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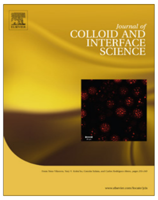

Colloidal stability of iron oxide nanoparticles with multivalent polymer surfactants

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ABSTRACT

This paper introduces a new approach for preparing magnetic colloidal suspensions with electrostatic repulsion between particles and polyelectrolyte surfactants. The surface charge of the iron oxide particles was positive in acidic aqueous conditions; however the surface charge of the colloid was negative in basic aqueous conditions due to the amphoteric property of Fe_2O_3. The long-term colloidal stability and particle distribution of the multivalent charged polymers, Poly(4-vinylbenzenesulfonate sodium salt) (PSS), Poly(acrylic acid) (PAA), and Poly(allylamine hydrochloride) (PAH) were compared with the monovalent surfactant sodium dodecyl sulfate (SDS). Both mono- and multivalent surfactant molecules showed good colloidal stability for extended periods of time. However, the particle distribution was dependent on the hydrophobicity of the surfactants' functional groups. Polyelectrolytes with a negatively charged functional group showed good long-term stability of particles and a narrow particle distribution regardless of the acid dissociation constant (pK_a) of the polymer.

1. Introduction

Magnetic particles have been integrated into the fields of data storage, wave absorbers, magnetic resonance contrast-enhancing media, immobilizing proteins, enzymes, medicine, and biotechnology because of their unique physical and chemical properties [1–4]. In particular, colloidal suspensions of iron oxide particles, ferrofluids, that possess a unique combination of fluidity and the capability to interact with a magnetic field have many applications [5–7]. For biomedical applications, the stability of colloids and the suitability of specific surface coating for prevention of undesirable adhesion are the most important factors. However, uncoated magnetic particles have hydrophobic surfaces which, due to interactions between the particles, agglomerate and form large clusters, resulting in increased particle size. When two large particle clusters approach one another, each particle in the magnetic field is further magnetized. The adherence of remnant magnetic particles causes mutual magnetization, resulting in increased aggregation [8,9]. To achieve stable suspension and desirable surface functions of particles, studies have been conducted using several methods such as covalent attachment of small-molecule ligands [10], adsorption of passivating polymers [11], and ligand-initiated growth of silica [12] and polymer shells around particles [13]. Among these methods, electrostatic interactions between particles and surfactants are of particular interest due to the stability of suspensions of charged particles in a liquid medium. Additionally, polyelectrolytes have great potential as surfactants because their functional groups provide greater flexibility for surface modification of particles [14–16].

Polymer conformation and particle charge have important roles in particle dispersion during particle–particle or particle–polymer interactions in solution. When particles and polymers interact, either stabilization or destabilization can occur. Electrostatic and steric stabilizations are both common in particle and polymer systems. When a solution is destabilized, colloidal particles can form aggregates. Many researchers have reported that, in mixtures of particles and polyelectrolytes with equal charges, aggregations can result from depletion interactions. Additionally, aggregation through adsorption interactions can occur in a system of oppositely charged components. According to the DLVO (Derjaguin, Landau, Verwey, Overbeek) theory, stability or instability of charged colloidal systems is governed by competition between London-van der Waals forces of attraction and electrostatic double-layer forces of repulsion [17–19].

Recently, several researchers suggested simple surface modification methods to simultaneously introduce both water stability

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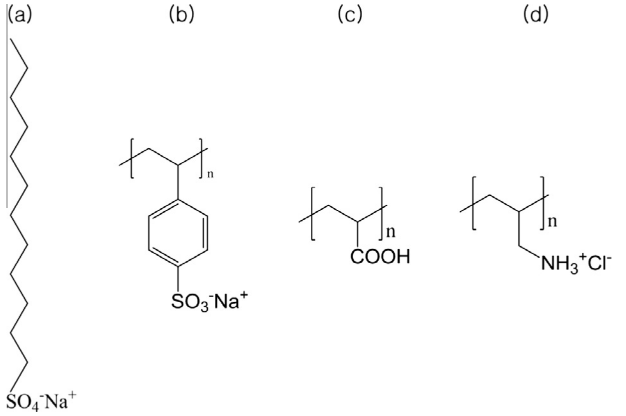

Fig. 1. The molecular structures of charged surfactants; (a) sodium dodecyl sulfate (SDS), (b) Poly(4-vinylbenzenesulfonate sodium (PSS), (c) Poly(acrylic acid) (PAA), and (d) Poly(allylamine hydrochloride) (PAH).

and surface functionality. Steiz et al. showed that polyethylenimine (PEI) coating of superparamagnetic iron oxide nanoparticles (SPIONs) led to colloidally stable beads even in high salt concentrations over a wide pH range [20]. In another study, Szpak et al. showed that highly stable dispersions of SPIONs in water can be induced by oppositely charged chitosan derivatives [9].

Although there are so many researches using the opposite charge stabilizer with charged particles, there are very few study about charge control of iron oxide particles. Meriguet et al. showed that the surface charge of Fe_2O_3 is positive at low pH and negative at high pH, with an isoelectric point around pH 7 [21]. Hydroxo-complexes of the multivalent metals are amphoteric in character; they may dissociate protons from coordinately bound water molecules, or they may add protons to hydroxide ions. The acidity or basicity of the metal hydroxide depends on the polarization of the water molecules or hydroxide ions which, in turn, depend on the charge and radius of the metal ion. Other factors influencing the character of the metal–oxygen bond are the coordination number, the filling of the *d*-orbitals and the nature of other ligands. In this paper, we focused on the amphoteric properties of particles. If the charge of metal oxide change significantly in aqueous solution, differently charged polyelectrolytes can play as a good stabilizer through the electrostatic repulsion stabilization [28,29].

We discussed three objectives in this study. First, we considered the colloidal stability of mixtures of monovalent surfactants and multivalent polyelectrolytes. We selected sodium dodecyl sulfate (SDS) as a mono-charged molecule and Poly(4-vinylbenzenesulfonate sodium salt) (PSS) as multi-charged molecule. Second, we considered the colloidal stability of mixtures of weak polyelectrolytes and strong polyelectrolytes. We chose Poly(4-vinylbenzenesulfonate sodium salt) as a strong polyelectrolyte and Poly(acrylic acid) (PAA) as a weak polyelectrolyte. Third, we considered colloidal stability as a function of surface charge on probe particles. We chose PSS as a negatively charged polymer surfactant and strong polyelectrolyte, and Poly(allylamine hydrochloride) (PAH) as a positively charged polymer surfactant. Fig. 1 shows the molecular structures of these molecules. In this paper, the colloidal stabilities of suspensions were measured using dynamic light scattering (DLS).

2. Materials and methods

2.1. Chemicals and sample preparations

Fe_2O_3 nanoparticles (15–25 nm), sodium dodecyl sulfate (SDS), and Poly(allylamine hydrochloride) (PAH; M.W. = 70,000) were purchased from Aldrich. Poly(4-vinylbenzenesulfonate sodium salt) (PSS; M.W. = 70,000) and Poly(acrylic acid) (PAA; M.W. = 90,000) were obtained from Polyscience Inc. Deionized (DI) water (18 MΩ cm) was used for preparing and rinsing all samples. All chemicals were used as received without further purification.

To obtain the most stable suspensions of iron oxide solution, 10 mg of each chemical (SDS, PSS, PAA, PAH) was dissolved in 10 ml of optimized buffer solution. Then, 1 mg iron oxide powder was added to each solution, and solutions were sonicated for 1 h.

2.2. Dynamic light scattering

Dynamic light scattering (DLS) experiments were performed using an Otsuka Electronics ELS-Z with a wavelength of $\lambda_0 = 632.8$ nm. The scattering data were recorded at 20 ± 0.1 °C in backscattering mode at a scattering angle of $2\theta = 165°$. The hydrodynamic radius, R_H, was obtained using the Stokes–Einstein equation, $D_T = k_bT/6\pi\eta R_H$, where k_b is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity.

2.3. Scanning electron microscopy and focused ion beam

Samples were deposited on silicon substrate and fully dried at room temperature for 24 h. All SEM images were obtained using the Nova nanolab-FEI model at an accelerating voltage of 5 kV.

2.4. ξ-Potential

The titration curve of the nanoparticles was determined using an automatic titrator (Otsuka Electronics). This system can titrate between pH 1 and pH 13 using a small sample volume. In this experiment, titration was performed with two titrants (0.1 M HCl and 0.1 M NaOH) in order to allow for accurate adjustment of pH with minimal increase in volume.

3. Results and discussion

3.1. Surface charge and colloidal stability of Fe_2O_3 particles

The ζ-potential experiment was conducted at various pH conditions to confirm the amphoteric property of iron oxide particles. Depending on the oxidation state of a metal oxide, many metals can form amphoteric oxide or hydroxide. Fig. 2 clearly shows the pH-dependent changes in surface charge of bare iron oxide particles. The ζ-potential of the Fe_2O_3 particles was 79.20 ± 7.15 mV at pH 3 and −53.63 ± 3.77 mV at PH 11, with an isoelectric point near pH 8. That is, the surface charge of iron oxide particles was positive in acidic conditions and negative in basic conditions.

The time-dependent DLS technique was used to determine the aggregation behavior of particles. Fig. 3 shows time-dependent variation in the hydrodynamic radii of particles in DI water over five minutes. At the onset of the experiment, iron oxide particles were dispersed in the water; however, after five minutes, the particles had precipitated, as shown in the inset of Fig. 3. Two different signals, slow and fast decay modes, were observed in the DLS experiment as shown in Fig. 3. The fast decay mode signal represented small dispersed aggregates, and the other signal showed large aggregates of particles. Fig. 3 shows that the large-aggregate signal of the colloidal solution remained constant during the experiment, while the small-aggregate signal shifted from 700 nm to 300 nm after three minutes. This phenomenon can be explained as aggregation growth in the simple water condition. The iron oxide particles did not easily disperse in the aqueous solution because of their hydrophobic surfaces. Although the original particle size was smaller than 50 nm, DLS revealed that this size increased to greater