at pH values of 1.5, 5.5 and 8.5 were 5.9, 6.4 and 6.9 g/l, respectively.

Ultrasonic treatment

A dramatic change in the effect of D on the course of sedimentation was observed after the suspensions were exposed to an ultrasonic tip. After one 50-kJ treatment of 500 cm^3 of a 2.68 g/l suspension of Mn montmorillonite, the entire settling process became much slower. Sedimentation was fastest in the cylinder with smallest D, but the rest of the series did not follow a regular pattern. However, after additional ultrasonic treatment with the same energy, a consistent correlation was observed between D and the length of the latency period. In complete contrast to the results obtained with corresponding suspensions that had only been stirred and/or tumbled, the latency period after ultrasonication increased with increasing D. The rate of the entire process decreased by 1–2 orders of magnitude (Figs. 7, 8).

Repeated ultrasonication also inverted the effect of the different heights of the settling columns on the latency period. This decreased with the height of the settling column, in contrast to stirred or tumbled suspensions. Similar effects were observed with suspensions of Ca montmorillonite, but the ultrasonic energy required to achieve these results was considerably greater.

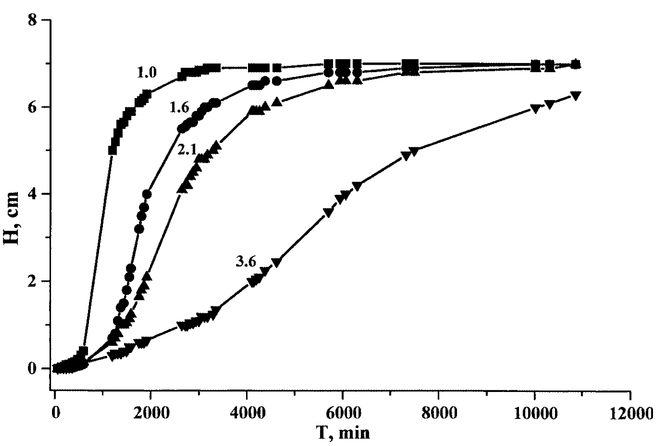

Fig. 7 H/T plots for a 2.68 g/l suspension of Mn montmorillonite (+0.4 g/l $MnCl_2$) after two 50-kJ ultrasonic treatments, in cylinders with D (cm) as shown, $H_i = 9$ cm

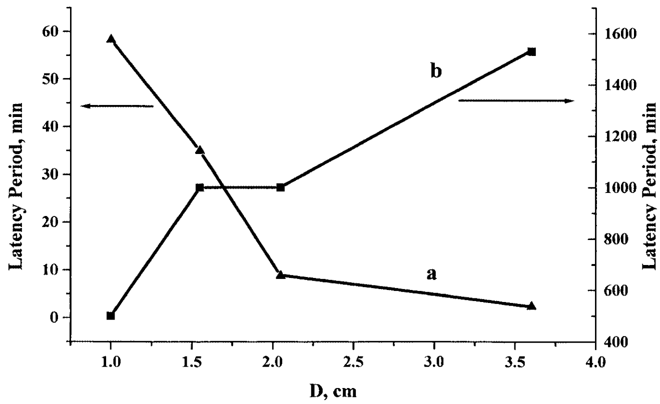

Fig. 8 Plots of latency period versus D for 2.68 g/l suspensions of Mn montmorillonite (+0.4 g/l $MnCl_2$): **a** after 20-h magnetic stirring and **b** after ultrasonication (50 kJ twice). Note the different time scales for **a** and **b**

The sediments formed after ultrasonification were more voluminous than those obtained from stirred or tumbled suspensions. Thus, c_f/c_i for an ultrasonicated 3.1 g/l suspension of Mn montmorillonite at pH 5.5 was 3.6 g/l; for an ultrasonicated 2.5 g/l suspension of Ca montmorillonite it was 4.4.

The changes effected by ultrasonication were reversed on storage of the suspensions, but this required several days.

Discussion

H/T plots of an inverse S shape have frequently been reported in the literature. Indeed, according to Poon et al. [6] they are almost ubiquitous for weakly flocculated suspensions. However, the present series of experiments exhibits some unusual features. The effect of vessel diameter exceeds any described in the literature. The principal effect was observed in the first stage, the latency period. This decreased with increasing D with samples that had been magnetically stirred or gently tumbled, but increased with D with samples after treatment with an ultrasonic tip (Fig. 8). These features were only observed in the presence of electrolytes. In the absence of electrolytes the settling plots of the smectites were approximately linear and independent of D.

A reduced rate of settling in tubes of small diameter owing to a "wall effect" is a well-known phenomenon. This effect is attributed to friction, which enhances the stability of the transient structure in tubes of smaller diameter. However, the predicted magnitude of this effect is very small. For example, the rate of settling of particles sedimenting under gravity according to Stokes' law in unbounded vessels and in a cylinder of diameter 0.5 cm is expected to differ by no more than 0.04–4% for particles of 1- and 100-μm diameter, respectively [7]. For a flocculated suspension of kaolinite of volume concentration 0.032, which has a settling curve of inverted S shape, the error introduced by using a vessel of 6-cm diameter should not exceed 4% [8].

Glasrund et al. [9] observed differences between the settling curves of iron oxides in tubes of 1.0 and 2.0-cm diameter, when the concentration of the suspensions was high (3.3% by volume). At low concentrations the effect of vessel diameter was negligible. The settling curves of the magnetic and nonmagnetic samples differed, although they had the same morphology. Allain et al. [10] did not observe a "wall effect" for calcium carbonate settling in tubes of only 1.2-cm diameter. Holdrich and Butt [5] found no difference between calcite or aragonite settling in tubes of 6.5- and 14-cm diameter, whereas similar experiments with talc showed a significant effect of vessel diameter on the process. On the basis of a study of settling of a well-aggregated clay, Lovell and Rose [11] recommended a minimum tube diameter of 4.5 cm to avoid retarded settling. Other investigators also reported effects of vessel diameter on the sedimentation of dilute suspensions without, however, providing detailed results [6, 12].

The literature data suggest that the significant effects of vessel diameter at D values of several centimeters cannot be attributed to "wall effects". Comparison between the settling of calcium carbonates and talc [5] or between magnetic and nonmagnetic iron oxide [9] suggests that the effect is due to a material characteristic of the sedimenting species. This is in agreement with the results of the present study and is illustrated by the effect of pH on the settling process. It is expected that montmorillonite particles form edge-to-face associations at low pH values, whereas arrangements of tactoids of parallel platelets predominate when the pH is raised [13]. It is reasonable to infer that the bulky flocs formed at low pH give rise to a more stable transient gel, which is firmly anchored in the cylinders, particularly in those of smaller diameter. When the transient gel collapses, flocs of lower density are formed in the lower pH range, accounting for the slower rate of settling and the larger sediment volume.

The reversal of the effects of D on sedimentation of montmorillonite observed after ultrasonic treatment further confirms that wall effects cannot explain the differences due to vessel diameter, but that these must be attributed to the structure of the transient phase.

To explain the effect of D on the latency period, it is necessary to understand the phenomenon of delayed sedimentation, but, unfortunately, no satisfactory explanation has yet been proposed. Poon et al. [6] pointed out the apparent paradox in the behavior of the transient structures, which are stable for a period of time and then collapse under their own weight. They invoked a "healing ability" of the structure during the transient stage, which they attributed to the development of tendrils connecting the particles. Collapse occurs when the self-healing ability is lost. The nature of the connecting tendrils was, however, not revealed. Allain et al. [10] observed a period of slow settling followed by rapid collective settling with aqueous suspensions of calcium carbonate. The beginning of rapid settling coincided with the appearance of a fracture within the suspension, along which water could flow upwards. Glasrund et al. [9] attributed channeling to the action of air bubbles in suspensions of iron oxides in oil. It appears from the present results and from the literature data that the effect of D on the settling process is a function of a material characteristic of the suspended matter. With the samples of montmorillonite studied this characteristic developed only after addition of electrolyte to the suspensions. It was affected by changes in pH and by various pretreatments and was drastically changed by ultrasonication.

Like the container diameter, H_i of the settling column affected the settling process. The latency period and the maximum settling rate attained increased with H_i and the subsiding suspensions were stratified. These observations also indicate that a process of self-organization occurred. After ultrasonication the latency period decreased with column height, reflecting a change in structure of the transient phase.

H/T plots of inverse S shape showing systematic changes in parameters with D were only observed within a certain range of concentration of the suspensions, which differed for the two clays. Within that range, sedimentation was accelerated by decreasing the concentration of the suspension. This is compatible with Stokes' law, which predicts a reduction in the uniform velocity of settling with concentration [14], and with the empirical equations for monodisperse systems given by Richardson and Zaki [15]. An increase in the rate of the settling process with decreasing concentration of the suspension has been reported in many studies [11, 16, 17], including those of polydisperse systems which show delayed sedimentation, for example, kaolinite or Na montmorillonite in the presence of electrolytes [8, 18]. The effect was attributed to the greater pore volume of the more dilute suspensions, which facilitates sedimentation.

The concentration of the final sediment decreased with increasing concentration of the initial suspension, i.e. the final sediments were more voluminous, the higher the concentration of the suspensions. It is reasonable to assume that the settling fragments are larger in the more concentrated suspensions, which have a smaller pore volume. Smaller particles pack more efficiently than larger ones, leading to a higher final concentration of the sediment. The observation that the final sediment volume did not vary significantly with either the container diameter or the column height is compatible with this interpretation.

The effect of increasing pH of the suspension on the final sediment volume also conforms to this concept. At low pH values, basal planes and edge faces of the clay carry opposite charges and therefore form more voluminous aggregates. With increasing pH, the edge charges become negative and attraction between basal and edge surfaces changes to repulsion. This reduces the stability of the transient stage, the latency period is decreased and the rate of rapid sedimentation is increased. Greater repulsion leads to smaller aggregates, which pack more efficiently, accounting for the smaller sediment volume observed at higher pH.

According to this interpretation the decrease in the concentration of the final sediment caused by ultrasonication of the suspensions indicates that these transient gels break up into voluminous fragments, which do not pack closely on settling. The long induction periods and low settling rates testify to the stability of the transient gels.

Conclusions

The data obtained in this study are insufficient to provide a detailed model of the settling processes. Very tentatively the following concepts may be suggested.

At the beginning of the settling experiments a transient space-filling network was formed. This underwent internal reorganization, without a significant overall change in volume, until interconnected water channels developed. This is a probabilistic process. The probability of opening a water channel is a function of the nature of the suspensions, which is affected by their prehistory. The rate of expulsion of water is limited by the rate of reorganization of the water–gel system. When water was expelled, by a process akin to syneresis, lenticular horizontal strata of concentrated clay suspensions were formed. These subsided slowly, until the rate of sedimentation was reduced and finally terminated by restricted diffusion of water. The process is based on self-organization of the suspensions throughout the entire available volume.

These concepts leave many questions unanswered, including the effects of D and H on the settling process and the changes caused by ultrasonic treatment. Possible chemical changes cannot account for either the effects of the ultrasonic treatment or those caused by altering the pH of the suspensions, because these effects were reversible on storage. Further research is required to interpret the novel features of the sedimentation of colloidal clay suspensions reported in this study.

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