Ionic magnetic fluids in polar solvents with tuned counter-ions

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ABSTRACT

The aim of the present study is to propose a new reproducible method for preparing colloidal dispersions of electrostatically charged nanoparticles (NPs) in polar solvents with different kinds of counter-ions. Maghemite NPs are here dispersed in solvents of different dielectric constant, namely water, di-methylsulfoxide (DMSO) and an ionic liquid, ethylammonium nitrate (EAN). If the existence of a NP superficial charge happens to be necessary for the colloidal stability of the dispersions in these three solvents, the standard DLVO theory cannot be used any more to describe the colloidal stability in EAN. The structure of the dispersions and the strength of the interparticle repulsion are investigated by small angle X-ray scattering measurements, in association with Ludwig–Soret coefficient determinations. Specificities, associated to the nature of the counter-ions are identified in this work on the colloidal stability, on the interparticle repulsion and on the Ludwig–Soret coefficient.

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1. Introduction

Ionic dispersions of electrostatically charged nanoparticles (NPs) in polar solvents bring potential applications in terms of producing electricity from an external heat flux. Indeed under a thermal gradient $\vec{\nabla} T$, the thermal drift of ionic species induces an internal electric field $\vec{E} = S_e \vec{\nabla} T$ (Seebeck effect) [1–3] and also concentration gradients leading to the well-known Ludwig–Soret effect [4–7]. In polar media, thermoelectric and thermophoretic properties are then interconnected through Eastman entropies of transfer $\hat{S}_i$, which characterize the individual interaction of each species (i), present in the dispersion, with the surrounding medium [1,8–10]. A positive (resp. negative) value of $\hat{S}_i$ is associated to a thermophobic (resp. thermophilic) behavior of the considered species.

Among polar solvents, there are several good potential candidates to develop such thermoelectric applications. We select here three of them, water with a permittivity $\epsilon_r = 80$, dimethyl sulfoxide (DMSO) with $\epsilon_r = 46$ and also ethylammonium nitrate (EAN), which is a well known ionic liquid (IL) with $\epsilon_r = 26$ (at 25 °C).

The goal is then to be able to control, in a reproducible manner, the quantity and the nature of all the ionic species in the dispersions contributing to Seebeck (and Ludwig–Soret) effect(s), including all the free ions and electrostatically charged NPs dispersed in the medium. We propose here a method to prepare controlled magnetic fluids in these three solvents, method that can be extended to other ones in the future. One of the main difficult points is to tune (and in the case of IL, understand the origin of) colloidal stability in these polar solvents. That is why, we choose here to disperse electrostatically charged maghemite (γ-Fe$_2$O$_3$) NPs, as quite a lot is already known about their dispersions in water [11]. The method allows to probe various kinds of counter-ions, finely tuning the quantities introduced, in order to point out ionic specific effects on the colloidal stability and to probe various parameters inducing either a thermophilic or a thermophobic NP behavior.

In the first section, we present the method of preparation of these dispersions, the properties of the selected solvents and the nature of the used counter-ions. Only dispersions with an inter-particle interaction more repulsive than hard spheres (HS) (in terms of osmotic second virial coefficient) are selected here thanks to a small angle X-ray scattering (SAXS) probing. In the second section, the measurement of the Ludwig–Soret coefficient S_T using a simple Rayleigh forced scattering method based on the illumination of a grid is presented. We finally discuss in the third section, the separate influence of several colloidal parameters on S_T, and show in particular how the nature of the counter-ion may change its sign and influence of NP Eastman entropy of transfer $\hat{S}_{NP}$.

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2. Magnetic fluid samples

2.1. Synthesis

Following the method of Massart (described in [12]), precursor magnetic fluids, based on maghemite NPs, are prepared by co-precipitation in aqueous alkaline medium of ferric and ferrous salts. To obtain maghemite NPs (and not magnetite or a partially oxidized magnetite) with a long-term chemical stability even in strongly acidic medium, a chemical oxidation is performed at 80 °C with $Fe(NO_3)_3$. After several washing, the positively charged NPs are dispersed in an aqueous nitric acid solution (thus with NO_3^- counterions) at a pH ranging between 1.5 and 2. By adding a large quantity of strong base, the NP charge becomes negative, thanks to the acid–base properties of the superficial hydroxyl groups. The NPs can then be redispersed in an alkaline medium, usually with tetramethylammonium (TAM^+) counterions. To disperse them at neutral pH where superficial hydroxyl groups do not provide any charge to the NPs, a subsequent NP coating by citrate species can be performed, the standardly used counterion is then Na^+ [13].

To precisely control the superficial charges of the NPs and the concentration of ions in the solvent around them, is not easy. In this preparation process, it is usually done after the synthesis, by using several kinds of titration methods [14,15] and dialysis is usually undertaken to modify the salt concentration [16]. Starting from the precursor colloid in acidic medium, other types of magnetic fluids can be obtained [14] by various steps of salt addition, precipitation, washing, redispersion. Even if these methods are globally efficient, they present serious weaknesses. First, it is not easy to check if some initial (and undesired) nitrate counterions are still in the dispersion. Second, at the end of the process, the total amount of salt is not precisely known and has to be determined. Third, it is very difficult to prepare exactly twice the same sample.

We propose here to start from flocculated dispersions at the point where the average NP charge is zero and where all extra-ions have been removed by repeated appropriate washing. All the water molecules that can be removed are then eliminated by repeated washing with dry organic solvents. Then the NPs are charged in the chosen medium (see further on), following a controlled and reproducible process. It is here applied either to NPs coated with hydroxyl groups (zero NP charge at pH 7) or to citrate coated NPs (zero NP charge at pH 2).

An ultracentrifugation of the dispersion ($2 \times 10^5 g$) is performed to obtain magnetic fluids of typical volume fraction 4%. Assuming that ultracentrifugation does not perturb local equilibria around the NPs, the concentrations of free co-ions and counterions are determined by conductivity measurements in the supernatant (except in EAN, concentration of counterions is then determined by flame atomic absorption spectroscopy). As the total quantity of counterions introduced is known, the density of structural surface charge is then deduced [17], without any potentiometric determination [14,15]. The dynamic effective charge of the NPs $e\xi_0$ is determined by the measurement of NP electric mobility (except in EAN) and mass diffusion coefficient at infinite dilution by quasi-elastic light scattering.

2.2. The chosen solvents and their properties

Among the polar solvents that we choose here to redisperse the NPs, water and DMSO presents similarity in that sense that "standard" (=DLVO type) electrostatic stabilization is known to be possible [10]. They are miscible in all proportions at room temperature. The permittivity of water ($\epsilon_r=80$) is roughly twice that of DMSO ($\epsilon_r=46$). It allows solvation of ionic species even if it is slightly less favorable in DMSO.

DMSO is a dipolar aprotic solvent, which is H bond acceptor and solvates better cations than anions. It is recyclable and biodegradable. This green grade solvent has a low toxicity and is used in pharmacological applications. It is possible to prepare stable dispersions with a long term stability (15 years for acid ones) with positively charged NPs (hydroxyl surface group – alkaline medium) or negatively charged NPs (either hydroxyl groups – acidic medium or citrate groups – neutral medium).

For its part, ethylammonium nitrate (EAN) is a room temperature IL. It is a molten salt only constituted of ions, with $\epsilon_r=26$ [18]. ILs [19,20] present numerous applications in the fields of NP synthesis [21], catalytic materials [22] and dye-sensitized solar cells [23]. EAN is used as a model-system to identify the parameters to be tuned for controlling colloidal stability of dispersions in ILs. A pH scale going from 0 to 10 can be defined in EAN [24], and molecules of EAN form a network of hydrogen bonds, similar to water molecules. However DLVO model of colloidal stability is null and void in this solvent only constituted of ions [25]. It has been shown that with a sufficient superficial charge, maghemite NPs can be dispersed in EAN [26]. Another study with citrate-coated NPs has shown that a short range interparticle repulsion, most probably produced by an ionic structuration around the NPs, can stabilize NP dispersions [27,28]. However the tuning is delicate, for example with too large NPs at a too large concentration a phase separation in two liquid phases is observed [28].

In these three solvents, specific effects related to the nature of the counter-ions exist. Stable dispersions cannot be obtained with all counterions in all polar solvents. We only take few examples here.

In acid DMSO, nitrate counterions NO_3^- cannot be used however perchlorate counterions ClO_4^- perfectly work [10,17,29]. In acid water, both ClO_4^- and NO_3^- can be used, however in the same conditions of pH and concentration, interparticle NP repulsion with ClO_4^- is less strong than with NO_3^- [17]. In water at pH=7 with citrate-coated NPs, a large spectrum of monovalent counterions can be used, for example lithium Li^+, sodium Na^+, ethylammonium EA^+, tetramethylammonium TMA^+ and tetrabuthylammonium $TBuA^+$ [17]. In EAN with citrate-coated NPs, a more efficient stabilization is obtained with Na^+ than with Li^+ et EA^+ [27,28].

2.3. The selected samples

We only consider here NP dispersions with an interparticle repulsion, which is (on average) stronger than that of hard spheres. Small angle X-rays scattering (SAXS) experiments give the opportunity to probe this point [16]. The SAXS experiments are performed at the SOLEIL synchrotron (SWING beamline, Gif-sur-Yvette, France) at a beam energy 15 keV in the range of scattering vector 3.2×10^{-3} Å^{-1} $< Q < 4 \times 10^{-1}$ Å^{-1}. Fig. 1 plots the SAXS intensity (normalized by the NP volume fraction) as a function of Q for aqueous samples of Table 1, based on the same citrate-coated NP with a volume fraction 3.5–3.7%. Fig. 1 compares the scattered intensities to the form factor $F(Q)$ of the NPs (deduced thanks to a Zimm plot) multiplied by the NP contrast $\Delta\rho^2$ [17].

The $I(Q)$ shapes of Fig. 1 show that the interparticle interaction is on average strongly repulsive for these samples. An easy way to quantify this repulsion is to determine an experimental compressibility χ_{exp} of the NPs system thanks to:

$$\chi_{\mathrm{exp}} = \frac{I(Q=0)/\varPhi}{\Delta\rho^2 F(Q=0)} \tag{1}$$

Here both $I(Q=0)$ and $F(Q=0)$ are approximated by their value at $Q = 3.2 \times 10^{-3}$ Å^{-1}. The measured χ_{exp} values are collected in Tables 1 and 2.

For a system of hard spheres, the volume fraction dependence