Tailoring ionic liquids: structure, acidity and catalytic activity of a new class of protic ionic liquids based on oligomeric $[(HSO_4)_xH_{x-1}]^-$ anions

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Supplementary Information

^{1}H NMR spectra of ionic liquids

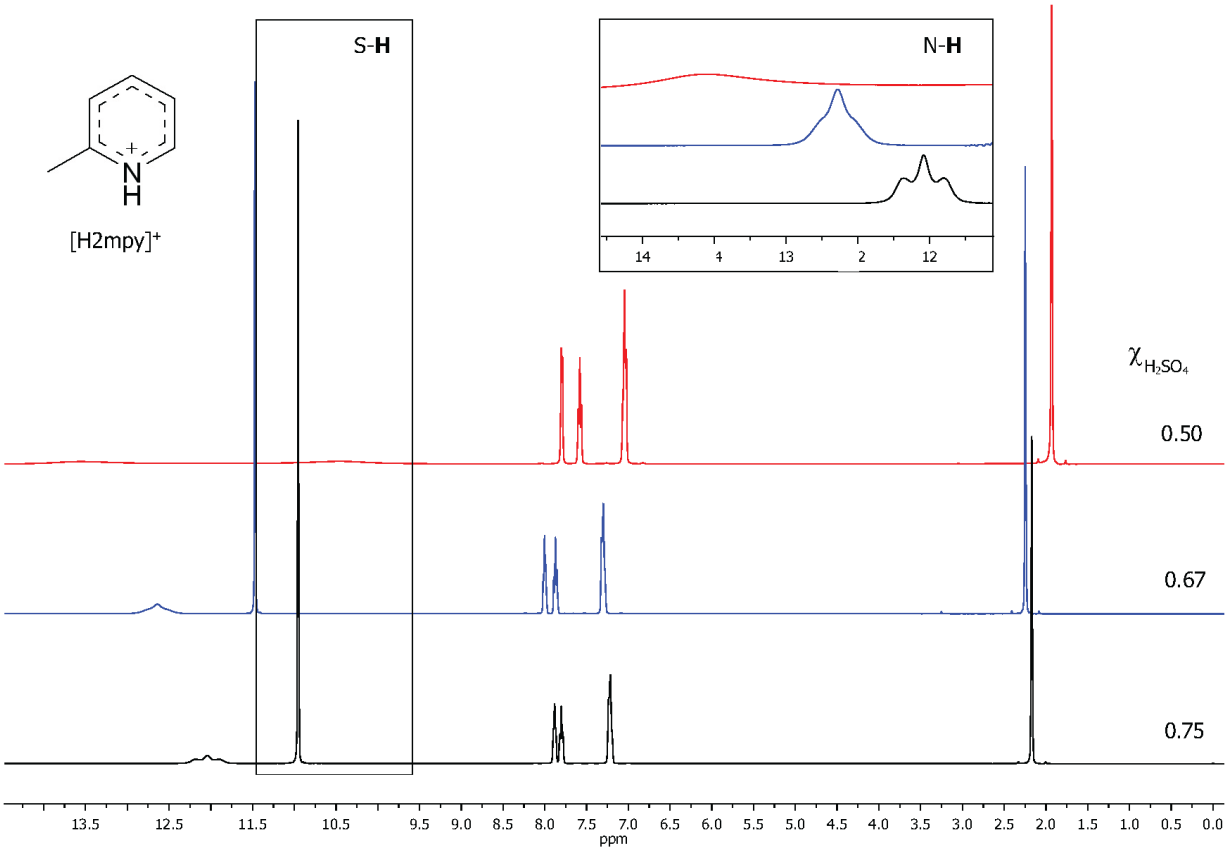

Figure 1-SI. ^{1}H NMR spectra (400.112 MHz, 80 °C, neat) of the [H2mpy][$(HSO_4)(H_2SO_4)_n$] system, for χ_{H2SO4} = 0.50, 0.67 and 0.75.

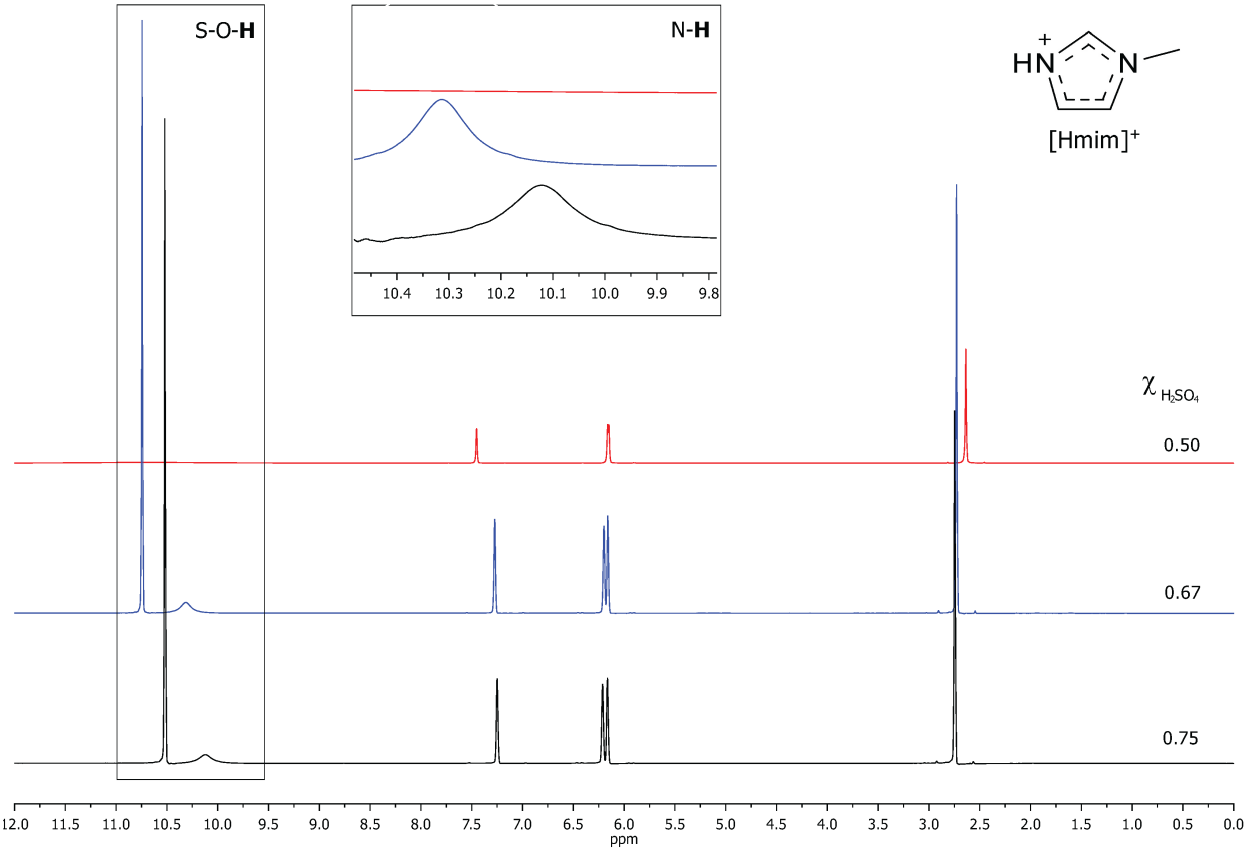

Figure 2-SI. ^{1}H NMR spectra (400.112 MHz, 80 °C, neat) of the [Hmim][$(HSO_4)(H_2SO_4)_n$] system, for χ_{H2SO4} = 0.50, 0.67 and 0.75.

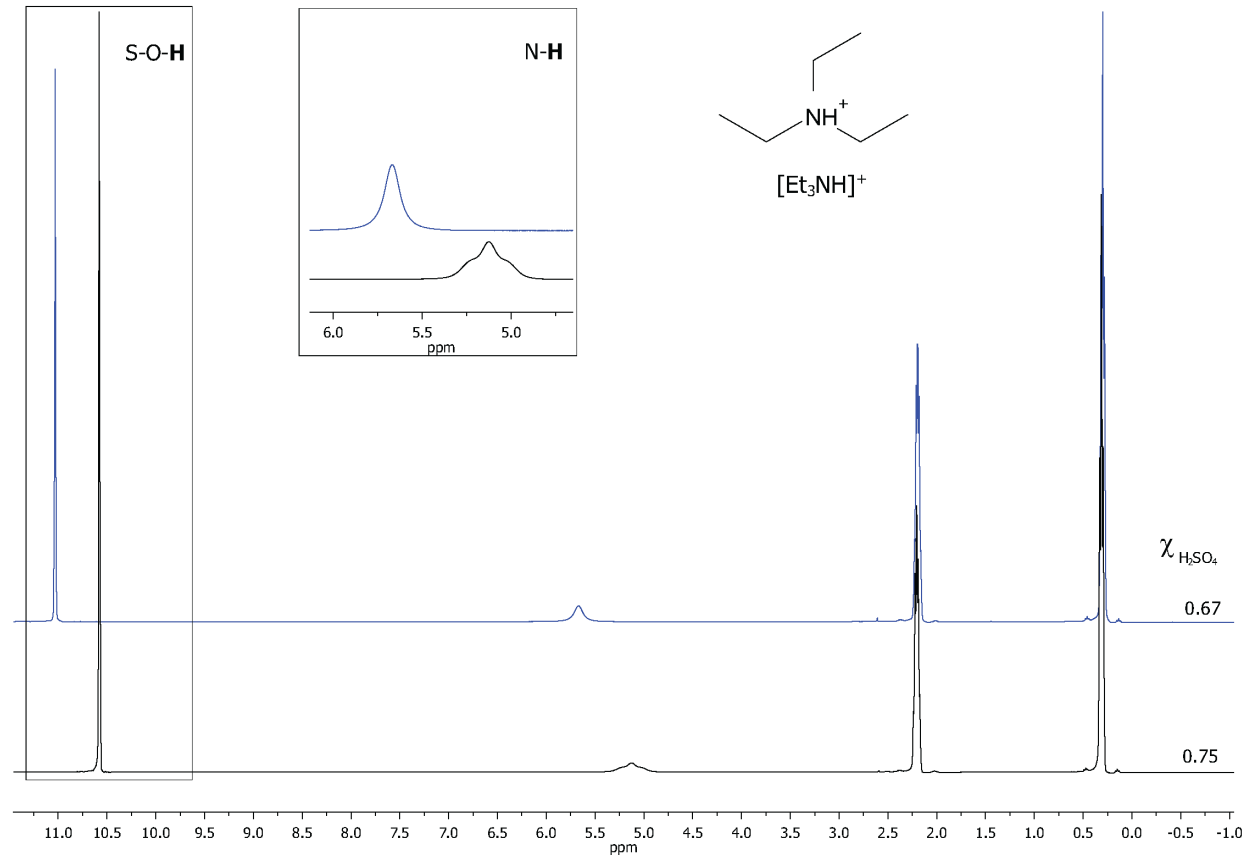

Figure 3-SI. ^{1}H NMR spectra (400.112 MHz, 80 °C, neat) of the [Et_3NH][$(HSO_4)(H_2SO_4)_n$] system, for χ_{H2SO4} = 0.50, 0.67 and 0.75.

Thermal properties of ionic liquids

In general, all ionic liquids had good thermal stability (T_d >200 °C). In all cases, loss of small amounts of water can be observed ('step' around 100 °C).

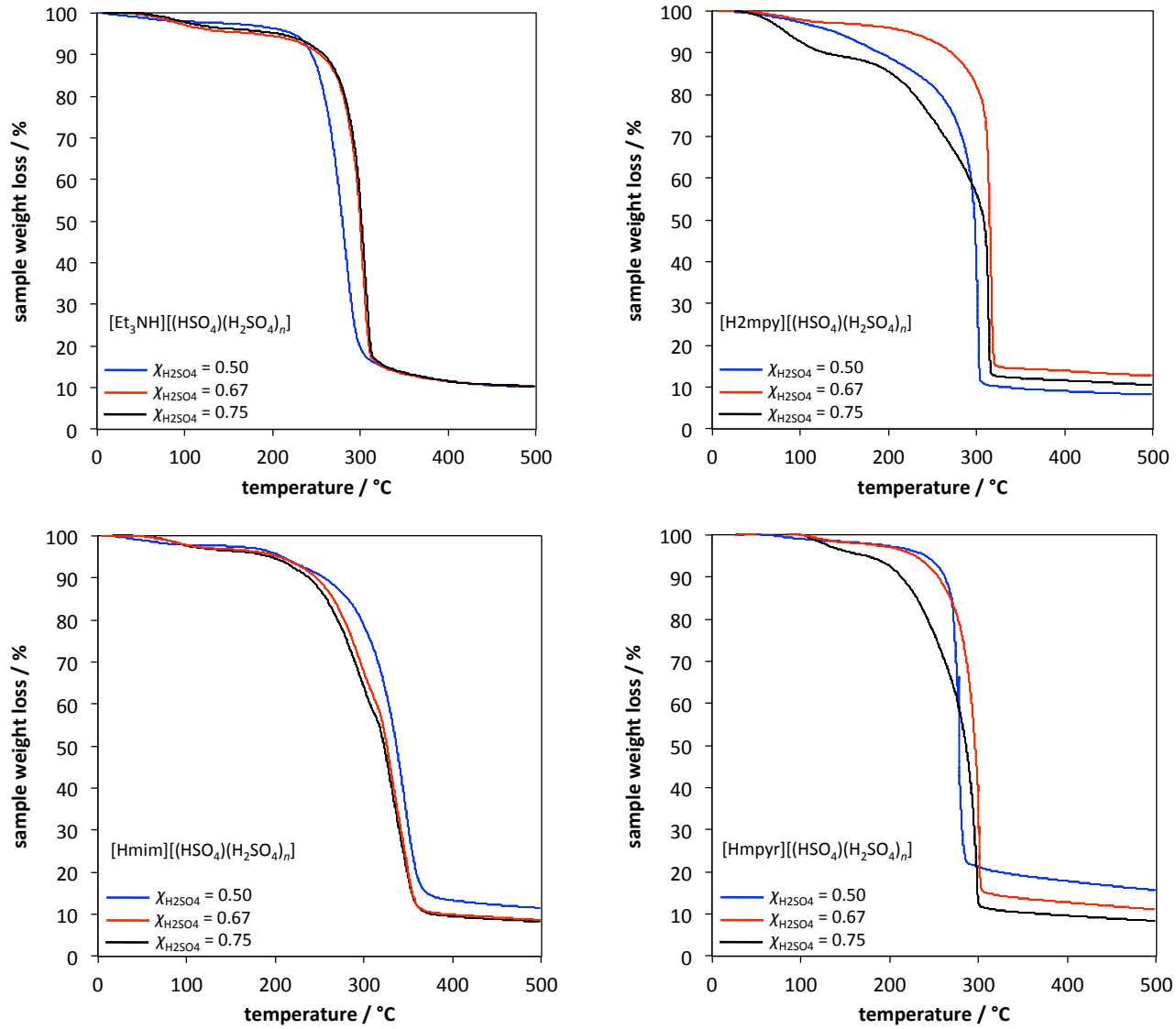

Figure 4-SI. Thermogravimetric analysis curves, depicting water loss and thermal decomposition of ionic liquids based on four protic cations, as a function of temperature.

Melting points could be measured only for ionic liquids prepared from equimolar amounts of a base and sulfuric acid (χ_{H2SO4} = 0.50), as listed in Table 1-SI; for χ_{H2SO4} > 0.50 room temperature ionic liquids were obtained, with glass transitions, T_g < 0 °C.

Table 1-SI. Melting points of protic ionic liquids (χ_{H2SO4} = 0.50).

ionic liquid	**melting point / °C**
[H2mpy][HSO_4]	62.63
[Hmim][HSO_4]	18.38 and 40.63
[Et_3NH][HSO_4]	75.18
[Hmpyr][HSO_4]	2.56