Surprising Particle Stability and Rapid Sedimentation Rates in an Ionic Liquid — Source link 🗗

Jacob Smith, Oliver Werzer, Grant B. Webber, Gregory G. Warr ...+1 more authors

Institutions: University of Sydney, University of Newcastle

Related papers:

- At the interface: solvation and designing ionic liquids

- Structure in Confined Room-Temperature Ionic Liquids

- Double-layer and solvation forces measured in a molten salt and its mixtures with water

- Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis

- Amphiphilicity determines nanostructure in protic ionic liquids.

NOVA

University of Newcastle Research Online

nova.newcastle.edu.au

Surprising Particle Stability and Rapid Sedimentation Rates in an Ionic Liquid

Jacob A. Smith,[1] Oliver Werzer,[1] Grant B. Webber,[2] Gregory G. Warr[3] and Rob Atkin.[1]

[1] Centre for Organic Electronics and [2] Centre for Advanced Particle Processing, The University of Newcastle, Callaghan, NSW 2308, Australia

[3] School of Chemistry, The University of Sydney, NSW, 2006, Australia

In this letter we demonstrate that particle suspensions in room temperature ionic liquids differ from aqueous suspensions in some surprising and remarkable ways. Two results are of key importance. Firstly, suspensions of 1 μm diameter silica spheres do not aggregate in pure ethylammonium nitrate (EAN) despite interparticle electrostatic repulsions being completely screened by its 11M ionic strength. However these dispersions become unstable in the presence of small amounts of water. Using silica colloid probe atomic force microscopy (AFM), optical microscopy and dynamic light scattering we show that this unusual stability is imparted by repulsions between well formed solvation layers, which decreases in number and strength upon addition of water. Secondly, particle suspensions in pure EAN settle six times more rapidly than predicted by the hindered Stokes equation. This remarkable result is unprecedented in the literature to our knowledge, and could foreshadow interesting lubrication effects for surfaces in EAN.
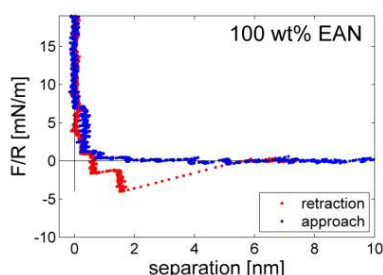
Keywords: ionic liquids, particle, stability, settling, suspension, aggregation.

Ionic liquids (ILs) consist entirely of ions and have melting points below 100°C. The first reported room temperature IL was ethylammonium nitrate (EAN) in 1914,[1] a protic IL synthesized by transfer of a proton from nitric acid to ethylamine. ILs are known as "designer solvents" because physical properties can be

coarsely controlled via the choice of cation and anion species, with fine control facilitated by subtle variation in molecular achitecture.[2]

Our group has made considerable progress elucidating the bulk and interfacial nanostructure of protic ionic liquids over the last few years. Small angle neutron scattering experiments and data fitting have shown that EAN has a sponge like structure in the bulk liquid,[3] on account of electrostatic interactions between the ammonium cation and nitrate anion favouring the creation of ionic domains. Hydrogen bonds intensify the attraction between ionic groups. Alkyl groups are solvophobically[4] repelled from the ionic regions, and cluster together forming apolar domains. Atomic force microscopy (AFM) has been used to determine how this structure changes at the solid liquid interface. There are five main factors that control the level of interfacial IL order: whether the bulk liquid is structured,[3,5] and if so how strongly;[6] the strength of interaction between the surface and the cation, which can be electrostatic[7,8] or solvophobic;[7] the molecular flexibility of the ions;[6,8,9] the surface roughness;[7] and the temperature.[8] In general terms, the bulk IL sponge morphology is transformed to a lamellar structure at the surface, reminiscent of surface-induced sponge to lamellar transitions that occur in lyotropic systems.[10]

For aqueous systems in the absence of stabilizers (surfactants and polymers), colloid stability is determined by the balance between attractive van der Waals and repulsive electrostatic interactions, which are mediated by the electrolyte concentration. The high ionic strength of ILs (e.g. 11 M salt for EAN) effectively swamps electrostatic repulsions between charged particles (effective Debye length ~1Å at 25°C),[11] negating this mechanism of particle stabilization. Ueno et al[11] studied colloidal dispersions of silica nanoparticles in aprotic ILs, concluding from both theory and experiment that electrostatic charge stabilization was likely to be ineffective due to the ILs' high ionic strength and the resulting surface-charge screening; surface grafted polymers served to stabilize particle suspensions, provided the polymer was IL soluble. Surprisingly, several articles have reported that colloidal suspensions displaying long term stability can be obtained in aprotic ILs even in the absence of stabilizers.[12-15] However, the mechanisms that lead to particle stability or instability in ILs remain unclear, although a second article by Ueno et $al.$ have begun to address this issue.[16] To our knowledge, no study has previously examined colloidal stability in protic ILs.

The stability of particle suspensions to aggregation in pure water, pure EAN, and the various water – EAN mixtures was assessed using DLS (Table 1) and optical microscopy (Figure 1). The particle diameter quoted by the manufacture was 1 μm, so measured z-average particle diameters of greater than 2 μm is taken to be evidence of aggregation. The actual size of the aggregates is not important for this work; DLS is used to assess whether aggregation occurs or not. In pure water the silica dispersions are stable, yielding a narrow, mono-modal particle size distribution with a z-average diameter equal to 1163 nm. The measured particle size is slightly greater than that quoted by the manufacturer due to the fact that DLS measures an effective hydrodynamic size rather than a physical particle size.

For all EAN concentrations between 0.5 wt% and 95 wt% the z-average particle sizes measured a few minutes after dispersion were greater than 2000 nm indicating rapid aggregation. When the same samples were re-examined over several hours the measured sizes increased, and in some instances was greater than the 6 μm limit of the instrument. The data presented in Table 1 was obtained 2 hours after dispersion. Remarkably, suspensions of silica particles in pure EAN are stable to aggregation over long time periods (at least 6 months).

Table 1. Measured particle size 2 hours after dispersion, particle suspensions stability to aggregation, calculated terminal settling velocity ($V_{T(calc)}$), batch settling experimental settling velocity ($V_{T(obs)}$), and the ratio of $V_{T(obs)}$ to $V_{T(calc)}$ for 1 wt % silica suspensions in water – EAN mixtures.

EAN (wt%)	Particle Size (nm)	Stability to Aggregation	$V_{T(calc)}$ x 10^{-7} (m.s^{-1})	$V_{T(obs)}$ x 10^{-7} (m.s^{-1})	$V_{T(obs)} : V_{T(calc)}$
0.00	1163	Stable	6.4	4.4*	0.7
0.5	2767	Unstable	6.4	77	12.0
1	2685	Unstable	6.4	94	14.7
5	2843	Unstable	6.3	70	11.1
10	3216	Unstable	5.7	160	28.1
25	3585	Unstable	5.1	150	29.4
50	5214	Unstable	4.2	42	10.0
75	4012	Unstable	3.5	34	9.7
90	3591	Unstable	2.4	30	12.5
95	3371	Unstable	1.3	23	17.7
100	1278	Stable	0.14	0.86*	6.1

*settling velocities for pure EAN and pure water were also measured using *Turbiscan*^{tm} and found to be 0.78 x 10^{-7} and 6.3 x 10^{-7} m.s^{-1} respectively.

The particle stability and instability classifications in Table 1 were confirmed using optical microscopy (Figure 1). Single particles were present in pure water and pure EAN, while large aggregates were noted for all EAN water mixtures. The image shown for 10 wt% EAN is representative for these aggregated samples. The image shown for the pure EAN system has poorer contrast than the pure water system due to the similarities in the refractive indices of silica and EAN.

In order to explain these differences in stability, AFM experiments using a silica colloid probe tip and a silica substrate were completed in pure water (pH = 5.8), pure EAN, and various water – EAN mixtures (Figure 2). The data obtained in pure water is characterized by an exponentially decreasing repulsive region at separations greater than about 5 nm extending to about 80 nm, which stabilizes the particles aggregation.

At close separations on approach attractive dispersive forces cause the colloid probe and silica surface to jump into contact, while upon retraction the colloid probe is electrostatically repelled from the substrate once the interaction force is reduced to ~10 mN.m^{-1}. This data is in good agreement with published results for similar experiments.[17]
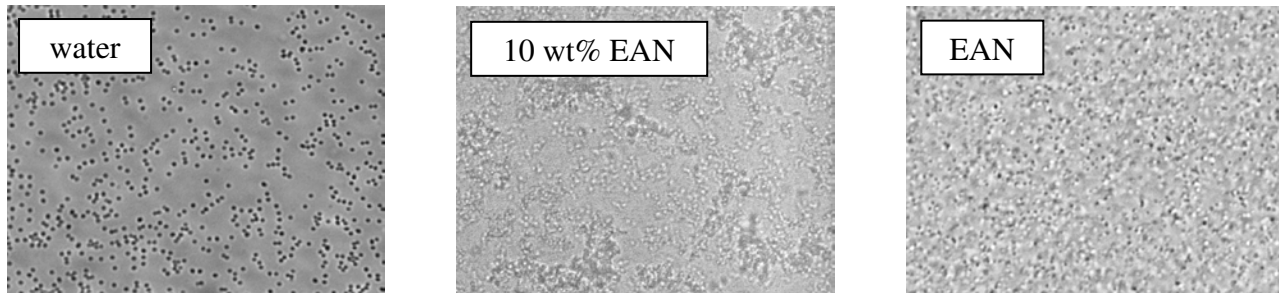

Figure 1. Optical micrographs showing the appearance of a 1 wt% 1 μm silica particle suspension in pure water, a 10 wt% EAN in water solution and in pure EAN.

Figure 2 shows force profiles obtained using a silica colloid probe and a silica surface in pure EAN. The data is broadly consistent with that presented previously for silicon nitride AFM tips on solid surfaces in various protic[7,8,18] and aprotic[9,19] ILs, although the small steps noted on approach at about 4 nm, and the clear steps seen on retraction, were not apparent, suggesting greater sensitivity is obtained with the colloid probe. As the ionic strength of pure EAN is 11.2 M, the electrostatic interactions that dominate in pure water are swamped, allowing small solvation forces to be measured. Three clear steps are seen in the force data on approach, and two on retraction, due to near surface EAN solvation layers. In the absence of electrostatic repulsions, long term particle stability in EAN must be a consequence of these solvation forces. As the colloid probe approaches the substrate it experiences no force until a separation of approximately 4.5 nm, where the AFM tip encounters an EAN solvation layer and the force increases slightly above the baseline level. When the applied force is sufficiently high the solvation layer is ruptured and the probe jumps inward by the diameter of an EAN ion pair,[7] about 0.5 nm, into contact with the next layer. This process is repeated as the probe moves towards the surface, with the force required to rupture each layer increasing closer to the surface as the layers become more ordered. The innermost layer is thinner than those further from the substrate because it consists primarily of ethylammonium cations adsorbed onto the negatively charged silica. From the force profile alone it can not be determined whether this layer is associated with the silica

substrate or colloid probe, or whether a layer of cations is present on one of the surfaces at zero separation, although experiments using forces greater than 100 mN.m^{-1} did not reveal subsequent steps. Steps in the force profile are also noted upon retraction due to layer reformation. These are more pronounced than those measured previously using a standard AFM tip,[7,18] and result from solvophobic attractions between cations adsorbed to the silica surfaces for the first layer, and between cations adsorbed to the colloid probe and cations in reformed layers for subsequent steps.
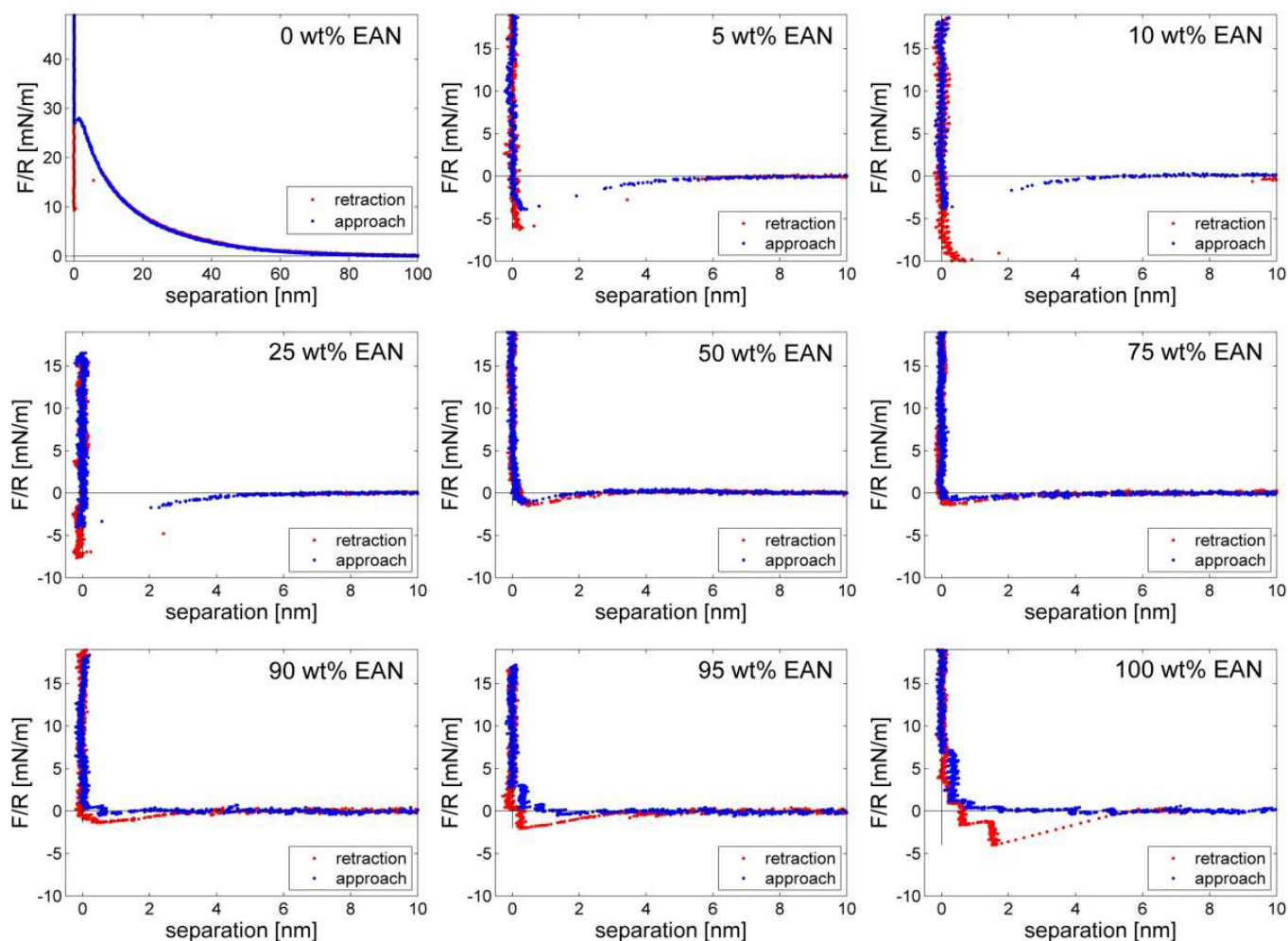

Figure 2. Force versus separation data for the approach and retraction of a 4.8 μm colloid probe AFM tip to a silica substrate immersed in water – EAN solutions at 21 °C. All force curves were recorded with the same colloid probe on the same day. The order of experiments was from pure EAN to pure water.

The force profiles determined for the approach of the colloid probe and a silica substrate for various water – EAN mixtures are also presented in Figure 2. Even at the lowest concentration of EAN investigated, 5 wt%, electrostatic repulsions are completely masked and an attractive dispersion force produces a jump into contact from 5 nm separation. The range of the attractive force decreases as the EAN weight fraction

increases up to 50 wt%, as a consequence of reduction in the Hamaker constant; the Hamaker constant for pure EAN has not been reported but is certainly much smaller than that of water.[20]

When the EAN concentration reaches 75 wt%, near-surface solvent structure becomes apparent in the force profile; a very small step was consistently seen on approach, superimposed on a weak attraction. This small step is consistent with a layer of electrostatically adsorbed cations. When the water is further reduced to 10 wt%, the solvation layer nearest the substrate is now clear, and there is little evidence of any attraction between the two surfaces. Force curves for 95 wt% and pure EAN data are similar in many respects; the important difference is that the force required to rupture the innermost solvent layer is reproducibly twice as high in pure EAN. Thus, the addition of even small amounts of water reduces both the number and resilience of EAN solvation layers; all evidence of solvent structure has disappeared once the water content is 50 wt%. This finding is consistent with previously published surface forces apparatus data for two mica surfaces in pure EAN and water – EAN mixtures.[20]

The force profiles presented in Figure 2 reveals the cause of suspension instability in EAN water mixtures. From 5 wt% to 75 wt% EAN the forces on approach are purely attractive, hence there is no barrier to particle – particle contact and rapid aggregation results. While the small solvation forces measured for 90 and 95 wt% EAN will hinder aggregation, they are clearly not sufficiently strong to prevent it on long time scales; the energy associated with thermal motion of particles is sufficient to overcome the weak solvation forces in these systems.

Bench-top batch settling experiments were used to determine the particle terminal settling velocity $V_{T(obs)}$, presented in Table 1. For comparison, the terminal settling velocity $V_{T(calc)}$, was calculated for each system using the hindered settling equation of Khan and Richardson.[21] These data are also included in Table 1. In pure water $V_{T(obs)}$ is approximately 30% less than $V_{T(calc)}$, however the terminal settling velocity for this system determined using Turbiscan[TM] is almost identical to $V_{T(calc)}$. This indicates the level of the error in the batch settling experiments, but also demonstrates the applicability of hindered settling equation of Khan and Richardson to systems of well-dispersed particles. For the unstable systems it is clear that the terminal settling velocity measured in the batch settling experiments is significantly greater than the calculated value.

This is to be expected since $V_{T(calc)}$ uses the single particle size, whereas for the unstable systems the size of the aggregates is much larger.

A quite unexpected and remarkable result is noted for particles suspended in pure EAN. The terminal settling velocity measured using both batch settling experiments and Turbiscan^{TM} is approximately six times greater than the calculated value. These experiments have been repeated a number of times, and the results are statistically significant. This faster than expected terminal settling velocity is not the result of particle aggregation as both the optical micrographs and DLS data confirm that the silica particles remain singly dispersed in pure EAN over a long periods of time.

We have considered a number of possible causes for this unusual behaviour. Multiple body interactions, such as slipstreams, are not significant at this relatively small particle concentration; indeed, recall that for pure water the terminal settling velocity measured using Turbiscan^{TM} is almost identical to $V_{T(calc)}$. EAN as a bulk liquid was confirmed to behave as a Newtonian fluid, so does not exhibit macroscopic shear thinning behavior. We are currently employing AFM friction measurements to investigate whether localized microscale shear thinning between solvent layers could be responsible for faster than expected settling by varying the structure of the IL cation and anion. Stable suspensions have been also been identified in other protic ILs including ethylammonium formate and diethylmethyl-ammonium formate, and the settling velocities appear to vary in a manner consistent with the level of interfacial IL order.

Experimental Section

EAN (M.P. = 12 °C) was prepared by reacting equimolar amounts of ethylamine (Aldrich) and conc. nitric acid (Merck) to produce an aqueous solution, as described by Evans *et al.*[22] Excess water was removed by first purging the EAN solution with nitrogen, then heating at 110–120 °C for several hours under a nitrogen atmosphere. This leads to water contents undetectable by Karl Fischer titration (<0.01 %) and prevents the formation of nitrous oxide impurities that, if present, produce a yellow discoloration. Silica colloidal particles (Fiber Optic Center, New Bedford, USA) were used as received. The particles are of low polydispersity and were confirmed to be 1 μm in diameter by the manufacturer via scanning electron microscopy. All water used was filtered, distilled and passed through a Millipore Gradient filtration unit before use.

A Malvern NanoSeries ZetaSizer Nano-ZS (Malvern Instruments, UK) with a 633 nm He-Ne laser source (4.0 mW power) was used for dynamic light scattering examination of the as-prepared suspensions and the re-dispersed settled particles. Scattering data for each sample were obtained by averaging 50 separate measurements of 20 seconds. Optical micrographs were obtained using a Zeiss Axioskop microscope in bright field mode with a 40x lens. Liquid densities were obtained by accurately weighing a known volume of liquid. An AR-G2 rheometer (TA Instruments, Delaware, USA) was used for rheological characterization of the EAN.

Force curves were obtained using a Digital Instruments Nanoscope IV Multimode atomic force microscope equipped with a Pico-Force controller. The substrates were silicon wafers with thermally grown oxide of 100 nm thickness. The substrate was cleaned by ultrasonication in a 10 wt% sodium hydroxide solution and subsequently in a 0.01 wt% cetyltrimethylammonium bromide solution followed by rinsing with Milli-Q water and ethanol, and dried under a nitrogen stream. Finally the surface was irradiated with ultraviolet light for 30min. The AFM probes were conventional sharpened Si_3N_4 cantilevers (Veeco Instrument, USA) modified by attachment of a 4.8 µm glass colloid (Bangs Lab., Inc, USA) with Asaldite™ epoxy. The probe was cleaned in ethanol and Milli-Q water, dried under a nitrogen stream and finally irradiated with UV-light for 30 min. The spring constant was determined by thermal vibration method[23] to be 4.38 N.m^{-1}. Force curves were taken on the same substrate and with same probe by subsequently injecting 1 ml solution with the different ratios of EAN and H_2O into the liquid cell. The scan sizes for all measurements were 100 nm and velocities of 10 nm.s^{-1} were used for the approach and retraction.

Batch settling experiments were performed to determine the settling velocity of the particles in each of the solvents. The concentration of the silica particles in each of the suspensions was 1% by mass. Freshly prepared suspensions of well-dispersed particles were placed into standard cuvettes, and the settling of the particles was monitored for up to 72 hours by digital photography. The distance moved by the interface between the particle suspension and the clear supernatant was measured as a function of time, and the terminal settling velocity of the particles calculated. The particle terminal settling velocity in pure water and pure EAN was confirmed using a Turbiscan^{TM} MA2000 (Formulaction, France).

Acknowledgements.

References.

(1) Walden, P. "Über die Molekulargröβe und elektrische Leitfähigkeit einiger geschmolzener Salze", *Bull. Acad. Imp. Sci.* **1914**, 1800.
(2) Belieres, J. P.; Angell, C. A. "Protic Ionic Liquids: Preparation, Characterization, and Proton Free Energy Level Representation", *J. Phys. Chem. B* **2007**, *111*, 4926.
(3) Atkin, R.; Warr, G. G. "The Smallest Amphiphiles: Nanostructure in Protic Room-Temperature Ionic Liquids with Short Alkyl Groups", *J. Phys. Chem. B* **2008**, *112*, 4164.
(4) Ray, A. "Solvophobic interactions and micelle formation in structure forming nonaqueous solvents", *Nature* **1971**, *231*, 313.
(5) Triolo, A.; Russina, O.; Bleif, H. J.; DiCola, E. "Nanoscale Segregation in Room Temperature Ionic Liquids", *J. Phys. Chem. B* **2007**, *111*, 4641.
(6) Atkin, R.; Warr, G. G. Bulk and Interfacial Nanostructure in Protic Room Temperature Ionic Liquids. In *Ionic Liquids V: From Knowledge to Application*; Plechkova, N., Seddon, K., Rogers, R., Eds., 2009; pp in press.
(7) Atkin, R.; Warr, G. G. "Structure in Confined Room-Temperature Ionic Liquids ", *J. Phys. Chem. C.* **2007**, *111*, 5162.
(8) Wakeham, D.; Hayes, R.; Warr, G. G.; Atkin, R. "Influence of Temperature and Molecular Structure on Ionic Liquid Solvation Layers", *The Journal of Physical Chemistry B* **2009**, *113*, 5961.
(9) Hayes, R.; El Abedin, S. Z.; Atkin, R. "Pronounced Structure in Confined Aprotic Room-Temperature Ionic Liquids", *The Journal of Physical Chemistry B* **2009**, *113*, 7049.
(10) Hamilton, W. A.; Porcar, L.; Butler, P. D.; Warr, G. G. "Local membrane ordering of sponge phases at a solid--solution interface", *The Journal of Chemical Physics* **2002**, *116*, 8533.
(11) Ueno, K.; Inaba, A.; Kondoh, M.; Watanabe, M. "Colloidal Stability of Bare and Polymer-Grafted Silica nanoparticles in Ionic Liquids", *Langmuir* **2008**, *24*, 5253.
(12) Gelesky, M. A.; Umpierre, A. P.; Machado, G.; Correia, R. R. B.; Magno, W. C.; Morais, J.; Ebeling, G.; Dupont, J. "Laser-Induced Fragmentation of Transition Metal Nanoparticles in Ionic Liquids", *J. Am. Chem. Soc.* **2005**, *127*, 4588.
(13) Torimoto, T.; Okazaki, K.; Kiyama, T.; Hirahara, K.; Tanaka, N.; Kuwabata, S. "Sputter deposition onto ionic liquids: Simple and clean synthesis of highly dispersed ultrafine metal nanoparticles", *Appl. Phys. Lett.* **2006**, *89*, 243117.
(14) Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. "Molecular Ordering of Organic Molten Salts Triggered by Single-Walled Carbon Nanotubes", *Science* **2003**, *300*, 2072.
(15) Wojtko´w, W.; Trzeciak, A. M.; Choukroun, R.; Pellegatta, J. L., *J. Mol. Catal. A: Chem.* **2004**, *224*, 81.
(16) Ueno, K.; Imaizumi, S.; Hata, K.; Watanabe, M. "Colloidal Interaction in Ionic Liquids", *Langmuir* **2009**, *25*, 825.
(17) Hartley, P. G.; Larson, I.; Scales, P. J. "Electrokinetic and Direct Force Measurements between Silica and Mica Surfaces in Dilute Electrolyte Solutions", *Langmuir* **1997**, *13*, 2207.
(18) Atkin, R.; De Fina, L.-M.; Kiederling, U.; Warr, G. G. "Structure and Self Assembly of Pluronic Amphiphiles in Ethylammonium Nitrate and at the Silica Surface", *The Journal of Physical Chemistry B* **2009**, *113*, 12201.
(19) Atkin, R.; Abedin, S. Z. E.; Hayes, R.; Gasparotto, L. H. S.; Borisenko, N.; Endres, F. "AFM and STM Studies on the Surface Interaction of [BMP]TFSA and [EMIm]TFSA Ionic Liquids with Au(111)", *The Journal of Physical Chemistry C* **2009**.
(20) Horn, R. G., Evans, D. F., Ninham, B. W. . "Double-layer and solvation forces measured in a molten salt and its mixtures with water ", *J. Phys. Chem.* **1988**, *92*, 3531.

(21) Kahn, A. R.; Richardson, J. F. "Fluid–particle interactions and flow characteristics of fluidized beds and settling suspensions of spherical particles", *Chemical Engineering Communications* **1989**, *78*, 111.

(22) Evans, D. F.; Chen, S.-H.; Schriver, G. W.; Arnett, E. M. "Thermodynamics of solution of nonpolar gases in a fused salt. Hydrophobic bonding behavior in a nonaqueous system", *Journal of the American Chemical Society* **1981**, *103*, 481.

(23) Notley, S. M.; Biggs, S.; Craig, V. S. J. "Calibration of colloid probe cantilevers using the dynamic viscous response of a confined liquid", *Rev. Sci. Instrum.* **2003**, *74*, 4026.