

# A GELATION PROCESS IN SiO<sub>2</sub> - H<sub>2</sub>O SYSTEM IN THE PRESENCE OF CALCIUM ACETATE MONOHYDRATE

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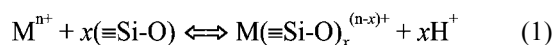
**Keywords:** Sol SiO<sub>2</sub>, Hydrosilicate gel, Zeta potential, Isoelectric point

*A sol of silicon dioxide has been used for modeling of the interactions of calcium salt with SiO<sub>2</sub> - H<sub>2</sub>O in high dispersive system. The dependence of the zeta potential on concentration of calcium acetate in SiO<sub>2</sub> - H<sub>2</sub>O system has been characterized at lower concentration of acetate by negative values. Isoelectric point has been determined at ratio molar concentration of acetate to silicon dioxide  $r = c_{\text{calciumacetate}}/c_{\text{SiO}_2} = 0.347$ . This work is focused on determination of optimum conditions for gelation, control of sol stability and explaining of gelation mechanism by ion exchange on silica surface.*

## INTRODUCTION

In recent years, silicate technologies have undergone remarkable development. Colloidal silicon dioxide may be applied in many branches of industry, such as in the production of heat resisting materials, surface treatment and processing of fibers and textiles, as well as treating the surfaces of packing materials. Another possibility is its application in building industry, namely for prevention of the masonry wetting. Matijevec and Allen [1] followed conditions of coagulation of silica sol particles with using Na<sup>+</sup>, Ca<sup>2+</sup>, La<sup>3+</sup>, and Al<sup>3+</sup> ions. In next work [2] they determined stability of colloidal silica sols in the presence of NaCl, LiCl, KCl, CsCl, NaBr, NaI, CaCl<sub>2</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> at various concentration of electrolytes. In that study is shown the dependence of mobility on pH value and molar concentration of electrolytes.

Ion exchanging on the colloidal silica surface (Ludox) in the presence of various electrolytes (LiCl, NaCl, KCl, CsCl) was discussed also [3]. Concentrations of critical coagulation of electrolytes were determined at various pH value. The coagulation process was followed using light scattering and transport parameters were determined by electrophoretic mobility values. The process of exchange of metal ions on silica surface may be described by equation :



Where M<sup>n+</sup> is a cation of charge  $n$ , which reacts with  $x$  surface silanol groups ( $\equiv\text{Si-OH}$ ).

The stability of silica hydrosols (Ludox), has been studied by Allen and Matijevec [4] as a function of pH in presence of electrolytes Al(NO<sub>3</sub>)<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, La(NO<sub>3</sub>)<sub>3</sub> and coagulation regions for the electrolytes were determined. Electrophoretic mobilities were measured by the moving boundary technique.

Kerner and Leiner [5] and as well as Iler [6] studied the rate of the SiO<sub>2</sub> sol gelation in dependence on pH and concentration of sodium chloride. Electrokinetic potential of SiO<sub>2</sub> particles was measured by Kosmowski and Matijevec [7] in KCl solution in presence of various types of alcohols.

In our previous works [8,9], the weighting method of measuring of zeta potential by MICROMERITICS Zetapotential analyzer 1202 was employed to the study the effect of calcium sulphate dihydrate [8] on the hydration or gelation of the SiO<sub>2</sub> - H<sub>2</sub>O system. In our work [9], the influence of calcium chloride was reported. These additives play an important role in transport processes through gel layer on surface of calcium silicates during hydration process in cement setting. Another common additive is soluble sodium chloride, which positively influences the gelation process of the SiO<sub>2</sub> sol in aqueous medium [2].

The presented work is focused on behaviour of the system SiO<sub>2</sub> - H<sub>2</sub>O - calcium acetate monohydrate. The goal of this work is to assess the calcium salt effect on the character of gelation by electrokinetic potential measurement. The additive, which was added to a solution of silicon dioxide sol in the form of a solution, influences the pH and leads to the gelation of the sol in the vicinity of the isoelectric point of the system.

## EXPERIMENTAL

The SiO<sub>2</sub> sol Tosil (Silchem, Ústí nad Labem, Czech Republic) containing 31.47 wt.% of silicon dioxide was used as the starting colloid solution. The sol has the density 1.21 g/cm<sup>3</sup> and *pH* value 9.10 at 25°C. The particle diameter of 0.524 mol/l silica sol was in the range of 5.9 and 14.8 nm. The samples were prepared by mixing of the sol and the solution of calcium acetate monohydrate (United Chemical and Metallurgical Works Ltd., Ústí nad Labem, Czech Republic).

The concentration of calcium acetate varied in the interval 2.84 10<sup>-2</sup> - 8.51 10<sup>-1</sup> mol/l. The ratio *r* was calculated as molar concentration of additive divided by molar concentration of SiO<sub>2</sub>.

$$r = \frac{C_{\text{calciumacetate}}}{C_{\text{SiO}_2}}$$

Range of molar ratio *r* was in the interval 0.054-1.624. The solubility of calcium acetate monohydrate is 46.4 g in 100 g water at 25°C [10].

The chemical composition of the sol was monitored using an ICP method by Thermo Jarrel Ash instrument, type Iris AP. For measurement of size of the particles, Zetasizer 3000HS (Malvern Instruments) was used. Zeta potential measurements were performed using Zeta Potential Analyzer, type 1202, Micromeritics, based on mass transport charged particles in electrical field. This analyzer can be used for the measurement of an electrokinetic potential of water disperse with high concentration of solid phase. Measuring cell of apparatus contains reservoir, cuvette and two stainless steel electrodes. During the experiment, the turning cell homogenizes the suspension sample. The volume of the sample was at least 110 cm<sup>3</sup>. The used current was in interval from 5 A to 20 mA. The values of current and the time of the experiment were set up with correspondence of observed sample conductivity.

The value of electrophoretic mobility *e* (s<sup>-1</sup> V<sup>-1</sup>) and parameter were calculated from equation (2) and (3) presented in [11].

$$V_e = \frac{\Delta m \cdot k}{R \cdot t \cdot I \cdot \phi (1 - \phi) \cdot (\rho_d - \rho_l)} \quad (2)$$

where  $\Delta m$  (g) is mass difference, *k* the conductance cell constant (cm<sup>-1</sup>), *R* sample resistance (Ω), *t* time period of test (s), *I* the applied current (A),  $\rho_d$  the density of the dispersed phase (g/cm<sup>3</sup>), and  $\rho_l$  the density of the liquid phase (g/cm<sup>3</sup>). Distance between conductometer electrodes *l* is 1 cm.

For the parameter representing the volume ratio of the components may be written relation:

$$\phi = \frac{(m_d / \rho_d)}{(m_d / \rho_d) + (m_l - \rho_l)} \quad (3)$$

where *m<sub>d</sub>* is the mass concentration of the dispersed

phase (g) and *m<sub>l</sub>* the mass concentration of the liquid phase (g).

The value of zeta potential (V), is calculated from Helmholtz - Smoluchowski relation [12,13]

$$\xi = \frac{3.6 \cdot 10^5 \cdot \pi \cdot v_e \cdot \eta}{\epsilon_r} = 1.131 \cdot 10^6 \cdot v_e \cdot \left( \frac{\eta}{\epsilon_r} \right) \quad (4)$$

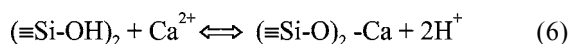
where *m<sub>d</sub>* is the mass concentration of the dispersed phase (g) and *m<sub>l</sub>* the mass concentration of the liquid phase (g).

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## RESULTS AND DISCUSSION

The results are summarized in figures 1 to 4. The dependence of zeta potential on the molar ratio logarithm in figure 1 shows that increasing values of the molar ratio of the system are accompanied by the increase of zeta potential, from negative values within the molar concentration of calcium acetate monohydrate from 0.284 to 0.851 mol/dm<sup>3</sup> (log *r* from -1.266 to 0.211). When a solution of the salt is added, dissociation takes place in the aqueous medium followed by transport of ions to surface of the sol particles. The system of SiO<sub>2</sub> - H<sub>2</sub>O - calcium acetate is characterized by the isoelectric point within the studied interval of molar ratio *r*. If log *r* = -1.266, the negatively charged surface of SiO<sub>2</sub> sol is insufficiently compensated by present a positively charged calcium ions.

Low concentration of calcium acetate in the system leads to rapid change of surface charge from negative value  $\xi = -18$  mV to  $\xi = -3$  mV. Negative charge of particles is caused by non saturated silica surface.



As is shown in diagram of dependence of zeta potential on log *r*, zero value = 0 was determined at *r* = 0.347 (log *r* = -0.46). The concentration of calcium acetate monohydrate was 0,182 mol/dm<sup>3</sup>. For *r* values exceeding 0.347 the zeta potential reaches positive values. In these conditions, the system is characterized by a surplus of calcium ions in solution and these ions may be used for formation of bigger particles of gel. The particles are composed probably of SiO<sub>2</sub> aggregates and a surface layer of *k* CaO . *l* SiO<sub>2</sub> . *m* H<sub>2</sub>O (calcium silicate hydrate gel).

The effect of logarithm of calcium acetate concentration on *pH* value is represented in the figure 2. There are evident three steps of stability. The first step represents dissociation of calcium acetate and formation of

(Si-O)<sub>2</sub>-Ca layer, and saturation of surface by Ca<sup>2+</sup> ions (values from pH = 7.8 to 7.5). Plateau at pH 7.5 is caused by dominant role of acetate acid. Dissociation of acetate acid, acetate ions, calcium ions and (poly)silicate acid on the colloid particles surface (step 2) plays a role in equilibrium.

At concentration of 0.227 (log *c* = -0.644) the isoelectric point and start of gelation was observed. The decreasing of pH value up to isoelectric point (step 3) may be explained by reducing the influence of (poly)silicate acid.

Figure 3 shows the dependence of zeta potential on pH in the presence of acetate. Initial pH value at *r* = 0 (pure sol) was 9.05. Increasing molar concentrations of calcium acetate in the system of SiO<sub>2</sub> - H<sub>2</sub>O obviously lead to a gradual decrease in the pH of the system. In the case of calcium acetate the pH value of the isoelectric point was determined at pH = 7.50.

Electrical conductivity (figure 4) increases with molar ratio interval *r* from 3.9 to 30.3 mS/cm. The relative changes of conductivity at higher *r* are lower than that at a low value. On the other hand, continuous particle shape development illustrates small effect of parti-

cle shape of colloid system on a conductance. The decrease of the slope d*G*/*dr* may be explained by formation of gel. The measured value of pure silica sol conductivity is 0.439 mS/cm, while the isoelectric point at *r* = 0.347 exhibits the value 17.72 mS/cm.

### CONCLUSIONS

The zeta potential measurement was used for determination of electrophoretic mobility of the colloid particles of SiO<sub>2</sub> in calcium acetate monohydrate solution. Calculated zeta potential values of the system increased with increasing amount of calcium acetate. Gelation process begins in isoelectric point when additional amount of calcium ions is bonded on silica surface. System of SiO<sub>2</sub> - H<sub>2</sub>O - calcium acetate monohydrate is characterized by isoelectric point at *r* = 0.347, (log *r* = -0.46). This zero point was obtained for calcium acetate molar concentration *c* = 0.182 and pH = 7.5. In comparison with systems SiO<sub>2</sub> - H<sub>2</sub>O - CaSO<sub>4</sub> [8] and SiO<sub>2</sub> - H<sub>2</sub>O - CaCl<sub>2</sub> [9] the isoelectric point was found at lower salt concentration.

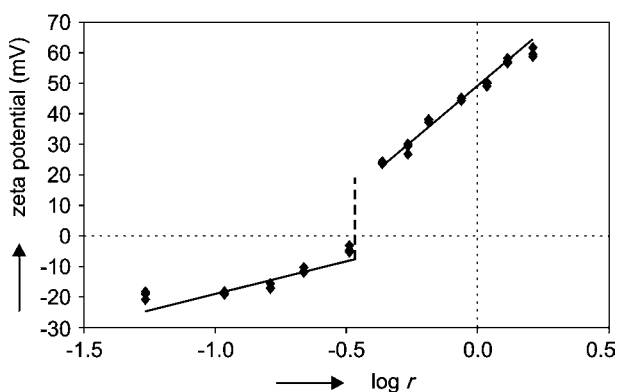


Figure 1. The dependence of zeta potential on logarithm of molar ratio of the system SiO<sub>2</sub> - H<sub>2</sub>O containing calcium acetate.

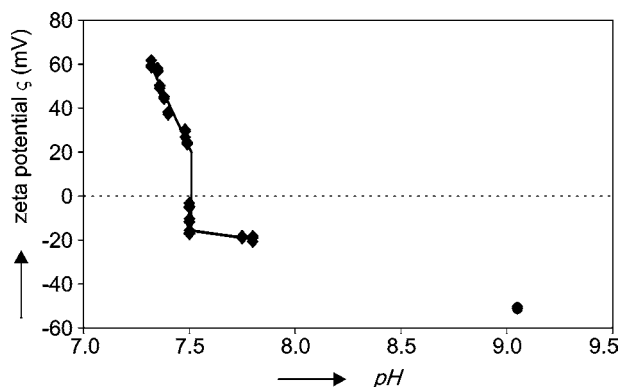


Figure 3. The dependence of zeta potential on pH value of SiO<sub>2</sub> - H<sub>2</sub>O - calcium acetate. The point (") represents the value of pure sol SiO<sub>2</sub>.

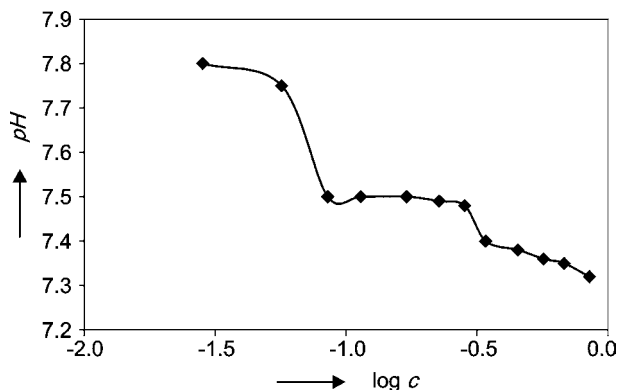


Figure 2. The dependence of pH value on logarithm of concentration of calcium acetate.

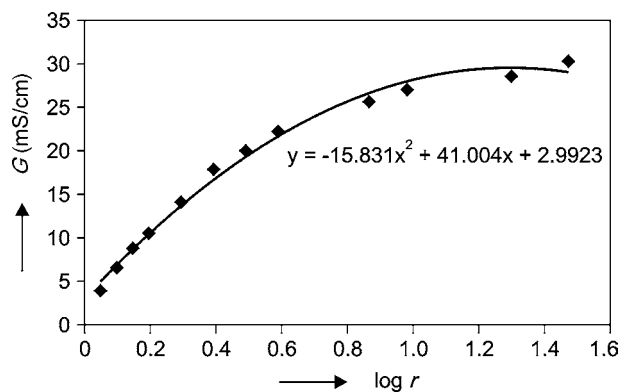


Figure 4. Representation of sample conductivity on logarithm of molar ratio, silica sol with calcium acetate. Concentration of silica sol is 0.52 mol/l.

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#### GELACE SYSTÉMU SiO<sub>2</sub> - H<sub>2</sub>O V PŘÍTOMNOSTI MONOHYDRÁTU OCTANU VÁPENATÉHO

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Interakce solu SiO<sub>2</sub> s monohydrátem octanu vápenatého, jako aditivní látky která urychluje gelaci soustavy, byla sledována měřením zeta potenciálu. Byly hodnoceny podmínky gelace, která probíhá tvorbou agregátů kyseliny křemičité, kdy v přítomnosti vápenatých iontů dochází k iontové výměně na povrchu SiO<sub>2</sub> částic. Se zvyšováním koncentrace vápenatých iontů v soustavě dochází k vzrůstu zeta potenciálu ze záporných do kladných hodnot. Hodnota *pH* systému klesá s rostoucí koncentrací octanu vápenatého. Byl určen izoelektrický bod soustavy, který při *pH* = 7,5 odpovídá molárnímu poměru *r* = 0,347 (log *r* = -0,46) a to odpovídá molární koncentraci octanu vápenatého *c* = 0,182 a 0,524 mol/dm<sup>3</sup> SiO<sub>2</sub>.