

## Supplementary Information

# Dynamic Acid/Base Equilibrium in Single Component Switchable Ionic Liquids and Consequences on Viscosity

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### Table of Contents

Abbreviations	2
Blue Moon Ensemble Simulation	2
Figure S1	2
Metadynamics Simulations	3
Figure S2	3
Table S1	4
Figure S3	4
Table S2	5
Additional Discussion on CO <sub>2</sub> Capture Capacity	5
Dipole Moments and Dielectric Constant Calculations	6
Table S3	6
Table S4	7
Classical Molecular Dynamics	8
Table S5	8
Table S6	9
Table S7	9
Additional Viscosity Discussion	9
Calculation of Percent Internal Hydrogen Bond	10
Figure S4	10
Figure S5	10
Angle and Dihedral Parameters	11
Classical MD Box Dimensions	12

## Abbreviations

AIMD: ab initio molecular dynamics

MD: molecular dynamics

IPADM-2-BOL: 1-((1,3-dimethylimidazolidin-2-ylidene)-amino)-propan-2-ol

IPATFMM-2-BOL: fluorinated variant of IPADM-2-BOL (see Figure 3 in main text)

EODM-2-BOL: oxime variant of IPADM-2-BOL (see Figure 3 in main text)

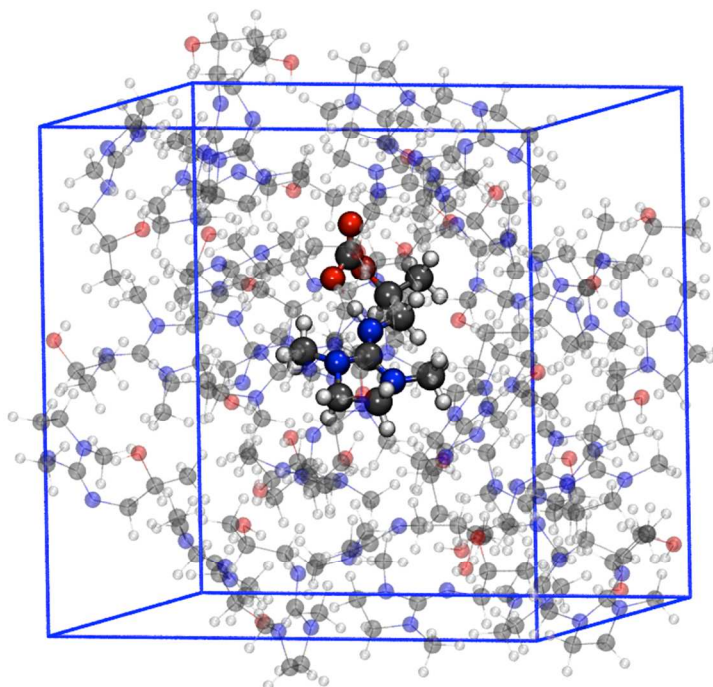
## Blue Moon Ensemble Simulation and Free Energy Calculations

Carbon capture was simulated in solvent boxes containing 34 IPADM-2-BOL molecules (example Figure S1) with a single CO<sub>2</sub> molecule with AIMD. An initial solvent box was prepared with classical MD to obtain a box size with the correct density (0.96 g/cm<sup>3</sup> computed compared to 1.0 g/cm<sup>3</sup> experiment for IPADM-2-BOL), and to relax the solvent structure. Independent simulation boxes were then made for each frame along the capture reaction coordinate, where the CO<sub>2</sub> was placed at varying distances from an IPADM-2-BOL molecule.

In the Blue Moon ensemble method, a potential of mean force is constructed from the forces on the constraint, in this case the distance between the CO<sub>2</sub> carbon atom and the alcohol oxygen atom of an IPADM-2-BOL molecule ( $r_{C-O}$ ). By integrating the mean force, free energies along the reaction coordinate are obtained. The error bars were estimated by calculating the potential of mean force using two halves of the equilibrated simulation time interval. The average internal energy  $\langle \Delta E \rangle$  is computed from the potential (i.e. Kohn-Sham energy) and kinetic energies over the equilibrated portion of the AIMD trajectory. See Figure 2 of main text for resulting energy and Free energy curves.

### Figure S1: IPADM-2-BOL solvent box used for AIMD simulations

CO<sub>2</sub>-bound IPADM-2-BOL molecule in its zwitterionic state surrounded by unbound IPADM-2-BOL molecules. 989 atoms, red is O, gray is C, white is H, and blue is N.

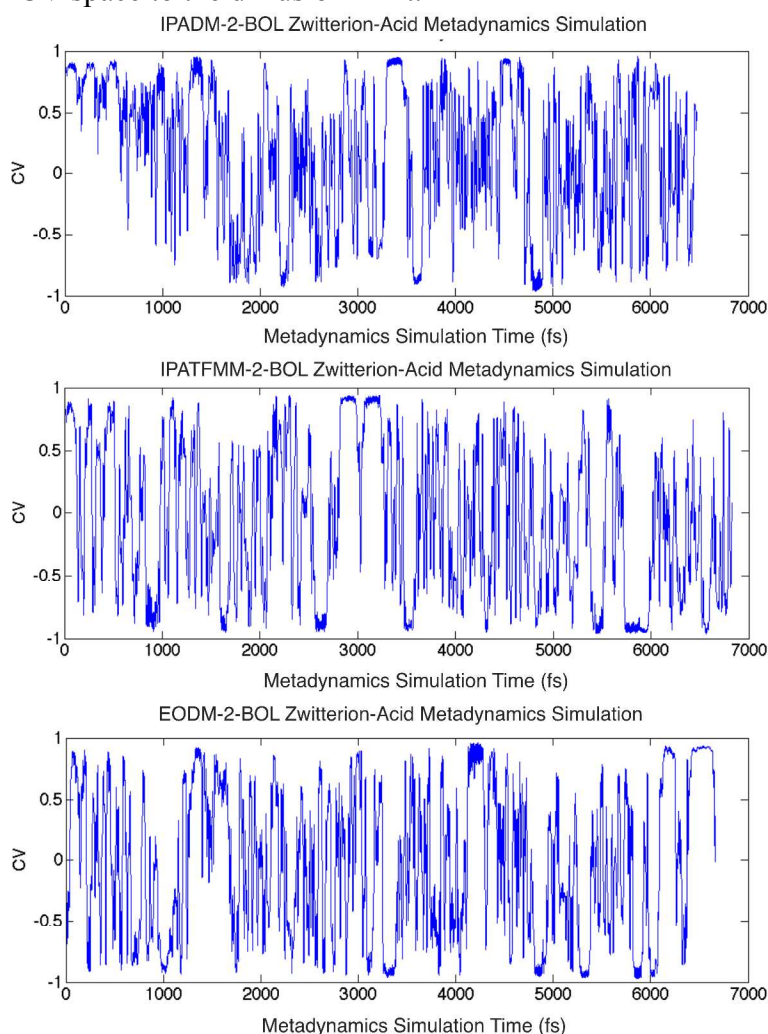


## Metadynamics Simulations and Free Energy Calculations

To determine the preferred CO<sub>2</sub>-bound, as well as calculating the acid-zwitterion equilibrium, a single CO<sub>2</sub>-bound CO<sub>2</sub>BOL molecule was placed in a solvent box of unbound molecules. The solvent box containing 34 CO<sub>2</sub>BOL molecules, one CO<sub>2</sub>-bound and the rest not binding, was initially prepared with classical MD. The carbon loaded CO<sub>2</sub>BOL was initially in its zwitterionic conformation. AIMD simulations using the metadynamics technique were used to accelerate the proton transfer to/from the carboxylate oxygen (acid) and guanidium nitrogen (zwitterion) atoms and construct a free energy profile of the internal proton transfer process. From that, relative acid/zwitterion populations and transfer energy barrier required can be obtained. This was done for IPADM-2-BOL, IPATFMM-2-BOL, and EODM-2-BOL solvents. By summing the energy hills added during the metadynamics simulation, the free energy profiles is built, and barriers, free energy differences, and relative populations can be calculated.

### Figure S2: CV values and metadynamics simulation time

The values of the CV over the IPADM-2-BOL, EODM-2-BOL, and IPATFMM-2-BOL metadynamics simulations had multiple crossings (from negative to positive values) to assure proper sampling of CV space to the diffusion limit.



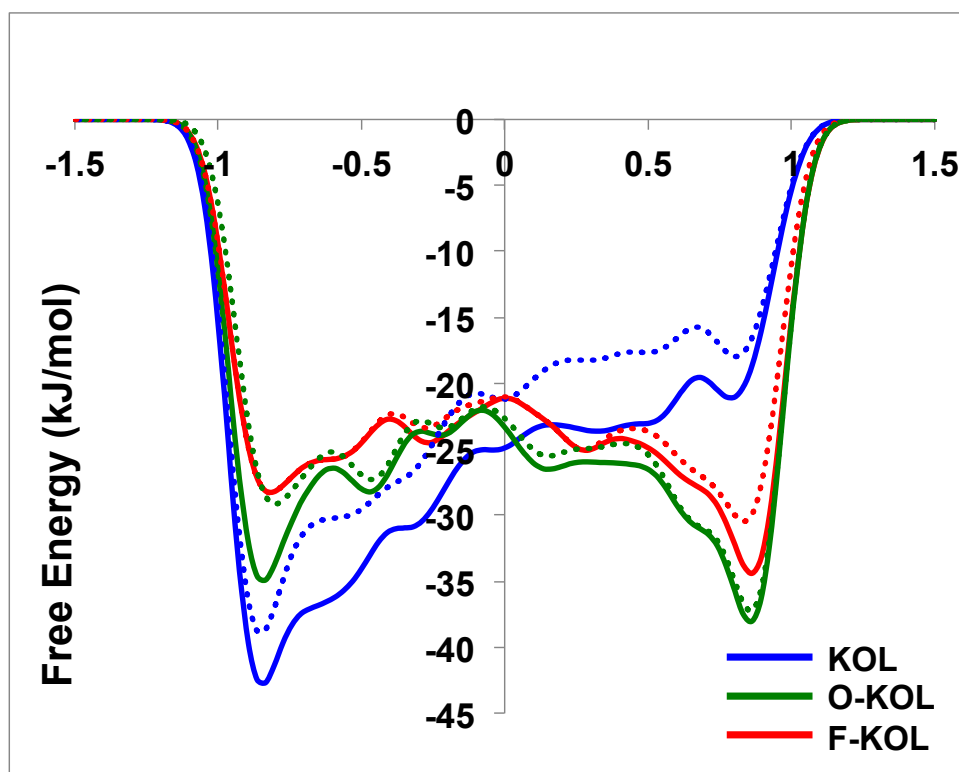
**Table S1: AIMD metadynamics calculations and error analysis of acid and zwitterionic states.**

System	Barrier $A \rightarrow Z$	Barrier $Z \rightarrow A$	$\Delta G (A - Z)$	$K_{eq}=[A]/[Z]^b$
IPADM-2-BOL(KOL)	1.3 +/- 0.5	22.9 +/- 0.1	21.6 +/- 0.6	1/4000
EODM-2-BOL (O-KOL)	15.9 +/- 0.5	12.8 +/- 4.4	-3.1 +/- 4.9	3/1
IPATFMM-2-BOL (F-KOL)	13.2 +/- 3.8	7.8 +/- 0.6	-5.4 +/- 4.4	8/1

<sup>a</sup>Free energy barriers (kJ/mol) and difference (kJ/mol) between the acid and zwitterionic states.

<sup>b</sup>Equilibrium constants estimated using  $\Delta G = -RT \ln(K_{eq})$  at 40 °C.

**Figure S3.** Two profiles for each compound: one constructed with all the hills added for the full simulation time ( $t_{final}$ ), and new profiles (dashed lines) built by summing the hills up to 1 ps before the full simulation time ( $t_{new} = t_{final} - 1ps$ ). The error in energy barrier and  $\Delta G$  values was estimated as the difference between those at  $t_{final}$  and  $t_{new}$ .



**Table S2: Electronic structure calculations of acid and zwitterionic states**

Free energy differences (kJ/mol) between acid and zwitterionic states for varying dielectric constants, equilibrium constants estimated using  $\Delta G = -RT \ln(K_{eq})$  at 40 °C.

	IPADM-2-BOL		IPATFMM-2-BOL		EODM-2-BOL	
Dielectric	$\Delta G(A-Z)$	$K_{eq}=[A]/[Z]$	$\Delta G(A-Z)$	$K_{eq}=[A]/[Z]$	$\Delta G(A-Z)$	$K_{eq}=[A]/[Z]$
78 (water)	*	-	12.5	1/125	2.2	1/2
24 (ethanol)	*	-	-0.8	1/1	1.2	1/1
17 (1-butanol)	20.0	1/2200	-1.7	1/1	0.5	1/1
12 (1-hexanol)	19.6	1/1900	-4.5	6/1	-2.5	3/1
7.4 (THF)	16.8	1/650	-9.1	34/1	-11.9	100/1
6.8 (Aniline)	16.1	1/500	-9.6	40/1	-12.5	125/1
5.9 (1-chloro-hexane)	15.2	1/350	-12.1	105/1	-13.6	185/1

\*Acid state optimization not possible without a constraint, turned into zwitterion

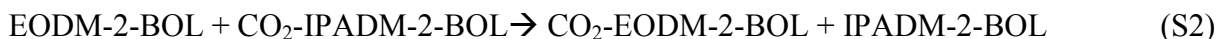
## Additional Discussion on CO<sub>2</sub> Capture Capacity

For a viable CO<sub>2</sub> capture solvent, the CO<sub>2</sub> capture (solvation and binding) enthalpy is estimated to be within the range of ~60-90kJ/mol. To gauge the capacity of CO<sub>2</sub> capture of IPATFMM-2-BOL and EODM-2-BOL, we consider the relative  $\Delta G$  for CO<sub>2</sub> capture compared to that of IPADM-2-BOL, which has been experimentally characterized to have a capture enthalpy of -80kJ/mol and a capture free energy of -10kJ/mol at low CO<sub>2</sub> loading.<sup>1</sup> Performing implicit solvent single molecule calculations on the CO<sub>2</sub> capture of IPADM-2-BOL resulted in  $\Delta E$  -29 kJ/mol, indicating that CO<sub>2</sub> solvation is not adequately reproduced by implicit solvent calculations.

Implicit solvation models cannot provide reliable estimates for the absolute capture energies due to insufficient parameterization. Our AIMD simulations, with the CO<sub>2</sub> solvated in the simulation box, can only accurately represent CO<sub>2</sub> binding. To our knowledge, there is no existing methodology at the AIMD level that can provide reliable description of the solvation free energy. Thus we resort to a simple measure based on an isodesmic reaction scheme. Here, the relative free energies of CO<sub>2</sub> bound to various CO<sub>2</sub>BOLs species are compared by computing the free energy of the reaction:



or



We used the experimental  $\Delta G_{\text{IPADM-2-BOL}}$  of -10 kJ/mol and  $\Delta H_{\text{IPADM-2-BOL}}$  of -80 kJ/mol of CO<sub>2</sub> capture as our reference states. The free energy of CO<sub>2</sub> capture can then be approximated by  $\Delta G_{\text{COMPOUND}} = \Delta G_{\text{IPADM-2-BOL}} + \Delta \Delta G_{\text{S1/S2}}$ , which can be approximated by  $\Delta G_{\text{COMPOUND}} = \Delta G_{\text{IPADM-2-BOL}} + \Delta \Delta E_{\text{S1/S2}}$ , since the vibrational and solvation energy/entropy terms will largely cancel from one solvent system to the next. Likewise, the relative enthalpy of reaction can also be approximated by  $\Delta H_{\text{COMPOUND}} = \Delta H_{\text{IPADM-2-BOL}} + \Delta \Delta E_{\text{S1/S2}}$ . We compute  $\Delta \Delta E_{\text{S1/S2}}$  using gas phase single molecule calculations. For IPATFMM-2-BOL our estimate is  $\Delta G$  -23 kJ/mol and  $\Delta H$  -93

<sup>1</sup> Mathias et al *Energy Environ. Sci.*, (2013), 6, 2233.

kJ/mol for CO<sub>2</sub> to be captured. Conversely for EODM-2-BOL we estimate  $\Delta G$  -11.2 kJ/mol and  $\Delta H$  -81.2 kJ/mol for CO<sub>2</sub> capture, which would indicate a similar higher CO<sub>2</sub> loading capacity to IPADM-2-BOL. A more quantitative approach for the evaluation of the entropic/enthalpic components of CO<sub>2</sub> sorption is currently being developed and will be the subject of forthcoming publications.

## Dipole Moments and Dielectric Constant Calculations

Molecular dipole moments calculated with different methods.

**Table S3: Dipole moments from different methods in Debye.**

System	$\mu_{\text{QM}}^{(a)}$	$\mu_{\text{PC}}^{(a)}$	$\mu_{\text{FF}}^{(a)}$	$\mu_{(l)}^{(a)}$
IPADM-2-BOL	4.9	5.1	4.9	5.0
EODM-2-BOL	4.0	4.1	4.0	4.5
IPATFMM-2-BOL	6.3	6.7	6.3	6.7
CO <sub>2</sub> -IPADM-2-BOL	14.3	16.5	14.3	15.6
CO <sub>2</sub> -EODM-2-BOL	10.7	14.9	10.7	20.3
CO <sub>2</sub> -IPATFMM-2-BOL	15.4	18.3	15.4	18.3

<sup>(a)</sup>  $\mu_{\text{QM}}$  is the single molecule dipole moment from the quantum chemistry calculations,  $\mu_{\text{PC}}$  is the single molecule dipole moment in a polarizable continuum,  $\mu_{\text{FF}}$  is the single molecule dipole moment using the ESP charges in a classical FF, and finally  $\mu_{(l)}$  is the dipole moment as an ensemble average  $\langle \mu_{\text{FF}} \rangle$  from all molecule conformations taken from the classical MD simulation at 25% mol CO<sub>2</sub> loading.

Molecular dipole computed with different methods (Table S4) show very little variation except for the CO<sub>2</sub>-loaded oxime species (CO<sub>2</sub>-EODM-2-BOL). This can be largely attributed to the conformational changes in the extended liquid structure ( $\mu_{(l)}$ ) relative to the gas phase ( $\mu_{\text{FF}}$ ).

Based on the values from Table S4, the static dielectric constant  $\epsilon_0$  can be computed and compared, using the basic Debye-Onsager theory.<sup>2</sup> In a classical MD *ansatz*, the static dielectric constant is  $\epsilon_0 \propto \langle M \cdot M \rangle$ , where  $M$  is the instantaneous dipole moment of the simulation box.  $M$  is approximated as a linear combination of the all the individual molecular dipole moments  $\mu_i$ ,  $M = \sum_i^N \mu_i$ . Consequently, the dielectric constant may be written as:

$$\epsilon_0 \propto \langle \sum_i^N \sum_j^N \mu_i \cdot \mu_j \rangle \quad \text{Eq. S1}$$

By re-ordering the terms in the summation, we have:

$$\epsilon_0 \propto \sum_i^N \langle \mu_i \rangle^2 + \sum_i^N \sum_{j \neq i}^N \langle \mu_i \cdot \mu_j \rangle \quad \text{Eq. S2}$$

<sup>2</sup> L. Onsager, *J. Am. Chem. Soc.* (1936), 58(8), 1486-1493.

The first term of Eq. S2 corresponds to the Debye-like term for the uncorrelated dipoles, while the second term represents the dipole correlations between molecules. Noting from Table S4 that the dipole moment of the ionic species is appreciably larger than the neutral ones, we can use a simple Debye-Onsager relationship to approximate  $\epsilon_0$ :

$$\epsilon_0 = n^2 + \frac{4\pi(\mu)^2}{3kT} N_s \quad \text{Eq. S3}$$

where  $n$  is the refractive index  $\sim 1$ ,  $\mu$  is the dipole (D) and  $N_s$  the concentration (molecules  $\text{m}^{-3}$ ).

Values of  $\epsilon_0$  computed from Eq. S3, are summarized in Table S4 and compared with values taken from Table S5 (simulation).

**Table S4: Computed dielectric constants.**

System	Loading (mol%)	$\epsilon_{0,FF}$ <sup>a</sup>	$\epsilon_{0,(l)}$ <sup>a</sup>	$\epsilon_{0,MD}$ <sup>b</sup>
CO <sub>2</sub> -IPADM-2-BOL	10	7.7	9.0	12.3 $\pm$ 1.3
	25	17.8	21.1	6.1 $\pm$ 0.5

<sup>a</sup> Calculated from Eq. S3 and the dipole values in Table S3. <sup>b</sup> Calculated with the g\_dipoles program in the GROMACS package. Error estimated by calculating the dielectric constant using two halves of the time interval.

Although the Debye-Onsager equation provides reasonable estimates at low loading, it will not predict the same trends in dielectric constant, as a function of carbon loading, as obtained from classical MD (see Table S5), since in this equation the dielectric constant is proportional the number of ionic species. In this zwitterionic system the arrangement between different molecules results in a smaller net dipoles of the extended liquid structure. This clearly proves the statement that as the number of charged species increases, inhomogeneity in the liquid leads to a decrease in the dielectric constant, see Table below for extended data presentation.



## Classical Molecular Dynamics

**Table S5:** Properties of IPADM-2-BOL at 40 °C calculated from classical molecular dynamics simulations.

Loading (mol %)	Self-Diffusion Coefficient <sup>a</sup> (10 <sup>-5</sup> cm <sup>2</sup> /s)	Dielectric Constant <sup>b</sup>	Viscosity (cP)			
			Green-Kubo <sup>c</sup>	Non- Equilibrium <sup>d</sup>	From Self- Diffusion <sup>e</sup>	Experi- ment <sup>f</sup>
0%	0.1228 ±0.0025	12.4 ±3	14.6 ±8.0	8.6 +1.0 -0.8	12.2 +0.2 -0.3	8.3
<i>All CO<sub>2</sub>-loaded molecules zwitterionic</i>						
10%	0.0373 ±0.0021	12.3 ±1.3	43.9 ±8.7	23.6 +4.6 -3.3	40.2 +2.4 -2.1	22.5
15%	0.0220 ±0.0008	11.2 ±4	60.3 ±22.8	48.9 +8.4 -6.2	68.2 +2.6 -2.4	43.9
20 %	0.0134 ±0.0017	7.5 ±0.3	94.5 ±44.5	80.2 +22.2 -14.3	111.9 +16.3 -12.6	75.4
25%	0.0081 ±0.0012	6.1 ±0.5	145.0 ±41.0	149.5 +21.2 -16.5	185.2 +32.2 -23.9	165.0*
30%	0.0051 ±0.0013	4.7 ±2.2	272.2 ±187.5	219.6 +107.9 -54.4	294.1 +100.6 -59.7	318.7*
<i>CO<sub>2</sub>-loaded molecules 1:1 acid to zwitterion</i>						
10%	0.0366 ±0.0013	7.9 ±0.4	22.4 ±11.7	25.1 +3.1 -2.5	41.0 +1.5 -1.4	N/A
15%	0.0220 ±0.0005	11.3 ±1.9	68.2 ±37.1	40.4 +7.6 -5.5	68.2 +1.6 -1.5	N/A
20%	0.0155 ±0.0040	6.8 ±1.1	72.3 ±69.4	53.2 +19.2 -11.2	96.8 +33.7 -19.9	N/A
25%	0.0102 ±0.0011	6.4 ±0.2	81.3 ±68.1	77.7 +31.3 -17.3	147.1 +17.8 -14.3	N/A
30%	0.0051 ±0.0003	6.0 ±0.1	Not converged	139.2 +69.9 -34.9	294.1 +18.4 -16.3	N/A

**a:** Calculated with g\_msd program in the GROMACS package. Error estimate as reported in the output.

**b:** Calculated with the g\_dipoles program in the GROMACS package. Error estimated by calculating the dielectric constant using two halves of the time interval.

**c:** Viscosity calculated using the Green-Kubo approach by calculating the integral of the pressure tensor autocorrelation function. Calculation was done with the P<sub>XZ</sub>, P<sub>XY</sub>, and P<sub>YZ</sub> tensors independently, and error estimated as the largest viscosity difference obtained between two tensors components

**d:** Non-equilibrium method was used as implemented in the g\_energy program in the GROMACS package to obtain 1/viscosity values after applying an acceleration. Error calculated based on the 1/viscosity error estimate as reported in the output, that result in different + and – variations.

**e:** Estimated from the calculated self-diffusion coefficient, and the self-diffusion coefficient and viscosity of water. Error estimates calculated from those of the self-diffusion coefficient, that result in different + and – variations.

**f:** Experimental viscosity measurements at 40 °C. From “P.M., M. *et al.* Measuring the Absorption Rate of CO<sub>2</sub> in Nonaqueous CO<sub>2</sub>-Binding Organic Liquid Solvents with a Wetted-Wall Apparatus. *ChemSusChem*, doi:10.1002/cssc.201500288 (2015)”.

\*: Predicted from an exponential fit to data from 0 to 23.8 %mol loading.



**Table S6:** Percent difference between calculated and experimental IPADM-2-BOL viscosities.

$$\%Diff = 100 * \frac{abs(\eta_{calc} - \eta_{exp})}{\eta_{exp}} \quad \text{Eq. S4}$$

Loading (mol %)	%Diff		
	Green-Kubo	Non-Equilibrium	Self-Diffusion
0%	75.9	3.6	47.2
10%	95.1	4.9	78.7
15%	37.4	11.4	55.3
20%	25.3	6.4	48.5
25%	12.1	9.4	12.2
30%	14.6	30.9	7.5

**Table S7:** IPATFMM-2-BOL and EODM-2-BOL viscosities calculated with the non-equilibrium method.

25% mol CO <sub>2</sub> loading	IPATFMM-2-BOL Viscosity (cP)	EODM-2-BOL Viscosity (cP)
All zwitterion	328.5 +415.4 -117.7	45.5 +8.0 -5.9
1:1 acid:zwitterion	214.2 +45.0 -31.7	17.9 +1.9 -1.6
All acid	137.9 +21.3 -16.3	14.2 +0.7 -0.6

### Additional Discussion on Viscosity Calculations

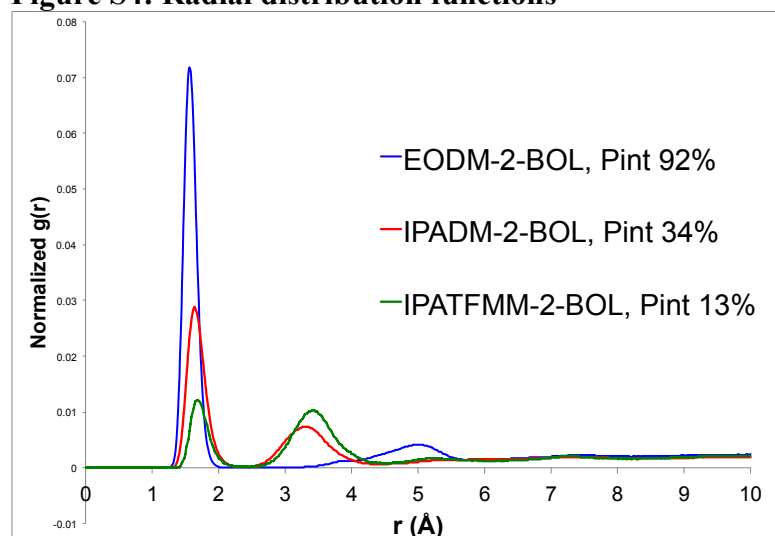
The non-equilibrium method performed best compared to experimental values and had the smallest error estimate (Tables S3 and S4). Calculated values are within 11% of the experimental ones for 25% mol CO<sub>2</sub> loadings or lower, supporting that the non-equilibrium method should also give accurate calculations of the 1:1 systems. The estimated error in the calculations increase with carbon loading, ranging from ~15% error for the lower viscosity range (<50 cP), ~30% error at the mid-range (50-150 cP), and >100% error for high viscosities (>200 cP).

Although the viscosities obtained are consistent with the experimental data, the statistical error bars are appreciable. When comparing to experiment, errors obtained with the non-equilibrium method performed better than those with a Green-Kubo approach at low CO<sub>2</sub> loading, or calculated from the self-diffusion coefficient (Table S6, Eq. S4). Despite this fact, all methods provide the same trends in change in viscosity with respect to variation of CO<sub>2</sub> loading and change of molecule type. Calculating accurate viscosities of condensed phases with highly charged species is challenging, and becomes more so as viscosity increases.

## Calculating the Percent of Internal Hydrogen Bond

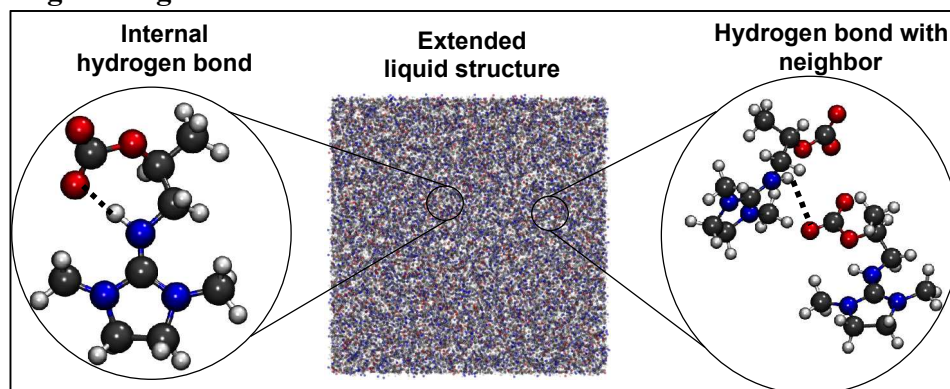
Radial distribution functions between the  $\text{H}(\text{H}^+\text{N})$  and  $\text{O}(\text{COO}^-)$  atoms in the extended solvent structure were computed to observe the distances between the two atoms in the extended liquid structure.

**Figure S4: Radial distribution functions**



Internal hydrogen bonds are less than  $2.5\text{\AA}$ , and the  $g(r)$  curves indicate hydrogen bonds for greater distances, so between different molecules. Note a higher 1<sup>st</sup> peak for EODM-2-BOL, which has 95% of  $\text{CO}_2$ -bound molecules with an internal hydrogen bond at 25% mol  $\text{CO}_2$  loading. Subsequently, the distance between of  $\text{H}(\text{H}^+\text{N})$  and  $\text{O}(\text{COO}^-)$  atoms for all molecules during NVT equilibrated runs were calculated, and counted the molecules for which the distance was below  $2.5\text{\AA}$  to calculate the percentage of  $\text{CO}_2$ -bound molecules with an internal hydrogen bond (Pint).

**Figure S5: Visual representation of the internal hydrogen bond, and bonding with neighboring molecules.**



## Special Angle and Dihedral Parameters

Angle parameters not present in the OPLS force field were estimated. For harmonic angle potentials, equilibrium values ( $\Theta_{ijk}^0$ ) were taken from the electronic structure optimized structures (see Methods), and force constants ( $k_{ijk}^\theta$ ) were estimated by doing constrained geometry optimizations for varying  $ijk$  angle values. For dihedral angles, a series of constrained geometry optimizations was done, and the resulting potential energies were used to fit the Ryckaert-Bellemans potentials, as implemented in GROMACS for proper dihedral angle types.

Harmonic angle potential:

$$V_a(\theta_{ijk}) = \frac{1}{2} k_{ijk}^\theta (\theta_{ijk} - \theta_{ijk}^0)^2$$

Dihedrals: Ryckaert-Bellemans function

$$V_{rb}(\phi_{ijkl}) = \sum_{n=0}^5 C_n (\cos(\psi))^n$$

where  $\psi = \phi - 180^\circ$

Parameters added:

Angles	$k_{ijk}^\theta$ (kJ/mol rad <sup>2</sup> )
EODM-2-BOL C-N-O	483.0
EODM-2-BOL N-O-C	485.0

Dihedrals	C <sub>0</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>
IPADM-2-BOL and IPATFMM-2-BOL N-C-C-O	13	20	-5	-3	7	0
EODM-2-BOL N-C-N-O	5	48	-5	-5	15	0

## Classical MD Simulation Box Dimensions

Compound, Loading (% mol)	Box (nm <sup>3</sup> )
IPADM-2-BOL	
0	507.1
10 all zw	505.3
15 all zw	505.9
20 all zw	506.9
25 all zw	507.0
30 all zw	508.2
10 1:1 ac:zw	505.4
15 1:1 ac:zw	505.8
20 1:1 ac:zw	507.8
25 1:1 ac:zw	508.6
30 1:1 ac:zw	509.1
EODM-2-BOL 25	491.7
IPATFMM-2-BOL 25	546.2