



Spherical α -Al₂O₃ suspensions layered sequentially with anionic and cationic polyelectrolytes: Chemistry, rheology and TEM images

Wei Zhang^{a,b}, Pek-Ing Au^{b,e}, X. Zhang^c, H. Fan^c, Chunbao Sun^a, M. Saunders^d, Yee-Kwong Leong^{b,*}

^a Department of Mineral Processing Engineering, School of Civil and Resource Engineering, University of Science and Technology Beijing, 100083, China

^b Department of Chemical Engineering, University of Western Australia, Crawley 6009, Australia

^c State Key Laboratory of Polymer Reaction Engineering Zhejiang University Hangzhou, 310027, China

^d Centre for Microscopy, Characterisation and Analysis & School of Molecular Sciences, The University of Western Australia, Crawley 6009, Australia

^e Department of Chemical Engineering, Curtin University, Miri, Sarawak 98009, Malaysia

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ABSTRACT

The zeta potential-pH and yield stress-pH behaviour of washed spherical α -Al₂O₃ suspensions with and without adsorbed multilayer polyelectrolytes up to 4 layers of poly(styrene sulphonic acid) sodium salt or PSSNa (100 kDa) and polyethyleneimine or PEI (70 kDa) adsorbed sequentially were characterised. The maximum yield stress ($\tau_{y,max}$) of washed spherical α -Al₂O₃ is 81.8 Pa located at $pH_{\xi=0}$ at ~ 9.2 . Particles with the first layer (layer 1) of PSSNa displayed negative zeta potential over the whole pH range of 3 to 8. Particles containing 3 layers with layer 3 being PSSNa also displayed negative zeta potential over the same pH range. The magnitude of the Layer 3 PSSNa is smaller. Similarly, the zeta potential remained positive for layer 2 and layer 4 PEI over the whole pH range of 3 to 8. At the dosage of 0.5 dwb% PSSNa and 0.1 dwb% PEI, monolayer coverage of PSSNa for layer 1 and 3 and of PEI for layer 2 and 4 should be achieved if the adsorption is uniform. The maximum yield stress of layer 1 PSSNa and layer 2 PEI was much larger than that without adsorbed additives despite the zeta potential being not zero. Additional attractive forces such as bridging, hydrophobic and hydrogen bonding must be present. TEM images showed that the adsorbed PSSNa-PEI layer surface is undulating and not uniform in thickness. This suggests that adsorption of these polyelectrolytes is not uniform. Extensive particle bridging showing the merging of layers at the interacting surface of the particles was observed from these TEM images. In contrast, α -Al₂O₃ suspensions with bilayer DIBMA-PEI, trilayer DIBMA-PEI-DIBMA and 4 layers DIBMA-PEI-DIBMA-PEI formed by 14 kDa DIBMA and 1.8 kDa PEI performed effectively as steric layer reducing the maximum yield stress significantly. TEM image of α -Al₂O₃ particles with bilayer DIBMA-PEI did not show the presence of polyelectrolyte layer suggesting that the polyelectrolyte layer is too thin to be observable.

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1. Introduction

Layer-by-layer formation via sequential adsorption of polyelectrolytes and other active ingredients to produce functionalized surfaces and particles for a range of applications, has drawn considerable interest from researchers all over the world [1, 2]. Investigations into the layer-by-layer method of functionalising nanoparticles, colloids and surfaces involving polyethyleneimine (PEI) and polystyrene sulphonic acid (PSS) which is a strong acid, and other ingredients are quite numerous [3–5]. Several layers were formed in most cases. However the integrity of each layer in terms of clear separation of polyelectrolyte material between layers is difficult to establish experimentally. In this study, the sequential layering of PSS and PEI on spherical alumina suspension was evaluated in terms of its effect on the zeta potential-pH and yield

stress-pH behaviour. TEM images of particles with two layers PSS-PEI and 4 layers PSS-PEI-PSS-PEI were captured. These images together with interparticle force information derived from yield stress data may provide an indication of the integrity of the multilayers. The concentration of additives or surface coverage chosen was such that if adsorption is uniform, the surface of all particles will be coated with a monolayer of PSS for the first and third layers and PEI for the second and fourth layer. A weaker acid, diisobutylene maleic acid alternating copolymer was also used in the layering.

A good use of layer-by-layer adsorption of additive molecules is to build up the layer thickness on the particle surface to achieve complete steric stabilization in aqueous medium. The layer must be thick enough such that the van der Waals interparticle attractive force at the point of zero charge is too weak to be important. This also requires the layer to be non-interacting i.e., the layer functions as a hard wall steric barrier. At this stage, the fully steric stabilised suspension should be insensitive to the pH environment as long as the layer maintained its integrity or

* Corresponding author.

E-mail address: yeekwong.leong@uwa.edu.au (Y.-K. Leong).

remained strongly adsorbed. A fully sterically stabilised system allows maximum volume fraction aqueous colloidal and nanoparticle suspensions to be prepared. Sequential layering of negatively and positively charged polyelectrolytes on a carbon nanotube by a dipping method produced a layer of composite polyelectrolytes with an overall thickness as large as 6 nm [6]. The thickness was however not uniform as seen from the TEM image provided. At 6 nm thickness, the van der Waals force of attraction is weakened quite considerably, by >500 times assuming the minimum separation of the interacting particle without the adsorbed polyelectrolyte is 0.5 nm. If the Brownian forces of water molecules were able to break the bond of the interacting coated particles at the point of zero charge, a fully steric stabilized suspension system can be claimed.

The layering of appropriate adsorbed polyelectrolytes can also be exploited to produce a range of surface forces such as bridging, steric, electrosteric, hydrophobic, patch charge and depletion forces in the suspensions [7–11]. When the layers on a pair of interacting particles interact attractively, we considered the adsorbed layer as interacting. Surface forces play a crucial role in determining the effectiveness and efficiency in the processing of colloidal suspensions and emulsions in processes such as mixing, pumping, flotation, filtration, coating and spreading, solid-liquid separation, flocculation and others [7]. Depending upon the property requirement of the suspension, these surface forces can be deployed to produce the desired flow or rheological properties. Paint and drilling muds required a yield stress attribute such that upon the cessation of shear the paint will not flow and the drill cuttings will not fall through the mud. In other particulate processes, a low viscosity suspension that is not affected by pH or ionic strength may be necessary. Particles with a thick non-interacting steric layer should meet the requirement.

Multiple additives are commonly added to commercial dispersion products such as paints, food and personal care products to control their rheological and texture properties. Many of these additives are adsorbed, altering the surface and rheological properties of the dispersions. Avadiar and Leong evaluated the zeta potential and yield stress of silica suspension first adsorbed with PEI and then with citric acid [12]. The positively charged PEI must be adsorbed first as the silica particles remained negative at very low pH ~ 2. PEI being a hyperbranched polymer with dendritic structure should adsorb forming a mesh-like layer. PEI alone increases the maximum yield stress of silica suspension very significantly by as much as 50-fold [12, 13]. The second citrate layer broadened the pH range of yield stress behaviour and did not cause the maximum yield stress to decrease significantly. Particle bridging by citrate linking the PEI coated particles was attributed as the cause. This result is an example showing that interacting adsorbed layers negate the steric effect formed by the physical presence of the layers causing the yield stress and viscosity of the suspension to increase. Such properties could be desirable in certain suspension applications.

Polystyrene sulphonic acid is a linear polymer and a strong acid [14–16]. It has a pKa value of -1.5 [14]. Adsorbed poly(styrene sulphonic acid) sodium salt (PSSNa or PSS-Na) was reported to impart patch charge attraction in zirconia suspension at low surface coverage [17]. At high surface coverage of PSSNa, the maximum yield stress located at very low pH did not decrease as much as predicted by steric effect. Another attractive force must be present as patch charge attraction is not important at high surface coverage. Intramolecular hydrogen bonding or hydrophobic interactions are the possible attractive force [18]. At low pH, PSSNa loses its charges and should become more hydrophobic. Hydrophobic interaction depletes the water layer near the adsorbed layer surface as the charge on the adsorbed PSS acid molecule becomes greatly diminished at low pH.

Unlike silica, α -Al₂O₃ has a point of zero charge at pH ~ 9 [19–25]. Adsorption of PEI can only occur at pH >9 where the positive charge density of the PEI is low. Desorption is expected to be considerable when PEI becomes uncharged. The effect of this adsorbed PEI on the maximum yield stress or maximum strength of the interparticle

attractive force of α -Al₂O₃ suspension located at pH > 9, is not known. The point of zero charge can be shifted to a lower more acidic pH by adsorbing PSSNa first and then followed by PEI adsorption. This investigation studied the effect of this sequential adsorption on the zeta potential–pH and yield stress–pH behaviour of the α -Al₂O₃ dispersions.

The hyperbranched PEI structure is shown in Fig. 1. The amine groups are fully charged at low pH ~ 2. PEI loses its positive charges gradually with increasing pH [26]. The degree of dissociation of 0.9 at pH 3 decreased to zero at pH ~ 10 at 0.01 M NaCl. At higher ionic strength the decrease in the degree of dissociation is much more gradual; 0.05 at pH >10 in 0.1 M NaCl. At a given pH and PEI dosage, the amount adsorbed on a silica wafer however increased very significantly with ionic strength. A strong nonelectrostatic affinity of PEI to silica was attributed by Meszaros [26]. PEI increased the yield stress of the SiO₂ suspension very significantly [13]. The yield stress–pH curve displayed a much sharper peak for lower molecular weight PEI. However, the parabolic yield stress–pH curve broadened considerably for the higher molecular weight PEI. Non-electrostatic forces may have played a role.

In this research, we investigated the yield stress–pH and zeta potential–pH behaviour of spherical alumina suspension sequentially layered with i) PSS-Na or PSSNa and PEI, and ii) DIBMA and PEI.

2. Materials and methods

The spherical α -alumina or α -Al₂O₃ powder, AO802, used in this research was purchased from Japan (Admatech). The median size (d_{50}) of this α -alumina powder is 0.43 μm , with the specific surface area (S.S.A) of 3.90 $\text{m}^2 \cdot \text{g}^{-1}$ and the density of 3970 $\text{kg} \cdot \text{m}^{-3}$. A Malvern Mastersizer Microplus was used to characterise the particle size distribution (PSD) of this powder. This powder has a d_{10} of 0.21 μm , d_{50} of 0.43 μm and d_{90} of 1.52 μm . The PSD is shown in Fig. 2.

The SEM image of AO802 α -Al₂O₃ particles shown in Fig. 3a was obtained by a Zeiss 55 VPSEM. The scale bar was 200 nm. The TEM image of α -Al₂O₃ shown in Fig. 3b was captured by JEOL2100. The scale bar was 100 nm. Fig. 3a showed that the diameter of these α -Al₂O₃ particles displayed wide variation consistent with the PSD result shown in Fig. 2. However only a few particles were shown in the TEM image. Both images showed the particles are highly spherical in nature.

This spherical α -alumina powder was washed with 0.2 M sodium hydroxide solution (low concentration alkali) to remove adsorbed impurities. The first washing stage involved mixing 200 g of powder with 2000 g 0.2 M sodium hydroxide solution. The mixture was then sonicated using a BRANSON Digital Sonifier for 1 min, which was set at 70% amplitude to break the agglomerates, until the suspension dispersed completely. The suspension was left to settle for 2 h forming a clear supernatant layer. The supernatant with the impurities was collected and weighed and the same amount of DI water was added to the settled layer and agitated. Approximately 1.5 kg supernatant was collected in the first washing representing a 75% impurities removal. The second washing removed another 1.5 kg of supernatant representing a total removal of impurities of 94%. The decrease in the ionic strength caused by washing and replacing with DI water caused the particles in the suspension to become dispersed as the pH remained high ~ 11 to 12. Concentrated nitric acid (5.9 M HNO₃) was added dropwise to bring the suspension close to the point of zero charge of the particle, pH ~9, in order to enhance the settling rate of the particles. After the 4th washing ~ 99% of the impurities were removed and the supernatant solution removed was not replaced. The settled layer of washed α -alumina suspension remained relatively dilute and was centrifuged to concentrate the suspension.

The polyelectrolytes additives used were polystyrene sulphonic acid sodium salt (PSS-Na or PSSNa) of Mw 100 kDa and polyethyleneimine of Mw 70 kDa and 1.8 kDa. Both these polymers were sourced from Polysciences, Inc. The number of repeating units per molecule is 485 for PSSNa and, 1628 and 42 for PEI.

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