Supporting Information

Are Ionic Liquids Pairwise In Gas Phase?

A cluster Approach and *In-situ* IR Study

Kun Dong[a], Lidong Zhao[a], Qian Wang[a], Yuting Song[a] and Suojiang Zhang*[a]

1.   TGA experiment and Enthalpies measurement of [Emim][Cl] and [EtAm][NO₃]

The [Emim][Cl] and [EtAm][NO$_3$] ILs were purchased from Beijing Zhongke AnyIn Technology Co. Ltd. Prior to use, all the ILs were dried in a vacuum at 55℃ and more than 48h.

In this work, we used a Q5000IR（TA Instruments-Waters） TGA. Mass calibration was performed with help of a standard weight of 100 μg. The uncertainty of temperature calibration was less than 0.5 K. In the experiments, the IL sample was placed in a plane platinum crucible with vertical walls, diameter of 10 mm and height 3 mm and was stepwise heated inside of the measuring head of the TGA. A mass loss was recorded at each temperature step (seeing Fig. S1 and Fig. S2). Prior to the measurement, a conditioning of the sample inside the TGA have been performed. A heating ramp of 1 K·min^{-1} was used, followed by a 4 h.
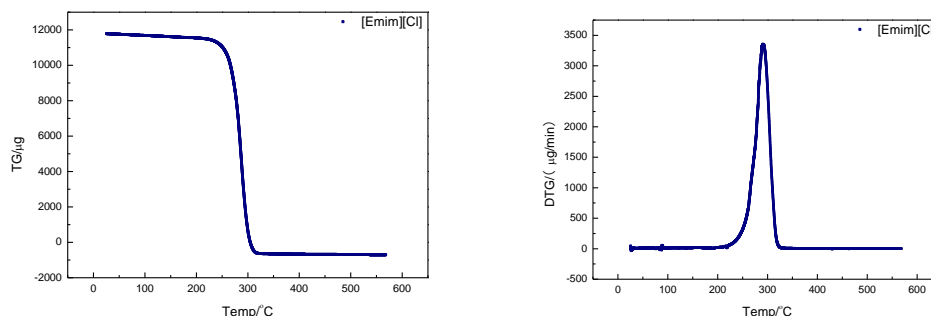

Fig. S1 TGA of [Emim][Cl] with initial about 11mg IL sample
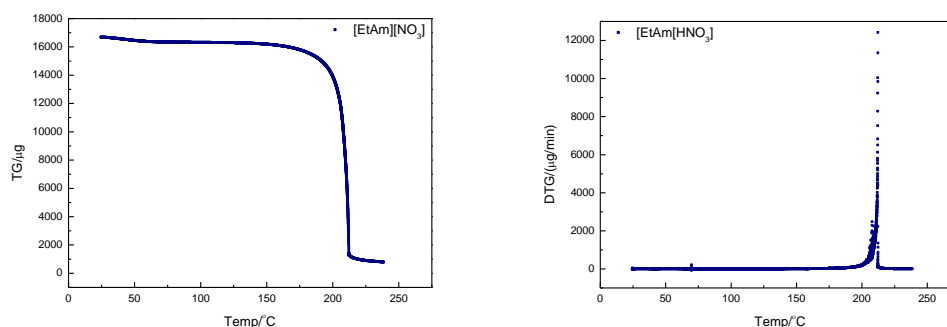

Fig. S2 TGA of [EtAm][NO$_3$] with initial about 16mg IL sample

The optimal conditions for reliable TGA determinations of vaporization enthalpies of ILs was

referred to Verevkin et al. works. [1] The relationship between the mass loss $r = dm/dt$ and the vaporization enthalpy was derived according to the Clausius-Clapeyron equation (1) but by using the mass loss rate dm/dt measured by the TGA (instead of the absolute pressure):[2]

$$\ln(\frac{dm}{dt}\sqrt{T}) = A' - \frac{\Delta_l^g H(T_0) - \Delta_l^g C T_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_l^g C}{R}\ln\left(\frac{T}{T_0}\right) \qquad (1)$$

with a constant A' which is essentially unknown and which includes parameters specific for our setup but is independent from the substance studied. T_0 appearing in Equ. (1) is an arbitrarily chosen reference temperature (which here has been chosen to be 298 K) and is the difference of the molar heat capacities. Enthalpy of vaporization obtained at the proper average temperature T_{av} range in which the sample can not be decomposed. Then the enthalpy has been adjusted to the reference temperature $T = 298.15$ K using the previously acknowledged for ILs value $\Delta_l^g C = 100$ J·K^{-1}·mol^{-1} for the sake of comparison with our earlier work. For [Emim][Cl], the $\Delta_l^g H(298.15) = 158.6$ kJ/mol with R^2=0.9994 at T_{av}= 220~250℃ temperature range. For [EtAm][NO$_3$], $\Delta_l^g H(298.15) = 148.7$ kJ/mol with R^2=0.9944 at T_{av} =180~195℃.

2. The cluster approach

Thermodynamic computation in Gaussian code is based on Statistical Mechanics. The partition function q of a single cluster can be expressed into equ. (2)

$$q = q_{trans}q_{rot}q_{vib}q_{elec} \qquad (2)$$

q_{trans} represents the translational partition function, q_{rot} represents rotational partition function, q_{vib} represent vibrational partition function and q_{elec} is electronic partition function. Vibrational energy levels are added within the harmonic approximation. Rotational energy levels are estimated treating each cluster as a classical rotator with its three moments of inertia. The translational energy levels stem from an approximate treatment of cluster translation as a particle in a three-dimensional box.

The entropy S and internal energy E of a cluster can be expressed:

$$S = R(\ln(q_{trans}q_{rot}q_{vib}q_{elect}e) + T(\frac{\partial \ln q}{\partial T})_V) \qquad (3)$$

$$E = Nk_BT^2 \left(\frac{\partial \ln q}{\partial T}\right) \qquad (4)$$

It is assumed that each cluster partition function q can be factored in the usual way into translational, rotational, vibrational and electronic contributions.

In the translational partition function be expressed into equ. (5)

$$q_{trans} = \frac{V}{\Lambda^3} \quad (5), \quad \text{where} \quad \Lambda = \frac{h}{(2\pi m k T)^{1/2}} \quad \text{is the thermal de Broglie wavelength. If being}$$

the an ideal gas, the volume can be estimated from $pV = nRT$ and the translational partition function becomes:

$$q_{trans} = \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \frac{KT}{P} \qquad (6)$$

Then entropy

Rotational partition function be expressed into equ. (7)

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2} \quad (7), \quad \text{where} \quad \Theta_{A,B,C} = \frac{\hbar^2}{2I_{A,B,C}K} \quad \text{is rotational temperatures.}$$

Vibrational partition function be expressed into equ. (8)

$$q_{vib} = \prod_{i=1}^{3n-6} \frac{1}{1-e^{-\theta_i/T}} \quad (8), \quad \text{where} \quad \theta_i = \frac{h v_i}{k} \quad \text{is vibrational temperatures.}$$

Finally, electronic partition function be expressed into equ. (9)

$$q_{elec} = \omega_0 e^{-E_0/kT} \quad (9), \quad \text{where} \quad \omega \quad \text{is the degeneracy of the energy level.}$$

Having the total partition function q of a cluster, entropy S and energy E can be calculated, then other thermodynamic properties such as H, G can be calculated.

3. The predicted enthalpies of the four ILs

Tab. S1 Calculated $\Delta_{vap}H$ (kJ/mol, 298.15K) of [Emim][NTf$_2$] when the gas species were assumed to the II, PM and IP, respectively.

	IP1@[Emim][NTf$_2$]	IP2@[Emim][NTf$_2$]	PM@[Emim][NTf$_2$]	II@[Emim][NTf$_2$]
2	30.82	79.22	304.92	444.9
4	116.67	165.07	390.77	530.75
6	131.20	182.23	405.30	545.28

8	130. 05	178. 45	404. 15	544. 13
10	97. 62	134. 34	360. 03	500. 02
12	128. 39	128. 26	338. 45	466. 84

Tab. S2 Calculated $\Delta_{vap}H$ (kJ/mol, 298.15K) of [Emmim][NTf$_2$] when the gas species were assumed to the II, PM and IP, respectively.

	IP1@[Emmim][NTf$_2$]	IP2@[Emmim][NTf$_2$]	IP3@[Emmim][NTf$_2$]	II@[Emmim][NTf$_2$]
2	48. 87	56. 88	114. 91	463. 39
4	80. 63	88. 64	146. 67	495. 15
6	104. 49	112. 51	170. 54	521. 65
8	111. 58	119. 59	177. 62	526. 10
10	114. 31	122. 33	180. 35	536. 71
12	123. 63	131. 64	189. 67	538. 15

Tab. S3 Calculated $\Delta_{vap}H$ (kJ/mol, 298.15K) of [Emim][Cl] when the gas species were assumed to the II, PM and IP, respectively.

	IP1@[Emim][Cl]	IP2@[Emim][Cl]	IP3@[Emim][Cl]	PM@[Emim][Cl]	II@[Emim][Cl]
2	79. 55	82. 18	121. 73	219. 42	512. 16
4	123. 19	125. 82	165. 37	263. 06	555. 80
6	116. 58	119. 20	158. 76	256. 44	549. 18
8	125. 64	128. 26	167. 82	265. 50	558. 24
10	125. 89	128. 51	168. 07	265. 76	558. 50
12	134. 46	137. 08	176. 64	274. 33	567. 07

Tab. S4 Calculated $\Delta_{vap}H$ (kJ/mol, 298.15K) of [EtAm][NO$_3$] when the gas species were assumed to the II, PM and IP, respectively.

	IP1@[EtAm][NO$_3$]	IP2@[EtAm][NO$_3$]	PM@[EtAm][NO$_3$]	II@[EtAm][NO$_3$]
2	81. 33	237. 91	254. 10	694. 36
4	116. 91	273. 48	289. 68	729. 94
6	129. 07	285. 64	301. 84	742. 09
8	148. 9	305. 47	321. 67	761. 93
10	149. 19	305. 76	321. 95	762. 21
12	206. 98	363. 55	378. 78	820. 00

4. The predicted free energies and entropies of vaporization of the [Emim][NTf$_2$] IL

Tab. S5 Calculated $\Delta_{vap}G$ (kJ/mol, 298.15K) of [Emim][NTf$_2$] when the gas species were assumed to the II, PM and IP, respectively.

	IP1@[Emim][NTf$_2$]	IP2@[Emim][NTf$_2$]	PM@[Emim][NTf$_2$]	II@[Emim][NTf$_2$]
2	9. 81	52. 07	220. 76	362. 76
4	68. 41	110. 90	279. 60	421. 58
6	76. 63	119. 12	287. 82	429. 81
8	74. 92	117. 41	286. 11	428. 10
10	25. 56	68. 05	236. 74	378. 73
12	75. 62	118. 10	286. 80	428. 79

Tab. S6 Calculated $\Delta_{vap} S$ (J/K·mol, 298.15K) of [Emim][NTf$_2$] when the gas species were assumed to the II, PM and IP, respectively.

	IP1@[Emim][NTf$_2$]	IP2@[Emim][NTf$_2$]	PM@[Emim][NTf$_2$]	II@[Emim][NTf$_2$]
2	71. 25	91. 09	282. 26	275. 28
4	161. 87	181. 72	372. 81	365. 91
6	183. 04	202. 88	394. 06	387. 07
8	184. 90	204. 75	395. 92	388. 94
10	202. 51	222. 36	413. 53	406. 55
12	207. 17	227. 01	418. 19	411. 20

5. The clusters of [Emim][NTf$_2$] at size 2~12

2 ion-pairs 4 ion-pairs 6 ion-pairs
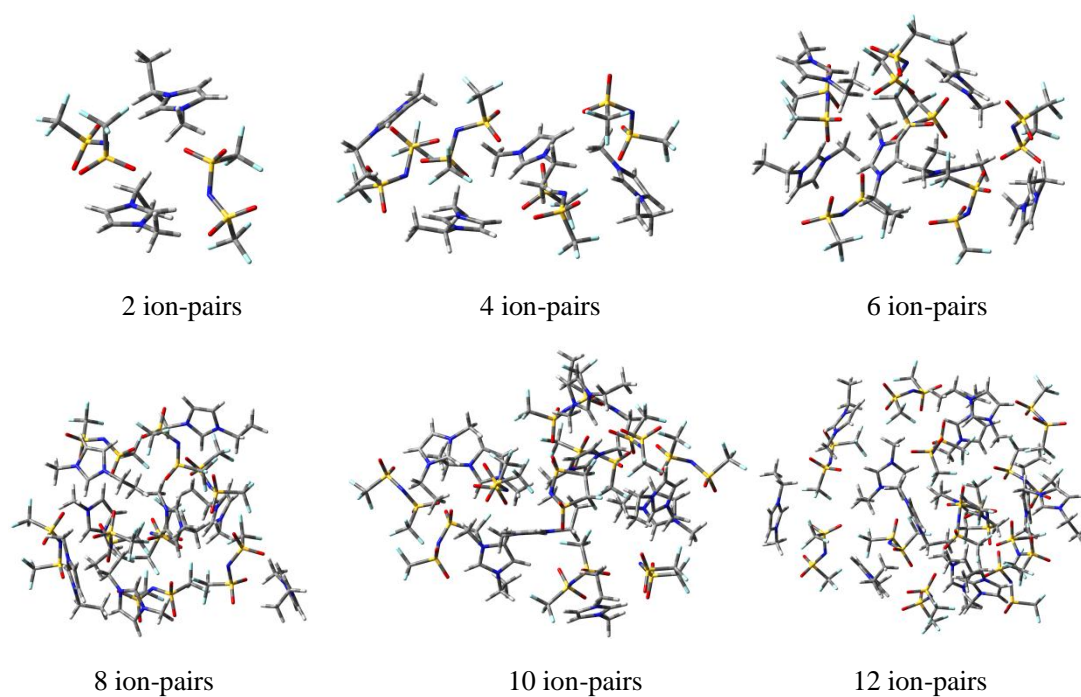
8 ion-pairs 10 ion-pairs 12 ion-pairs

Fig. S3 The optimized geometries of [Emim][NTf$_2$] at M062X/3-21G* level.

1. V. N. Emel'yanenko, S. P. Verevkin and A. Heintz, *J. Am. Chem. Soc.*, 2007, 129, 3930-3937.
2. M. S. Kelkar and E. J. Maginn, *J. Phys. Chem. B*, 2007, 111, 9424-9427.