Paramagnetic Ionic Liquids for Measurements of Density Using Magnetic Levitation

SUPPORTING INFORMATION

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EXPERIMENTAL SECTION

Chemical and Materials

The salts 1-butyl-3-methyl imidazolium chloride (BMIM Cl), 1-butyl-2,3-methyl imidazolium chloride (BDMIM Cl), iron (III) chloride, manganese (III) chloride, gadolinium (III) chloride, holmium (III) chloride, holmium (III) bromide, dysprosium (III) chloride, trioctylmethylammonium chloride (Aliquat® Cl), trioctylmethylammonium bromide (Aliquat® Br), trihexyl(tetradecyl)phosphonium dicyanamide ([PR$_4$] [DCA]), L-alanine methyl ester chloride (L-AlaC1 Cl), and Melamine were obtained from Sigma-Aldrich and used as received. Glass beads with known density were purchased from American Density Materials (Stauton, VA) and Delrin beads having known density were obtained from McMaster-Carr. Whole milk was purchased from CVS pharmacy (Cambridge, MA).

Synthesis of paramagnetic ionic liquids (PILs)

We synthesized the PILs in nearly quantitative yield by combining imidazolium, amino acid ester, or ammonium halides. These reactions can be performed either without solvent or by mixing the salts in methanol followed by removal of the solvent under high vacuum. Except for [BMIM][FeCl$_4$], [BMIM]$_2$[MnCl$_4$], all PILs were synthesized by mixing appropriate equivalents of the halide starting materials in methanol and allowed to stir overnight (12 hrs). The solvent was removed by rotary evaporation and then dried under high vacuum for 12 hours affording PILs in nearly quantitative yield. The synthesis of [BMIM][FeCl$_4$] was carried out by following reported literature procedure.[1-3] Specifically, [BMIM][Cl] and FeCl$_3$ were mixed together in a 1:1 molar ratio and stirred under nitrogen atmosphere. After stirring for 10 minutes at room temperature, [BMIM][FeCl$_4$] was obtained as a brown colored liquid. We used similar procedure

to synthesize [BMIM]$_2$[MnCl$_4$] except that we heated the mixture (2:1 molar ratio of [BMIM][Cl]:MnCl$_2$) at 60ºC for 10 minutes.

Characterization of PILs

We characterized the synthesized PILs using elemental (C, H, N) analysis (Robertson Microlit Systems, NJ). We measured the glass transition temperature (T$_g$) and decomposition temperatures (T$_d$) of the synthesized PILs, respectively, using dynamic scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). We carried out the measurement of glass transitions by equilibrating a sample of the PIL (5-10 mg) at 25 ºC, cooling the sample to -75 ºC at a ramp rate of 5 ºC/min followed by heating to 50 ºC at 5 ºC/min. We performed thermal gravimetric analysis by monitoring the change in weight of the PILs sample (15-20 mg) as it is heated at 10 ºC/min from room temperature to 700 ºC under nitrogen flow (25 ml/min) and measured the decomposition temperatures (T$_d$) at the onset of decomposition (~ 10% mass loss).

Elemental analysis (% C, H, N)

[Aliq]$_3$[GdCl$_6$], Calculated for C$_{75}$H$_{162}$Cl$_6$GdN$_3$: C, 61.03; H, 11.06; N 2.85. Found: C, 61.91; H, 12.38; N, 2.44.

[Aliq]$_3$[HoCl$_6$], Calculated for C$_{75}$H$_{162}$Cl$_6$HoN$_3$: C, 60.71; H, 11.00; N, 2.83. Found: C, 59.15; H, 11.26; N, 2.38.

[Aliq]$_3$[HoBr$_6$], Calculated for C$_{75}$H$_{162}$Br$_6$HoN$_3$: C,51.46; H ,9.33; N, 2.40. Found: C, 50.11; H, 10.05; N, 2.14.

[BMIM]$_3$[DyCl$_6$], Calculated for C$_{24}$H$_{45}$DyCl$_6$N$_6$: C, 36.36; H, 5.72; N, 10.60. Found: C, 35.43; H, 7.32; N, 8.40.

[BMIM][FeCl$_4$], Calculated for C$_8$H$_{15}$Cl$_4$FeN$_2$: C, 28.50; H, 4.45; N, 8.31. Found: C,30.60; H, 4.95; N, 9.04.

[BMIM]$_3$[HoCl$_6$], Calculated for C$_{24}$H$_{45}$Cl$_6$HoN$_6$: C, 36.24; H, 5.70; N, 10.57. Found: C, 35.48; H, 5.84; N,10.17.

[BDMIM][FeCl$_4$], Calculated for C$_9$H$_{17}$Cl$_4$FeN$_2$: C, 30.81; H, 4.88; N,7.98. Found: C, 29.86; H, 4.93; N, 8.51.

[BDMIM]$_3$[DyCl$_6$], Calculated for C$_{27}$H$_{51}$Cl$_6$DyN$_6$: C, 38.84; H, 6.16; N,10.04. Found: C, 36.70; H, 6.60; N, 9.07.

[BDMIM]$_3$[GdCl$_6$], Calculated for C$_{27}$H$_{51}$Cl$_6$GdN$_6$: C, 39.09; H, 6.20; N, 10.13. Found: C, 37.65; H, 5.88; N, 9.67.

[AlaC1][FeCl$_4$], Calculated for C$_4$H$_{10}$Cl$_4$FeNO$_2$: C, 15.92; H, 3.34; N, 6.11. Found: C,14.35; H, 3.94; N, 4.41.

[AlaC1]$_3$[DyCl$_6$], Calculated for C$_{12}$H$_{30}$Cl$_6$DyN$_3$O$_6$: C, 20.96; H, 4.40; N, 6.11. Found: C, 20.33; H, 4.71; N, 5.90.

[AlaC1]$_3$[GdCl$_6$], Calculated for C$_{12}$H$_{30}$Cl$_6$GdN$_3$O$_6$: C, 21.12; H, 4.43; N, 6.16. Found: C, 20.77; H, 4.58; N, 6.20.

[AlaC1]$_3$[HoCl$_6$], Calculated for C$_{12}$H$_{30}$Cl$_6$HoN$_3$O$_6$: C, 20.89; H, 4.38; N, 6.09. Found: C, 17.90; H, 4.20; N, 5.10.

[AlaC1]$_3$[MnCl$_4$], Calculated for C$_8$H$_{20}$Cl$_4$MnN$_2$O$_4$: C, 23.72; H, 4.98; N, 6.92. Found: C, 22.22; H, 5.01; N, 6.23.

Figure S1. Picture illustrating that a droplet of $[Aliq]_3[HoCl_6]$ PIL in water responds to, and is attracted by a $Nd_2Fe_{14}B$ magnet. The droplet (A) before and (B) after a magnet is placed above the vial.

A)

No magnet

B)
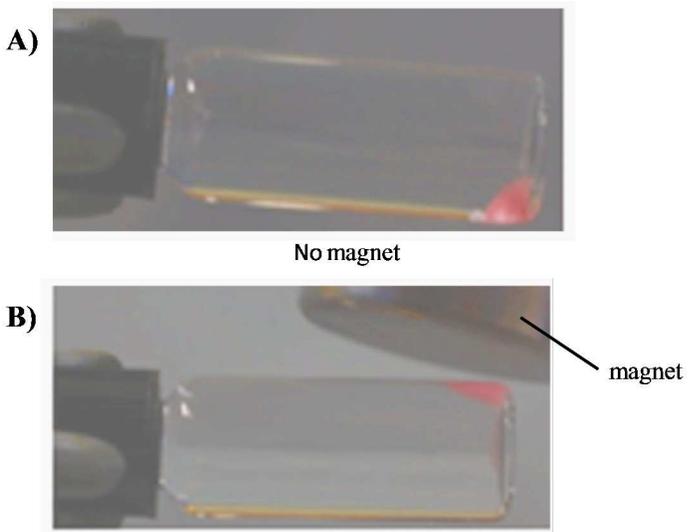
magnet

Determining the density and magnetic susceptibility of the PILs.

We used MagLev device with the magnets having like poles facing, arranged parallel at 4.5 cm apart, as we have previously described.[4] The magnetic field strength (B_0) at the surface of the magnets (measured using a handheld magnetometer) is 0.38 T. We measured the levitation height of beads having known density in the PILs at room temperature. Equation S1 shows that there is a linear relationship between the levitation height and density of the object. We plot the levitation height of density-standard beads versus their density and fitted the plot to Eq. S1. In this equation, ρ_{bead} and ρ_{PIL} (both kg/m^3) are the densities, and χ_{bead} and χ_{PIL} (SI, unitless) are the magnetic susceptibilities of the bead and the paramagnetic ionic liquid (PIL), respectively, d (m) is the distance between the magnets, B_0 (Tesla) is the magnitude of the magnetic field at the surface of the magnets (0.38 T), g (9.8 m/s^2) is the acceleration due to gravity, and μ_0 (T·m·A^{-1}) is the magnetic permeability of free space. In equation S1 (a), A is the slope, and B is the intercept, of the plot of levitation height of density-standard beads versus their density levitated in PILs. The magnetic susceptibility and density of each PIL are obtained by solving for the values of χ_{PIL} and ρ_{PIL} in equation S1(b) and S1(c), respectively, and are tabulated in Table 1.

$$h = \frac{(\rho_{bead} - \rho_{PIL})g\mu_0 d^2}{(\chi_{bead} - \chi_{PIL})4B_0^2} + \frac{d}{2} \tag{S1}$$

$$h = -A \times \rho_{PIL} + B \tag{S1a}$$

$$A = \frac{\mu_0 g}{\chi_{PIL} - \chi_{bead}}\left(\frac{d}{2B_0}\right)^2 \tag{S1b}$$

$$B = \frac{\mu_0 g \rho_{PIL}}{\chi_{PIL} - \chi_{bead}}\left(\frac{d}{2B_0}\right)^2 + \frac{d}{2} \tag{S1c}$$

Calculating densities of samples from their levitation heights.

We determined densities of samples levitated in PILs using calibration standards as previously reported.[4] We measured unknown densities by first levitating objects with known densities in the PILs. From the measured levitation heights, we plot the levitation height versus density (Equation S2). We then determine the values of parameters α and β in eq. S2 empirically, and use these values for calculating the unknown densities from the levitation heights of the sample. This approach does not require an accurate knowledge of experimental parameters in eq. S2. The uncertainty in measurement of density ($\delta\rho$) of the object is calculated from the product of the calibration parameter (α) and the uncertainty in measurement of height (δh) using Equation S3.[4,5]

$$\rho_s = \alpha h + \beta \qquad \text{(S2)}$$

$$\delta\rho_s = \left|\frac{d\rho_s}{dh}\right|\delta h = |\alpha|\delta h \qquad \text{(S3)}$$

Figure S2. Graphs showing the relationship between the levitation height and density of standard-beads levitated in (A) $[Aliq]_3[HoBr_6]$, (B) $[BDMIM]_3[DyCl_6]$, and (C) $[Aliq]_3[HoCl_6]$, at room temperature (298K) and at -20 °C (253K).
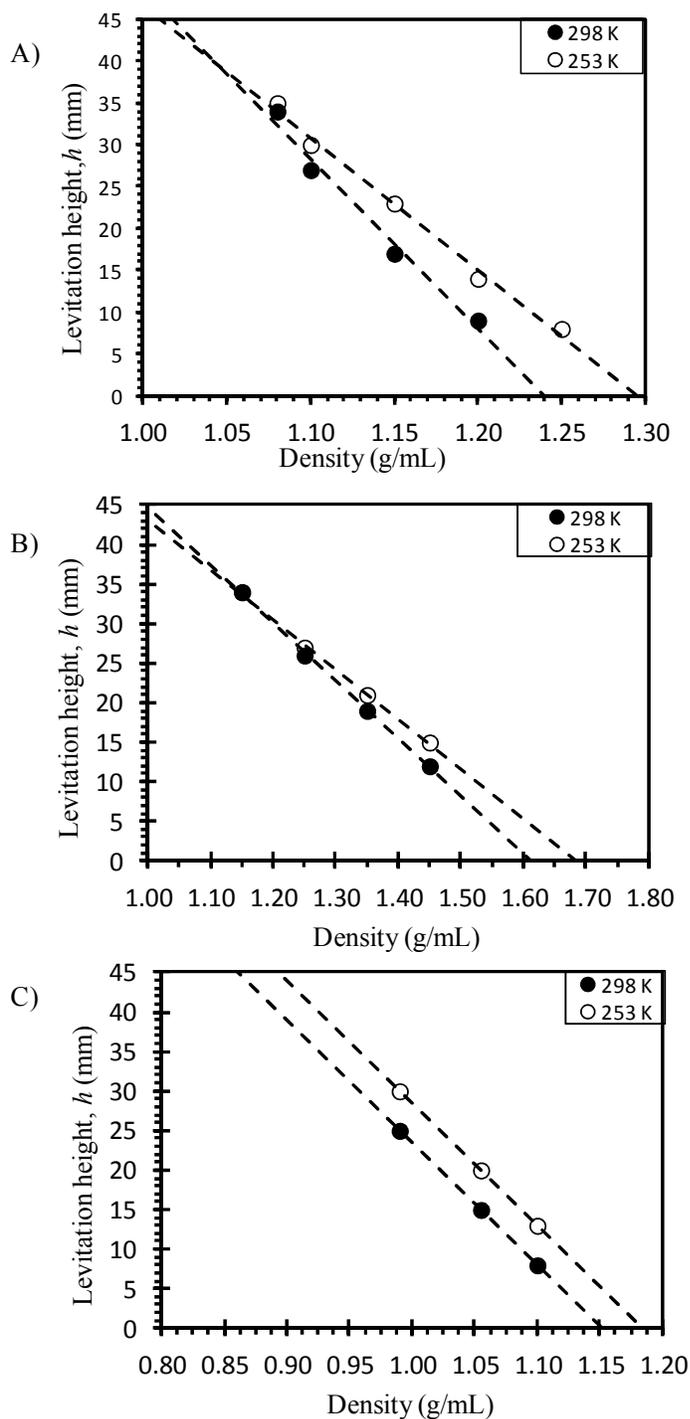
**Figure S3.** Milk droplets levitating in a mixture of [Aliq]$_3$[HoBr$_6$] PIL and trihexyl(tetradecyl)phosphonium dicyanamide, [PR$_4$][DCA], ionic liquid (55:45 v/v): (A) Whole milk (top), and whole milk containing 10% Melamine (w/v) (bottom). (B) Whole milk (bottom), and whole milk adulterated with an equal volume of water (top). We added [PR$_4$][DCA] ionic liquid to adjust density and magnetic susceptibility of [Aliq]$_3$[HoBr$_6$] PIL. Scale bars are 2 mm.
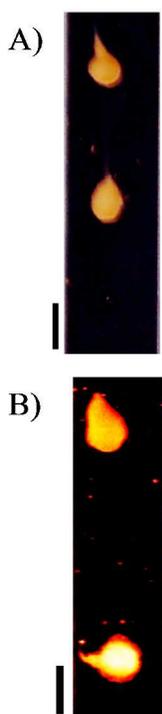
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