Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Understanding Positive and Negative Deviations in Polarity of Ionic Liquid Mixtures by Pseudo-solvent Approach

*Vijay Beniwal and Anil Kumar**

Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Homi Bhabha Road, Pune-411 008, India

*Author for correspondence: a.kumar@ncl.res.in Tel: 91-20-2598 2278

Contents:

1. Synthesis of aprotic ionic liquids:

The synthesis of $[C_4C_1im]^+$ and $[C_4C_1C_1im]^+$ based ionic liquids was carried out through the quarternization reaction followed by the anion exchange reaction. Distilled 1-bromobutane was added slowly to the previously distilled 1-methyimidazole. 1-bromobutane was taken 1.2 times (molar ratio) than that of 1-methylimidazole. The reaction mixture is subjected to the reflux condenser for about 12 h at 65° C. Excess of 1-bromobutane was washed out through using ethyl acetate. Leftover impurities were then removed using high vacuum at about 70°C, resulting in purified 1-Butyl-3-methylimidazolium bromide $[C_4C_1im]Br$. Similar procedure has been followed for the synthesis of 1-Butyl-2,3-dimethylimidazolium bromide $[C_4C_1C_1im]Br$, using 1,2-dimethylimidazole in place of 1-methylimidazole. Second step involves the anion exchange reaction. For this, $[C_4C_1im]Br$ and $[C_4C_1C_1im]Br$ were mixed with the required salts containing respective anion such as, sodium tetrafluoroborate, sodium dicyanamide and silver nitrate using DCM as solvent. The salts were taken 1.2 times (molar ratio) than that of $[C_4C_1im]Br$ and $[C_4C_1C_1im]Br$. Excess of salts were filtered out through Buckner's funnel using celite and DCM as solvent. Ionic liquids were subjected to rota vapour at 60° C in order to evaporate the DCM and then were put under high vacuum at 70°C for 6-12 h to remove leftover water and DCM.

2. Synthesis of protic ionic liquids:

Protic ionic liquids were synthesized via single step 1:1 acid-base reaction also known as atom economy method. Acids containing the required anion were added drop-wise into 1-methylimidazole in a round bottomed flask placed in an ice bath. The reaction mixture was allowed to stir for 6 h. The ionic liquids thus

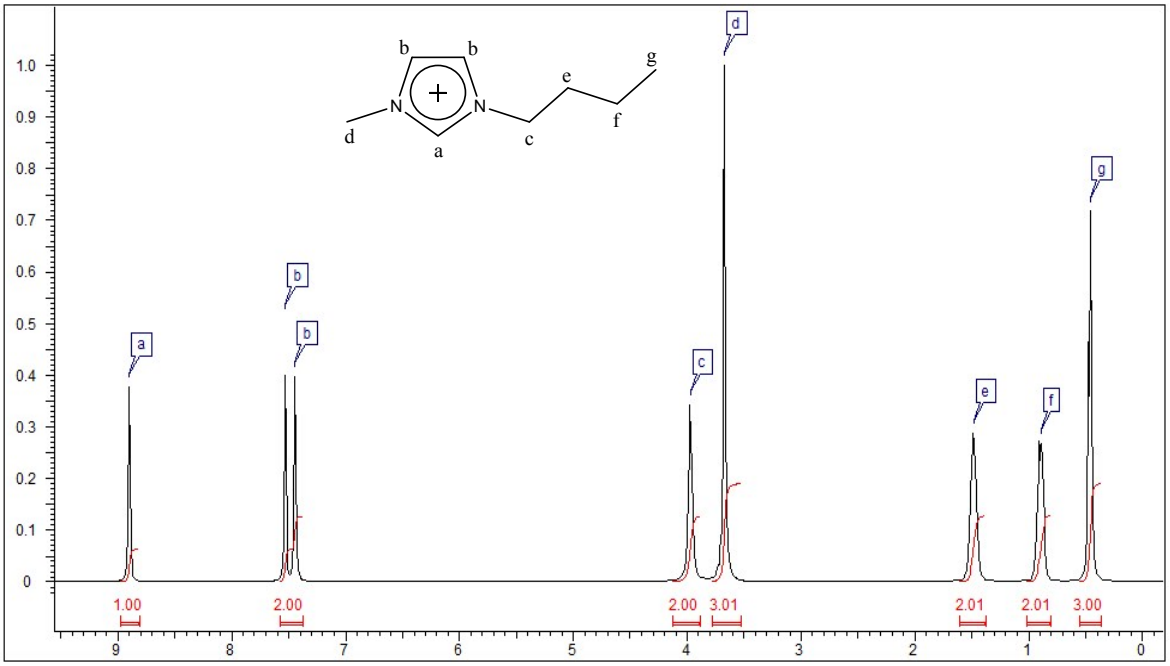
prepared were subjected to the rotavapour at 75° C to remove the excess of water. Then the ionic liquids were dried thoroughly under high vacuum for 12 h at 75° C.

3. Residual halide and water contents of the ionic liquids

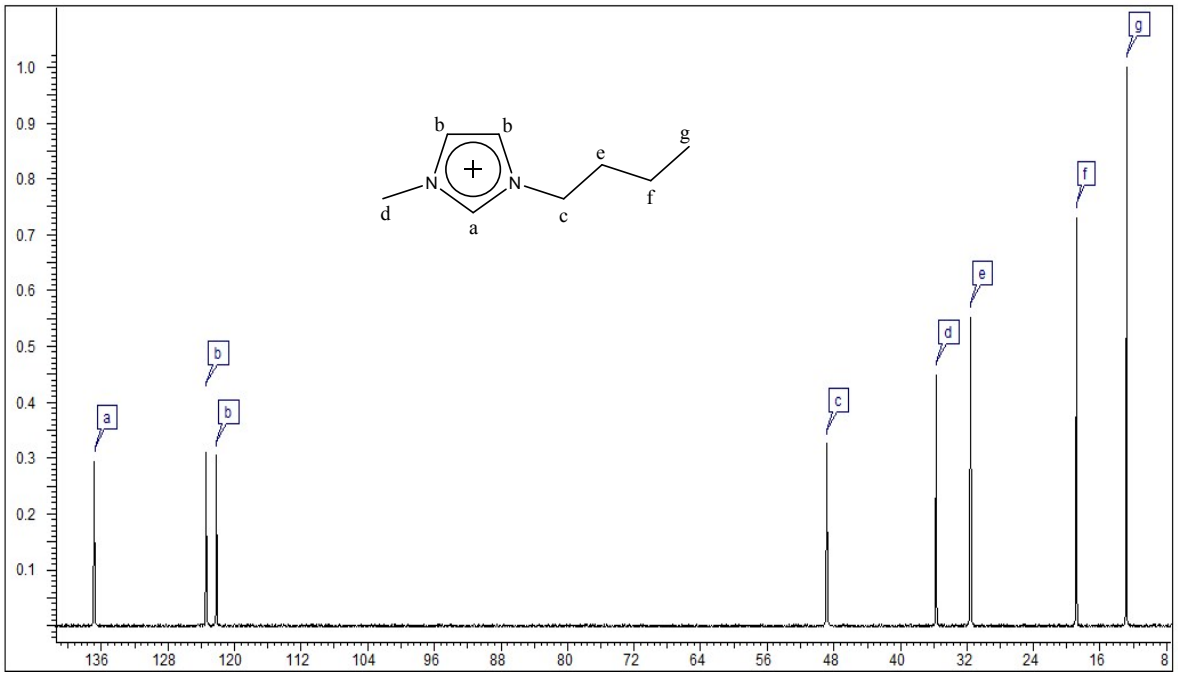
Ionic liquid	Halide contents	Water contents
$[C_4C_1im][BF_4]$	21-23 ppm	36-42 ppm
$[C_4C_1im][N(CN)_2]$	22-23 ppm	40-46 ppm
$[C_4C_1im][NO_3]$	16-18 ppm	43-48 ppm
$[C_4C_1C_1im][BF_4]$	26-27 ppm	30-36 ppm
$[C_4C_1C_1im][N(CN)_2]$	28-29 ppm	34-38 ppm
$[C_4C_1C_1im][NO_3]$	21-24 ppm	37-41 ppm
$[C_1im][HCOO]$	0-5 ppm	60-68 ppm
$[C_1im][CH_3COO]$	0-5 ppm	57-64 ppm

4. ^{1}H NMR and ^{13}C NMR spectra of the ionic liquids

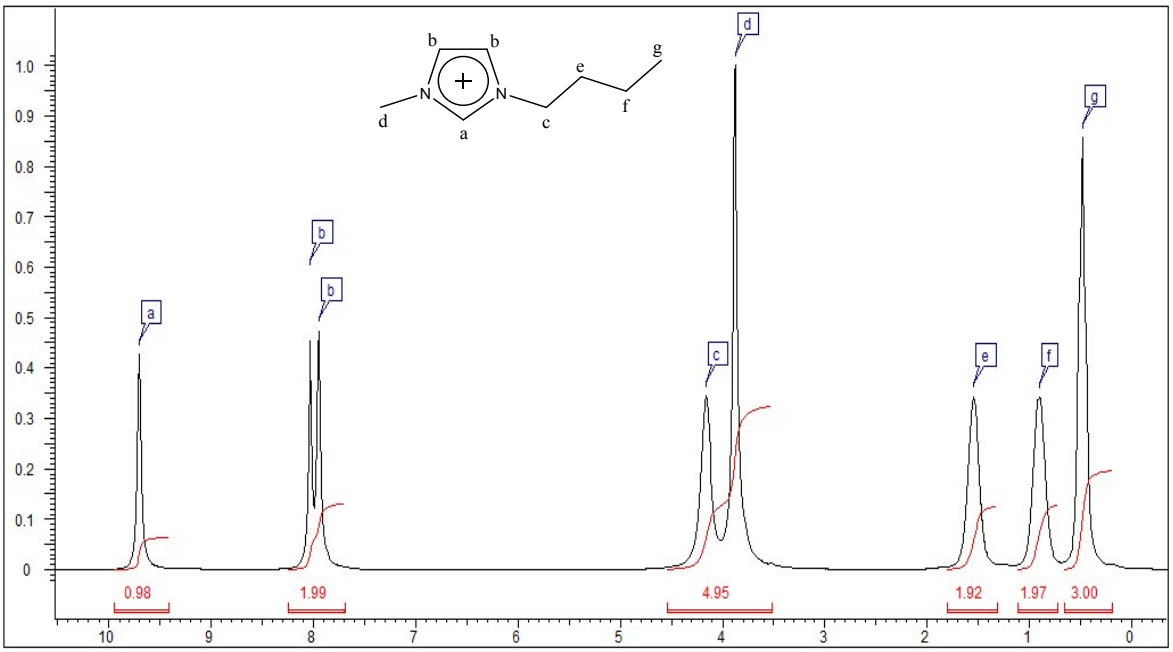
(a) ^{1}H NMR spectrum of pure $[C_4C_1im][BF_4]$ in neat condition at 200 MHz using $CDCl_3$ capillary:



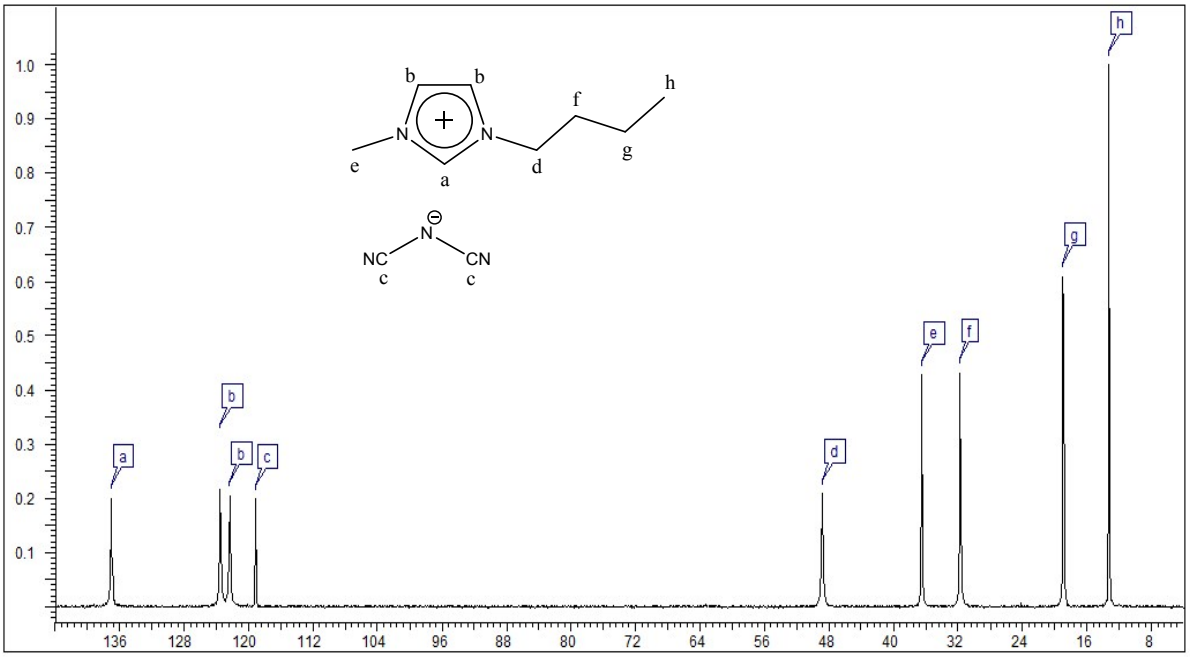
(b) ^{13}C NMR spectrum of pure $[C_4C_1im][BF_4]$ in neat condition at 500 MHz using $CDCl_3$ capillary:



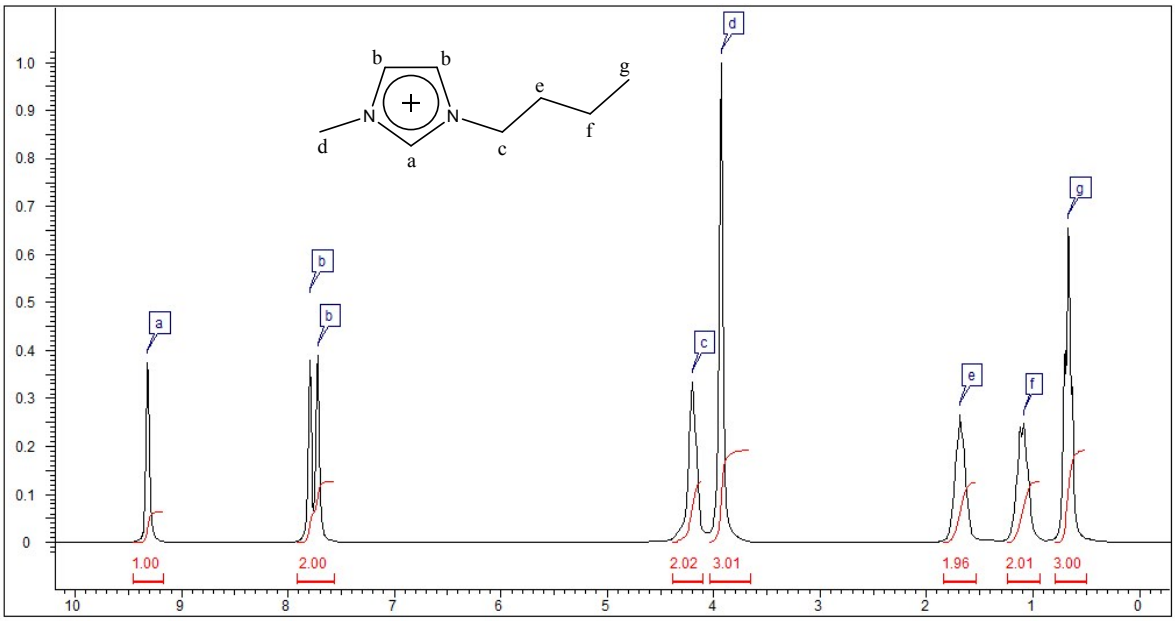
(c) ^{1}H NMR spectrum of pure $[C_4C_1im][N(CN)_2]$ in neat condition at 200 MHz using $CDCl_3$ capillary



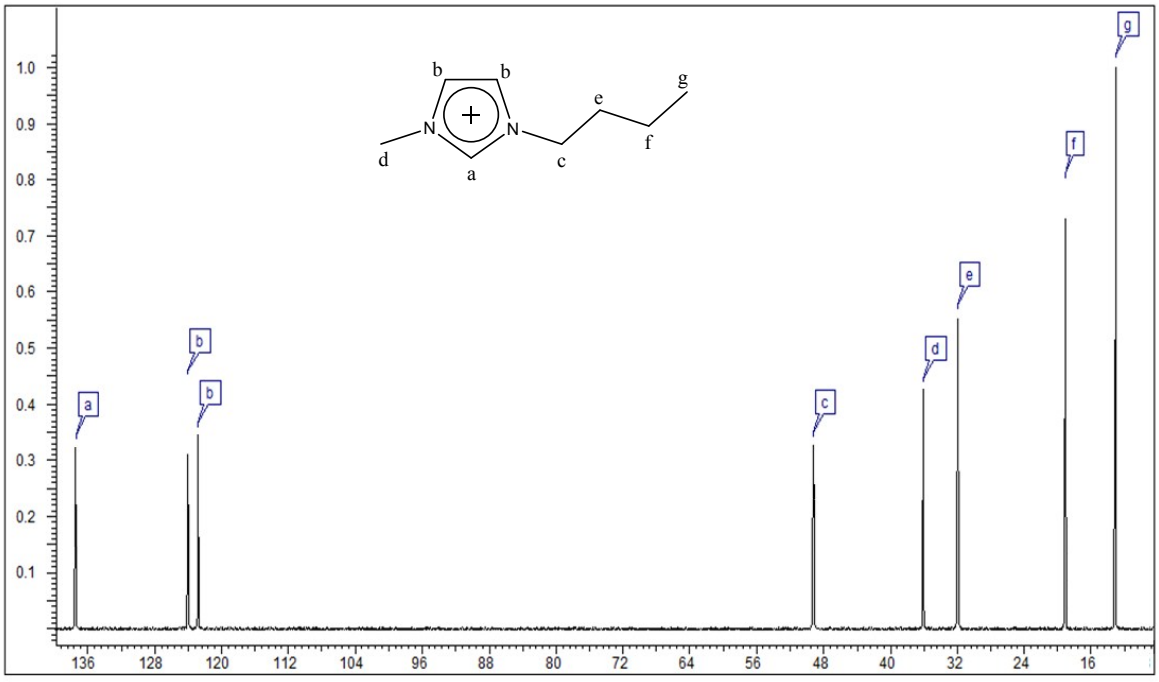
(d) ^{13}C NMR spectrum of pure $[C_4C_1im][N(CN)_2]$ in neat condition at 200 MHz using $CDCl_3$ capillary



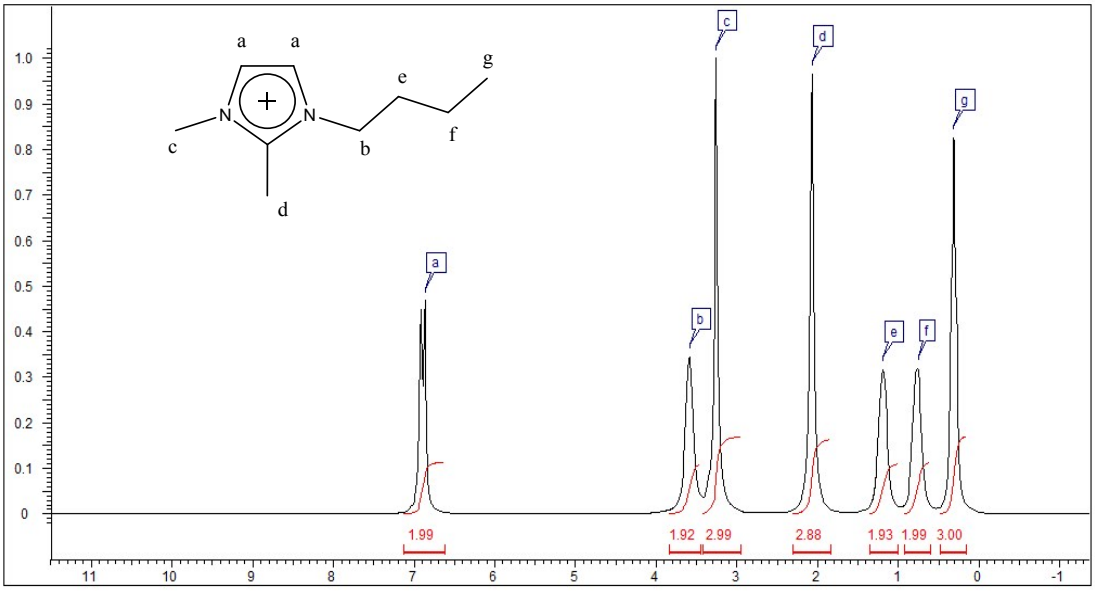
(e) ^{1}H NMR spectrum of pure $[C_4C_1im][NO_3]$ in neat condition at 200 MHz using $CDCl_3$ capillary



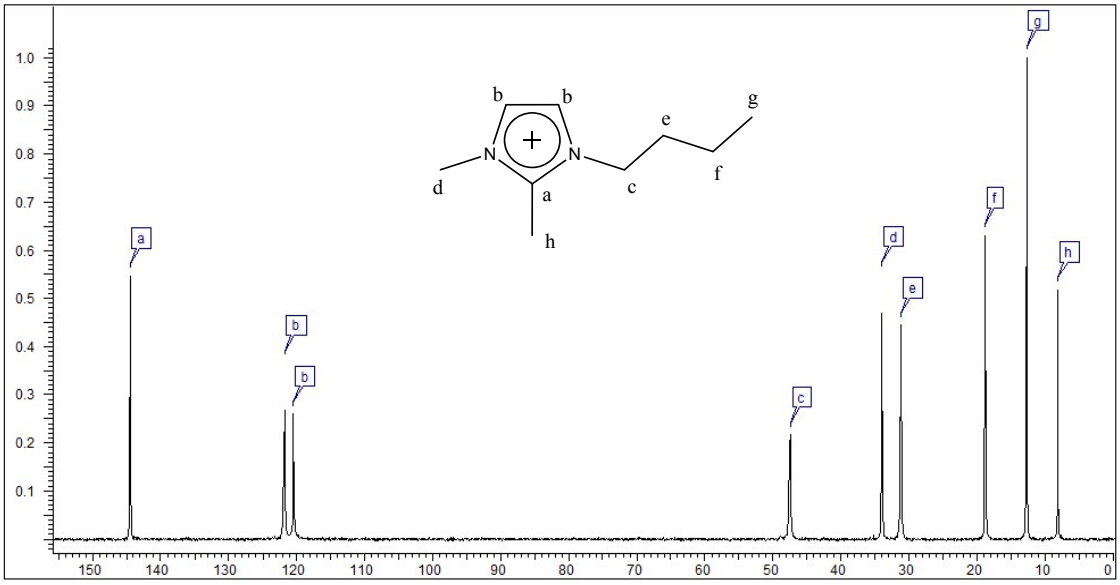
(f) ^{13}C NMR spectrum of pure $[C_4C_1im][NO_3]$ in neat condition at 200 MHz using $CDCl_3$ capillary



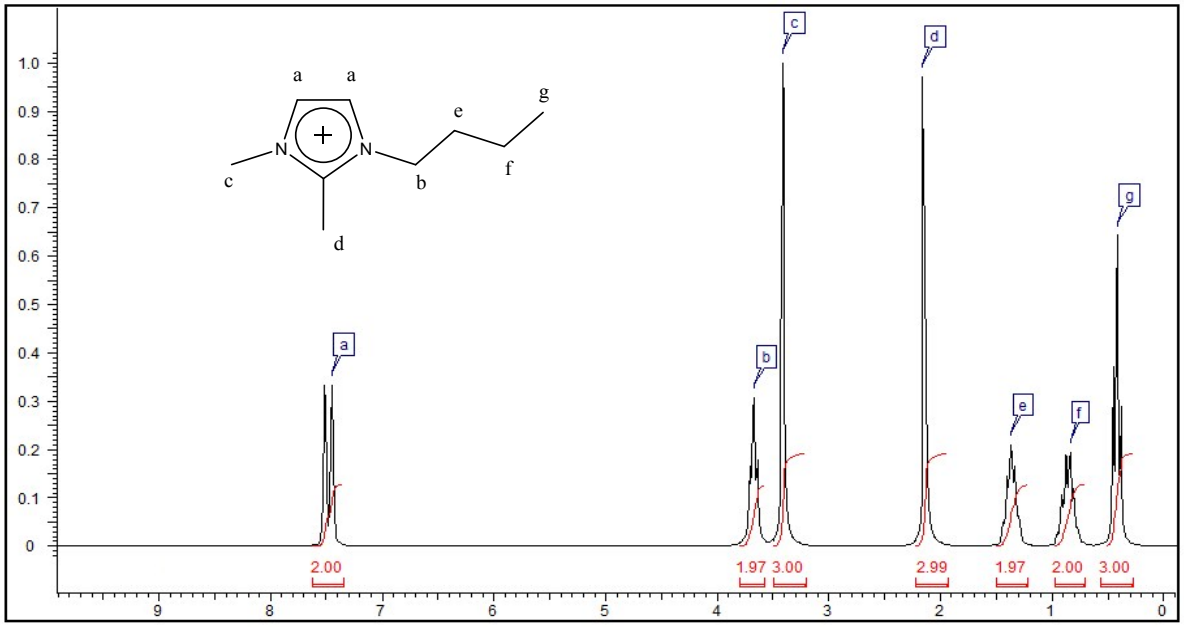
(g) ^{1}H NMR spectrum of pure $[C_4C_1C_1im][BF_4]$ in neat condition at 200 MHz using $CDCl_3$ capillary



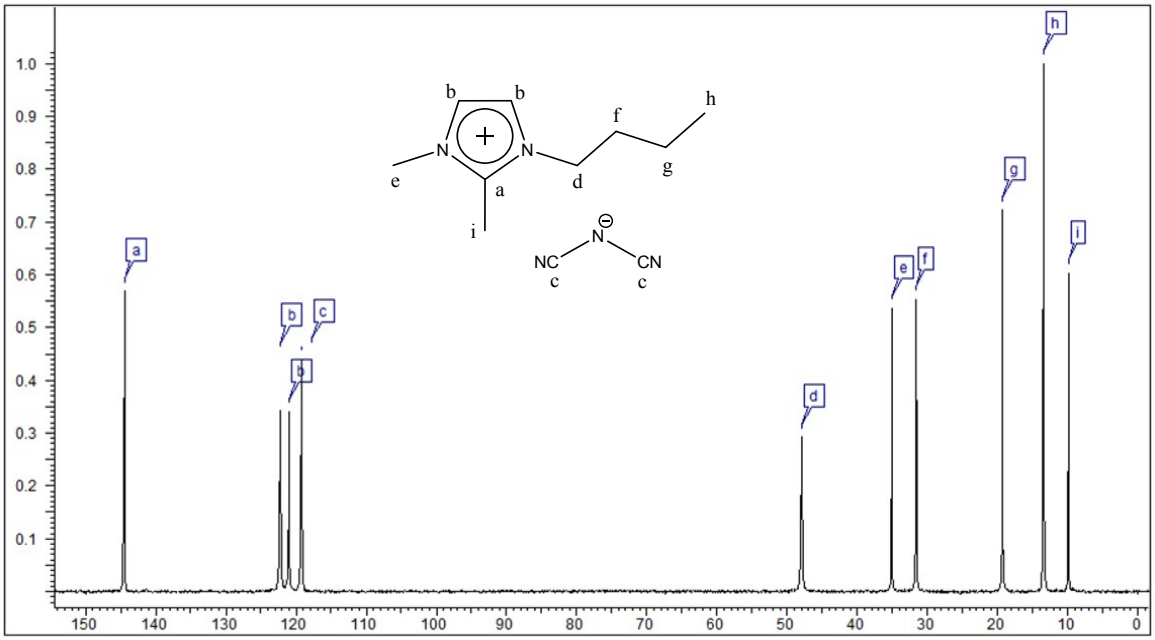
(h) ^{13}C NMR spectrum of pure $[C_4C_1C_1im][BF_4]$ in neat condition at 200 MHz using $CDCl_3$ capillary



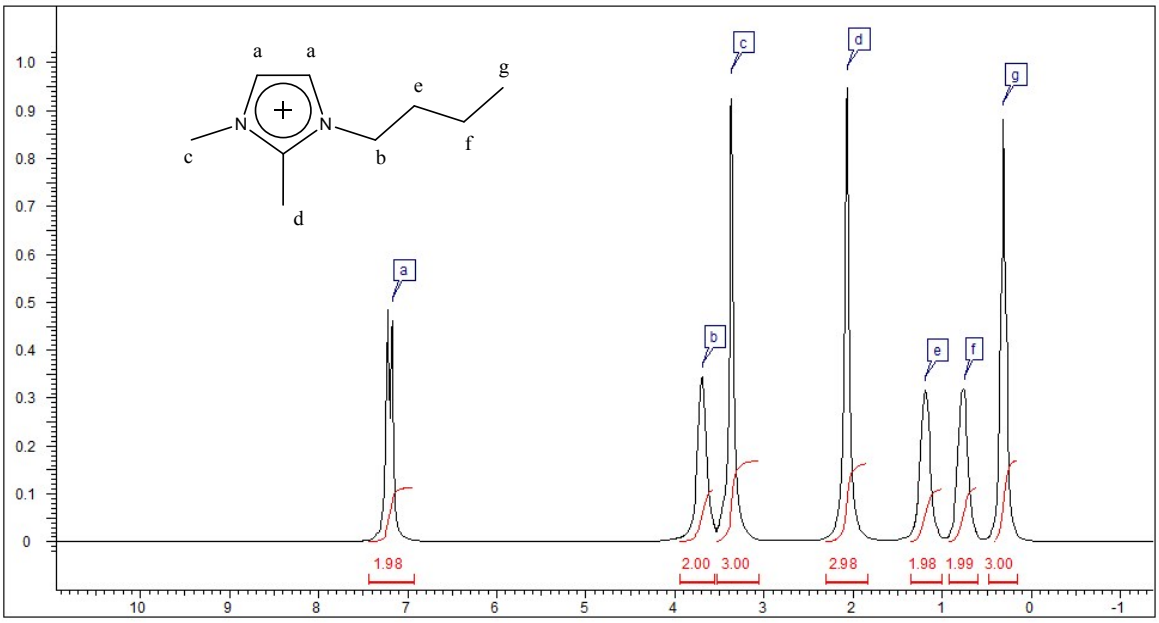
(i) ^{1}H NMR spectrum of pure $[C_4C_1C_1im][N(CN)_2]$ in neat condition at 200 MHz using $CDCl_3$ capillary



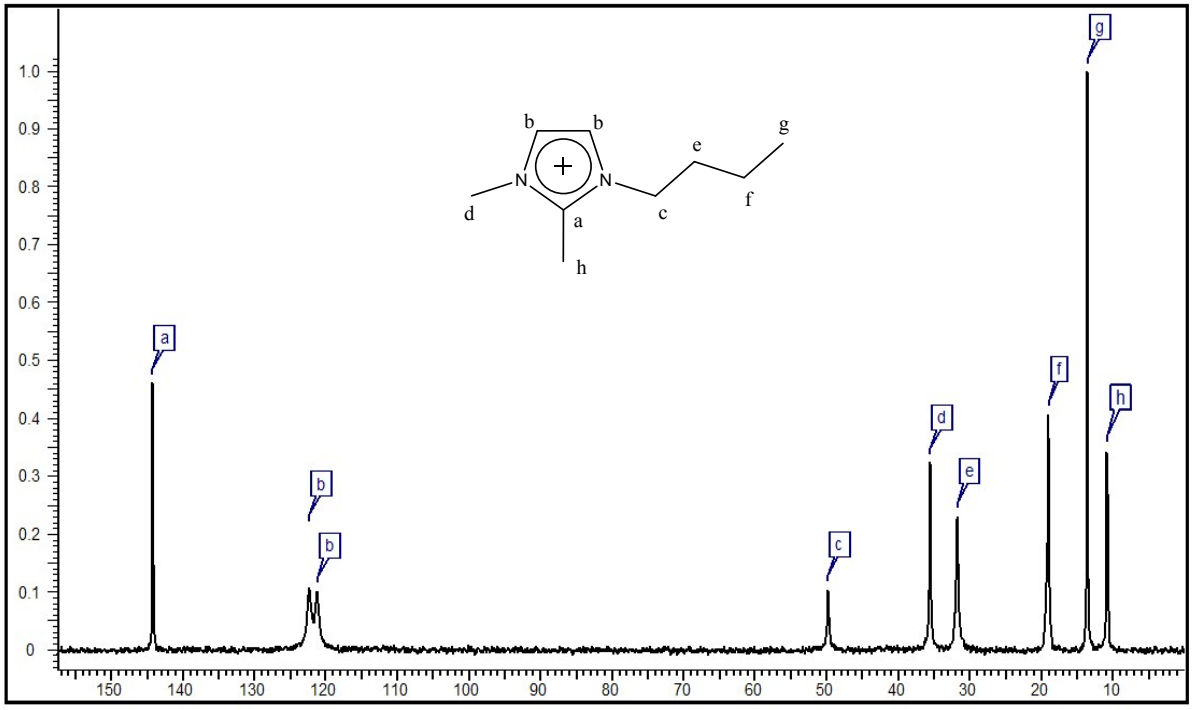
(j) ^{13}C NMR spectrum of pure $[C_4C_1C_1im][N(CN)_2]$ in neat condition at 200 MHz using $CDCl_3$ capillary



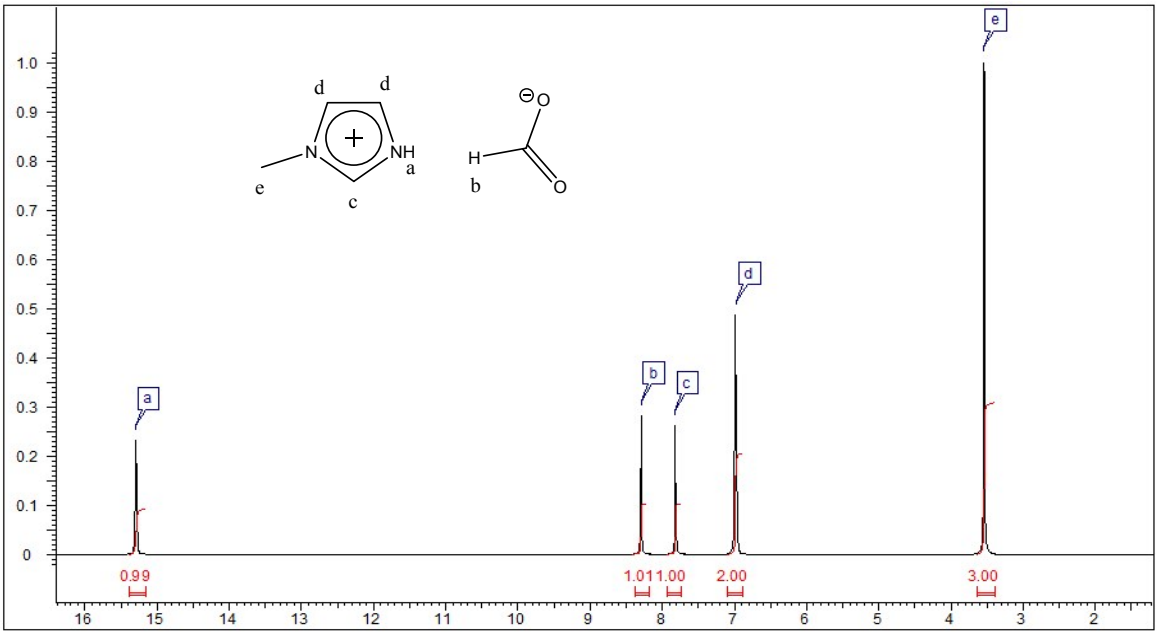
(k) ^{1}H NMR spectrum of pure $[C_4C_1C_1im][NO_3]$ in neat condition at 200 MHz using $CDCl_3$ capillary



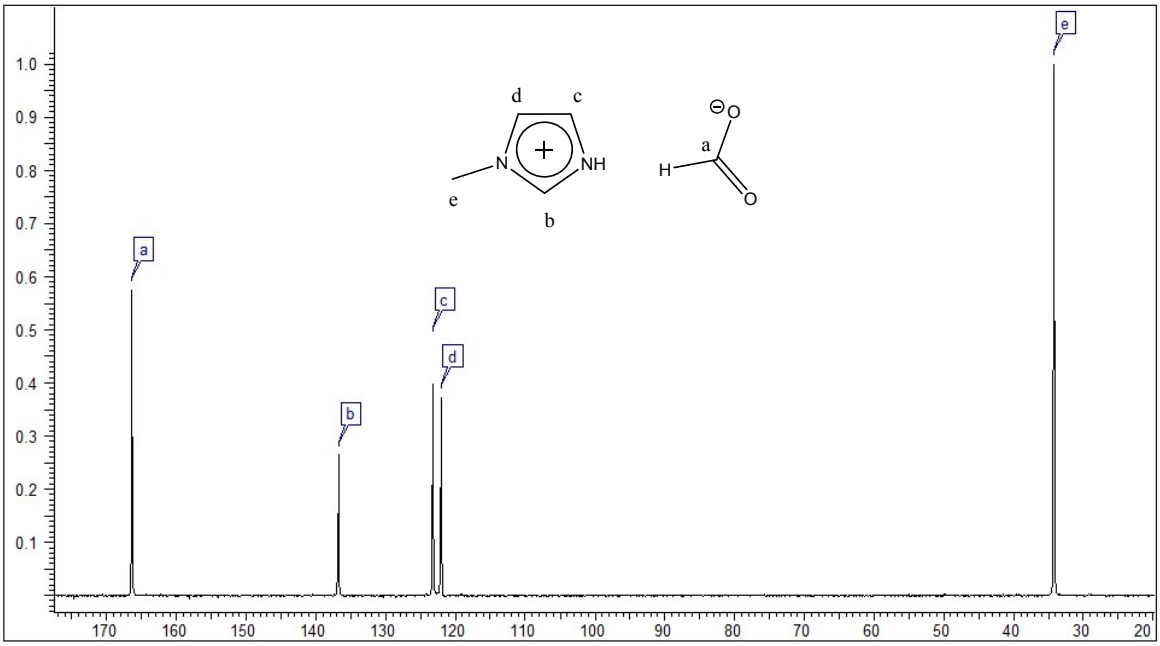
(l) ^{13}C NMR spectrum of pure $[C_4C_1C_1im][NO_3]$ in neat condition at 200 MHz using $CDCl_3$ capillary



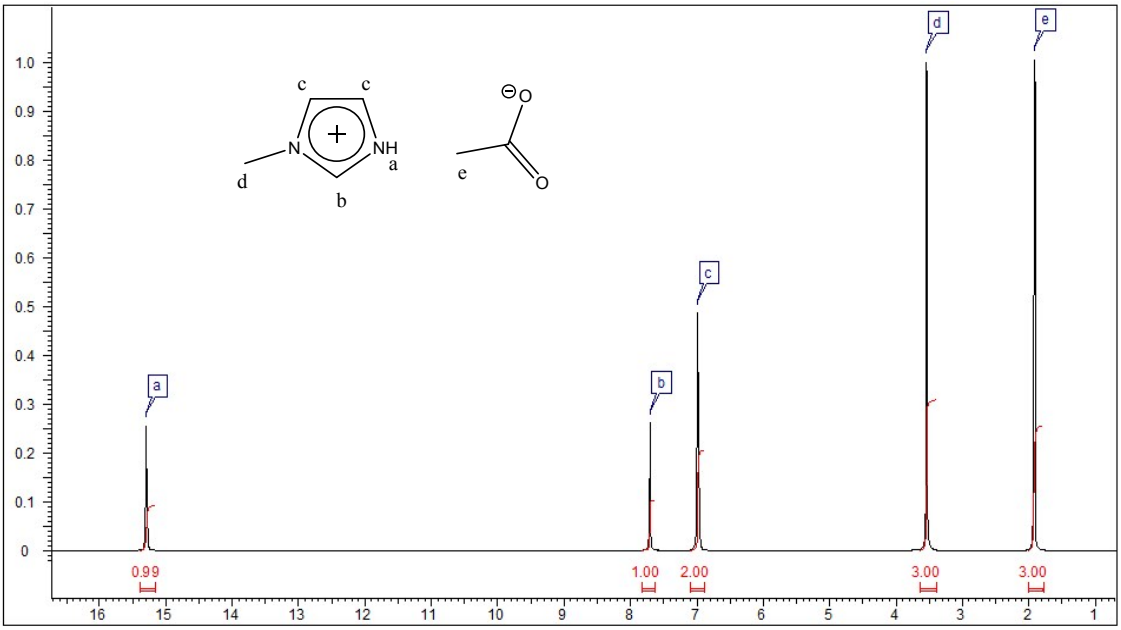
(m)[1]H NMR spectrum of pure [C_1im][HCOO] in neat condition at 200 MHz using $CDCl_3$ capillary



(n) [13]C NMR spectrum of pure [C_1im][HCOO] in neat condition at 200 MHz using $CDCl_3$ capillary



(o) ^{1}H NMR spectrum of pure $[C_1im][CH_3COO]$ in neat condition at 200 MHz using $CDCl_3$ capillary



(p) ^{13}C NMR spectrum of pure $[C_1im][CH_3COO]$ in neat condition at 200 MHz using $CDCl_3$ capillary