Studies on kinetic behaviour of colloidal dispersion of Mg-Al hydrotalcite-like compounds

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Hydrotalcite-like compounds (HTlc) have a layered structure similar to that exhibited by natural Mg(OH)2, also known as brucite. The permanent positive charge in the layers has been acquired by isomorphic substitution. In recent years, there has been tremendous interest in the preparation, characterization and properties of the HTlc, because the HTlc may be widely utilized in many fields such as catalysts, antacids, the treatment of the waste water, antiscaling agents, medicine, antionic exchangers, and rheology modifiers. In industrial applications, the phenomena of aggregation and stabilization of colloidal dispersions are of great importance and are mainly determined by parameters such as particle size and density, the surface chemistry, the water chemistry, and the hydrodynamic flow rates.

The HTlc are the only known family of layered solids with permanent positive charge and rare in the nature but relatively simple and cheap to prepare in the laboratory. Extensive studies on the HTlc preparation and on the chemical properties of this kind of material have been carried out. However, studies on the aggregation kinetics of this permanent positively charged and plate-like particle model has received little attention. We report herein, the colloidal stability of Mg-Al HTlc colloidal dispersion at various KCl concentrations (C_{KCl}), investigated by dynamic light scattering (DLS), electrophoresis and interaction energy calculations.

Materials and Methods

The Mg-Al HTlc samples used were synthesized by the co-precipitation method. The chemical composition of the HTlc was determined by chemical analysis to be Mg_{0.18}Al_{0.82}(OH)_{3.52}Cl_{0.44}. With acid-base potentiometric titration, the point of zero net charge (pH_{ZPC}) of the Mg-Al HTlc was measured to be 12.30, and its permanent charge density (q_p) was 2.78 mmol/g (4.40 C/m^2). A near-monodisperse particle distribution was obtained by sequential centrifugation, decanting and filtering. Particle size was determined using a JEM-100cxII model transmission electron microscope. Average platelet diameter, here taken as the statistical average of several measurements, was 30±5 nm, as shown in Fig. 1. The mean hydrodynamic diameter (d_{mean}), determined by the method of DLS, was equal to 72.6 nm with the relative standard deviation of about 0.15.

Total solids concentration of Mg-Al HTlc dispersion was determined by gravimetric analysis. The specific density of Mg-Al HTlc was here assumed to be 2.15. Average particle concentration was 0.241±0.009 kg/m^3. The particle number

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concentration was estimated to be \((5.55\pm0.26)\times10^{10}\) particles per ml for the diluted dispersion used in all aggregation experiments. The pH of dilute dispersions were adjusted to 9.6 and measured directly before a sample was placed in the testing cell.

All aggregation experiments were performed at 25°C. Aggregation was induced by adding known amounts of KCl electrolyte solution to the prepared particulate dispersion to achieve a final KCl concentration ranging from 20-300 mM. Observed differences in particle aggregation rates can therefore be ascribed to differences in solution chemistry, i.e., ionic strength.

The particle aggregation rate for the initial stage of the aggregation process was estimated using DLS. DLS measurements were performed using an apparatus consisting of a BI-200SM goniometer (version 2.0), a BI-9000AT digital autocorrelator (Brookhaven Instruments Corp., Holtsville, NY), and a ILT5500BSL argon-ion laser (IOI Technology Ltd., Shanghai, China). All data were gathered at 25°C, a scattering angle of 90°, and a wavelength of 488 nm. The data were analyzed with the Brookhaven BI-9000AT program, which employs the method of cumulants to determine the mean hydrodynamic diameter \((d_{\text{mean}})\) of the particle via the Stokes-Einstein equation. The polydispersity from cumulant analysis was around 0.1 prior to adding electrolytes and was not expected to affect the results to a significantly larger degree than other experimental errors\(^9\). For analysis purposes, the dispersion can be considered monodisperse\(^9\). Experiments were repeated several times to ensure data reproducibility. Measurements of the hydrodynamic size within a single day varied about 1.1% on average, while measurements from one day to the next varied about 0.7% on average. Reported values are averages taken over several such experimental runs.

Electrophoretic mobility \((\mu)\) of the HTlc dispersion prepared for the aggregation experiment was measured on ZetaPALS (Brookhaven) apparatus thermostated at 25°C. The \(\zeta\)-potentials at the shear plane were estimated from \(\mu\) by the Smoluchowski relationship.

### Results and Discussion

#### Aggregation

At different \(C_{\text{KCl}}\) in the Mg-Al HTlc dispersions, three different regimes can be observed. In these regimes the phenomena of stability or aggregation upon addition of electrolyte are characterized as mostly stable, slow aggregating and fast aggregating, respectively.

**Region I: \(0 < \text{C}_{\text{KCl}} < 20 \text{ mM}\)**

In Region I (see Fig. 2), the majority of particles, which do not form aggregates, diffuse freely and the colloidal dispersions can be considered as stable. The \(d_{\text{mean}}\) value of particles initially decreases slightly with ionic strength and above 10 mM increase slowly. The same results were found after 4 months for the repeated DLS experiments.

The variation of hydrodynamic size with ionic strength can be interpreted by including diffuse layer effects in the particle size calculation. Polarization of the ion cloud has a noticeable effect on the diffusivity
and, therefore, the calculated hydrodynamic size. Seebergh et al.\textsuperscript{12} and Gittings et al.\textsuperscript{13} found a decrease in size with increasing ionic strength similar to that seen in the present study. The increase in size at low ionic strength (up to 8 nm) had been interpreted as evidence of the gradual expansion of a surface layer, but this must be viewed cautiously since the calculation assumes a smooth surface\textsuperscript{13}. Naturally, electrokinetic effects do not fully account for the differences between sizes measured by DLS and TEM. This may be partly due to particle shrinkage when drying samples for TEM.

**Region II: 20 < C_{KCl} < 205 mM**

With further increase of electrolyte concentration, the colloid dispersion turns into Region II and Region III, in which aggregation has taken place. Aggregation kinetics, as quantified by the change in hydrodynamic particle size, provides an indirect measure of the net interparticle interactions. Figure 3 shows the increase of hydrodynamic diameter with time for different electrolyte concentrations in Region II and Region III. At 25 mM KCl, the mean diameter increases slowly. Electrostatic repulsive forces opposing particle-particle contact play a dominant role in limiting the rate of aggregation; only a small fraction of the particles have thermal energies sufficient to overcome the electrostatic barrier. The slope of the hydrodynamic diameter versus time curve, i.e., the aggregation rate, increases with increasing electrolyte concentration till the electrolyte concentration is about 205 mM.

**Region III: C_{KCl} > 205 mM**

At C_{KCl} higher than 205 mM, the same slope is observed (see Fig. 3), and the aggregation rate reaches a maximum. This is an indisputable indication of the fast aggregation regime, where the aggregation rate constant is independent of the electrolyte concentration. Further increase in electrolyte concentration has little effect on the aggregation rate, since the van der Waals attractive is weakly affected by the intervening electrolyte\textsuperscript{14}. The Region III is characterized by particle aggregation in the absence of an energy barrier. At higher electrolyte concentrations, the rate of aggregation slows down abruptly after the initial rapid growth phase. The early and late phases of aggregation have been observed in various particulate systems, such as polystyrene, gold, and silica colloids\textsuperscript{15}.

Figure 4 shows the stability ratios (W) determined from the slope of the mean hydrodynamic diameter with time at different ionic strengths. The shape of the curve is typical of colloids stabilized by electrostatic repulsions\textsuperscript{16}. It displays the typical form with the plateau of the fast aggregation regime on the right-hand side and the slope of the slow aggregation regime as a function of the decreasing electrolyte concentration on the left-hand side. As the electrolyte concentration is increased, the aggregation rate increases (W decreases), and above a critical electrolyte concentration (C), the aggregation rate

\[
C_{KCl} = \frac{K}{C_{KCl}}
\]
approaches a constant value. The $C_\infty$ for this particle was found to be 205 mM.

In the absence of viscous drainage effects, fast aggregation with no electrostatic repulsive barrier is determined by Brownian motion alone, and theoretical $W$ would be close to unity. Experiment yields $W_{\text{meas}} > 1$, a value explained, in part, by drainage effects as the particles approach one another. The viscous interactions associated with high surface potentials and thick double layers affect the aggregation rate, resulting in the high stability ratio for fast aggregation.

**ζ-potential of the HTlc particles**

The electrophoresis experiments show that the HTlc particles are positively charged. Figure 5 represents the decrease of $\zeta$-potential of Mg-Al HTlc with the increase of ionic strengths. According to the DLVO theory\(^1\), the double-layer repulsion energy is proportional to the surface potential squared, which can be estimated from the $\zeta$-potential at the slip plane. Although the $\zeta$-potential does not coincide with the surface potential, it has a predictive value with respect to colloidal stability, because a high $\zeta$-potential will always favour the double-layer repulsion.

**Interaction energy**

The repulsive interaction required for colloidal stability originates from double-layer interactions. To verify the effect of electrolyte concentration on colloidal stability when only the double-layer repulsion is taken into account, we have calculated the interaction energy between HTlc particles and present the results in Fig. 6.

![Fig. 5—ζ-potential versus KCl concentration for the Mg-Al HTlc sample.](image)

![Fig. 6—Interaction energy for two plate-like particles in water as a function of the surface-to-surface distance (D). The Hamaker constant is calculated to be 55.6 kT at $T = 298$ K. Surface potential $\zeta_0 = 83$ mV has been used. $[\text{KCl}] = 0.1$ mM (curve 1); 5 mM (curve 2); 50 mM (curve 3); 180 mM (curve 4); 210 mM (curve 5); 300 mM (curve 6).](image)

This aggregation behaviour is attributed to electrical double layer compression in the presence of Brownian motion. By adding KCl the double layer is compressed, and the $\zeta$-potential and the effective charge of HTlc particles decrease. In the Region I, the $\zeta$-potential and the effective charge have a high value. Hence, the repulsive interaction keeps dominant during the particles approaching each other and thus reduces the collision probability. Further addition of KCl causes a lowering of the repulsive energy barrier. At the same time, the Brownian motion promotes aggregation by overcoming the barrier between particles and by increasing collision frequencies. The system turns into Region II, characterized by slow aggregation and in this region the second minimum interaction energy is to be expected for HTlc particles. When fast aggregation takes place, a large amount of electrolyte compresses the double layer heavily and lowers the $\zeta$-potential to a large degree. The repulsive energy barrier fades away and the attractive van der Waals forces play the important role. To simplify the DLVO picture, the structural or hydration forces with repulsive feature have been ignored. Every surface with hydration layer sees short range ordering of the electrolytic solution in its vicinity. When two such surfaces mutually approach each other, the overlap of these ordered solvent layers occur which creates a mutual repulsive force between the approaching
surfaces of particles. The aggregation region obtained by DLS experiments is a little different from that of theoretical analysis.

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