

Flocculation of Latex P articles of Varying Surface Charge Densities by Chitosans

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A series of well-characterized chitosan samples spanning a wide range of molecular weights, having been homogeneously acetylated to produce varying degrees of linear charge density, were used to flocculate “model colloid” polymer latices. Latices were selected to cover a wide range of charge densities and were sized between 85 nm and 2.1 μm . The optimum flocculation concentrations were identified using both residual turbidity and initial rate methods together with electrophoretic mobility measurements. A charge neutralization mechanism with an enhancement of rate in comparison to the rate of rapid coagulation indicative of a “charge patch” effect was confirmed, except in the case of the 2.1 μm particles. The optimum flocculation concentration of the latter fell below that of rapid coagulation, an effect ascribed to the influence of adsorbed chitosan upon the drainage between particles on close approach. Both molecular weight and degree of acetylation of the chitosans had a small effect upon the optimum flocculation concentration, with efficiency increasing with increases in both molecular weight and linear charge density. Increasing the ionic strength of the dispersion medium broadened the flocculation concentration range and diminished the enhancement of rate produced by the charge patch mechanism. With doses of chitosans in excess of the optimum for flocculation, charge reversal occurred and the cationic latices were rather more stable to electrolyte addition than their anionic precursors but were electrostatically rather than sterically stabilized.

Introduction

Chitosan, a biodegradable, nontoxic, and renewable resource commodity, is a naturally occurring copolymer of poly[β (1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose] and poly[β (1 \rightarrow 4)-2-amino-2-deoxy-D-glucopyranose], which becomes soluble and positively charged in acidic media and may therefore be used as an environmentally friendly flocculant.¹ The linear charge density depends on the level of acetylation. The mechanism by which chitosans flocculate particulate dispersions has been a matter of debate and disagreement in the published literature,^{2–7} often because the systems used have been insufficiently well-defined, particularly in large scale applications.^{8–10} A recent publication¹¹ has addressed this problem by reporting results for a series of well-characterized chitosans with a single particle size model colloid latex. This paper reports the effects of using well-characterized polystyrene latices of differing surface charge densities in studies of flocculation by chitosans of differing linear charge densities and molecular weights.

Experimental Section

Materials. All water used was doubly distilled from an all-Pyrex apparatus. Acetic acid was GPR grade (>99.5%) supplied by BDH, Poole, Dorset, U.K. Styrene (>99%) was supplied by Sigma Aldrich, Poole, Dorset, U.K. and was distilled under reduced pressure of nitrogen gas to remove the stabilizer. Sodium dodecyl sulfate (SDS) (>98%) was supplied by Fluka, Gillingham, Dorset, U.K. Potassium persulfate (KPS) SLR grade (>97%) recrystallized from distilled water, cetyltrimethylammonium bromide (CTAB) AR grade (>99%), sodium chloride SLR grade (99.6% after drying), hydrochloric acid SLR, and carbonate-free sodium hydroxide for volumetric analysis were all supplied by Fischer Scientific, Loughborough, Leicestershire, U.K.

In the preparation and use of solutions of cationic materials, all vessels were conditioned to allow for losses by adsorption onto the walls;¹² that is, the vessels were first equilibrated over a period of 12 h with a solution of the desired concentration which was then discarded and replaced with a new solution at the desired concentration.

Chitosans. Chitosan samples are coded according to their fractional acetylation F_A and their molecular weight; for example, $F_A[0.02]O$ is 2% acetylated oligomeric (O) (relative molecular mass (RMM) ca. 2×10^3) chitosan. Medium molecular weight (M) (RMM ca. 5×10^5) and high molecular weight (H) (RMM ca. 1×10^6) samples were also used and were homogeneously reacylated to increasing degrees which were then quantified by dye adsorption.¹¹

Latex Particles. Surfactant-free polystyrene latex particles, stabilized solely by surface sulfate groups and spanning the full range of surface charge densities available, were obtained from the Interfacial Dynamics Corp., Portland, OR as follows: 350 nm diameter, $0.33 \mu\text{C cm}^{-2}$ (product no. 1–300, batch no. 401–1); 400 nm diameter, $3.38 \mu\text{C cm}^{-2}$ (product no. 1–400, batch no. 2–63 \leq 44.186,1); 2.1 μm diameter, $8.6 \mu\text{C cm}^{-2}$ (product no. 1–2000, batch no. 780).

Latex particles (85 nm, coefficient of variance 6%) were prepared by emulsion polymerization of styrene at 40 °C using SDS emulsifier at $10 \times$ its critical micelle concentration, and the initiator was KPS. The latex particles were cleaned by exhaustive dialysis, acid washed with 0.01 M HCl, and then serum exchanged

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