Poly (N-isopropylacrylamide) (PNIPAM) as a flotation collector: Effect of temperature and molecular weight

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ABSTRACT

Poly (N-isopropylacrylamide) (PNIPAM), a temperature responsive polymer, was tested for its potential use as a collector in a quartz flotation system. The effect of PNIPAM on the surface characteristics of quartz particles were studied using induction time, contact angle and zeta potential measurement and analysed in terms of the probability of bubble/particle attachment and the probability of formation of stable bubble/particle aggregates. It was found that probability of bubble/particle attachment of quartz significantly increases in the presence of PNIPAM, particularly at temperatures above the lower critical solution temperature (LCST) of 32 °C. Furthermore, the probability of bubble/particle attachment increases with increasing PNIPAM molecular weight. This was attributed to the increased hydrophobicity of the quartz surface as well as the decrease in the double layer repulsion between bubbles and particles. This leads to the conclusion that PNIPAM could act as an effective collector in a flotation system.

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1. Introduction

Poly (N-isopropylacrylamide) (PNIPAM) is a temperature responsive polymer. At temperature below its lower critical solution temperature (LCST) of 32 °C, PNIPAM is soluble in water and hydrophilic. The polymer macromolecules are hydrated and fully extended, with extensive intermolecular hydrogen bonding between water molecules and polymer chains (Saunders et al., 1999; Sakohara et al., 2002; Sun et al., 2004). At temperatures above the LCST, the hydrogen bonds between water molecules and polymer chains are broken and instead, intramolecular and intermolecular hydrogen bonds between the C=O and N–H groups are formed. The formation of intramolecular bonds causes the molecule to coil up, exposing its hydrophobic core. This renders the polymers hydrophobic and insoluble in water (Saunders et al., 1999; Sakohara et al., 2002; Sun et al., 2004).

The studies of PNIPAM in the context of mineral processing applications, originate in its potential use as a temperature responsive flocculant at temperatures above the LCST. It can be used as a reversibly responsive flocculant and dispersant (Guillet et al., 1985; Deng et al., 1996; Sakohara et al., 2002; Sakohara and Nishikawa, 2004; Franks, 2005; Li et al., 2007, 2009). The reversibility of the state of aggregation and dispersion can be used to produce both rapid sedimentation (at temperatures above the LCST) and enhance sediment consolidation and dewatering (at temperatures below the LCST). At high temperature, the inter-particle forces in a mineral suspension are changed from repulsive to attractive; causing the formation of hydrophobic particle aggregates (flocs). After the flocs settle, the temperature can be reduced, which produces repulsion between particles as the polymer becomes hydrophilic. The repulsion allows for additional consolidation of the mineral sediment leading to improved water recovery.

As well as being an effective flocculant/dispersant, preliminary investigations demonstrated that PNIPAM can be an effective collector in the flotation of oxide minerals (Franks et al., 2009). In current flotation practice, flotation of oxide minerals is generally achieved using short chain surfactant collectors (e.g. dodecyl amine and sodium dodecyl sulphate) (Quast, 2000; Araujo et al., 2005). Preliminary testing in a simple flotation system showed that at temperatures above the LCST, the presence of PNIPAM induced flotation of both silica and kaolinite, achieving recoveries significantly greater than those in the presence of dodecyl amine (Franks et al., 2009). The ability of PNIPAM to induce both flocculation and flotation of previously dispersed hydrophilic particles (at temperatures above the LSCT) potentially makes it a highly valuable reagent in the flotation of ultrafine mineral particles. Furthermore, PNIPAM is a non-toxic polymer, which can potentially provide an environmentally friendly substitute to industrial collectors which

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are often environmentally harmful (Davis et al., 1976). However, there is still insufficient evidence to determine whether or not PNI-PAM would present a commercially viable substitute for collectors currently used in industry.

The likelihood that a mineral particle is floatable is generally expressed in terms of probabilities, as shown in Eq. (1), where P is the overall flotation probability, P_C is the probability of bubble/particle collision, P_A is the probability of bubble/particle attachment and P_S is the probability of formation of a stable bubble/particle aggregate (Laskowski, 1986; Ralston, 1992).

$$P = P_C \cdot P_A \cdot P_S \tag{1}$$

The probability of collision (P_C) is strongly related to hydrodynamic factors such as cell turbulence, pulp viscosity and particle size (Schulze, 1984). As such, collision probability is unlikely to be influenced by the presence of collector in the flotation system, and is not considered further.

The probability of formation of stable bubble/particle aggregates (P_S) is a very strong function of the magnitude of the three phase contact angle between the air bubble, mineral particle and aqueous medium, which directly determines the strength of the bubble/particle bond (Laskowski, 1986). The increased strength of this bond determines how likely a particle is to detach from a bubble. For this reason, in some publications this term (P_S) is replaced by the probability of bubble/particle detachment (P_D), where P_S is inversely related to P_D (Laskowski, 1986; Ralston, 1992).

The probability of bubble/particle attachment (P_A) is largely dependent on the surface forces existing between a bubble and a particle. It has been shown that in an aqueous medium, the interactions between a negatively charged mineral particle and a bubble are similar to those between two negatively charged mineral particles (Derjaguin, 1954; Laskowski, 1986). Therefore, the probability of bubble particle attachment is subject to double layer forces, as described by the modified DLVO theory, mainly: van der Waals forces, electrical double layer repulsion and hydrophobic attraction. It follows that the probability of bubble particle attachment will decrease with increasing double layer repulsion between mineral particles and bubbles and increase with increasing particle hydrophobicity.

Induction time measurements are one way of characterising the probability of particle/bubble attachment (Nguyen et al., 1997). Induction time is defined as the time for the thinning of the intervening liquid film between an air bubble and a hydrophobic particle to a critical thickness at which the film will rupture spontaneously (Laskowski, 1974). Induction time is measured by bringing captive bubbles into contact with a bed of particles for a controlled time interval (typically between 10 and 1500 ms), to determine whether or not mineral particles attach to bubbles such that they can be lifted up from a particle bed. The particle/bubble contacts are repeated numerous times, estimating the probability of bubble/particle pickup at each contact time. The contact time corresponding to 50% probability of particle pickup is termed the induction time. This technique allows for a simple and reliable estimate of the strength of particle/bubble attachment (Eigeles and Volova, 1968; Yordan and Yoon, 1986, 1988; Holuszko et al., 2008; Burdukova and Laskowski, 2009).

The purpose of this work is to study the effect of temperature sensitive PNIPAM on the probability of attachment of quartz particles to air bubbles, using induction time measurements. These measurements are then interpreted by characterising the particle surfaces in terms of their hydrophobicity (as indicated by contact angle measurements) and electrical double layer repulsion (as indicated by zeta potential measurements).

2. Experimental details

2.1. Materials

2.1.1. Temperature sensitive polymers

A temperature sensitive, non-ionic polymer – poly (N-isopropylacrylamide) (PNIPAM), was used in this work. Three molecular weights of this polymer were used, termed: low, medium and high. The low molecular weight (0.23 MDa) PNIPAM was purchased from Sigma–Aldrich, Australia. The PNIPAMs with the medium molecular weight (1.32 MDa) and the high molecular weight (3.6 and 4.5 MDa) were synthesized in our laboratories as described in detail elsewhere (O'Shea et al., 2007). The synthesis process of these high molecular weight polymers is such that relatively small quantities of the polymer can be produced per batch and it is not easy to obtain consistent molecular weights of polymers between batches. For this reason the high molecular weight polymer used in the different sections of the work varies in molecular weight between 3.6 and 4.5 MDa. In the case of contact angle measurements, the PNIPAM with medium molecular weight (2.0 MDa) was purchased from Polymer Source Inc., Canada.

2.1.2. Quartz

Quartz powder (Silica 400G) was obtained from UNIMIN Australia Limited for use in zeta potential measurements. The particles had a size distribution of d_{50} 10 µm, and a BET surface area of 1.7 $m^2\,g^{-1}$. The powder contained 99.6% SiO_2 and traces of alumina, ferric oxide, titania and lime. For the use in induction time measurements, quartz particles (Silica 100 WQ) were obtained from UNIMIN Australia Limited. The particles were dry sieved to obtain a particle size distribution of 90 µm < D_p < 150 µm. The particles contained 99.5% SiO_2 and traces of alumina, ferric oxide, titania and lime.

3. Methods

3.1. Contact angle measurement

The sessile drop technique was used for the measurement of advancing contact angle, using the OCA Dataphysics measurement system, provided by the Department of Chemistry, University of Melbourne. Silica glass surfaces were cleaned by first washing them in surfactant solution followed by dilute NaOH, then finally rinsing with deionised water. For each molecular weight PNIPAM, three clean silica glass slides (26 × 76 mm) were coated with polymer solutions so as to produce the surface concentration of 0.1 g of polymer per m^2 of glass surface. The slides were dried in an oven at 80 °C for about 30 min. The temperature of the glass slides during contact angle measurements was controlled by placing the slides on the top surface of an aluminium stage which has its temperature controlled by a water bath in order to achieve the temperature of either 22 °C (below the LCST) or 50 °C (above the LCST). Five minutes were allowed to make sure that the slide had reached the desired temperature. A drop of deionised water at pH 6, with 3 µL volume, was introduced onto the slide through a computer controlled micro-syringe. The measurement was taken 10 s after the liquid drop was put on the glass slide. The measurements were conducted in triplicate.

3.2. Zeta potential measurements

Zeta potential measurements were performed using the Zeta Acustosizer, manufactured by Colloidal Dynamics Inc., Sydney, Australia. The instrument is equipped with a recirculating water bath, which allowed for the measurement being performed at both 22 °C and 50 °C. Suspensions of quartz (5 wt.%) were prepared using deionised water containing 40 ppm of PNIPAM (corresponding to