On the Arrangement of Ions in Imidazolium-Based Room Temperature Ionic Liquids at the Gas−Liquid Interface, Using Sum Frequency Generation, Surface Potential, and Surface Tension Measurements

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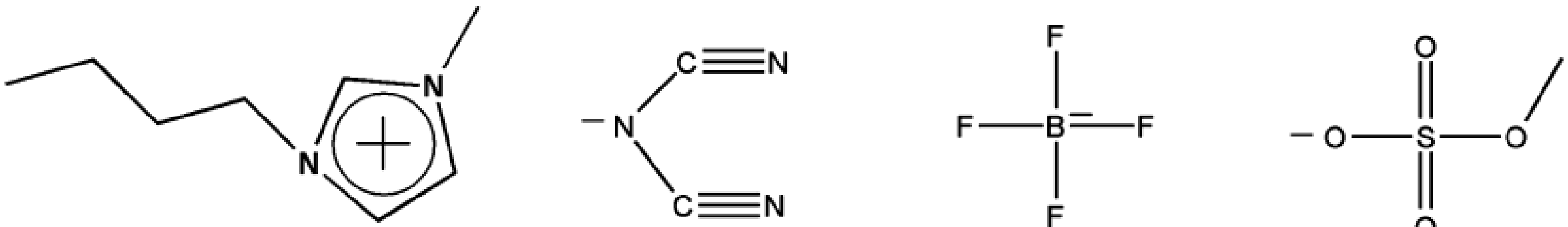
The characterization of three ionic liquids [BMIM][BF_4], [BMIM][DCA], and [BMIM][MS] having a common cation and with anions of varying sizes and shapes was performed with three complementary surface techniques: sum frequency generation-polarization mapping, surface tension measurement, and surface potential measurement. Custom vacuum cells were designed for each technique to be able to perform measurements in a highly controlled environment minimizing the presence of water and other contaminants, which may compromise measured values. SFG results show evidence of having anions and cations present on the surface with the butyl chain of the cation positioned toward the gas phase and the imidazolium ring mostly parallel to the surface plane. Results from the surface potential measurements reveal the relative positions of the ions where the anions are located at a slightly lower plane compared to the cations. Observed values from the surface tension measurements denote surface intermolecular interactions indicative of both van der Waals and Coulombic interactions suggesting the presence of alkyl chains as well as ions on the surface. A model on the gas−liquid interface of ionic liquids is described based on the concurring results from these three surface characterization techniques, as well as current literature.

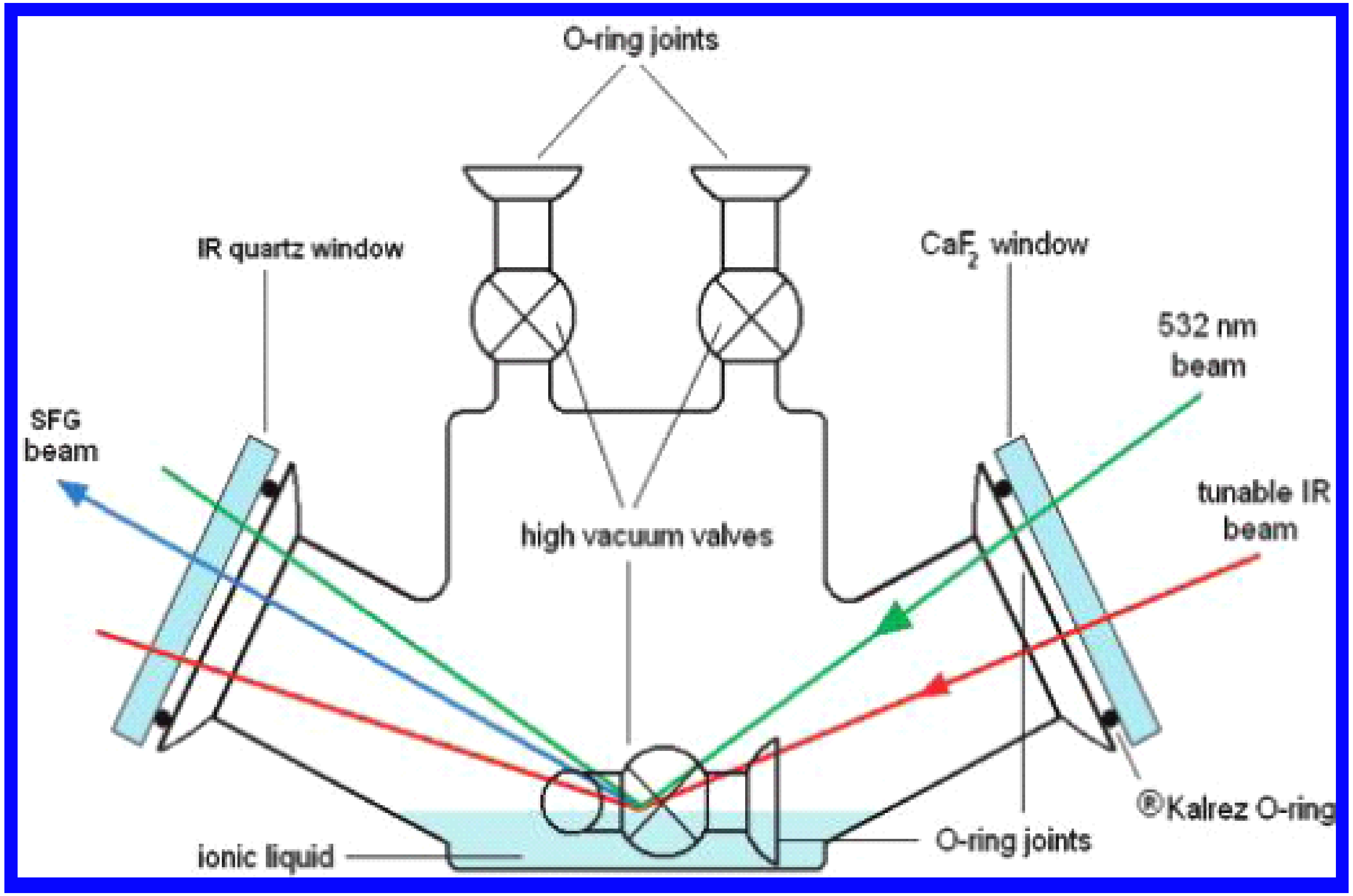
Methods



(a) **BMIM** (b) **DCA** (c) **BF_4** (d) **MS**

- SFG-Polarization Mapping Method
- Surface Potentials
- Surface Tension

SFG-Polarization Mapping Method



Sample holder

SFG-Polarization Mapping Method

Visible beam — 45º from the s polarization direction (**$\sigma_1 = 45^\circ$**)

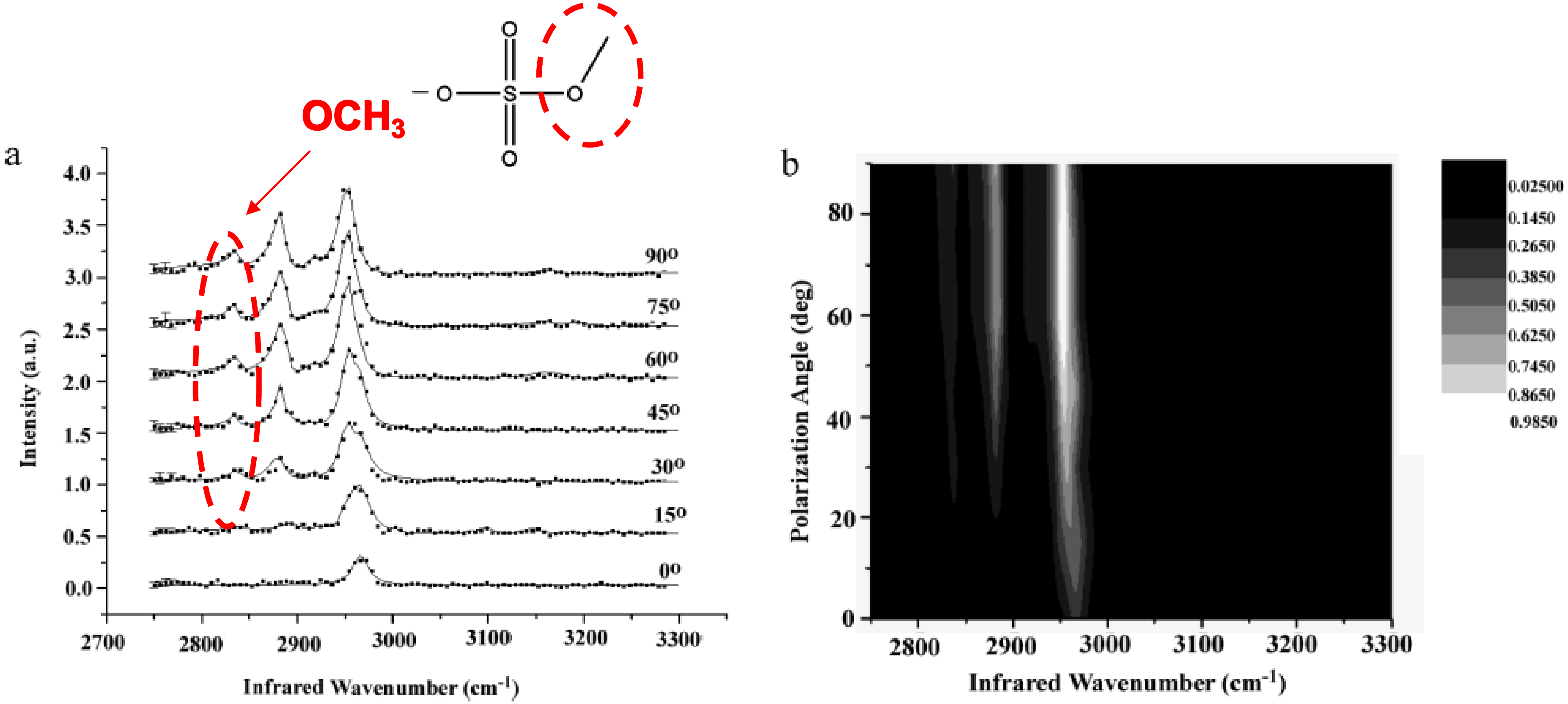
IR beam — p polarization direction (**$\sigma_2 = 90^\circ$**)

SFG — **σ_s**

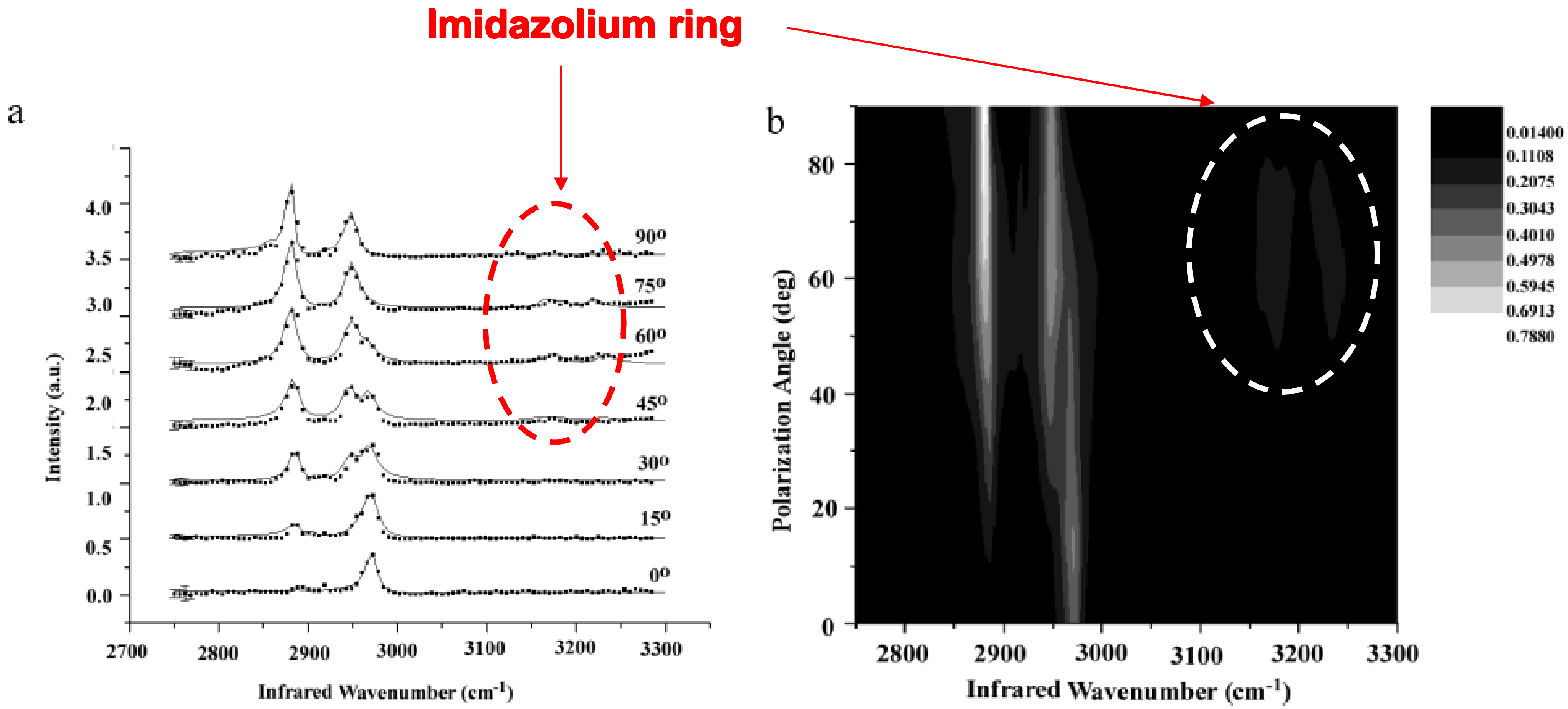
$$\chi^{(2)}_{\mathrm{eff}} = \chi^{(2)}_{\mathrm{eff},yyz} + \chi^{(2)}_{\mathrm{eff},xxz} + \chi^{(2)}_{\mathrm{eff},xzx} + \chi^{(2)}_{\mathrm{eff},zxx} + \chi^{(2)}_{\mathrm{eff},zzz} \qquad (8)$$

$$\begin{aligned} I(\omega_s) \propto\ & |L_{yyz} \cos\sigma_s \cos\sigma_1 \sin\sigma_2 \sin\beta_2 \chi^{(2)}_{yyz} - \\ & L_{xxz} \sin\sigma_s \cos\beta_s \sin\sigma_1 \cos\beta_1 \sin\sigma_2 \sin\beta_2 \chi^{(2)}_{xxz} - \\ & L_{xzx} \sin\sigma_s \cos\beta_s \sin\sigma_1 \sin\beta_1 \sin\sigma_2 \cos\beta_2 \chi^{(2)}_{xzx} + \\ & L_{zxx} \sin\sigma_s \sin\beta_s \sin\sigma_1 \cos\beta_1 \sin\sigma_2 \cos\beta_2 \chi^{(2)}_{zxx} + \\ & L_{zzz} \sin\sigma_s \sin\beta_s \sin\sigma_1 \sin\beta_1 \sin\sigma_2 \sin\beta_2|^2 \propto \\ & 1/2|F_{yyz}\chi^{(2)}_{yyz} \cos\sigma_s + (-F_{xxz}\chi^{(2)}_{xxz} - F_{xzx}\chi^{(2)}_{xzx} + F_{zxx}\chi^{(2)}_{zxx} + \\ & F_{zzz}\chi^{(2)}_{zzz}) \sin\sigma_s|^2 \propto \underline{1/2|\chi^{(2)}_{\mathrm{eff,ssp}} \cos\sigma_s + \chi^{(2)}_{\mathrm{eff,ppp}} \sin\sigma_s|^2} \qquad (9) \end{aligned}$$

SFG-Polarization Mapping Method

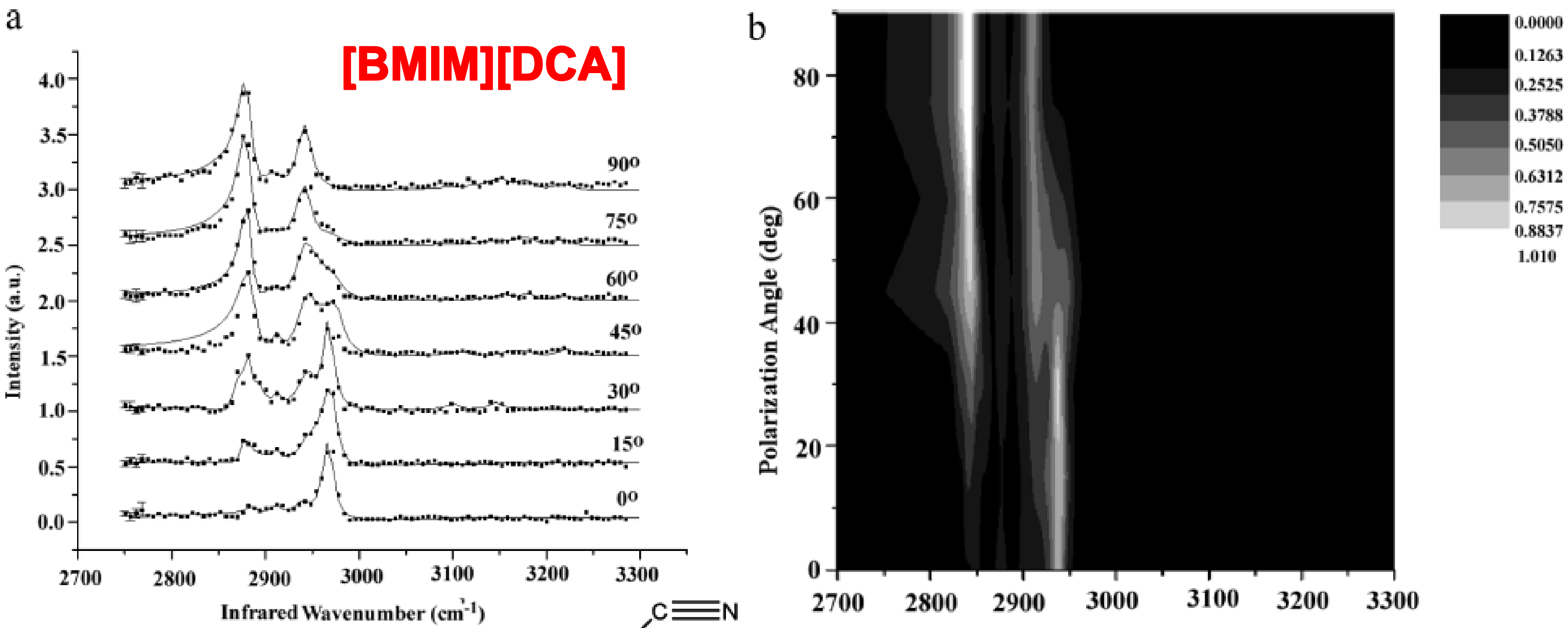


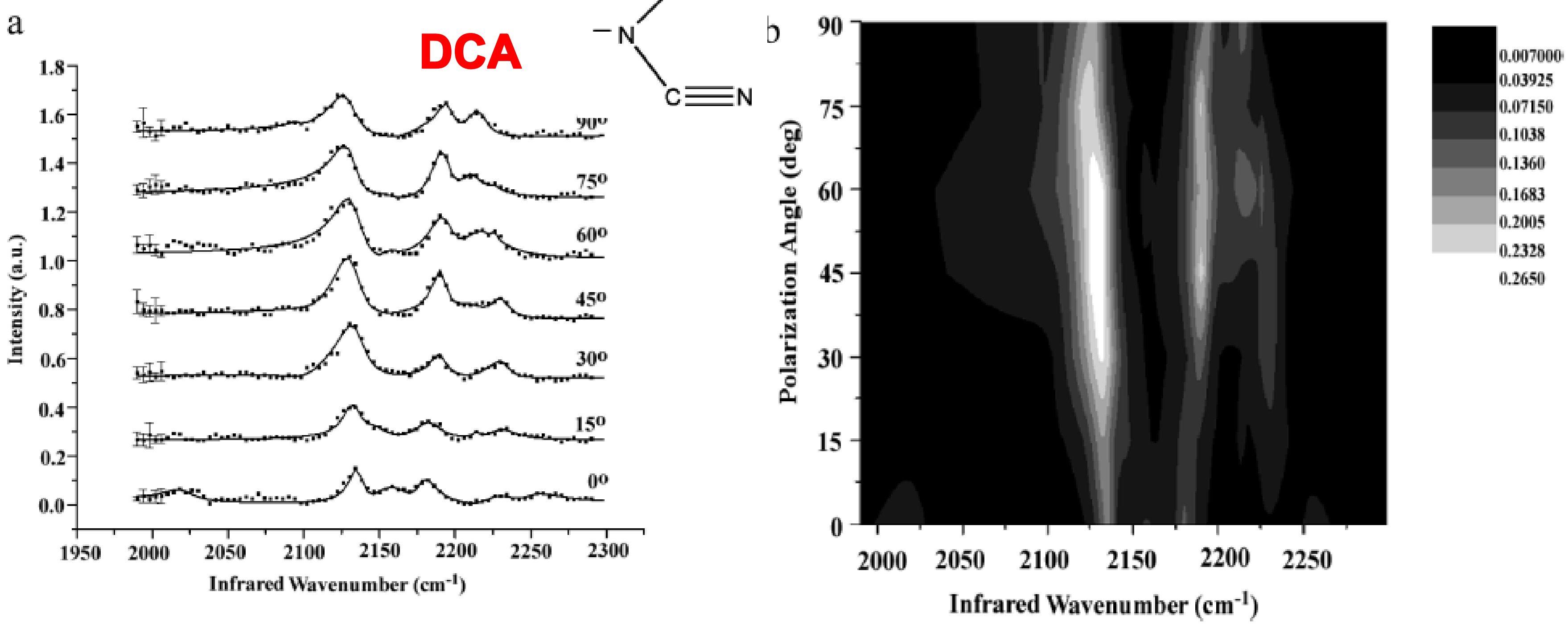
[BMIM][MS]



Imidazolium ring
a
Intensity (a.u.)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
90°
75°
60°
45°
30°
15°
0°
2700
2800
2900
3000
3100
3200
3300
Infrared Wavenumber (cm-1)
b
Polarization Angle (deg)
80
60
40
20
0
2800
2900
3000
3100
3200
3300
Infrared Wavenumber (cm-1)
0.01400
0.1108
0.2075
0.3043
0.4010
0.4978
0.5945
0.6913
0.7880

[BMIM][BF$_4$]

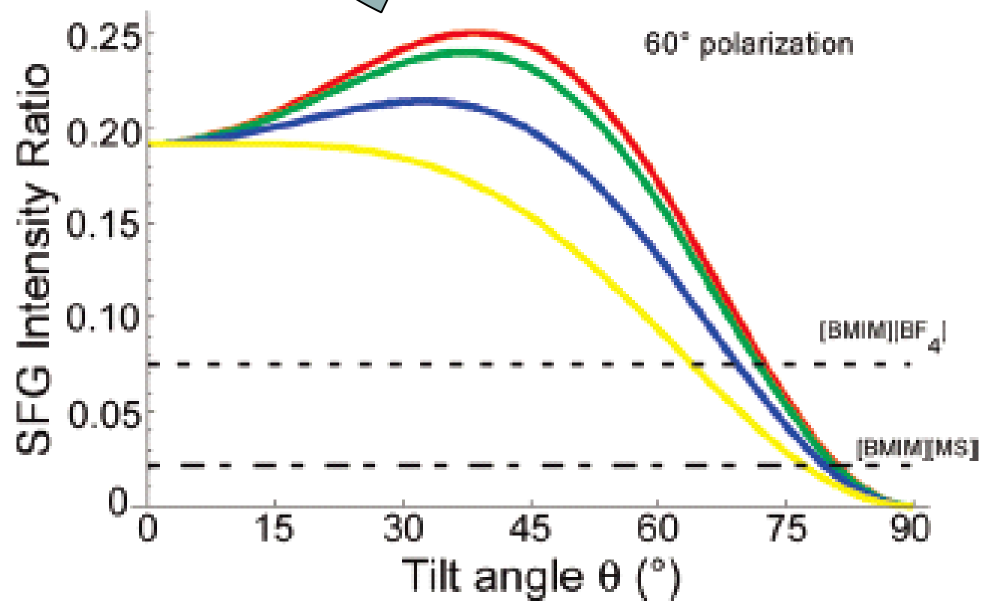

a
[BMIM][DCA]
90°
75°
60°
45°
30°
15°
0°
Intensity (a.u.)
Infrared Wavenumber (cm^{-1})
b
Polarization Angle (deg)
0.0000
0.1263
0.2525
0.3788
0.5050
0.6312
0.7575
0.8837
1.010


a
DCA
C≡N
N
C≡N
90°
75°
60°
45°
30°
15°
0°
Intensity (a.u.)
Infrared Wavenumber (cm^{-1})
b
Polarization Angle (deg)
0.007000
0.03925
0.07150
0.1038
0.1360
0.1683
0.2005
0.2328
0.2650
Infrared Wavenumber (cm^{-1})

Orientational Analysis

	Butyl Chain	Imidazolium ring
[BMIM][BF4]	47º	~70º
[BMIM][MS]	45º	~80º
[BMIM][DCA]	47º	

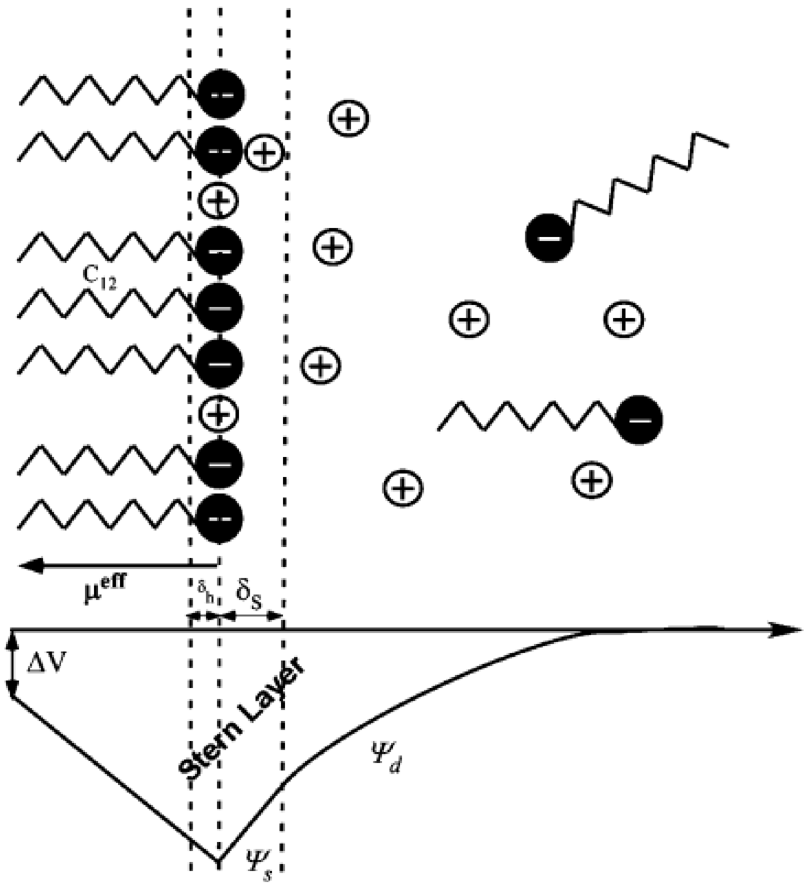
Butyl chain toward the gas phase, and imidazolium ring mostly parallel to the surface plane.



The curves from red to yellow are for the various twist angle around the C2 axis of imidazolium ring

Surface Potential

Stern-Gouy Chapman Model



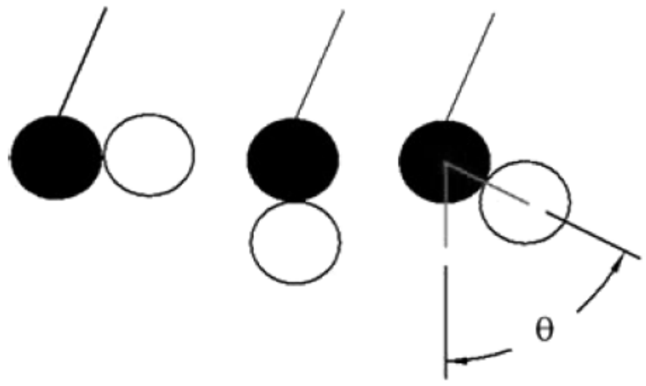
$$\Delta V = N_a \Gamma_s \frac{\mu_\perp^{eff}}{\epsilon_o \epsilon_t}(\Gamma_s) + \frac{\sigma \delta_s}{\epsilon_o \epsilon_s} + \frac{2kT}{e}\sinh^{-1}\left(\frac{\sigma e}{2\epsilon_o \epsilon_s kT\kappa}\right)$$

Dipolar contribution — Stern Potential — Diffuse Potential

$$\sigma = (z_s F \Gamma_s + z_c F \Gamma_c)$$

Pure Ionic Liquid:

$$\Delta V = \frac{N_a}{\epsilon_o \epsilon_s}(\Gamma_c \mu_{\perp c}^{eff} \cos\theta_c) + \frac{\sigma \delta_s}{\epsilon_o \epsilon_t}$$

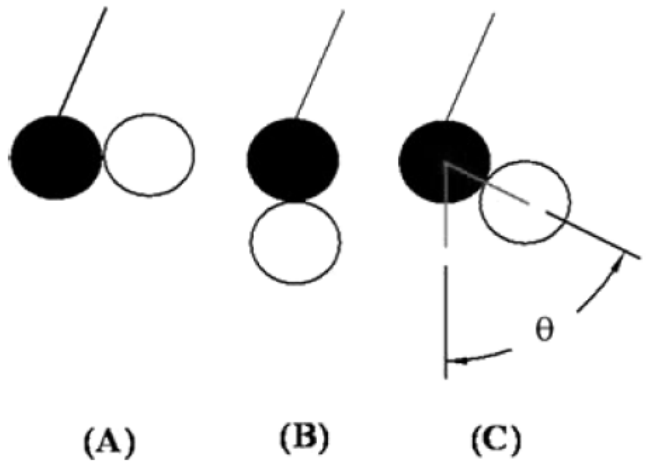


(A) (B) (C)

$$\delta_s = 0 \qquad \delta_s = \delta_{s,\max} \qquad \delta_s = \delta_{s,\max}\cos\theta$$

IL	ε_t	μ_c (D)	θ_c (deg)	θ_a (deg)	$\delta_{s,max}$ (Å)	ε_s	A_c (Å^2)	A_a (Å^2)
[BMIM][BF_4]	2	0.38	47		3.27	11.7[70]	22.25[71]	19.63[72,73]
[BMIM][DCA]	2	0.38	47	70	3.57	11.3[74]	22.25	24.63[72,73]
[BMIM][MS]	2	0.38	45	65[12]	3.65	14.8[75]	22.25	26.06[71,76,77]

$$\Delta V = \frac{N_a}{\epsilon_o \epsilon_s}(\Gamma_c \mu_{\perp c}^{\text{eff}} \cos\theta_c) + \frac{\sigma \delta_s}{\epsilon_o \epsilon_t}$$



$\delta_s = 0$ $\delta_s = \delta_{s,\max}$ $\delta_s = \delta_{s,\max} \cos\theta$

TABLE 4: Calculated Surface Potentials at Specific Cation−Anion Configurations

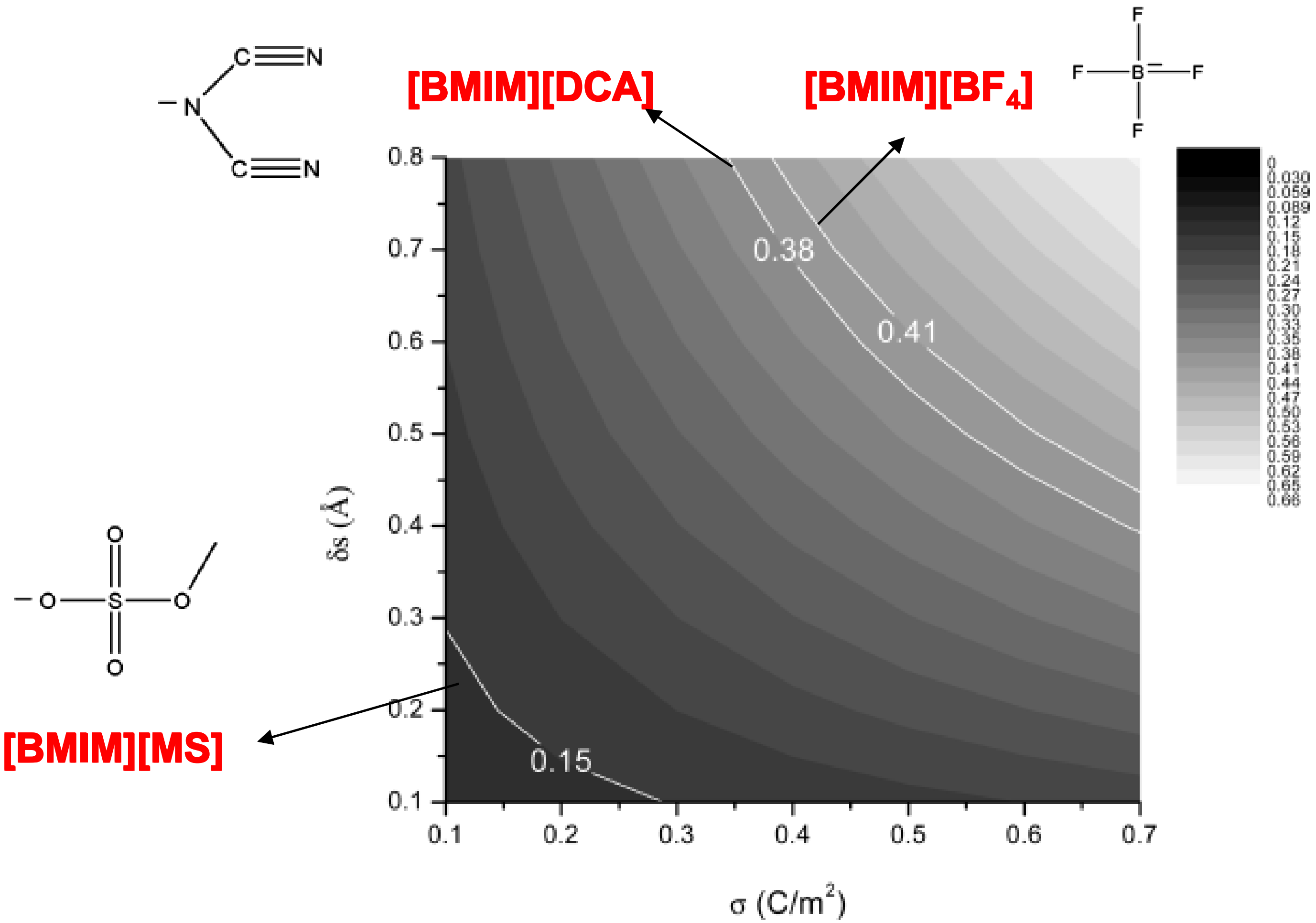
	$[BMIM]^+$ ionic liquid					
	$[BF_4]^-$		$[DCA]^-$		$[MS]^-$	
configuration	δ_s	ΔV	δ_s	ΔV	δ_s	ΔV
A	0	0.12	0	0.10	0	0.11
B	3.27	2.49	3.57	2.79	3.65	2.23

TABLE 2: Surface Potential of Ionic Liquids

	ϕ (V)	
IL	average	± deviation
$[BMIM][BF_4]$	0.42	0.02
[BMIM][DCA]	0.37	0.02
[BMIM][MS]	0.14	0.02

Configuration (A) < Experimental data < Configuration (B)

Configuration (C) is favored



Stern Length

[BMIM][MS]	**0.15Å ~ 0.30Å**
[BMIM][DCA]	**0.40Å ~ 0.80Å**
[BMIM][BF4]	**0.50Å ~ 0.80Å**

MS is closest to the gas phase

Surface Tension

TABLE 5: Surface Tension of Ionic Liquids

	γ (V) $\pm$ Δ			
IL name	trial 1	trial 2	trial 3	average
[BMIM] [BF_4]	42.76 ± 0.53	40.12 ± 0.47	41.47 ± 1.53	41.29 ± 1.53
[BMIM] [DCA]	43.36 ± 1.33	44.97 ± 2.49	42.23 ± 1.50	43.55 ± 1.50
[BMIM] [MS]	43.25 ± 2.03	44.07 ± 1.37	43.17 ± 2.03	43.47 ± 1.53

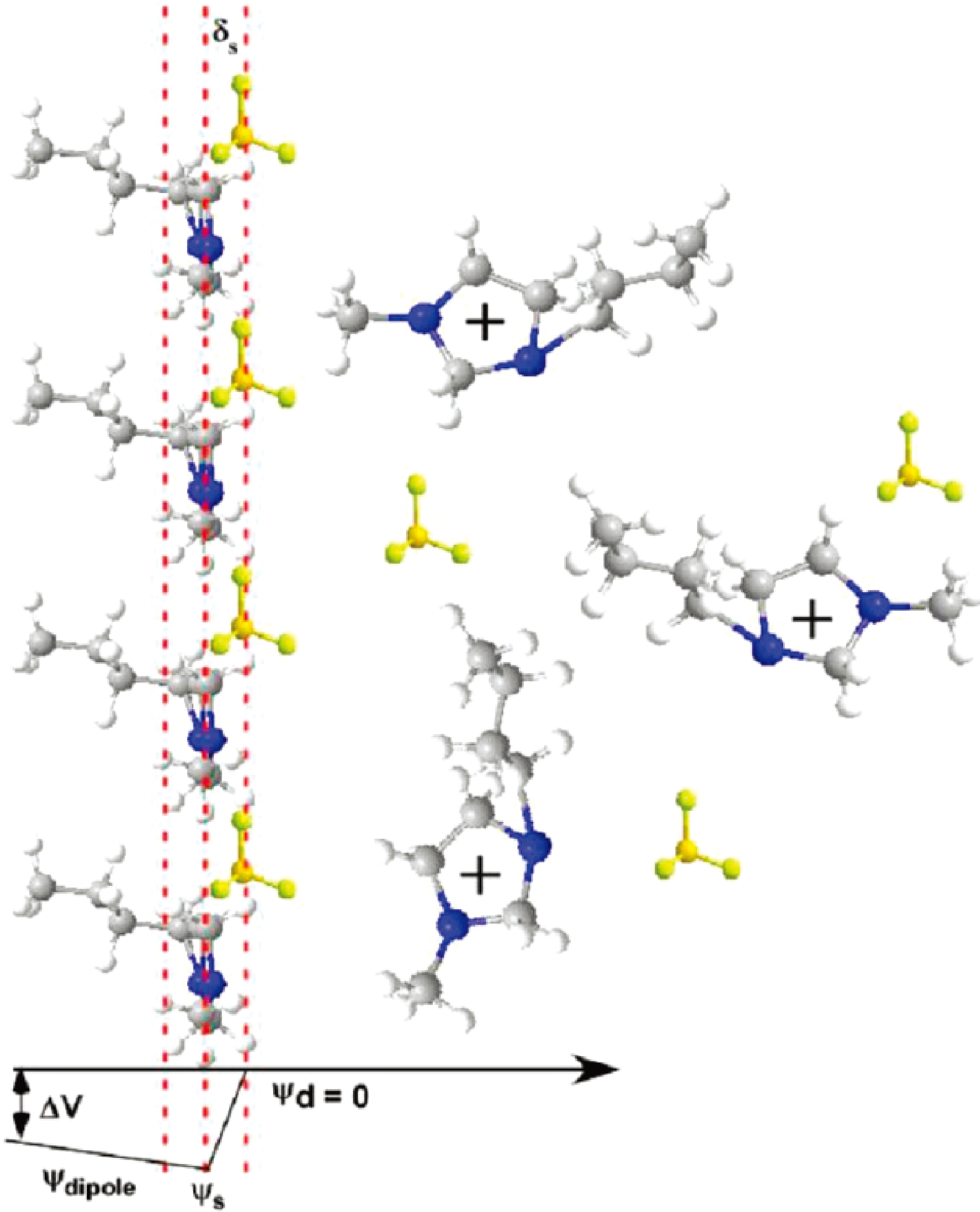
Surface Tension Values:

Alkane < Ionic Liquid < Electrolyte Solution

Van der Waals interaction

Van der Waals and Coulombic interaction

Coulombic interaction



δ_s
+
+
+
ΔV
$\Psi d = 0$
Ψ_{dipole}
Ψ_s