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Nanoscale forces of interaction between glass in aqueous and non-aqueous media: A theoretical and empirical study

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ABSTRACT

The interfacial forces that control colloid stability in aqueous and non-aqueous systems are functions of the polar and apolar properties of the medium. This study presents a complete empirical and theoretical description of the forces and energies between a glass microsphere and a glass surface in aqueous and non-aqueous n-decane solutions that were amended systematically to enhance various colloidal interactions. Force data were measured using colloid probe atomic force microscopy (AFM) and both classical DLVO and extended-DLVO (XDLVO) theories were used to calculate the free energy of each system. The successes and failures of each theory in predicting force data were evaluated and the results indicate the importance of minor amounts of impurities, especially in the non-aqueous solutions, which impart measurable electrostatic charges on the colloidal particles. Data were also collected in a complex non-aqueous solution (commercial motor oil) and the recorded forces were significantly different compared to data collected in n-decane; long-range repulsive forces were measured by AFM. These results document the significance of aqueous impurities in non-aqueous systems which will likely dominate interactions between colloids in natural systems. Our results also indicate that DLVO and XDLVO theory predict colloidal interactions in aqueous systems. However these theories are unable to predict colloid stability in natural and chemically complex non-aqueous media.

1. Introduction

Colloids are a unique group of particles ranging in size from 0.01 to 10.0 μm [1], that have variable composition, phase, and geometry and exist in many biological, chemical, and geological systems. The stability of a colloidal system is ultimately controlled by a combination of interfacial forces which include, but are not limited to, van der Waals, electrostatic, and acid–base interactions. The dominance of any particular interaction is determined by both the liquid dispersant medium and the solid colloidal particle. Although the size, shape, and charge of the colloid are also important parameters, which must be quantified to understand the colloidal system, the chemical properties of the medium are equally necessary to properly predict and understand the system's stability. Thus, the focus of this research is to understand and quantify the fundamental differences between aqueous and non-aqueous dispersant media, involving one type of particle.

Colloidal forces in aqueous and non-aqueous media differ for several reasons. van Oss [2] and others [3–6] provide a thorough background and understanding of colloid stability in aqueous media; however, colloid stability in non-aqueous media is not completely described. In aqueous solutions electrolytes tend to dissociate completely until saturated, thus making ions readily available to associate with surfaces. The association of ions with a surface creates an electric double layer whose thickness varies with ionic strength; the thickness of the double layer is defined by the distance at which the radius of shear is differentiated from the bulk solution and is quantified in terms of a zeta-potential [4].

In non-aqueous solutions diffuse layers of charge form less readily due to limited solubility of ions and the mechanisms that govern colloidal interactions differ from aqueous solutions [7–11]. The lack of ions in non-aqueous solutions generates much thicker double layers relative to aqueous solutions [7]. Additionally, Lewis acid–base interactions are reduced in non-aqueous solutions, where there are generally no electron donor (γ_L^-) or acceptor (γ_L^+) properties of the medium, and the only acid–base interactions are those of the colloid (γ_S), which occur roughly at the minimum equilibrium distance [12]. Although acid–base interactions may not exist between a particle and non-aqueous solution theoretically, the presence of very small quantities of water may result in electron donor/acceptor properties that influence colloid stability. For example, water has a solubility of 0.007% (w/w) in n-decane at 25 °C [13]. Trace amounts of water may cause the particle sur-

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face to acquire a greater charge potential or form a water meniscus between the colloid and the substrate [11,14].

The objectives of this research are to (1) measure the nanoscale interfacial forces between a colloid and surface in simple aqueous and non-aqueous solutions, (2) determine the effectiveness of Derjaguin, Landau, Verwey, and Overbeek (DLVO) and Extended-DLVO (XDLVO) theories in predicting those forces in both the aqueous and non-aqueous simple systems, and (3) apply our knowledge of forces in a simple non-aqueous system to a more complex non-aqueous fluid. The forces between a glass colloid and glass planar surface were measured in water and n-decane with various chemical amendments using colloid probe atomic force microscopy (AFM). The chemical amendments selected for this study are common additives to commercial motor oils. Inverse modeling was used to fit XDLVO theory to empirical AFM force data. Thus, we present a complete theoretical and empirical description of the major forces present in aqueous and non-aqueous solutions for a given colloid-surface system. We use our results from the simpler aqueous and non-aqueous systems to describe and quantify colloidal forces in commercial motor oil, a more complex non-aqueous system comprised mostly of n-decane.

2. Materials and methods

2.1. Materials

All aqueous solutions were prepared with deionized water (DIW) as the solvent. All non-aqueous solutions were prepared with practical grade n-decane (J.T. Baker) as the solvent. For the aqueous portion of the study, a 10.0 mM $NaCl_{(aq)}$ solution was made by dissolving sodium chloride salt (A.C.S Reagent grade, EMD) in DIW, and a 2.0 mM sodium di-2-ethylhexylsulfosuccinate (AOT) solution was made by dissolving AOT surfactant (TCI-EP) in DIW. For the non-aqueous portion of the study a 0.045% (v/v) (H_2O/n-decane) solution was prepared by injecting a small aliquot of DIW into the n-decane, which was stirred in a covered beaker overnight. 0W-20 motor oil was purchased for AFM experiments.

The colloids used in all experiments were borosilicate glass microspheres (Polysciences, Inc.). Each AFM colloid probe was imaged using a scanning electron microscope (SEM) to determine the particle's size and cleanliness. All force data were collected using microspheres that measured $6 \pm 0.5\ \mu\text{m}$ in diameter.

2.2. Atomic force microscopy experiments

Colloid probe cantilever preparation and force measurements were completed using an MFP-3D AFM coupled to an inverted optical microscope (Asylum Research, Santa Barbara, CA). AFM colloid probes were prepared by attaching a single glass colloid to the apex of a tipless silicon nitride cantilever using 5-min epoxy (LOCTITE® Quick Set™). Using the AFM microscope stage, the cantilever was lowered into a miniscule drop of epoxy, raised up, and then lowered down onto a single colloid. In total, five colloid probes were prepared for this research. Once the epoxy had set (24 h) the spring constant of each colloid probe was calibrated using the "Engage-and-Thermal" method outlined by Asylum Research [15]. The calculated spring constants of the cantilevers were ±0.01 N/m of the reported value (0.06 N/m). However, the thermal plots of the cantilevers in solution were dampened by approximately 1/3. Each colloid probe was imaged using an SEM to ensure the proper placement of the microsphere and confirm that no other particles, dirt, or epoxy were on the cantilever or colloid (Fig. 1).

The colloid probe cantilevers were cleaned between each experiment. Colloid probes were rinsed in 70% (v/v) reagent alcohol and air dried for 20 min, then rinsed with 30% H_2O_2 and air dried for 10 min, and finally rinsed with DIW and then dried in an oven at 60 °C for 24 h. The cantilever was then allowed to cool to room temperature prior to collecting force data.

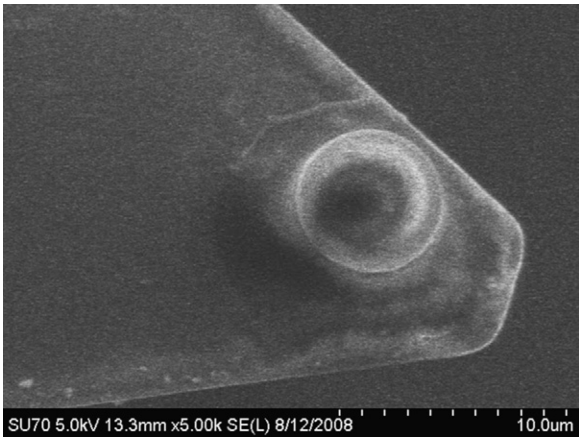

Fig. 1. SEM image of glass microsphere attached to tipless cantilever.

Force data were collected between the glass colloid on the AFM colloid probe and the glass bottom of the fluid cell. The planar glass bottom of the fluid cell was washed between all experiments using the same method described for the colloid probe, except that the surface was wiped dry in the final step.

Force data were collected at room temperature in contact-mode with a set point force of 0.5 V and an integral gain of 10.00. All force data were collected using the same piezo approach/retraction velocity and trigger point, 1.25 μm/s and 0.5 V, respectively. Due to the greater viscosity of the commercial motor oil, integral gain, velocity, and trigger point values of 6.50, 350 nm/s, and 0.7 V, respectively, were used to improve reproducibility and signal-to-noise (S/N) ratio.

Force data were plotted as force (nN to pN) versus colloid-to-surface separation distance (nm). Each force–distance curve was inspected individually, and force curves with obvious noise or irregularities were removed. Approximately 15–20 force curves were analyzed in each system and the average force curve of each system was calculated using the IGOR subroutine. To compare measured force data to DLVO and XDLVO modeling, the average AFM force curve from each experiment was integrated with respect to separation distance to calculate interaction energy [16]. The integration of each force curve was done from a separation distance that corresponded to the initial measurable force in each system (16–100 nm) to the point of colloid-surface contact (0 nm). All reported AFM data were normalized to the radius of the colloid and are presented as such in the results.

2.3. DLVO and XDLVO modeling

Classical DLVO and XDLVO modeling were performed for each colloidal system using the sphere-to-flat plane model [12]. Classical DLVO modeling is expressed as the sum of the van der Waals [13] and electrostatic (EL) interaction energies, as a function of separation distance:

$$\Delta G_{121}^{Tot}(d) = \Delta G_{121}^{LW}(d) + \Delta G_{121}^{EL}(d) \qquad (1)$$

where ΔG_{121}^{LW} is the attractive van der Waals free energy of interaction (negative by convention), and ΔG_{121}^{EL} is the repulsive electrostatic free energy of interaction (positive by convention) between materials 1 immersed in a liquid 2. The van der Waals