



## Behavior of a Weak Polyelectrolyte at Oil-water Interfaces under Different Environmental Conditions

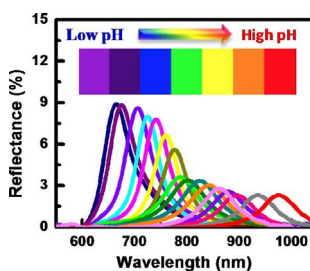
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### GRAPHICAL ABSTRACT

TOC: Bragg spectra change for PAA covered droplets at different pH. With appropriate choice of droplets, visual manifestation of the stretching and collapse of polymers is possible from the color changes.



### ARTICLE INFO

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### ABSTRACT

Understanding the behavior of macromolecules adsorbed to a surface or interface under different environmental conditions is very important in stabilization of colloidal formulations, coating, drug delivery and lubrications. However, the experimental understanding on polyelectrolyte behavior at interfaces under different environmental conditions is lacking. Here, we probe the conformational changes of a weak polyelectrolyte (Polyacrylic acid, PAA) adsorbed at an oil-water interface, under different physiochemical condition such as pH and salt of various concentrations and valences, using a simple spectroscopic approach. The conformational change of PAA adsorbed at magnetically polarizable emulsions droplets is manifested from the Bragg spectral shift or interdroplet spacing change from an array of droplets. In addition, the intermolecular repulsive interaction between the polyelectrolyte covered droplets is studied in details. In the pH range of 3–11.8, at zero salt concentration, the interdroplet spacing increased from 40 to 173 nm, indicating a large extended conformation of adsorbed PAA, which undergoes a sharp collapse in the presence of multi valence salt. The decay length obtained from the force measurement results, at zero salt concentration and at low pH, suggest that the adsorbed PAA exhibits a compact structure at an oil-water interface whereas it adopts an extended structure at high pH. Interestingly, the scaling exponents observed from the force decay length during swelling and collapse of the adsorbed PAA at different pH and salts are in good agreement with mean field theory and counter-ion fluctuation theory, though the interface and anchoring behavior of polyelectrolyte are quite different. Our results provide new experimental insights into macromolecular conformation at oil-water interfaces under different practical situations and offer new possibilities in probing macromolecular behavior at interfaces, for creating stimuli responsive nanostructures (pH, temperature, ion etc), lubrication and better stabilization of colloids.

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## 1. Introduction

Colloidal suspensions are widely used in many industrial products such as pharmaceutical formulations, cosmetics, paints etc. The shelf life of these products is dictated by the effective interaction forces acting between suspended particles or the net forces acting between them. To achieve net repulsive interactions throughout its storage and use, various stabilizations techniques are attempted by industries, which includes electrostatic, steric or electro-steric approaches. More recently particle stabilization (pickering approach) [1–4] is also attempted widely because of their effectiveness in achieving long term stability. Emulsions are liquid–liquid (oil–water) suspensions, are a class of colloids widely used in various industries. As electrostatic stabilization is not effective under high ionic strength [5] and sensitive to solvent conditions, in general, polymer or polyelectrolyte based stabilization is widely used in many products to achieve the effective steric or electro-steric repulsive forces [6]. In addition, these macromolecules also acts as rheological modifiers to achieve the viscosity and flow behavior. Though the above approaches are adopted by industries, a proper scientific understanding of the interaction mechanism of macromolecules at interfaces is still lacking. Such an understanding is absolutely essential to produce durable product formulations with an extended shelf life. Though the formulations with a superior stability is made by industries by using various stabilizing entities and their combinations, the know-how is secretly guarded by them considering the commercial interest. Therefore, understanding the behavior of macromolecules adsorbed to a surface or interface is important for stabilization of emulsions based products. Further it has important implications in coating, drug delivery [7] and lubrications applications [8]. The present study attempts to gain new insights into the behavior of polyelectrolyte at interfaces under different environmental conditions.

Here, the behavior of a weak polyelectrolyte (PE), Polyacrylic acid (Hereafter mentioned as PAA) adsorbed at emulsion interfaces in an aqueous media is studied. It is a water soluble anionic PE that undergoes reversible conformational transitions under varying pH and ionic strength. At low pH, it is neutral in nature and adopts a compact globule structure but at relatively high pH, they are charged and thus swell because of the ionization of carboxyl group at the backbone of the PE. However, at very low molecular weight, PAA exhibits pH independent behavior [9].

The main objective of this work was (1) to study the conformational changes of an adsorbed weak PE at liquid–liquid interface under varying salt and pH (2) comparing the scaling exponents with the theoretical prediction and (3) to study the effect of salt valence on the conformational change of adsorbed PE and the resultant colloidal stability from the force measurement. To realize the above criteria, we have used a nanoemulsion adsorbed with PAA and studied its behavior under different physiochemical conditions by probing the interdroplet spacing under a given magnetic force and looking at intermolecular force using magnetic chaining technique [10].

## 2. Materials and methods

### 2.1. Materials

The PE used in this study was PAA of average molecular weight 450,000 g/mol, ( $M_w/M_n < 1.1$ ), obtained from Sigma-Aldrich. AR grade salts, of sodium chloride (NaCl), calcium chloride ( $\text{CaCl}_2$ ) and ferric sulphate ( $\text{Fe}_2(\text{SO}_4)_3$ ) were obtained from Sigma Aldrich and used without further purification. Surfactants, sodium dodecyl sulphate (SDS) and nonylphenol ethoxylate (NP-9) were obtained Sigma Aldrich and also used without any further purification. The pH of the medium were changed using AR grade hydrochloric acid (HCl) or sodium hydroxide (NaOH). Milli Q water, filtered with 0.22  $\mu\text{m}$  Millipore filter, was used to make polymer and salt solutions.

### 2.2. Magnetic emulsion

The preparation of magnetic nanoemulsion was discussed in the previous publications which is briefly discussed [10]. The superparamagnetic nanoparticle ( $\text{Fe}_3\text{O}_4$ ) used in the ferrofluid was prepared by co-precipitation technique and the particles were stabilized against aggregation by oleic acid and dispersed in octane [11]. The ferrofluid nanoemulsion was prepared by shearing ferrofluid oil, water and surfactant using a IKA, T-25 ultra turrax high speed homogenizer at room temperature [12]. This leads to formation of emulsions with a wide polydispersity. Fractionation technique is used to produce mono-dispersed emulsion from the coarse emulsion [13]. Here, the excess surfactant is added into the continuous medium to induce an attractive interaction between droplets to phase separate smaller droplets from larger droplets. The dilute phase is removed and the dense phase is diluted with surfactant solution further and the process is repeated several times to obtain a highly monodisperse emulsion. The mono-dispersed emulsion stabilized by SDS with an average droplet size of  $\sim 200$  nm was used in the present study. The polydispersity (PDI) of the emulsion was found to be 0.07, which is defined as the ratio of square of the standard deviation ( $\sigma^2$ ) to the square of the mean particle size ( $H_b^2$ ) as  $PDI = \frac{\sigma^2}{H_b^2}$ . To stabilize the emulsion with PAA, the master emulsion was washed with SDS (CMC/10) and then with NP – 9 solution. The application of a strong magnetic field augmented the separation of droplets from the aqueous phase. The supernatant was removed and the bottom is diluted with fresh NP – 9 solution and mixed thoroughly. After 3–4 washes, the pH of the dispersion is adjusted to the desired value. After surface charge neutralization, PAA solution of 0.5 wt% was added to the emulsion and then left it for 3 days to equilibrate.

### 2.3. Measurement techniques

The hydrodynamic size distribution and zeta potential were obtained using a Malvern Nanosizer (Zetasizer Nano-S) at 25 °C. A folded capillary cell was employed to measure both hydrodynamic size and zeta potential. For measuring hydrodynamic size and zeta potential, less concentrated emulsion (diluted by 100 times from master emulsion) is used. An inverted phase contrast optical microscope (M/s Leica DM IRM) equipped with a digital camera (JVC) and a frame grabber card is used to obtain the phase contrast optical microscopy images of emulsion droplets. 100X oil-immersion objective (having numerical aperture of 1.4) is used. Image pro software is used for processing the images. Intermolecular force measurement was carried out at 25 °C using an in house developed system comprised of a fiber optic based spectrometer (Avaspec, Netherlands) with a white light as source, a custom made solenoid and a programmable power supply (Agilent Technologies—N5770A). 200  $\mu\text{L}$  emulsion in a cylindrical cuvette is used for the force measurement study. The details of the intermolecular force measurement were discussed in our earlier publications [10,14]. The present approach enables measurement of weak forces between nanodroplets (with a force resolution of 0.1 pN) as a function of interdroplet spacing with a resolution of 1 nm.

## 3. Results and discussion

### 3.1. Force profile for surfactant and PE stabilized emulsion

The Fig. 1 shows the intermolecular force measurement for SDS and PAA stabilized emulsion at pH  $\sim 7$ .

For SDS stabilized emulsion, the corresponding zeta potential is found to be  $-35$  mV, which shows that the interface is negatively charged. The theoretical electrostatic repulsive force for diffused double layer with  $ka > 5$  is,  $F_r(r) = 4\pi\epsilon\psi_0^2 a^2 \left[ \frac{1}{r} + \frac{1}{r^2} \right] \exp[-(r-2a)]$ , and for thin electrical double layers with  $ka < 5$ ,  $F_r(r) = 2\pi\epsilon\psi_0^2 a \frac{\exp[-(r-2a)]}{1 + \exp[-(r-2a)]}$  [16], where  $r$  is the droplet separation

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