

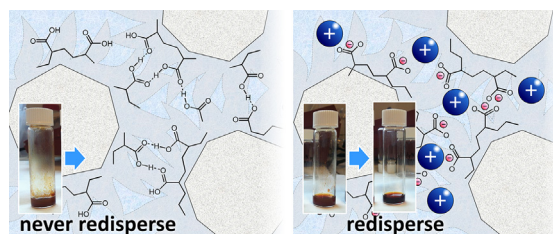
Regular Article

Dispersion mechanism of polyacrylic acid-coated nanoparticle in protic ionic liquid, *N,N*-diethylethanolammonium trifluoromethanesulfonateRyo Kanzaki ^{a,*}, Clément Guibert ^{b,1}, Jérôme Fresnais ^b, Véronique Peyre ^b^a Graduate School of Science and Engineering, Kagoshima University, 1-21-35, Korimoto, Kagoshima 890-0065, Japan^b Sorbonne Université, CNRS, Laboratoire Physico-Chimie des Electrolytes et des Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France

HIGHLIGHTS

- pAA-coated nanoparticle (CNP) was stably dispersed in a protic ionic liquid diethylethanolammonium trifluoromethanesulfonate.
- CNP dispersed when the degree of dissociation of pAA α was $\alpha < 0.1$ or $\alpha > 0.7$.
- CNP aggregation was swelling well and could be reversibly redispersed.

GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Ionic liquids (ILs) are extremely concentrated electrolyte solutions. The ubiquitous presence of ions induces specific behaviors for chemical reactions compared to reactions in water solutions. This is also the case for the stability of colloidal dispersions, for which the DLVO model cannot be applied as the ionic strength is out of the model range. In a previous work, in the protic IL ethylammonium nitrate (doi: <https://doi.org/10.1016/j.jcis.2015.04.059>), we observed an unexpected influence of the pH on the stability of dispersion of maghemite nanoparticles coated with poly(acrylic acid) (pAA).

Experiments: To clarify and generalize these observations, we investigated here the pH response of the dispersion in a second protic ionic liquid with a different acid-base nature, diethylethanolammonium trifluoromethanesulfonate. pH titrations of the dispersions were achieved with an IS-FET electrode and the associated thermodynamic constants determined. The colloid structural properties were examined by small angle X-ray scattering.

Findings: Under acidic or mildly basic condition, a stable dispersion was obtained, i.e., when the degree of dissociation of pAA, α , was $\alpha < 0.1$ or $\alpha > 0.7$. Dispersions form quite dense but reversible aggregates in the intermediate α range. A model for the solvation layer around the particles is proposed and generalizes the former findings.

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1. Introduction

Nano-scale chemistry interconnects the molecular-scopic physicochemistry and the macroscopic world. When nano-sized particles are dispersed in a solution, the visible state reflects

sensitively the chemical function of the surface of the particle, which is submitted to the bulk chemical environment. Indeed, colloidal stability is the result of the balance between attractive van der Waals forces, always present, short ranged and involving the whole volume of the particles, and repulsive forces of various origins related to the surface of the particle, highly related to the solvent chemical environment. This repulsion can stem from intrinsic surface charges inducing electrostatic repulsion, coating molecules preventing the approach of particles etc. Therefore, the precise characterization of the surface is mandatory to properly describe

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colloidal stability. In protic solvents, one key parameter for colloidal stability is thus the pH. It controls the surface potential of the particle by varying the degree of dissociation of the functional group on its surface, such as hydroxyl and carboxyl groups. In water, well established models such as DLVO provide a good description for the stability behavior in relation with the surface charge, but this model cannot hold in all cases and in particular in highly salted conditions. Within this context, ionic liquids form a special class of solvents. They are electrolytes whose melting point is lower than 100 °C [1–4]. Thanks to their interesting properties such as high conductivity, wide electrochemical window, high chemical and thermal stability, and negligible vapor pressure, ionic liquids have received great interest for the last few decades. Illimitable impacts will be produced by the combination of nanoparticle and ionic liquid for its unforeseeable potentiality. Ionic liquids are considered as extremely concentrated electrolyte solutions, and hence, they are supposed not to be “good” solvents for colloidal stability in particular owing to DLVO theory. Despite those predictions, stable dispersions of nanoparticles have already been obtained in various ILs and the mechanisms for colloidal stability are still under investigation. The formation of solvation layers or the use of steric repulsions are often invoked for this purpose [5–7].

In our previous study, we have investigated the pH response of the colloidal stability of maghemite nanoparticles, whose surface is functionalized with polyacrylic acid (coated nanoparticle, CNP), in ethylammonium nitrate (EAN), a typical protic ionic liquid (PIL) [8]. PIL is a subclass of ionic liquids consisting of onium salt, and can be a medium of acid-base reaction [9–16]. Their acid-base properties can be tuned by choosing the constituent anion and cation [13–19]. In EAN, we have evidenced an unexpected behavior of colloidal stability of CNP by varying its protonation state. Dispersions were stable at high pH and flocculated at intermediate pH, as in water, but they surprisingly redispersed at low pH. This was attributed to the formation of hydrogen-bond between the protonated carboxylic acid group on the nanoparticles' surface and the nitrate ion of the solvent. In the present work, we want to validate if this behavior can be generalized to other PILs and clarify the influence of the pH on colloidal stability in PILs. For this purpose, we chose diethylethanolammonium trifluoromethanesulfonate ([DEEAH⁺][TfO⁻]) to disperse the same well-known CNPs. With the help of acid-base titrations, a careful characterization of ionization equilibrium was obtained. The CNP dispersion was examined at the nanometer scale by small-angle X-ray scattering (SAXS), and was related to surface protonation state. We can thus propose a model of ion distribution at the vicinity of the charged CNP that can explain the unexpected colloidal behavior.

2. Experimental section

2.1. Nanoparticle and coating

Maghemite nanoparticles were synthesized by coprecipitation of Fe²⁺ and Fe³⁺ following Massart's method [20,21]. Then, a size-sorting was done to reduce the size polydispersity based on a selective flocculation of the largest particles upon increase of ionic strength by using HNO₃ [22,23]. The size-sorted nanoparticles were then coated with polyacrylate (pAA) by means of the precipitation-redispersion protocol [24,25]. The mean molecular weight of the pAA is 2100 g/mol in its sodium salt (Sigma-Aldrich, used as received), corresponding to 22 carboxylate monomers. The coated nanoparticles (CNP) were redispersed into pH = 10–11 in ammonia-ammonium nitrate buffer and dialyzed with a molecular weight cut off 12–14 kDa membrane for two or three times of 8 h. In Fig. 1, the TEM picture and the size distribution of CNP thus

prepared are shown. The obtained TEM diameter, fitted with a log-normal distribution, is $D_0^{\text{TEM}} = 6.9$ nm with $\sigma = 0.18$. The concentrations of the dispersions (mass fraction of maghemite) were evaluated through iron content (Fe) determination by flame atomic absorption spectrometry (AAnalyst 100, Perkin Elmer).

2.2. Ionic liquid

Aqueous solution of trifluoromethanesulfonic acid (TfOH, Sigma-Aldrich, 99%) was added drop by drop into aqueous diethylethanolamine (DEEA, Sigma-Aldrich, 99.5%) with stirring in –10 °C methanol bath until a mildly acidic sleet-like product was obtained. During the mixing, the temperature of the solution did not exceed –5 °C. Then, this aqueous solution of the onium salt, diethylethanolammonium trifluoromethanesulfonate ([DEEAH⁺][TfO⁻]), was freeze-dried overnight to yield a clear viscous liquid. Hereafter, this liquid salt is referred to as simply PIL. The water content was 2800 ppm (coulometric Karl Fischer determination, Schott TitroLine KF Trace). Density of 1.3357 g/cm³ (Anton Paar DSA5000M) and viscosity of 180 mPa·s at 298 K (with the falling ball method, on an Anton Paar Automated Microviscometer AMVn) compare well with already published values [26]. Refraction index at 656 nm (on the Arago refractometer from Cordouan technologies) was 1.4179 at 298 K.

2.3. Potentiometric titration

Potentiometric titration was carried out with IS-FET electrode (HORIBA 0040-10D). The output potential of IS-FET, E , obeys the Nernstian equation.

$$E = E_0 + \frac{(\ln 10)RT}{F} \log \left(\frac{[\text{H}^+]}{\text{mol dm}^{-3}} \right) \quad (1)$$

where E_0 is the practical standard electrode potential, and R , T , and F are the gas constant, temperature, and Faraday constant, respectively. $[\text{H}^+]$ is the concentration of the solvated proton in the PIL. IS-FET was confirmed to work well in the PIL obeying Eq. (1) by the separate titration of the strong acid TfOH with the strong base DEEA in PIL. Then, 1 cm³ of the CNP dispersion in PIL containing an excess TfOH was titrated with the basic DEEA solution of the PIL using a 500 mm³ micro syringe ([DEEA] ca. 0.4 mol dm⁻³). For the sake of reproducibility, titrations were carried out three times with different CNP concentrations (mass fraction of maghemite $\Phi_w = 0.50\%$, 0.74%, and 1.17%).

2.4. Small angle X-ray scattering (SAXS) measurements

Dispersions and suspensions were analyzed by SAXS measurements on the SWING beamline of the synchrotron SOLEIL (Saint Aubin, France). The beam energy of 7 keV, corresponding to $\lambda = 1.77$ Å, is chosen to avoid X-rays absorption by iron. Two configurations were used, giving access to the scattering vector range $3.0 \times 10^{-3} \text{ \AA}^{-1} < Q < 0.4 \text{ \AA}^{-1}$. Standard correction procedures were applied for sample volume, empty cell signal subtraction and detector efficiency to obtain scattered intensity in absolute unit (cm⁻¹). Such reduction of data was done using the software Foxrot[®]. Scattering length densities are $40.62 \times 10^{-6} \text{ \AA}^2$ for maghemite, $9.33 \times 10^{-6} \text{ \AA}^2$ for water and $11.74 \times 10^{-6} \text{ \AA}^2$ for PIL.

3. Results and discussions

3.1. Dispersion of nanoparticle in ionic liquid

CNP were successfully dispersed in the PIL by adding 1–3 mL of aqueous CNP dispersion ($\Phi_w \approx 0.5\%$) into 1 mL of basic PIL containing a small excess of DEEA (checked by dropping on a

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