



# Characterization and magnetic properties of nickel and nickel-iron nanoparticle colloidal suspensions in imidazolium-based ionic liquids prepared by magnetron sputtering

A. Cigáň<sup>a</sup>, P. Lobotka<sup>b</sup>, A. Dvurečenskij<sup>a</sup>, M. Škrátek<sup>a</sup>, G. Radnóczy<sup>c</sup>, M. Majerová<sup>a</sup>, Z. Czigány<sup>c</sup>, J. Maňka<sup>a,\*</sup>, I. Vávra<sup>b</sup>, M. Mičušík<sup>d</sup>

<sup>a</sup> Institute of Measurement Science, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia

<sup>b</sup> Institute of Electrical Engineering, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia

<sup>c</sup> Centre for Energy Research, Hungarian Academy of Sciences, H-1525, Budapest, Hungary

<sup>d</sup> Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia

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## ABSTRACT

Colloids of Ni and Ni-Fe nanoparticles in two imidazolium-based ionic liquids were prepared by magnetron sputtering of nickel and co-sputtering of nickel and iron, respectively, on the surface of the ionic liquids. The liquids consist of the same cation 1-butyl-3-methylimidazolium [BMIM] and two different anions: hexafluorophosphate [PF6] or bis(trifluoromethylsulfonyl)imide [Tf2N]. The nanoparticle preparation method was based on extremely low vapour pressures of the ionic liquids, which allowed them to be used in vacuum. Magnetic properties of the metal nanocolloids (NCs) and the pure ionic liquids were analysed in detail, including the effect of ageing over a period of more than 30 months. The NCs were studied by TEM microscopy, UV–Vis spectroscopy and SQUID magnetometry. They were stable in time. No sedimentation or agglomeration of nanoparticles was observed after more than 24 months. The ionic liquid ions play more than the role of a surfactant, e.g. magnetic data gave evidence of a strong interaction between the ionic liquids and metal nanoparticles.

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## 1. Introduction

Ionic liquids (ILs) (or more precisely Room-Temperature Ionic Liquids - RTILs) are solely composed of ions (often with delocalized charges). They are liquid at room temperature and at temperatures  $\leq 100$  °C. ILs have unique physical-chemical properties: high ionic conductivity, non-flammability, high thermal and chemical stability, high polarity, and negligible vapour pressure. Nano-range ordering exists in ILs, especially in those that are imidazolium-based. The ordering gives rise to aggregates composed of cations and anions. Neutron diffraction studies on some ILs indicated that the charge ordering endures in the liquid phase. Furthermore, molecular dynamics calculations proved that the ion nanoclusters remain locked in place and the cations and anions cease to behave as discrete units but act rather as larger supermolecules [1]. The

ordered structures of cation and anion chains are formed as a result. Such ordering stems from typical interactions between the cations and anions, including Coulombic, van der Waals, and other specific interactions, such as H-bonding [1–3]. There is evidence that ILs interact relatively strongly with the surface of colloidal metal nanoparticles (NPs). Contradictory conclusions disregarding various properties of ILs (differing in the choice of cations or anions) were made as regards to IL ions adjacent to nanoparticle surface. It is suggested that for isolated NPs in ILs containing hexafluorophosphate anion [PF6], the interaction between the surface metal atoms and fluorine atoms is more pronounced [1] and that the interaction between cations and anions in the IL itself is dependent on the length of the alkyl chain of the cation (e.g. [BMIM] in [BMIM.PF6]). If the alkyl chains are short, as it is the case of [BMIM], the [PF6] anions interact not only with the ring of the cation but also with alkyl chains [4]. Dupont et al. in Ref. [1] reported the application of ILs to the formation and stabilization of transition metal NPs, and also structural and surface properties of the systems. They claim that very small metal NPs (1–10) nm are

\* Corresponding author.

E-mail address: [jan.manka@savba.sk](mailto:jan.manka@savba.sk) (J. Maňka).

undoubtedly stabilised thanks to positive charge on their surface, which is ultimately induced by the adsorption of the anionic IL species on the coordinatively unsaturated, electron-deficient, and initially neutral metal surface.

Although ILs are used in chemistry for many years (the term “green chemistry” was coined about 20 years ago), their application is still rare in the fields of physics or materials science. As late as 2006, Torimoto et al. [5] performed the first experiment with ILs, in which they used their exceptional property: very low vapour pressure of about  $10^{-11}$  mbar. The authors sputtered gold on the surface of an IL in a vacuum deposition machine, which was normally used for the deposition of thin films. The IL played the role of a “liquid substrate”. They surprisingly acquired a colloid containing well-dispersed 6 nm gold NPs with a remarkably narrow size distribution, because a thin Au film was expected to form, as such films were obtained if silicon oil or grease were used as the “substrate”. They subsequently succeeded in preparing composite Au-Ag NPs from a composite sputtering target [6].

We used the same procedure as that reported in Ref. [6] to prepare nickel and Ni-Fe NPs using two ILs: [BMIM.PF6] and [BMIM.Tf2N]. The main motivation was to study magnetic properties of the pure ILs and possible effects of the ILs on magnetic properties of the prepared NPs in the colloids. It is necessary to point out that our NCs, although they contain a magnetic material, differ from the so-called magnetic ionic liquids, e.g. [BMIM.Fe<sub>2</sub>Cl<sub>7</sub>], where every anion contains two iron atoms. Our NCs could be described rather as magnetic nanoparticles embedded in an ionic liquid matrix. We presume that the paper brings the first detailed characterization of magnetic properties of colloids of metal nanoparticles in the imidazolium-based ILs.

More detailed information on synthesis methods and applications of free or NPs incorporated of ILs or polymeric ionic liquids, can be found in the papers [7–11].

## 2. Materials and methods

### 2.1. Sample preparation

For the NCs preparation, we used an UHV vacuum machine with a load-lock chamber, pumped by turbomolecular pumps and equipped with two tilted 2-inch magnetrons forming a common V-shaped plasma (the angle between their axes was about 75°), enabling independent and fully controlled deposition of materials from two sputtering sources. This arrangement ensures perfect mixing of both materials (Ni and Fe in our case) within the common plasma region. This leads, together with sample holder rotation, to very good thickness homogeneity of the deposited film. Typical inhomogeneity at the level of the sample holder is only 1% on the diameter of 100 mm. The base pressure of the apparatus is  $\sim 10^{-8}$  mbar.

The metals were deposited onto an ionic liquid (2 or 5 ml) poured into a Petri dish with a diameter of 60 mm situated about 40 mm beneath the plasma in order to avoid IL radiation damage. Before deposition, the ILs (of 99% purity, purchased from IoLiTec Ionic Liquids Technologies GmbH) were kept overnight in vacuum ( $\sim 10^{-6}$  mbar) in the load-lock chamber in order to get rid of the residual volatile solvents and humidity present in the ILs. The sputtering rates of Ni and Fe magnetrons were calibrated in separate experiments. Then, the power ratio of both magnetrons was set to 80:20, which corresponded to the composition of permalloy (Ni<sub>0.8</sub>Fe<sub>0.2</sub>). The sputtering time varied from 5 to 90 min.

### 2.2. Characterization

In this way, we prepared several NCs. All of them were

investigated for the presence of NPs by UV–Vis spectrophotometry. UV–Vis spectra were measured by a Shimadzu UV-1650PC dual beam spectrophotometer.

TEM micrographs were acquired by JEOL-1200EX or Philips CM20 electron microscopes. The samples for TEM observation were usually prepared by short heating of a tiny NC drop that was carefully placed on an amorphous carbon membrane suspended on a copper mesh.

The temperature dependences of the DC magnetic moment of the pure ILs and metal NCs were measured by a Quantum Design SQUID magnetometer MPMS XL-7. The dependences were measured in the zero field cooling (ZFC), and field cooling (FC) mode. The ZFC procedure consists of cooling the sample from the room temperature to  $\sim 2$  K in the zero applied magnetic field,  $H = 0$ . Thereafter,  $H$  was set to 20 Oe or 2 kOe and the magnetic moment of the sample was measured at an increasing temperature up to 300 K. After that, the FC characteristics were obtained by the measurement of the magnetic moment at a decreasing temperature at the magnetic field. More details about magnetic measurements (e.g. the sample preparation, the determination of metal content in NCs) are in the Supplementary information section.

The DC mass magnetization  $M(H)$  was measured at 300 K, 5 K or 1.8 K. Every magnetization curve at the given temperature consisted of two loops; the first one was measured at a weak magnetic field, and the second one was measured up to 70 kOe immediately after the first curve was finished.

For a detailed study of magnetic properties of Ni and Ni-Fe NPs colloids, the molar magnetic susceptibility,  $\chi$ , per formula unit (f.u.) was determined after correcting the measured data for the sample holder, diamagnetism of pure IL or inner shell electrons of metal atoms in the ILs, and also for temperature independent paramagnetic/diamagnetic contributions. The diamagnetism (DM) of pure IL was evaluated also using the tabulated values of diamagnetic susceptibilities of cations and anions given by Bain and Berry [12]. The temperature independent contributions of magnetic susceptibility was estimated from experimental  $\chi T$  vs.  $T$  dependences as a slope of the linear fit of the measured data in the temperature range of (50–200) K, taking into account the effect of the glass transitions occurring in the ILs above 200 K.

## 3. Results and discussion

Surprisingly, right after the metal deposition on the surface of ILs, the obtained colloids were completely black. Then, the solution started to clarify (without any external intervention - agitation or sonication or heating) and after several hours, it became yellowish (see Fig. 1). It must be noted that the pure ILs are transparent and colourless, as can be seen in Fig. 1 on the left.

In our understanding, the sputtered metallic material during the deposition forms NPs on (or just below) the IL surface, but they immediately coagulate and form agglomerates of NPs (as can be seen in the Supplement, Figs. S1 and S2), which gives the black appearance to the solution due to the agglomerates (of the size  $> 100$  nm) that absorb the light quite efficiently. After several hours, remarkable disentangling and dissolving abilities of IL [13] cause disassembling of the agglomerates to single NPs, the NC clarifies and becomes yellowish. There is no return of agglomeration for more than two years, which is superior to other types of NCs that are ethanol- or water-based. Moreover, IL-based NCs are special in the sense that ions from IL itself play the role a surfactant.

### 3.1. TEM micrographs

In Fig. 2, TEM micrograph of the Ni-Fe NPs prepared in [BMIM.Tf2N] is shown. The average size of the NPs is about 12 nm.

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