



Sequestration ability of task specific ionic liquids towards cations of environmental interest



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ABSTRACT

The metal speciation behavior of the amino functionalized 1-(2'-diethylamino)ethyl-3-methylimidazolium-based ILs, bearing anions featured by different coordination properties (chloride, perchlorate, acetate) is reported. Sequestering ability of this family of ILs towards Hg^{2+} , CH_3Hg^+ , Sn^{2+} , $(\text{CH}_3)_2\text{Sn}^{2+}$, UO_2^{2+} , evaluated by the determination of $pL_{0.5}$ parameter, was found to be a function of the nature of anions and/or pH. The acetate IL displayed a high affinity towards Hg^{2+} and CH_3Hg^+ , both at acidic and basic conditions, with respect to chloride and perchlorate derivatives, suggesting that a cation-anion cooperation mechanism is operating in the sequestering process. Conversely, UO_2^{2+} sequestration resulted a function of pH and independent on the nature of the anion. The extraction capabilities of hydrophobic 1-(2'-diethylamino)ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide towards Hg^{2+} and CH_3Hg^+ after treatment with acetate IL were also checked. AAS measurements showed the almost complete removal of both mercury species from water solution.

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1. Introduction

Ionic liquids (ILs), i.e. salts melting below 100 °C, emerged as a large class of functional materials with applications in many fields. The huge interest towards these “novel” materials results from their large number of tunable properties, such as good chemical, thermal and electrochemical stability, high ionic conductivity, good solvation ability and so on. Among others, they are characterized by nonflammability, minimal vapour pressure associated to a wide liquid range, making them ideal “green and designer” solvents and utilized as viable alternatives to conventional ones in synthesis [1], catalysis [2], extractions [3,4] processes. Their unique tailorable properties stem from their intrinsic ionic nature, which allows their fine modulation by the proper selection of cation/anion couples. ILs anchoring to appropriate substrates (nanostructures, polymers, etc.) emerged as a successful strategy to overcome the limitations arising from their liquid nature leading to a significant enhancement of their functions, their processing and hence applications [5–8]. ILs and the so called “supported ILs” (i.e. anchored ILs) had a relevant impact in analytical chemistry playing a significant role in the context of separation science [9–11]. In chromatography, they have been largely utilized as stationary [12,13] and mobile phases [14], as additives for

mobile phases [15], in supported liquid membrane processes and extractions [both liquid-liquid partitioning from water [16–20] and solid-liquid [21]. Hydrophobic ILs, on the other hand, result efficient metal ions extractants from aqueous solutions. Differently from conventional strategies which involve the employment of metal complexation followed by water/ILs phase-transfer process [22–26], ILs can be properly functionalized to interact with specific metal ions. These ILs, referred as Task Specific Ionic Liquids (TSILs) [27–31], can exert their sequestering function via cation or anion [32], or as a result of a synergy of both [33].

Despite the large body of research regarding ILs employment in extracting processes, only random studies regarding ILs metal speciation in aqueous medium are reported [28,34]. As it is well known, speciation models represent a useful means to establish the sequestration behavior of a ligand towards metals in traces. This information is in turn helpful in selecting the best operating conditions to reduce the metal free activity in water avoiding long time requiring processes. The ionic nature of ILs and, hence, the possibility to access to a large variety of cation/anion combinations represents a huge source of ligands to be applied in water metal speciation. Besides, by changing systematically the cation and/or anion nature, systems with high selectivity can be properly designed.

In the present paper we report on the metal speciation/sequestration behavior of the amino functionalized 1-(2'-diethylamino)ethyl-3-methylimidazolium-based ILs, bearing anions featured by different

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coordination properties, i.e. chloride (**L1**), perchlorate (**L2**), acetate (**L3**). Metals of environmental interest, such as i.e. Hg^{2+} , CH_3Hg^+ , Sn^{2+} , $(\text{CH}_3)_2\text{Sn}^{2+}$, UO_2^{2+} , were chosen to test the speciation/sequestering ability of this family of ILs. The preliminary assessment of the element distribution among defined chemical species (i.e. speciation studies [35]) allowed the quantification of ILs sequestering power through the determination of an empirical parameter that represents the concentration of IL required to sequester 50% of the metal ion.

The results showed that the sequestering ability of these ILs is a function, besides of pH, of the nature of anions. In fact, the acetate **L3** displayed a high affinity towards Hg^{2+} and CH_3Hg^+ , both at acidic and basic conditions, with respect to chloride and perchlorate derivatives, suggesting that a cation-anion cooperation mechanism is operating in the sequestering process.

Preliminary investigations on extraction properties of 1-(2'-diethylamino)ethyl-3-methylimidazolium ILs were also carried out. To this aim the bis(trifluoromethylsulfonyl)imide hydrophobic derivative (**L4**) was tested as extractant phase towards Hg^{2+} and CH_3Hg^+ species, after complexation with acetate IL. The extraction efficiencies were evaluated by atomic absorption spectrometry determinations, which showed the almost complete removal of both Hg^{2+} and CH_3Hg^+ from water solution.

2. Experimental section

2.1. Materials

Solutions of metal ions were prepared by weighing the corresponding salts: HgCl_2 (Riedel-de-Haen), CH_3HgCl (Aldrich), $(\text{CH}_3)_2\text{SnCl}_2$ (SigmaAldrich), $\text{SnCl}_2(\text{II})$ (SigmaAldrich), $\text{UO}_2(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (SigmaAldrich). Purity of dioxouranium(VI) cation, checked gravimetrically after precipitation as U_3O_8 by gaseous ammonia, was $\geq 99.5\%$. Particular attention was paid to the preparation of tin(II) solutions, in order to avoid the oxidation of Sn(II) to Sn(IV) and the formation of sparingly soluble hydrolytic species. The solutions were acidified with known amounts of standard HCl to reach $\text{pH} = 2$ and a little piece of metallic tin was added to the solutions after the preparation. Solutions were standardized with EDTA standard solutions, and the purity was always $\geq 99\%$. Phosphate and arseniate solutions were prepared from $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (Fluka >99%) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Carlo Erba) salts and their purity was checked potentiometrically by alkalimetric titrations.

Concentrated ampoules of hydrochloric acid and sodium hydroxide (Fluka) were used to prepare the corresponding diluted solutions. The solutions of hydrochloric acid were standardized against sodium carbonate, those of sodium hydroxide against potassium hydrogen phthalate. All solutions were protected from atmospheric CO_2 using soda lime traps. Grade A glassware and twice-distilled water were employed in the preparation of all the solutions.

All the chemicals used for the syntheses (see later) were purchased from SigmaAldrich and used as received.

2.2. Measurements

^1H NMR solution spectra were recorded with a Bruker AMX R-300 spectrometer operating at 300.13 MHz. Elemental analyses were performed by the Redox Microanalytical Laboratory, Cologno Monzese, Milan (Italy). Thermogravimetric investigations were performed by means of Perkin-Elmer Pyris TGA7 in the temperature range between 50 and 800 °C, under nitrogen flow (60 mL min^{-1}) and heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetry measurements were carried out by using a TA Q20 instrument equipped with a Refrigerant Cooling System (RCS 90) with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, under an anhydrous N_2 atmosphere (60 mL min^{-1}). The cooling rates were fixed at $10 \text{ }^\circ\text{C min}^{-1}$. The positive MALDI-TOF mass spectra were collected by a Voyager DE (PerSeptive Biosystem) using a delay extraction

procedure (25 kV applied after 2600 ns with a potential gradient of 454 V mm^{-1} and a wire voltage of 25 V) with ion detection in linear mode [36,37]. The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2). In order to avoid fragmentation of the polymers, the laser irradiance was maintained slightly above threshold. Each spectrum was an average of 32 laser shots. The MALDI investigations were performed by loading on the plate a 0.1 mmol sample and 40 mmol matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldene]-malonitrile (DCTB), with CHCl_3 as solvent. Both 5,10-di(p-dodecanoxyphenyl)-15,20-di(p-hydroxyphenyl) porphyrin ($\text{C}_{68}\text{H}_{78}\text{N}_4\text{O}_4$, 1014 Da), tetrakis(p-dodecanoxyphenyl)porphyrin ($\text{C}_{92}\text{H}_{126}\text{N}_4\text{O}_4$, 1350 Da) and a PEG sample of known structure were used as external standards for *m/z* calibration [38].

The spectrophotometric measurements on aqueous solutions were recorded using a Varian Cary 50 UV-vis spectrophotometer equipped with an optic fibre probe having a fixed 1 cm path length. The spectrophotometer was connected to a PC for the acquisition of the experimental data (absorbance vs wavelength), by Varian Cary WinUV (version 3.00) software. Simultaneously, in the thermostated measurement cell, the pH of the solutions was measured by a combined glass electrode (Ross type 8102, from Thermo/Orion) connected to a Metrohm 713 potentiometer. The combined glass electrode was standardized before each experiment in terms of $\text{pH} = -\log[\text{H}^+]$. In this order, both data A vs λ (nm) and pH vs volume of titrant (mL) were simultaneously recorded. The titrant was delivered in the measurement cell by means of a 665 Metrohm automatic burette; to ensure the systems homogeneity during the titration the solutions were vigorously stirred. During each experiment, N_2 was bubbled in the solutions for at least 5 min in order to exclude the presence of CO_2 and O_2 . Preliminary absorbing spectra were recorded to detect the wavelength interval where the ligands absorbed ($200 \leq \lambda \leq 300 \text{ nm}$). In order to check ionic liquids acid-base behavior, 20 mL of solutions containing the specific IL (**L**) ($0.05 \leq \text{C}_L \leq 0.3 \text{ mmol L}^{-1}$) and HCl ($0 \leq \text{C}_{\text{HCl}} \leq 1 \text{ mmol L}^{-1}$) were analyzed by varying the pH through alkalimetric titration. For the investigations on metal complex species formation constants, 20 mL of solutions containing different amounts of IL (**L**) ($0.1 \leq \text{C}_L \leq 0.5 \text{ mmol L}^{-1}$), HCl ($0 \leq \text{C}_{\text{HCl}} \leq 1 \text{ mmol L}^{-1}$) and metal ($0.1 \leq \text{C}_M \leq 0.4 \text{ mmol L}^{-1}$) under study, at different metal-ligand concentration ratios ($0.4 \leq \text{C}_M/\text{C}_L \leq 2$), were analyzed in a wide pH range ($2.5 \leq \text{pH} \leq 11$). Small increments of standard NaOH solution were added to each solution in order to obtain the maximum absorbance for each predominant species, according to the speciation diagrams of the systems. Analogously, investigations on PO_4^{3-} and AsO_4^{3-} -**L3** systems were performed by titrating 20 mL of solutions containing **L3** ($0.1 \leq \text{C}_{\text{L3}} \leq 0.5 \text{ mmol L}^{-1}$), HCl ($0 \leq \text{C}_{\text{HCl}} \leq 1 \text{ mmol L}^{-1}$) and Na_2HPO_4 or Na_2HAsO_4 salt ($0.1 \leq \text{C}_S \leq 0.4 \text{ mmol L}^{-1}$) in the $2.5 \leq \text{pH} \leq 11$ range. UV spectra were analyzed by the HypSpec programs [39], which allowed to calculate the protonation or formation constants and the molar absorption coefficient spectrum of each absorbing species, using experimental absorbances, analytical concentrations of reagents and the proposed chemical model as input. ES4ECI program [40] was used to calculate formation percentages of the species and to plot speciation diagrams.

The metal extraction experiments were carried out by employing 5 mL of water solution (Hg^{2+} or CH_3Hg^+ 1 mM, 1-(2'-diethylamino)ethyl-3-methylimidazolium acetate (**L3**) 2 mM, $\text{pH} = 8$) and 1 mL of bulk 1-(2'-diethylamino)ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide **L4**. The two phases were sonicated for 15 h and then centrifuged for 5 min at 2000 rpm, to ensure their complete mixing and separation. The aqueous layer was then removed, the metals remaining in water determined by means of Atomic Absorption Spectrometry and the amount of the extracted Hg^{2+} or CH_3Hg^+ in the IL phase calculated as the difference between the initial concentration of metal ion in water solution (1 mM) and the concentration of metal ion after extraction. Each extraction experiment was performed in duplicate and the results agreed to within 5%.

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