Molecular modeling studies of interactions between sodium polyacrylate polymer and calcite surface

A. Ylikantola [a], J. Linnanto [a,b,*], J. Knuutinen [a], A. Oravilahti [a], M. Toivakka [c]

[a] University of Jyväskylä, Department of Chemistry, P.O. Box 35, University of Jyväskylä, FI-40014, Finland
[b] University of Tartu, Institute of Physics, Riia 142, EE-51014 Tartu, Estonia
[c] Åbo Akademi University, Laboratory of Paper Coating and Converting and Center for Functional Materials, FI-20500 Turku/Åbo, Finland

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ABSTRACT

The interactions between calcite pigment and sodium polyacrylate dispersing agent, widely used in papermaking as paper coating components, were investigated using classical force field and quantum chemical approaches. The objective was to understand interactions between the calcite surface and sodium polyacrylate polymer at 300 K using molecular dynamics simulations. A quantum mechanical *ab initio* Hartree–Fock method was also used to obtain detailed information about the sodium polyacrylate polymer structure. The effect of water molecules (moisture) on the interactions was also examined. Calculations showed that molecular weight, branching and the orientation of sodium polyacrylate polymers influence the interactions between the calcite surface and the polymer. The force field applied, and also water molecules, were found to have an impact on all systems studied. *Ab initio* Hartree–Fock calculations indicated that there are two types of coordination between sodium atoms and carboxylate groups of the sodium polyacrylate polymer, inter- and intra-carboxylate group coordination. In addition, *ab initio* Hartree–Fock calculations of the structure of the sodium polyacrylate polymer produced important information regarding interactions between the polymers and carboxylated styrene-butadiene latex particles.

1. Introduction

1.1. Calcite surface

Calcium carbonate is the most widely used mineral in paper coating in Europe [1]. Calcium carbonates can be categorized as natural ground calcium carbonate (GCC) or synthetically precipitated calcium carbonate (PCC) [1,2]. The average particle size of PCC is 0.4–2.0 μm [2]. PCC has an extremely narrow particle size distribution and high purity. Therefore it has been successfully used for improving paper quality, *e.g.*, brightness [1,3]. The PCC surface is known to embody calcium ions which have a Lewis acid character [4–7]. These acids are able to bind to numerous basic organic groups, *e.g.*, carboxylate, phosphonate, phosphate and amide groups [4,6]. Most interactions between virgin PCC surfaces and organic additives can be explained by acidic Ca^{2+} sites [6]. Huang et al. [7] reported that at the monolayer saturation a PCC surface can adsorb one Ca^{2+} ion for every 1.05 nm^2 of the PCC surface from calcium chloride solutions. On the other hand, H$^+$, OH$^-$, CO$_3$$^{2-}$ and other ions are able to adsorb onto a PCC surface as well.

A PCC surface has a cationic surface charge [2]. According to Knez et al. [8], Ca^{2+} ion activity especially affects processes such as initial charging of the $CaCO_3$ surface in base PCC dispersions, surface charge regulation and dispersion stabilization efficiency of the polyacrylate dispersing agent. Carbonate ions are unstable under low pH conditions, and they hydrolyze to $HCO_3$$^-$ ions and further to dissolved CO_2 released from the solution. Consequently, the activity of Ca^{2+} ions in the solution at low pH exceeds the activity of the $CO_3$$^{2-}$ ion, and the surface of $CaCO_3$ is positively charged. It has also been found that the fundamental potential-determining ion system for PCC is a Ca^{2+}/anion pair rather than an H$^+$/OH$^-$ pair [9], and Ca^{2+} and $CO_3$$^{2-}$ ions are the major surface ions of the calcite surface [10]. Hydrogen and hydroxide ions do not have an impact on the surface charge of calcite when the pH is between 7 and 12. On the other hand, zeta potential measurements at pH 7.5–11 have suggested that a calcite surface has a positive charge because $CO_3$$^{2-}$ ions are released easier from the calcite surface than Ca^{2+} ions [11].

Calcite is the most common natural calcium carbonate [2,3]. In addition to paper coating colors, calcite is also one of the most abundant minerals in the environment and of fundamental importance in many fields, both inorganic and biological [12–15]. The $10\bar{1}4$ family of crystal faces is the most stable morphology of

* Corresponding author at: University of Tartu, Institute of Physics, Riia 142, EE-51014 Tartu, Estonia. Tel.: +358 408401766.
E-mail address: juha.m.linnanto@gmail.com (J. Linnanto).

calcite [14,16,17]. The above family of crystal faces is also the most commonly discovered morphology of calcite *in situ* [14,17,18].

1.2. Sodium polyacrylate polymer

Polyacrylic acid (PAA) salts have been widely used as dispersing agents in paper coating and sodium polyacrylate polymers are common polyelectrolyte dispersing agents. Molecular weight and composition are two major properties used for describing the effectiveness of the polymer as dispersing agent [19]. Sodium polyacrylate polymers have long chains which can act as spatial steric hindrance, and their surface charge can have the function of electrostatic stability. Consequently, sodium polyacrylate polymers can also prevent the agglomeration of particles and reduce the viscosity of the slurry [20].

Chiefari et al. [21] were the first to describe the reversible addition-fragmentation transfer (RAFT) polymerization process. The same researchers were also the first to introduce controlled polymerization of acrylic acids [21,22]. The RAFT technique suits for example polymers which contain acrylic, styrenic or vinylic monomers [23]. An advantage of the RAFT process is that it produces polymers with controlled molecular weight and narrow polydispersity values [21]. According to experimental data [24,25], sodium polyacrylate polymers with a low molecular weight manufactured by the RAFT are linear since those polymers contain only 1.9% of branches. On the other hand, the polymers with a high molecular weight should not be considered as ideal linear polymers.

The molecular weight and molecular weight distribution of sodium polyacrylate polymers seem to affect the adsorption process [24]. Lamarche et al. [26] reported that maximum efficiency in rheological properties of sodium polyacrylate polymers with the molecular weight between 700 and 20,000 g/mol was found at 2000–4000 g/mol. Sodium polyacrylate chains with a molecular weight between 2000 and 4000 g/mol were also found to attach on the calcium carbonate energetically in a more efficient way. Geffroy et al. [27] stated that sodium polyacrylate chains with a molecular mass below 1500 g/mol do not adsorb on the calcite surface. Those polymer chains were not able to displace $CO_3{}^{2-}$ and $HCO_3{}^{-}$ ions and to bind onto Ca^+ sites at the calcite surfaces. It is also evident that larger macromolecules are able to replace small macromolecules bound on the surface. Sodium polyacrylate polymers with a medium molecular weight were found to adsorb energetically in a more advantageous way on the calcite surface than larger polymers [27]. However, larger polymers were also able to bind on the calcite surface, but they were rejected by the medium macromolecules that arrived first on the surface.

Lamarche et al. [26] suggested that the explanation of the dispersion efficiency of sodium polyacrylate polymers with a molecular weight between 2000 and 4000 is electrostatic repulsion between similarly charged particles. When polydisperse sodium polyacrylate chains are used, only chains with a molecular weight of 5000 g/mol adsorb on the surface in a flat conformation while others stay in solution [24]. Chen et al. [20] reported that electrostatic interactions between the nano-sized $CaCO_3$ particles which were modified by sodium polyacrylate polymers were found to be the main factor contributing to the dispersion of nano-sized $CaCO_3$ in water. According to experimental data [27], sodium polyacrylate polymers with a medium molecular weight are able to attach on the calcite surfaces. Those polymers were able to find conformations where the Ca^+ sites at the hydrated calcite surfaces were chelated. Polyacrylate polymers were also able to chelate Ca^+ surface sites by the same mechanism that they chelated Ca^{2+} counterions in the solution. Eriksson et al. [11] also reported that sodium polyacrylate polymers are able to act as chelating agents on the surface

indicating that those polymers were able to change the surface charge of calcite from positive to negative.

Sodium polyacrylate polymers are able to interact endothermically with precipitated calcium carbonate [4], and they can interact quickly and strongly with PCC because Ca^{2+} ions on the surface attract the carboxylate groups of the polymers [4,28,29]. Dissolved Ca^{2+} ions also interact with the carboxylate groups of sodium polyacrylate polymers [4]. The conformation of a polyacrylate dispersant on the PCC surface depends on the concentration of Ca^{2+} surface sites [29].

1.3. Previous modeling results

The adsorption behavior of PAA on the calcite surface has been reported [30]. However, adsorption studies for the system containing calcite surface and sodium polyacrylate polymer have not been reported earlier. Our previous report deals with molecular modeling studies of interactions between styrene-butadiene latex and a sodium polyacrylate polymer surface [31]. On the other hand, various molecular modeling studies of calcite have been carried out earlier using *ab initio*, semi-empirical, density functional, molecular mechanics and molecular dynamics methods [13–17,30,32–59]. There are also numerous publications where water molecules have been included in the calculations concerning calcium carbonate or calcite [13–17,35,36,38,39,41–46,48–51,53–57,59]. In addition, results concerning the development of force field applicable for calcite or calcium carbonate have been reported [16,17]. The calcite surface 1 0 1̄ 4 has been found to be the most stable surface in modeling studies [16,53,54] which agrees with experimental studies [14,16,17].

Atomic charges are important in classical force field calculations because in these methods intermolecular interactions are based on point charges/charge density distributions [60–62]. Yamamoto et al. [34] used a rigid-ion-model analysis to propose effective charges for calcite. Effective charges were $Z_{Ca} = 1.21$ [e], $Z_C = 0.20$ [e] and $Z_O = -0.47$ [e] in calcite. Partial atomic charges for calcite have also been reported with charge values $Z_{Ca} = 2.0$ [e], $Z_C = 0.985$ [e] and $Z_O = -0.995$ [e] [52]. Both a rigid-ion-model and a shell model were used in the above study. Catti *et al.* [58] calculated partial atomic charges for bulk atoms in calcite by an *ab initio* periodic Hartree–Fock (HF) method, the charge values being $Z_{Ca} = 1.865$ [e], $Z_C = 1.075$ [e] and $Z_O = -0.980$ [e]. Ruuska et al. [51] calculated charges of the central surface calcium of water-stabilized and nonwater-stabilized cluster models by an *ab initio* periodic HF method. The atomic charge of surface calcium atoms in calcite clusters varied between 0.839 and 1.521 [e]. Partial atomic charges for water molecules have also been reported [63]. These charge values were obtained by using a rigid-molecule model, where oxygen and hydrogen had charges of −0.82 [e] and 0.41 [e], respectively.

There are various adsorption studies available for calcite. Kerisit and Parker [36] studied the free energy of adsorption of water and calcium as well as water and metal ions (magnesium, calcium and strontium) [55] on the 1 0 1̄ 4 calcite surface by using the computer code DL_POLY. de Leeuw and Parker [53] investigated molecular adsorption of water onto the stepped and planar 1 0 1̄ 4, 0 0 0 1, 1 0 1̄ 0, 1 0 1̄ 1 and 1 1 2̄ 0 surfaces using atomistic simulation techniques and METADISE code. The competitive adsorption of water and formic acid on calcite and fluorite surfaces, and the adsorption of formic acid onto low-index calcite and aragonite surfaces by atomistic simulation techniques have also been studied [44,56]. The adsorption energies for polyacrylate and polymaleate on calcium fluoride were calculated at different pH values using a DREIDING 2.21 force field in molecular dynamic (MD) simulations by ter Horst et al. [64]. The most important adsorption behavior study relating to this work has been published by Liu et al. [30]. They studied the deformation and adsorption behavior of PAA on