Aqueous solutions of Ionic Liquids

- Imidazolium cation & halide anion
- Studied by NMR Spectroscopy

2012.8.11

Seoncheol Cha

What is ionic liquids?

Materials exist at **liquid state** at room-temperature even though having ionic bonding

Low vapor pressure

Low combustibility

Excellent thermal stability

Wide liquid region

Good solvent for
polar/non-polar compounds

Green solvent for alternating organic solvent

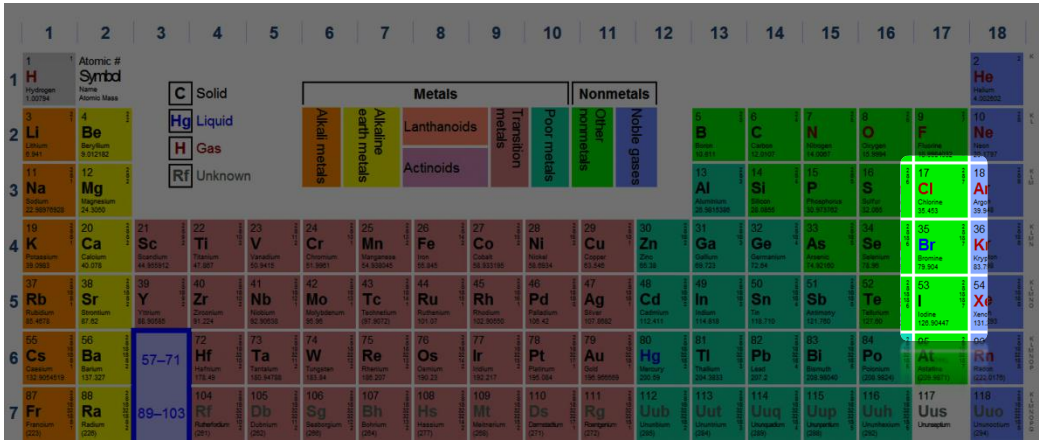
Special solvent to synthesis unique chemical

Recycling material

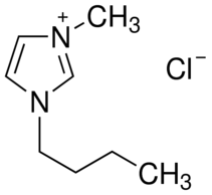
Solar thermal energy transfer/storage medium

Battery electrolyte

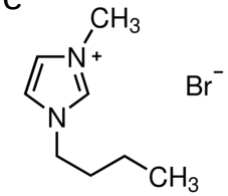
[bmim][X] ionic liquid (X : Cl, Br, I)



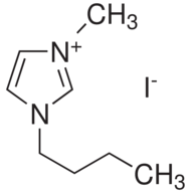
1-Butyl-3-methylimidazolium chloride



1-Butyl-3-methylimidazolium bromide

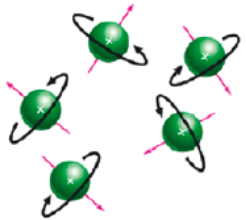


1-Butyl-3-methylimidazolium iodide



NMR Spectroscopy

Nuclear Spin Magnetic Moment vs. Energy (In the case of s = 1/2)



External H^o

H^o

α-Spin

&

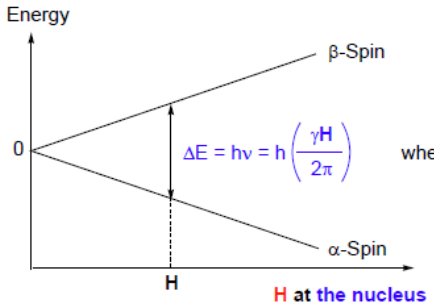
β-Spin

- Parallel orientaion
- More stable
  → More populated

- Anti-parallel orientaion
- Less stable
  → Less populated

In the absence of H^o, the energy of nuclei with any nuclear spin magnetic moment are the same
→ The spins of magnetic nuclei are oriented randomly

Boltzman distribution : $\frac{P(\alpha)}{P(\beta)} = e^{-\frac{E(\alpha)-E(\beta)}{kT}}$

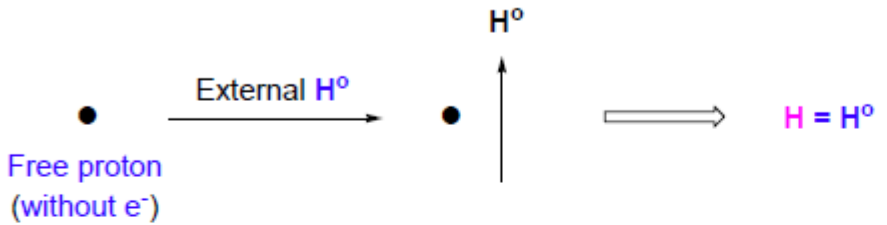


where
- H : Magnetic field at the nucleus (not H^o)
- γ : Magnetogyric ratio of the nucleus (Characteristic & different for each nucleus !)

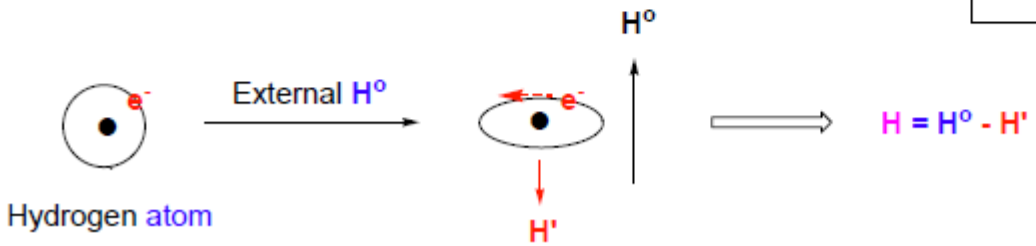
($\gamma = 2.6753 \times 10^4$ radians / sec Gauss for ^1H
$\gamma = 6.7328 \times 10^3$ radians / sec Gauss for ^{13}C)

Chemical Shift

Shielding / Deshielding



H : Effective field felt by the nucleus
H° : Applied external magnetic field
H' : Induced magnetic field by e⁻
(Diamagnetic shielding)



Upfield, Downfield

- Fixed ν & vairable **H°** : e^- Density around proton ↑
  → Shielding ↑
  → Induced magnetic field (**H'**) ↑
  → **H°** for matching ΔE = hν (fixed value !) ↑
  → Upfield

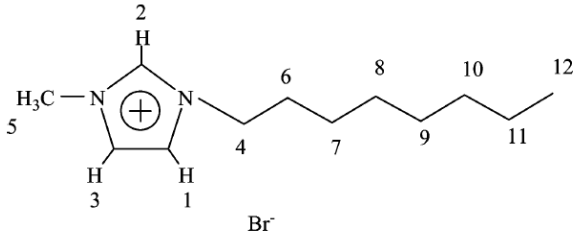
- Fixed **H°** & vairable ν (Modern Instrument) : e^- Density around proton ↑
  → Shielding ↑
  → Induced magnetic field (**H'**) ↑
  → **H** ↓
  → ν ↓

Context

2003 The structure of a Room-Temperature Ionic Liquid with and without trace amount of water :
The role of C-H…O and C-H…F Interactions in [$C_n$mim[BF_4]
- NOE / ROE NMR Spectroscopy for [$C_n$mim][BF_4]
- type of water-cation interaction / site of interaction
Andrea Mele, Chieu D. Tran, Silvia H. De Paoli Lacerda
Angew. Chem. Int. Ed (2003) **42** 4364

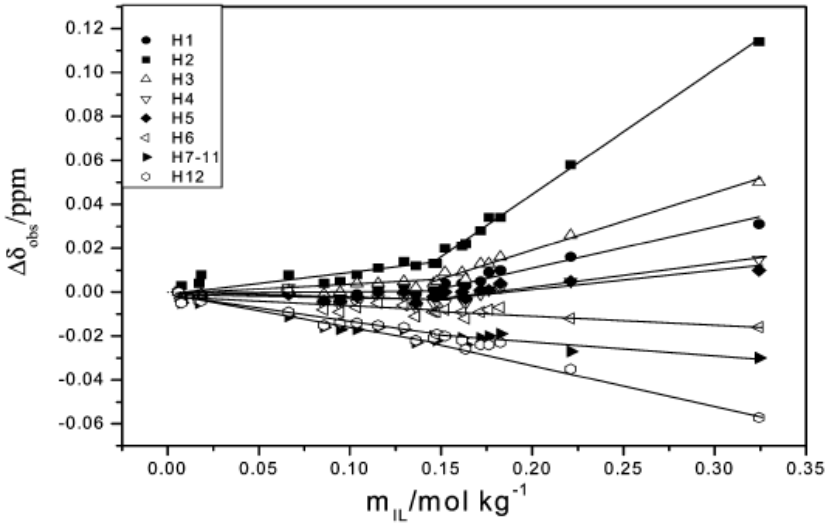
2008 Aggregation of Ionic Liquids [$C_n$mim]Br (n=4,6,8,10,12) in D_2O : A NMR Study
- 1H NMR, 1H-1H ROESY NMR
- aggregation in aqueous solution of ionic liquid
Yang Zhao, Shanjiao Gao, Janji Whang, Junming Tang
J.Phys.Chem.B (2008) **112** 2031

2008 Aggregation of Ionic Liquids [Cnmim]Br (n=4,6,8,10,12) in D2O : A NMR Study



$\delta_{obsd} = \delta_{obsd} - \delta_{obsd,m}$

$\delta_{obsd,m}$ = observed chemical shift of a given IL at the lowest concentration



Dependence of proton chemical shifts of [C_8mim]Br on the IL concentration in D_2O.

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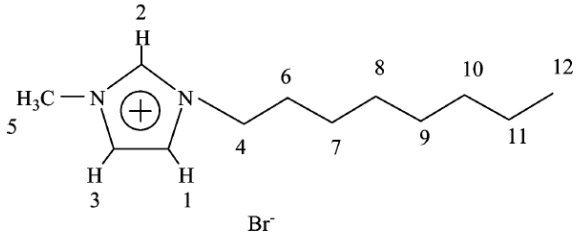
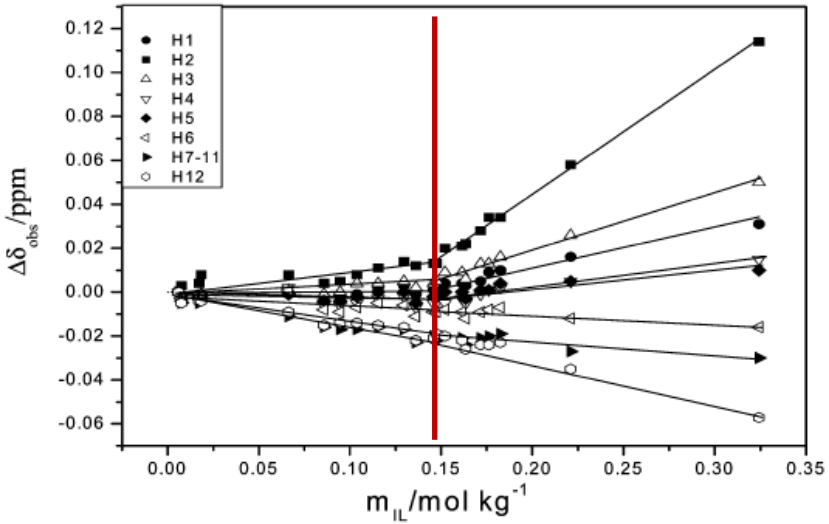


CAC (critical aggregation concentration)

Fast exchange of monomer and aggregate assumption (faster than NMR time scale)

$\delta_{obsd} = \delta_{mon} m_{mon}/m_{tot} + \delta_{mic} m_{mic}/m_{tot}$



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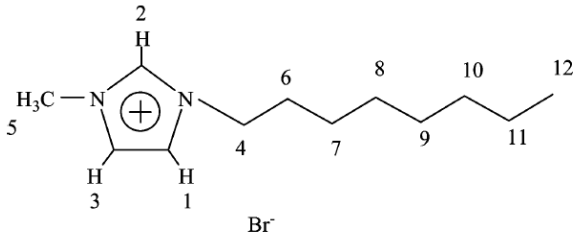

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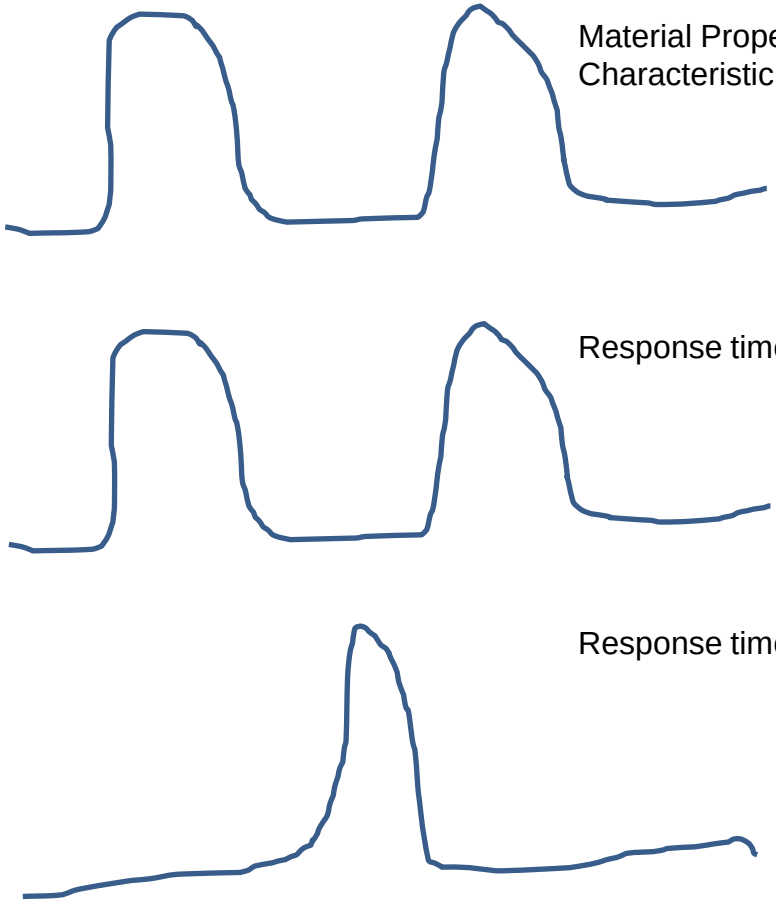

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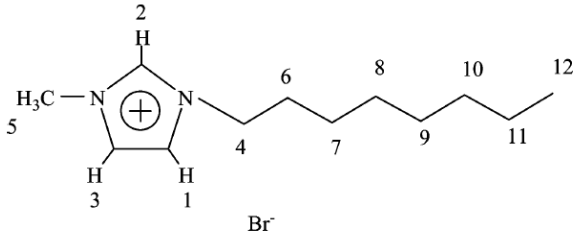


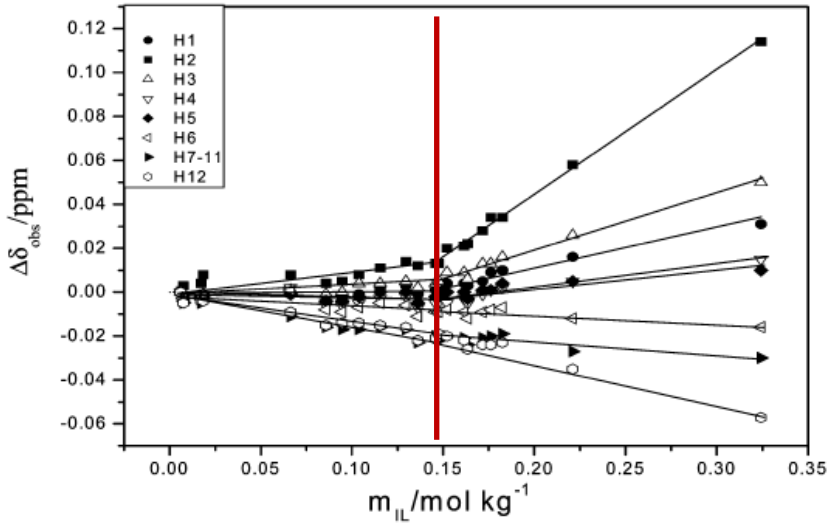
CAC (critical aggregation concentration)

Fast exchange of monomer and aggregate assumption (faster than NMR time scale)

$\delta_{obsd} = \delta_{mon} m_{mon}/m_{tot} + \delta_{mic} m_{mic}/m_{tot}$

No aggregation assumption below CAC

$\delta_{obsd} = \delta_{mic} - CAC(\delta_{mic}-\delta_{mon})/m_{tot}$



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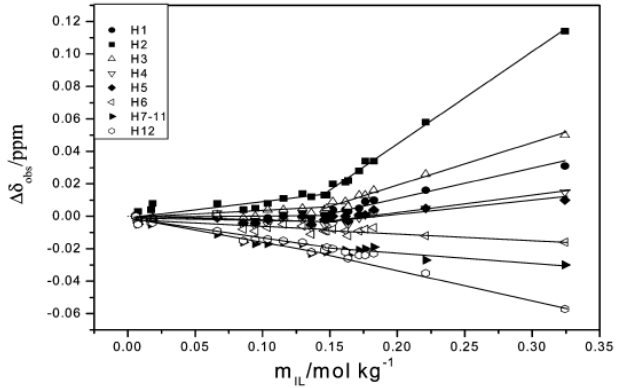


Dependence of proton chemical shifts of [C8mim]Br on the IL concentration in D_2O.

CAC1

$$\delta_{obsd} = \delta_{mon} m_{mon}/m_{tot} + \delta_{mic} m_{mic}/m_{tot}$$

CAC2

$$\delta_{obsd} = \delta_{mic} - CAC(\delta_{mic}-\delta_{mon})/m_{tot}$$

Ref1 : Goodchild *et al* (2007)
Ref2 : Wang *et al* (2007)

No aggregate for short chain

Difference between H_2O and D_2O (??)

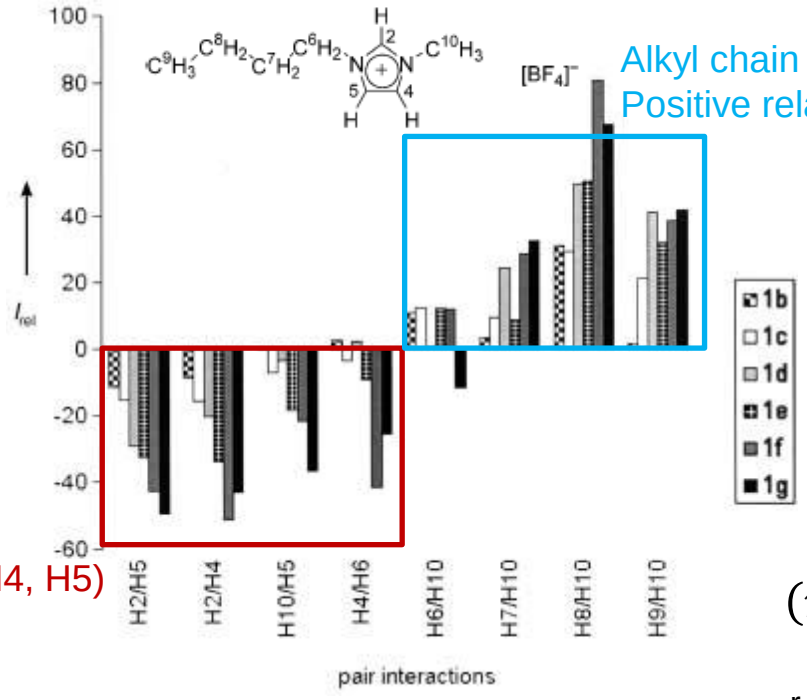
IL	CAC1 (mol / kg)	CAC2 (mol / kg)	Surface tenstion (mol/ L) Ref1	Electric conductivity (mol / L) ref1	Electric conductivity (mol / L) ref2
[C_4mim][Br]	-	2.579	0.8±0.1	0.7±0.3	0.97
[C_6mim][Br]	0.732	0.849	0.6±0.2	0.4±0.3	0.77
[C_8mim][Br]	0.142	0.140	0.15±0.05	0.15±0.06	0.16
[C_{10}mim][Br]	0.030	0.032	0.04±0.02	0.03±0.01	0.039
[C_{12}mim][Br]	0.011	0.011			0.009

[BMIM][BF_4] Rosey

Ring proton is hydrogen bond donor to F atoms in F (in BF_4)

H_2O involved in Hydrogen bonds H2 – BF_4

Increased distance -> breaking of ring stacking



Alkyl chain Interaction (H6-H10)
Positive relative intensity

Intensity increase :
Protons in n-butyl chain group shifting to ring parts

(gauche to trans?)

Ring proton Interaction (H2, H4, H5)
Negative relative intensity

$$(r_{CD})^6\left(\frac{d\,I/d\,t_{CD}}{d\,I/d\,t_{AB}}\right) = (r_{AB})^6$$

r_{ij} : internuclear distance
dI/dt_{ij} : intensity of cross-peaks

Table 1: Composition of samples of compound **1**.

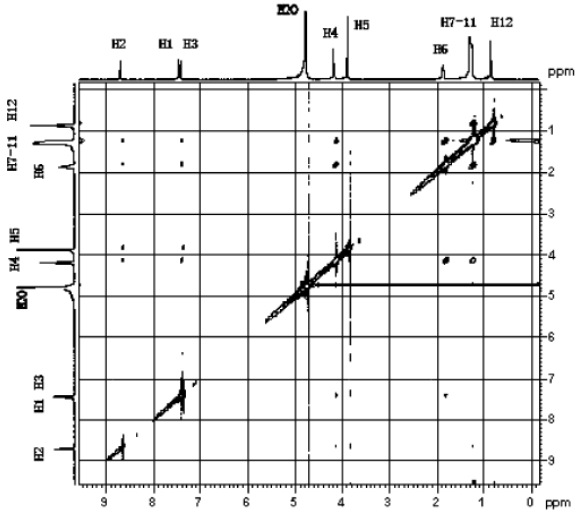
	1a[a]	1b	1c	1d	1e	1f	1g
Water:**1** mole ratio	0	0.10	0.20	0.37	0.56	0.81	1.09
Water mole fraction	0	0.09	0.17	0.27	0.36	0.45	0.52

[a] Pure liquid, reference sample.

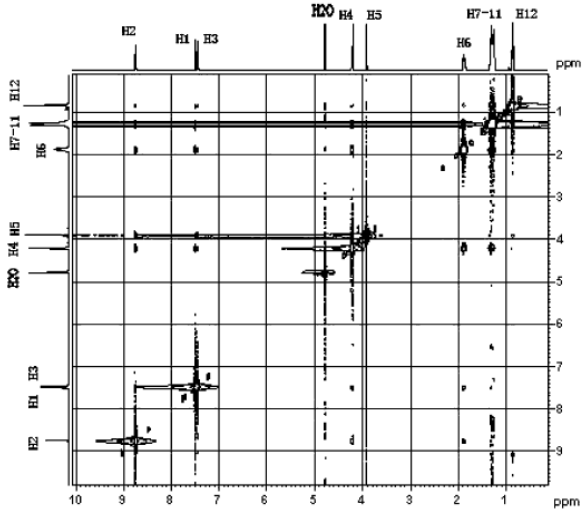
Andrea Mele *et al.*, Angew. Chem. Int. Ed.

[BMIM][Br] Rosey

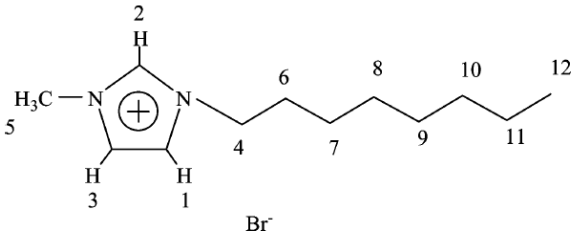
below CAC



above CAC



Many cross-peaks appear

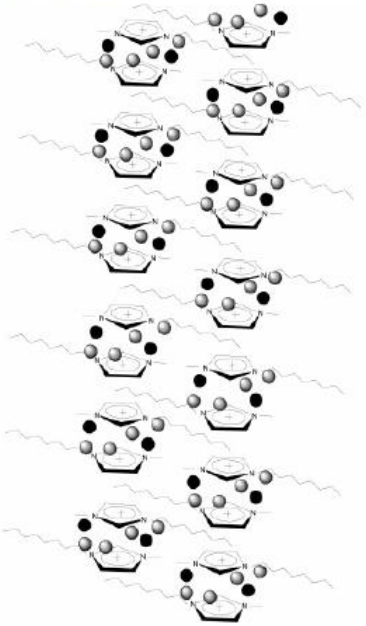


H2-H1,H3 | H5-H4,H6 : intermolecular interaction

H12/H1-H5 : ring-alkyl chain contact (intramolecular)

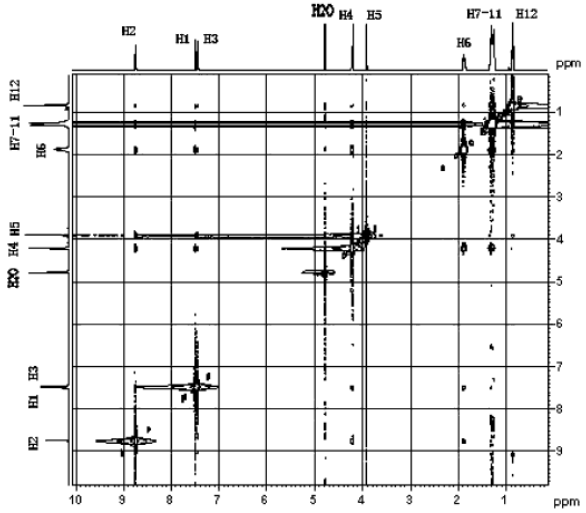
[BMIM][Br] Rosey

SCHEME 2: Possible Structure Illustrating Aggregation of [C8mim]Br in D_2O[a]



[a] With aggregation number $N = 25$; (black balls) Br^- and (gray balls) D_2O.

above CAC



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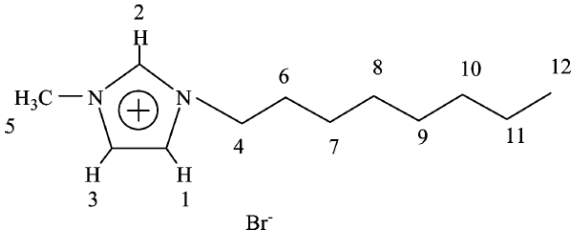

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