

A unique conformational equilibrium of polyacrylic acid at the solid/liquid interface

Joy T. Kunjappu, P. Somasundaran *, K. Sivadasan ¹

Langmuir Center for Colloids and Interfaces, Columbia University, New York 10027, NY, USA

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Abstract

The adsorption of polyacrylic acid onto an alumina surface is shown using fluorescence spectroscopy to be followed by a rearrangement of its macromolecular segments in the adsorbed state. The adsorption of pyrene-labelled polyacrylic acid has been investigated from its solutions and from solutions mixed with unlabelled acid. The excimer efficiency of the emission of the pyrene-labelled polymer species indicates a pH-independent equilibrium conformation of adsorbed polymer chains. While the slow conformational rearrangement may not affect rapid flocculation processes, it could affect slow flocculation as well as deaggregation and reaggregation processes.

Keywords: Conformation; Polyacrylic acid; Solid/liquid interface

Introduction

Polymers and surfactants find wide application in the flocculation and stabilization of colloidal particles [1,2]. The aggregation and deaggregation potential of colloidal particles in a dispersion is a complex function of the properties of the polymer, such as its molecular weight, size distribution and functionality, as well as the nature of the solvent, pH and temperature [3]. Although the kinetics of transfer of polymer from bulk to interface (adsorption) is fairly well understood, the kinetics of post-adsorption changes, as well as the effect on the kinetics of the aggregation process, is not [4].

The conformation of polymers at solid/liquid interfaces can dictate the course of flocculation by virtue of the effect of the conformation on the

electrostatic and steric forces of stabilization [5]. Fluorescence has been used to investigate the extent of coiling of polymer chains by monitoring the emission properties of the fluorophore [6,7]. In particular, the excimer-forming properties of pyrene moiety labels on polyacrylic acid (PAA) have been utilized for studying the pH-dependent conformational equilibria of polyelectrolytes [8]. In general, high excimer yields result at low pH, and low yields at high pH. In the latter case, ionization of carboxylic acid groups gives rise to mutual repulsion of the segments, leading to stretching of the polymer chain. Under these conditions, the possibility of two randomly labeled pyrene groups being close enough to undergo the effective overlapping necessary for excimer formation is limited. The fluorescence spectra of pyrene-labeled polymer at two different pH values are given in Fig. 1. The structure of the pyrene-labeled polyacrylic acid (PyPAA) polymer as well as the

* Corresponding author.

¹ Present address: Chemistry Division, ONGC, Bombay, India.

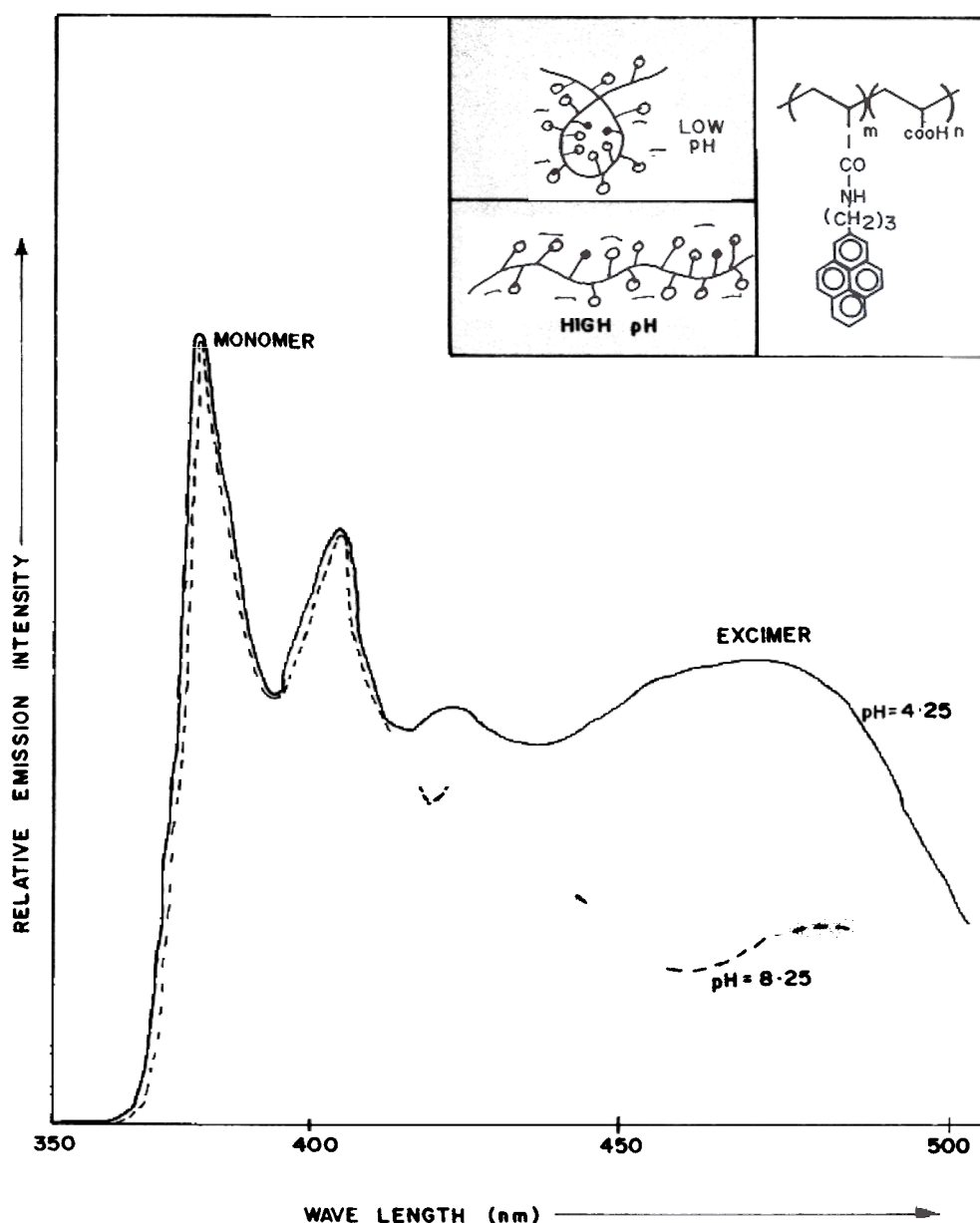


Fig. 1. Fluorescence spectra of PyPAA at two different pH values. The structure of the polymer with the label and a model presentation of the two conformations at low and high pH values are shown as insets.

model representation of conformations at extreme pH values are shown as insets. In this paper, we report the results obtained for the adsorption of PyPAA at the alumina/water interface, with special emphasis on the time-dependent variation in

the excimer efficiency of pyrene. The variation in excimer efficiency is also studied at different concentrations of unlabeled PAA with a fixed concentration of PyPAA, both in solution and at the interface. The adsorption isotherms of PAA on

Al₂O₃ at the two different pH values of interest are also determined for correlation purposes.

Experimental

The alumina used in this study was of Linde A grade from Union Carbide with a specific surface area of 13.4 m² g⁻¹ and a particle size of 0.3 μm. PyPAA was synthesized according to a procedure reported earlier [9]. This polymer had 1.5 mol.% of pyrene label, a molecular weight of 40 000 and a degree of polymerization of about 510. The unlabeled PAA with a molecular weight of about 35 000, was purchased from Polysciences Inc. ($M_w/M_n = 1.6$).

The pH of the solutions was adjusted with 1N HCl or 1N NaOH.

In order to generate the adsorption isotherms, the polymer depletion from solution was determined by monitoring the residual polymer concentrations, using a total organic carbon analyzer (TOC) – Dohrmann Carbon Analyser. The fluorescence spectra (uncorrected) for calculating the I_E/I_M values (I_E = intensity of excimer at 480 nm, and I_M = intensity of monomer at 373 nm) were recorded at an excitation wavelength of 320 nm on a Spex Fluorolog fluorescence spectrometer.

The samples for determining the excimer efficiency with PyPAA were prepared as follows. 0.2 g of Al₂O₃ was prepared in 2 ml of water at the required pH in a cuvette, and mixed with added PyPAA solution pre-adjusted to the same pH. The first emission scan was done within 30 s of mixing. The spectral scanning was repeated for various time intervals up to about 3 h. Each scan (350–600 nm) was done in a minute and the average value was plotted as the excimer/monomer ratio (I_E/I_M) for an assigned time. Simultaneously, the I_E/I_M values were also determined in homogeneous solutions. The temperature was maintained at 23 ± 0.5°C.

In the experiments to investigate the effect of the coadsorption of PyPAA and unlabelled PAA, the required amounts of the two polymer solutions were mixed at the appropriate pH and the I_E/I_M was measured. Each of these samples was added to alumina slurry at the pre-adjusted pH and the

emission spectra were recorded 5 min after mixing, as in the previous set. In all of the above cases, supernatant analysis was performed to determine the amount of residual unadsorbed PyPAA, which was found to be less than 10% of the initial concentration.

The samples for adsorption isotherms were prepared as follows. Alumina (0.5 g) was allowed to equilibrate in water (5 g) at the required pH, and shaken with a wrist-action mechanical shaker for 3 h. The same solid/liquid ratio was maintained as in the above experiments. A polymer solution at a pre-adjusted pH value was then added, and the solution was shaken for another 20 h while the pH of the adsorption samples was maintained at the desired values by the addition of acid or alkali. The samples were centrifuged and the supernatant was used for polymer analysis according to the following procedure. 5 ml of the supernatant was acidified with a drop of phosphoric acid and purged with oxygen to removed dissolved CO₂. 200 μl of the above solution (pH 2) was injected into the injection port of TOC for determining the residual concentration.

3. Results and discussion

A plot of the ratio of the intensities of the excimer and monomer fluorescence of the PyPAA at the solid/liquid interface is shown in Fig. 2 as a function of time. In homogeneous solutions, the I_E/I_M ratio remained essentially constant at both pH values (0.40 at pH 4.25 and 0.22 at pH 8.25). However, at the Al₂O₃/water interface, I_E/I_M decreased from 0.40 to about 0.25 at low pH for an hour, and then remained at this same value. Under high pH conditions, I_E/I_M increased slowly for about an hour from about 0.22 to 0.25, and then remained constant. The gradual changes occurring in the excimer efficiency during the first hour are indicative of the segmental motion of the polymer chains after adsorption, culminating in conformational changes. Interestingly, the adsorbed polymer molecules attain the same equilibrium conformation with time, irrespective of pH. The adsorption itself may be a fast process; soon after the adsorption, the adsorbate seems to retain

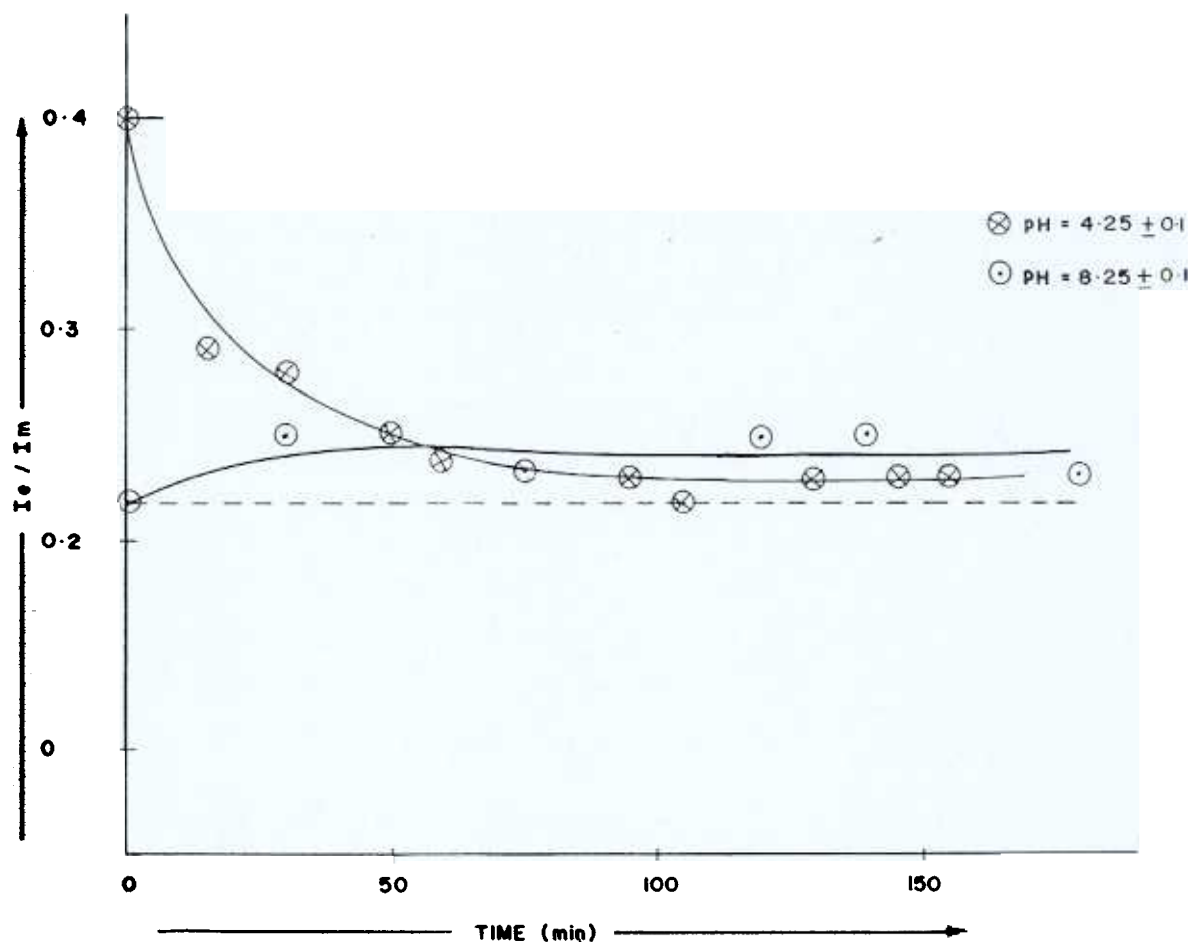


Fig. 2. Excimer-forming efficiency ($\pm 0.5\%$) of PyPAA (50 p.p.m.) during adsorption onto alumina at pH 4.25 and 8.25 as a function of time. Broken lines (---) represent the I_E/I_M values in homogeneous solution.

the same different conformation at the solid/liquid interface at different values of pH as in the homogeneous solution. However, with time, the polymer chains tend towards the same average conformation at both pH values. Even though conformational changes of the adsorbed polymer molecules at the solid/liquid interface can be expected to occur, their exact nature is not yet well understood. The above results clearly show that the PAA adsorbates on alumina tend to relax and reach an equilibrium conformation with the same average properties indicated by the constant excimer/monomer ratios. Some degree of uniqueness may be

connected with this observation. It should also be noted that the polymer molecules retain the same solution conformation immediately after the adsorption. It may be noted here that monitoring the excimer/monomer emission alone cannot distinguish between depletion of the polymer from the solution or adsorption continuing over the course of the experiment. It can only suggest the various surface rearrangements occurring after adsorption, manifested as changes in conformation responsible for excimer emission. It is observed that conformational rearrangement occurs on the surface, although the maximum adsorption density

attained at a given concentration and pH is quite different.

The above set of experiments was carried out at a PyPAA concentration of about 50 p.p.m., at which the adsorption density is well below the maximum plateau adsorption. The adsorption isotherms at two different pH values are given in Fig. 3. The adsorption density at the low pH is about an order of magnitude greater than at the higher pH. The higher adsorption density at the low pH is attributed to the highly coiled conformation at this pH, with the result that more of the polymer is needed for complete surface coverage. At the high pH value, however, since the polymer is more stretched (fewer effective *random walk* segments) the maximum adsorption density that can be achieved is lower. However, after adsorption, the unbound regions tend to either stretch or coil, which is reflected in the gradual change in the I_E/I_M value. The alumina surface is positively charged at both the pH values, (isoelectric point = 8.5) and PAA adsorption occurs predominantly

through an electrostatic mechanism, hence, the initial state of the adsorbate is dictated by the effective solution conformation.

The excimer forming efficiency of PyPAA in solution and at the interface in the adsorbed state are given in Fig. 4 for different initial concentrations of unlabeled PAA. I_E/I_M reaches the same final value at higher adsorption densities independently of the pH. Pyrene fluorescence in the polymer is not quenched by free PAA even at a concentration as high as 3000 p.p.m. Thus at increasing adsorption densities the pyrene groups can be considered to be describing an equilibrium position (Fig. 5) which is comparable to the mean position (conformation) obtained for the adsorption of PyPPA (50 p.p.m.) alone. Note that the excimer efficiency does not change merely by trivial quenching of pyrene fluorescence by PAA. Fig. 4 also shows that the same effect is observed at both pH values.

The flocculation properties of these samples, such as percentage solid settled and settling rate,

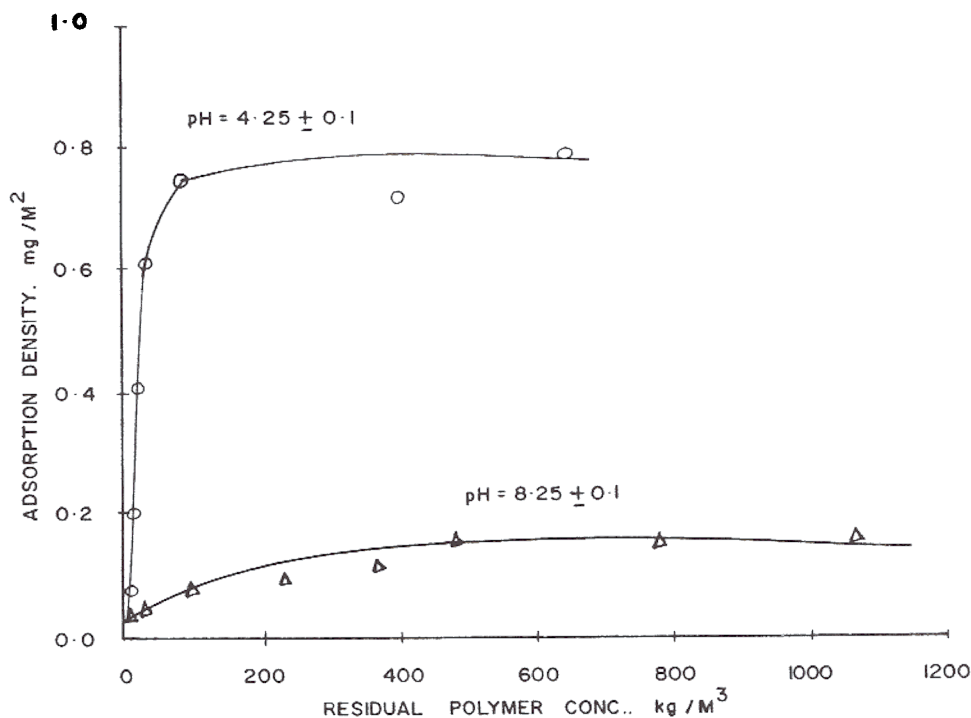


Fig. 3. Adsorption isotherm of polyacrylic acid (unlabeled) on alumina at two pH values.

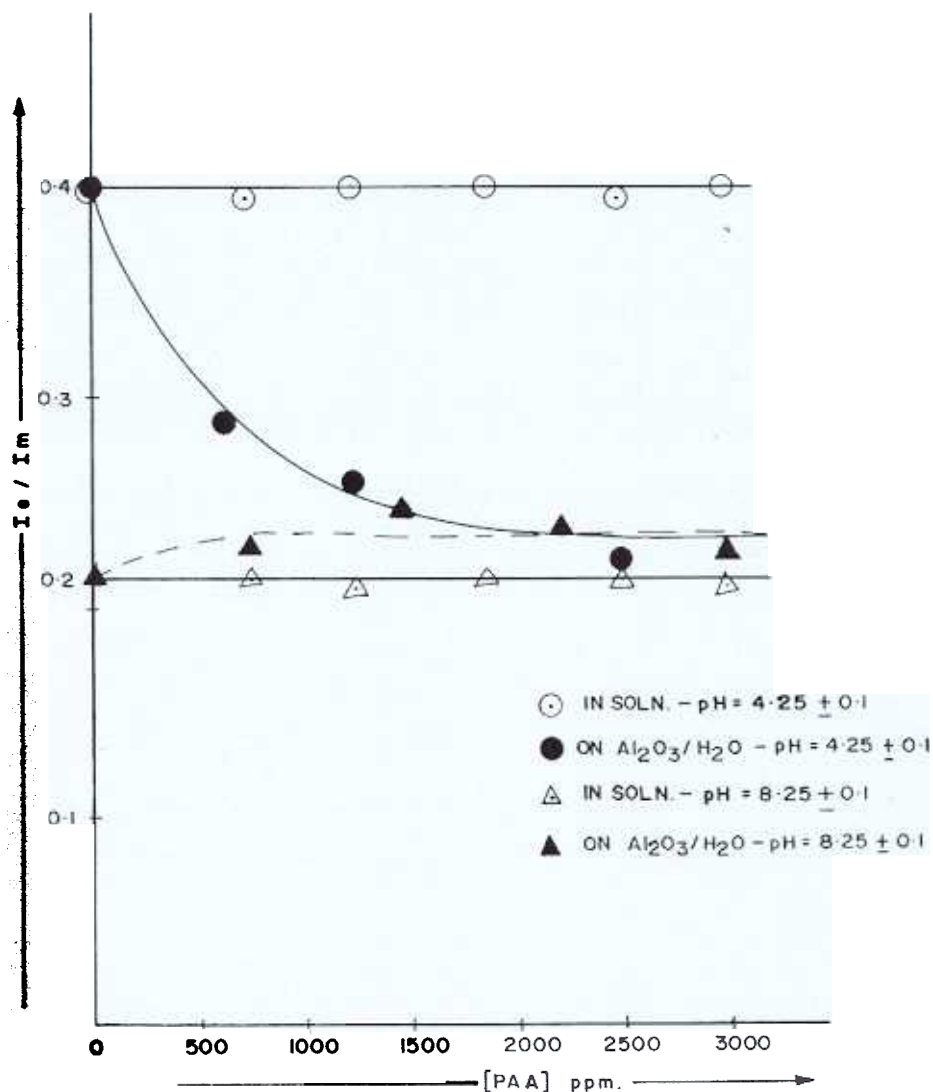


Fig. 4. Excimer-forming efficiency ($\pm 0.5\%$) of PyPAA (50 p.p.m.) in solution and at the alumina/water interface at different concentrations of PAA.

have been found to increase with pH [10]. This has been attributed to polymer chains with a stretched conformation at high pH dangling out into the solution phase and anchoring onto the surface. The phenomenon of flocculation begins immediately upon the adsorption of the polymer onto the particles. The flocculation process is initiated by the bridging of particles through polymer segments stretching out from the surface into the

solution phase. Apparently, the segments lying in the vicinity of the surface under high pH conditions undergo some coiling with time, as suggested by the increase in excimer formation. Whether the forces involved in this process originate from the surface or the thermodynamic instability involving the interaction between the polymer segments and solvent is not currently known. At low pH values, the adsorbed species possessing the coiled con-

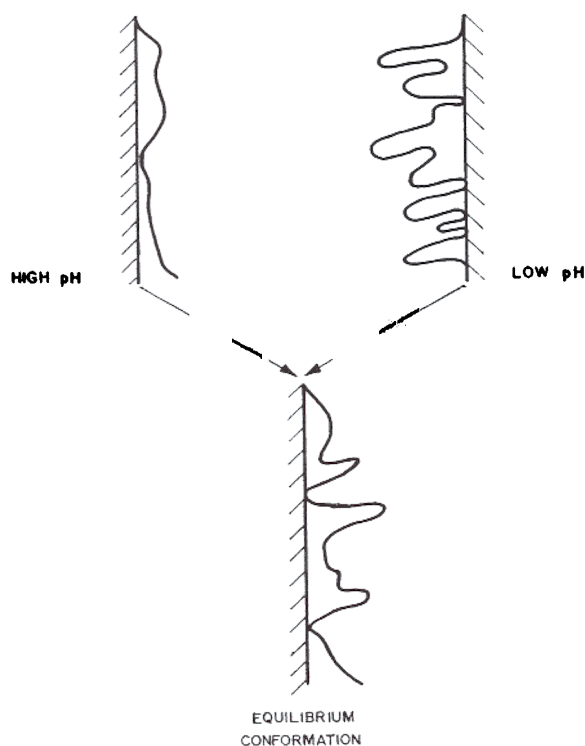


Fig. 5. Visualization of the PAA conformation on alumina immediately after adsorption at low and high pH values, and after reaching equilibrium.

formation in solution tend to stretch until the adsorbed polymer molecules attain a conformation close to that normally reached under high pH conditions at the interface. Since quenching of pyrene fluorescence does not occur with free PAA, changes in the I_E/I_M value can be attributed to the change in conformation of the adsorbed polymer chain.

Aggregation of particles by a bridging mechanism can be considered to be initiated simultaneously to the onset of adsorption of the polymer in a particular conformation. Thus, the aggregation centers having been nucleated, any change in the conformation of the polymer segments at the interface not directly involved in bridging may not

appear to affect the flocculation property of the particles. However, the various time scales involved in the adsorption and flocculation processes will depend on the polymer concentration and molecular weight (i.e. polymer diffusivity), particle concentration and pH. Thus, the rearrangement of the polymer adsorbate may yield an equilibrium excimer efficiency without affecting the flocculation efficiency. It may be noted that if the system is subjected to severe shearing, deflocculation and even reflocculation can occur. It is indeed possible that these processes might be affected by the change in conformation of the adsorbed polymer species.

Acknowledgments

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