VIP Nanoparticles in Ionic Liquids

DOI: 10.1002/ange.201103096

Solvation and Stabilization of Metallic Nanoparticles in Ionic Liquids**

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Some room-temperature ionic liquids can hold stable suspensions of nanoparticles without additional surface-active agents[1] through mechanisms of solvation and stabilization that are not understood at present, particularly for metallic nanoparticles. These systems are relevant for applications in catalysis, lubrication, electrochemical devices, and chemical processes. We address this issue by studying the interactions and ordering of ionic liquids around metallic nanoparticles using molecular dynamics simulations, which is a suitable tool because the arrangement of the ions around a 2 nm particle is difficult to observe experimentally. The fundamental obstacle to modeling resides in the description of the interactions between metals and ionic fluids, a problem not only for nanometer-scale objects but for extended surfaces as well. In this work we devised an original strategy to represent accurately the molecular interactions and gain insight into the solvation and stabilization mechanisms of nanoparticles in ionic liquids.

Experimental studies of metallic nanoparticles in ionic liquids provide different clues about the stabilization of the colloid. Some postulate an electric double layer (the Deryagin–Landau–Verwey–Overbeek model) in which a first solvation shell of anions surrounds the metal cluster, followed by a less ordered layer of cations, and so on.[2] Other studies present evidence of close interactions of the nanoparticles with the cations, through deuterium exchange on positively charged imidazolium rings[3] and through surface-enhanced Raman spectroscopy on gold nanoparticles in imidazolium liquids.[4] Correlations have been established between the size of metallic nanoparticles synthesized in situ with the anion volume.[5] Still other studies suggest that nanoparticles are solvated in nonpolar regions formed by aggregation of the hydrophobic alkyl side chains of the ions, as there is a relationship between the length scale of the structural heterogeneities of the ionic liquid[6] and the size of nanoparticles synthesized therein.[7]

Measurements of the thickness of the electrostatic double layer of ionic liquids at metal surfaces have been performed by different techniques. Atomic force microscopy of two ionic liquids $[C_2C_1im][Ntf_2]$ and $[C_4C_1pyrr][NTf_2]$ at the Au(111) surface[8] yielded a surface layer with a thickness of 6 Å. Capacitance and Stark effect measurements on $[C_4C_1im][BF_4]$ at a Pt surface[9] yielded an interfacial layer with one-ion thickness of 3.3 to 5 Å. This is consistent with the Debye length of the order of 1 Å estimated for an electrolyte with a concentration around 4 or 5 M, such as a pure ionic liquid, and constitutes an argument against DLVO-type stabilization. However, measurements on macroscopic flat surfaces may not be immediately transposed to nanoparticle suspensions.

Suspensions of metallic nanoparticles in an ionic liquid are governed by three kinds of molecular interaction: ion–ion, metal–metal, and metal–ion, which are all nontrivial and each offers its own difficulties to a description. We adopted an atomistic description for both the nanoparticle and for the ionic liquid, providing a high level of detail regarding the interactions and conformations. We considered a ruthenium nanoparticle in $[C_4C_1im][Ntf_2]$, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (Figure 1). This system was chosen in the context of hydrogenation catalysis using metallic nanoparticles.[10]

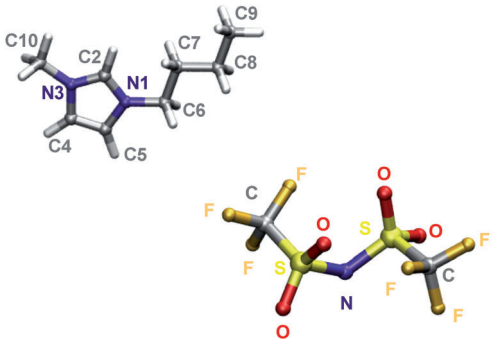

Figure 1. Molecular structure of the $[C_4C_1im][NTf_2]$ ionic liquid.

Ionic liquids are composed of large, flexible organic ions, usually with delocalization of electrostatic charge and with nonpolar side chains in their molecular structure, leading to structurally and dynamically complex liquids. The highly cohesive charged groups tend to segregate from the side chains if these are long enough,[6a] resulting in liquids with a heterogeneous structure at the nanometer scale that offer both ionic and nonpolar solvation environments.[11] In $[C_4C_1im][Ntf_2]$, both the cation and the anion are flexible molecular entities, with the electrostatic charge distributed over several atoms: positive charge mainly on the imidazolium ring in the cation, and negative charge on the nitrogen and the four oxygen atoms of the anion. Also, both ions contain weakly polar groups, notably the butyl side chain on

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[**] We thank Dr. Ekaterina Izgorodina (Monash University, Australia), Dr. Patricia Hunt (Imperial College London (UK)), and Dr. Bruno Chaudret (LCC CNRS Toulouse, France) for fruitful discussions and advice. This work was supported by the Agence National de la Recherche, France (CALIST) and by the supercomputing centers IDRIS (France) and CESGA (Galicia, Spain). A.S.P. was a recipient of an Ánxeles Alvariño fellowship from Xunta de Galicia, Spain.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201103096.

the cation and, to a minor degree, the CF_3 groups of the anion. Therefore, a too simplified representation of the ions by, say, spherical models with integer point charges would not be adequate to convey the balance of electrostatic and dispersive interactions present in ionic liquids, or their rich conformational behavior. Interactions within the ionic liquid were described by a classical, all-atom force field[12] specifically parameterized for the ionic liquid studied herein. This model uses fixed electrostatic charges, therefore polarization in not specifically included. This is an identified drawback when calculating dynamic properties of ionic liquids, although for equilibrium properties and liquid-state structure the effect of inclusion of explicit polarizability is less significant.

Metal–metal interactions are described by a model of the Finnis–Sinclair type,[13] a density-dependent potential derived from the tight-binding approximation, which can describe bonding of metal atoms in terms of the local electron density, and is suitable to calculate the properties of metals, including ruthenium.[14]

Metal surfaces are conducting, thus highly polarizable, and their interactions with charged entities incorporate many-body effects that are expected to be non-negligible even for small clusters of metal atoms. A specific model of the metal–ionic liquid interactions was developed here based on quantum chemical calculations. Polarization of the metal surface by the ions was also taken into account. This model is one of the main original contributions of the present work and will be described in some detail.

We employed density functional theory (DFT) methods to determine the interactions between the ionic liquid and the Ru(0001) surface of a cluster of metal atoms. We considered three different fragments of the ionic liquid: 1,3-dimethylimidazolium ($C_1C_1im^+$), bis(trifluoromethanesulfonyl)amide (Ntf_2^-), and *n*-butane (C_4H_{10}). The adsorption of *n*-butane on transition-metal surfaces is a typical weak physisorption originating in van der Waals dispersive and repulsive interactions between the nonpolar molecule and the metal surface. DFT methods tend to account poorly for dispersion interactions,[15] but in recent years an important effort to improve this situation was undertaken by several groups, with specially parameterized functionals proposed to describe noncovalent interactions and the dependence of the attractive energy at long range. In the present study we considered several of these functionals, namely B97-D, a generalized gradient approximation (GGA) functional including an explicit dispersion term in C_6r^{-6},[16] and M06 L, which is a local *meta*-GGA functional.[17]

The calculations were carried out using Gaussian 09,[18] with the TZVP basis set[19] and the Stuttgart/Dresden ECP28MWB effective core potential[20] for ruthenium. The basis set superposition error was corrected by the counterpoise technique.[21] The interaction energy at a given distance r of the closest atom of the molecular fragment from the ruthenium cluster, and for each orientation, is the difference between the energy of the pair minus that of the isolated fragment and metal cluster. In preliminary calculations, we tested the performance of both B97-D and M06 L functionals by determining the adsorption energy of *n*-butane on a cluster of 20 Ru atoms. Experiment show that propane[22] and cyclobutane[23] adsorption energies on Ru are of about $-40\ kJ\,mol^{-1}$. We can estimate that for *n*-butane the adsorption energy is similar. The adsorption energy obtained with B97-D and M06 L are -48 and $-29\ kJ\,mol^{-1}$, respectively. Considering that the lateral intermolecular interaction energy can be as large as 25%, as evaluated for the adsorption of *n*-butane in several metallic surfaces,[15a] we conclude that the energies obtained with M06 L are in better agreement with experiment, so we chose this functional for the present study.

Sections of the potential energy surfaces are represented in Figure 2, where it is shown that the calculated adsorption energy of the three fragments of the ionic liquid range from $-30\ kJ\,mol^{-1}$ for *n*-butane to $-100\ kJ\,mol^{-1}$ for $C_1C_1im^+$. The discrete points of DFT energy were fitted by a classical atom–atom interaction potential function to be used in molecular dynamics simulations of a ruthenium nanoparticle solvated in ionic liquid. For simplicity, hydrogen atoms in the ionic liquid fragments are not explicit and are incorporated in a united-atom description of the interactions with the metal. The potential of interaction represents the potential energy surface correctly and the parameters obtained are given in the Supporting Information.

To account for the polarization of the metal surface by the ions we employed a Drude-rod model,[24] in which a polarizable atom is obtained by incorporating in each metal atom a freely rotating dipole composed of two opposite charges q and $-q$ constrained at a given distance l_0 and having mass m. Values for these parameters were proposed[24] to reproduce the interaction energy between a charged entity and a conducting surface. Thus, the surface of the metal nanoparticle can be charge-polarized.

The development of an interaction model between an ionic liquid and a metal surface is an important result of this work, which is applicable not only to nanoparticles but also in general whenever ionic liquids interact with metal (ruthenium) surfaces. The model is expected to represent the interactions independently of the surface topology, defects, or roughness, as it is an atom–atom model. The methods adopted herein can be used to develop interaction models for other metals, or non-metals, and ionic liquids.

To study the mechanism of solvation and stabilization of ruthenium nanoparticles in an ionic liquid, two nanoparticles of about 2 nm diameter consisting of 323 Ru atoms were simulated. One nanoparticle is fully crystalline with the hcp structure, whereas the other underwent a process of simulated annealing, resulting in a crystalline core and an amorphous external shell. Both structures are plausible and supported by some structural evidence.[25] Systems containing one ruthenium nanoparticle (crystalline or amorphous-shell) and 828 ion pairs of $[C_4C_1im][Ntf_2]$ were simulated in periodic cubic boxes, as shown in Figure 3, using the DL_POLY molecular dynamics package.[26] The initial configuration was a low-density configuration containing only the ionic liquid. Equilibrations of this solvent took 500 ps at constant NpT ($T = 423$ K, $p = 1$ bar) with a timestep of 2 fs. Once the equilibrium density was reached, the nanoparticles were inserted in the center of the simulation boxes (the overlapping ions removed in pairs) and a 500 ps equilibration period followed. Then,

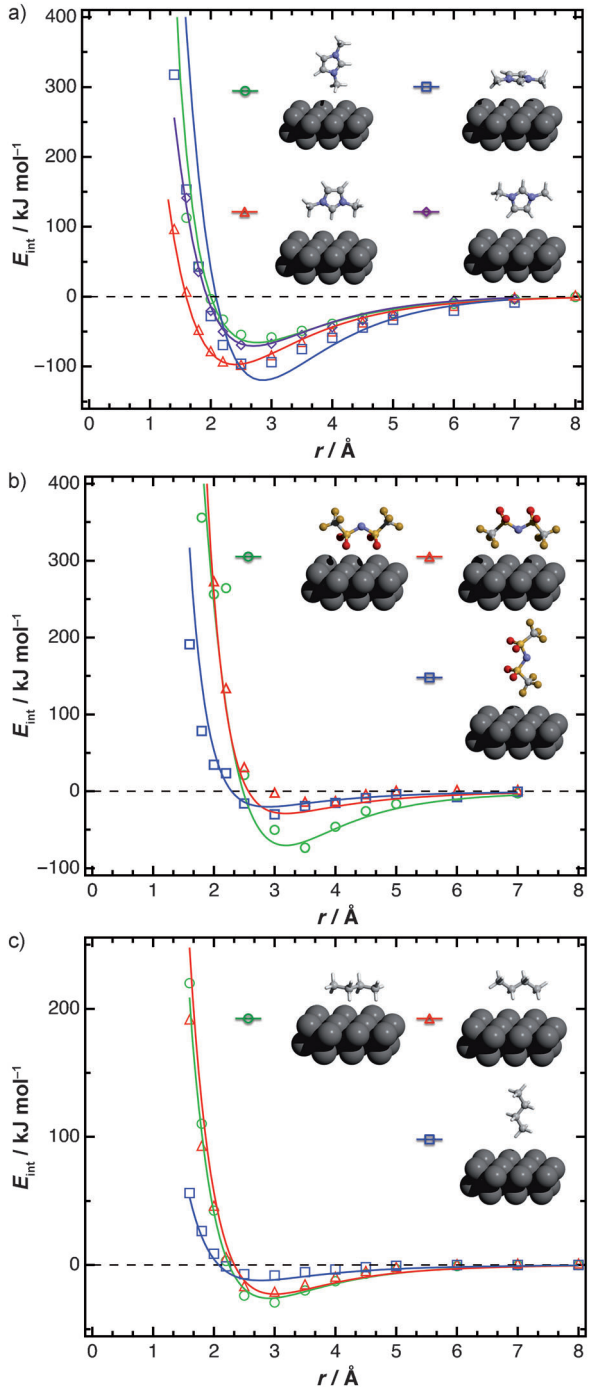

Figure 2. Interaction energies of a) $C_1C_1im^+$, b) Ntf_2^-, and c) *n*-butane on Ru(0001) as a function of separation *r*, evaluated between the closest atoms of the fragment and cluster, for several orientations of the fragments calculated using M06 L/TZVP,ECP28MWB (BSSE). Lines represent the fit of the calculated interaction energies to a classical intermolecular potential of Born–Huggins–Meyer analytical form between each atom of the metal cluster and united-atom sites in the fragments of the ionic liquid.

molecular dynamics runs of 1 ns were performed from which several thousand configurations were sampled, yielding representative averages of structural quantities.

The aim of this work was to elucidate the mechanism solvation of ruthenium nanoparticles in an ionic liquid. The

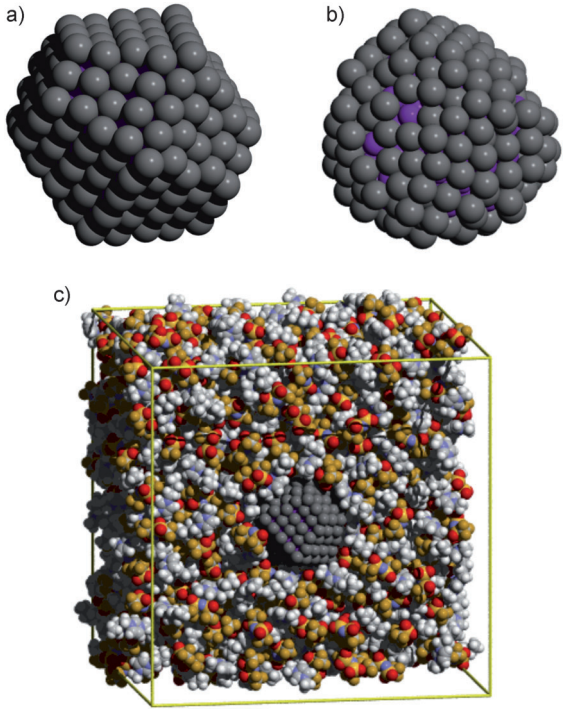

Figure 3. a) Crystalline and b) amorphous-shell models of ruthenium nanoparticles; c) a sliced view of a cubic simulation box with the nanoparticle solvated in the ionic liquid (828 ion pairs). The sides of the simulation boxes are approximately 75 Å long and the systems contain close to 30000 atoms. The size of the system is large enough to avoid influence of a nanoparticle on its periodic images.

structural picture (Figure 4) corresponds to an interfacial layer of ionic liquid that is essentially one ion think. The regions of highest probability of presence of cation head groups and anions coincide in the vicinity of the nanoparticle, therefore charge separation is small in the ionic liquid. This is confirmed by the plots of radial charge distribution that indicate an electrostatic interface layer of 4–5 Å. After a first small positive peak, one large negative and then one large positive peak form the interfacial layer. The multiplicity and spread of peaks depends on the nonspherical shape of the nanoparticles: atoms of the ionic liquid near the center of faces are found at a shorter distance from the center of the particle than atoms close to the edges and vertices. This effect is less marked for the amorphous-shell nanoparticle.

The terminal atoms of the alkyl side chain of the imidazolium cations are found further away from the nanoparticle, at distances around 18 Å from its center. This is a result of the stronger attractive interaction of the charged moieties with metal surfaces. Notwithstanding, there is a small probability of finding the end of the alkyl chains as close as 12 Å from the center of the nanoparticle. The CF_3 groups of the anions are also directed away from the nanoparticles (Supporting Information, Figure S4).

The orientation of the cations with respect to the surface of the nanoparticle (Figure 5) shows that the imidazolium ring lies most probably perpendicular to the nanoparticle surface, with the CH_3 group attached to the N_3 closer to the metal. The interaction of the imidazolium ring with neighboring anions is

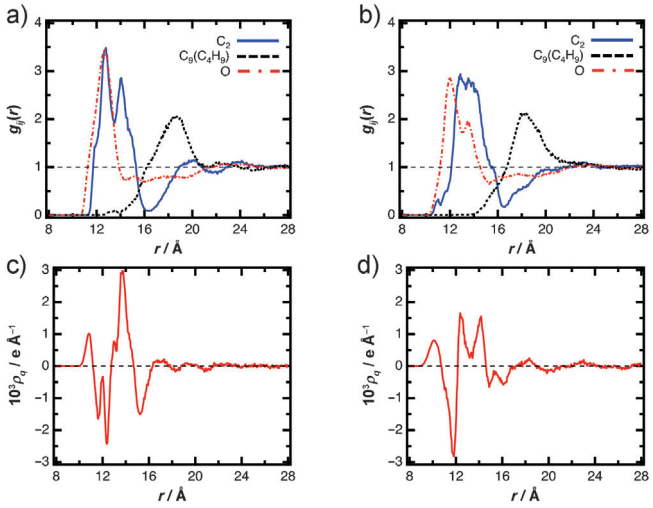

Figure 4. a,b) Radial distribution functions of atoms of the ionic liquid from the center of the nanoparticles (crystalline (a) and amorphous shell (b)). In both cases the oxygen atoms of the anion are closest, followed by the C_2 carbon of the imidazolium ring. Terminal carbon atoms of the alkyl side chain of the cation are not found with a high probability close to the surface. c,d) Radial distributions of electrostatic charge. These results are averages over 1 ns molecular dynamics trajectories.

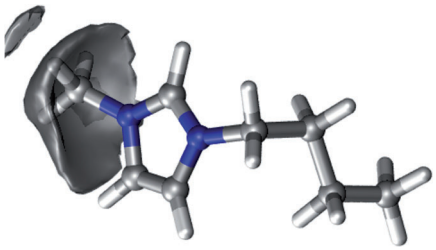

Figure 5. Spatial distribution function around the imidazolium ring of the cation showing the most probable locations of ruthenium atoms of the nanoparticle. The gray surface corresponds to an isoprobability of 3.5 times the average of finding a ruthenium atom around the imidazolium head group, sampled over a 1 ns molecular dynamics run.

thus maximized. This strong interaction of has been observed by surface-enhanced Raman spectroscopy on gold nanoparticles.[4] The H_2 and $H_{4,5}$ protons of the imidazolum ring are thus not the main sites of interaction with the nanoparticle, and configurations in which the imidazolium ring lies flat at the surface are not prevalent in our trajectories.

Inclusion of surface hydrides is expected to increase the nonpolar character of the nanoparticle.[27] We investigated this effect by incorporating H atoms at the surface of a nanoparticle, keeping a ratio of one hydrogen atom per surface ruthenium atom. Hydride atoms were modeled by a Lennard–Jones potential with a point electrostatic charge. Details are provided in the Supporting Information, Figure S5 and S8. The results of radial distribution functions confirm an increase of the hydrophobic character of the metallic nanoparticle, with a higher probability of finding the nonpolar groups of the ionic liquid near of the surface, but without disrupting the preferential solvation by the charged moieties.

In conclusion, metallic nanoparticles in ionic liquids are solvated preferentially by the charged moieties of the ions, with an interface layer that is one ion thick. Therefore, both cations and anions are present in contact with the metal. Nonpolar groups and side chains are preferentially directed away from the surface. The stabilization mechanism of metallic nanoparticles is therefore not due to an electrostatic double layer, and it is also not likely to be due to steric effects of the alkyl chains in the cations, which are too short in the present case. The narrow size distribution of nanoparticles synthesized in situ in ionic liquids and the link between their size and characteristic lengths of the ionic liquid (represented either by the anion volume or by the size of structural heterogeneities) means that the length scales of the ionic liquid do affect the nucleation and growth of the nanoparticles, and also the stability of the resulting colloid. This is a stabilization effect of the solvent as structural matrix or template, and not a result of electrostatic double layer or steric repulsion.

Received: May 5, 2011
Published online: July 29, 2011

Keywords: ionic liquids · molecular interactions · molecular simulations · nanoparticles · solvation

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