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Macromolecular conformation changes at oil-water interface in the presence of cations

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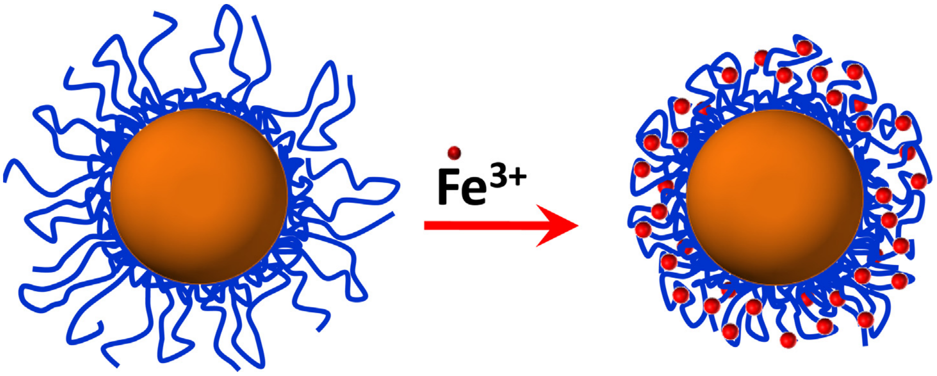
HIGHLIGHTS

- Interaction forces between nanoemulsion droplets in the presence of cations are probed.
- Results suggest a collapsed conformation of polymer at O/W interface in presence of hydrated ions.
- On increasing the cation concentration the onset repulsion decreases drastically.
- Hydrated ion environment does not result in the total displacement of adsorbed polymers.

GRAPHICAL ABSTRACT

Conformation of adsorbed polymers at O/W interface upon addition of cations.



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ABSTRACT

We probed the interaction forces between di-block co-polymer covered oil-in-water nanoemulsion droplets in the presence of monovalent, divalent and trivalent chloride salts using equilibrium force-distance measurements to understand the effect of hydrated ionic environment on the adsorbed macromolecular conformation. Without added cations, the force-distance curve decays exponentially with a characteristic decay length comparable to the polymer radius of gyration (R_g). With 5 mM concentrations of Na^+, Ca^{2+} and Fe^{3+} cations, the decay lengths were found to be ~0.9, 0.8 and 0.6 R_g, respectively. The interdroplet spacing at the minimum measurable repulsive force ($\approx 10^{-13}$ N) in the presence of Na^+, Ca^{2+} and Fe^{3+} cations at 0.24 mM were 76.6, 70.5 and 54 nm, respectively for PVA-Vac (molecular weight 40000) stabilized emulsion. On increasing the cation concentration and valency, a dramatic decrease in the onset repulsion was observed. The observed change in the force parameters with increasing cation concentrations and valency suggests a collapsed conformation of polymers at O/W interface in the presence of hydrated ionic surface structures due to the strong coulombic attraction between cations and oxygen, leading to bridging of PVA chain segments. However, the hydrated ion environment has not resulted in the total displacement of adsorbed polymers. Similar experimental results were observed with Ni^{2+}, Mn^{2+} cations and PVA-Vac of higher molecular weight. Finally, the correlation between the onset of repulsion and the hydration thermodynamic properties of

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cations are compared and the possible mechanisms for cation–polymer interactions are discussed. Our results provide several new insights into ion-macromolecular interactions that may find useful applications in the design of multi-scale biological systems and industrial formulations.

1. Introduction

Adsorption and conformation of polymers at different interfaces in the presence of ions that are common in natural environments are very important from practical application point of view (e.g., Colloidal assembly, protein folding, enzyme activity, bacterial growth and transport across membranes). This topic has been an area of intense research both experimentally and theoretically over the last four decades [1–5]. The tremendous interest in such studies stems from the biological implications of specific ion effect in living systems, which is abundant with macromolecular assemblies containing amphiphilic molecules and water [4,6–9]. The specific ion effect and hydrophobic effects greatly influence the membrane formation, interfacial contact thickness, and stability of structures [10–12]. Also, hydrated highly charged metal ions play critical roles in mineral formation and extraction, biochemical reactions and in the transport of toxic materials [13]. The understanding of specific ion effects is still elusive because of complicated solvation structure near interfaces [11,14]. The recent advances in high-resolution atomic force microscopy with atomic level precision made it possible to directly visualize the adsorption of various ions to solid surfaces in contact with aqueous electrolytes [15]. The indirect techniques such as attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and vibrational sum frequency spectroscopy (VSFS) have been extensively used to study the association between different molecule, and the chloride salts of different valencies in bulk solution [11]. In addition, specialized tools such as X-ray photoelectron spectroscopy [16], second harmonic (SH) generation [11], resonant SH reflection [17] and sum frequency generation [7,18] have been used to probe the interfacial structures in the presence of various ions. Recently the effect of anions on the phase behaviors of a triblock copolymer was investigated with an automated melting point system [19].

As polymers along with other additives (e.g., surfactant, nanoparticles and cations of different valencies) are often used as stabilizers and rheological modifiers of industrial formulations [20] (e.g., food, pharmaceuticals, personal care products, cosmetics) [21], it is important to understand the intermolecular and surface forces between interfaces in the presence of adsorbing polymers, solvent molecules and other additives. The phase behavior and the stability of colloidal dispersions can be strongly influenced by adsorbing moieties such as cations, anions and neutral materials [19,22]. Measurement of interaction forces such Van der Waals, electrostatic, steric, hydrophobic, and hydrogen bonding provides better insights into the complex interaction between various components in aqueous dispersions. Irrespective of intense research efforts, both theoretically and experimentally, the experimental data on macromolecular conformational changes at interfaces in the presence of specific ions is limited mainly because of the lack of highly sensitive experimental tools capable of probing such subtle interactions and the very complex intermolecular and surface forces between macromolecule covered interfaces [23]. Surface force apparatus [24], atomic force microscopy [25–27], optical tweezers [28,29], etc. have been extensively used to probe the intermolecular forces, which provided valuable insights into our current understanding of intermolecular forces. [30,31] However, the above tools do not allow measurement of forces between Brownian colloidal particle in solution, though such measurements are extremely important in the understanding of stability of colloidal formations with multiple additives. This limitation was overcome with the introduction of magnetic chaining technique (MCT) [32], which is a unique technique that allows probing of intermolecular forces between the magnetic colloidal droplets/particles. This technique is based on the diffraction of light by chains of magnetic particles under an applied magnetic field. MCT has been extensively used to probe electrostatic [23], steric [33] and electro-steric forces [34].

Although the effect of surfactant and free polymers on inter surface forces between polymers stabilized droplets are studied, the effect of cation valency on forces between polymer covered O/W interfaces is not studied yet. Here we report the effect of cation valency on the intermolecular force between neutral polymers stabilized emulsion droplets using magnetic chaining technique. The questions we try to address from this study are the following: (1) How cations in solutions interact with adsorbed polymers at an O/W interface? (2) Can cation interaction lead to a desorption of polymers from an O/W interface? (3) How the polymer conformation at an O/W interface is altered under cations interaction? (4) What is the effect of cation valencies on such interaction forces and the stability of emulsions? As hydration of ions is crucial in colloidal formulations [35–37], protein folding [2,38], adhesion and growth of bio-films [39], phase transition in polymer solutions[22,40] and biological activities [41], the role of hydrated ions on interaction forces and the stability of emulsions is important and warrants a systematic study.

2. Experimental

2.1. Materials

A statistical block copolymer of vinyl alcohol-vinyl acetate (CH_2CHOH [88%] – CH_2CH ($OCOCH_3$) [12%]), with an average molecular weight of 40,000 and 155,000 (referred as PVA 40 K and PVA 155 K, respectively) purchased from Aldrich, USA is used as such for the present study. PVA-Vac is a water soluble polymer at room temperature and its theta temperature in water is around 97 °C. The unperturbed radius of gyration (R_g) of the polymer was measured from viscosity measurements at a concentration well below the overlap concentration (C^*). In the dilute concentration limit, the viscosity follows Einstein law $\eta/\eta_0 = 1 + 2.5\phi$, where η is the polymer solution viscosity, η_0 is the pure solvent viscosity and ϕ is the coil volume fraction, which is related to the hydrodynamic radius of the polymer [42]. The R_g values of PVA 40 K and PVA 155 K, is found to be ~8 and 16 nm, respectively. Experiments were performed at a polymer concentration (0.6 wt%), which is well below the overlap concentration.

2.2. Emulsion preparation

The stimuli-responsive magnetic nanoemulsion was prepared by shearing ferrofluid oil in the presence of an anionic surfactant and water using a homogenizer (IKA werke, T 25 Germany) [33]. The ferrimagnetic Fe_3O_4 particle of size ~10 nm, sterically stabilized with oleic acid and dispersed in octane constitutes the oil phase.