

Supporting Information

Stable iron carbide nanoparticle dispersions in [Emim][SCN] and [Emim][N(CN)₂] ionic liquids

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Experimental

Materials. FeCl₂*4H₂O (Sigma Aldrich), Fe(CO)₅ (Acros Organics), Urea (Riedel-de Haen, 99 %), absolute ethanol (VWR Prolabo), and anhydrous FeCl₃ (Aldrich) were used as received. Ionic Liquids (ILs) based on the 1-ethyl-3-methylimidazolium [Emim] and the 1-

butyl-3-methylimidazolium [Bmim] cation and the ethylsulfate [ES], methanesulfonate [MS], trifluoromethylsulfonate (triflate) [TfO], tetrafluoroborate [BF₄], dicyanamide [N(CN)₂], and thiocyanate [SCN] were purchased from Iolitec and used as received. All ILs were colorless or slightly yellow. All ILs were checked for purity via NMR, IR, and elemental analysis prior to use.

Iron carbide nanoparticle synthesis. In a typical synthesis, 0.244 g of FeCl₂*4H₂O were mixed with 0.118 g of Fe(CO)₅ and then dissolved in 1 g of absolute ethanol. Urea was added to the iron precursor solution such that the urea/iron chloride molar ratio was equal to 3:1. After stirring for 1h, a dark brown gel was obtained, which was subsequently treated at 700 °C under nitrogen flow for 2 hours. The resulting black magnetic (when an external field is applied) powder consists of crystalline Fe₃C nanoparticles with diameters between 5 and 10 nm dispersed in a matrix of amorphous carbon. The final material still contains between 10 and 15 % carbon, which cannot be removed.

Dispersion of nanoparticles in ILs. Iron carbide nanopowders were dispersed in ILs at various temperatures. In a typical dispersion experiment, 1 to 10 mg of iron carbide nanopowder were mixed with 1 g of IL at room temperature and subsequently stirred at 20, 120, 160, or 180 °C for 72 hours. In some cases, only incomplete dispersion of the iron carbide powder was observed even after 72 hours. Solid residuals were removed by decantation.

X-ray scattering. Wide-Angle X-ray scattering (WAXS) was done on a Bruker D8 using CuK α (λ = 1.542 Å) radiation. Silicon was used as external calibration standard, 2D data were converted to 1D data, and analyzed with Diffrac Plus EVA.¹ Small angle X-ray scattering (SAXS) measurements were performed with a SAXSess camera (Anton Paar, Austria) attached to a laboratory X-ray generator (PW3830, PANanalytical) operated with a fine focus glass X-ray tube at 40 kV and 50 mA (CuK α , λ = 0.1542 nm). Samples were filled in a reusable vacuum tight 1 mm quartz capillary to attain the same scattering volume and

background contribution. The scattering vector is defined in terms of the scattering angle θ and the wavelength of the radiation, thus $q = 4\pi/\lambda \sin(\theta)$. SAXS data were recorded as 120 x 5 s repetitions in a q -range from 0.06 nm⁻¹ to 1.0 nm⁻¹ with a CCD detection system (Anton Paar). The two-dimensional intensity data were converted to one-dimensional data and deconvoluted using the software SAXSQuant (Anton Paar). Data were fitted using an analytical model² assuming a Schultz distribution^{3, 4} of the radii, using Igor Pro 6.0.4 (Wavemetrics) and the NIST SANS Data Analysis Package.⁵

Electron microscopy. Transmission electron microscopy (TEM) was done on a Philips CM10 operated at 100 kV and a Zeiss 912Ω operated at 120 kV. The nanoparticle dispersions were directly deposited on formvar-coated grids as neat samples in IL and allowed to air-dry for 24 hrs prior to imaging.

UV/Vis spectroscopy. UV/Vis spectroscopy was done at room temperature on a Perkin Elmer Lambda Agilent spectrometer from 200 to 1000 nm with a resolution of 3 nm. Experiments were done in standard quartz cuvettes (Hellma) with an optical path length of 1 cm. Undiluted samples were used for all measurements and the respective ionic liquids were used for baseline correction. FeCl₃ solutions used for comparison experiments were made by dissolving a few crystals of FeCl₃ in [Emim][SCN].

Table S1. Physico-chemical parameters typically used in the explanation of phenomena in ILs. MW = molecular weight, T_m = melting temperature, R.I. = refractive index, DK = dielectric constant. Unless given otherwise, values are for 25 °C.

Cation	Anion	MW g/mol	Viscosity cP	Density g/cm ³	T _m °C	Hydrophilicity	Decomposition Temperature °C	Electr. Conductivity μS/cm	DK
EMIM	[ES]	236.2 ⁹	122 RT) ⁶ 14 (80°C) ⁶	1.2369 ³ (25°C) ⁷ 1.20 (80°C)	65 ⁸	hydrophilic	300 ⁹	2970 ⁹ 7200 (80 °C) ¹⁰	27.9 ¹

	[MS]	206.2 ₇	109 (RT) ₆ 13 (80°C) ₆	1.24 (RT) ₆ 1.21 (80°C) ₆	35 ⁶	hydrophilic	250 ⁹	2700 ⁹ 2600 ¹⁰	
	[TfO]	260.2 ₃	53 ⁸ 45 ¹²	1.330 ⁸ 1.3572 ₃ ¹	-9 ¹²	hydrophilic	250 ⁹	9200 ⁹	15.1 ₁ ¹
	[BF ₄]	197.9 ₇	37.7 ¹⁴	1.2695 ₅ ¹	-65 ₅ ¹	hydrophobic	150 ¹⁵	3150 ⁹	
	[N(CN) ₂]	177.2 ₁	16.8 ⁹	1.113 ¹⁶	-21 ⁹		80 ⁹	25300 ⁹	
	[SCN]	169.2 ₅	21 ¹⁷ 24.7 (80°C) ₉ 5.8 (80°C) ₁₀	1.1140 (RT) ₁₅ 1.0829 (80°C) ₁₀	-24 ⁹	Hydrophilic ⁹	80 ⁹	2700000 ¹⁷	
BMIM	[ES]	236.2 ₉	240 ¹⁵		-17 ₅ ¹	hydrophilic		8300 ¹⁵	
	[MS]	234.3 ₂	15.7 (100°C) ₁₅	1.128 (100°C) ₁₅	75 -80 ₅ ¹			210 (80°C) ₁₀	
	[TfO]	302.3 ₄	109.0 ⁹	1.292 (20°C)	16 ⁹		250 ⁹	3049 ⁹	
	[BF ₄]	226.0 ₂	233 ¹⁸ 136.7 ⁹	1.1961 (20°C) ₁₅	-75 ⁹	hydrophobic	100 ⁹	3145 ⁹	
	[N(CN) ₂]	205.2 ₆		1.06 ¹⁶					
	[SCN]	197.3	51.7 ¹⁵ 9.34 (80°C) ₁₀	1.0696 (25°C) ₁₅ 1.0384 (80°C) ₁₀	-24 ₅ ¹	Hydrophilic ¹⁰	100 °C ¹⁵	40 ¹⁰	

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