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Eu^{3+} as a dual probe for the determination of IL anion donor power: A combined luminescence spectroscopic and electrochemical approach

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ABSTRACT

This work is aimed at giving proof that $Eu(Tf_2N)_3$ (Tf_2N = bis(trifluoromethanesulfonyl)amide) can act as both an optical and electrochemical probe for the determination of the Lewis acidity of an ionic liquid anion. For that reason the luminescence spectra and cyclic voltammograms of dilute solutions of $Eu(Tf_2N)_3$ in various ionic liquids were investigated. The $Eu^{2+/3+}$ redox potential in the investigated ILs can be related to the Lewis basicity of the IL anion. The IL cation had little influence. The lower the determined halfwave potential, the higher the IL anion basicity. The obtained ranking can be confirmed by luminescence spectroscopy where a bathochromic shift of the $^5D_0 \rightarrow {}^7F_4$ transition indicates a stronger Lewis basicity of the IL anion.

1. Introduction

Ionic liquids (ILs) are receiving growing attention as solvent replacements for conventional organic solvents [1]. Often they are considered to be environmentally more benign and chemically safe because many ILs have low flammabilities and flash points. However, the most important advantage that ionic liquids offer over conventional organic solvents (and water) is the tuneability of their solvent properties through the choice of the respective cation/anion combination. It is estimated that roughly 10^{18} ionic liquids are accessible [2]. Each ionic liquid with a specific cation–anion combination offers a new set of chemical and physical properties. In consequence, ILs can be truly designed for a certain application. However, to do so, it is important to be able to know and predict fundamental solvent properties such as polarity and acidity.

Solvent polarity and acidity will determine the solubility of substances and are able to influence the outcome of chemical reactions, the position of chemical equilibria as well as reaction rates [3]. It is not an easy task to determine the acidity of non-aqueous media, but several methods have been used to describe the solvent power of ionic liquids addressing their polarity. A common approach for determining the solvent polarity is to evaluate the UV–Vis spectra of optical probes such as solvatochromic dyes or transition metal complexes in the solvents under investigation. The absorption or emission bands of the probe show a strong shift in their optical spectra (solvatochromic shift) which can be related to the polarity of the solvent in which they are dissolved [4,5]. However, it has been realized that it is difficult to analyze and separate specific interactions in the liquid which becomes even more important in non-classical, highly structured solvents such as ionic liquids.

For ionic liquids Kamlet–Taft parameters derived from solvatochromic studies of organic dyes have been associated with different solvent properties, such as π^* with dipolarity and polarizability, α with the hydrogen bond acceptor capability and β with the hydrogen bond acceptor capability. Although it was noticed that α is largely dependent on the IL anion and β on the IL cation, an analysis of separate influences of cation and anion that would ultimately allow for a designed choice of the cation–anion combination was not possible. But the unique power of ionic liquids is that through a smart choice of the cation and anion a solvent with designed properties can be created. For that reason it would be interesting to have probes that allow testing specifically for certain solvent properties.

Solvent polarity as such is rather complex. IUPAC defines solvent polarity as being "the overall solvation capability (or solvation power) for (i) starting materials and products, which influences chemical equilibrium; (ii) reactants and activated complexes ("transition states"), which determines reaction rates; and (iii) ions or molecules in their ground and first excited state, which is responsible for light absorptions in the various wavelength regions. This overall solvation capability depends on the action of all, non-specific and specific, intermolecular

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solute–solvent interactions, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute" [6].

According to Reichardt solvent–solute interactions can be divided into specific and non-specific interactions [7]. Non-specific interactions are instantaneous/induced dipole forces (dispersion or London forces), dipole/induced-dipole forces (induction or Debye forces), dipole/dipole forces (orientation or Keesom forces) and ion/dipole forces (Coulomb forces) which might quite well get addressed through measurements of continuum properties such as dielectric constants. Specific interactions include hydrogen bond donor and/or hydrogen bond acceptor interactions, electron pair donor/electron pair acceptor or charge–transfer interactions, solvophobic interactions (which can become important only in highly structured solvents). As ionic liquids contain, in contrast to conventional molecular solvents, charged ions it is expected that electron–donor–acceptor interactions have a rather high influence. In consequence, an important property of ionic liquids as solvents is their Lewis acidity and basicity or, in other words, their electron acceptor and donor capability. It is anticipated that the electron acceptor properties of an IL depend largely on the cation whereas the IL anion governs the IL electron donor properties.

We could confirm this hypothesis through evaluation of spectroscopic properties of certain transition metal compounds in different ionic liquids. They made it possible to separate the anionic influence, hence Lewis basicity. We were able to rank various IL anions with respect to their Lewis basicity by evaluating the absorption spectra of the indicator complex (Ni(tmen)(acac)][B(Ph)$_4$] (tmen = tetramethylethylendiamine, acac = acetylacetonate) [8]. In a second step we transferred Duffy's concept of the *optical basicity* [9] to ILs by using Mn(Tf$_2$N)$_2$ as a spectroscopic probe [10].

When investigating in a different context the solvation and ligand exchange processes of ytterbium(III) salts in ionic liquids such as (C$_4$mpyr)(Tf$_2$N) (C$_4$mpyr = N-butyl-N-methylpyrrolidinium) or (C$_4$mpyr)(TfO) we made an interesting observation: We found that the Yb^{2+}/Yb^{3+} redox potential strongly depends on the local chemical environment and coordination of Yb^{3+} by the IL anion. It was found that the more coordinating the IL anion is, the less negative the redox potentials (vs. Fc/Fc$^+$) [11]. Thus, it also should be possible to electrochemically determine the Lewis basicity of an IL with a given anion by investigating the redox potential of a dissolved lanthanide bis(trifluoromethanesulfonyl)amide, Ln(Tf$_2$N)$_3$. An additional advantage of using lanthanide salts as a probe is, that many of the trivalent lanthanides show distinct photoluminescence. As Yb^{3+} is spectroscopically inactive in the visible range of the electromagnetic spectrum, we choose for this study Eu^{3+} which is commonly used as a structural probe. To date several Eu^{3+} containing ionic liquids and liquid crystals are known [12]. In case of Eu^{3+} it is possible to monitor the electron donation power of the anion via the shift of (hyper-) sensitive transitions in the luminescence spectra. Thus, by using the same probe, Eu(Tf$_2$N)$_3$, but different analytical tools, namely cyclic voltammetry and luminescence spectroscopy, it should be possible to access the electron donor power of an IL anion. To check whether Eu(Tf$_2$N)$_3$ can work as both, an optical and electrochemical probe for the anion Lewis basicity we have investigated solutions of Eu(Tf$_2$N)$_3$ in a set of ionic liquids with anions of weak (e.g. Tf$_2$N$^-$), middle (e.g. TfO$^-$) and strong (e.g. DCA$^-$) Lewis basicity and recorded the respective luminescence spectra and cyclic voltammograms.

2. Experimental section

2.1. Chemicals and synthesis

LiTfO (98%), Eu(TfO)$_3$ (98%) and Eu$_2$O$_3$ (99.9%) were purchased from Sigma-Aldrich, Schnelldorf, D. LiTf$_2$N, (N$_{4441}$)(Tf$_2$N), (C$_2$mim)(MeSO$_3$), (C$_2$mim)(TfO) and (C$_4$pyr)(Tf$_2$N) (all 99%) were purchased from IoLiTec, Heilbronn, D. (P$_{666\ 14}$)Cl (95%) was provided by Cytec, Stamford, USA. All commercial ILs were purified prior to the experiments. Methylimidazole (98%), *N*-methylpyrrolidine (98%), the respective halogen alkanes (>98%) were purchased from Acros, Geel, B and distilled prior to use.

2.2. General purification procedure for ILs

The respective IL was diluted with CH$_2$Cl$_2$ or CHCl$_3$ and washed several times with deionized water to remove any excess of halides or alkali metal salts (AgNO$_3$ test) as well as unreacted starting material. After filtration of the solution over a column with neutral Al$_2$O$_3$ and active charcoal the solvent was removed under high vacuum and the ILs dried under dynamic vacuum for 1–2 days at 80–90 °C.

2.3. Synthesis of HTf$_2$N

HTf$_2$N was obtained by sublimation at 70 °C from a solution of LiTf$_2$N in concentrated sulfuric acid under reduced pressure (10^{-3} mbar). The crude product was resublimed for further purification. Yield: 90%.

$$^{1}\mathrm{H{-}NMR(D_2O)}:\delta(\mathrm{ppm}) = 4.77(s, 1\mathrm{H})$$

$$^{19}\mathrm{F{-}NMR(D_2O)}:\delta(\mathrm{ppm}) = -79.16(\mathrm{s}, 6\mathrm{F})$$

$$^{13}\mathrm{C}\left\{^{19}\mathrm{F}\right\}\mathrm{{-}NMR(D_2O)}:\delta(\mathrm{ppm}) = 19.27(\mathrm{s}, 2\mathrm{C})$$

2.4. Synthesis of Eu(Tf$_2$N)$_3$

Eu$_2$O$_3$ was suspended in deionized water and five-fold molar excess of an aqueous HTf$_2$N solution was added dropwise. After complete dissolution of Eu$_2$O$_3$ the water was boiled off until a slurry solid appeared. This slurry was transferred to a Schlenk tube and dried at 140–160 °C under high vacuum. The residual solid was sublimed for purification under reduced pressure at 270 °C.

$$\text{Elemental analysis}:\mathrm{Eu(Tf_2N)_3}$$

$$\text{calc.N } 4.23\%.\text{C } 7.26\%, \text{H } 0.00\%, \text{S } 19.39\ \%$$

$$\text{found N } 4.19\%.\text{C } 7.25\%, \text{H } 0.10\%, \text{S } 20.34\%$$

2.5. Synthesis of 1-alkyl-3-methylimidazolium bromides

(C$_n$mimBr) bromides (n = 2, 3, 4 and 6) were obtained by alkylation of 1-methylimidazole with the respective halogen alkane [13]. All bromides except C$_6$mimBr, which is liquid, were obtained as crystalline white powders.

$$\begin{aligned}&(\mathrm{C_2mim})\mathrm{Br}{:}^{1}\mathrm{H{-}NMR\ (CDCl_3)}:\delta\ (\mathrm{ppm})\\ &\quad = 1.23\ (\mathrm{t}, 3\mathrm{H}, \mathrm{J} = 7.4\ \mathrm{Hz}); 3.75\ (\mathrm{s}, 3\mathrm{H}); 4.06\ (\mathrm{q}, 2\mathrm{H}, \mathrm{J} = 7.2\ \mathrm{Hz});\\ &\qquad 7.39\ (\mathrm{s}, 2\mathrm{H}); 9.82\ (\mathrm{s}, 1\mathrm{H})\end{aligned}$$

$$\begin{aligned}&(\mathrm{C_3mim})\mathrm{Br}{:}^{1}\mathrm{H{-}NMR\ (CDCl_3)}:\delta\ (\mathrm{ppm})\\ &\quad = 0.44\ (\mathrm{t}, 3\mathrm{H}, \mathrm{J} = 7.4\ \mathrm{Hz}); 1.45\ (\mathrm{hex}, 2\mathrm{H}, \mathrm{J} = 7.2\ \mathrm{Hz}); 3.61\ (\mathrm{s}, 3\mathrm{H});\\ &\qquad 3.82\ (\mathrm{t}, 2\mathrm{H}, \mathrm{J} = 7.2\ \mathrm{Hz}); 7.82\ (\mathrm{d}, 2\mathrm{H}, \mathrm{J} = 1.7\ \mathrm{Hz}); 9.67\ (\mathrm{s}, 1\mathrm{H})\end{aligned}$$