Electronic Supporting Information

Theoretical Studies on CO_2 Capture Behavior of the Quaternary Ammonium-Based Polymeric Ionic Liquids

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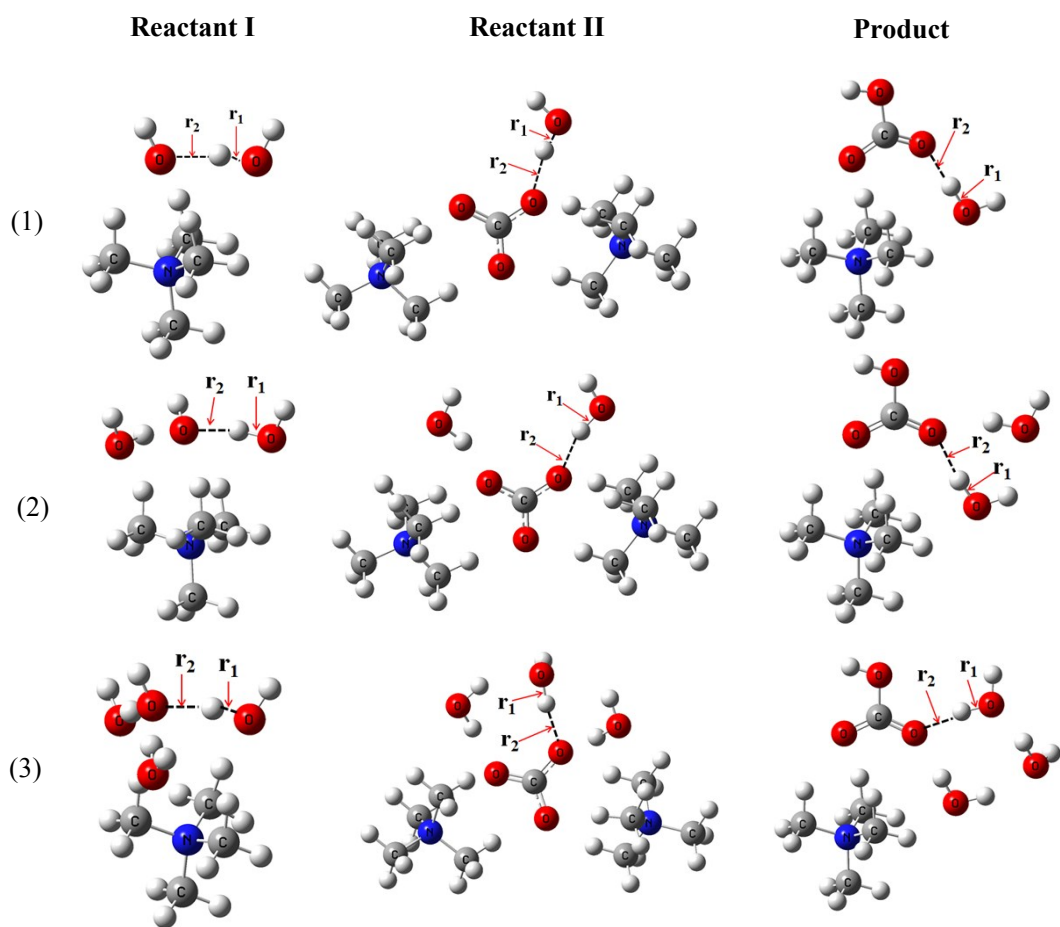
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Fig. S1 Optimized structures of model compounds of PILs with different anions and one (1), two (2) or three (3) hydrated water molecules. r_1 is the O-H bond length in the most active hydrated water r_2 is the length of H-bond. The optimized structure is calculated at B3LYP/6-311++G** level. PILs with certain number of water molecules could have different conformers (see Figure S2) and Figure S1 shows the most stable ones in our calculations.
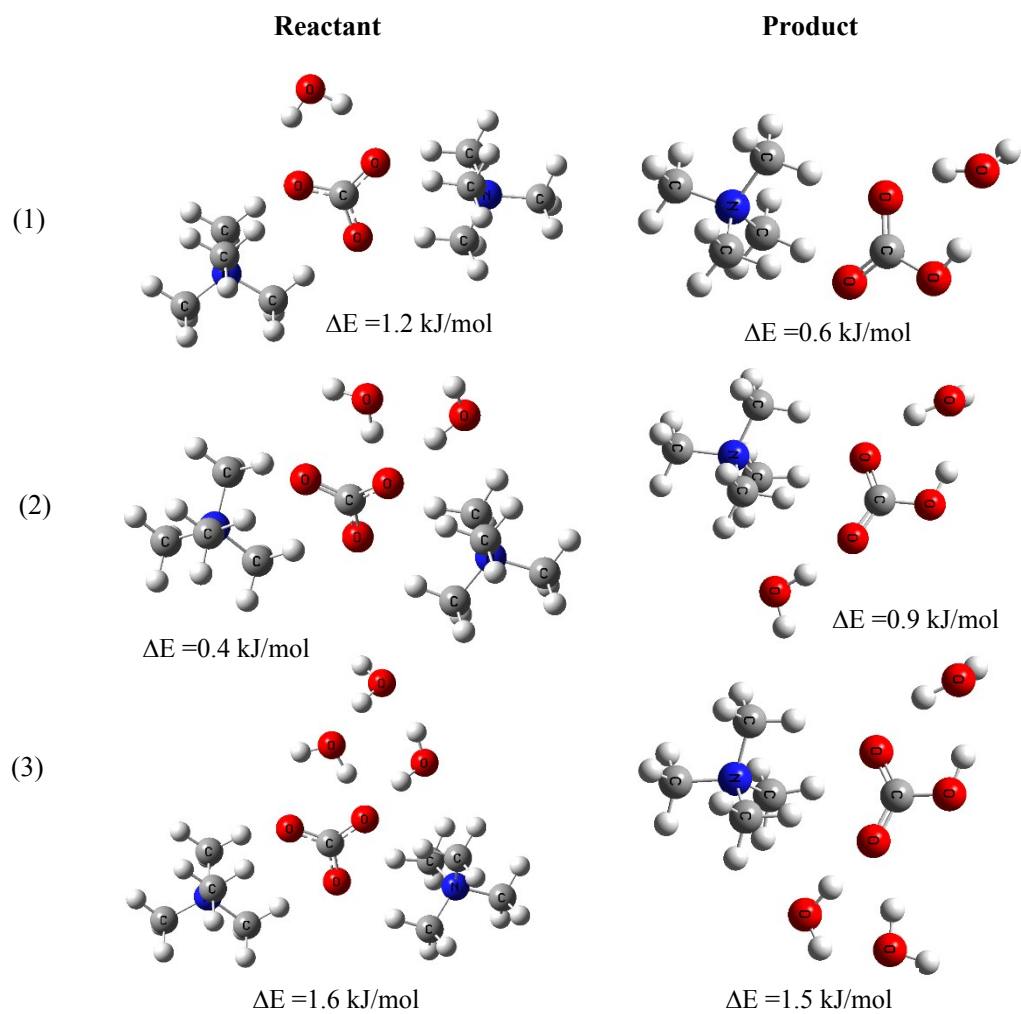
	Reactant	Product

(1)

ΔE =1.2 kJ/mol

ΔE =0.6 kJ/mol

(2)

ΔE =0.4 kJ/mol

ΔE =0.9 kJ/mol

(3)

ΔE =1.6 kJ/mol

ΔE =1.5 kJ/mol

Fig. S2 Optimized structures of conformers other than the most stable ones shown in Figure S1. ΔE is the relative
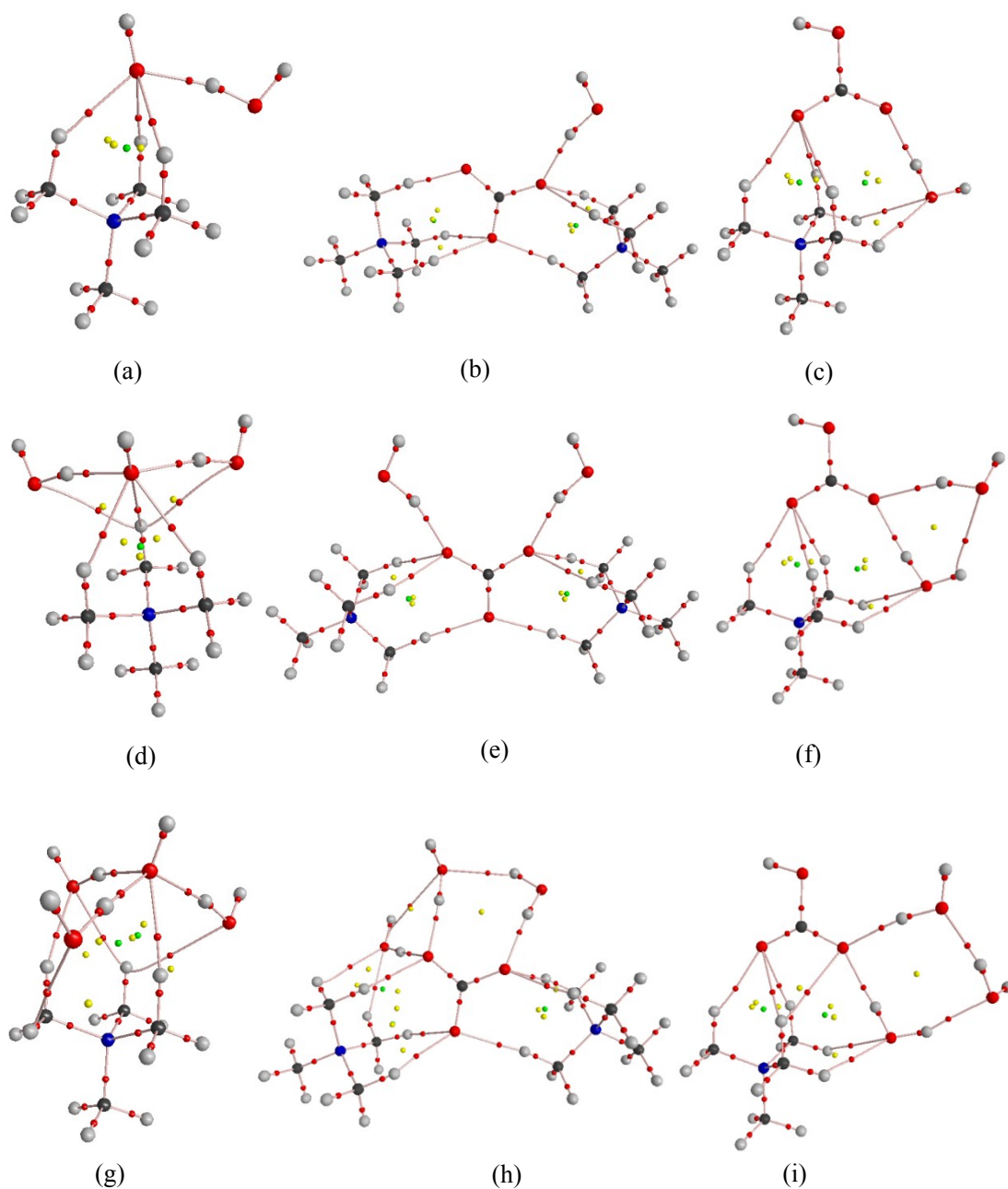
energy compared with the most stable one.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

Fig. S3 Atoms in molecules (AIM) analysis for optimized structures of model compounds with (a) hydroxide anion and one hydrated water molecule, (b) carbonate anion and one hydrated water molecule, (c) bicarbonate anion and one hydrated water molecule, (d) hydroxide anion and two hydrated water molecules, (e) carbonate anion and two hydrated water molecules, (f) bicarbonate anion and two hydrated water molecules, (g) hydroxide anion and three hydrated water molecules, (h) carbonate anion and three hydrated water molecules, (i) bicarbonate anion and three hydrated water molecules

Relevant binary critical points (BCPs), ring critical points (RCPs) and cage critical points (CCPs) are displayed.

Small red dots BCPs, small yellow dots RCPs, small green dots CCPs, black spheres carbon atoms, gray spheres

hydrogen atoms, blue spheres nitrogen atoms, red spheres oxygen atoms, pink lines bond paths.

Table S1 Electron Density (ρ) and Laplacian of the Electron Density ($\nabla^2\rho$) in the BCPs of H-bonds displayed in Fig. S2. The electron density associated with all critical points (ρ) involved in the interaction is correlated to its strength. On the other hand, the Laplacian of the density ($\nabla^2\rho$) indicates regions with concentration of local charge and presents a negative sign when a bond occurs, and a positive one defining a weak interaction.

	hydroxide			carbonate			bicarbonate		
		ρ	$\nabla^2\rho$		ρ	$\nabla^2\rho$		ρ	$\nabla^2\rho$
1^+	OH^--H_2O (1*)	0.0613	0.1422	CO_3^--H_2O (1*)	0.0505	0.1496	HCO_3^{2-}-H_2O (1*)	0.0427	0.1407
	OH^--CH_3 (3*)	0.0248	0.0896	CO_3^--CH_3 (6*)	0.0243	0.0798	HCO_3^{2-}-CH_3 (3*)	0.0179	0.0564
		0.0245	0.0885		0.0296	0.0999		0.0161	0.0600
		0.0257	0.0818		0.0339	0.1036	H_2O-CH_3 (2*)	0.0132	0.0459
2^+	OH^--H_2O (2*)	0.0566	0.1430	CO_3^--H_2O (2*)	0.0454	0.1492	HCO_3^{2-}-H_2O (2*)	0.0308	0.1162
		0.0568	0.1434		0.0462	0.1497		0.0337	0.1226
	OH^--CH_3 (3*)	0.0137	0.0524	CO_3^--CH_3 (6*)	0.0262	0.0887	HCO_3^{2-}-CH_3 (3*)	0.0146	0.0449
		0.0138	0.0531		0.0263	0.0891		0.0163	0.0506
		0.0209	0.0652		0.0273	0.0933		0.0154	0.0559
	H_2O-CH_3 (2*)	0.0078	0.0294		0.0276	0.0949	H_2O-CH_3 (2*)	0.0128	0.0474
		0.0078	0.0298		0.0291	0.0905		0.0133	0.0442
					0.0290	0.0901	H_2O-H_2O (1*)	0.0112	0.0388
3^+	OH^--H_2O (3*)	0.0481	0.1312	CO_3^--H_2O (3*)	0.0386	0.1257	HCO_3^{2-}-H_2O (2*)	0.0418	0.1347
		0.0496	0.1325		0.0475	0.1365		0.0279	0.1059
		0.0628	0.1518		0.0405	0.1320			
	OH^--CH_3 (1*)	0.0190	0.0690	CO_3^--CH_3 (6*)	0.0278	0.1007	HCO_3^--CH_3 (4*)	0.0090	0.0304
					0.0215	0.0718		0.0168	0.0529
		0.0069	0.0221		0.0258	0.0845		0.0129	0.0396
					0.0224	0.0708		0.0143	0.0508
	H_2O-CH_3 (4*)	0.0088	0.0298		0.0224	0.0703	H_2O-CH_3 (2*)	0.0149	0.0541
					0.0237	0.0805			
		0.0108	0.0375	H_2O-CH_3 (2*)	0.0073	0.0247		0.0141	0.0476
					0.0113	0.0415			
		0.0178	0.0609	H_2O-H_2O (2*)	0.0182	0.0590	H_2O-H_2O (2*)	0.0342	0.1195
					0.0054	0.0209		0.0266	0.0925

$^+$ The number of hydrated water in hydrated ionic pairs

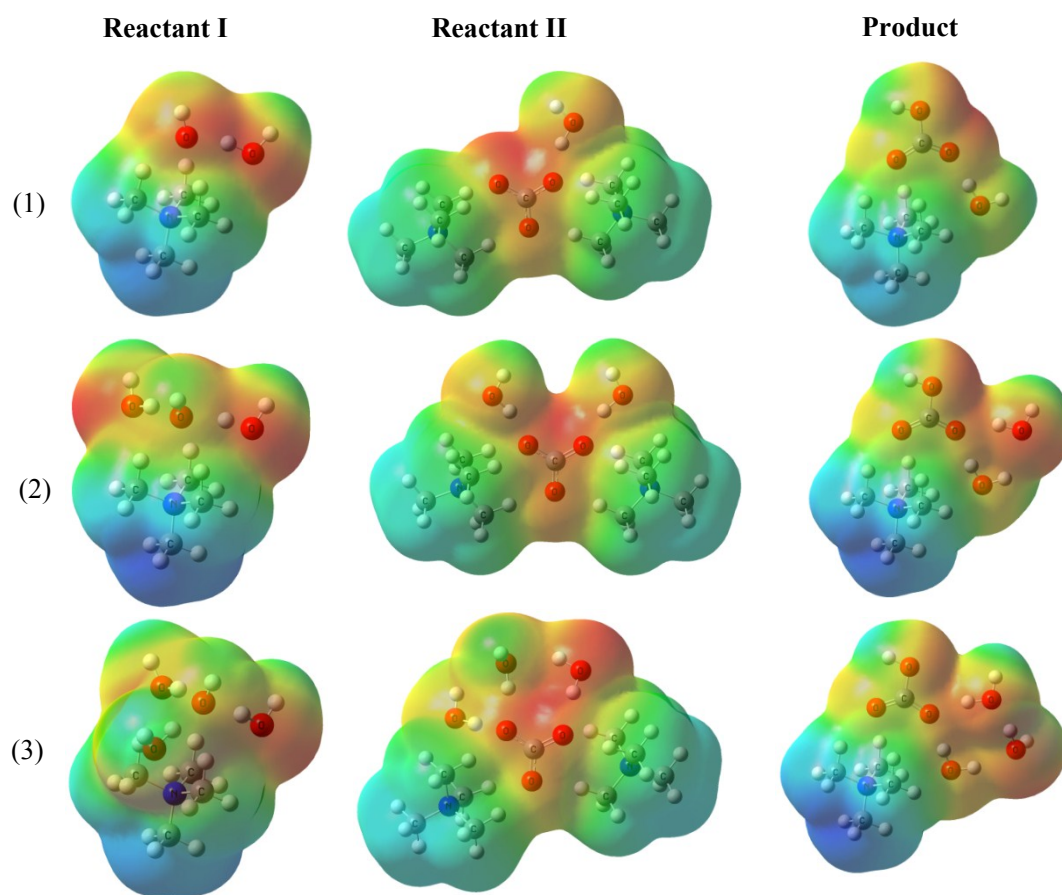* The number of H-bond of the displayed types

Fig. S4 Electrostatic potential maps of model compounds of PILs with different anions and one (1), two (2) or

three (3) hydrated water molecules.

The electrostatical potential surfaces were calculated through populational analysis at B3LYP/6-311++G** level.

Electron density projected onto electrostatic potential isosurface (mapped at 0.01 a.u.). The red zones represent

negative charge center and the blue zones represent positive charge center.

The AIM analysis of model compounds of PILs with different anions and different number of hydrated water molecules is shown in Figure S3 and the values of ρ and $\nabla^2\rho$ of BCPs are shown in Table S1. The AIM analysis confirms the strong H-bonds between water and anions. The H-bonds between water molecules are remarkable for model compounds of PILs with bicarbonate anion, because water molecules have self-association distribution. However, these H-bonds are ignorable for model compounds of PILs with hydroxide or carbonate anion, which is the result of mutual independence distribution of water molecules. The variation of the maximum strength of H-bonds between water and model compounds has a similar tendency with that of atomic charge of oxygen-atom in hydrated water and O-H bond length and H-bond length, which indicates that there is a direct relation between the maximum strength of H-bonds and their charge parameters or structure parameters [1].
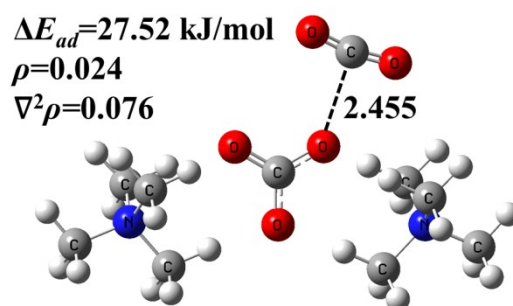
ΔE_{ad}=27.52 kJ/mol
ρ=0.024
$\nabla^2\rho$=0.076
2.455

Fig. S5 Direct interaction of CO_2 and model compounds of P[VBTEA][CO_3^{2-}].

Literature Cited

[1]   M. Shahabi, H. Raissi, F. Mollania, *Struct Chem* **2015**, 26, 491–506.