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INVESTIGATION OF THE FLOCCULATION OF COLLOIDAL SUSPENSIONS BY CONTROLLING ADSORBED LAYER MICROSTRUCTURE AND POPULATION BALANCE MODELLING

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The stability of colloidal suspensions is determined primarily by the interactions among suspended particles, which in turn depends on pH, electrolyte concentration, temperature and so on. In most practical systems, flocculation or stabilization is controlled by adsorbing polymers, surfactants or their mixtures. In this paper, the role of adsorbed layer microstructural properties, particularly polymer conformation at solid–liquid interface, in controlling stability and efficiency of flocculation is examined. When polymers are used, their conformation can be manipulated by changing solution conditions such as pH and/or by the addition of a secondary polymer or surfactant. A multi-pronged approach involving the use of fluorescence, ESR, Raman and NMR spectroscopic techniques along with measurements of surface charge and hydrophobicity was employed to explore the structure of the adsorbed layer. A detailed population balance model for coagulation and flocculation of colloidal suspensions by inorganic salts and polymers is then presented incorporating the modern theories of surface forces. In particular, the classical DLVO theory is modified for flocculation by polymers and integrated in a population balance framework for the kinetics of flocculation. The open and irregular structure of flocs is accounted for by embedding the mass fractal dimension of flocs in the model. For demonstration, the evolution of mean floc size with time is simulated for flocculation of hematite and polystyrene latex suspensions. The model predictions are in reasonable agreement with experimental data. As it is computationally less intensive, the proposed model can be utilized for online optimization and control of solid–liquid separation processes that are widely encountered in water treatment, mineral processing, waste management, and so on.

Keywords: colloidal suspensions; flocculation; polymer; conformation; population balance modelling; surface forces.

INTRODUCTION

Flocculation of colloidal suspensions is a critical step in solid–liquid separation operations in many industrial processes dealing with particulate solids, for example, pulp and papermaking (Pelton, 1999), mineral processing (Somasundaran *et al.*, 1996) and water treatment (Thomas *et al.*, 1999). Inorganics, polymers/polyelectrolytes and surfactants are commonly used as coagulants or flocculants. Flocculation by polymers is a complex phenomenon, which involves several steps or sub-processes such as colloid aggregation, polymer adsorption and reconformation, and floc fragmentation and restructuring, occurring sequentially or concurrently. Nonetheless, polymers and polyelectrolytes are employed as flocculating agents in industrial operations, presumably because it is possible to control stability as well as rate of flocculation of flocculating suspensions by controlling polymer adsorption and conformation at the solid-solution interface by manipulating variables such as pH, ionic strength, polymer concentration and temperature.

Flocculation by adsorbing polymers occurs by any one or more of the three well-known mechanisms: simple charge neutralization, charge patch neutralization and polymer bridging (Levine and Friesen, 1987). Polymer conformation at the solid–liquid interface is one of the most critical parameters in stabilization and flocculation. The conformation

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of polymers in solution and at the solid–liquid interface depends on pH, ionic strength, temperature, polymer concentration and its molecular weight distribution (MWD), solids concentration and the nature of solvent and substrate. Process variables such as solids settling rate, viscosity and turbidity are strongly affected by polymer conformation as it governs the mechanism of flocculation. Flocculation occurs by bridging if the polymer adsorbs in the form of long tails while it takes place by charge or patch neutralization if the polymer adsorbs in the form of trains or coils at the interface. Polymer conformation can be controlled by manipulating pH, ionic strength, polymer concentration and temperature.

The efficiency of flocculation is usually measured in terms of parameters such as supernatant turbidity, rate of settling, sediment volume and percent solids settled, all of which are actually functions of floc size distribution. Population balances have been applied extensively for modelling flocculation and for predicting the evolution of floc size distribution with time (Thomas *et al.*, 1999). The kinetics of flocculation is influenced strongly by the frequency of collisions between particles and/or clusters and the efficiency of such collisions. Depending on the process operating conditions, collisions occur due to Brownian motion, applied shear and differential sedimentation. The frequency of collisions is accounted for by including an appropriate kernel in the population balance. The collision efficiency, on the other hand, has been mostly used as a fitting parameter. It is actually a function of the interaction forces between particles which, in turn, depend critically on the type of flocculant used. Because collision efficiency factor is treated as a fitting parameter, the existing population balance models are restricted in their applicability to specific industrial processes.

We have been studying polymer-induced flocculation of colloidal suspensions employing a multi-pronged approach involving fluorescence, ESR, Raman and NMR spectroscopic techniques in order to deduce the properties of solid–liquid interfacial structure and their effect on easily measurable parameters such as solids settling rate, percent solids settled and supernatant turbidity. Simultaneously, we have also been working on the development of a reasonably comprehensive mathematical model for flocculation that accounts for colloid aggregation, floc fragmentation in stirred suspensions, irregular floc structure and surface forces. In this paper, experimental results on polymer conformation and its influence on flocculation by single and dual polymer systems are presented first followed by a population balance model for flocculation and its validation with experimental data from literature.

ROLE OF POLYMER CONFORMATION IN POLYMER-INDUCED FLOCCULATION

Depending on the affinity of the polymer to the surface, polymer chains can have one or a combination of the three conformations (Figure 1): trains (stretched on the surface), loops (coils), and tails (stretched or dangling into the solution at some angle to the surface) (Tjipangandjara *et al.*, 1990; Fleer *et al.*, 1993). Polymer conformation can now be determined using fluorescence and electron spin resonance spectroscopy. This involves measuring monomer (I_m) and excimer (I_e) emission peaks, for example, of the pyrene-labelled polymer. The coiling index, defined as the ratio of the excimer to monomer peak, I_e/I_m, gives a measure of the conformation. A high ratio indicates coiled conformation while a low ratio indicates dangling or flat conformation (Chandar *et al.*, 1987). The dynamics of polymer conformation and its subsequent effect on flocculation are discussed in this section for flocculation by single and dual polymer systems.

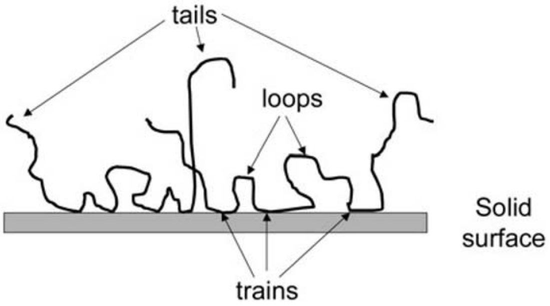

Figure 1. Schematic representation of trains–loops–tails conformations of adsorbed polymer chains at the solid–liquid interface.

Effect of pH on Polymer Conformation and Flocculation Kinetics

One of the most important variables in flocculation is solution pH because it influences not only the electrochemical nature of particle surfaces but also the dissociation of polyelectrolytes and hence their conformation in solution and at the interface. Oxide materials such as hematite and alumina are positively charged below their isoelectric point (IEP) and become negatively charged at pH above the IEP. Similarly, polyelectrolytes remain in compact coiled form below their dissociation pH and attain stretched conformation at higher pH due to the repulsion between charged polymer segments. For example, polyacrylic acid (PAA) has a relatively high coiling index of about 0.7 at pH 4 and a low value of about 0.2–0.3 at pH 10.5 (Tjipangandjara and Somasundaran, 1991). The coiling index of an adsorbed polymer also changes if pH is perturbed. The results of our studies (Yu and Somasundaran, 1996b) on dynamics of polymer conformation and its effect on rate of flocculation of alumina in the presence of a hydrolysed polyacrylamide are presented here to demonstrate the influence of varying pH. The experimental procedure is briefly described below. More details can be found in the cited reference.

Linde A alumina powder having a mean diameter of 0.3 μm and BET surface area of approximately 14 $m^2 g^{-1}$ was dispersed in 110 ml of 0.03 $mol\,l^{-1}$ NaCl solution in a 150 ml beaker. The suspension was magnetically stirred for 45 min for uniform dispersion of particles. The pH was then adjusted to the desired value and the suspension was further stirred for 45 min for equilibration. The magnetic bar was removed and further mixing was carried out using a propeller of 1 cm radius. 1 ml of 600 $mg\,l^{-1}$ pyrene-labelled hydrolysed polyacrylamide solution (PyHPAM) (molecular weight: 76 000 $g\,mol^{-1}$, degree of hydrolysis: 22.6% and pyrene content: 1 mol%) was then added for 1 min using a Sage syringe pump,