# Stable and Water-Tolerant Ionic Liquid Ferrofluids

Nirmesh Jain, Xiaoli Zhang, Brian S. Hawkett, and Gregory G. Warr*

School of Chemistry and Key Centre for Polymers and Colloids, The University of Sydney, New South Wales 2006, Australia

Ⓢ Supporting Information

ABSTRACT: Ionic liquid ferrofluids have been prepared containing both bare and sterically stabilized 8−12 nm diameter superparamagnetic iron oxide nanoparticles, which remain stable for several months in both protic ethylammonium and aprotic imidazolium room-temperature ionic liquids. These ferrofluids exhibit spiking in static magnetic fields similar to conventional aqueous and nonaqueous ferrofluids. Ferrofluid stability was verified by following the flocculation and settling behavior of dilute nanoparticle dispersions. Although bare nanoparticles showed excellent stability in some ILs, they were unstable in others, and exhibited limited water tolerance. Stability was achieved by incorporating a thin polymeric steric stabilization layer designed to be compatible with the IL. This confers the added benefit of imbuing the ILF with a high tolerance to water.

KEYWORDS: ferrofluid, ionic liquid, steric stabilization, nanoparticle, dispersion, solvation
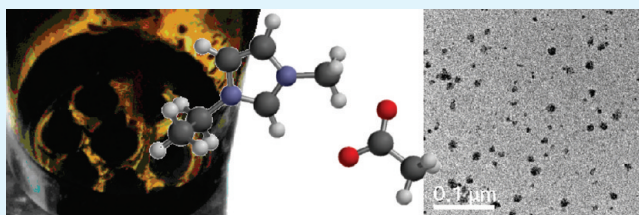
■ INTRODUCTION

Iron oxide nanoparticles are an important class of magnetic materials.[1] Their concentrated dispersions have been widely used as ferrofluids in various applications since their first preparation.[2,3] Ferrofluids are colloidal dispersions of small, single-domain magnetic particles suspended in a carrier liquid, and whose rheological behavior can be controlled by means of magnetic field.[4−7] Thus ferrofluids can change from a liquid to a solid-like state and vice versa almost instantaneously. Ferrofluids characteristically have both magnetic and fluid properties. Applications of ferrofluids include semiactive shock absorbers in the automotive industry, dampeners for seismic damage controls in civil engineering, in seals, valves, robotics, and microelectronic devices.[8−10] Magnetic nanoparticles have also been widely used in biology and medicine for enzyme and protein immobilization, radiopharmaceuticals, magnetic resonance imaging, diagnostics, immunoassays, purification, and drug delivery and cancer therapeutic methods.[11−17]

It is often desirable that ferrofluids are prepared in a carrier liquid that does not evaporate or decompose easily at high temperatures, especially for applications in bearings, seals, and for lubrication and heat transfer.[18] Many commercial ferrofluids therefore use heavy oils, which have low vapor pressures, as carrier liquids instead of lighter organic solvents. Ionic liquids (ILs) are composed entirely of ions and which melt below 100 °C. They have appeared in recent years as novel substances attracting considerable interest in many fields of chemistry and in the chemical industry.[19−22] Typical applications of ionic liquids include entrainers to break common azeotropes in separation processing, electrolytes for highly reversible lithium batteries and phase change materials for the storage of solar energy.[23] Their unique physicochemical properties may include negligible vapor pressure, nonflammability, high conductivity, and thermal and electrochemical stability,[24,25] which endow them with a further potential to replace conventional organic solvents in purifications, chemical and catalytic reactions.[26−29] Recently, ILs have been demonstrated to act as nonaqueous designer solvents to self-assemble amphiphilic biomacromolecules without requiring their prior modifications.[30] Because of their unique physicochemical properties, ILs are also prospective candidates for colloidal dispersion media for nanomaterials. A number of colloidal systems with ILs have recently been reported for the dispersion of metal and semiconductor nanoparticles, including in situ nanoparticle synthesis in ILs,[31,32] enhancement of colloidal stability in ILs,[33−35] phase transfer to ILs from other dispersed media,[36,37] and catalysis using metal nanoparticles in ILs.[38] The physical properties of ILs (e.g., viscosity, solubility, electrical conductivity, melting point, etc.) are readily tuned by varying their constituent ions. Owing to these characteristics, the use of ILs as ferrofluid carriers may be expected to expand and/or improve their applications in different areas of science and engineering such as in bearings, seals, lubrication and heat transfer.

Efforts have recently been made to obtain stable dispersions of magnetic nanoparticles in ILs.[39,40] Oliviera et al.[39] have reported stable dispersions of magnetic nanoparticles of γ-Fe_2O_3 and $CoFe_2O_4$ in 1-n-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$). However these dispersions became unstable above about 30% w/w, and upon addition of water. Also, it has recently been reported that the composition of an ionic liquid affects the stabilization of dispersions and colloidal interactions.[41,42] For instance, Smith et al.[41] found that bare silica particles do not

Table 1. Physical Properties of the Carrier Liquids Employed in Current Study

solvent	melting point (°C)	viscosity (cP)	density (g mL^{-1})	surface tension (mN m^{-1})	refractive index	ionic conductivity (μS cm^{-1})
water[45]	0	1^a	1.00^b	72.8^a	1.33	0.055^c
EMIMAc[46]	<−20	93^c	1.10^c		1.50	2500^c
EMIMSCN[47]	−6	22^c	1.11^c	57.8^c	1.55	220^c
BMIMBF$_4$[48]	−81	219^c	1.21^c	46.6^c	1.52^c	3520^c
EAN[49]	14	32^c	1.20^c	47.6^c	1.45^c	26900^c

^{a} 20 °C. ^{b} 4 °C. ^{c} 25 °C.

aggregate in pure ethylammonium nitrate, but are unstable in 1-alkyl-3-methylimidazolium based ILs, according to Ueno et al.[42] Here, we examine the stability of dispersions of magnetic nanoparticles in different types of protic and aprotic ILs, in order to determine the design features required of concentrated dispersions that will be suitable as IL ferrofluids, and how to control their tolerance to water.

■ EXPERIMENTAL SECTION

Fe(II) chloride tetrahydrate (99%), Fe(III) chloride hexahydrate (98%), Sigma-Aldrich (USA), Fe(III) nitrate nonahydrate (99%), Merck (Germany), ammonium hydroxide (28% w/w NH$_3$ in water), nitric acid, Fluka, and ethylamine, Sigma, were used as supplied. Milli-Q water was used throughout the work. Acrylic acid-b-acrylamide copolymer (AA$_{10}$-b-AM$_{14}$) was prepared and characterized as reported previously.[43] Ethylmethylimidazolium acetate and thiocyanate, EMIMAc and EMIMSCN, and n-butyl-methyl-imidazolium tetrafluoroborate, BMIMBF$_4$, were obtained from Sigma-Aldrich, and were used as received.

Ethylammonium nitrate, EAN, was prepared as described previously by Evans et al.[44] by adding nitric acid dropwise to ethylamine while keeping the reaction temperature below 15 °C. Excess water was removed by rotary evaporation followed by nitrogen purging and heating at 108−110 °C under a nitrogen atmosphere overnight. This leads to water contents undetectable by Karl Fischer titration.

Bare and polymer-coated iron oxide (maghemite) nanoparticles were synthesized in water as reported previously.[43] These particles have been extensively characterized using various methods such as TEM, X-ray diffraction, magnetometry, etc., as described in ref 43.

Ionic liquid ferrofluids (ILFs) were prepared by mixing an aqueous dispersion of (bare or polymer-coated) iron oxide nanoparticles with each IL, and ultrasonication for 2 min. Water was then removed by rotary evaporation followed by nitrogen purging overnight. Many of the dispersions became unstable in the IL/water mixtures, but were subsequently redispersed by sonication after water was removed.

The size and the morphology of nanoparticles was determined using a JEOL 1400 transmission electron microscope operated at 120 kV, yielding nanoparticle core diameters of 8−12 nm. A small droplet of the dispersion in each solvent was placed on a Formvar-coated and carbon-sputtered copper grid and excess solvent was carefully removed by blotting with a piece of filter paper. Their size distribution and state of aggregation in each continuous phase was measured by laser light scattering (Malvern Zeta Sizer 3000H) at 25 °C on samples at 0.1% w/w nanoparticle concentration. The main physical properties of carriers employed in this study are listed in Table 1.

To further evaluate the water tolerance, a series of nanoparticle dispersions in IL−water mixtures with different weight ratios were also prepared. The aqueous nanoparticle dispersions with known concentrations were weighed initially and added to small glass vials. The pure ILs were then mixed quantitatively with these weighed aqueous dispersions to obtain the required concentration of 0.1% w/w for each dispersion in
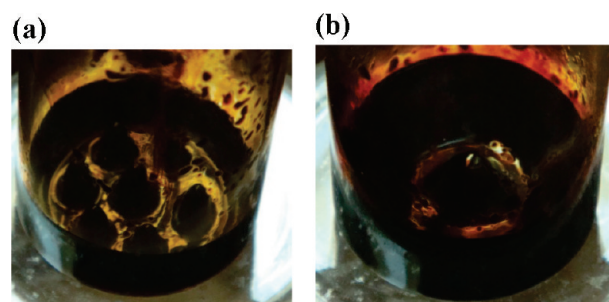

Figure 1. Maghemite IL ferrofluids showing characteristic spiking in a static magnetic field. (a) 45% w/w bare in EMIMAc; (b) 37% w/w polymer-coated in EAN.

IL−water mixtures. These mixtures were then sonicated for 2 min in a sonic bath and equilibrated overnight prior to their measurements.

■ RESULTS AND DISCUSSION

One of the primary goals of this work is to prepare stable, concentrated dispersions of iron oxide nanoparticles in ionic liquids suitable as ferrofluids. Formation of a ferrofluid requires the stabilization of a concentrated dispersion of single domain superparamagnetic nanoparticles containing at least 1×10^{17} particles/mL,[54] so that their induced dipoles will align in an external magnetic field, resulting in spiking. This feature can only be observed at or above a threshold concentration of magnetic nanoparticles, typically around 10% v/v. Bare nanoparticle dispersions are thus favored for ferrofluids as they lead to greater loadings and stronger responses to external fields. Stable dispersions of magnetic nanoparticles in ILs[39,40] have been reported recently in the literature, but these did not meet this criterion, becoming unstable at particle concentrations above 30% (w/w). In this work, we were able to obtain very stable dispersions at high concentration such as 45% (w/w) of bare particles dispersed in EMIMAc, and comparable results in EMIMSCN. No phase separation was seen when ILFs were subjected to the external magnetic field (∼0.3 T), indicating that particles were well-stabilized and dispersed in the IL. However, no ferrofluid could be prepared using bare magnhemite nanoparticles in the protic IL, EAN. In this carrier, the particles sedimented within minutes.

Figure 1 illustrates the characteristic spiking behavior exhibited by bare maghemite (45% w/w or 2.7×10^{17} particles/mL) ferrofluid using EMIMAc in a static magnetic field. This concentration vastly exceeds the maximum nanoparticle loading achieved by Oliveira et al.[39] and is comparable to traditional aqueous ferrofluids. This ferrofluid remains stable for at least several months, with no evidence for flocculation or settling. Their stability is unaffected by exposure to static magnetic fields such as those used in Figure 1.
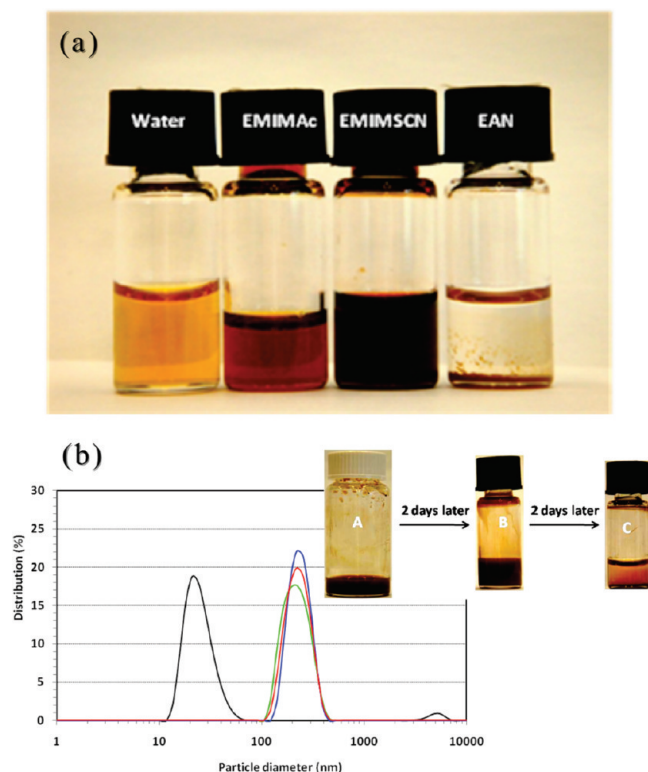
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Figure 2. (a) 0.1% w/w maghemite nanoparticle dispersions in various solvents; (b) hydrodynamic diameters of maghemite (0.5% w/w) nanoparticles in BMIMBF$_4$ 10 min (green) and 2 days (blue) after dispersion, and 4 days following redispersion by 10 min sonication (red). An aqueous dispersion (black) is also shown for comparison. Inset: settling occurring in these dispersions over the same period.

Table 2. Hydrodynamic Diameters of Bare Maghemite (0.1% w/w) Nanoparticles in Water and Various Ionic Liquids; No Particle Size Is Reported if the Dispersion Was Unstable

solvent	mean diameter (nm)
water	26 ± 0.8
EMIMAc	38 ± 3.0
EMIMSCN	44 ± 2.8
BMIMBF$_4$	220 ± 24.0[a]
EAN	

[a] Unstable dispersion settles over 2−4 days.

The high concentration of the nanoparticles in a ferrofluid makes it impossible to employ physical methods such as TEM, light scattering, etc., to characterize the particles and investigate their stability. To overcome this, we examined dilute dispersions of nanoparticles in various ILs. These were prepared by adding concentrated aqueous dispersion of nanoparticles to pure ILs, followed by overnight purging with nitrogen to remove water (confirmed by Karl Fischer titration). The colloidal stability of particle dispersions in ILs was investigated by following their flocculation and settling behavior, and also by measuring the size of particles by dynamic light scattering. Figure 2 shows dilute dispersions of bare maghemite nanoparticles in a variety of carriers. Dispersions in imidazolium ILs such as EMIMAc and EMIMSCN were, to the naked eye, stable for at least several months, as shown in Figure 2a. Maghemite particles dispersed in
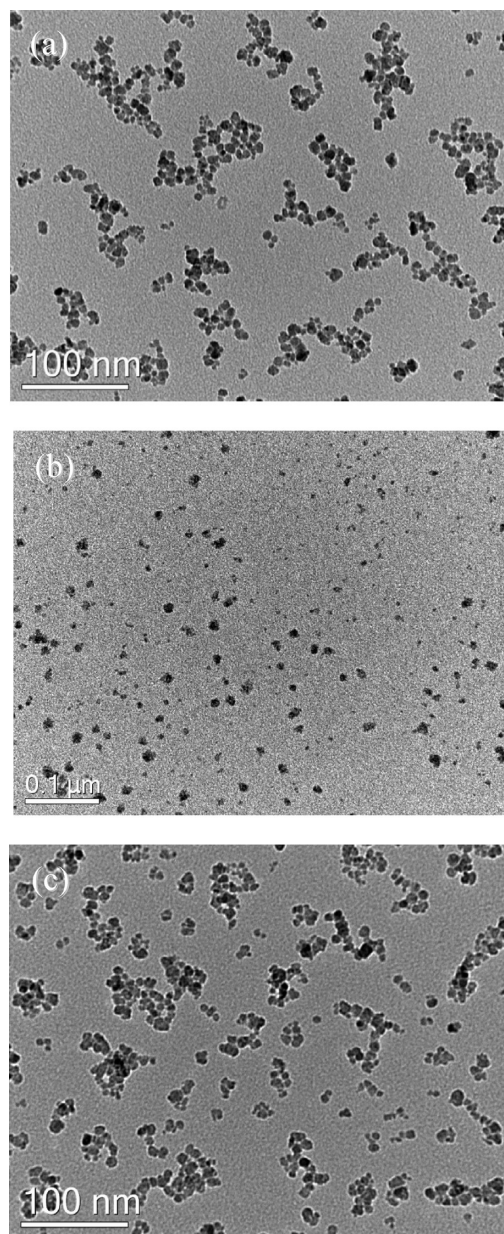

Figure 3. TEM images of maghemite (0.1% w/w) nanoparticle dispersions in (a) water; (b) EMIMAc; (c) polymer-coated nanoparticles in water.

carefully dried EAN, however, aggregated and settled very quickly leaving a clear supernatant, consistent with our observed inability to prepare an EAN-based ferrofluid. This was an unexpected result, as silica dispersions in EAN have been reported to be stable,[41] and EAN has been shown to form multiple solvation layers on macroscopic silica surfaces.[50] This suggests that the surface chemistry of maghemite must not favor the binding of the ethylammonium cation layer, as occurs on silica. Ueno et al.[42] have reported similar differences in stability of silica particle dispersions in 1-alkyl-3-methylimidazolium ILs with different anions.

Hydrodynamic diameters of maghemite particles dispersed in water and various ILs are listed in Table 2. The average values in water are larger (26 nm) than the typical diameters of 8−10 nm measured in TEM images (Figure 3a). This is due to a

Table 3. Hydrodynamic Diameters of Bare Maghemite (0.1% w/w) Nanoparticles in IL−Water Mixtures; No Particle Size Is Reported if the Dispersion Was Unstable

ionic liquid, wt%	hydrodynamic diameter (nm)	
	EMIMAc	EMIMSCN
0	26 ± 0.8	26 ± 0.8
5−85		
90	38 ± 3.8	
95	37 ± 3.3	49 ± 3.4
100	38 ± 3.0	44 ± 2.8

Figure 4. Dilute, polymer-coated maghemite dispersions in various solvents.

combination of effects including (i) the polydispersity of the nanoparticles, and that dynamic light scattering reports a z-average of the hydrodynamic diameter, which (ii) includes a solvation layer around the particle, and (iii) is very sensitive to the presence of a small number of aggregates. This is similar to effects reported by us previously for aqueous nanoparticle dispersions.[43] The key result is that the measured size distribution is stable over time. Figure 2b shows the size distribution of such an aqueous dispersion obtained from dynamic light scattering, which shows a distribution of particle diameters from 10 to 50 nm contributing to the reported average. The z-average particle diameters in EMIMAc and EMIMSCN were slightly larger than in water. Small-angle X-ray scattering (see Supporting Information) yields the same particle diameters of 9 nm in water and EMIMAc, consistent with primary particle size from TEM studies.

Figure 3 (a and b) shows TEM images of maghemite nanoparticles deposited on the TEM grid from aqueous dispersions and EMIMAc. The particles are quite polydisperse, which is not unusual for particles prepared by this method and has been reported previously.[43] Individual primary particle sizes obtained from the micrographs in both the cases range from 8 to 12 nm. The flocs in Figure 3a are a common observation, and result from capillary action during the drying process. Although the quality of the image in the IL is not as good as in water, Figure 3b clearly shows that maghemite particles are not flocculated in EMIMAc, which does not evaporate from the TEM grid before imaging.

Oliveira et al.[39] have reported stable maghemite nanoparticle dispersions in BMIMBF$_4$ at concentrations up to 30%w/w. However, our investigations on the stability of maghemite nanoparticles in BMIMBF$_4$ suggest that even dilute dispersions are relatively short-lived. Figure 2b shows the sedimentation of maghemite nanoparticles dispersed in BMIMBF$_4$. Dynamic light scattering shows that aggregation into particles over 200 nm in diameter occurs rapidly in BMIMBF$_4$, leading to settling over 2−4 days (Table 2). Redispersion of the sediment by sonication only regenerates the population of flocs, and primary particles with diameters below 50 nm cannot be detected.

Water-tolerance will be a key issue in the use of IL ferrofluids, either through deliberate formulation or adventitious uptake. The presence of very little water in ILs can drastically reduce their viscosity.[55−57] This is desirable for a number of industrial applications since viscosity significantly influences the ionic conductivity, mass transfer of solutes, mixing, dispersion, filtration, and equipment selections.[58] Therefore, this characteristic feature of the low-viscosity nanoparticle dispersion in IL−water mixtures promises to expand their potential applications. However, the stability of many nanoparticle dispersions in ILs is very sensitive

to the presence of water.[39,41,42,59] Rubim et al.[59] found that even very small amounts of water caused the aggregation of silver nanoparticles in BMIMBF$_4$. Smith et al.[41] also observed that water destabilized silica particles dispersed in EAN.

Bare aqueous nanoparticle dispersions are electrostatically stabilized, whereas solvent structural forces appear to be the primary stabilization mechanism in ILs. The stability of particulate dispersions in ILs has been attributed to the formation of semiorganized protective layers such as $[(BMIM)_2(BF_4)_3]^-$ and $[(BMIM)_3(PF_6)_4]^-$ aggregates around magnetic oxide and Pt(0) nanoparticles.[39,59] There also is considerable evidence in the literature for the layering of EAN, imidazolium and other aprotic ILs at interfaces,[50−53] and also around dispersed particles, leading to "solvation" repulsions between particles. The extent of structuring depends strongly on the structure of both cation and anion, as well as the solid substrate.[50,60,61] Water has been shown to reduce the strength and number of solvation layers at an EAN/silica surface,[41] allowing dispersion forces to dominate. This results in aggregation of the particles and destabilization of the colloidal dispersion. Table 3 lists hydrodynamic particle diameters in both EMIMAc-water and EMIMSCN−water mixtures. Both form stable dispersions in pure water and pure IL, but are unstable in mixtures over a very broad range of compositions. With as little as 5% w/w IL in water, either IL acts as an aqueous electrolyte and screens the electrostatic stabilizing forces. Addition of 5−10% w/w water to the IL similarly destabilizes the dispersion, probably by disrupting or displacing solvation layers on the particle surface.

As we have recently shown,[43] a thin coating of a short acrylic acid-b-acrylamide copolymer (AA_{10}-b-AM_{14}) can stabilize aqueous ferrofluids in high electrolyte aqueous environments. Figure 1b shows that this approach is also effective in stabilizing particles in a pure EAN ferrofluid, leading to spiking and long-term stability at a coated particle loading of 37% w/w. The acrylic acid groups of this copolymer bind strongly to the maghemite surface, generating a thin stabilizing layer of poly(acrylamide) at little cost to maximum particle loading. Figure 4 shows that dilute dispersions of sterically stabilized maghemite were also stable in EAN and EMIMAc, but not in EMIMSCN (the flocculated particles can be clearly seen on the wall of the glass vial in the inset) or BMIMBF$_4$ (not shown). This is simply a consequence of the insolubility of the polyacrylamide block of acrylic

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Table 4. Hydrodynamic Diameters of Polymer-Coated Maghemite (0.1% w/w) Nanoparticles in IL-Water Mixtures

ionic liquid, wt%	hydrodynamic diameter (nm)	
	EMIMAc	EAN
0 (water)	57 ± 6.0	57 ± 6.0
10	67 ± 6.3	55 ± 5.5
30	70 ± 6.8	57 ± 5.8
50	66 ± 7.3	62 ± 6.1
60	67 ± 6.0	64 ± 7.0
80	74 ± 7.7	62 ± 6.7
100	67 ± 8.0	62 ± 5.7

acid-*b*-acrylamide in these ILs, making it an ineffective steric stabilizer for these carriers; alternative stabilizing blocks could readily be identified by screening a range of candidate homopolymers such as poly(ethylene oxide), which have been shown to exhibit good solubility on various ILs.[62−65] Similar effects have been observed by Ueno and co-workers[42] for the dispersions containing PMMA layers grafted onto silica particles in BMIM-based ILs.

Table 4 shows the hydrodynamic diameters of the polymer-coated particles dispersed in IL-water mixtures. These are noticeably larger than the bare particle diameters (Table 2), but vary little over the entire composition range, indicating that dispersions of polymer coated particles are stable at all compositions: No sedimentation was observed in any of these systems over many months. Figure 3c shows that the maghemite cores of the polymer-coated particles are identical to the bare particles, and flocculate similarly under capillary action when deposited from water onto TEM grids.

CONCLUSIONS

Ferrofluids in ionic liquids and IL/water mixtures at all compositions were successfully prepared, and the stability verified by dynamic light scattering. Bare nanoparticle stability arises in several aprotic ILs, due to solvation structure surrounding nanoparticles. Where bare nanoparticle dispersions are unstable, a thin adsorbed polymer layer can form an effective steric barrier if the ionic liquid is a good solvent for the grafted copolymer. Steric stabilization is also effective at generating a high water tolerance for nanoparticle dispersions in ILs. The result is unprecedented in the literature to our knowledge, and could expand the range of practical applications of IL ferrofluids where water may be present as an impurity, or is deliberately incorporated to manipulate carrier viscosity or conductivity.

ASSOCIATED CONTENT

S **Supporting Information.** Graph of SAXS spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: gregory.warr@sydney.edu.au

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