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Redox chemistry, solubility, and surface distribution of Pt(II) and Pt(IV) complexes dissolved in ionic liquids

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ABSTRACT

An X-ray photoelectron spectroscopy (XPS) study of Pt(II) and Pt(IV) complexes dissolved in ionic liquids (ILs) revealed the occurrence of a rich redox chemistry, which is partly induced by X-ray radiation. Depending on the IL anion either a reduction of Pt(IV) to Pt(II) in the case of ethylsulfate ($[EtOSO_3]^-$)-based ILs, or an oxidation of Pt(II) to Pt(IV) in the case of bis[(trifluoromethyl)sulfonyl]imide ($[Tf_2N]^-$)-based ILs was observed upon X-ray irradiation. Moreover, surface enrichment or depletion effects of the Pt complexes were deduced from angle-resolved XPS (ARXPS) data; while the Pt complexes dissolved in imidazolium-based ILs tended to deplete from the surface, in pyrrolidinium-based solutions a surface enrichment of the Pt complexes was observed.

1. Introduction

Ionic liquids (ILs) – salts with a melting point below 100 °C – possess unique physico-chemical properties, such as unusual solvation and miscibility properties [1], a large temperature range of their molten state [2], a large electrochemical window, extremely low volatility [3,4], and low flammability [5], electroconductivity [6]. These properties open manifold routes to applications in catalysis [7,8], electrochemistry [9], and analytics [10], and as "engineering fluids" (*e.g.*, in separation technologies [11]), some of which have been already adopted by industry [12]. With respect to catalysis, one advantage of ILs over conventional molecular solvents is related to their low vapor pressure and their tunable miscibility behavior with common organic solvents. These properties enable an easier separation of reaction products by evaporation or decantation from the IL catalyst phase. Consequently, the use of ILs is able to overcome one of the major challenges of homogeneous catalysis, namely the recovery and recycling of the dissolved, molecular catalyst. One example is the biphasic, Pt-catalyzed hydrosilylation [13,14], where the starting materials and the products form one phase (the organic phase), and the active Pt complex is immobilized in the IL phase (the ionic catalyst phase). For most ILs used in this reaction, high conversion rates have been achieved and recycling of the catalyst up to 10 cycles was possible without a pronounced decrease in activity [13].

The first utilization of ILs as solvents for homogeneous transition metal catalysis with Pt complexes was already reported in 1972 by Parshall et al., who studied the Pt-catalyzed hydroformylation of ethylene in tetraethylammonium trichlorostannate [15]. Since then, a variety of other homogeneous Pt-catalyzed reactions in ILs have been tested [8,16], including hydroformylation [17], hydrogenation [18], hydroamination [19], alkane oxidation [20], and C–C coupling reactions [21–23]. In some cases, higher conversion rates and selectivities were found compared to the use of conventional solvents.

One particularly interesting concept is supported ionic liquid phase (SILP) catalysis [24,25]. Here, thin films of ILs on high surface area supports are used to immobilize catalytically active, homogeneously dissolved transition metal complexes. The very low vapor pressure of ILs helps to avoid loss of solvents by evaporation during the catalytic process. Thus, the SILP concept combines the easy manageability of heterogeneous catalysts with the well-defined molecular reaction environment of a homogeneous catalyst. In such systems, the diffusion of the reagents from the substrate/product phase (gas) to the reactive ionic catalyst phase (liquid) is an important step. This step can even be rate limiting due to the relatively high viscosity of the ionic liquid [26]. Consequently, an enrichment of the dissolved catalyst complex in the surface region of the IL would be advantageous for increasing the catalyst utilization. A very suitable tool, in order to study the surface activity of substances in ILs, is angle-resolved X-ray photoelectron spectroscopy (ARXPS) under ultrahigh vacuum (UHV) conditions. The surface sensitivity of ARXPS originates from the low mean free pathway of electrons in matter [27]. For normal emission (0° with respect to the surface normal) of the emitted electrons, the near-surface region is probed with an information depth (ID) of ~7–9 nm, depending on the kinetic energy of the excited photoelectrons [28]. The ID can be further reduced by increasing the emission angle, *e.g.*, to ~1-1.5 nm at 80°. Consequently, an increase in signal intensity with increasing emission angle (*i.e.*, with increasing surface sensitivity) reveals the enrichment of the respective element at the surface.

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A previous ARXPS study of $[Pt^{II}(NH_3)_4]Cl_2$ dissolved in the IL 1-ethyl-3-methylimidazolium ethylsulfate ($[C_2C_1Im][EtOSO_3]$) showed the enrichment of the Pt complex at the surface, while the chloride counter ion was depleted from the surface [29]. The different surface activities of the dissolved species were attributed to their differences in molecular volume and in polarizability; the larger and more polarizable a dissolved component, the higher is its surface activity [29]. Later, it has been shown that surface enrichment of a catalyst can also be influenced by a suitable ligand; while the catalytic–active complex $[Rh(acac)(CO)_2]$ displayed no surface activity in $[C_2C_1Im][EtOSO_3]$, upon exchanging at least one CO ligand with tris(3-sulfonatophenyl) phosphine (tppts) an enrichment of the modified Rh-complex at the IL surface was found [30].

Apart from surface activity, also the stability of complexes dissolved in ILs is of concern. Already in the first XPS study on ILs, Smith et al. reported the reduction of $[Pd^{II}(OAc)_2(PPh_3)_2]$ in $[C_2C_1Im][EtOSO_3]$ to a Pd(0) species, which was explained by the formation of N-heterocyclic carbene complexes and the subsequent reduction to the metal [31]. While for this process X-ray radiation seemed not to play a role, the stability of complexes can also be affected directly by X-ray irradiation as has been shown in XPS studies of neat Pt(IV) salts, where a reduction to Pt(II) was observed upon X-ray irradiation in the solid state [32,33].

In this work, we present ARXPS data of 12 different IL solutions of platinum salts. One important issue in this context is the solubility of the Pt complexes. While Pt contents even below 0.01 mol% might be still sufficient for running catalytic reactions, the detection limit of XPS requires more than 0.2 mol% of Pt within the near-surface region to obtain satisfactory signal-to-noise ratios. Hence, one of the goals of this study was to increase the solubility limits. For this purpose, Pt(II) and Pt(IV) salts with counter ions identical to the IL ions were employed. Table 1 summarizes all utilized Pt salts and ILs with their chemical structure and IUPAC name. The Pt(II) salts used were $K_2[PtCl_4]$ and $[Pt(NH_3)_4][Tf_2N]_2$; the Pt(IV) salts were $H_2[PtCl_6]$, $[C_2C_1Im]_2[PtCl_6]$ and $[C_2C_1Pyrr]_2[PtCl_6]$. The influence of the IL cation and anion on the solubility, surface activity, and stability of the dissolved Pt complexes was probed in the ILs $[C_2C_1Im][EtOSO_3]$, $[C_2C_1Im][Tf_2N]$, $[C_2C_1Pyrr][EtOSO_3]$, and $[C_4C_1Pyrr][Tf_2N]$. The studied homogeneous solutions are summarized in Table 2 with their respective concentrations in mol%; the latter were derived from inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements.

2. Experimental

2.1. Materials and synthesis

Unless otherwise stated, all commercially available reagents and solvents were purchased at the highest available purity and used as received. The NMR spectra were recorded at 25 °C on a JEOL ECX 400 MHz spectrometer. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were conducted with a SPECTRO CIROS-CCP spectrometer, using either bi-distilled water or absolute ethanol as solvent. The synthesis of the commercially non-available reagents is described in the following.

2.1.1. 1-Ethyl-1-methylpyrrolidinium ethylsulfate $[C_2C_1Pyrr][EtOSO_3]$

1-Methylpyrrolidine (0.2 mol) was dissolved in anhydrous methylene chloride (200 mL). To this solution, diethylsulfate (0.2 mol) was added drop-wise at room temperature. The resulting mixture was stirred overnight and then the solvent evaporated. The oily residue was washed with diethyl ether (3 × 100 mL) and then dried under vacuum resulting in a 96% yield of a colorless liquid, which tends to solidify with time. ^1H NMR, D_2O: δ 1.2 (t, J = 7 Hz, 3, CH_3); 1.3 (t, J = 7 Hz, 3, CH_3); 2.1 (mult, 4, CH_2-ring); 2.9 (s, 3, CH_3); 3.4 (mult, 6, CH_2-ring and CH_2-alkyl); 4.0 (quart, J = 7 Hz, 2, CH_2). ^{13}C-{^1H}: δ 8.7; 14.4; 21.5; 47.6; 59.7; 63.9; 65.4.

2.1.2. 1-Ethyl-1-methylpyrrolidium chloride $[C_2C_1Pyrr]Cl$

10.00 g of 1-ethyl-1-methylpyrrolidinium ethylsulfate was dissolved in 10 mL of bi-distilled water and the solution was passed through a column of Dowex 1 × 8® in chloride form (3 × 10 cm). The product was further eluted with 150 mL of bi-distilled water. The water was then evaporated leaving 1-ethyl-1-methylpyrrolidium chloride as white solid in quantitative yield. ^1H NMR, D_2O: δ 1.2 (tquart, $J_1 = 7$ Hz, $J_2 = 2$ Hz, 3, CH_3); 2.0 (mult, 4, CH_2-ring); 2.9 (s, 3, CH_3); 3.3 (mult, 6, CH_2-ring and CH_2-alkyl). ^{13}C-{^1H}: δ 8.6; 21.4; 47.6; 59.6; 63.9.

2.1.3. Bis(1-ethyl-1-methylpyrrolidium) hexachloroplatinate(IV) $[C_2C_1Pyrr]_2[PtCl_6]$

1-Ethyl-1-methylpyrrolidium chloride (1.8720 g, 12.50 mmol) and $PtCl_4$ (2.1069 g, 6.25 mmol) were placed in a 100 mL Schlenk flask under argon. To the solids, dry acetonitrile (50 mL) was added and the mixture was refluxed under argon until the suspension became clear. The reflux was continued for 1 h and then the deep orange solution was allowed to cool by means of an ice bath. An orange solid precipitated, which was decanted, washed with cold acetonitrile (10 mL) and diethyl ether (3 × 10 mL), and then dried under vacuum yielding 2.2687 g (57%) of an orange powder. ^1H NMR, DMSO-d_6: δ 1.2 (t, J = 7 Hz, 3, CH_3); 2.0 (mult, 4, CH_2-ring); 2.9 (s, 3, CH_3); 3.4 (mult, 6, CH_2-ring and CH_2-alkyl). ^{13}C-{^1H}: δ 9.5; 21.6; 47.5; 58.9; 63.5. ICP-AES analysis gave a Pt content of 31.03% (expected 30.66%).

2.1.4. Bis(1-ethyl-3-methylimidazolium) hexachloroplatinate(IV) $[C_2C_1Im]_2[PtCl_6]$

This complex was synthesized in 79% yield following the above procedure. ^1H NMR, DMSO-d_6: δ 1.4 (t, J = 7 Hz, 3, CH_3); 3.8 (s, 3, CH_3) 4,2 (quart, 2, CH_2); 7.5 (t, J = 1,6 Hz, 1, CH-ring) 7.6 (t, J = 1,6 Hz, 1, CH-ring) 9.0 (s, 1, CH-ring). ICP-AES analysis gave a Pt content of 30.13% (expected 30.96%).

2.1.5. Tetraaminoplatinum(II) di{bis[(trifluoromethyl)sulfonyl]imide} $[Pt(NH_3)_4][Tf_2N]_2$

Tetraaminoplatinum(II) chloride hydrate (0.8157 g, 2.3 mmol) and $Ag[Tf_2N]$ (1.7983 g, 4.6 mmol) were placed in a 100 mL Erlenmeyer flask and dissolved in 50 mL bi-distilled water. A white precipitate immediately formed. After stirring for 15 min at room temperature, the suspension was carefully filtered and the filtrate evaporated by means of a rotavapor. The obtained very viscous yellow liquid was further dried by high vacuum. It solidified upon standing in a desiccator over silica gel. ICP-AES analysis of the waxy solid gave a Pt and S content of 23.57 and 15.73%, respectively (expected: Pt 23.69%; S 15.57%). ^{195}Pt-NMR in deuterated water showed a singlet at −2560 ppm which was attributable to the $[Pt(NH_3)_4]^{2+}$ cation [34]. Accordingly, ^{19}F NMR showed a singlet at −79.2 ppm and ^{13}C NMR a quartet centered at 121.2 ppm with $J_{CF} = 318$ Hz.

2.1.6. Preparation of saturated Pt complex solutions in ILs

The Pt compound was added to the relevant ionic liquid (~2.0 g) in the amount required to obtain a 0.1 mol/mol solution. The solutions of $H_2[PtCl_6]$ were prepared with its commercially available hexahydrate $H_2[PtCl_6] \times 6\ H_2O$. For the solutions of $H_2[PtCl_6]$ in $[C_2C_1Im][Tf_2N]$, of $[C_2C_1Im]_2[PtCl_6]$ in $[C_2C_1Im][EtOSO_3]$ and in $[C_2C_1Im][Tf_2N]$, and of $[Pt(NH_3)_4][Tf_2N]_2$ in $[C_2C_1Im][EtOSO_3]$ and in $[C_2C_1Im][Tf_2N]$, acetonitrile was additionally added as a co-solvent. The resulting suspensions were stirred at room temperature for ~6 h. After the removal of the co-solvent (and water, in case of the $H_2[PtCl_6]$ solutions) by vacuum, the suspensions were centrifuged in order to remove all un-dissolved material. The supernatant fluids were separated and analyzed for the Pt content by means of ICP-AES. The obtained Pt concentrations are listed in Table 2 in mol%.