Aggregation of nanoparticles in aqueous solutions of ionic liquids

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ARTICLE INFO

ABSTRACT

In this work we were concerned with interactions between ionic liquids (IL) and nanoparticles (NPs) dispersed in aqueous solutions leading to the formation of NP clusters of finite size. The NPs used were Al_2O_3 ($d = 80$ nm), TiO_2 ($d < 100$ nm), and Fe_3O_4 ($d < 100$ nm). ILs were 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) and 1-methacryloyloxypropyl-3-methylimidazolium bromide, [mcpmim][Br]. The latter compound was a new IL synthesized in our laboratory. It was demonstrated that ILs actively participate in the formation of NP aggregates suspended in aqueous solution filling the inter-particle space. The aggregates saturated with IL were used as extractors making it possible for the elimination of compounds dissolved in water. Results of the extraction of anthracene and salicylic acid from aqueous solutions were presented.

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1. Introduction

ILs may be used to replace the usual organic solvents in extraction processes. They have been recognized as important novel solvents showing specific properties including high heat capacity, high density, extremely low volatility, non-flammability, high thermal stability, and wide temperature range for liquid state. Their properties may be easily tuned by changing either a cation or an anion [1–7]. ILs have been successfully used not only for designing new separation processes but also as solvents for numerous catalytic reactions, including polymerization, alkylation, and acylation [8–11]. It was demonstrated that NPs of transition metals dispersed in ILs display interesting catalytic properties [12,13]. The ILs stabilize NP dispersion through interactions of the metal surface with aggregates of ILs surrounded by ions [14]. These interactions are M–O (metaloxide) and M–F contributions in most cases [12]. The stabilization of NPs in ILs is rather due to the effect of the solvent as structural matrix or template, and not a result of electrostatic double layer or steric repulsion. Indeed, the 1,3-dialkylimidazolium salts form a 3D arrangement of cations and anions connected together by hydrogen bonds [15].

Hayes et al. [16], used atomic force microscope measurements to characterize the nanoscale forces at the mica–IL interface. They observed significant differences in liquid order with molecular structure, due to the changes in interionic forces. In the case of 1-butyl-3-methyl imidazolium hexafluorphosphate six solvation layers were detected. It

was concluded that in the case of ILs the mica surface acts to align the order pre-existing in IL bulk solution that leads to formation of solvation layers. According to K. Ueno and M. Watanabe [17], the structure forming property of ILs, can promote the encapsulation of colloidal particles in the well-defined layered structure of ILs due to the IL-based solvation force.

A 3D arrangement of the imidazolium ILs is generally formed through the chains of the imidazolium rings generating polar channels in which the anions are accommodated. Thus, IL arrangement is built with separated polar and non-polar domains. Since metal NPs surrounded by IL aggregates may interact through either ionic channels or non-polar domains created by imidazolium alkyl chains, the extractive NP/IL system may solubilize solutes of different polarity. It is well known [6] that ILs may be successfully used for solute recovery from aqueous media. The findings reported here suggest that in certain cases, the use of IL with NPs may improve the extraction capacity of ILs. Moreover, this technique potentially allows to avoid problems inherent with the use of bulk ILs resulting from high viscosity, high cost and toxicity.

Recently we have used IL (benzyl-dimethyl-alkyl-ammonium nitrate, [BA][NO_3]) and alumina (Al_2O_3) NPs to extract salicylic acid from aqueous solutions [18]. The average size of particles in solution as determined with DLS technique was in the range of 130 to 230 nm depending on IL and NP concentration and corresponded to small aggregates of NPs. The extraction occurred between the bulk solution and dispersed aggregates of NPs coated with the adsorbed IL. The high contact surface between solution and NP/IL clusters allowed a good mass transfer in spite of the high IL viscosity. The phase separation after extraction was done by filtration but other techniques such as centrifugation or (in the case of ferrous NPs) magnetic force driving may be used.

The extractive capacity of NP/IL systems depend on numerous factors. A better understanding of the extraction processes implies the knowledge of the mechanism of aggregate formation as well as the molecular interaction between NPs and ILs. Both these issues should be discussed taking in consideration not only the inherent properties of ILs and NPs but also the colloidal character of NP/IL systems.

Particles in the size range of 10 to 100 nm are characterized by a high ratio of surface-to-volume atoms leading to important surface effects. Attractive/repulsive interactions between particles that lead to aggregate formation depend on the geometrical factors that change strongly with decreasing particle size and are solvent mediated [19]. On the other hand, properties of solvent contained inside the aggregates are influenced by interaction between solid surfaces. The confinement of non-polar liquids in pores with a diameter of a few nanometers influences the physical properties of the liquid and can induce a phase transition as was observed with cyclohexane and toluene solidifying between solid walls with a distance of approximately 5–10 molecular diameters [20,21]. In the case of ionic liquids the nano-scale ordering arises from the association of polar and non-polar moieties [22–24] leading in some cases to alternate layers of cations and anions at the charged surface [25] with 3–10 layers distinguishable before the liquid becomes bulk-like. In the case of non-polar surfaces ILs stack in bilayers rather than ion-pair layers in the film. The strong ordering of the ILs adjacent to the surface does not induce the long range order and the IL crystallization. The range of interactions of two solid surfaces across IL goes to 10 nm due to solvation forces [22]. Results reported in the literature support the idea that the molecular ordering present in bulk ILs is enhanced in confined spaces due to the interaction of solid surfaces. The effect of confinement on the liquid properties is very complex and depends not only on the chemical properties of NPs and the geometry of pores but also on the ordering of ILs characteristic for a given anion–cation pair.

Therefore, the separative capacity of NP/IL systems in respect to solutes present in aqueous solution would depend on numerous factors resulting as well from chemical properties of NPs and ILs as from the colloidal specificity of the IL/NP system.

In this work we have studied the mechanism of aggregation of NPs in aqueous solutions of ILs. We were also concerned with interactions between ionic liquids (IL) and dispersed nanoparticles (NP) leading to the formation of the finite size clusters of NPs.

At first, we have determined the sorption isotherms of [BMIM][Br] IL with respect to different NPs. We looked to establish the amount of IL adsorbed or sorbed by aggregates.

Next we have used the IL/NP system to extract solutes from aqueous solutions. Two examples have been dealt with. Firstly, extraction of anthracene from aqueous solutions containing [BMIM][Br]/Al$_2$O$_3$ phase was studied. Next, extraction of the salicylic acid from aqueous solutions containing 1-methacryloyloxypropyl-3-methylimidazolium bromide, [mcpmim][Br]/Al$_2$O$_3$ phase was considered. The [mcpmim][Br] is a new IL synthesized in our laboratory displaying very good selectivity in respect to numerous separation systems [26].

2. Materials and methods

2.1. Materials

The ionic liquid 1-butyl-3-methylimidazolium bromide, [BMIM][Br] has a purity of >0.98 mass fraction and was supplied by Sigma-Aldrich. The ILs were further purified by subjecting the liquid to a very low pressure in a vacuum desiccator at a temperature of about 300 K for approximately 5 h. This procedure removed any volatile chemicals and water from the IL.

The ionic liquid 1-methacryloyloxypropyl-3-methylimidazolium bromide, [mcpmim][Br] was prepared via esterification using Dean–Starck apparatus, so 1 eq. of 3-bromo-1-propanol was added to 0.1 eq. of paratoluenesulfonic acid (PTSA) with few ppm of 4-ethoxyphenol

and the mixture was dissolved in cyclohexane and stirred at 80 °C for 1 h. Then, the solution of 1.2 eq. methacrylic acid and cyclohexane was added drop by drop and the reaction mixture was left at 80 °C over 12 h. After cooling, the preparation was washed three times with NaOH 10%. The organic solution was dried with MgSO$_4$ and the solvent was evaporated leading to the pure 3-bromopropyl methacrylate. The 1-methacryloyloxypropyl-3-methylimidazolium bromide was obtained through the bromine atom substitution using N-methylimidazole at 50 °C over 24 h without solvent. The reaction mixture was stirred in diethyl ether and filtered in order to obtain a white powder. The product, the melting temperature of which was 103 °C, was characterized using ^{1}H NMR, ^{13}C NMR: ^{1}H NMR (Bruker Avance 250 Mhz; deuterated solvent DMSO), δH: 1.77 (s, CH$_3$), 2.21 (q, CH$_2$), 3.81(s, NCH$_3$), 4.15 (t, CH$_2$N), 4.25 (t, CH$_2$O), 5.60 (d, CH), 5.92 (d, CH), 7.34 (d, NCH), 7.40 (d, NCH), 8.66 (s, N(H)CN); ^{13}C NMR δC: 17.3 (CH$_3$), 28.3 (CH$_2$), 35.7 (NCH$_3$), 47.1 (CH$_2$N), 62.4 (CH$_2$O), 122.4 (NCH), 123.7 (NCH), 126.8 (CH), 135.7 (CH), 169.4 (CO), and by FTIR: $\nu_{C=O}$: 1698 cm^{-1}, ν_{C-C-O}: 1168 cm^{-1}, ν_{O-C-C}: 1254 cm^{-1}, $\nu_{C=C}$: 1626 cm^{-1}, $\nu_{CH3\ umb}$: 1376 cm^{-1}, $\nu_{C=N^+-}$: 1572 cm^{-1}, ν_{C-H} aro: 3051/3101 cm^{-1}.

The anthracene was purchased from Sigma-Aldrich, 0.98 +. Water was bidistilled, deionized and degassed.

The NPs Al$_2$O$_3$, $d = 80$ nm, TiO$_2$, $d < 100$ nm, and Fe$_3$O$_4$, $d = 10$–20 nm were supplied by Sigma-Aldrich.

Water content was analyzed by using the Karl–Fisher titration technique (method TitroLine KF) and was lower than 0.0004 mass fraction.

2.2. Analytical methods

2.2.1. UV–vis spectroscopy

UV–vis spectroscopy was used to determine the concentration of organic compounds in solution. UV–vis absorption spectra were obtained by using Analytik Jena Specord 205 UV–vis double beam spectrophotometer with a wavelength ranking between 190 and 300 nm. The path length of a quartz cell was 10.00 mm. Concentration of the organic compounds was determined using the reference calibration curve.

2.2.2. Potentiometric titration

Concentrations of IL in aqueous solutions were determined by potentiometric titration of bromide ions with silver nitrate solution using silver/calomel electrodes.

2.3. Dynamic light scattering (DLS)

The mean particle size was determined using a Malvern 48000 photon correlation spectrometer (Malvern Instruments, Malvern, UK) with a light source from a 35-mW, 633 nm He–Ne laser. The autocorrelation function of the scattered light was determined with 7032 Malvern UK, 8-bit, high-speed, 72 channel correlator. The data were analyzed by the standard program using CONTIN method [27] obtaining the average value of the diameter of dispersed solid particles. Measurements were performed using samples conditioned at first at constant temperature during 24 h, and just before experiment in an ultrasonic bath during 20 min. Ultrasonic treatment disintegrates aggregates and allows the following of the aggregation occurring during the experiment. Therefore, DLS experiments give information about the size and the stability of aggregates formed in the solutions studied.

3. Results and discussion

3.1. Aggregation of nanoparticles in aqueous solutions of ionic liquids

The sorption of [BMIM][Br] from aqueous solutions by suspensions of three nanopowders: Al$_2$O$_3$ ($d = 80$ nm), TiO$_2$ ($d < 100$ nm), and