



Boehmite suspension behaviour upon adsorption of methacrylate–phosphonate copolymers



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ABSTRACT

Two novel methacrylate–phosphonate copolymers were successfully synthesised with varying proportions of methacrylate and phosphonate groups. The dispersant ability of the copolymers was investigated using boehmite colloidal suspensions as a function of pH and polymer concentration. The adsorption and electrochemical behaviour of these methacrylate–phosphonate copolymers onto the boehmite surface was studied as a function of polymer concentration at pH values below and above the IEP of boehmite.

It was found that the anionic copolymers adsorbed slightly more on boehmite at pH values below the boehmite IEP (pH 9.4) than above the IEP due to electrostatic attraction with the positively charged aluminate hydroxide groups at the boehmite surface. As a result, boehmite becomes more negatively charged, increasing electrostatic repulsion between boehmite particles and therefore the stability of the boehmite particulate suspension, especially at alkaline pH values around the IEP. It was also found that, for a boehmite surface partially covered by adsorbed copolymer, heterogeneous electrical double layer interaction could occur between a positively charged bare boehmite patch (pH < IEP) and the polymer covered patch, resulting in increased electrical attraction between particles. The increased electrical attraction causes the suspension to be less stable when compared to that either in the absence of polymer or at full polymer surface coverage. Very little differences between the two copolymers were observed in their boehmite adsorption or in their particle dispersion ability which is likely to be due to the low proportion of phosphonate groups that were able to be incorporated in these polymers.

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1. Introduction

Titania pigment particles have a wide range of applications such as in paints, plastics, paper making and pharmaceuticals. Pigment particles are coated with thin layers of solution-deposited silicate and aluminate to improve pigment gloss and degradation resistance [1,2]. Being a colloidal process, the system is very sensitive to solution conditions and any subsequent changes will have major effects on product characteristics and ultimately performance [1]. The conditions encountered during processing when inorganic oxide coatings are applied, involve temperatures in excess of 70 °C with pH values ranging from 7 and as high as 11. When dispersion is inadequately controlled during the application of the inorganic oxide coatings, pigment particles aggregate, which is detrimental to gloss, hiding power and colour.

Polyphosphates are commonly used industrially to provide electrosteric stabilisation of the pigment particles [3]; however, they degrade at high temperatures and under alkaline solution conditions [4] which are present during the pigment production process. Degradation can lead to a loss of dispersion stability and higher aggregation of the

pigment particles. A dispersant having a higher level of stability under pigment processing conditions is therefore essential to prevent particle aggregation, avoiding detrimental optical properties in the final pigment products. Phosphonates have been reported to stabilise oxide particles and offer greater thermal and pH stability than phosphates, due to the presence of the P–C bond [5]. In addition to phosphonates, acrylic acid–phosphonate copolymers have also been reported to provide improved dispersion properties particularly when compared to polyacrylic acid homopolymer [6]. These carboxylate and phosphonate copolymers are commonly synthesised by interfacial polymerisation using readily available reagents [7].

The aim of this study is to investigate the interaction of synthesised, novel methacrylate–phosphonate copolymers, with varying proportions of phosphonate and carboxylate groups, with boehmite particles and their particle dispersant ability. The study investigates the copolymer dispersion properties with boehmite particle suspensions as a function of pH and polymer concentration, proposing a mechanism for boehmite stabilisation provided by the polymer's phosphonate and carboxylate functional groups. For simplicity, boehmite was used in this study as a model of the titania pigment as several studies have shown that the surface of the titania pigment after inorganic oxide treatment is in a form very similar to boehmite [2,8].

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2. Materials and methods

2.1. Materials

High purity boehmite, Apyral AOH 60, used throughout this study was obtained courtesy of Nabaltec, Germany. The BET surface area of the boehmite particles measured by N_2 adsorption was $6.5 \text{ m}^2/\text{g}$. The average particle size measured by scanning electron microscopy was $0.75 \mu\text{m}$, which is identical to the D_{50} value obtained in solution by laser diffraction. The major surface elements determined by X-ray photoelectron spectroscopy were O, Al, Na, and the adventitious C (57, 35, 0.8, and 7 at.%, respectively). The boehmite isoelectric point (IEP) was pH 9.4, determined using an Acoustosizer II, which is well within the range of IEP values reported for boehmite in the literature [9,10].

The method reported by Matta et al. [7] was used to synthesise methacrylate–phosphonate copolymers by reacting methacrylic acid and vinylphosphonic acid in the presence of water, isopropanol and sodium persulfate under nitrogen at 80°C for 1 h, as schematically presented in Fig. 1. Purification of the product was conducted by removing isopropanol under vacuum, followed by dialysis. The overall yield of the reaction (Fig. 1) was 70 wt.% for MAPO₃H(4.4) and 76 wt.% for MAPO₃H(7.6); the numbers 4.4 and 7.6 refer to the percentage of phosphonate groups in these copolymers containing phosphonate and carboxylate groups (see Table 1). Characterisation of the purified product was undertaken using ¹H, ¹³C and ³¹P NMR and FT-IR [11]. The structure of the copolymers is calculated based on their molecular weight (Table 1) and elemental analysis (values for C, H, P and O of 49.45, 6.23, 0.76 and 33.75 for MAPO₃H(4.4) and 47.51, 6.02, 2.99 and 32.97 for MAPO₃H(7.6), respectively). The copolymers consist of 612 carboxylate groups and 28 phosphonate groups for MAPO₃H(4.4) and 513 carboxylate groups and 42 phosphonate groups for MAPO₃H(7.6). It was not possible to incorporate a higher proportion of phosphonate groups in these copolymers using this polymerisation method. The average molecular weight, number average molecular weight and degree of polydispersity of these polymers are presented in Table 1 [11].

High purity water (Milli-Q) was produced by the following sequential treatment: reverse osmosis, two stage mixed bed ion exchange, two stage activated carbon treatment and a final filtering step through a $0.22 \mu\text{m}$ filter. The conductivity of the Milli-Q water was less than $0.5 \mu\text{S}/\text{cm}$ at 20°C . All other reagents used were of analytical grade (unless otherwise stated).

2.2. Adsorption isotherms

Adsorption isotherm measurements were conducted at 25°C at pH values of 7.5 and 10.0 which lie on either side of the boehmite IEP. Boehmite suspensions (4.2 wt.%) were conditioned by stirring continuously overnight in 0.01 M KNO₃ electrolyte solution at the boehmite

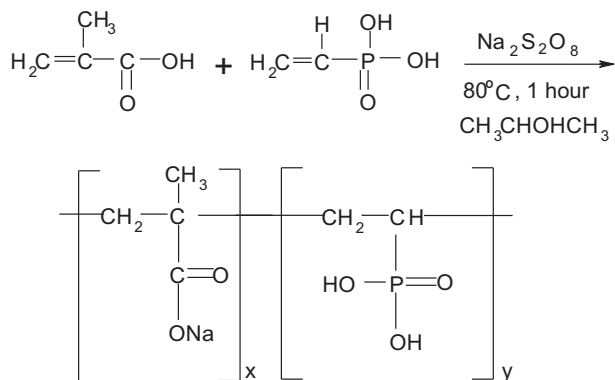


Fig. 1. Reaction scheme showing the synthesis of MAPO₃H(4.4) and MAPO₃H(7.6) (see Table 1 for values of x and y).

Table 1

Average molecular weight (Mw), number average molecular weight (Mn), degree of polydispersity (Mw/Mn), obtained by gel permeation chromatography, and number of functional groups in MAPO₃H(4.4) and MAPO₃H(7.6) (see text and Fig. 1 for explanation).

Copolymer	Mw (g/mol)	Mn (g/mol)	Mw/Mn	Number of functional groups	
				carboxylate (x)	phosphonate (y)
MAPO ₃ H(4.4)	61,000	19,300	3.17	612	28
MAPO ₃ H(7.6)	54,000	18,000	3	513	42

natural suspension pH (pH 8.8). After pH adjustment to the desired value with a small amount of HNO₃ or KOH solution, a known concentration of copolymer stock solution was introduced into the vessel and stirred continuously for 20 min, the time required to reach adsorption equilibrium indicated by the adsorption kinetics studies. The pH was monitored throughout the adsorption experiment and adjusted if required. A sample of the suspension was removed and centrifuged with an Eppendorf 5416 centrifuge at 10,000 rpm for 3 min. The supernatants were analysed to determine the concentration of the remaining copolymer. A series of individual adsorption measurements were performed over a range of copolymer concentrations with the amount of copolymer depleted from the solution assumed to have adsorbed onto the boehmite surface.

The antimony–molybdate/ascorbic acid reduction method [4] was used to obtain the phosphorus concentration in solution and therefore the concentration of copolymer remaining in solution. It was assumed that the amount of polymer depleted from solution had adsorbed onto the boehmite surface.

2.3. Zeta potential measurements

The zeta potential (ζ) of the particles was determined from the dynamic mobility measurements using an Acoustosizer II (Colloidal Dynamics, Australia) at 25°C . The boehmite suspensions (4.2 wt.%) were conditioned by continuous stirring overnight in a 0.01 M KNO₃ solution at a natural pH value. The pH sweep was made by adjusting the suspension to pH 11 with KOH followed by the titration addition of HNO₃ to pH 3. Suspension pH was incrementally reduced allowing 15 min equilibration between measurements. For the measurement of zeta potential with polymer addition, the suspension was titrated with polymer solution from 0 to 6 mg/g.

2.4. Rheology

Rheological measurements were undertaken on 58 wt.% boehmite slurry in 0.01 M KNO₃ at 25°C as a function of solution pH and copolymer concentration. The vane technique was used for shear yield stress (τ_y) measurements. The advantage of the vane technique is that it eliminates wall slip which can be particularly problematic with strongly attractive slurries [12]. A vane rheometer fitted with a six bladed vane (diameter = 24 mm; height = 17 mm) was inserted slowly into the boehmite suspension, insuring that sufficient distance was maintained between the vane edges and the vessel wall. The vane was powered by a Haake VT550 and rotated slowly at a constant rate ($\gamma = 0.021 \text{ s}^{-1}$) such that the yield stress was independent of shear rate.

3. Results and discussion

3.1. Adsorption studies

Adsorption isotherms of MAPO₃H(4.4) and MAPO₃H(7.6) onto boehmite particles in 0.01 M KNO₃ were obtained at pH 7.5 and pH 10.0 and are presented in Fig. 2. The general trend is that more polymer adsorbs at pH 7.5 than at pH 10.0 and MAPO₃H(7.6) adsorbs slightly more than MAPO₃H(4.4). All polymer added at low polymer

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