

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

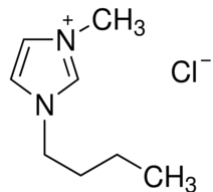
Solar thermal energy transfer/storage medium

Battery electrolyte

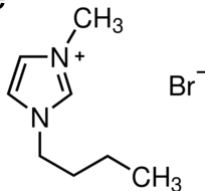
[bmim][X] ionic liquid (X : Cl, Br, I)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.00794	2 He Helium 4.002602	<div> <div>Atomic #</div> <div>Symbol</div> <div>Name</div> <div>Atomic Mass</div> </div> <div> <div>C Solid</div> <div>Hg Liquid</div> <div>H Gas</div> <div>Rf Unknown</div> </div> <div> <div>Metals</div> <div>Alkali metals</div> <div>Alkaline earth metals</div> <div>Lanthanoids</div> <div>Actinoids</div> <div>Transition metals</div> <div>Poor metals</div> <div>Other nonmetals</div> <div>Noble gases</div> </div>															
3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.0064	8 O Oxygen 15.999	9 F Fluorine 18.9984	10 Ne Neon 20.1797	11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050	13 Al Aluminum 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.06	17 Cl Chlorine 35.453	18 Ar Argon 39.948	19 K Potassium 39.0983	20 Ca Calcium 40.078
21 Sc Scandium 44.955912	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62
39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9062	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29	55 Cs Cesium 132.90545	56 Ba Barium 137.327
57-71 Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.96657	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.9804	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222	87 Fr Francium 223	88 Ra Radium 226
89-103 Actinoids	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bh Bohrium 264	108 Hs Hassium 277	109 Mt Meitnerium 268	110 Ds Darmstadtium 271	111 Rg Roentgenium 272	112 Uub Ununbium 285	113 Uut Ununtrium 284	114 Uuq Ununquadium 289	115 Uup Ununpentium 288	116 Uuh Ununhexium 292	117 Uus Ununseptium 294	118 Uuo Ununoctium 294	119 Uuh Ununennium 295	120 Uuo Unbinilium 296

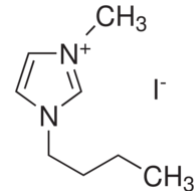
1-Butyl-3-methylimidazolium chloride



1-Butyl-3-methylimidazolium bromide

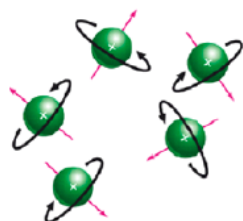


1-Butyl-3-methylimidazolium iodide

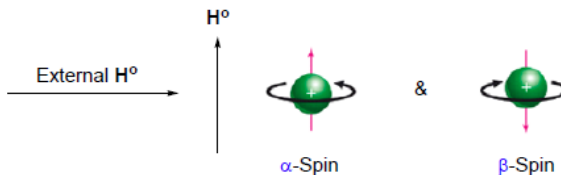


NMR Spectroscopy

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

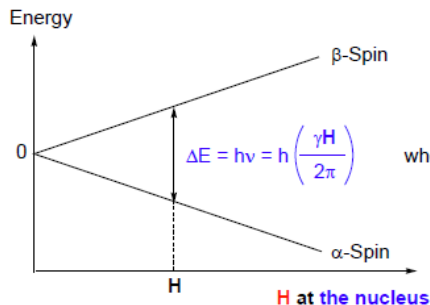


In the **absence** of H^0 , the **energy** of nuclei with any nuclear spin magnetic moment are the **same**
 → The spins of magnetic nuclei are oriented **randomly**



- **Parallel** orientation
- **More stable**
→ More populated
- **Anti-parallel** orientation
- **Less stable**
→ Less populated

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

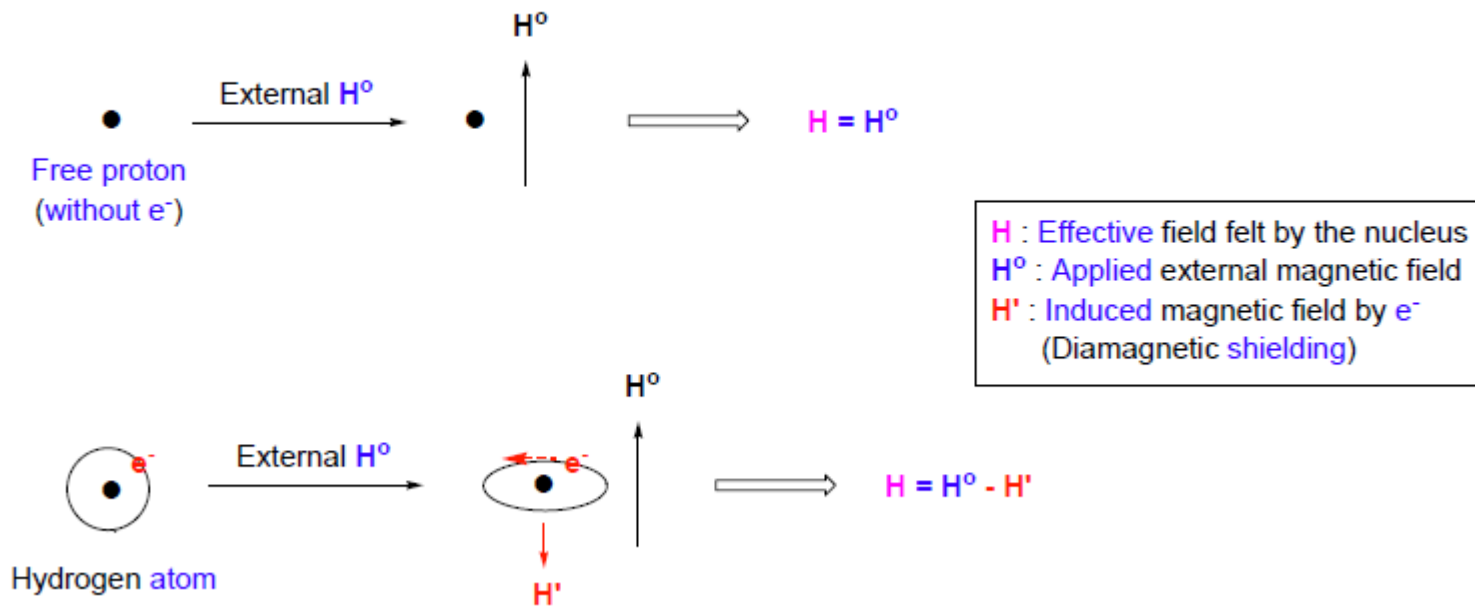


where { H : Magnetic field **at the nucleus** (not H^0)
 γ : Magnetogyric ratio of the nucleus
 (Characteristic & different for each nucleus !)

$$\left(\begin{array}{l} \gamma = 2.6753 \times 10^4 \text{ radians / sec Gauss for } ^1\text{H} \\ \gamma = 6.7328 \times 10^3 \text{ radians / sec Gauss for } ^{13}\text{C} \end{array} \right)$$

Chemical Shift

Shielding / Deshielding



Upfield, Downfield

- Fixed ν & variable H^0 : e^- Density around proton \uparrow
 - Shielding \uparrow
 - Induced magnetic field (H') \uparrow
 - H^0 for matching $\Delta E = h\nu$ (fixed value !) \uparrow
 - Upfield
- Fixed H^0 & variable ν (Modern Instrument) : e^- Density around proton \uparrow
 - Shielding \uparrow
 - Induced magnetic field (H') \uparrow
 - H \downarrow
 - ν \downarrow

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 $[C_n\text{mim}][BF_4]$

- NOE / ROE NMR Spectroscopy for $[C_n\text{mim}][BF_4]$

- 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 $[C_n\text{mim}]\text{Br}$ ($n=4,6,8,10,12$) in D_2O : A NMR Study

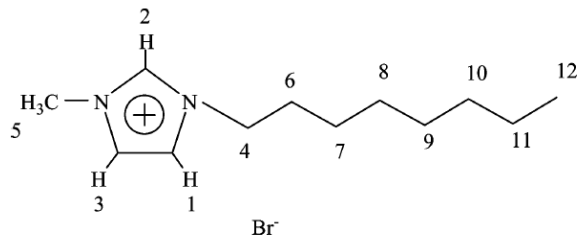
- 1H NMR, 1H - 1H ROESY NMR

- aggregation in aqueous solution of ionic liquid

Yang Zhao, Shanjiao Gao, Janji Whang, Junming Tang

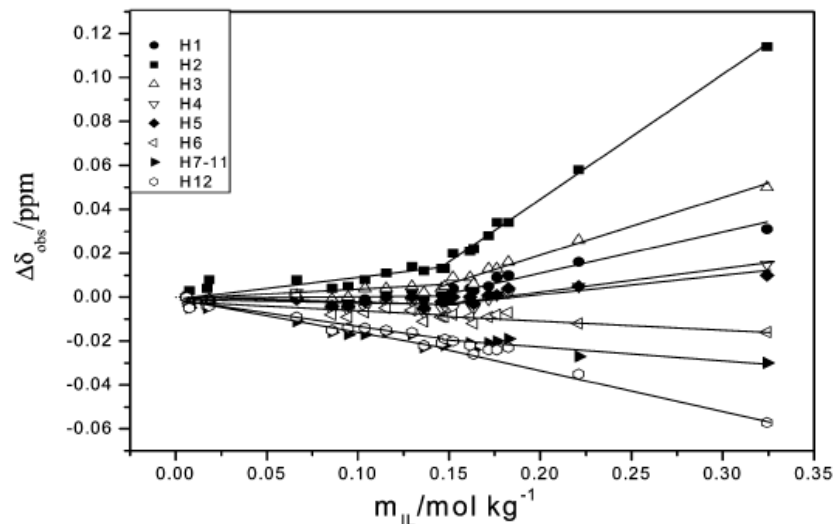
J.Phys.Chem.B (2008) **112** 2031

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



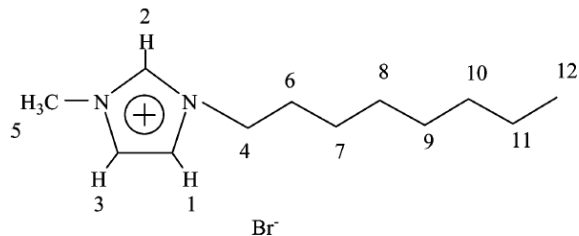
$$\delta_{\text{obsd}} = \delta_{\text{obsd}} - \delta_{\text{obsd},m}$$

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



Dependence of proton chemical shifts of [C₈mim]Br on the IL concentration in D₂O.

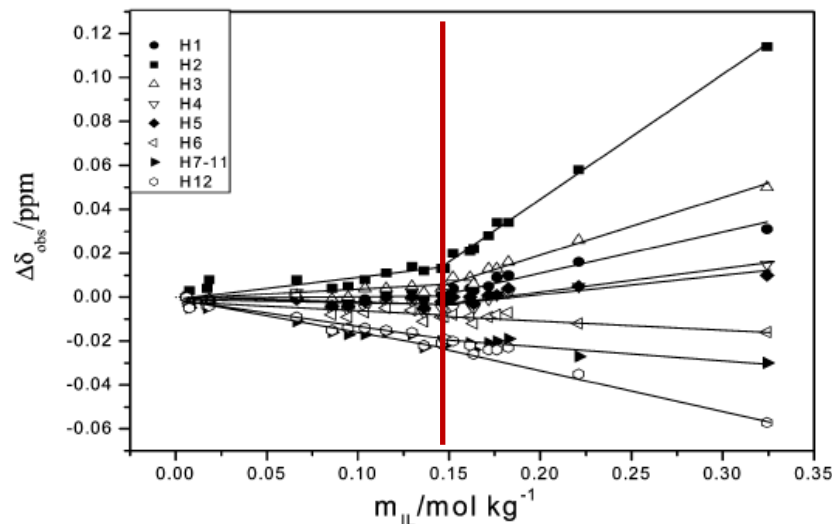
2008 Aggregation of Ionic Liquids [Cnmim]Br (n=4,6,8,10,12) in D2O : A NMR Study



CAC (critical aggregation concentration)

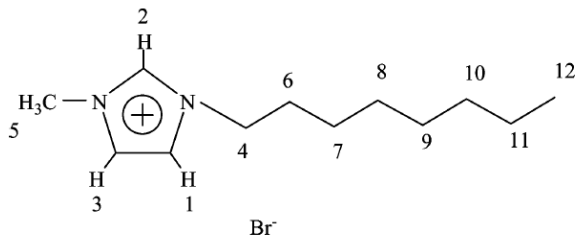
Fast exchange of monomer and aggregate assumption (faster than NMR time scale)

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



Dependence of proton chemical shifts of [C₈mim]Br on the IL concentration in D₂O.

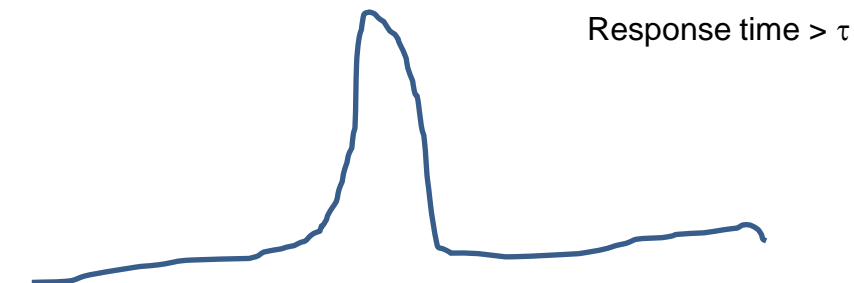
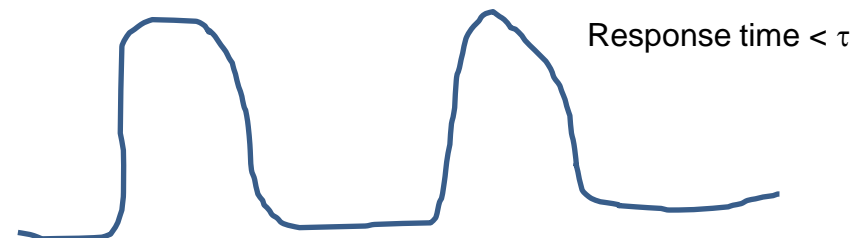
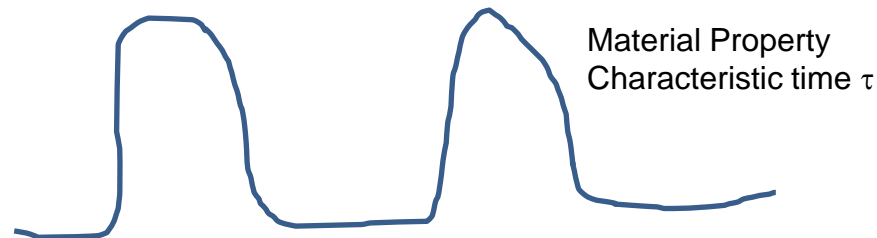
2008 Aggregation of Ionic Liquids [Cnmim]Br (n=4,6,8,10,12) in D2O : A NMR Study



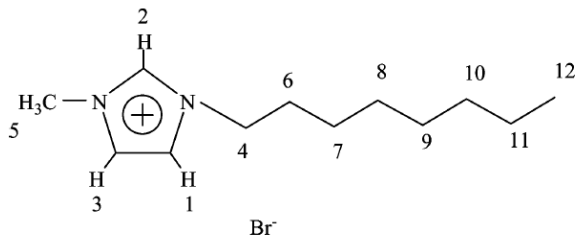
CAC (critical aggregation concentration)

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

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



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



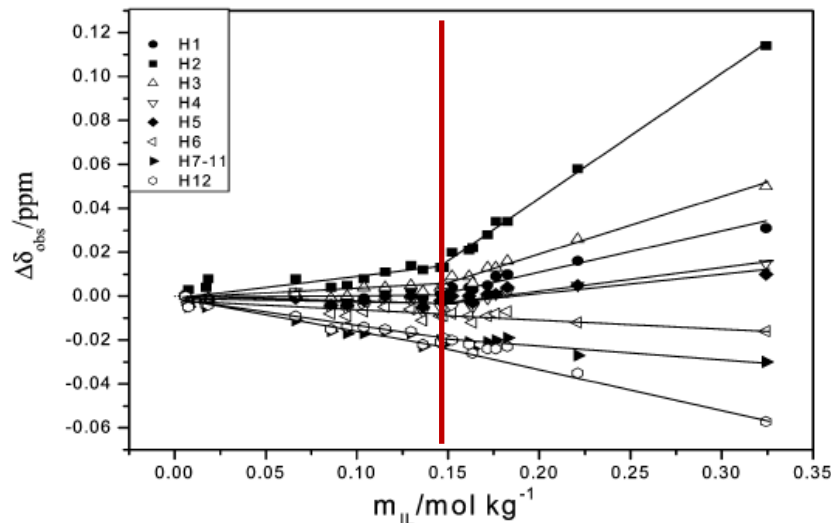
CAC (critical aggregation concentration)

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

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

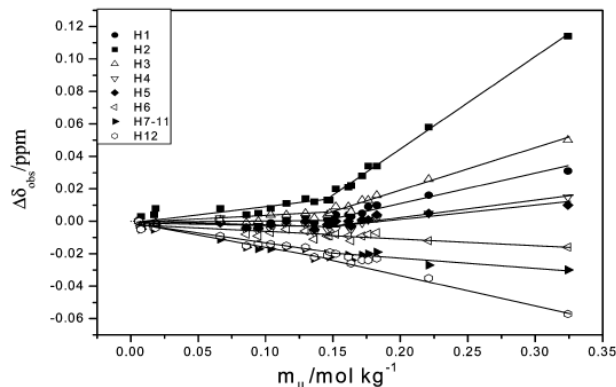
No aggregation assumption below CAC

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



Dependence of proton chemical shifts of [C₈mim]Br on the IL concentration in D₂O.

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



Dependence of proton chemical shifts of [C₈mim]Br on the IL concentration in D₂O.

CAC1

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

CAC2

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

Ref1 : Goodchild *et al* (2007)

Ref2 : Wang *et al* (2007)

No aggregate for short chain

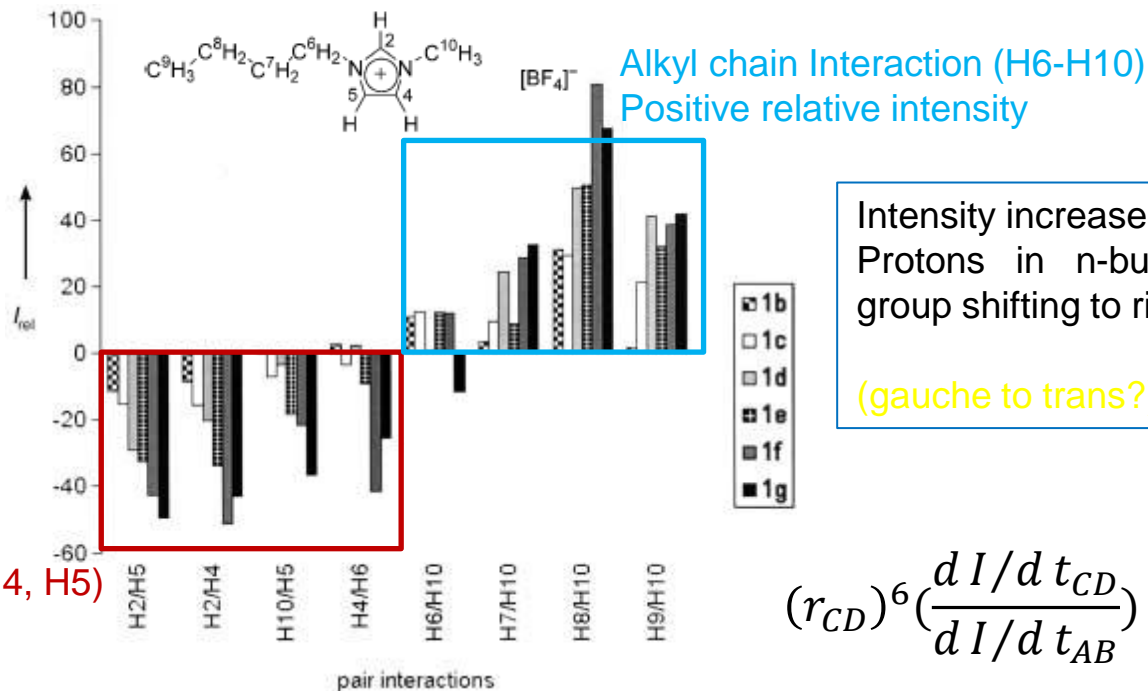
Difference between H₂O and D₂O (??)

IL	CAC1 (mol / kg)	CAC2 (mol / kg)	Surface tension (mol/ L) Ref1	Electric conductivity (mol / L) ref1	Electric conductivity (mol / L) ref2
[C ₄ mim][Br]	-	2.579	0.8±0.1	0.7±0.3	0.97
[C ₆ mim][Br]	0.732	0.849	0.6±0.2	0.4±0.3	0.77
[C ₈ mim][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

Ring proton is hydrogen bond donor to F atoms in F (in BF₄)

H₂O involved in Hydrogen bonds H2 – BF₄

Increased distance -> breaking of ring stacking



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

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

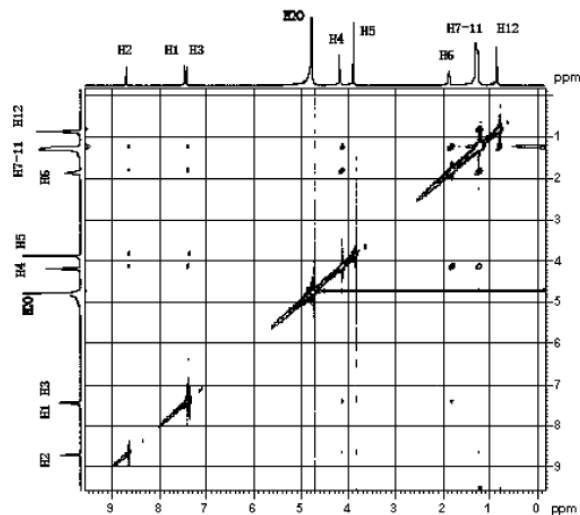
[a] Pure liquid, reference sample.

$$(r_{CD})^6 \left(\frac{dI/dt_{CD}}{dI/dt_{AB}} \right) = (r_{AB})^6$$

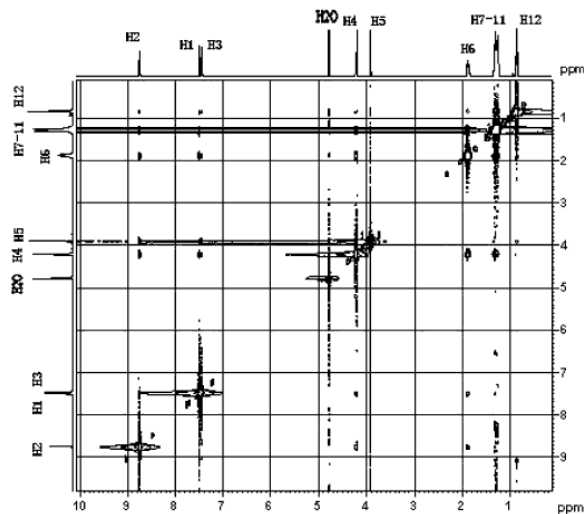
r_{ij} : internuclear distance
 dI/dt_{ij} : intensity of cross-peaks

[BMIM][Br] Rosey

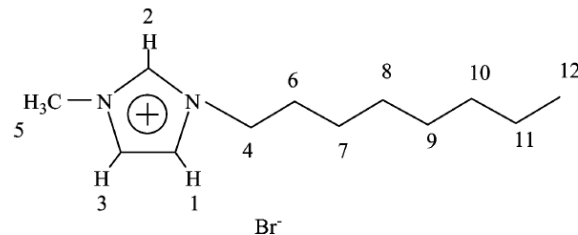
below CAC



above CAC



Many cross-peaks appear

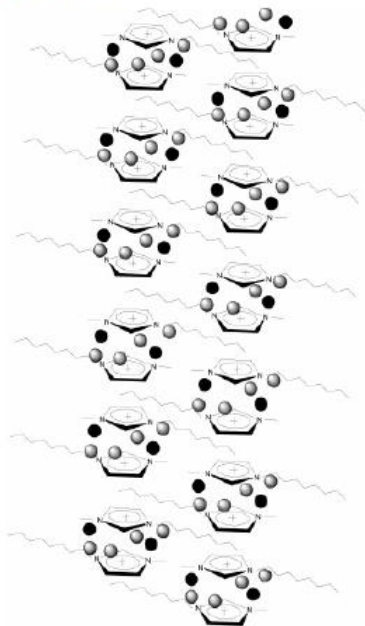


H2-H1,H3 | H5-H4,H6 : intermolecular interaction

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

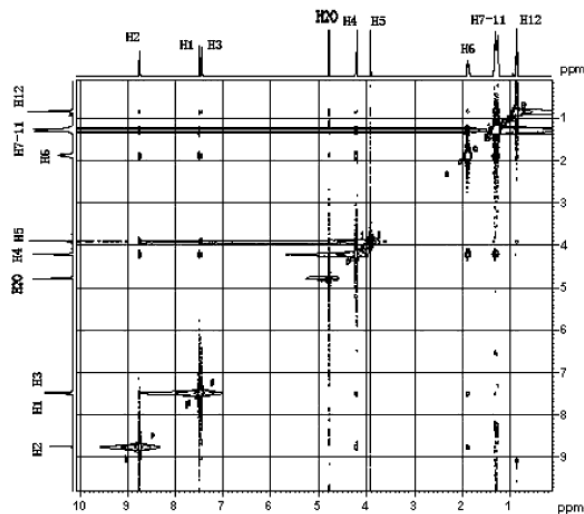
[BMIM][Br] Rosey

SCHEME 2: Possible Structure Illustrating Aggregation of [C₈mim]Br in D₂O^a

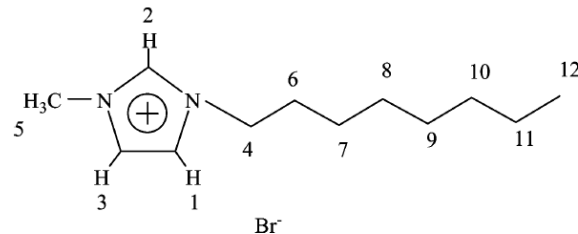


^a With aggregation number $N = 25$; (black balls) Br⁻ and (gray balls) D₂O.

above CAC



Many cross-peaks appear



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

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