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Temperature sensitive polymers as efficient and selective flotation collectors ☆

Elizaveta Forbes [a,*], Dee J. Bradshaw [b], George V. Franks [a]

[a] Department of Chemical and Biomolecular Engineering, Australian Mineral Science Research Institute, University of Melbourne, VIC 3010, Australia
[b] Julius Kruttschnitt Mineral Research Centre, University of Queensland, QLD 4068, Australia

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ABSTRACT

This study investigates both the efficacy and selectivity temperature responsive of poly(N-isopropylacrylamide) PNIPAM as a flotation collector. The results of this study showed that charged poly(N-isopropylacrylamide) polymers selectively increased both the probability particle/bubble attachment as well as the floatability of coarse alumina and quartz particles respectively. These results provide a basis for considering PNIPAM as both an effective and selective collector in a flotation system. Coupled with previous studies that demonstrate the efficacy of PNIPAM as a flocculant in mineral suspensions, these results clearly demonstrate the potential use of PNIPAM as a dual function reagent which acts as both selective flotation collector and flocculant in the flotation of ultrafine particles.

1. Introduction

One of the major challenges facing minerals processing operations is the flotation of ultrafine mineral particles. It is well known that the floatability of fine particles is poor, due to the low probability of collision with air bubbles (Trahar and Warren, 1976). However, the continuous depletion of higher grade ores requires the comminution of mineral particles to increasingly finer sizes to achieve mineral liberation. For this reason, producing large aggregates of fine particles is gaining an increasing level of importance in the mineral processing industry.

In order for particle aggregation methodologies to be successful in a flotation system, they must satisfy two criteria: Aggregation must be selective and the resultant aggregates must be hydrophobic (Laskowski and Lopez-Vladivieso, 2004). Over the years, a number of techniques have been devised to attempt to satisfy these criteria, such as shear flocculation, selective polymer flocculation, carrier flotation and oil agglomeration (Fuerstenau, 1980; Laskowski and Lopez-Vladivieso, 2004; Matis et al., 1993).

An alternative methodology for the flotation of mineral aggregates is the use of temperature sensitive polymers, such as poly(N-isopropylacrylamide) (PNIPAM). At temperatures below its lower critical solution temperature (LCST) of 32 °C, PNIPAM is hydrophilic and soluble in water. At temperatures above the LCST, the hydrogen bonds between water molecules and polymer chains are broken and instead, intramolecular and intermolecular hydrogen bonds formed. The formation of such bonds causes the molecule to coil up, exposing its hydrophobic core. This renders the polymers hydrophobic and insoluble in water, which causes them to precipitate from solution in the form of hydrophobic colloidal particles (Sakohara et al., 2002; Saunders et al., 1999; Sun et al., 2004).

The studies of PNIPAM in the context of mineral processing applications originate in its potential use as a temperature responsive reagent for flocculation and solid/liquid separation. It has been comprehensively demonstrated that at temperatures above the LCST, PNIPAM can act as an effective flocculant (Deng et al., 1996; Guillet et al., 1985; Li et al., 2007, 2009; O'Shea et al., 2010; Sakohara et al., 2002; Sakohara and Nishikawa, 2004). As well as being an effective flocculant, preliminary investigations also demonstrated that PNIPAM could act as an effective collector in a flotation system (Franks et al., 2009). At temperatures above the LCST, the presence of PNIPAM was shown to increase the hydrophobicity of silica glass surfaces as well as induce flotation of both silica and kaolinite in a very simple flotation system. The floatability of kaolinite in the presence of PNIPAM was shown to be significantly greater that in the presence of dodecyl amine, a common flotation collector (Franks et al., 2009).

The above studies have shown that PNIPAM is able to act as both a flocculant and a flotation collector. Its presence in a suspension of ultrafine hydrophilic particles is able to induce the formation of particle aggregates that are both large and hydrophobic. This satisfies both criteria for successful particle aggregation in a flotation system (Laskowski and Lopez-Vladivieso, 2004).

The aim of this work is to study the effect of different types of PNIPAM on the selective floatability of mineral particles. Floatability is generally discussed in terms of three components: bubble/particle collision, bubble/particle attachment and bubble/particle

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* Corresponding author.

E-mail address: forbese@unimelb.edu.au (E. Forbes).

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detachment (Laskowski, 1986; Ralston, 1992). Of the three components, bubble/particle attachment is the one that is most affected by collectors, as it is chiefly dependent on the surface forces between bubbles and particles and is unaffected by hydrodynamic factors such as cell turbulence and particle size. The probability of bubble/particle attachment is largely dependent on the surface forces existing between a bubble and a particle. Therefore, the probability of bubble particle attachment is subject to surface forces, as described by the modified DLVO theory, mainly: van der Waals forces, electrical double layer repulsion and hydrophobic attraction. It follows that the increase in the probability of bubble particle attachment will likely be caused by an increase in mineral hydrophobicity and a decrease in double layer repulsion between particles and bubbles.

Particle/bubble attachment can be characterised using induction time measurements (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 and can be lifted out of the particle bed. The contacts between bubbles and a bed of particles 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 (Burdukova and Laskowski, 2009; Eigeles and Volova, 1965; Holuszko et al., 2008; Yordan and Yoon, 1986, 1988).

In this paper, charged PNIPAM polymers are evaluated in terms of their efficacy and selectivity as collectors in a model flotation system. The effect that these polymers have on the properties of mineral surfaces is characterised using zeta potential measurements. The effect of the charged polymers on the probability of bubble/particle attachment is studied using induction time measurements. Finally, the selective floatability of mineral particles in the presence of different types of PNIPAM is tested using microflotation and compared to that of other common reagents based on literature.

2. Experimental methods

2.1. Materials

Temperature sensitive poly(N-isopropylacrylamide) (PNIPAM), was used in this work. Cationic and anionic random co-polymers of roughly equivalent molecular weights and charge densities were used. The cationic polymer had a molecular weight of 1.18 MDa and a charge density of 15%. The anionic polymer had a molecular weight of 1.84 MDa and a charge density of 15%. All the polymers used were synthesised in our laboratories as described in detail elsewhere (O'Shea et al., 2008, submitted for publication, 2007). The general structure of the two polymers is schematically represented in Fig. 1.

Quartz powder (Silica 400G) was obtained from UNIMIN Australia Limited for the 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. The powder contained 99.6% SiO_2 and traces of alumina, ferric oxide, titania and lime. For the use in induction time and flotation measurements, quartz particles (Silica 100 WQ) were obtained from UNIMIN Australia Limited. The particles were dry sieved to obtain a particle size distribution of $90\ \mu m < D_p < 150\ \mu m$. The particles contained 99.5% SiO_2 and traces of alumina, ferric oxide, titania and lime.

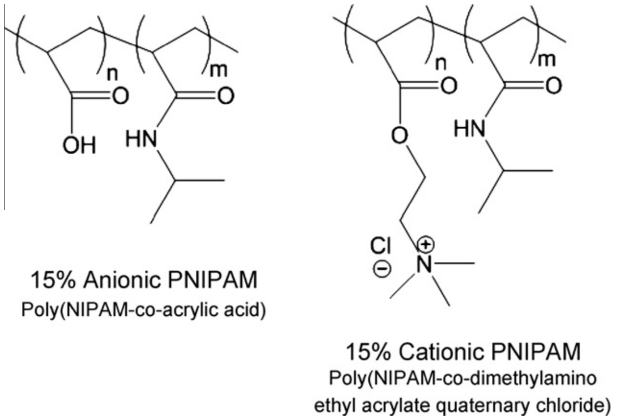

Fig. 1. General structure of anionic and cationic random copolymers of PNIPAM, adapted from O'Shea et al. (2011).

Alpha alumina powder was obtained from Sumitomo, Japan for the use in zeta potential measurements. The particles had a size distribution of d_{50} 1 μm, and a BET surface area of 7 m^2/g. The powder contained 99.9% alumina and traces of silica, calcium, fluoride and sulphur. For the use in induction time and flotation measurements, alumina particles (CA 100) were obtained from UNIMIN Australia Limited. The particles were crushed in a ring mill and dry sieved to obtain a particle size distribution of $90\ \mu m < D_p < 150\ \mu m$. The particles contained 97.5% Al_2O_3 and traces of silica, soda, lime and ferric oxide.

2.2. Methods

2.2.1. Zeta potential measurements

Zeta potential measurements were performed using the Zeta Acoustosizer, manufactured by Colloidal Dynamics, Sydney Australia. The instrument is equipped with a re-circulating water bath, which allowed for the measurement being performed at 50 °C. 10 wt.% suspensions of quartz and alumina respectively were prepared using deionised water containing 40 ppm of PNIPAM (corresponding to 400 g/ton of mineral). The solution concentration of 40 ppm has previously been shown to correspond to optimum levels of polymer adsorption of cationic and anionic PNPAM onto quartz and alumina surfaces respectively (O'Shea et al., submitted for publication). The suspensions were allowed to stand for 24 h prior to measurement. The measurements were performed in a pH range between 2 and 11. 1 M NaOH and 1 M HCl solutions were used for pH adjustment, with the background electrolyte of 10^{-2} KCl.

2.2.2. Induction time measurements

Quartz and alumina particles were treated with both anionic and cationic PNIPAMs, prior to induction time measurement. 10 g of mineral were placed in a beaker containing 100 ml of deionised water adjusted to pH 8 using 1 M NaOH solution for pH adjustment, with the background electrolyte of 10^{-2} KCl. The beaker was immersed in a water bath controlled to 50 °C. Each suspension was dosed with 40 ppm of PNIPAM, which corresponded to 400 g of polymer per ton of mineral. The suspensions were allowed to equilibrate of one hour, while being continuously agitated with a magnetic stirrer. After one hour, the solids were filtered out and gently washed with deionised water heated to 50 °C. The PNIPAM coated solids were placed in the oven to dry at 70 °C.

Induction time measurements were performed with the MCT 100 Induction Time Meter, provided by the Julius Kruttschnitt Mineral Research Centre, University of Queensland. The temperature of