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The coagulation of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in aqueous electrolyte solutions

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With 8 figures and 1 table

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Introduction

When $\text{Ca}_3\text{Al}_2\text{O}_6$ (a component of Portland cement) and water react, hydrates are formed (such as $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$) and the system hardens (see, e.g., ref. (1)). The rheological properties of the paste and the strength of the resulting hydrate structure depend on the total energy of interaction between the particles. This interaction is thought to be composed of a van der Waals attraction and an electrostatic repulsion (2). We studied this interaction by following the coagulation behaviour of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ suspensions in various aqueous electrolyte solutions.

Experimental

Materials

$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ was prepared by hydrating $\text{Ca}_3\text{Al}_2\text{O}_6$ in water in an agate ball mill for 10 days at room temperature with continuous milling. The $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ formed was washed with water, filtered and washed with absolute ethanol and dried in vacuo (10 mm Hg at 80 °C). The $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ particles had an almost spherical, icositetrahedral form (fig. 1). No impurities could be detected by X-ray analyses or SEM. The particle size distribution, determined by measuring the particle radius obtained by SEM on 2491 particles, is given in figure 2. The specific surface of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ calculated from the particle size distribution (on the hypothesis of the particles being spheres) is 4.9 m²/g, the specific surface measured by N₂ adsorption in an Areameter ("Ströhlein") is 5.1 m²/g.

The water used was distilled twice and redistilled under reduced pressure shortly prior to use. Solutions saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ were prepared as described previously (3). During all preparations and experiments care was taken to avoid contamination by

CO₂ and where possible a glove-box with N₂-atmosphere free of CO₂ was used.

Fig. 1. S. E. M. of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ particles

Fig. 2. The particle size distribution of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ particles. The line indicates a lognormal particles size distribution: $n(r) = C \exp -k(\ln r/r_0)^2$ where $r_0 = 110$ nm, $k = 2.3$ and $C = 0.1947$

Methods

Calcium and aluminium were determined as described previously (3). The ζ -potential was calculated from the electrophoretic mobility, measured in a *Smith and Lisse* cell (4), using the relations given by *Wiersema et al.* (5). In concentrated electrolyte solutions (0.3 M and 1 M) the mobility of only a few particles could be measured, due to fast polarization of the electrodes.

The rate of coagulation was determined by following the change in extinction of a $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ suspension at a wavelength of 486 nm using a Vitatron MPS spectrophotometer. The suspensions were prepared by dispersing $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ particles into a solution previously saturated towards this compound using an ultrasonic bath (Megason Ultrasonic, frequency 80.000 Hz, 240 Watts) for 30 minutes. The concentration of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ particles in suspension was adjusted until an extinction $E=0.4$ was reached (≈ 130 mg/l $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$). 10 ml of this suspension was placed in a thermostated ($25.0^\circ\text{C} \pm 0.1$) cylindrical glass tube (inner diameter 1 cm) and was stirred using a teflon coated magnet at 240 rpm in order to avoid settling. During the coagulation the extinction decreased forming a S-type curve when plotted as a function of time. $E(t)$ curves obtained at different electrolyte concentrations can be made to coincide by adjustment of the time scale (fig. 3). This shows that the coagulation between primary particles (prevailing at the start of a coagulation experiment) is influenced by changes in electrolyte concentrations in the same way as coagulation between agglomerates (prevailing at later stages). Thus the maximum rate of decrease of the extinction $\left(\frac{dE}{dt}\right)_{\max}$ can be used as a relative measure of the coagulation rate.

Results

Figure 4 shows the maximum rate of decrease of the extinction $\left(\frac{dE}{dt}\right)_{\max}$ as a

Fig. 3. Comparison of the changes of extinction of a $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ suspension with different electrolyte concentrations, as a function of time. The time necessary to reach $E=0.3$ was taken 1 in all cases

function of the Debye parameter

$$\kappa = \left(\frac{e \sum n_i z_i^2}{\epsilon_0 \epsilon_r k T} \right)^{1/2}$$

(with n_i = the number of ions with charge $z_i e$ in 1 m^3 of solution) for $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ suspensions in H_2O , NaOH , NaNO_3 and saturated $\text{Ca}(\text{OH})_2$ solutions. In KNO_3 solutions a similar coagulation behaviour was found as in NaNO_3 solutions: for comparison some values of $\left(\frac{dE}{dt}\right)_{\max}$ in KNO_3 solutions are included in figure 4.

The concentrations of ions in the liquid phase are shown together with κ in table 1. The $\text{Ca}(\text{OH})^+$ concentration was calculated as described previously (3). The increase of solubility with increasing ionic strength in NaNO_3 solutions has e.g. also been found for $\text{Ca}(\text{OH})_2$ (6). For sake of brevity the solutions will be indicated henceforth by their initial concentrations but in calculations, due account will be taken of $\text{Al}(\text{OH})_4^-$, Ca^{2+} , $\text{Ca}(\text{OH})^+$, NO_3^- and OH^- ions. It is supposed that aluminate ions in the solutions are present as $\text{Al}(\text{OH})_4^-$ or $\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2^-$ ions; for the possible role of poly-aluminate ions, see later.

The ζ -potential and surface charge behind the electrokinetic slipping plane σ_ζ are also

Fig. 4. $1 / \left(\frac{dE}{dt}\right)_{\max}$ for $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ -suspension in water and NaOH , NaNO_3 , KNO_3 and saturated $\text{Ca}(\text{OH})_2$ -solutions, saturated towards $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$

Table 1. Data on $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ suspensions used for coagulation

Initial liquid phase	Ca^{2+}	$\text{Ca}(\text{OH})^+$	$\text{Al}(\text{OH})_4^-$	Concentration (mmoles/l) $\kappa (\times 10^9 \text{ m}^{-1})$	ζ (mV)	σ_ζ (mC/m ²)
H_2O	2.82	0.17	1.72	0.3054	-15.4	- 3.5
0.01 M NaNO_3	3.04	0.16	2.04	0.4565	-16.8	- 5.5
0.03 M NaNO_3	3.37	0.15	2.65	0.6596	-15.3	- 6.9
0.1 M NaNO_3	3.88	0.14	3.35	1.099	-14.1	-10.4
0.3 M NaNO_3	4.63	0.15	3.94	1.842	- 9.3	-11.5
1 M NaNO_3	5.18	0.18	3.98	3.313	- 8.1	-19.7
0.01 M KNO_3	2.98	0.16	1.96	0.4542	-15.8	- 5.0
0.1 M KNO_3	3.94	0.14	3.42	1.101	-12.4	- 9.1
1 M KNO_3	5.23	0.18	4.01	3.314	- 8.8	-21.4
0.01 M NaOH	1.95	0.29	1.53	0.4177	-17.7	- 5.2
0.02 M NaOH	1.40	0.30	1.31	0.5146	-23.6	- 8.6
0.03 M NaOH	1.19	0.32	1.25	0.6042	-24.4	-10.4
0.04 M NaOH	0.89	0.27	1.08	0.6812	-25.4	-12.1
0.1 M NaOH	0.47	0.21	0.74	1.048	-29.8	-21.7
0.3 M NaOH	0.30	0.19	0.84	1.804	-23.6	-29.3
1 M NaOH	0.17	0.15	1.31	3.289	-20.0	-49.0
sat. $\text{Ca}(\text{OH})_2$	15.50	5.80	0.20	0.7510	+10.7	+ 5.7

shown in table 1. σ_ζ was calculated taking the change of activity coefficients of the ions in the diffuse double layer into account as described previously (3).

Discussion

In the system investigated, coagulation is dependent on electrolyte concentration to a minor degree only, as compared with other systems investigated (see e.g. *Reerink and Overbeek* (7), *Ottewill and Shaw* (8) and *Wiese and Healy* (9)). In addition the trend of the $\log W - \log \kappa$ curve is at electrolyte concentrations up to 0.1 M NaNO_3 or 0.3 M NaOH contrary to that predicted by the DLVO-theory (2). The differences in stability are considered to be larger than the experimental error because the differences found were reproducible and similar differences were found for other solid phase concentrations.

The dependence of $\left(\frac{dE}{dt}\right)_{\max}$ on solid phase concentration agreed with the kinetics of a "bimolecular" type of reaction (fig. 5); $\left(\frac{dE}{dt}\right)_{\max} = k \cdot c_0^2 = k \cdot (10 \cdot E_0)^2$ where k is a constant, E_0 is the initial extinction, and c_0 the initial concentration of the solid phase.

In order to investigate the influence of

Fig. 5. Dependence of coagulation rate on the solid phase concentration

differences in surface potential, we calculated the stability ratio W as a function of κ on the basis of the following model:

a) For attraction (V_A) the Hamaker equation for spheres of equal size was employed (10).

b) For repulsion, the equation derived by *Bell et al.* (11) for symmetric electrolytes, as modified by *Lyklema and de Wit* (12) was used:

$$V_R = 4\pi\epsilon_0\epsilon_r \left(\frac{kT}{e}\right)^2 Y^2 \frac{a + \Delta}{s'} \exp \{-\kappa(a + \Delta)(s' - 2)\} \quad [1]$$

where Δ is the thickness of a layer around the particle not belonging to the diffuse part of the double layer (e.g. Stern-layer); $s' = \frac{R}{a + \Delta}$,

where R is the distance between the particle centers and a is the particle radius; k , T , e , ϵ_0 and ϵ_r have their usual meaning. Y is the "effective reduced potential at large values of $\kappa(R - a)$ " (12). At large values of κa , as are considered here, $Y = 4 \tanh(e\psi_\delta/4kT)$, where ψ_δ is the potential in the plane near the solid where the diffuse double layer begins. When the influence of the bivalent Ca^{2+} ions on the potential distribution in the diffuse part of the double layer is not small compared to that of the univalent cations (in water, NaNO_3 and NaOH concentrations lower than 0.1 M and saturated Ca(OH)_2 solutions respectively) the assumption $Y = 4 \tanh(e\psi_\delta/4kT)$ introduces a significant error. We calculated the influence the Ca^{2+} ions on Y by comparing two potential distributions: a) the potential distribution calculated as described previously (3), from the data given in table 1; b) the potential distribution for an 1-1 electrolyte of equal ionic strength. In this latter calculation the potential at the interface was chosen such as to make the potential distribution at large values of $\kappa(r - a)$, equal to potential distribution a). The reduced value of this potential was used to calculate Y . Combination of the Hamaker equation with eq. [1] gives the total energy of interaction $V_T = V_A + V_R$.

The stability ratio for "primary" coagulation (i.e. coagulation leading to agglomerated particles situated at the primary minimum in the $V_T - R$ curve (2), at the shortest distance between the solid particles) due to Brownian motion in a force field was calculated according to *McGrown and Parfitt* (14). In these calculation ψ_δ is unknown. However, we considered two models for the situation at the $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ -electrolyte solution interface:

Model (1): Ions from the solution are present in the space between the electrokinetic slipping plane (ζ -plane) and the plane with average potential ψ_δ (ψ_δ -plane); this space will henceforth be referred to as " ψ_δ - ζ -layer"; $\psi_\delta^{(1)}$ can then be calculated by extrapolating the potential distribution in the diffuse double layer outside the ζ -plane, as calculated from the

Fig. 6. The potential distribution outside of the ψ_δ -plane 1) Potential distribution with ions present in the ψ_δ - ζ -layer; 2) Potential distribution with a charge-free ψ_δ - ζ -layer ("ice-like" structure behind the ζ -plane)

Gouy-Chapman theory, to the ψ_δ -plane (fig. 6), with the thickness of the ψ_δ - ζ -layer (δ_ζ) as a parameter. In this case the ψ_δ - ζ -layer is part of the diffuse double layer and does contribute to the repulsion energy; the repulsion energy can be calculated using eq. [1] taking $\Delta = 0$ and $\psi_\delta = \psi_\delta^{(1)}$. δ_ζ is expressed as "equivalent distance" i.e. the distance (in nm) if the relative dielectric constant between the ζ - and ψ_δ -planes would be $= 80$. If, however, the dielectric constant is lower, than the real distance becomes proportionally lower.

Model (2): The water in the ψ_δ - ζ -layer has an ice-like structure not penetrable for ions from the liquid phase. Then $\psi_\delta^{(2)}$ (fig. 6) can be calculated from the ζ -potential by assuming a linear dependence of the potential on the distance from the interface in the ψ_δ - ζ -layer, with gradient equal to that at the ζ -plane. In this case the ψ_δ - ζ -layer does not contribute to the repulsion energy. In eq. [1] ψ_δ can be taken equal to the ζ -potential and Δ is equal to the thickness of the ice-like ψ_δ - ζ -layer ($\Delta = \delta_\zeta$). Again, δ_ζ as used as an parameter in the calculations is the "equivalent distance" i.e. the distance if the relative dielectric constant would be $= 80$.

When a suspension coagulates by primary coagulation, the stability of the suspension is determined primarily by the height of the energy barrier between the particles. We tried to calculate the stability ratios found experimentally (fig. 4) by varying δ_ζ (0-1 nm) and the Hamaker constant $\mathcal{A}_{1(2)}$ taking the particle radius $a = 120$ nm. In these calculations we

Fig. 7. Y values for transition from fast to slow coagulation for different values of $A_{1(2)}$, for a diffuse situation in the $\psi\delta\zeta$ -layer; $A_{1(2)}$ in 10^{-20} J as a parameter. Initial liquid phase: $\bullet$ H_2O ; $\circ$ NaNO_3 solutions; $\times$ NaOH solutions

assumed a constant viscosity and dielectric constant of the liquid phase in the diffuse double layer, for all electrolyte concentrations. The variation in $\delta\zeta$ and $A_{1(2)}$ changed the height of the energy barrier between the particles. Figure 7 shows the result of these calculations, as a diagram indicating the regions of stability and instability of a suspension, assuming an ion-distribution in the $\psi\delta\zeta$ -layer agreeing with the Gouy-Chapman theory (model 1). The lines, drawn for different values of $A_{1(2)}$ indicate the value of Y , at constant $A_{1(2)}$ at which the maximum in the $V_T - R$ curves as a function of the distance between the particles is situated at $V_T = 0$ (ref. 2 p. 304). Although in principle the transition from fast to slow coagulation is a gradual one, in practice the transition is reasonably sharp especially in more concentrated electrolyte solutions; if $\frac{kT}{e} Y$ is a few mV larger than the value indicated in figure 7, coagulation becomes very slow (ref. 13, p. 169).

Figure 8 shows the same curves for an ice like structured $\psi\delta\zeta$ -layer with $\delta\zeta = 0.4$ nm. Analogous diagrams were calculated for other $\delta\zeta$ -values up to 1 nm. For interpreting these results we start from the following facts:

a) The differences found experimentally in the coagulation rate of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ at different electrolyte concentrations were small

Fig. 8. Y values for transition from fast to slow coagulation for different values of $A_{1(2)}$ for an ice-like structure in the $\psi\delta\zeta$ -layer, with $\delta\zeta = 0.4$ nm; $A_{1(2)}$ in 10^{-20} J as a parameter

as compared to those usually found in coagulation (13).

b) No combination of $\delta\zeta$ and $A_{1(2)}$ can be found, which explains the coagulation behaviour of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ at low concentrations as being due to changes in electrolyte content of the solutions. Especially the relatively large stabilities at $\kappa = 0.6596 \cdot 10^{-9} \text{ m}^{-1}$ (in NaNO_3) and $\kappa = 1.804 \cdot 10^{-9} \text{ m}^{-1}$ (in NaOH) cannot be explained in this way. It follows that at all concentrations, lower than those corresponding to the stability maxima mentioned, either fast coagulation or slow coagulation must prevail. Fast primary coagulation, however, is improbable in view of the low $\left(\frac{\Delta E}{\Delta t}\right)_{\max}$ values; the flocculation time estimated for the suspensions concerned on the basis of the von Smoluchowski-Müller theory of fast flocculation (15) employing a log-normal distribution as mentioned in figure 2 would be 100 sec. ($c_0 = 1.6 \times 10^{15}$ particles m^{-3}), whereas at the stability maximum it took 1 hour, for a unstirred suspension, to effect a extinction change of 0.4 to 0.37.

c) On the other hand, the stability decrease at larger concentrations and the difference between NaNO_3 and NaOH containing suspension, in this region can be attributed to the increase in electrolyte content. If we assume, e.g. $\delta\zeta = 0.3$ nm and $A_{1(2)} = 0.28 \times 10^{-20}$ J, for model (1) a stability decrease in

NaNO_3 solutions of the concentrations concerned is expected (fig. 7) whereas in NaOH solutions, primary coagulation remains slow. For model (2) the same conclusion holds for $A_{1(2)} = 0.3 \times 10^{-20}$ J for $\delta_\zeta = 0.4$ nm (fig. 8).

d) In order to prevent fast coagulation at the largest NaNO_3 concentration investigated for δ_ζ (ζ -plane coinciding with the ψ_δ -plane a maximum value for the Hamaker constant of $0.03 \cdot 10^{-20}$ J is calculated.

The question may be asked whether the assumption of secondary coagulation (ref. 2 p. 325) might explain the coagulation experiments. In this case the stability ratio can be estimated according to *Hogg and Yang* (16)

$$V_2 = \frac{\int_{s_2}^{\infty} \exp(V_T/kT) \frac{ds}{s^2}}{1 - \exp(V_2/kT)} \simeq \frac{1}{1 - \exp(V_2/kT)} \quad [2]$$

where $s = R/a$, R_2 = the distance from the center of a solid particle to the secondary minimum in the $V_R - R$ curve, $V_2 = V_T$ at the secondary minimum and $s_2 = R_2/a$. This equation is only valid in the beginning of the coagulation because disaggregation of agglomerates caused by stirring is not accounted for (17). V_2 is primarily dependent on $A_{1(2)}$ and the electrolyte concentration; the surface potential, however, has a minor influence only. The increase in stability with increasing κ at low electrolyte concentration (fig. 4) cannot be explained as secondary coagulation, because theory predicts in this case a decreasing stability. Secondary coagulation might account for the decreasing stability in concentrated NaNO_3 solutions, however, it cannot account for the difference between NaNO_3 containing and NaOH containing suspensions, respectively. Therefore we prefer primary coagulation as an explanation for the decreasing stability with increasing κ in concentrated NaNO_3 -solutions.

The increasing stability with increasing κ at low concentrations cannot be explained either as primary or as secondary coagulation. A third possibility is that the differences in coagulation rate in this region might be ascribed to differences in viscosity of the bulk solutions or of the liquids near the interfaces, either caused by local ion concentrations or by the local electrical field (18). However, the

viscosity of the bulk solution is not significantly changed by NaNO_3 or NaOH in the concentration range concerned. A predominant influence of the electrical field strength at the interface is excluded by the fact that the coagulation rate in a solution saturated towards both Ca(OH)_2 and $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ is situated in figure 5 on the curve representing the coagulation behaviour in NaOH solutions in view of the differences in ζ -potential. The same argument excludes differences in local ion concentrations as cause for the difference in stability.

The following model, although tentative, is in agreement with the experiments.

The general increase in stability with increasing κ at relatively low electrolyte concentration (whether NaOH , NaNO_3 , KNO_3 or Ca(OH)_2 solutions) suggests that this effect is caused by a property connected with ionic strength. One such effect might be the depolymerization of poly-aluminate ions, caused by the lowering of the activity coefficient of monomeric Al(OH)_4^- or $\text{Al(OH)}_4^- \cdot (\text{H}_2\text{O})_2$ ions. Whether polyaluminate ions are present in the solutions concerned is not clear (studies of the aluminate ions in solutions are usually carried out at much higher aluminate concentrations, cf. ref. 20–22). However, the presence of poly-aluminate ions in the liquid phase of the suspension obtained by dispersing $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in water is supported by the fact that the concentrations in this liquid phase are situated near the line indicating the "solubility" of amorphous Al(OH)_3 (23) (this liquid is supersaturated towards crystalline $\gamma\text{-Al(OH)}_3$). In addition, surface precipitation of amorphous Al(OH)_3 on $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in the concentration region concerned has been postulated for explaining some characteristics of the reaction of $\text{Ca}_3\text{Al}_2\text{O}_6$ with water (24).

The poly-aluminate ions might stimulate the coagulation of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ by forming bridges between the particles; a similar action of polymeric Zn(OH)_2 species in solution has been postulated by *Healy and Jelett* for explaining the coagulation of ZnO (25). On the other hand, adsorbed polymeric molecules might stabilize a suspension through loss of configurational entropy of the adsorbed molecules on the approach of a second particle (26). Apparently, in the present case the destabilizing action through bridge formation pre-

dominates. Thus, the increase in stability with increasing κ at low concentration is ascribed to depolymerization of poly-aluminate ions and the decrease in stability in concentrated NaNO_3 solutions to primary coagulation under influence of electrolytes. The decrease in stability in very concentrated NaOH solutions is at present not sufficiently understood; however, this decrease can be due to increase of aluminate concentrations (table 1) at these NaOH concentrations.

Conclusion

The DLVO theory is capable of explaining the coagulation of aqueous $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ suspensions, in NaNO_3 solutions and NaOH solutions at concentrations larger than 0.1 M assuming $\delta\zeta = 0$ nm and $\mathcal{A}_{1(2)} = 0.03 \times 10^{-20}$ J or $\delta\zeta = 0.3$ nm and $\mathcal{A}_{1(2)} = 0.3 \times 10^{-20}$ J. The relatively low stability at low electrolyte concentrations, however, is contrary to the trend predicted by the theory for the influence of electrolytes. It can be ascribed to bridge-formation, by poly-aluminate ions, between the particles.

Summary

Coagulation rate measurements of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ in different aqueous electrolyte solutions (NaOH , NaNO_3 , $\text{Ca}(\text{OH})_2$) show that, at concentrations lower than 0.1 M NaNO_3 and 0.3 M NaOH respectively, the stability increases with increasing ionic strength. This fact cannot be explained as either primary or secondary coagulation according to the DLVO theory. However, polymeric ions such as poly-aluminate ions, present in the liquid phase can cause the observed coagulation behaviour at these concentrations. At NaNO_3 concentrations higher than 0.1 M NaNO_3 the coagulation behaviour can be explained as primary coagulation according to the DLVO theory assuming $\psi_\delta = \zeta$ with $\mathcal{A}_{1(2)} = 0.03 \times 10^{-20}$ J. Assuming a distance between the plane with average potential ψ_δ and ζ of 0.3 to 0.4 nm, $\mathcal{A}_{1(2)} = 0.28 - 0.30 \times 10^{-20}$ J depending on the conditions between these two layers.

Zusammenfassung

Koagulationsgeschwindigkeitsmessungen an $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ -Suspensionen zeigen, daß in wässrigen Elektrolytlösungen (NaOH , NaNO_3 , $\text{Ca}(\text{OH})_2$) bei Konzentrationen niedriger als 0.1 M NaNO_3 bzw. 0.3 M NaOH die Stabilität größer wird, wenn die Elektrolytkonzentration zunimmt. Weder primäre noch sekundäre Koagulation nach der DLVO-Theorie kann diesen Effekt erklären. Die Anwesenheit von polymeren Ionen (z.B. Polyaluminationen) in der Lösung kann das beobachtete Koagulationsverhalten bei diesen Konzentrationen aber deuten. Bei NaNO_3 -Konzentrationen größer als 0.1 M kann das Koagulationsverhalten erklärt werden als primäre Koagulation

nach der DLVO-Theorie mit der Annahme, daß $\psi_\delta = \zeta$ und $\mathcal{A}_{1(2)} = 0.03 \times 10^{-20}$ J. Nimmt man an, daß der Abstand zwischen den Flächen mit durchschnittlichen Potentialen ψ_δ und ζ etwa 0.3–0.4 nm beträgt, so wird $\mathcal{A}_{1(2)} = 0.28 - 0.30 \times 10^{-20}$ J, abhängig vom Zustand zwischen diesen Flächen.

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