Probing the acidity level of ionic liquids: implementation of Hammett acidity functions in Raman spectroscopy

Aurélie Rensonnet, Gauthier Eppe, and Cedric Malherbe

Mass Spectrometry Laboratory, MolSys Research Unit, University of Liège | Aurelie.Rensonnet@uliege.be

Introduction

The level of acidity achievable in ionic liquids (ILs) is related to the solvation properties of the solvent towards the proton and is critical in many applications: liquid and gas chromatography, electrochemical systems and organic synthesis/catalysis[1,2], for which a correlation between the catalytic activity and the Bronsted acidity of ILs is regularly observed.[3]

Yet, the experimental measurement of the acidity in these media is not straightforward and difficult to predict.

One common method to assess the acidity in ILs involves the measurement of the Hammett acidity functions, H_0, based on the protonation equilibrium of a family of colour indicators (CIs), usually nitroanilines[4]:

$$H_0 \equiv pK_{IC,\,\boldsymbol{H_2O}} + \log\left(\frac{a_{In,\boldsymbol{IL}}}{a_{HIn^+,\boldsymbol{IL}}}\right) = pH_{\boldsymbol{H_2O}} + \log\left(\frac{\Gamma^{HS}_{H_2O}(HIn^+)}{\Gamma^{HS}_{H_2O}(In)}\right)$$

$\log \Gamma_t(i)^{IL}_w$

Extra-thermodynamic hypothesis of Hammett

The protonation equilibrium is followed by UV-Visible spectroscopy (UV-Vis), but this method suffers from a few limitations:

- Limited to colour indicators as pH-probes, and transparent systems
- Use of nitroanilines: possible π interactions between the IC and IL

⇒ **Implementation in Raman spectroscopy, which will enable to use other pH probes, extending the systems that can be studied, for instance**

Experimental section

1. Due to the sensitivity of the ILs to moisture, all solutions were prepared in a glovebox, and kept under inert atmosphere in crimp cap vials.
   Solutions of CI in the probed ILs were prepared with increasing concentration of acid (i.e. increasing acidity), as shown in **Fig 1**.

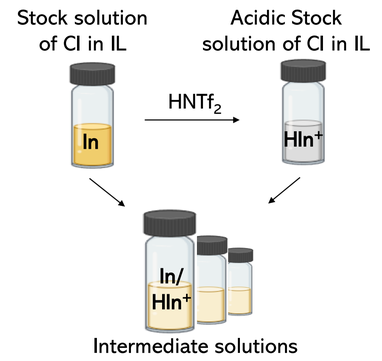

Fig 1. Preparation of solutions of CI in ILs with increasing amounts of acid ($HNTf_2$).

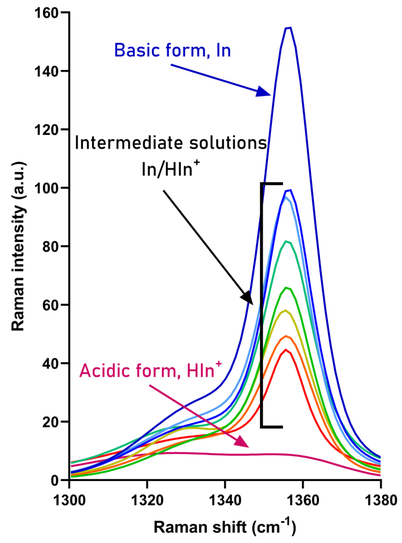

Fig 2. Evolution of the Raman spectrum in the 1300-1380 cm^{-1} range of 2,6-dichloro-4-nitroaniline in $[HMIm]NTf_2$ with increasing amounts of $HNTf_2$.

2. Raman spectra of the solutions were recorded using a Horiba Labram 300 spectrometer interfaced with 532 or 785 nm DPSS lasers.

3. The contribution of the IL was subtracted, and the ionisation ratio of the CI and the Hammett acidity functions were determined through:

$$H_0 \equiv pK_{IC,\,\boldsymbol{H_2O}} + \log\left(\frac{[In]_{IL}}{[HIn^+]_{IL}}\right)$$

$$= pK_{IC,\,\boldsymbol{H_2O}} + \log\left(\frac{I - I_{HIn^+}}{I_{In} - I}\right)$$

Results

1. Effect of different anions

Constant cation (1-butyl-3-methylimidazolium) and different anions: different acidity levels are obtained

⇒ Observed both in Raman and UV-Vis spectroscopies

BUT the H_0 acidity functions are systematically shifted towards higher values (less acidic) in Raman spectroscopy

⇒ Deviate more from the "absolute" acidity of the medium

It might originate from the higher concentration of CI used in Raman spectroscopy (~ 55 mM *vs.* ~ 1-2 mM in UV-Vis)

⇒ Acts as a basic impurity in the IL, decreasing the acidity of the medium

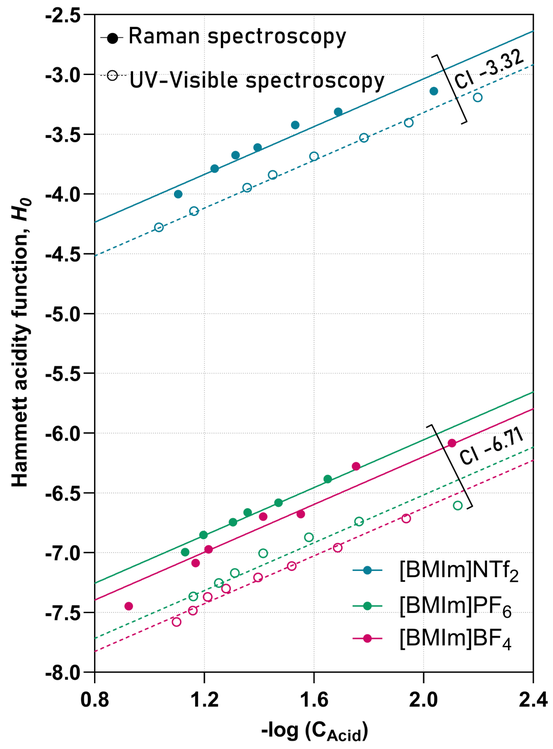

Fig 3. Hammett acidity functions H_0 obtained by Raman (●) and UV-Visible (○) spectroscopies as a function of the cologarithm of $HNTf_2$ concentration in $[BMIm]NTf_2$ (●, CI = 2,4-dichloro-6-nitroaniline, pK_a -3.32), $[BMIm]PF_6$ and $[BMIm]BF_4$ (● and ●, CI = 2-bromo-4,6-dinitroaniline, pK_a -6.71)

2. Effect of the alkyl chain length on the cation

Increasing acidity as the length of the alkyl chain on the cation gets shorter (constant anion, bis(trifluoromethane)sulfonimide)

⇒ Octyl < Hexyl < Butyl < Ethyl

⇒ Observed both in Raman and UV-Vis spectroscopies

⇒ H_0 acidity functions shifted again in Raman spectroscopy

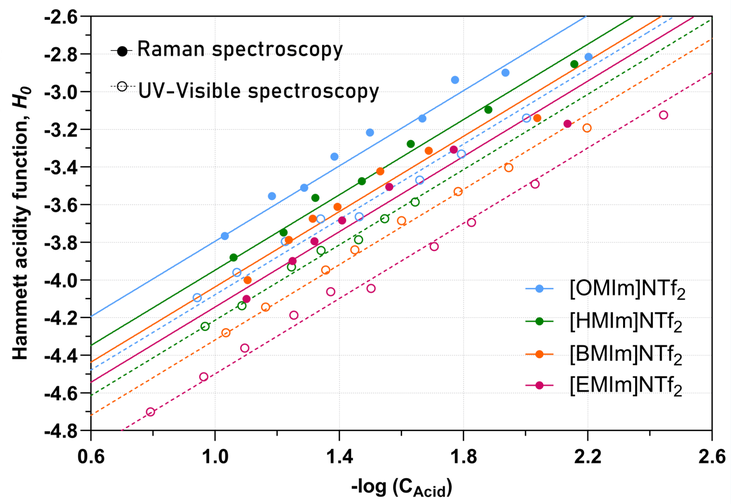

Fig 4. Hammett acidity functions H_0 obtained by Raman (●) and UV-Visible (○) spectroscopies as a function of the cologarithm of $HNTf_2$ concentration in 2,6-dichloro-4-nitroaniline solutions in [EMIm]NTf2 (●), [BMIm]NTf2 (●), $[HMIm]NTf_2$ (●) and [OMIm]NTf2 (●).

Compared to the difference in acidity obtained when the anionic moiety is varied (order of units, cfr. Part I), the H_0 acidity functions vary only by several tenths of unit only[5].

⟹ **Acidity in ILs not governed prominently by the cation, yet a small effect is measured**

3. Ion pairs in ionic liquids

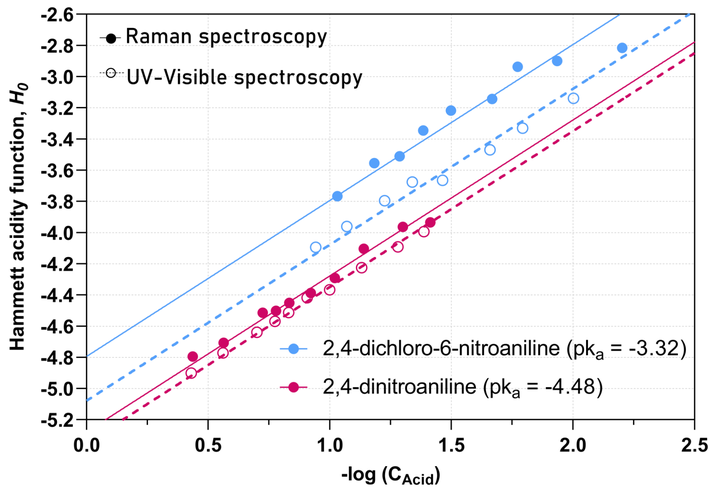

Fig 5. Hammett acidity functions H_0 in $[OMIm]NTf_2$ obtained by Raman (●) and UV-Visible (○) spectroscopies as a function of the cologarithm of $HNTf_2$ concentration for CI = 2,4-dichloro-6-nitroaniline (●) and 2,4-dinitroaniline (●).

When two different CIs are used in the same solvent: different H_0 acidity functions, as already described in the literature[6]

⇒ Observed both in Raman and UV-Visible spectroscopies

Linked to the possible fully non-dissociating behavior of ILs, leading to ion pairs between the CI and acid:

$$In + X^- \rightleftarrows InH^+X^-$$

Definition of an **apparent acidity function** $(H_0)_{app}$[6]:

$$(H_0)_{app} = pK_{IC,\,H_2O} + \log\left(\frac{[In]_{IL}}{[HIn^+X^-]_{IL}}\right) = pK_{IC,\,H_2O} + pK_f^{InH^+X^-} - \log(C_{HX})$$

⇒ Shifted H_0 acidity functions towards less acidic values due to the formation of ion pairs

Conclusion

- The Hammett acidity functions was implemented for the first time in Raman spectroscopy, leading to similar results as in UV-Visible spectroscopy:
  - Small influence of the IL cation on the achieved acidity, compared to the anion
  - Ion pairs seem to form between the CI and the acid
- However, lower acidities are measured by Raman, which could originate from the high CI concentration, acting as a basic impurity in the medium
- Nonetheless, **Raman spectroscopy possesses many advantages over UV-Visible spectroscopy**:
  - ✓ Not limited to CIs: possibility to use colourless pH probes and study coloured media
  - ✓ Use other pH probes than nitroanilines: non-aromatic, better meeting the Hammett hypothesis
  - ✓ Possibility to perform in-situ measurements through optical fibres

Perspectives

- Study of the CI concentration
- Study of other cations to probe specific interactions between the IC and IL (e.g. 1-butyl-3-methylpyrrolidinium cation)
- Probing the non-dissociating behaviour of ILs: determine formation constant of ion pairs in the ILs

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(4) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54* (7), 2721–2739.
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(6) Bruckenstein, S., *J. Am. Chem. Soc*. **1960**, *82 (2)*, 307-310

Acknowledgements
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