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# Colloids and Surfaces A: Physicochemical and Engineering Aspects

# Effects of inorganic and organic anions on the stability of illite and quartz soil colloids in Na-, Ca- and mixed Na–Ca systems

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## HIGHLIGHTS

► CCC of $Ca^{2+}$ and $Na^+$ for illite and quartz WDC with different anions.

► CCC of low soluble $Ca^{2+}$-oxalate tested with oxalate-modified illite in $CaCl_2$.

► Coagulating $Ca^{2+}$ dominates the colloidal dispersion effect of oxalate compared to $Na^+$.

► Attraction energy between mineral colloids at CCC is scaled.

► CCC in pure Na- and Ca-systems can be used to predict CCC in mixed systems.

## GRAPHICAL ABSTRACT

Increase of colloidal illite stability ($CCC_{Na+Ca}$) in suspension at different molar ratios of calcium to sodium, X, after oxalate modification in the presence of chloride anion compared to pristine illite in the presence of sulfate anion.
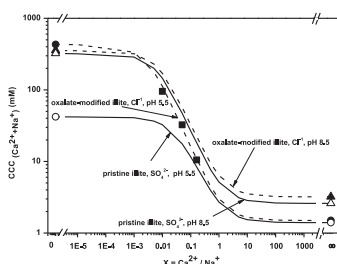
## ABSTRACT

The colloidal behavior of soil mineral colloids (quartz and illite) in Na, Ca and mixed Na–Ca systems was systematically investigated. The critical coagulation concentrations (CCCs) were determined for $Na^+$ and $Ca^{2+}$ solutions containing anions of a different nature ($Cl^-$, $SO_4^{2-}$ and ubiquitous soil organic anions formate and oxalate) at pH 5.5 and pH 8.5. Higher CCC values in the presence of $Na^+$ at pH 8.5 were related to a lower screening effect of monovalent cations and the ionization properties of the soil mineral colloids. Attraction energy between colloids was experimentally scaled at CCC from zeta potential and aggregation kinetics measurements. In the Na-system, a higher stability for colloidal illite and quartz particles suspensions in the presence of oxalate anions confirmed surface complexation at an acidic pH. In the Ca-system, slight CCC variations in illite suspensions in the presence of $Cl^-$, $SO_4^{2-}$, formate and oxalate supported attractive ion–ion correlation forces between equally highly charged clay mineral colloids. It was shown that the CCCs of mixed Na–Ca systems close to soil chemical conditions can be calculated using the CCCs for colloidal illite and quartz particles in pure Na and Ca systems at pH 5.5 and pH 8.5. Sensitive dispersion effects due to adsorbed oxalate can be analyzed as a function of the molar ratios of calcium to sodium in solution.

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## 1. Introduction

Water dispersible colloids (WDCs) are soil particles <2 μm from soil clay fractions that can be easily dispersed in contact of soil water. They mainly include aluminosilicate and metal oxide particles which can be released from soil aggregate structures and contribute to soil erosion. They have large surface area and exhibit low gravitational velocities which facilitate the sorption and transport of organic matter and pollutants including oxyanions,

radionuclides, pesticides and other hydrophobic compounds in the subsurface environment [1,2]. The release and transport of WDCs in soils are conditioned by the hydrodynamic water flow due to rainfall or irrigation and the solution chemistry. Thus, solution chemical conditions such as presence of natural organic matter (NOM), varying pH, electrolyte concentration and the sodium adsorption ratio (SAR) are crucial factors for the concentration and stability of mobile WDC and they have been widely documented [3–9]. These factors control the equilibrium between repulsive electrostatic forces and van der Waals attractive forces between particles, which govern the stability of WDC dispersions according to the Deryagin–Landau–Verwey–Overbeek (DLVO) theory [10]. Based on physical–chemical parameters such as particle size, surface electrokinetic potential (zeta potential, $\zeta$) and the material Hamaker constant ($A$), DLVO theory can satisfactorily describe interactions between particles [6,11].

Illite and quartz particles are ubiquitous minerals which are found in soil clay fractions. Under typical soil electrolyte conditions, they carry an overall negative charge which makes them potential stable WDCs. However, the heterogeneous chemical composition of the illite phyllosilicate structure at edge sites and basal planes contrasts with the more homogeneous chemical composition of quartz surfaces. The peculiar properties of illite surfaces are characterized by pH-dependent titrating aluminol ($>$AlOH) and silanol ($>$SiOH) groups at edge sites. The aluminol group of octahedral sheets can protonate and deprotonate along the pH under soil electrolyte conditions according to the ionization reaction $-Al-OH^{+1/2} \leftrightarrow Al-O^{-1/2} + H^+$, resulting in positive or negative surface charge with an apparent $pk_a$ 6–8 at a low ionic strength [12]. A net negative charge is also formed under alkaline conditions due to the dissociation of the $>$SiOH group from the tetrahedral sheets. On the other hand, the particle basal plane is characterized by a permanent negative charge mainly resulting from isomorphous substitutions of silicium ($Si^{IV}$) by aluminum atoms ($Al^{III}$). These anisotropic surface properties induce various models of particle aggregations between the edge surface and basal planes. The formation of a card-house structure [13–16] under acidic and neutral conditions is favored where contacts between the positively charged edges of illite [12] due to the protonated aluminol groups and negatively charged basal planes are established. At a basic pH, an overwhelming negative charge characterizes the illite surface. In the case of quartz particles, a point of zero charge (PZC) 2–4 [17] can be measured where surface silanol groups ($pk_a$ 7–8) are predominantly anionic at basic pH [12,18].

The anisotropic surface properties of illite particles render their dispersion/coagulation behavior complex along the pH, which merits to be systematically investigated in comparison with quartz particles. It has been demonstrated that under soil electrolyte conditions, the mobilization of WDC depends on the relative saturation of the medium with major available cations (Ca-system and Na-system) [19]. It must be noted that ionic correlation forces between highly negatively charged particles in the presence of divalent Ca give rise to a net attractive double layer interaction [20–22]. However, the modeling of WDC mobilization in mixed Na–Ca systems, which are more related to soil conditions, has not been investigated as thoroughly [23]. A large distribution of mineral and organic anions also exists in soil, which necessitates a comparative investigation of anionic ligand effects on WDC dispersion phenomena [23,24]. It has been shown that the adsorption extent of anions at the surface of metal oxyhydroxide mineral components depends on their chemical reactivity. Thus, outer-sphere and inner-sphere complexations with metal cations of surface metal oxyhydroxide characterize the electrostatic and chemical adsorption of anions, respectively. Chloride anions mainly interact as an outer-sphere surface complex while $SO_4^{2-}$ and low molecular weight (LMW) organic

acids are known to form both outer- and inner-sphere surface complexes depending on the nature of anions, the surface metal oxyhydroxide and pH [25–27]. In most soils $SO_4^{2-}$ thus competes for the same adsorption sites with LMW anions from plant roots and microorganisms [28]. Among them, NOM in the form of oxalic and formic acids is largely distributed and ubiquitous in forest and agricultural soils [29,30]. In the long term, the surface modification of metal oxyhydroxide by organic acids results in the release kinetics of metal cations in solution by complexation as is the case with oxalic acid [18,26,27,31]. However, in the short term, a surface coating causes variations in the colloidal behavior of WDC depending on the pH, cation nature and concentration [32–34]. It must be noted that the interactions of LMW organic acids with minerals based on ligand exchange and $Ca^{2+}$ bridging/$Ca^{2+}$-LMW organic acid precipitation have been recognized as an important pathway of organic matter stabilization against microbial degradation in soils [5,35,36].

The objective of this study is to investigate the stability of illite and quartz colloids dispersion under various solution chemistry conditions in order to approach the environmental behavior of soil colloids. In this work, we considered $Na^+$ (monovalent) and $Ca^{2+}$ (divalent) salts of simplest largely distributed organic anions, formate (monocarboxylate form, $CHO_2^-$) and oxalate (dicarboxylate form, $C_2O_4^{2-}$) in soils. The results were compared to the $Na^+$ and $Ca^{2+}$ salts with major $Cl^-$ (monovalent) and $SO_4^{2-}$ (divalent) anions. The critical coagulation concentration (CCC) was systematically measured in Na-, Ca- and Na–Ca systems at pH 5.5 and 8.5. The combination of PCS and microelectrophoretic ($\zeta$-potential) methods allowed us to determine parameters, which control the stability of illite and quartz dispersions according to the DLVO theory [10,37]. The coagulation property of low soluble calcium oxalate was investigated with oxalate-modified illite in the presence of $CaCl_2$. In mixed Na–Ca systems, the results were tested and modeled in order to detail the effects of NOM compounds such as oxalate and pH on the stability of WDC under soil conditions.

## 2. Materials and methods

### 2.1. Materials

Colloidal fractions of crushed quartz F32 from Quarzwerke GmbH (Frechen, Germany) and illite from Cs-Ker Illit Bt (Bekecs, Hungary) were obtained after a fractionation procedure based on a 12 h sedimentation period and high-speed centrifugation ($10,000 \times g$; 90 min) of the colloidal dispersion without any filtration [6]. Water purified through Millipore filters was used in all experiments. Colloidal phases of illite and quartz in water were vigorously shaken for 12 h before coagulation investigations. The oxalate-modified illite particle preparation was detailed in Supplementary material. $CaCl_2$, $CaSO_4$, Ca-formate ($Ca(HCOO)_2$), NaCl, $Na_2SO_4$ and Na-oxalate ($Na_2C_2O_4$) (certified ACS reagent) were purchased from Merck (Germany). Stock solutions were prepared and diluted to a series of concentrations in order to acquire the maximum aggregation kinetic gradually. The pHs of colloidal suspension and chemical solutions at 5.5 and 8.5 were adjusted by adding of small amount of HCl and NaOH, respectively (see Supplementary material S.1). According to the $pk_a$, (formic acid: 3.75 and oxalic acid: 1.25 and 3.81 at 25 °C), it can be assumed that formic and oxalic acids are in their carboxylate forms [38].

### 2.2. Methods

The photon correlation spectroscopy (PCS) measurements were performed using a Malvern Nano-ZS apparatus (Malvern Instruments Ltd., Malvern, WR, UK). Measurements were made at the