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Regular Article

Extended hierarchical solvent perturbations from curved surfaces of mesoporous silica particles in a deep eutectic solvent

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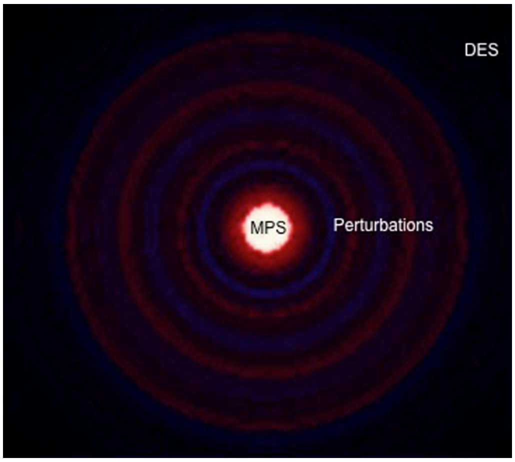
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Many applications of deep eutectic solvents (DES) rely on exploitation of their unique yet complex liquid structures. Due to the ionic nature of the DES components, their diffuse structures are perturbed in the presence of a charged surface. We hypothesize that it is possible to perturb the bulk DES structure far (>100 nm) from a curved, charged surface with mesoscopic dimensions.
Experiments: We performed in situ, synchrotron-based ultra-small angle X-ray scattering (USAXS) experiments to study the solvent distribution near the surface of charged mesoporous silica particles (MPS) ($\approx$0.5 μm in diameter) suspended in both water and a common type of DES (1:2 choline Cl-:ethylene glycol).
Findings: A careful USAXS analysis reveals that the perturbation of electron density distribution within the DES extends $\approx$1 μm beyond the particle surface, and that this perturbation can be manipulated by the addition of salt ions (AgCl). The concentration of the pore-filling fluid is greatly reduced in the DES. Notably, we extracted the real-space structures of these fluctuations from the USAXS data using a simulated annealing approach that does not require *a priori* knowledge about the scattering form factor, and can be generalized to a wide range of complex small-angle scattering problems.

Abbreviations: USAXS, ultra small angle X-ray scattering; APS, Advanced Photon Source; SAS, small angle scattering; DES, deep eutectic solvent; MPS, mesoporous silica.

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1. Introduction

Particle-solvent interactions are fundamental to understanding and manipulating particle-particle interactions in colloidal dispersions. Historically, particle-particle interactions have been characterized by colloidal stability, with unstable colloids flocculating out of solution. Electrostatic stability of colloids is achieved by surface-charge induced inter-particle repulsions. In aqueous solutions, a charged particle surface attracts oppositely charged ions to form an electrostatic double layer [1]. In general, the electric field is highest in the Stern layer, adjacent to the surface (<1 nm), and decreases monotonically throughout the Guoy-Chapman layer [2]. Consequently, the ion concentrations increasingly deviate from the bulk solution as they approach the particle surface. Typical double-layer thicknesses in aqueous solutions are below 1 nm and would be difficult to resolve with scattering techniques such as small angle X-ray scattering (SAXS). Rather, other experimental techniques, such as differential capacitance [3] and atomic force microscopy [4], can be used to validate the theoretical predictions.

Contrary to simple aqueous solutions, a charged surface in a room temperature ionic liquid (RTIL) is known to induce an oscillating multilayer structure where the ion concentration deviates from the bulk in an oscillatory fashion, as ions approach the surface [5]. In many RTILs, this behavior is attributed to charge overscreening, whereby the bulky ions pack together in localized regions [5,6]. Typically, these “packed” regions are on the nanometer-scale and are experimentally accessible [7–14]. At the same time, many RTILs have bulk structure that is related to their complex molecular interactions, including ionic attraction and repulsion [15]. Therefore, the presence of an electric field may perturb the bulk structure over large distances from the surface charge. When colloidal particles are suspended in a RTIL, it is more difficult but not impossible to characterize the particle-solvent interactions. For example, it has been proposed that a protective shell forms around charged particles in RTILs [16–18]. However, the extent of the solvent perturbation from the surface, including the characteristic length scale and strength of perturbation, is not understood. In this work, we performed in situ, synchrotron-based ultra-small angle X-ray scattering (USAXS) experiments from mesoscopic charged colloidal particles to resolve the electron density fluctuations near the surface. As a technique, USAXS is sensitive to electron-density inhomogeneities from the nanometer to micrometer scale, a size range of particular importance to answering this challenging scientific question.

Deep eutectic solvents (DESs) consist of at least two otherwise solid components that, when mixed together in the right proportions, are liquid solutions at room temperature [19]. Since the realization of their potential [20], this broad class of solvents has attracted interest in particle synthesis [21], assembly [22], toxin removal [23–25] and other nanoparticle technologies [26], as they are often considered green [27], cost-effective alternative solutions that have potential in many applications [28,29]. Similar to most RTILs, DESs contain a high concentration of ions. Even though the constituent species of the DES are smaller than that of most RTILs, multilayers with dimensions larger than those of RTILs have been observed in DES solutions [30,31]. In these prior studies, it was proposed that the perturbations were induced by species adsorption onto nanometer-sized particles, which then disrupts both the electric field and hydrogen bond network of the DES near the surface. As the hydrogen bond networks in DESs are quite extensive [32–34], it was hypothesized that solvent perturbations could also be extended much further out in the solution. Such long-range perturbations could, in principle, be manipulated to change the solvent structure or fine-tune interactions of the particles. Our study aims to experimentally test this hypothesis, with mesoscopic particles suspended in DES solutions to confirm the presence of long-range solvent perturbation.

Deep Eutectic Solvents have proven to be effective solutions to facilitate assembly for several nanoparticles including: Au [35], PbS [36], Pt [37], Pd [31,38] and Ni [39]. In each of these cases, nanoparticles assemble in a specific “non-random” way to form various morphologies. The role that the DES plays in directing the assembly is difficult to elucidate but is likely a complex process. One possible pathway for irreversible assembly is via particle-solvent interactions whereby the particle precursor and DES composition is not uniform across the particle surface. These non-uniform particle-solvent interactions could affect the way that surface particles aggregate [31,40] or the way that the particles grow. On the other hand, the solvent fluctuations near a continuous phase transition play a role in reversible particle assembly through the so-called critical Casimir Force [41]. If the perturbations observed in prior work extend far enough out into the solution to other particles, it may be possible to achieve larger particle assemblies. Though no particle assembly is observed in this study, the aim was to explore the possibility of such long-range perturbations.

A second aspect of this study is that the mesoscopic porous silica (MPS) particles used in this study are mesoporous. Porous colloids are used in a wide variety of technologies whereby guest species are contained or released within the particles. A few notable examples include: hollow and mesoporous carbon for faradaic [42] and capacitive [43] energy storage, hollow [44] and mesoporous [45] silica for drug release, synthesis templates, molecular sieves [46] or storage for triggered release [47]. In many of these applications, the pore-filling fluid can have different thermophysical properties as a result of the confinement within the nanopores [48]. Moreover, these thermo-physical properties can be dependent on the pore size and the chemistry of the pore-filling fluid [49]. USAXS is sensitive to changes in the pore size, and the composition and electron density of pore-filling fluid, which make it a well-suited technique to understand the pore-filling activity. Hence, a secondary focus of this study is to probe the pore-filling behaviors of DES in commercially available and broadly used MPS particles to understand the technologically important pore activity and colloidal stability. Even though the presence of pores complicates the SAS modeling, they can play an important role in the functionality of the MPS. To our knowledge, it is unknown whether or not the DES can penetrate the MPS as other molecules. For these reasons, MPS was used in this study, than other nanoporous colloids.

2. Method, materials, and experiments

2.1. Materials

In this study, MPS particles were dispersed in three different solutions at different volume fractions. Silica powder with diameter of 0.5 μm was acquired from Bangs Laboratories Inc, IN[1]. The colloids were dispersed with three different solutions: Millipore water, 1:2 choline Cl-:ethylene glycol DES and 1:2 choline Cl-:ethylene glycol DES with 0.011 wt.% AgCl. Each solution was prepared in a plastic tube then sealed. Care was attended to ensure proper dispersion using a combination of repeated and rigorous vortex mixing and ultrasonic bath for over 12 h. Volume fractions of 1%,

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[1] Certain trade names and company products are mentioned in the text or identified in illustrations in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.