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Adsorption of hybrid polyacrylamides on anisotropic kaolinite surfaces: Effect of polymer characteristics and solution properties

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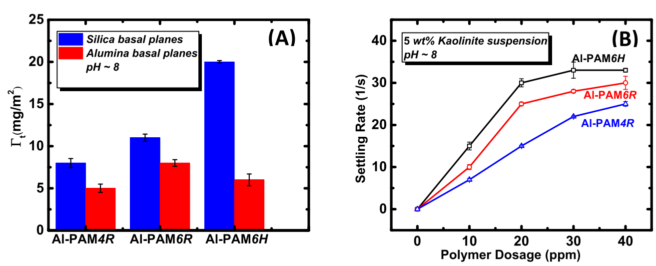
HIGHLIGHTS

- Increasing the molecular weight resulted in an increase of the mass uptake of the polymer on silica and alumina basal planes.
- The amount of the polymer adsorbed on silica increased by increasing Al content in contrast to the adsorption on alumina.
- Fitting of the adsorption data to the Langmuir adsorption isotherm revealed spontaneous adsorption of Al-PAM on silica.
- The adsorption of Al-PAM on silica was shown to decrease in plant recycle water compared to deionized water at pH ~8.
- Maximum coverage of Al-PAM on silica basal planes is lower at higher temperatures.

GRAPHICAL ABSTRACT

(A) Comparison of the total amount of adsorbed mass of different Al-PAMs on silica and alumina basal planes of kaolinite measured by QCM-D and; (B) Comparison of settling rates of 5 wt% kaolinite suspensions after flocculation by Al-PAMs. Settling rates (1/s) was obtained by plotting the normalized mudline height (h/H, where “h” is the mudline height at settling time “t” and “H” is the initial suspension or mudline height) versus the settling time. Molecular weight: Al-PAM*6R* = Al-PAM*6H* > Al-PAM*4R*; Aluminum content: Al-PAM*6R* = Al-PAM*4R* < Al-PAM*6H*.



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ABSTRACT

Adsorption kinetics of organic-inorganic (hybrid) $Al(OH)_3$-polyacrylamide (Al-PAM) with different molecular weights (for organic characteristics) and contents of aluminum hydroxide nanoparticles (for inorganic characteristics) on kaolinite basal planes was studied using a versatile quartz crystal microbalance with dissipation (QCM-D). The flocculation dynamics of kaolinite by Al-PAMs was assessed by measuring the initial settling rate of flocculated kaolinite particles and the turbidity of the supernatant after settling of flocculated solids. The areal mass (mg/m^2) of Al-PAMs adsorbed on tetrahedral silica and octahedral alumina basal planes of kaolinite increased with increasing molecular weight of the polymer. Increasing the content of Aluminum hydroxide nanoparticle in Al-PAM has resulted in an increase of the amount of the polymer adsorbed on silica basal planes while opposite trend was found on alumina basal planes. Results obtained from the adsorption kinetics study of Al-PAM*6R* (M_w = 2.2 million Dalton, 0.11 wt% Aluminum) on silica basal planes revealed that the early stage of adsorption is diffusion-controlled. Thus, initially the adsorption rate increased with increasing temperature while the maximum coverage decreased. Moreover, the adsorption of Al-PAMs on silica basal planes was shown to decrease significantly in plant recycle (process) water compared to deionized water. Al-PAMs of higher molecular weight and/or high content of inorganic

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$Al(OH)_3$ nanoparticles were found to be more effective in flocculating kaolinite as indicated by the faster settling rates and clearer supernatant.

1. Introduction

Interactions between water-soluble polymers and clay surfaces, at a molecular level, are of critical importance in controlling the stability of clay dispersions, depending on the type of polymers used and the nature of the interaction mecahnisms [1]. For example, in the field of waste water treatment and mineral tailings management, the use of high-molecular weight polymers as flocculants has been a dominant practice to enhance sludge dewatering. Dewatering is accomplished by bridge-flocculation and the subsequent sedimentation of suspended colloidal mineral particles [2–6]. In other processes such as flotation operations, relatively small molecular weight polymers are used to depress gangue minerals by blocking collector adsorption and dispersing the particles [7–10]. In both cases, the structural properties of polymer molecules used are one of the primary factors that determine the efficiency of the process. Therefore, fundamental investigations on the effect of polymer structure on the adsorption process are of great importance for solving industrial pollution problems and for developing more versatile and effective solutions for fine solid-liquid separation as being increasingly encountered in nanotechnology.

Organic-inorganic (hybrid) polymers are well-known for their unique structural properties [10]. Hybrid organic-inorganic macromolecules are not just a physical mixture of their organic and inorganic constituents. Their properties are not the sum of individual components, rather they offer totally new characteristics, depending on many factors including the spatial and size distribution, and the ratio of individual constituents of the polymer [11,12]. These hybrid organic-inorganic polymers have become the foundation for several new technologies. The functionalities of hybrid polymer molecules are determined mainly by their chemical composition, molecular size and structure, morphology and the configuration they adopt at different interfaces [13]. For example, in the field of solid-liquid separation, it was proposed that hybrid polymers with star-like structures are more effective than their linear counterpart in flocculating fine and ultrafine mineral particles, probably as a result of the secondary aggregation of the primary aggregates or floccules to form larger aggregates/flocs, creating a raspberry-like structure of the aggregates [14]. The structural properties of such novel molecules can always be tuned to meet a targeted application [11]. Organic-inorganic polyacrylamides are the focus of this work due to the importance of polyacrylamides and their co-polymers in a wide range of industrial processes such as soil erosion control, soil conditioning and irrigation control. They are also important flocculants for wastewater and industry effluent treatment, including the management of oil sands tailings [5,15,16].

In our previous publication, adsorption characteristics of $Al(OH)_3$-PAM (Al-PAM) on anisotropic T- (silica) and O- (alumina) basal planes of kaolinite were investigated using a quartz crystal microbalance with dissipation. Data from this work showed a preferential adsorption of the polymer on T-basal planes via strong electrostatic attractive forces and hydrogen bonds [17]. The adsorption of Al-PAM on O-basal planes is relatively weak, mainly governed by the hydrogen bonding mechanism [17].

In this study, the effect of structural properties of organic/inorganic hybrid Al-PAM on its adsorption on different kaolinite basal planes was investigated in the context of kaolinite flocculation using Al-PAMs of different molecular weight and $Al(OH)_3$ nanoparticle content. Adsorption kinetics was investigated using a quartz crystal microbalance with dissipation in combination with electrokinetics measurements. The effect of water chemistry and temperature on adsorption of Al-PAMs on kaolinite was also investigated. The flocculation performance was assessed by measuring the initial settling rate of kaolinite suspensions and the turbidity of the supernatant after settling of the flocculated kaolinite particles.

2. Materials and methods

2.1. Materials

Al-PAMs used in this study were synthesized in-house using the procedures described elsewhere [1,18,19]. The characteristics of the Al-PAMs used in current study are summarized in Table 1. The star-like molecular structure proposed is depicted in Fig. 1 [14,19]. Micron size kaolinite particles used in flocculation tests and nonionic polyacrylamide (PAM) of a molecular weight of 5 million Dalton were purchased from Fisher Scientific. Polymer stock solutions were prepared at a concentration of 500 ppm in MilliQ water two days prior to their use. Silicon dioxide-coated QCM-D sensors (simulating silica basal surface) and aluminum oxide-coated QCM-D sensors (simulating aluminum oxyhydroxyl basal surface) were purchased from Q-sense (Gothenburg, Sweden). High-purity kaolinite, kindly provided by Dr. Miller's research group at the University of Utah, was used for preparation of differentiated kaolinite basal planes by deposition of the particles on QCM-D sensors, a method developed by Miller's group [17,20]. ACS grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) from Fisher Scientific were used to adjust the pH as needed [1]. Deionized water with a resistivity of 18.2 MΩ cm, obtained using a Millipore-UV Plus water purification system (Millipore Inc., Canada), was used throughout this work, unless otherwise specified.

2.2. Experimental procedures

2.2.1. Determination of intrinsic viscosity and viscosity average molecular weight (M_w)

Intrinsic viscosity [η] measurements were conducted using an Ubbelohde viscometer (CANNON 75-J953, Fisher Scientific) at 25 °C. The flux time was recorded with an accuracy of ±0.05 s [19].

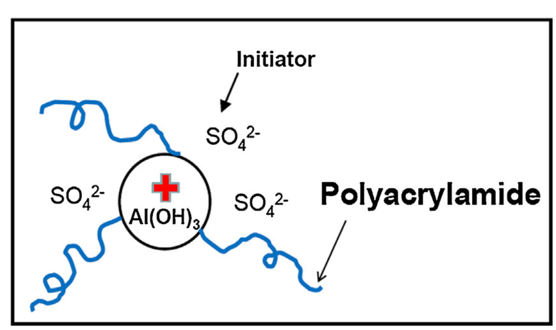

Fig. 1. Proposed molecular structure of $Al(OH)_3$-Polyacrylamide, Al-PAM [14,19]. (The typical size of $Al(OH)_3$ nanoparticles ranges from 30 to 50 nm while the hydrodynamic radius of Al-PAM varies between 270 and 300 nm.)