

Tuning the colloidal stability in ionic liquids by controlling the nanoparticles/liquid interface

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SUPPLEMENTARY INFORMATION

1. Synthesis of the ionic liquid ethylammonium nitrate (EAN)

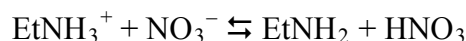
Ethylammonium nitrate (EAN) is prepared by a simple acid-base reaction: equimolar quantities of nitric acid (69.5% water solution) and ethylamine (70% water solution) are reacted in distilled water at $-10\text{ }^{\circ}\text{C}$. The product is a solution of the ionic liquid in water. Upon completion of the reaction, an excess of ethylamine solution is added until the pH becomes plainly basic ($\approx 10-12$). This ensures a stoichiometric reaction between the two species.

Excess amine removal is carried out via rotary evaporation, taking care as not to heat the water bath over $40\text{ }^{\circ}\text{C}$, which helps reduce the risk of degradation of the ammonium moiety. This is followed by overnight freeze-drying to pump most of the remaining water away: this is a “soft” technique for water removal that rests on the selective sublimation of water at low pressure from a deep-frozen sample, and it is of particularly convenient use in ILs since their negligible vapour tension allows them to stay in the liquid state at such low pressure conditions; also, freeze-drying is preferred to heating, so as to avoid the degradation of EAN.

In practice, freeze-drying consists in rapidly freezing the sample by immersion in liquid nitrogen, followed by pumping at about 10^{-6} bar.

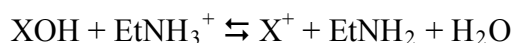
2. pH determinations in EAN

The acid-base properties of ethylammonium nitrate as an amphoteric solvent have been thoroughly studied^{1,2}. Pure EAN is characterized by the presence of the following autoprotolysis equilibrium:



where molecular nitric acid is the strongest acid (solvated proton) and ethylamine is the strongest base. Assimilating activities and concentrations, the pH is defined as $-\log[\text{HNO}_3]$ and the autoprotolysis constant is $K_s = [\text{EtNH}_2][\text{HNO}_3]$ ($pK_s = 10.0 \pm 0.2$).^{1,2} The neutral pH in EAN thus has a value of 5.0. Acidity scales can then be defined in EAN, and acid-base properties of various species can be described as in water. Strong acids and bases can be defined, as well as weak acids/bases characterized by an acidity constant¹.

Within this framework, since the constitutive strongest acid and base of EAN (*i.e.*, HNO_3 and EtNH_2) are not easy to manipulate in a condensed state at room temperature, we chose other compounds in order to control the pH of the EAN dispersions. The chosen strong acid is benzenesulfonic acid (BSA), already described in literature¹, and the chosen bases are tetramethylammonium hydroxide (TMAOH) and sodium hydroxide. TMA^+ is chosen because it is a classical non-flocculating counter-ion³ for aqueous alkaline ferrofluids, and Na^+ because of its intensive use in water. In order to test the experimental set up and the response of the glass electrode in neat EAN, the procedure described by Benlhima *et al.* was used¹. Growing amounts of a strong base (or acid) solution in EAN (concentration $C = 0.1 \text{ mol L}^{-1}$) were added to the pure ionic liquid, and the electric potentials E were recorded between a glass electrode and a saturated calomel electrode. Results for the bases are plotted in Figure S1. If XOH is a strong base in EAN, the expected reaction with the solvent can be written:



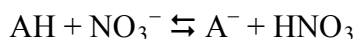
Using the definition of the autoprotolysis constant, the pH of the strong base of concentration C in EAN is:

$$pH = pK_s + \log C$$

The expected response of the glass electrode is $E = cst + RT/(F \ln 10) \log[\text{HNO}_3] = cst - RT/F pK_s - RT/(F \ln 10) \log C$, with cst a constant, F the Faraday constant and RT as usual. Here the experimental linear fit leads to $E_{\text{NaOH}} \text{ (mV)} = -132.1 - 65.4 \log C_{\text{NaOH}}$, and $E_{\text{TMAOH}} \text{ (mV)} = -133.5 - 63.3 \log C_{\text{TMAOH}}$, at $T = 25 \text{ }^\circ\text{C}$ (Fig. S1). Therefore we can conclude that (i) the experimental set-up properly responds and the glass electrode can be used even in pure ethylammonium nitrate where

the water content is inferior to 0.3%_w; (ii) both hydroxides are actually strong bases in EAN, so their pH can be calculated as explained above.

Symmetrically, if AH is a strong acid, its reaction in EAN can be expressed as:



with AH and A⁻ representing, respectively, the protonated and deprotonated forms of benzenesulfonic acid. The pH of a solution of strong acid of concentration C is then defined as: $\text{pH} = -\log [\text{HNO}_3] = -\log C$.

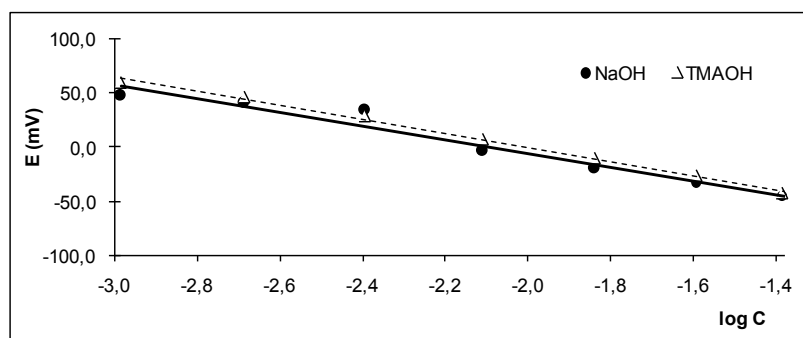


Figure S1: response of the glass electrode in NaOH and TMAOH solutions in EAN (C in mol L⁻¹). See text for the protocol.

For pH measurements in EAN, we prepare calibration buffers of known pH in order to convert the recorded electric potential into pH values as in water : (i) pH = 1.0: a 1 10⁻¹ mol L⁻¹ solution of benzenesulfonic acid (BSA); (ii) pH = 5.4: an equimolar solution of benzoic acid/sodium benzoate (concentration 2.0 10⁻¹ mol L⁻¹); (iii) pH = 9.0: since TMAOH showed a better solubility in EAN than NaOH, we could prepare a 1.0 10⁻¹ mol L⁻¹ solution of such hydroxide, and use it as a pseudo-buffer. These three solutions (BSA, benzoate buffer and TMAOH) were used for calibration prior to any pH measurement.

3. Dissociation constants of citric acid in EAN

We determined the dissociation constants of citric acid in EAN as it is not accessible in literature. Solutions of citric acid H₃Cit 1 10⁻² mol L⁻¹ and of trisodium citrate Na₃Cit 1 10⁻² mol L⁻¹ are prepared in EAN, as well as 1:1; 1:2 and 2:1 volume mixes of these two solutions, and their pH is measured. Table S1 summarizes the results. The acidic dissociation constants are calculated by

solving the first three equations, which are classical approximated formulas. This leads to $pK_1 = 4.1$; $pK_2 = 5.2$; $pK_3 = 6.6$. The last two solutions in Table S1 are used to ascertain the pK values.

In order to validate the use of such simple formulas even for pK_a of close values, we calculated a posteriori the expected pH of the 5 solutions, with the pK_a values listed above as input parameters, without any approximation. The differences between the exact calculated pH and the measured pH were within 0.2 pH unit, as indicated in the last column.

Composition	Measured pH	Approximated Formulae	Exact calculation of pH
$H_3Cit\ 10^{-2}\ M$	3.0	$pH = \frac{1}{2} (pK_1 - \log C)$	3.1
$H_3Cit\ 10^{-2}\ M : Na_3Cit\ 10^{-2}\ M\ (1:1)$	5.2	$pH = pK_2$	5.2
$Na_3Cit\ 10^{-2}\ M$	7.3	$pH = 5.0 + \frac{1}{2} (pK_3 + \log C)$	7.3
$H_3Cit\ 10^{-2}\ M : Na_3Cit\ 10^{-2}\ M\ (1:2)$	5.9	$pH = \frac{1}{2} (pK_2 + pK_3)$	5.9
$H_3Cit\ 10^{-2}\ M : Na_3Cit\ 10^{-2}\ M\ (2:1)$	4.5	$pH = \frac{1}{2} (pK_1 + pK_2)$	4.7

Table S1: pH measured for several ionic solutions in EAN, simplified formulas used and *a posteriori* calculated pH.

4. Dynamic Light Scattering (DLS)

Dynamic Light Scattering was performed on a VASCO particle size analyzer by Cordouan Technologies, an instrument able to evaluate the diffusion coefficient D of particles even in concentrated and dark/turbid media thanks to an original sample cell design. Each sample was analyzed at 25 °C at least 15 times for 60 seconds. Each correlogram was fitted using the Padé-Laplace^{4,5} method. The hydrodynamic radius R_H of the scattering particles was then calculated through the Stokes-Einstein equation $D = k_B T / 6\pi\eta R_H$ (k_B : Boltzmann constant, T : absolute temperature, η : viscosity of the medium). The viscosities are extracted from the literature⁶ (0.891 mPa s⁻¹ for water, 35.3 mPa s⁻¹ for EAN at 25 °C). Refraction indexes for EAN were measured on an Abbe refractometer at 25 °C.

5. Small angle neutron scattering (SANS)

After the standard correction procedures performed with PasiNet (available free of charge at <http://didier.lairez.fr>), the scattered intensity of the nanoparticles was obtained by subtracting from the total scattered intensity the quantity $(1-\Phi)*I_{\text{solvent}}$, where Φ is the volume fraction of nanoparticles and I_{solvent} is the scattered intensity of the solvent (measured independently). In a hydrogenated solvent as EAN, the intensity after subtraction of solvent is, as in water, largely dominated by the nuclear contribution of the nanoparticles⁷. Data treatment and curve fitting were carried out using the NIST software *Igor*⁸.

Table S2 presents the volume fractions calculated from the scattering invariant ($\Phi_{\text{NP_SANS}}$), which are in good agreement with the volume fraction deduced from iron determinations by FAAS (Φ_{NP_χ}). The calculation of $\Phi_{\text{NP_SANS}}$ was carried out using the following values of scattering length density (SLD): $6.96 \cdot 10^{10} \text{ cm}^{-2}$ for Fe_2O_3 , $-5.6 \cdot 10^9 \text{ cm}^{-2}$ for water, and $1.32 \cdot 10^{10} \text{ cm}^{-2}$ for EAN. The pH values measured in water and EAN dispersions are also given, showing no significant dependence on the nature of the counterion.

	Counter-ion	Φ_{NP_χ}	$\Phi_{\text{NP_SANS}}$	pH
WATER	Na^+ (W)	0.013	0.0120	7.5 ± 0.1
	Li^+ (W)	0.012	0.0120	7.5 ± 0.1
EAN	Na^+	0.007	0.0069	6.7 ± 0.1
	Li^+	0.003	0.0032	6.0 ± 0.1
	K^+	0.009	0.0075	6.2 ± 0.1
	Cs^+	0.008	0.0069	6.1 ± 0.1
	NH_4^+	0.008	0.0073	6.5 ± 0.1
	EtA^+	0.007	0.0069	6.1 ± 0.1
	TMA^+	0.007	0.0064	6.5 ± 0.1

Table S2: Characteristics of the dispersions obtained from aqueous ferrofluids and of the dispersions in EAN with different counterions, 2 months after their preparation. $\Phi_{NP,\chi}$: nanoparticles volume fractions from chemical determination (error bar = $\pm 10\%$); $\Phi_{NP,SANS}$: nanoparticles volume fractions from the scattering invariant.

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