Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

# Ion effects in the adsorption of carboxylate on oxide surfaces, studied with quartz crystal microbalance

Lei Wang*, Igor Siretanu, Michel H.G. Duits, Martien A. Cohen Stuart, Frieder Mugele

Physics of Complex Fluids Group, MESA+ Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, the Netherlands

HIGHLIGHTS

- Carboxylate adsorption on mineral surfaces is studied with Quartz Crystal Microbalance.
- On silica, Ca^{2+} can promote carboxylate adsorption via ion-bridges.
- On alumina, carboxylates adsorb mainly via ligand exchange, even in presence of Ca^{2+}.
- On gibbsite, carboxylates and Cl^- adsorb competitively via pre-adsorbed Ca^{2+}.

GRAPHICAL ABSTRACT
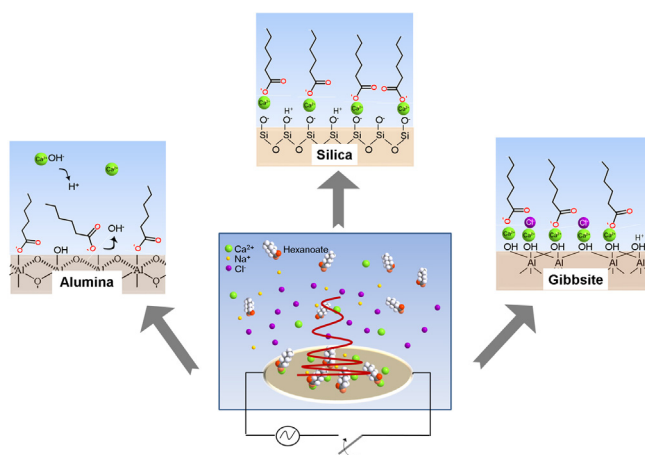
ARTICLE INFO

ABSTRACT

We chose water-soluble sodium hexanoate as a model organic molecule to study the role of salt ions (Ca^{2+}, Na^+, Cl^-) in the adsorption of carboxylates to mineral surfaces (silica, alumina, gibbsite) of variable surface charge and chemistry. Quartz crystal microbalance (QCM-D) measurements reveal a qualitatively different dependence of the adsorption behavior on the electrolyte composition for the different surfaces at near neutral pH. Overall, hexanoate adsorption is more pronounced on the positively charged alumina surfaces than on negatively charged silica surfaces. On silica, however, Ca^{2+} ions strongly enhance the adsorption of hexanoate, suggesting that the divalent cations act as bridges between carboxylate and deprotonated silanol surface groups. On alumina, hexanoate adsorption is found to depend only weakly on the salt composition, suggesting a direct interaction of the carboxylate group with the surface, consistent with a ligand-exchange mechanism. The adsorption behavior on partially gibbsite-covered silica surfaces is particularly rich and displays a strong non-monotonic dependence on the $CaCl_2$ concentration. Comparison to earlier work and control experiments suggest an important role of Cl^- anions, which compete with the carboxylate group for adsorption sites.

1. Introduction

Adsorption of organic molecules and other species at mineral (clay) water interfaces has been studied for a long time but still

* Corresponding author.
  E-mail address: l.wang@utwente.nl (L. Wang).

L. Wang et al. / Colloids and Surfaces A: Physicochem. Eng. Aspects 494 (2016) 30–38

31

attracts great interest of researchers. This is because the adsorption phenomena can have a multitude of effects: they can alter the wettability of macroscopic substrates [1], tune the rheology of particle suspensions [2], modify the sorptive properties [3], etc. As a result, this phenomenon is critical to many industrial applications such as water treatment [4], nanocomposites fabrication [5] and oil recovery [6,7].

Clay also known as phyllosilicate, mainly consists of aluminosilicate layers, containing silicon dioxide tetrahedral sheets and aluminum oxyhydroxyl octahedral sheets. Therefore in many fundamental studies silica, alumina or gibbsite are used as models of clay minerals. In particular, studies on interactions between organic molecules like carboxylates and the above mineral surfaces have been conducted [8–12], because carboxylates are commonly found in nature as well as in industrial processes. Effects of pH and ionic strength on the adsorption process have been well covered by several works [8,12–15]. However, only few studies were so far aimed at comparing the adsorption behaviors of carboxylates on different substrates and at different aqueous ion compositions (including salt mixtures). An exception is the recent work of Juhl, who reported that the bonding strength between a carboxylate and an alumina surface changes with the solution salinity, and that divalent ions can replace adsorbed monovalent ions on oxide surfaces [16]. Understanding the adsorption mechanism of carboxylates at the different clay surfaces, including the competition between ions during this process, would help to understand many industrial processes.

A good example is given by the water flooding process, which is routinely practiced in oil recovery to release (more) hydrocarbons from the subsurface. Traditionally, (highly saline) sea water is injected into the rock reservoir to repel the mobilized oil from the rock surface. However, it was recently found that the recovery can be enhanced by flooding with low salinity solutions [17,18]. This low salinity effect has been attributed to an alteration of the wettability: the rock becomes more water-wet when organic material is desorbed from the clay surface. However the underlying microscopic mechanisms behind the ad/desorption of organic molecules and other species at clay-mineral surfaces are still not clarified. In previous works, some progress was made along this line. Langmuir–Blodgett films were studied to demonstrate the role of divalent cations as bridging ions between silica substrates and stearic acid molecules [19]. Additionally, atomic resolution AFM was used to examine specific ion adsorption on gibbsite surfaces [20].

In this paper, we investigate the adsorption of a water soluble, short-chain carboxylate (hexanoate) on various oxide surfaces (silica, alumina and gibbsite). The aim is to understand the role of cations in particular from mixed electrolytes on the adsorption of carboxylate, as well as the adsorption mechanism of carboxylate on these oxides. The pH value was chosen to be around 7, which is close to the natural conditions. In this regime, the dissociation of the carboxylic acid and the surface charges of the oxides (silica, alumina and gibbsite) surfaces are all sensitive to the pH. Besides different concentrations of hexanoate, also various compositions of NaCl and $CaCl_2$ solutions were explored.

The principal technique we have used is the measurement of adsorbed mass using a Quartz Crystal Microbalance capable of quantifying also dissipation (QCM-D). Careful application of this sensitive method allowed us (for the first time) to perform semi-quantitative measurements of the adsorption isotherm for these very small molecules. To support our data analysis, also Atomic Force Microscopy (AFM) experiments were performed; these measurements provided information about the state of charge of the bare substrates. Based on the combined data, adsorption mechanisms on different solid surfaces are proposed.

2. Experimental

2.1. Materials

Sodium hexanoate (C6), Hexanoic acid, $CaCl_2 \cdot 2H_2O$, and NaCl were obtained from Sigma–Aldrich and used without further purification. Deionized water with a resistivity of $18.2\,M\Omega\,cm$ (Synergy-UV, Millipore) was used throughout this study.

Silica-coated and alumina-coated quartz crystal sensors were purchased from Q-sense (Gothenburg, Sweden). A suspension of gibbsite nanoparticles was kindly provided by the group of Prof. A.P. Philipse (University of Utrecht, the Netherlands). Synthesis and characterization of the material were described by Wierenga et al [21]. The gibbsite-coated sensor was prepared by depositing gibbsite particles from a suspension on the silica coated quartz crystal, following the procedures described by Siretanu et al. [20].

2.2. AFM imaging and force spectroscopy measurements

Topographical features of the QCM sensor surfaces were studied by using a Multimode8 Atomic Force Microscope with a Nanoscope V controller (Bruker Nano). A Dimension Icon AFM (Bruker) equipped with a Nanoscope V controller was used to study the surface charge of the sensors. All samples were analyzed in amplitude modulation mode. Silicon tips from MikroMasch, NSC36 ($f_0 = 52\,kHz$, $c_z = 3.6\,N/m$, $Q = 4.8$, tip radius $\sim$19 nm) and Bruker FASTSCAN-B cantilevers ($f_0 = 170\,kHz$, $c_z = 3\,N/m$, $Q = 10$, tip radius $\sim$3 nm) were used. Before the measurement, both the tip and cantilever were rinsed with an ethanol/isopropanol ($\approx$1:1) mixture and treated further with air plasma (Harrick Plasma) for 15 min. Image analysis was carried out with Nanoscope Analysis version 120 software (Bruker). Roughness data were extracted from three separate images obtained at different regions on each sample. The surface coverage of gibbsite sensor was $55\% \pm 10\%$. The surface charge of the substrates in electrolyte solution was determined from analysis of AFM interaction stiffness (force gradient) versus distance curves in the framework of DLVO theory, complemented by a charge regulation boundary condition. The AFM equipment, the operations, and details about force inversion and charge extraction have been described elsewhere [22,23].

2.3. Adsorption measurements by QCM

Adsorption experiments were performed as a function of the Na-hexanoate (C6) and salt concentrations. On each sensor, three concentration series were examined. In each of the series, the concentration of C6 was varied from 0 to 10 mM. Since this is far below the solubility (70 mM) [24,25], no precipitation should occur. The total Na^+ concentration (from C6 and NaCl) was always maintained at 10 mM, while the concentration of $CaCl_2$ was controlled at 0, 10 and 20 mM. In short, these series are denoted as: 1) C6-Na; 2) C6-Na-10Ca and 3) C6-Na-20Ca. The pH of the samples varies from 6 to 7 with the concentration of C6. Because hexanoic acid is a weak acid ($pK_a = 4.85$), the carboxylate groups will occur partly in protonated and partly in deprotonated form. According to Lee [26], at pH 7 the Critical Micelle Concentration (CMC) of Na-carboxylate is approximately 1 M, and that of Ca-dicarboxylate is higher than 0.03 M [27,28]. Our solutions are always more diluted than this, so that we can safely exclude the presence of micelles.

Adsorption studies are conducted with the QCM-D (E4) instrument from Q-sense (Gothenburg, Sweden). A standard AT-cut quartz crystal sensor with a diameter of 14 mm has a 100 nm thick gold layer as electrode. In our case silica-, alumina- and gibbsite-coated sensors were used. The QCM-D liquid chamber is mounted on a Peltier element, which controls the temperature accurately (at $22 \pm 0.1\,^\circ C$) to avoid signal drifts. The fundamental oscillation