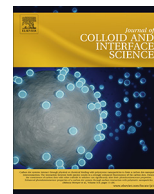




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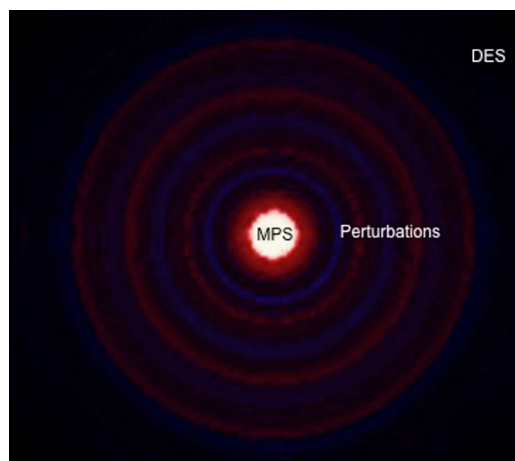
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Regular Article

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) ($\approx 0.5 \mu\text{m}$ 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 $\approx 1 \mu\text{m}$ 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.

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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 thermo-physical 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, rather 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, IN¹. 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%,

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.

5% and 10% were prepared for both the neat DES and H₂O, while volume fractions of 1% and 5% were prepared in the DES-AgCl solution. More details about sample preparation can be found elsewhere [50].

The DES was prepared by mixing fresh recrystallized (in absolute ethanol) choline Cl- (Sigma-Aldrich, MO) and 99.96% anhydrous ethylene glycol (Sigma-Aldrich, MO Lot SHBC8455V) in a 1:2 molar ratio in a glass beaker. The mixture was left to melt on a hot plate at 90 °C under an Ar blanket. Once a homogenous liquid was observed, the appropriate volume of solution was syringed out of the beaker and placed in the tube that contained the MPS and sealed. A second DES was prepared in the same way and then mixed with 0.011 wt.% AgCl (≈ 0.01 mM) at ≈ 50 °C and stirred under an Ar blanket for ≈ 6 h. The final AgCl/DES mixture was in the form of a clear solution, which was again syringed into the sealed tubes that contained the MPS. Millipore H₂O was obtained using a Millipore H₂O dispenser.

2.2. Small angle X-ray scattering

The technique of small angle X-ray scattering (SAXS) is broadly applied to characterize the structure and understand the behaviors of colloidal suspensions. In an SAXS experiment, the scattering intensity is measured as a function of the magnitude of the scattering vector q , where q is defined by:

$$q = \frac{4\pi \sin \theta / 2}{\lambda} \quad (1)$$

Here, λ is the wavelength of the X-rays and θ is the scattering angle [51]. For a scattering object with spherical symmetry, the scattering intensity, $I(q)$, depends on the radial scattering length density function, $\rho(r)$, following:

$$I(q) = \left[4\pi \int_0^R \rho(r) \frac{\sin qr}{qr} r^2 dr \right]^2 \quad (2)$$

Eq. (2) allows one to extract the physical function $\rho(r)$ from the scattering intensity. In this study, $\rho(r)$ is the primary objective of modeling. For nonhomogeneous $\rho(r)$, the integral in Eq. (2) allows $\rho(r)$ to be partitioned into discrete radial shells of discrete width, dr , in a formulation commonly known as construction of concentric shells. This forms the foundation of the USAXS modeling and allows the scattering length density distribution $\rho(r)$ to be extracted. We also emphasize that the MPS we used is highly monodisperse (size dispersity $\approx 6\%$, [50]). This limits the distortion and smearing that polydispersity brings, and maximizes our chances to elucidate the statistically meaningful solvent structure near the surface of MPS.

From a technique point of view, we need to resolve the weak scattering contrast variations around the MPS particles. This requires both very intense X-rays and access to low- q scattering, which are only satisfied by a synchrotron-based USAXS instrument. Analysis-wise, instead of adopting traditional ball-and-sticks SAXS analysis methods that can be assumption-heavy, we developed a heuristic approach based on the simulated annealing algorithm specific to mesoporous colloids. The aim of this approach is to elucidate the scattering length density function of the DES, $\rho_{DES}(r)$, which is proportional to radial electron density function of the DES. Here, r is the distance from the center of the MPS out into the bulk solvent. We constructed a universal scattering length density function $\rho_{DES}(r)$ and deduced the overall scattering intensity over a wide q range based on $\rho_{DES}(r)$. By minimizing the energy of the simulated annealing algorithm, we drew conclusions based on observations from multiple candidate functions of $\rho_{DES}(r)$.

2.3. USAXS experiment and analysis

Approximately 1 ml of each suspension and solution were pipetted out of each tube and immediately transferred to a sealed 1 mm thick cell (Grace bio-labs) for the USAXS experiments. From synthesis to measurement, this was the only time the solutions were exposed to air at room temperature. Hence, we expect that the disruption of atmospheric H₂O to the DES solution used in this study be minimal. The USAXS experiments were performed using 17 keV X-rays at beamline 9-ID-C at the Advanced Photon Source, Argonne National Laboratory, using a beam area of 0.6 mm² [52]. A second set of pinhole SAXS experiments were conducted on the same samples using an add-on pinhole camera, also available at the beamline [53]. The data reduction was performed using the *Indra* package for Igor Pro (WaveMetrics, OR). The scattering from the bulk solution (without MPS) was subtracted from USAXS data collected for each respective suspension. Detailed data analysis was performed in Python, using the least-squares module “lmfit” [54] and simulated annealing module “simanneal” [55]. The data analyses were performed using a computer with a 2.1 GHz Intel Xeon E5-2695 v5 processor and 128 GB of memory. Typical computation times for the least-squares fitting were minimal, while the simulated annealing procedures required 20–48 h each.

3. Results and discussion

3.1. SAXS data

The USAXS data from the MPS suspension, as shown in Fig. 1, bear much resemblance. In all cases, there is a broad Guinier knee at $\approx 10^{-3} \text{ \AA}^{-1}$, followed by a large number of Bessel oscillations and a feature at $\approx 0.1 \text{ \AA}^{-1}$ that appears more prominent than a conventional Guinier knee; this feature will be referred to as the “high- q ” feature. The low- q knee is associated with the mean MPS particle size. The large number of oscillation shows that the MPS particles are highly monodisperse. The high- q feature is associated with the nanoscopic pore structure within the MPS. Because these features do not shift in q , we conclude that the different solutions do not affect the particle size or the pore size.

Despite the similarities, Fig. 1 readily shows that the MPS particles in the DES solutions scatter X-rays differently than those in H₂O, which provides insight into particle-solvent interactions. First, the scattering uptick for the MPS in DES samples at $q < 10^{-3} \text{ \AA}^{-1}$ cannot be attributed to “fractal-like” particle aggregation [56] because the scattering intensity in the q -range ($10^{-4} \text{ \AA}^{-1} < q < 10^{-3} \text{ \AA}^{-1}$) is not a persistent power-law and also because the suspensions remained stabilized over an extended period of time (days) and did not precipitate. Second, the USAXS scattering intensity is absolutely-calibrated. Hence, for samples in different solvents with the same MPS volume fraction and sample thickness, the scattering intensity is directly comparable. We observed a systematic difference in scattering intensity at the Guinier knee near $q \approx 10^{-3} \text{ \AA}^{-1}$ and the following Bessel oscillation, with the scattering intensity being lower for samples in the DES solutions. This observation indicates that scattering length density around the particles is different than the bulk DES. Third, due to the size monodispersity, the Bessel oscillations continue as the scattering intensity decays according to $I(q) = Bq^{-4}$ in H₂O suspensions, a characteristic of Porod scattering [51]. In the DES suspensions, the scattering intensity in the same q region contains a broad feature that decays differently than what Porod scattering dictates, which indicates the presence of scattering inhomogeneities on the order of 100 nm. Moreover, scattering in this region and at $q < 10^{-3} \text{ \AA}^{-1}$ changes when AgCl is added to the DES, which suggests that the dissolved AgCl species affects the scattering inhomogeneities

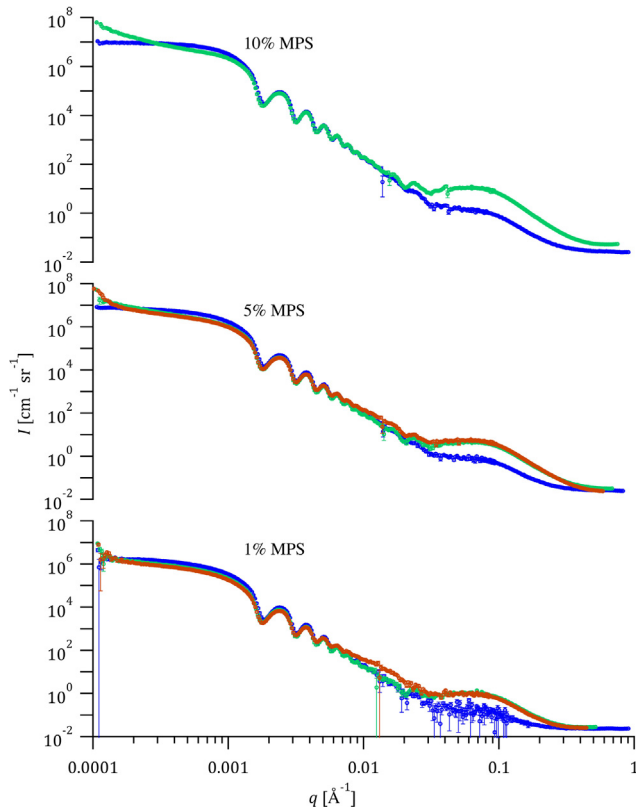


Fig. 1. log-log plot of the USAXS data collected from each MPS suspension in water (blue), DES (green) and 0.01% AgCl+DES (red) at different particle loadings, as shown from top (10%), middle (5%) and bottom (1%). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

corresponding to this q range. Finally, any scattering due to a non-fractal-like particle superstructure (e.g., aggregates) should be enhanced in the 10% MPS loading in the DES. Instead, the low- q scattering that precedes the MPS Guinier knee is suppressed, similar to the USAXS from 10% MPS in H_2O . This suppression is attributed to the excluded volume effect, which arises from time-averaged particle correlations. Therefore, the USAXS data suggests that the structure of the MPS in the DES at particle loadings $\leq 10\%$ is similar to that in water, i.e., the particles are well dispersed. Phenomenologically, these four observations indicate additional scattering features on the order of 100 nm that are adjacent to the MPS particles and extend at least 1 μm from the particle surface.

The high- q scattering ($q \approx 0.1 \text{ \AA}^{-1}$) demonstrates a drastic increase in intensity by a factor of 10 when the MPS is suspended in the DES, in comparison with in H_2O . Such a large increase cannot be due to an increase in the volume fraction of pores, v_{fp} , as both DES and H_2O are not expected to react with silica. Therefore, the increase can only be due to an increase in the pore contrast in DES suspensions compared with MPS in H_2O . In the context of small angle scattering theory, an increase in contrast means that either the electron density of the pores, ρ_{pore} , decreases or the electron density of the SiO_2 around the pores, ρ_{SiO_2} , increases. As there is no reason for ρ_{SiO_2} to increase, the increase in intensity scaling is due to a decrease in ρ_{pore} when the MPS is suspended in the DES. A lower ρ_{pore} (and larger X-ray contrast) is observed in all the DES suspensions compared with the H_2O suspensions, which serves as strong evidence showing that the DES does not penetrate the MPS as effectively as H_2O . The dependence of the high- q scattering intensity on particle loading or AgCl addition in the DES is weak,

indicating the constituent species of the DES have a low affinity for the pores within the MPS.

3.2. SAXS analysis

The goal of the modeling is to obtain the real-space scattering length density, $\rho_{DES}(r)$, within and near the surface of the MPS in the DES suspensions. Successful modeling requires MPS size distribution and pore morphology be known. These properties of the MPS are obtained from the MPS- H_2O suspensions and used in the MPS-DES modeling. The size distribution is assumed to be Gaussian and described by the mean radius, $\bar{R}$, and normalized standard deviation, σ_R , while the system of pores is described by a single-level unified equation [57] that describes a phase with one radius of gyration and rough surface [58,59]. With this equation, the pore scattering is described by four parameters: radius of gyration (R_g), volume fraction of pores per particle (v_{fp}), surface fractal dimension (d_s) and scattering length density within the pores (ρ_{pore}). With this formulation, the mean size of the pores (via R_g) and their degree of surface fine-structure, d_s , can be accounted for in the model fitting. The pore size distribution could be estimated from the modeling [60], but is not necessary because there is no evidence that the pore size changes in any solution; moreover, the width of the size distribution cannot be reliably extracted from the scattering data. The pores that encompass v_{fp} are accessible to the solution, which allows ρ_{pore} to vary. The individual scattering from the particle and pores are summed together and connected via the value of $\rho_{particle}$, which depends on the three parameters: v_{fp} , ρ_{pore} and the scattering length density of the SiO_2 around the pores, ρ_{SiO_2} . In this way, the relative scale between the low- q Guinier knee and high- q feature is directly related to the composition of the MPS.

3.3. Model calibration: MPS in H_2O

In the H_2O suspension, we assume that the pores are homogeneously filled with H_2O , and that the pore-filling H_2O has the same density as the bulk. The assumption that the pores are homogeneously filled is based on the Porod scattering that persists between the Guinier knee associated with the MPS size and the pore scattering. If there were any significant heterogeneity within the particle, an additional scattering feature would be observed in this region. Scattering length density of H_2O within the pore is coupled with the pore volume fraction, v_{fp} . Hence, the bulk scattering length density of H_2O is assumed as its initial value. Therefore, the scattering length density of the MPS is calculated by:

$$\rho_{particle} = v_{fp}\rho_{H_2O} + [1 - v_{fp}]\rho_{SiO_2} \quad (3)$$

The scattering intensity from a single particle in H_2O , I_{H_2O} , is calculated by the following equations:

$$I_{H_2O}(q, R) = [\rho_{particle} - \rho_{Bulk}]^2 F^2(q, R) V(R) + I_{pore}(q) \quad (4)$$

$$I_{pore}(q) = S_{static}(q) \left[G_{pore} e^{-\frac{q^2 R_g^2}{3}} + B_{pore} \left(\frac{\left(\text{erf} \left(\frac{q R_g}{\sqrt{6}} \right) \right)^3}{q} \right)^{d_s} \right] \quad (5)$$

$$G_{pore} = v_{fp} [\rho_{pore} - \rho_{SiO_2}]^2 V(R_g \sqrt{5/3}) \quad (6)$$

$$B_{pore} = \frac{G_{pore} e^{-d_s/2} [3/2 d_s]^{d_s/2}}{R_g^{d_s}} \quad (7)$$

where R is the radius, $F(q, R)$ is the form-factor for a sphere [51], $V(R)$ is the volume of a sphere and $S_{static}(q)$ is the structure factor of the pores within the particle, which assumes the inter-pore distances are static and can be represented by a distribution that has a mean distance, d_{mean} and standard deviation, σ_d [61]. The ρ_{Bulk} term in Eq. (4) is equal to pure water, ρ_{H_2O} , for dilute MPS concentrations used in this study; for higher MPS concentrations, one would have to include the contribution of the particles to the average bulk scattering length density. For the H_2O suspensions, the value of ρ_{pore} was set equal to ρ_{H_2O} at $9.42 \times 10^{10} \text{ cm}^{-2}$, as an approximation. Finally, the small angle scattering from each particle loading ($v_{particles}$) is modeled by assuming a Gaussian distribution of spheres, $P(R)$, by the equation:

$$I(q) = [v_{particles}] S(q) \sum I_{H_2O}(q, R) P(R, \bar{R}, \sigma_R) \Delta R \quad (8)$$

$$S(q) = \frac{1}{1 + pF(q, 2\bar{R})} \quad (9)$$

where $P(R, \bar{R}, \sigma_R)$ is the volume distribution that is described by the mean radius, $\bar{R}$, and standard deviation, σ_R ; and p is the packing factor that is related to the local volume fraction of particles [62]. Eq. (8) was fit to the MPS suspensions in H_2O that contained 1% and 5% MPS in volume without the structure factor $S(q)$. The sample that contained 10% volume fraction of SiO_2 required the fluid structure factor, $S(q)$, for the model to scale correctly. From these model fits, the particle specific parameters $\bar{R}$, ρ_{SiO_2} , σ_R , d_{mean} , σ_d , v_{fp} , d_s and R_g were obtained, averaged, and used as constants to model the USAXS data from the DES suspensions. These parameters are summarized in Table 1. The model fit and raw data are shown in Fig. 2.

From the model fitting of each particle loading, we found minor variation in $\bar{R}$, ρ_{SiO_2} and v_{fp} that is outside of the error obtained from the Jacobian matrix of χ^2 . This occurs because each USAXS measurement has its own measurement uncertainty dictated by the instrument [63]. The variation in $\bar{R}$ is less than 1% and within the standard deviation of the distribution, σ_R . For amorphous SiO_2 , a theoretical maximum value of $18.6 \times 10^{10} \text{ cm}^{-2}$ is expected for ρ_{SiO_2} , assuming vitreous SiO_2 with a mass density of 2.196 g cm^{-3} [64]. A lower mean value of $15.0 \times 10^{10} \text{ cm}^{-2}$ was found from the modeling, which is expected since the scattering length density around the pores, ρ_{SiO_2} , will decrease if the pores are connected. The volume fractions of these pores, v_{fp} , decrease slightly with particle loading. Because volume fraction and the scattering length density of the pore are coupled, this result indicates that pore- H_2O density may increase slightly with the higher particle loading. However, we reserve making this assertion since the trend is on the same order as the uncertainty. More particle loadings would be required to reach this conclusion. With these deviations in mind, the average value of $\bar{R}$, ρ_{SiO_2} and v_{fp} were used for the analysis of the scattering profiles of MPS in DES.

3.4. Model deployment: MPS in DES

Following the analysis of the MPS in H_2O suspensions, we acquired the average particle and pore morphology parameters, as shown in Table 1. These parameters were subsequently used as input to subsequent heuristic analyses of USAXS data of MPS in DES to extract structure information concerning DES in and around the MPS particles. The radial scattering length density, from the center of the MPS particle, is described by $\rho_{DES}(r)$. Similar

to Eq. (3), the scattering length density of the particle, $\rho_{particle}$, is calculated by:

$$\rho_{particle}(r) = v_{fp} \rho_{DES}(r) + [1 - v_{fp}] \rho_{SiO_2} \quad (10)$$

where the value of ρ_{SiO_2} is taken from Table 1 and $\rho_{particle}(r)$ terminates at $r = R$; to deal with the transition at the particle surface, $\rho_{particle}(r > R)$, is set to $\rho_{DES}(r)$. Beyond the particle surface ($r > R$), the scattering length density is contained in the function $\rho_{DES}(r)$ up to a maximum radial distance, which is defined by the parameter, f_{shell} . At $r = f_{shell}R$, the scattering length density is taken to be that of the bulk DES ρ_{Bulk} at $10 \times 10^{10} \text{ cm}^{-2}$. To a first-order approximation, $f_{shell} \geq \pi/[q_{min}R] \approx 13$, where q_{min} is $10^{-4} \text{ \AA}^{-1}$. For our analysis, we found a f_{shell} value of 13 was adequate to fit the data. A larger value of f_{shell} can be used, which leads to more data points in $\rho_{DES}(r)$, and consequently longer computation time.

The scattering intensity for a single particle in the DES, $I_{DES}(q, R)$, is calculated from $\rho_{DES}(r)$ by combining the scattering intensity from the particles, layers and pores in a way that resembles Eq. (4). To calculate $I_{DES}(q, R)$, both the internal and external contrast of the particle are modeled together as a system of concentric shells, $I_{cs}(q)$, with thickness, dr . The scattering from the pores, $I_{pore}(q)$, is modeled using a single unified equation [57]. The combined intensity is given by the equations:

$$I_{DES}(q, R, \rho_{DES}(r)) = I_{cs}(q, R, \rho_{DES}(r)) + \sum_{r=0}^{r=R} I_{poreN}(q, R, r) \quad (11)$$

$$I_{cs}(q, R, \rho_{DES}(r)) = \frac{[A_R(q, Rf_{shell}) + [\sum_{r=0}^{r=R} A_p(q, r)] + [\sum_{r=R}^{r=Rf_{shell}} A_{ml}(q, r)]]^2}{V(R)} \quad (12)$$

$$A_p(q, r) = [\rho_{particle}(r) - \rho_{particle}(r + dr)] V(r) F_{sphere}(q, r) \quad (13)$$

$$A_{ml}(q, r) = [\rho_{DES}(r) - \rho_{DES}(r + dr)] V(r) F_{sphere}(q, r) \quad (14)$$

$$A_R(q, r) = [\rho_{DES}(r) - \rho_{Bulk}] V(r) F_{sphere}(q, r) \quad (15)$$

$$I_{poreN}(q, R, r) = S_{static}(q) \left[G_{poreN}(R) e^{-\frac{q^2 R_g^2}{3}} + B_{poreN} \left(\frac{\left(\text{erf} \left(\frac{q R_g}{\sqrt{6}} \right) \right)^3}{q} \right)^{d_s} \right] \quad (16)$$

$$G_{poreN}(R, r) = \frac{V(dr)}{V(R)} v_{fp} [\rho_{DES}(r) - \rho_{SiO_2}]^2 V(R_g \sqrt{5/3}) \quad (17)$$

where the numerator in Eq. (12) is the same as that in Eq. (2), with partitioned limits of integration. Instead of having linearly spaced r , i.e., dr with constant value, we introduced randomness to dr to avoid aliasing-type numerical artifacts. Randomized dr also allows us to reduce the number of points in function $\rho_{DES}(r)$, thus reducing the overall computation time. Accounting for the size distribution of particles, the scattering intensity from the entire system, $I(q, \rho_{DES}(r))$, is given by the equation:

$$I(q, \rho_{DES}(r)) = v_{particles} S(q) \sum I_{DES} \left(q, R, \rho_{DES} \left(\frac{Rr}{\bar{R}} \right) \right) P(R) \Delta R \quad (18)$$

Table 1

Physical parameter of MPS obtained via least-squares fitting of the scattering profiles of MPS in H₂O suspensions. The mathematical formulations are described by Eqs. (3)–(9). The uncertainties were acquired from the Jacobian matrix during the least-squares fitting. Modeling of the weakest signal data ($v_p = 1\%$) required that some parameters be held constant, these parameters are denoted with a “*” symbol.

Volume Fraction of MPS	$\bar{R}$ (nm)	σ_R	d_{mean} (nm)	σ_d	v_p %	ds	ρ_{SiO_2} (10^{10} cm^{-2})	R_g (nm)
1%	242.7 ± 0.4	0.08 ± 0.01	5*	0.45^*	13.0 ± 2.0	3.38 ± 0.67	15.02 ± 0.14	2.0 ± 0.2
5%	241.2 ± 0.4	0.09 ± 0.01	5.1 ± 0.7	0.45 ± 0.05	12.1 ± 0.5	3.31 ± 0.20	15.18 ± 0.03	2.1 ± 0.1
10%	242.3 ± 0.4	0.09 ± 0.01	5.3 ± 0.6	0.45 ± 0.03	11.0 ± 0.3	3.35 ± 0.14	14.96 ± 0.02	2.0 ± 0.1
Mean	242.1	0.09	5.2	0.45	12.0	3.35	15.0	2.0

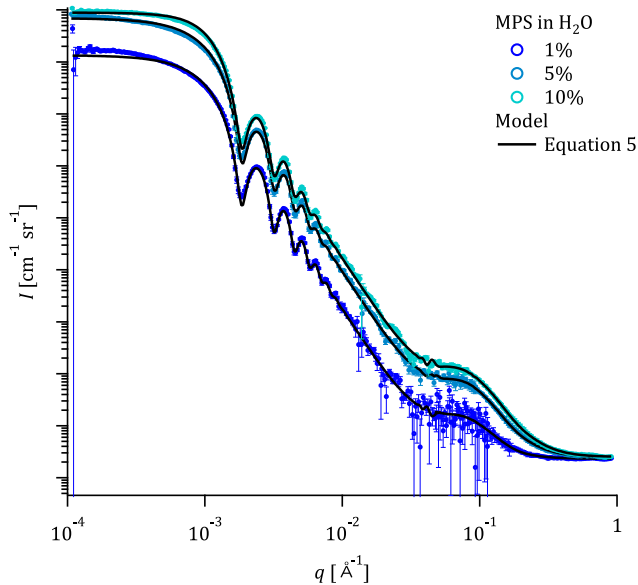


Fig. 2. log-log plot showing the data (circles) and model fits (black lines) of SiO₂ in H₂O suspensions at 1%, 5%, and 10% volume fractions, respectively. The least-squares fitting was performed following a composite scattering function outlined by Eqs. (3)–(9). The fitting parameters are summarized in Table 1.

where again $S(q)$ is one for all particle loadings except 10% and the average values for the particle and pore parameters (Table 1) are used so that the only unknown is the function, $\rho_{\text{DES}}(r)$. The same size polydispersity is assumed in $\rho_{\text{DES}}(r)$ as is present in the particles by multiplying the function, r , by the factor: $R/\bar{R}$. The purpose of this operation is to account for any thermal fluctuations in $\rho_{\text{DES}}(r)$, as these DES components are fluid, instead of solid.

As indicated by Eqs. (11)–(18), the fluctuations within $\rho_{\text{DES}}(r)$ determine the intensity profile in the entire q -range of the scattering model. On the one hand, the scattering intensity at $q < 10^{-3} \text{ Å}^{-1}$ only depends on $\rho_{\text{DES}}(r > \bar{R})$. On the other hand, the extent and dimensionality of fluctuations within and around the particles affect the appearance of $I(q)$ when $q > 10^{-3} \text{ Å}^{-1}$. Traditional SAS analysis methods, such as least-squares fitting using a predetermined scattering form factor, as discussed earlier, require exploration of a large parameter space, which is not only time-consuming but also subject to limitations imposed by local minima. Heuristic methods such as simulated annealing can, to some extent, address this challenge by providing different candidate functions to the function $\rho_{\text{DES}}(r)$. For the simulations reported in this work, we used 1100 points in $\rho_{\text{DES}}(r)$. With this many points, one single calculation for the intensity represented by Eq. (18) took ≈ 5 s, using an Intel Xeon EP 2.1 GHz processor with 128 GB of ram. For every dataset, we performed 8 sets of simulated annealing analysis, and acquired 8 candidate functions. For clarity, we will discuss the general trend observed from the 8 candidate functions and show the $\rho_{\text{DES}}(r)$ with the lowest energy (optimal solution among 8). All 8 functions can be found in the [supplementary information](#) Section S.1.

3.5. Simulated annealing

The simulated annealing procedure randomly perturbs the function, $\rho_{\text{DES}}(r)$, and evaluates the change in χ^2 . Each move is evaluated and accepted depending on the temperature and the change in χ^2 compared with the previous value; the temperature is a non-physical parameter and is therefore unitless. This routine is summarized by the following steps:

- (1) Establish the total number of steps, N , a maximum temperature, T_{max} , and a minimum temperature, T_{min} .
- (2) Calculate the initial χ^2 of the system.
- (3) Perturb the function $\rho_{\text{DES}}(r)$ with a randomly chosen Gaussian function that has a mode between 0 and R_{fshell} , a peak value between 0 and 0.1 and a standard deviation, σ_{anneal} between 1 and 30 points.
- (4) Calculate the new χ^2 and temperature, T , of the system by the equation:

$$T = T_{\text{max}} e^{-\frac{1}{N} \log T_{\text{max}} / T_{\text{min}}} \quad (19)$$

- (5) The new state obtained in step 4 is accepted if it meets one of the following conditions:

$$[\chi^2_i - \chi^2_{i-1}] < 0 \quad (20)$$

$$e^{-\frac{[\chi^2_i - \chi^2_{i-1}]}{T}} > U([0, 1]) \quad (21)$$

where $U([0, 1])$ denotes a random floating-point number between 0 and 1.

- (6) Steps 3 – 5 are repeated for N steps.

The optimal T_{max} was determined to be 500 for these data. The number of steps, N , was varied between 20,000 and 30,000. Complete discussions of T_{max} , σ_{anneal} and N are found in the supplementary Sections, S.2.a, S.2.b and S.2.c, respectively. A value of one was used for T_{min} . The lowest energy model fits to the USAXS data are shown in Fig. 3 and the resulting functions, $\rho_{\text{DES}}(r)$, are shown in Fig. 4.

As part of the effort, we also explored the influence of pore heterogeneity on the perturbations to ρ_{DES} around the particles. This was accomplished by evaluating different number of points in the function, $\rho_{\text{DES}}(r < \bar{R})$. In this attempt, we used 10 or 50 points in $\rho_{\text{DES}}(r < \bar{R})$ to simulate a homogenous and heterogeneous pore filling within the MPS, respectively. Typically, when we assume pore homogeneity, slightly lower values of χ^2 were obtained and more fluctuating features in the function $\rho_{\text{DES}}(r > \bar{R})$ were observed. Despite the slight improvement of fitting quality, we cannot validate this assumption (pore homogeneity). For the discussion below, we only present results from the simulations that allowed

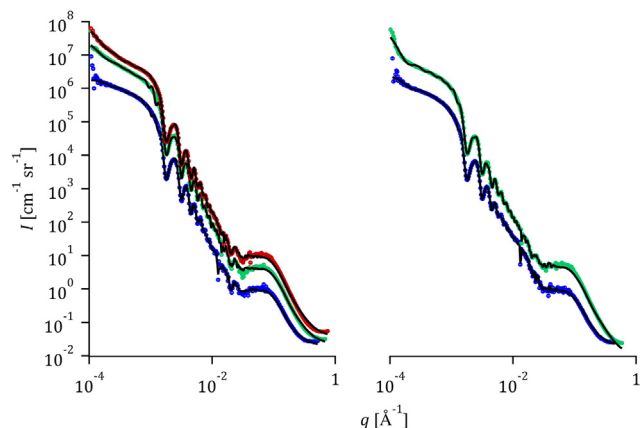


Fig. 3. Log-log plots of the 1% (blue) and 5% (green) MPS suspensions in the DES (Fig. 3a) and DES+AgCl (Fig. 3b). The model fit that was obtained from the simulated annealing is shown as black lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

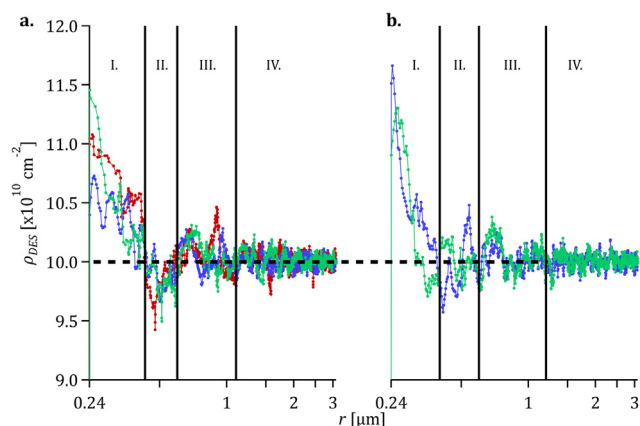


Fig. 4. Scattering length distribution $\rho_{DES}(r)$ obtained from the simulated annealing procedure for 1% (blue), 5% (green) and 10% (red) MPS in the DES (Fig. 4a) and 1% (blue), 5% (green) MPS in DES+AgCl (Fig. 4b). The r -axis is shown on a log-base 2 scale. $\rho_{DES}(r)$ is partitioned into four regions. Region I shows the oscillations near the surface. Region II is ≈ 200 nm wide in both solvents and is closer to the surface by ≈ 30 nm in the AgCl+DES suspensions. Region III spans ≈ 1 μm and contains two, broad, electron-rich oscillations. Region IV contains narrow spikes that gradually decay towards the bulk value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for pore heterogeneity and describe the trends in $\rho_{DES}(r > \bar{R})$ that were observed in both cases (homogeneous pore and heterogeneous pore). A comparison of the two cases can be found in the supplemental information Section S.3.

The model fits of the USAXS data (Fig. 3) capture the general shape of the $I(q)$ curve with some notable deviations. The slight oscillatory nature of $I(q)$ at low- q is unavoidable but can be smoothed by assuming a broader size distribution of scattering layers. In Eq. (12), the layers are assumed to have the same size-distribution as the particles for simplicity. However, the layers are fluid and are expected to contain some thermal fluctuations that change the layer dimensions during the measurement. Nevertheless, the simulated annealing is able to capture the intensity decay that is associated with the fluctuations in $\rho_{DES}(r > \bar{R})$.

3.6. Multi-layer perturbations

All of the $\rho_{DES}(r)$ functions shown in Fig. 4 oscillate about the bulk value of the DES, ρ_{bulk} , with some similarities. Oscillations

are greatest near the surface and decay in magnitude as the distance from the surface normal, r - R , increases. This behavior is consistent with an earlier report, where multilayer perturbations of DES was observed near the surface of small (≈ 5 nm) silver nanoparticles [30].

To aid the understanding of the multilayer perturbations near the surface of MPS, we partitioned the $\rho_{DES}(r)$ functions into four regions, as shown in Fig. 4. These general features are described as either electron-rich ($\rho_{DES}(r) > \rho_{bulk}$) or electron-poor ($\rho_{DES}(r) < \rho_{bulk}$) regions that persist for some radial distance, r . Fig. 4(a) shows the scattering length density distribution $\rho_{DES}(r)$ without AgCl, and Fig. 4(b) with AgCl. Overall, the electron-rich features deviate more from ρ_{bulk} than then electron-poor features, which was observed previously [30]. We observed a weak dependence of the extent and dimensionality of the multilayer perturbation on MPS loading. With the MPS loadings at 1%, 5% and 10% volume, the average interparticle distance is $4.6 \times$, $2.7 \times$, and $2.2 \times$ particle diameter, respectively. Fig. 4 suggests that the main modulation to $\rho_{DES}(r)$ caused by a MPS occurs near the particle surface, similar to what normally occurs in Stern layers in aqueous solutions. The interference between the multilayer perturbations caused by two neighboring MPS particles is not significant within the MPS volume fraction range of 1% and 5%. There is some evidence of particle contributions to $\rho_{DES}(R)$ in the 10% loading, as a strong peak is observed around 1 μm . However, positive perturbations on this length-scale are also observed in the lower particle loadings but with a lower magnitude.

When AgCl was present in the DES, Fig. 4 shows that the electron-rich regions in $\rho_{DES}(r)$ demonstrates more deviation from ρ_{bulk} than the electron-poor regions, similar to a previous observation [30]. This behavior is expected to the high electron density of AgCl, even though its concentration is low in DES.

The features within the first two regions shown in Fig. 4 provide insight into how the addition of AgCl changes the perturbations that determine the low- q X-ray scattering. Near the surface in region I, the function $\rho_{DES}(r)$ is always greatest near the MPS surface and decays towards ρ_{bulk} . In all simulations, this decay extends ≈ 30 nm further without AgCl, indicating that the presence of ions reduces the extent of electron density oscillations within the DES. In region II, $\rho_{DES}(r)$ contains more electron-rich regions with AgCl; in most simulations, two clear peaks are also observed with AgCl. Therefore, the addition of AgCl increases the electron density of region II where $\rho_{DES}(r)$ is otherwise electron-poor. On the other hand, the presence of AgCl decreases the distance from the surface (region I) where $\rho_{DES}(r)$ is electron-rich. Oscillations on the order of 100 nm within the first two regions are also more obvious with AgCl, which is reflected as a Guinier knee observed in the USAXS data at $q \approx 10^{-2} \text{ \AA}^{-1}$ (Fig. 1). While broad features are also observed in region III, there is no systematic difference with and without AgCl. Similarly, in region IV magnitude of the perturbations ($\approx 0.2 \times 10^{10} \text{ cm}^{-2}$) is the same. Based on the simulated annealing results, the dissolved AgCl increases $\rho_{DES}(r)$ in region II and acts as a parasitic species in region I.

One important conclusion from this analysis is that the DES composition can be perturbed far from a charged surface ($\approx 1 \mu\text{m}$). This potentially opens a pathway for solvent-directed assembly. However, the molecular interactions that determine these fluctuations are difficult to infer from Fig. 4 alone. One approach would be to compare the spatial composition of the DES components with a transport model. For USAXS/SAXS experiments, $\rho_{DES}(r)$ is a function of the spatial composition of the constituent species. As all the constituent species (except AgCl) have similar electron densities, it is not possible to obtain each constituent profile with X-rays. Neutron scattering is better suited for this purpose, and has been used to probe ionic liquid interactions [65–67]. Here, a high- Z salt with known speciation in the DES (AgCl) [68] was used as a “contrast-

marker” that increases $\rho_{DES}(r)$ in region II. If this accumulation were due to electrostatic forces then a high concentration of choline would be expected in region II. While electron-poor regions in $\rho_{DES}(r)$ were associated with choline abundance in prior work [30,31], it is difficult to make that conclusion here because the surface capacitance of the MPS was not measured. As the scattering length density in region I is not enhanced with the addition of AgCl, it is likely that this region is rich in Cl⁻ ions, which hydrogen bond strongly with electro-neutral ethylene glycol [34]. However, more experiments would be required to resolve the spatial composition of the DES constituents.

With the perturbation to $\rho_{DES}(r)$ extending far from the MPS surface, it becomes evident that care needs to be taken for future scattering measurements to ensure an adequate q (size) range is covered. We again emphasize that the low- q portion of the scattering data is not a strict power-law decay, which allows us to resolve the extended fluctuations in $\rho_{DES}(r)$. While it may be tempting to attribute the low- q scattering to aggregates [56], it was not observed experimentally. Our results demonstrate the importance of measuring into the USAXS region, as truncated data could easily be misinterpreted and the perturbation caused by MPS would have been lost.

3.7. Pore penetration

Based on the increase in the X-ray contrast of the porous scattering from the MPS-DES suspensions (Fig. 1), we concluded that the DES is not able to penetrate the MPS to the same degree as the H₂O. In other words, we observed a low concentration of the DES components within the ≈ 5 nm pores that were fully accessible to water molecules. While pore-filling behavior of DES in MPS is not the primary focus of this study, we show that USAXS can be used to measure the degree to which solution species can penetrate a mesoporous (nanoporous) colloid. Ultimately, the electron density within the pore, as measured by USAXS, depends on the species, concentration, and pore size. In the field of nano-pore infiltration, these are important parameters that could be extracted from small angle scattering with the right system and experimental data. Such a precise quantification is not possible here because v_p was extracted from the MPS-H₂O suspensions with the approximation that the scattering length density of the pore is equal to that of bulk water. As it is well known that fluids behave differently in nanopores [48], a better quantification of v_p might be achieved by calibrating the USAXS model from a dry MPS powder. Determining the spatial distribution of the DES species within the MPS cannot be accomplished with X-rays and is a task better suited for neutron scattering. Nevertheless, the approach taken in this study is sufficient to conclude that the DES does not penetrate the MPS as much as H₂O.

As there is a wide range of colloids with different porous structures [69], it is worth discussing briefly how Eq. (11) would change with the porous structure within the particle. For cases where no observable pores exist in the colloids, the second term in Eq. (11) that accounts for the porous structure would be ignored. Only where the pore structure is spherically symmetric, can Eq. (11) be modified to accommodate different pore morphologies by replacing Eq. (16) with the scattered intensity from the specific pore shape. In such cases where the pores are dilute, Eq. (16) could be replaced by the appropriate form factor, such cylindrical or worm-like shapes [51]. When the pore fraction is high and their shape is not well-defined, the internal particle morphology must be treated as a two-phase system whereby the pores and solid material between them both scatter [70]. Whether the pores are dilute or not, their scattering contribution can be accounted for in the simulated annealing using Eq. (11), with the caveat that their structure is not anisotropic [71].

4. Conclusions

With this work, we have demonstrated the unique interactions between MPS and a deep eutectic solvent far exceeds what has been observed in literature for DESs [30,31] and other RTILs [5,72]. Due to electrostatic interaction between MPS and DES, the DES electron density of the solution was measurably perturbed, which induced fluctuations that extended ≈ 1 μ m from the surface and changed with the addition of AgCl. The scattering from these long-range fluctuations is smooth and decays across a decade in q . Therefore, the electron density fluctuations are hierarchical in nature and cannot be associated with mass-fractal agglomerate scattering. While much work has focused on the individual, molecular interactions in DESs [34,73,74], this work demonstrates how these small-scale interactions, that comprise the bulk structure [15], can lead to fluctuations on the nanometer to micrometer scales in the presence of a charged colloid. Altogether, these long-range solvent fluctuations suggest that the colloidal interface in DESs can be far more complex and extends far into the solution.

The general approach to measuring and manipulating the solvent perturbations can be applied to a wide variety of different colloidal and DES systems and change the way we look at the colloidal interface. The pore contrast variations and solution perturbations were modeled from the USAXS data by using a simulated annealing approach. This approach required the MPS morphology and size distribution as input, which was obtained by least-squares fitting of the MPS suspensions in H₂O. Several simulated annealing procedures were performed on the data to extract possible candidate functions. Only features common to all candidate functions were considered. These features were partitioned into four regions with comparable behavior with and without AgCl. The effect of dissolved AgCl is to compress the dimensions of the first electron-rich region, and enhance the electron density of the second, otherwise electron-poor, region. These results demonstrate how the spatial concentration of DES species can be manipulated over relatively large length scales.

We have also shown that the constituent species of the DES do not penetrate the MPS as H₂O does. This observation suggests that the pores within the MPS can remain active in the DES and could be filled with a guest species. One example might be the CO₂ capture, which has been demonstrated for both functionalized MPS [75] and a DES [76]. The long-range solvent perturbations reported here might also play a role in reversible particle assembly [41]. While much work is needed to demonstrate such long-range assembly and tunability of the solvent structure, the general approach to resolving the DES perturbations presented here provides a means characterize a wide variety of DES solvents and nanoporous colloidal systems, *in-situ*.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcis.2018.02.078>.

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