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Transition Region at the n-Hexane/Nanocolloidal Silica Interface

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Introduction

A comprehensive understanding of the electrical double layer at the interface of an insulator/electrolyte solution is of fundamental importance in describing electrochemical processes in systems involving membranes, absorbers, catalysts, surfactants, or surfaces of other dielectrics [1, 2]. I report the findings from studies of a transition layer at the interface between n-hexane (insulator) and colloidal silica (electrolyte) solutions, with particle sizes typical for macromolecules (5 – 22 nm) and very large surface-charge densities (0.2 – 0.9 C/m^2). Its thickness is comparable with the Debye screening length, which is a typical width of the diffuse layer in the Goy-Chapman theory, between particles of the electrolyte solution ($\Lambda_D \sim 300$ – 1000 Å). In this paper I studied by x-ray reflectivity the dependence of the width of the transition region from the size of the nanoparticles.

Methods and Materials

All the data presented in this paper were obtained at beamline X19C, National Synchrotron Light Source, Brookhaven National Laboratory [3]. I used a monochromatic (wavelength $\lambda = 0.825 \pm 0.002$ Å) focused x-ray beam to explore the planar interface between n-hexane and silica solution, which do not mix. I used the same experimental procedure as described in details in Ref. 4. N-hexane was purchased from Aldrich-Sigma and purified by activated alumina in a chromatography column. DuPont supplied the suspensions of colloidal silica in water, stabilized by sodium hydroxide. Silica sol can be treated as strong electrolyte in which the solutes are completely ionized. Particles of amorphous silica in the sols carry a negative charge $Z \sim 400e - 700e$ per particle (e is the elementary charge). The tension, γ, of the hexane/sol interface was approximately ~ 40 mN/m measured by the Wilhelmy plate method.

Results

The forces between sol particles, cationic Na$^+$, and the charge density induced by them near the interface define the equilibrium structure of the interface, which can be described in accordance with a model wherein the potential gradient at the interface reflects the difference in the potentials of “image forces” between the cationic Na$^+$ and anions (nanoparticles) and the specific adsorption of surface charge [5]. The structure factor of the interface and the angular dependence of the grazing incidence small-angle scattering can be explained by the interfacial model, which consists of three layers, i.e., a thin layer of Na$^+$ (~ 20 Å), a monolayer of nanocolloidal particles as the part of the diffuse layer, and a low-density layer sandwiched between them (See Fig. 1). The transition layer of the 50-Å and 70-Å-particle solutions is the same thickness, while for the 120-Å and 220-Å-particle sol it is much wider (200 Å vs. 400 Å).

Discussion

The strongest interaction in this system is associated with the repulsion of the nanoparticles from each other and from the oil surface by the forces of electrical image that are ~ Z^2. As was shown in Ref. [6], 12-nm particles in the loose monolayer should carry at least a threefold higher charge than in the bulk of the solution to satisfy the condition of electro-neutrality at the interface. This means that the repulsion between particles in the bulk and those at the interface is weaker than the repulsion between the image charge and particles at the interface. On the other hand, the interaction of nanoparticles in the monolayer with the image charge should also be weakening with increasing distance from the interface due to the effect of screening by electrolyte ions ($\Lambda_D \sim 1000$ Å). Therefore, the Helmholtz plane (the plane of the closest approach to the interface) for 12-nm or 22-nm particles must be positioned further from the interface than for 5-nm or 7-nm particles. In closing, I refer readers to my recent publication exploring the density of water in a solution of 70 Å particles using of x-ray reflectivity and small-angle grazing incidence diffraction [4].

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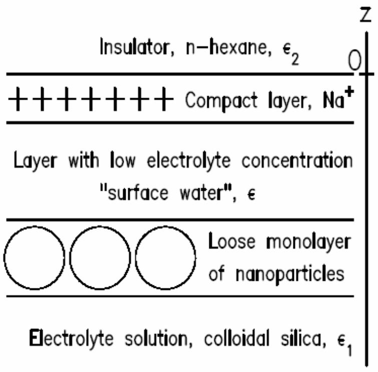

Fig. 1. Three-layer model of the transition layer at hexane/silica sol interface.