Carboxymethyl cellulose binding to mineral substrates: Characterization by atomic force microscopy–based Force spectroscopy and quartz-crystal microbalance with dissipation monitoring

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ABSTRACT

The attachment of the sodium salt of carboxymethyl cellulose (CMC) onto iron oxide and various silicate substrates in aqueous solution as a function of salt concentration and pH was studied by atomic force microscopy–based force spectroscopy (AFM) and quartz-crystal microbalance with dissipation monitoring (QCM-D). Both ionic strength and cation valency were found to influence substrate binding. Notably, QCM-D experiments strongly suggested that the solubility of CMC is directly impacted by the presence of $CaCl_2$. Such data are critical for the design of new molecules for stabilizing mineral floc dispersions and for assessing the mobility of CMC-coated particles in the subsurface. Modeling of AFM data with an extended Ohshima theory showed that van der Waals and steric forces played a major role in the interactions between CMC and mineral substrates, and that hydration forces were also important.

1. Introduction

The sodium salt of carboxymethyl cellulose (CMC) is a polymer derived from cellulose, yet, unlike cellulose, CMC is soluble in water and chemically reactive (Fig. 1). CMC is neutral at low pH values but hydrolyzes at high pH values. Specifically, at high pH, CMC loses its positive Na^+ counter-ion, acquiring a negative charge. The extent of CMC dissociation is both pH and ionic-strength dependent [1]. Like many other carbohydrates such as starch, guar-gum and dextrin, CMC finds application in a diverse number of industries. It is used to retain water and stabilize dispersions and as a thickener in the cosmetic and food industry [2,3]. In the mineral industry, CMC can be used to both inhibit mineral flotation and stabilize mineral suspensions [4–6]. In order to evaluate the usefulness of CMC either as inhibitor or stabilizer it is important to gain a basic understanding of CMC adsorption onto substrates such as alumina [7], pyrite [8], chalcopyrite [9], molybdenite [10], and talc [9,11–14]. CMC has been used to stabilize titanium nano-particles and zerovalent iron nano-particles, both of which are employed for remediation purposes [15–22]. When particles are employed for remediation purposes, it is important to understand how CMC coatings can affect their mobility in the subsurface.

To achieve this goal, it is crucial to probe CMC attachment onto minerals present in the soil.

In order to clearly understand how CMC functions as either a stabilizer or inhibitor of mineral dispersions and how CMC coatings can affect particle mobility in the subsurface, it is important to elucidate the nature of association of CMC with the mineral surface and how this association impacts subsequent interactions. The forces between polymers, such as CMC, and mineral surfaces arise as a consequence of a diversity of interactions, including van der Waals, hydration, electrostatic and steric forces, as well as hydrogen bonding and acid–base interactions. Repulsive steric forces in particular, arise due to compression of the polymer chains [23], and would be clearly dependent on the conformation of the polymer at the mineral surface. We therefore believe that repulsion between polymer-modified substrates is facilitated by polymers that adsorb and adopt an extended conformation protruding perpendicularly from the surface, potentially akin to a brush motif. Since polymer conformation is solvent-dependent, in the case of aqueous solutions, water chemistry (pH, ionic strength) would clearly influence steric forces. This is particularly true for charged polymers that extend away from the surface onto which they are grafted or physisorbed to minimize contact with each other [24].

Neutral in acidic environments, CMC is hydrolyzed under basic conditions, acquiring a negative charge. It is therefore expected that, at high pH, CMC adopts an extended conformation due to

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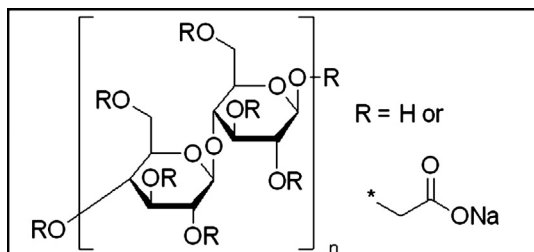E-mail address: sleep@ecf.utoronto.ca (B.E. Sleep).

Fig. 1. Structure of the sodium salt of carboxy-methyl cellulose employed in this study.

electrostatic repulsion between the polymer chains. At low pH, CMC is instead more likely to be coiled or collapsed, since the polymer chains are neutral and interchain repulsion decreases. This is consistent with the observation of enhanced swelling of CMC hydrogels under neutral and basic pH conditions [25]. Salts can have an effect similar to low pH values on the polymer conformation due to their ability to participate in electrostatic charge screening [9], which reduces interchain repulsion and favors a coiled conformation [26]. In the case of CMC, both mono- and divalent cations are known to readily associate with the polymer [27–29]. However, divalent salts were found to have a more significant effect than monovalent salts. In particular, it has been reported that the viscosity of CMC solutions decreased significantly in the presence of Ca^{2+} compared with Na^+ at the same ionic strength [30]. This was attributed to more effective screening by the divalent calcium ion and contraction of CMC chains upon chelation. This effect was reinforced by the observation that the sodium salt of CMC is soluble while its calcium counterpart is insoluble [31]. Based on these data, we believe that aggregation of the CMC occurs in the presence of Ca^{2+}, possibly due to adoption of a coiled conformation for CMC, which promotes flocculation.

Electrostatic forces between polymers such as CMC and mineral surfaces can be affected by the presence of other salts in solution. For example, charge neutralization or reversal in the presence of calcium was hypothesized to promote CMC sorption onto talc [13]. Alternatively, positively charged ions may bind at the negatively charged mineral surfaces, acting as positively charged sites to promote attractive interactions with CMC molecules (bridging effect).

The importance of hydrogen bonding between CMC and mineral surfaces was previously recognized by some authors [3,8], while other researchers propose acid–base interactions as the main sorption mechanism [4]. According to these authors, the characteristics of cations at the mineral surface (valence, radius, and coordination numbers) can affect acid–base interactions by influencing the basic properties of the mineral surfaces. In particular, they report that sorption of certain polymers (such as starch) onto calcium-bearing minerals is particularly favorable. It is noted that both hydrogen bonding and acid–base interactions act at separation distances shorter than electrostatic and van der Waals forces.

To date, the adsorption of CMC onto mineral surfaces has been studied by flotation tests [5,14], atomic force microscopy imaging [3,9], infra-red spectroscopy [3,13], and ToF-SIMS [12,14]. Also, QCM-D studies have been conducted to probe CMC sorption onto cellulose surfaces [32,33], but not onto the materials utilized in the present study. To the best of our knowledge, AFM-based force spectroscopy has only been used to measure the mechanical properties of individual CMC polymers [34]. In the present study, AFM-based force spectroscopy was used to probe the forces of interaction between CMC and several mineral surfaces as a function of water chemistry. The minerals employed in AFM experiments include iron oxide particles and silicate particles (silica, borosilicate,

and pumice stone). The silicate particles employed differed in mineral composition and surface roughness, which can affect surface forces. This study allowed assessing if different silicates interact with CMC in a similar manner, or if dissimilarities in surface roughness and mineral composition can have a major impact on the forces of interaction.

Parallel measurements using quartz-crystal microbalance with dissipation monitoring (QCM-D) were performed to assess the reversibility of CMC adsorption onto these surfaces. QCM-D experiments were conducted using magnetite, silica, and aluminum–silicate substrates. Modeling with extended DLVO theory combined with a modified Ohshima's theory [35,36] was conducted to assess the importance of van der Waals and steric forces. Our results will allow theoretical predictions of CMC polymer sorption onto mineral surfaces and may be useful in interpreting experimental studies, for example column adsorption studies, wherein interaction forces cannot be directly measured.

2. Materials and methods

2.1. Atomic force microscopy–based force spectroscopy studies

2.1.1. CMC-coated mica used for AFM studies

CMC polymer coatings were obtained by pipetting 0.1 mL of CMC solution (35 g/L) onto freshly cleaved mica disks. The excess polymer was gently blown off the disks with nitrogen gas, and the polymer solution was allowed to dry. The treatment was repeated at least two times to ensure complete coverage of the mica surface.

2.1.2. Iron oxide particles

Carbonyl iron particles (CIP, Alfa Aesar, product number 10214) were high purity micron-sized iron particles. The CIP were affixed onto AFM cantilevers as described in Section 2.1.4 and aged in pure water (milli-Q water) at room temperature (23 °C) overnight. After aging, the outer core of the particles was a mix of iron oxides and hydroxides, as determined by XPS and EDS analyses. The point of zero charge for aged CIP, ~9, was determined by potentiometric titration in milli-Q water and in 0.1 M $NaNO_3$ salt solution. This value is within the range previously reported for iron oxides [37,38] and nano-iron slurries [39].

2.1.3. Pumice stone particles

Natural pumice stone was crushed using a mortar and pestle to yield particles with a porous surface and irregular structure ranging in diameter from about 1–2.5 μm as determined by scanning electron microscopy (JEOL JSM6610-Lv). The mineral composition of the pumice stone was determined using powder X-ray diffraction (XRD), using a Philips XRD system equipped with a PW 1830 HT generator, a PW 1050 goniometer and PW3710 control electronics. Pumice stone was mainly quartz (SiO_2), with minor amounts of tobermorite (Ca_4Si_6). The particles were negatively charged up to a pH of 2.7, as determined through potentiometric titration conducted in Milli-Q water (titrations were not conducted at lower pH values). This result is consistent with the fact that the

Table 1
Zeta potential of pumice stone particles in different water chemistries.

Solution	pH	Average zeta potential (mV)	Standard deviation (mV)
Milli-Q	5.5	−22.4	5.4
Milli-Q	4	−16.6	5.0
Milli-Q	8	−27.2	5.9
NaCl, 100 mM	5.5	−25.5	0
CaCl2, 100 mM	5.5	−0.5	0