



The forces and physical properties of polymer particulate monolayers at air/aqueous interfaces



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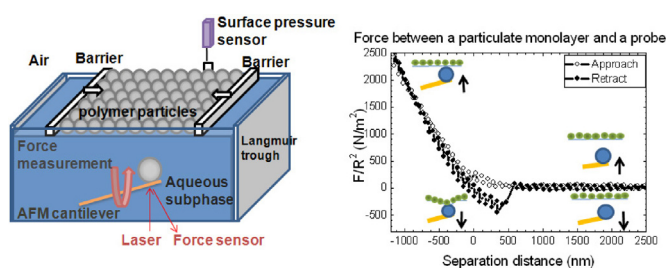
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HIGHLIGHTS

- Polystyrene (PS) particles with PDMA or PDEA hairs (PDMA-PS or PDEA-PS) were used.
- The particles formed incomplete monolayers at pH 2.5 subphases.
- Incomplete monolayers gave a low adhesion and stiffness.
- The particles formed close packed monolayers at pH 5.8 and pH 9 subphases.
- Increasing the monolayer density decreased the adhesion and stiffness.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 October 2014

Received in revised form 1 December 2014

Accepted 17 December 2014

Available online 31 December 2014

Keywords:

Charge
Hydrophobicity
Packing density
Langmuir monolayer
Stiffness
Adhesion

ABSTRACT

Polystyrene particles with poly[2-(dimethylamino)ethylmethacrylate] or poly[2-(diethylamino)ethylmethacrylate] hairs (PDMA-PS or PDEA-PS) formed monolayers at the air/water interface. We measured the forces between the particle monolayers and a positively charged hydrophilic particle attached to an atomic force microscope cantilever (probe particle) in the water subphase. Force–distance curves were recorded as a function of the surface pressure at different pH. In this way, we determined the effect of the particle charge, hydrophobicity and packing density on the forces.

PDMA-PS and PDEA-PS particles strongly adhered to the water surface and formed stable monolayers at pH 5.8 and pH 9.0. However, the particles did not attach to the water surface strongly at pH 2.5 and therefore only formed incomplete monolayers. This result was explained by the fact that the particles were highly positively charged and hydrophilic at pH 2.5, but became less charged and therefore more hydrophobic as the subphase pH was increased to pH 5.8 and pH 9.0. The effective stiffness of the air/water interface that was determined from the force measurements decreased with a surface pressure increase (particle packing density increase) for pH 5.8 and pH 9.0. A higher particle density gave a lower stiffness, due to the lower surface tension. The adhesion between the probe and the monolayer and the effective stiffness of the monolayer increased when the subphase pH was increased from 2.5 to pH 5.8 or 9.0. This increase was explained by the increased ability of the particles to adsorb to the air/aqueous interface, which resulted from the lower charge and therefore higher hydrophobicity of the particles. Increasing the charge density of the monolayer of the partially hydrophobic particles by decreasing the subphase pH from 9.0 to 5.8 tended to increase the effective stiffness in the wrinkling phase. This result was explained by the increased electrostatic repulsion between the particulate monolayer and the probe,

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which caused the probe to contact the monolayer less and therefore to physically perturb the monolayer less. Increasing the hydrophobicity of the particles increased the stiffness of the monolayer, due to the stronger inter-particle hydrophobic attractions.

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1. Introduction

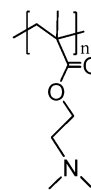
The ability to stabilize liquids and bubbles dispersed in liquids by the adsorption of particles determines the success of many applications, such as the formation of the long-circulating and target-specific carriers that are used to cure cancer in drug delivery [1], the improvement of the biocatalysis and bioseparation technology [2], the development of smart foods that reduce the risk of diseases [3], and the formation of new nanocomposites for use in nanotechnology [4]. A successful stabilization requires the correct number, size and type of particles to be adsorbed to the air or liquid interface with the correct packing density [5]. We therefore need to be able to control the effect of the number and type of particles and the surrounding environment on the physical properties of deformable interfaces, such as emulsions and foams. Such an ability can only be realized from an in-depth understanding of the mechanism and forces responsible for the adsorption of particles to deformable interfaces, and the factors and forces affecting the physical properties of the interface once particles have adsorbed.

The adsorption of a particle to an interface, the organization of the particles at the interface, and the resulting physical properties of the interface are controlled by the inter-molecular forces in the system, such as the forces between the particle and the interface and the lateral inter-molecular forces between neighboring particles at the interface. Inter-particle repulsions are influenced by the electrostatic forces between the particles, which are controlled by their surface charge. Inter-particle attractions depend on the hydrophobic, van der Waals, and capillary interactions between neighboring particles [6]. The strength of the attractions increases with particle hydrophobicity. Thus, the packing density, hydrophobicity and charge of the particles will affect the interactions of the particles at the interface and therefore the overall physical properties of the interface. It is therefore important to determine the effect of the hydrophobicity, particle charge, and packing density of a particle stabilized emulsion or foam on the forces in such a system, in order to better understand and control the properties and behavior of a system involving particles at deformable interfaces.

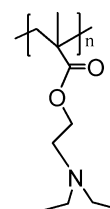
In contrast to particles adsorbed to hard surfaces, particles at liquid interfaces are free to move laterally and the interface undulates. The force data needed to understand a deformable interface cannot be obtained using the conventional methods of force measurement, such as the Atomic Force Microscope (AFM) and the Surface Force Apparatus. The Monolayer Particle Interaction Apparatus (MPIA) can be used to directly measure the forces between a particle in a liquid and a deformable interface [7–9]. As a particle stabilized emulsion or foam can be modeled by a monolayer of particles at the air/water interface, we can use the MPIA to determine the forces controlling the physical properties of a model emulsion or foam. For an easier analysis, the particles used to form the monolayer should be monodisperse. They also need to adsorb to an air/water interface and they should be two-dimensionally dispersed at the air/water interface, that is, they should not form clusters/islands. Polymer particles, Janus particles, and TiO₂ particles are known to form stable monolayers at air/liquid interfaces with the above properties [10–12].

Here, we use polystyrene particles that are coated with the stimuli-responsive polymers of poly[2-(dimethylamino)ethyl

A. PDMA



B. PDEA



C. hydrophilpos

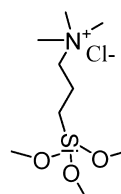


Fig. 1. Structures of the materials used for the particles in this study. (A) PDMA; (B) PDEA; (C) N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (*hydrophilpos*).

methacrylate] (PDMA) or poly[2-(diethylamino)ethyl methacrylate] (PDEA), referred to as PDMA-PS and PDEA-PS, respectively (Fig. 1A and B). The PDMA or PDEA coating allows the surface charge and the hydrophobicity of the particles to be controlled by the pH. The diethylamino group in PDEA-PS has a longer hydrocarbon chain-length than the dimethylamino group in PDMA-PS. Thus, the hydrophobicity influence of particles on the forces of a particle-stabilized emulsion can be obtained if the forces are measured using monolayers of the PDMA-PS or PDEA-PS particles. Additionally, PDMA and PDEA have pK_a values of 7.0 and 7.3, respectively [13]. Thus, a pH increase from 2.5 to 9.0 causes the protonation of the amino group on the particles to decrease [14]. This change in the charge of the particles with pH allows the effect of the charge of the particles in the particulate monolayer at the air/aqueous on the inter-molecular forces to be determined, if the pH of the subphase water on which the polymer particles are spread is adjusted. Finally, the packing density of a particulate monolayer increases with a surface pressure increase [15]. Thus, the effect of the packing density on the properties of particulate monolayers at air/aqueous interfaces can be determined by measuring the forces of the monolayers as a function of the monolayer surface pressure.

In this study, we used the MPIA to determine the effect of the particle charge, hydrophobicity and packing density on the forces and physical properties of a particulate monolayer at an air/water interface. The forces were measured between the PDMA-PS or PDEA-PS particulate monolayers at an air/aqueous

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