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Historical perspective

Dynamics of polyelectrolyte adsorption and colloidal flocculation upon mixing studied using mono-dispersed polystyrene latex particles

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ABSTRACT

The dynamic behavior of polyelectrolytes just after their encounter with the surface of bare colloidal particles is analyzed, using the flocculation properties of mono-dispersed polystyrene latex (PSL) particles. Applying a Standardized Colloid Mixing (SCM) approach, effects of ionic strength and charge density of polymer chain on the rate of flocculation, the electrophoretic mobility of particle coated with polyelectrolyte, and the thickness of adsorbed polymer layer were analyzed, focusing on distinguishing features of two modes of flocculation, namely bridging formation and charge neutralization. In the case of excess polymer dosage, the bridging flocculation clearly highlights the transient behavior of polymer conformation from random-coil-like in bulk solution to increasingly flatten on the surface. The adsorption of polymer chains leads to a stagnant layer of solvent near the solid wall, which is confirmed by electrokinetic data. In the regime near optimum dosage two cases emerge. For high charge density polymer, charge neutralization is dominant and advantageous for the continuous progress of flocculation by heterogeneous double layer interaction. As a function of elapsed time after the onset of mixing, crossover from bridging to charge neutralization is found. In the case of low charge density polymer, bridging flocculation is the mechanism. Fluid mixing is concluded to have an essential role in the formation of bridges.

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1. Introduction

The use of water soluble polymers as flocculants to control the stability of colloids has a long history. A very early introduction of the effect of adding polymer on the flocculation can be found in Sanskrit literature (ca. 2000 B.C.) [1]. Nowadays, flocculation is commonly used in, e.g., conventional water and waste water treatment processes [2], mineral processing [3], and pulp and paper making [4] to enhance the precipitation, floatation and filteration of suspended matter. Synthetic polymers usually displace the natural biopolymers extensively used in ancient times. Despite long history and widespread use, the scientific understanding of the flocculation mechanism is still under discussion, at an elementary level. The main difficulty is the lack of knowledge on the transient dynamics of polymer chains from their state in bulk solution to that at interface. Extraction of the elemental processes involved in the flocculation is also impossible in such notoriously chaotic mixing condition.

Two mechanisms of colloidal flocculation: bridging and charge neutralization, have been recognized [5–21]. Depletion flocculation, induced by non-adsorbing polymer (negative adsorption) [22,23], will not be discussed here. In Fig. 1, the role of nonionic polymer or polyelectrolyte in the flocculation and the stabilization is briefly illustrated. One can easily imagine that immediately after adding polymers to the colloidal dispersion, the polymers which have strong affinity to the particle surface start to adsorb onto the 'starved' particle surfaces. Bridging is formed when one polymer chain adsorbs on two or more particles (Fig. 1(a)). This concept was proposed in 1952 by Ruehrwein and Ward to explain the formation of soil aggregates [5]. In their experiment, the optimum polymer dosage exists and gives maximum flocculation efficiency. The presence of optimum dosage was explained by the concept of successful collision to result in floc formation. That is, the collisions between particles with polymer coated surfaces and uncoated surfaces are successfully making flocs [7]. For the polymer chains with opposite sign of charge to the colloidal particle, the polyelectrolyte adsorption will result in the reduction of the total amount of charge of the colloidal particle, and excess polyelectrolyte adsorption will eventually reverse the particle charge. Usually the most effective flocculation takes place near to complete charge neutralization [8] (Fig. 1(b)). However, in a concentrated cellar suspension, it is reported that the flexibility, size and charge density of polyelectrolyte chain will influence the optimum flocculation dosage [24]. Repulsion between two surfaces will appear when the amount of adsorption exceeds a certain threshold.

In the case of neutral polymer, the overlap of protruding part of adsorbed polymer layer will disturb the approach of two surfaces (Fig. 1(c)). In the case of polyelectrolyte conveying opposite charge, usually charge reversal takes place and colloidal dispersion will be electrostatically stabilized by the interaction between overcharged surfaces (Fig. 1(d)). For both mechanisms of flocculation, the key factor is a change of morphology of the adsorbing polymer chains from their initial conformation in bulk solution to a final state on the surface [9,25,26].

As is well known, sufficient efforts have been devoted to the statistical thermodynamics of nonionic polymer and polyelectrolyte, in solution as well as at interfaces [27–30]. However, there is limited information on the dynamics of polymer adsorption and subsequent flocculation. Probably, one of the biggest remaining issues is that the most important event of colloidal flocculation takes place at the beginning of mixing operation where the system is brought to non-equilibrium state in turbulent flow [31]. In the present review, our attempts to analyze the initial stage of flocculation, in terms of transport phenomena, started about two decades ago [32] are summarized.

Our original idea has been very simple, namely, to consider the collision process between mono-dispersion of colloidal latex [33] and to extend the same idea to the collision between colloidal particles and polymer molecules [26,32,34–41]. Accumulation of data for various conditions has made it possible to correlate the obtained results to the elementary description on the nonionic polymer and polyelectrolyte dynamics when chains get attached from bulk solution to the interface [20,25,42,43]. Although our study began as a fundamental study to understand flocculation in water treatment, the results are relevant for a general understanding of the non-equilibrium dynamic properties of polyelectrolytes at interfaces and therefore also relevant for other fundamental aspects of, e.g., biological interaction of DNA and protein [44,45], microbiological column sensing [46], cell glue [47], drug delivery systems [48], thin films and multilayers [49,50], and chemical sensors [51].

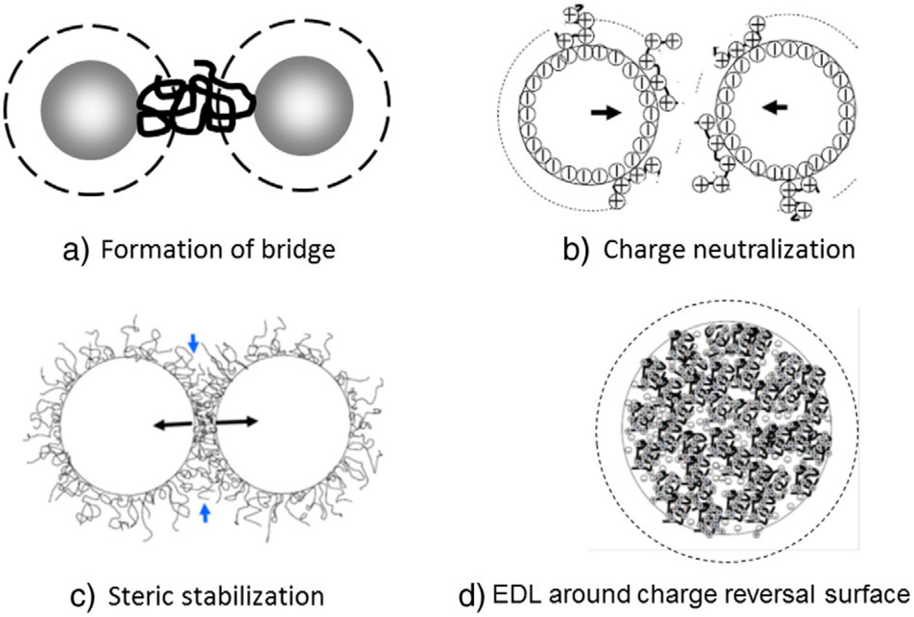

Fig. 1. Effects of water soluble polymers and polyelectrolytes with an affinity to colloidal surfaces. (a) Bridging. (b) Charge neutralization. (c) Steric stabilization. (d) Electric double layer formation due to the charge reversal of colloidal surface.