Short communication

Use of molecular dynamics to study the conformation of an anionic polyelectrolyte in saline medium and its adsorption on a quartz surface

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ABSTRACT

In seeking to gain insights on the performance of long chain water-soluble polymer flocculants when conducting mineral processing in highly saline liquors, molecular dynamic simulation was used to study the effect of NaCl concentration on the conformation of an anionic polyelectrolyte and its adsorption on a quartz surface at pH values above its isoelectric point. Increased salinity led to two competing effects on the overall flocculation process: (i) increased polyelectrolyte adsorption on the quartz surface favours the initial aggregate-forming collisions, but (ii) the radius-of-gyration of the polyelectrolyte is reduced, which then may limit the aggregate size achieved. Such results support reported experimental trends and show the advantages of computational methodologies to describe complex systems.

1. Introduction

Mineral processing to separate and concentrate valuable phases involves large volumes of water and the generation of tailings, i.e. fine gangue phases in dilute suspensions. The tailings are treated in gravity thickeners, large settling tanks in which water is recovered for upstream reuse and solid phases are concentrated for deposition or disposal, ideally over a low area footprint.

High volumetric throughputs require particles to settle at rates well in excess of what they would on the basis of their size. This is achieved by adding *flocculants* - high molecular weight water-soluble polyelectrolytes that adhere to specific active surface sites, bridging particles to form larger structures (aggregates) and accelerating settling by up to several orders of magnitude. Decisions on reagent management, such as polymer and dosage selection, are made empirically and often with little fundamental understanding, despite flocculation being highly sensitive to a variety of variables.

The physical characteristics of aggregates on a microscopic scale govern flocculation responses, which can in part be manipulated through knowledge of the flocculant's solution and adsorption properties. Mineral processing flocculants are based on hydrolysed polyacrylamide (HPAM), typically acrylamide and acrylate copolymerised at varying ratios, the latter's charged functionality favouring chain extension in aqueous solutions. Adsorption of a single functionality to a surface is weak, but adsorption of multiple functionalities from one chain (a "train") is effectively irreversible, with unadsorbed "tails" then able to offer bridging.

While tailings composition varies widely in mineralogy and size, in general the fines fraction ($< 20\,\mu m$) determining solid-liquid separation and flocculation behaviour is dominated by clays and fine quartz phases. Quartz surfaces consist of silanol groups (Si-OH), but clay surface chemistry is complicated by their plate-like structures. The major basal faces consist of silanol groups which are negatively charged over most pH values and effectively control the bulk particle charge, while the minor edge faces have a higher proportion of aluminol groups (Al-OH) with a greater prospect of providing neutral sites for flocculant adsorption at most slurry pH values (Hocking et al., 1999).

There is strong interest (and a need in some cases) to use highly saline liquors and even seawater in mineral processing (Cisternas and Moreno, 2014), which influences the flocculation process. At pH values > 3, minimal flocculant adsorbs on quartz surfaces in the absence of salt (Somasundaran and Zhang, 2000). Adsorption may then be through salt bridges, where cations link between the hydrolysed silanol sites and anionic HPAM groups. However, the measured flocculation trends in saline liquors can be complex and contrasting (Witham et al., 2012; Jeldres et al., 2017; Costine et al., 2018), making ultimate effects on separation processes difficult to predict.

Techniques such as viscometry, carbon analysis, x-ray spectroscopy

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and atomic force microscopy have been applied to probe the state of flocculants both in solution and adsorbed on surfaces (Girod et al., 1988, Lecourtier et al., 1990; Allen et al., 1998; Dalton et al., 2002), although most approaches give indirect information or require drying, the latter likely to induce changes. Molecular dynamics (MD) simulations offer the potential to describe how systems of interest behave on a microscopic scale. The quartz-water interface has been extensively simulated - for example, Quezada et al. (2017) showed ion adsorption obeys the concept of "like absorbs like", where weakly hydrated ions are better adsorbed on low isoelectric point quartz surfaces that are weakly hydrated. On the other hand, Chen et al. (2012) showed through MD that Na^+ ions reduce the HPAM size by decreasing the repulsion of its charged groups. Abdel-Azeim and Kanj (2018) predicted this effect to be even greater in the presence of divalent cations.

The interaction of biological molecules with mineral surfaces has been studied by MD (e.g. Emami et al., 2014). Simulations of the effect of salt type on HPAM adsorption to quartz at different pH have also shown better adhesion with cations of higher electrical density, such as Li^+ and Na^+, than with Cs^+ (Quezada et al., 2018). In this work, the effect of salinity (NaCl) on the phenomena involved in HPAM adsorption on a quartz mineral (1 0 1) surface is analysed, with particular emphasis on the density of adsorption and the polyelectrolyte conformation.

2. Methodology

Molecular dynamics simulations were carried out for: (i) a model polymer in the presence of salts for prediction of the radius-of-gyration in solution and (ii) a quartz surface in the presence of the polymer and salts for prediction of subsequent adsorption. The HPAM flocculant is represented by a 25% anionic polymer formed from 54 acrylamide and 18 acrylate evenly distributed monomers, the functionalities of the latter in deprotonated form ($-COO^-$) at pH > 6. The surface is crystalline quartz with an area of $5.8 \times 5.5\,nm^2$ and the face (1 0 1) exposed to the medium having explicit silanol groups; this face represents one the most common cleavages found in nature (de Leeuw et al., 1999). The ions are spheres of Na^+ and Cl^-, while the water used is the SPC/E model and is represented by three explicit site atoms. Computer simulations were carried out in the package Gromacs 5.1.2. The interaction potentials used were AMBER99SB for HPAM, CLAYFF for quartz and the potential shown in Li et al. (2015) for ions. The similarity of these functions facilitates their use together. For a correct representation of the electronic density of the quartz surface to incorporate pH effects through charge density, first principles calculations for partial charges of the HPAM and the surface deprotonation, respectively, were performed in Gaussian 09 using the DFT B3LYP method with the base functions 3-21G for the non-oxygen atoms and 6-31G (d,p) for the oxygens (Kroutil et al., 2015). An initial energy minimisation step was made by steepest descent, followed by (i) a constant particle, volume and temperature (NVT) simulation of 1 ns only as free water molecules to generate hydration layers, and (ii) a constant particle, pressure and temperature (NPT) step of 2 ns, initially using annealing with an increase to 430 K per 100 ps and then lower to 300 K, thus eliminating metastable HPAM configurations. Finally, an NVT simulation of 80 ns is used to generate results. The step of integration is 2 fs, and the constants of the thermostat and barostat of Berendsen are 0.1 and 2.0 ps, respectively.

3. Results

The predicted radius-of-gyration (r_g) of the HPAM polymer in response to increasing salinity (Fig. 1a) clearly shows a contraction in conformation. For context, r_g for the polymer in the absence of salt was 1.85 nm, and hence the presence of 0.6 M NaCl represents a reduction in size of one-third. Electrostatic repulsions between the $-COO^-$ groups serve to keep the polyelectrolyte chain stretched at low ionic
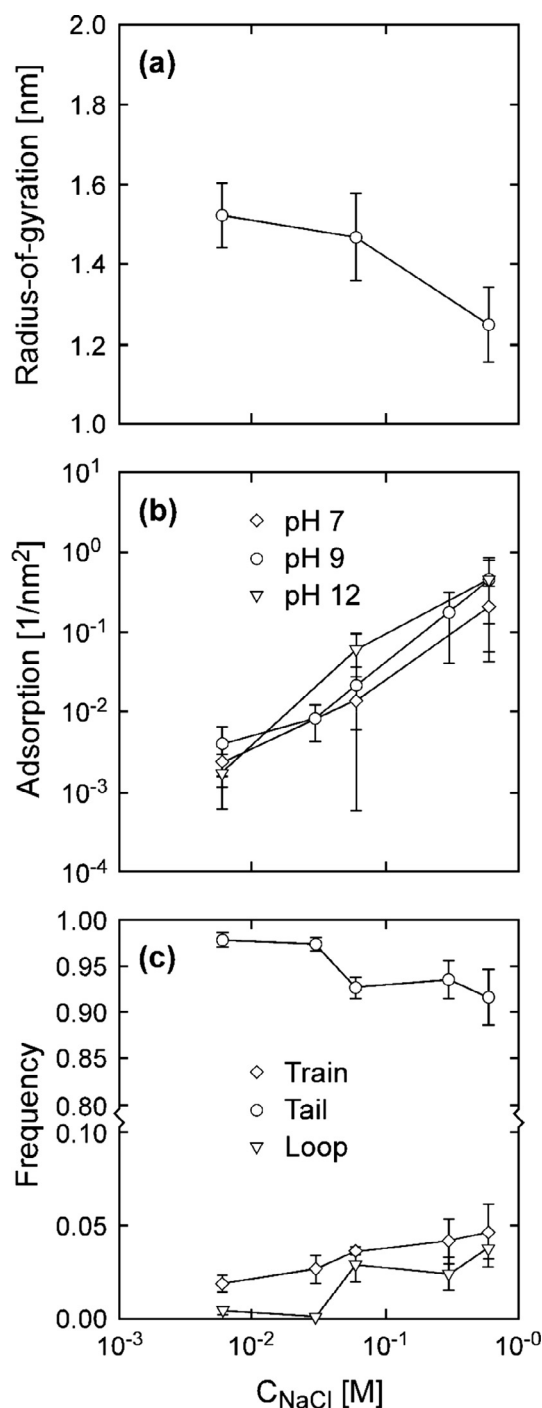

Fig. 1. Flocculant response to changes in salinity: (a) radius of gyration for pH > 6, (b) adsorption on a quartz surface, (c) flocculant conformation on a quartz surface.

strength, but such repulsions are reduced by shielding from increasing the counter-ion concentration (Na^+), and the polyelectrolyte's effective size decreases. Fig. 2a is a representation from the simulations of this behaviour, clearly showing the change in chain extension.

Simulation of the polyelectrolyte interactions with a quartz surface (Fig. 1b) indicated adsorption density was strongly influenced by higher salt concentration, increasing by more than two orders of magnitude on going from 0.006 M to 0.6 M NaCl, with pH having no discernible effect. The enhancement of adsorption is captured by the simulations in Fig. 2b, where the Na^+ cations that shield the $-COO^-$ groups of HPAM and also adsorb on the quartz surface combine to give closer approach