

# Supporting Information for: Water Sorption and Diffusivity in

[C<sub>2</sub>C<sub>1</sub>im][BF<sub>4</sub>], [C<sub>4</sub>C<sub>1</sub>im][OAc], and [C<sub>4</sub>C<sub>1</sub>im][Cl]

M. Alejandra Rocha and Mark B. Shiflett\*

Department of Chemical and Petroleum Engineering, University of Kansas,  
1450 Jayhawk Blvd, Lawrence, Kansas 66045, United States

\* To whom correspondence should be addressed. E-mail: mark.b.shiflett@ku.edu (M. B. Shiflett).

## **Table of Contents**

<b>Solubility Data</b> .....	2
<b>Density Values</b> .....	10
<b>NRTL Parameters <math>\tau_{ij}</math></b> .....	11
<b>Enthalpy</b> .....	12
<b>Rotational Motion Activation Energy</b> .....	15
<b>Diffusion</b> .....	17
<b>Modeling</b> .....	17
<b>Height in Calculating the Diffusion Coefficient</b> .....	20
<b>Diffusion Coefficient Results</b> .....	22
<b>References</b> .....	25

## **Solubility Data**

**Table S1.** Absorption and Desorption Solubility Data for [C<sub>2</sub>C<sub>1</sub>im][BF<sub>4</sub>] at 298.15 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0.00	0.00	0.0	0.0
Absorption	10.67	0.34	0.8	8.4
Absorption	30.67	0.97	2.8	24.3
Absorption	50.67	1.61	5.8	40.4
Absorption	70.67	2.24	11.8	59.4
Desorption	70.67	2.25	11.9	59.6
Desorption	50.67	1.61	5.8	40.4
Desorption	30.67	0.97	2.8	24.2
Desorption	10.67	0.34	0.8	8.5
Desorption	0.00	0.00	0.0	0.5

<sup>a</sup> Uncertainty was less than 0.1 mol%.

**Table S2.** Absorption and Desorption Solubility Data for [C<sub>2</sub>C<sub>1</sub>im][BF<sub>4</sub>] at 303.15 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0.00	0.00	0.0	0.0
Absorption	10.67	0.45	0.9	9.2
Absorption	30.67	1.30	3.0	25.6
Absorption	50.67	2.15	6.1	41.9
Absorption	60.67	2.58	8.5	50.5
Absorption	70.67	3.00	12.3	60.6
Desorption	70.67	3.01	12.1	60.3
Desorption	50.67	2.15	6.1	41.7
Desorption	0.00	0	0.0	0.0

<sup>a</sup> Uncertainty was less than 0.1 mol%.

**Table S3.** Absorption and Desorption Solubility Data for [C<sub>4</sub>C<sub>1</sub>im][OAc] at 294.85 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0	0.00	0.0	0.0
Absorption	1.67	0.04	5.6	39.5
Absorption	5.67	0.15	11.8	59.4
Absorption	10.67	0.28	15.5	66.9
Absorption	15.67	0.41	18.6	71.6
Absorption	20.67	0.54	21.4	75.0
Absorption	25.67	0.67	24.2	77.8
Desorption	25.67	0.67	24.2	77.8
Desorption	20.67	0.54	21.5	75.0
Desorption	15.67	0.41	18.6	71.6
Desorption	10.67	0.28	15.5	66.9

<sup>a</sup> Uncertainty was less than 0.1 mol%.

**Table S4.** Absorption and Desorption Solubility Data for [C<sub>4</sub>C<sub>1</sub>im][OAc] at 303.15 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0	0.00	0.0	0.0
Absorption	1.47	0.06	5.6	39.5
Absorption	1.67	0.07	6.4	42.9
Absorption	5.67	0.24	12.4	60.9
Absorption	10.67	0.45	15.7	67.1
Absorption	15.67	0.67	18.8	71.8
Absorption	20.67	0.88	21.8	75.4
Absorption	25.67	1.09	24.4	78.1
Desorption	25.67	1.09	24.4	78.0
Desorption	20.67	0.88	21.8	75.4
Desorption	15.67	0.67	19.0	72.1
Desorption	10.67	0.45	15.9	67.5
Desorption	5.67	0.24	12.2	60.4

<sup>a</sup> Uncertainty was less than 0.1 mol%.

**Table S5.** Absorption and Desorption Solubility Data for [C<sub>4</sub>C<sub>1</sub>im][OAc] at 315.15 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0	0.00	0.0	0.0
Absorption	1.47	0.12	5.1	37.3
Absorption	1.67	0.14	5.9	40.8
Absorption	5.67	0.47	11.7	59.2
Absorption	10.67	0.88	15.3	66.5
Absorption	15.67	1.29	18.3	71.2
Absorption	20.67	1.70	21.1	74.6
Absorption	25.67	2.11	23.7	77.4
Desorption	25.67	2.11	23.7	77.4
Desorption	20.67	1.70	21.1	74.6
Desorption	15.67	1.29	18.3	71.2
Desorption	10.67	0.88	15.3	66.6
Desorption	5.67	0.47	11.6	59.2
Desorption	1.67	0.14	6.0	41.3
Desorption	1.47	0.12	5.1	37.2
Desorption	0	0.00	0.4	4.2

<sup>a</sup> Uncertainty was less than 0.1 mol%.

**Table S6.** Absorption and Desorption Solubility Data for [C<sub>4</sub>C<sub>1</sub>im][Cl] at 283.15 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0	0.00	0.0	0.0
Absorption	1.66	0.02	6.3	39.6
Absorption	5.66	0.07	9.5	50.6
Absorption	10.66	0.14	12.4	57.9
Absorption	15.66	0.20	14.9	62.9
Absorption	20.66	0.26	17.2	66.8
Absorption	25.66	0.33	19.5	70.1
Desorption	15.66	0.20	14.9	62.9
Desorption	5.66	0.07	9.6	50.8
Desorption	1.66	0.02	6.3	39.6
Desorption	0	0.00	1.2	10.5

<sup>a</sup> Uncertainty was less than 0.1 mol%.

**Table S7.** Absorption and Desorption Solubility Data for [C<sub>4</sub>C<sub>1</sub>im][Cl] at 295.15 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0	0.00	0.0	0.0
Absorption	1.67	0.04	5.8	37.5
Absorption	5.67	0.15	9.2	49.6
Absorption	10.67	0.28	12.0	56.9
Absorption	15.67	0.41	14.4	61.9
Absorption	20.67	0.55	16.6	65.9
Absorption	25.67	0.68	18.9	69.3
Desorption	15.67	0.41	14.4	61.9
Desorption	5.67	0.15	9.2	49.4
Desorption	1.67	0.04	5.8	37.6
Desorption	0	0.00	0.5	4.6

<sup>a</sup> Uncertainty was less than 0.1 mol%.



**Table S8.** Absorption and Desorption Data for [C<sub>4</sub>C<sub>1</sub>im][Cl] at 303.15 K

Sorption	Relative Humidity	Partial Pressure of water	w <sub>H2O</sub>	x <sub>H2O</sub> <sup>a</sup>
	(%)	(kPa)	(mass %)	(mole %)
Absorption	0	0.00	0.00	0.0
Absorption	1.66	0.07	5.6	36.7
Absorption	5.66	0.24	9.0	49.1
Absorption	10.66	0.45	11.8	56.5
Absorption	15.66	0.67	14.2	61.7
Absorption	20.66	0.88	16.5	65.7
Absorption	25.66	1.09	18.7	69.0
Desorption	15.66	0.67	14.2	61.6
Desorption	5.66	0.24	9.0	48.9
Desorption	1.66	0.07	5.7	36.8
Desorption	0	0.00	1.6	13.3

<sup>a</sup> Uncertainty was less than 0.1 mol%.

### **Density Values**

The density used in the buoyancy correction for ionic liquids [C<sub>2</sub>C<sub>1</sub>im][BF<sub>4</sub>], [C<sub>4</sub>C<sub>1</sub>im][OAc], and [C<sub>4</sub>C<sub>1</sub>im][Cl].

**Table S9.** Density for buoyancy correction

Ionic Liquid	Temperatures (K)	Density (g/cm <sup>3</sup> )	Source
[C <sub>2</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	298.15 303.15	1.28 1.28	<sup>1</sup> Equation $d/g \cdot cm^{-3} = 1.5134 - 7.8297 \times 10^{-4} T/K$
[C <sub>4</sub> C <sub>1</sub> im][OAc]	294.85 303.15 315.15	1.05 1.05 1.04	<sup>2</sup> Equation 2 and 3 in literature
[C <sub>4</sub> C <sub>1</sub> im][Cl]	283.15 295.15 303.15	1.09 1.08 1.08	Linear equation fit to data from literature <sup>3-8</sup>

## **NRTL Parameters $\tau_{ij}$**

**Table S10.** NRTL parameters  $\tau_{ij}$  calculated for different temperatures of  $[\text{C}_2\text{C}_{1\text{im}}][\text{BF}_4]$ -water

T (K)	$\tau_{12}$	$\tau_{21}$
283	2.44	0.10
291	2.74	0.07
298	3.00	0.05
303	3.17	0.04

**Table S11.** NRTL parameters  $\tau_{ij}$  calculated for different temperatures of  $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ -water

T (K)	$\tau_{12}$	$\tau_{21}$
294.85	6.34	-7.14
303.15	6.35	-7.10
315.15	6.37	-7.05

**Table S12.** NRTL parameters  $\tau_{ij}$  calculated for different temperatures of  $[\text{C}_4\text{C}_{1\text{im}}][\text{Cl}]$ -water

T (K)	$\tau_{12}$	$\tau_{21}$
283.15	-3.58	-2.96
295.15	-3.15	-2.93
303.15	-2.88	-2.91

## **Enthalpy**

**Table S13.** Enthalpy of Absorption Data for [C<sub>2</sub>C<sub>1</sub>im][BF<sub>4</sub>]

x <sub>H2O</sub>	$\Delta H_{\text{abs}}$	$\Delta H_{\text{abs}}$ Error
(mole fraction)	(kJ/mol)	(kJ/mol)
0.05	39.0	0.1
0.10	39.3	0.1
0.15	39.7	0.1
0.20	40.0	0.1
0.25	40.3	0.1
0.30	40.6	0.1
0.35	40.9	0.2
0.40	41.3	0.2
0.45	41.6	0.2
0.50	41.9	0.2
0.55	42.3	0.2
0.60	42.6	0.2
0.65	43.0	0.3
0.70	43.4	0.3
0.75	43.8	0.3
0.80	44.2	0.3

**Table S14.** Enthalpy of Absorption Data for [C<sub>4</sub>C<sub>1</sub>im][OAc]

x <sub>H2O</sub> (mole fraction)	$\Delta H_{\text{abs}}$ (kJ/mol)	$\Delta H_{\text{abs}}$ Error (kJ/mol)
0.35	47.0	0.1
0.40	46.9	0.1
0.45	46.9	0.1
0.50	46.8	0.1
0.55	46.6	0.1
0.60	46.4	0.1
0.65	46.2	0.1
0.70	46.0	0.1
0.75	45.6	0.1
0.80	45.3	0.1

**Table S15.** Enthalpy of Absorption Data for [C<sub>4</sub>C<sub>1</sub>im][Cl]

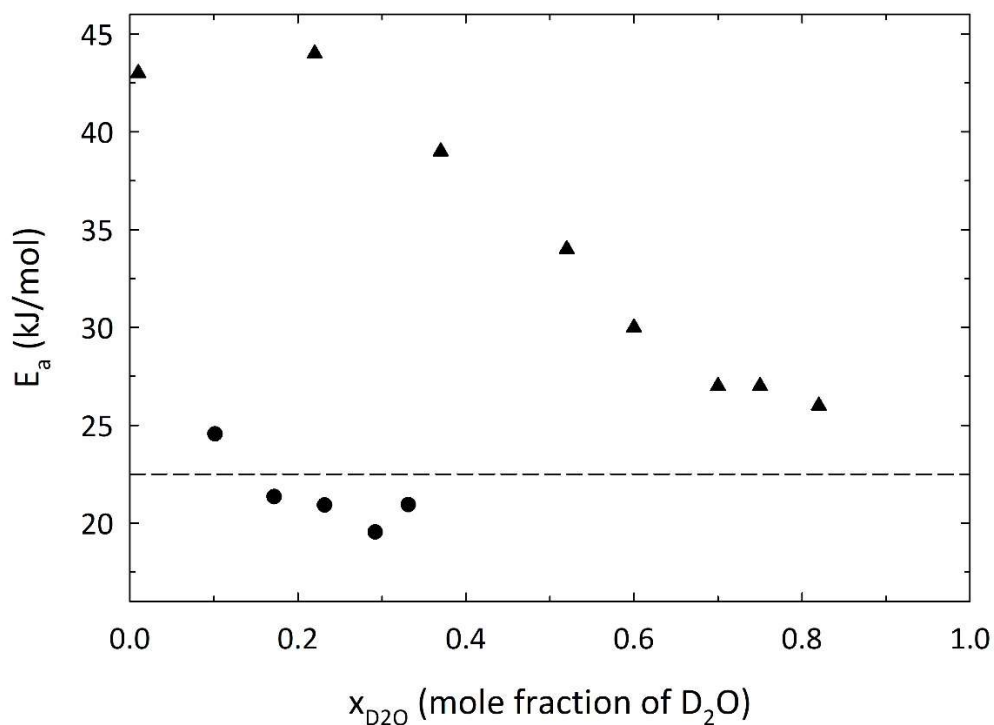
x <sub>H2O</sub>	ΔH <sub>abs</sub>	ΔH <sub>abs</sub> Error
(mole fraction)	(kJ/mol)	(kJ/mol)
0.35	54.6	0.2
0.40	51.6	0.1
0.45	49.5	0.1
0.50	48.1	0.1
0.55	47.1	0.1
0.60	46.4	0.1
0.65	45.8	0.1
0.70	45.4	0.1

Error for the enthalpy of absorption was calculated using Eq. S1 at each mole fraction shown in Tables S13-15, where  $C$  is the constant arising from the derivative. Then the excel LINEST function was used to obtain the slope error, which was multiplied by  $R$  and converted to  $\Delta H$ .

$$\ln(P) = \frac{1}{T} * \frac{\Delta H}{R} + C \quad (\text{S1})$$

## **Rotational Motion Activation Energy**

The interactions in the  $[\text{C}_2\text{C}_{1\text{im}}][\text{BF}_4]$  system are weaker than the water-water interactions (i.e. hydrogen bonding). The activation energies ( $E_a$ ) of the rotational motion of water molecules makes this slightly clearer. Published  $E_a$  values for  $\text{D}_2\text{O}$  in  $[\text{C}_2\text{C}_{1\text{im}}][\text{BF}_4]$ <sup>9</sup> and  $[\text{C}_4\text{C}_{1\text{im}}][\text{Cl}]$ <sup>10</sup> are shown in Figure S1. These measurements indicate that the rotational motion activation energy for  $\text{D}_2\text{O}$  in  $[\text{C}_4\text{C}_{1\text{im}}][\text{Cl}]$  is much larger than for  $\text{D}_2\text{O}$  in  $[\text{C}_2\text{C}_{1\text{im}}][\text{BF}_4]$ , which indicates that the rotational motion of water is more restricted in the  $\text{D}_2\text{O} + [\text{C}_4\text{C}_{1\text{im}}][\text{Cl}]$  system. This is likely due to the Coulombic forces between the  $\text{Cl}$  anion and the water molecules<sup>10</sup> and explains why the water diffusion in  $[\text{C}_2\text{C}_{1\text{im}}][\text{BF}_4]$  is overall faster than  $[\text{C}_4\text{C}_{1\text{im}}][\text{Cl}]$  at a given temperature and  $x_w$ . As the concentration of water increases, the  $E_a$  value for  $[\text{C}_4\text{C}_{1\text{im}}][\text{Cl}]\text{-D}_2\text{O}$  decreases and approaches the  $E_a$  value of pure  $\text{D}_2\text{O}$ , suggesting water molecules have more mobility and may diffuse more easily. On the other hand, the  $E_a$  of  $[\text{C}_2\text{C}_{1\text{im}}][\text{BF}_4]\text{-D}_2\text{O}$ , after having reached a value lower than  $E_a$  of pure  $\text{D}_2\text{O}$ , appears to be increasing at  $x_w > 0.3$ ; a behavior which has been attributed to the water-water hydrogen bonds restricting rotational motion.<sup>9</sup>



**Figure S1.** Activation energies of the rotational motion of water molecules in [C<sub>2</sub>C<sub>1</sub>im][BF<sub>4</sub>] and [C<sub>4</sub>C<sub>1</sub>im][Cl] plotted as a function of D<sub>2</sub>O mole fraction. The circles represent data measured by Takamuku et al. for [C<sub>2</sub>C<sub>1</sub>im][BF<sub>4</sub>], and the triangles are data measured by Yasaka, et al. for [C<sub>4</sub>C<sub>1</sub>im][Cl]. The dashed line is the rotational motion activation energy of pure D<sub>2</sub>O.<sup>11</sup>



## **Diffusion**

### **Modeling**

Initially, the COMSOL Multiphysics® Optimization interface was used to solve for  $D$  and  $C_s$  while minimizing the sum of square differences between the simulation measurements and the experimental data (mass vs. time). The experimental mass versus time data is the average water concentration (i.e., mass fraction) in the sample at a given time. The output of the COMSOL Multiphysics® Simulation is reported in moles of H<sub>2</sub>O per liquid volume ( $n_{H_2O}/V$ ) as a function of position and time. Therefore, the output  $n_{H_2O}/V$  was integrated over the 3D geometry to obtain total moles of H<sub>2</sub>O ( $n_{H_2O}$ ) and divided by the total mass to obtain concentration, as shown in Eqs. S2 and S3.

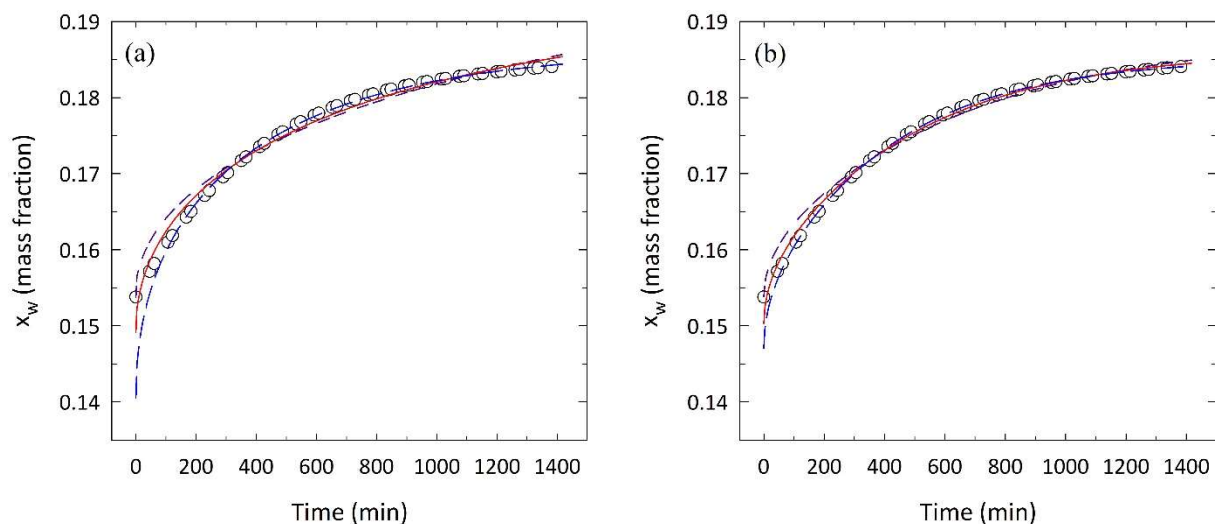
$$n_{H_2O} = \iiint \frac{n_{H_2O}}{V} dV \quad (S2)$$

$$C = \frac{n_{H_2O} * MW_{H_2O}}{n_{H_2O} MW_{H_2O} + (1 - n_{H_2O}) * MW_{IL}} \quad (S3)$$

This method was initially applied to the solubility data (mass versus time) for the H<sub>2</sub>O + [C<sub>4</sub>C<sub>1</sub>im][OAc] system at 294.85 K and 15.67 % RH, where the  $C_0$  value was specified ( $C_0 = 15.38$  wt. %), based on the measured water concentration in the ionic liquid when the RH becomes stable. The comparison between the simulation (lines) and the experimental data (circles) shown in Figure S2a indicates that the fit is reasonable but could be improved. Next, the  $C_0$  value was included as a variable to be optimized along with  $D$  and  $C_s$ . This method provides a better fit, as shown in Figure S2a by the solid line but also could be improved if the first few data points were deleted. Therefore, the final COMSOL optimization trial was performed deleting the first 3 measured points. The  $D$ ,  $C_s$ ,  $C_0$ , and standard errors of regression (S) for each method are listed in Table S16, and the methods are listed below:

- Method 1:  $C_0$  value was specified,  $D$  and  $C_s$  were calculated using all data points.
- Method 2:  $D$ ,  $C_s$ , and  $C_0$  were calculated using all data points.
- Method 3:  $D$ ,  $C_s$ , and  $C_0$  were calculated using all data except for the first 3 points.

Method 1, with a specified value for  $C_0$ , was not optimum for either the 2D or 1D models, and Method 3 eliminated the first three data points which was not preferred; therefore, Method 2, which used all the experimental data to determine  $D$ ,  $C_s$ , and  $C_0$ , was utilized.



**Figure S2.** A comparison between using (a) the COMSOL 2D mass transfer simulation and (b) the 1D diffusion Eq. 17 to determine the binary  $D$  coefficient for water in ILs by fitting the mass fraction per time data. Open circle symbols are experimental data. Purple short-dashed line represents the fit where  $C_0$  value was specified,  $D$  and  $C_s$  were calculated using all data points; red solid line represents the fit where  $D$ ,  $C_s$ , and  $C_0$  were calculated using all data points; long-dashed line represents the fit where  $D$ ,  $C_s$ , and  $C_0$  were calculated using all data points except for the first 3 measured points.

**Table S16.** D, C<sub>s</sub>, and C<sub>0</sub> determined by the 2D COMSOL simulation and the 1D diffusion equation (Eq. 17) for the solubility of water in [C<sub>4</sub>C<sub>1</sub>im][OAc] at 15 % RH and 294.85 K

Approach	Method	D (x 10 <sup>-11</sup> m <sup>2</sup> /s)	C <sub>s</sub> , meas (wt. %)	C <sub>s</sub> , calc (wt. %)	C <sub>0</sub> , meas (wt. %)	C <sub>0</sub> , calc (wt. %)	S (wt. %)
2D COMSOL Simulation	1	0.5	18.6	20.3	15.4	15.4	0.2
	2	1.1	18.6	19.2	15.4	14.9	0.1
	3	2.2	18.6	18.6	15.4	14.1	0.2
1D Equation (Eq. 17)	1	0.8	18.6	18.8	15.4	15.4	0.1
	2	1.1	18.6	18.6	15.4	15.0	0.1
	3	1.3	18.6	18.5	15.4	14.7	0.1

The Standard Error of Regression (S) or also known as RMSE (Root Mean Square Error) was calculated using Eq. S4, where  $\hat{y}_i$  is the predicted concentration,  $y_i$  is the measured concentration, and  $n$  is the number of measurements. It represents the error for how the model fits the overall data.

$$S = \sqrt{\sum_{i=1}^n \frac{(\hat{y}_i - y_i)^2}{n}} \quad (\text{S4})$$

### **Height in Calculating the Diffusion Coefficient**

The diffusion coefficient of each IL was calculated at the highest RH measured for each temperature using the average “wet” cylinder height and also using the “dry” height to observe the effect of height ( $L$ ) on the diffusion coefficient. The “wet” height was calculated by taking the average of the height from beginning to end at a specified  $T$  and RH condition. The ionic liquid can expand as water absorbs and the height increases; therefore, an average “wet” height was used to determine the effect versus using the initial “dry” height at the beginning of the isotherm when no water had been absorbed. For example, for  $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$  at 294.85 K and 25.67 % RH ( $x_w = 77.8$  mol%), the calculated molar volume was  $0.0718 \text{ cm}^3$ ; and at 294.85 K and 20.67 % RH, ( $x_w = 75.0$  mol%), the calculated molar volume was  $0.0692 \text{ cm}^3$ ; and the average molar volume was  $0.0705 \text{ cm}^3$ . Using Eq. 19 in the main article, the average cylinder height was calculated to be 0.1054 cm. The dry height was calculated assuming the IL contained no water, which for  $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$  at 294.85 K was 0.0904 cm.

The diffusion coefficients using the average “wet” and “dry” heights are provided in Table S17. On average the diffusion coefficient increased by 27 % when using the average height including volume expansion versus the initial height without volume expansion; therefore, the average height for each  $T$ , % RH condition was used to calculate the diffusion coefficients.

**Table S17.** Effect of Height on the Diffusion Coefficient

Ionic Liquid	Temperature (K)	RH (%)	Dry Cylindrical Height (cm)	$D_{\text{Dry Height}}$ ( $\times 10^{-11} \text{ m/s}^2$ )	Average “wet” Cylindrical Height (cm)	$D_{\text{Avg Wet Height}}$ ( $\times 10^{-11} \text{ m/s}^2$ )
[C <sub>2</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	298.15	70.67	0.0810	2.6	0.0864	2.9
[C <sub>2</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	303.15	70.67	0.0811	2.7	0.0876	3.2
[C <sub>4</sub> C <sub>1</sub> im][OAc]	294.85	25.67	0.0904	1.3	0.1054	1.7
[C <sub>4</sub> C <sub>1</sub> im][OAc]	303.15	25.67	0.0907	2.1	0.1059	2.8
[C <sub>4</sub> C <sub>1</sub> im][OAc]	315.15	25.67	0.0909	3.9	0.1056	5.2
[C <sub>4</sub> C <sub>1</sub> im][Cl]	283.15	25.66	0.0948	0.8	0.1072	1.0
[C <sub>4</sub> C <sub>1</sub> im][Cl]	295.15	25.67	0.0934	1.7	0.1052	2.1
[C <sub>4</sub> C <sub>1</sub> im][Cl]	303.15	25.66	0.0953	2.8	0.1072	3.5

## Diffusion Coefficient Results

Tables S18-S20 show the diffusion coefficients for the ILs investigated, using the 1D Diffusion equation (Eq. 17 from main article) and using the average wet height.

The total error in the diffusion coefficients was calculated using the error of regression from the MATLAB fit ( $<0.1 \times 10^{-11} \text{ m}^2/\text{s}$ ), which captures the instrumental error, and the systematic error due to the use of the average height. The systematic error due to L “average” is shown in Eq. S5, where  $D_{Li}$  and  $D_{Lf}$  represent the diffusion coefficient calculated at the initial L and final L for a specific  $T$  and % RH, respectively. The total error calculation is shown in Eq. S6.

$$\text{Systematic Error} = (D_{Li} - D_{Lf})/2 \quad (\text{S5})$$

$$\text{Total Error} = \sqrt{\text{Instrumental Error}^2 + \text{Systematic Error}^2} \quad (\text{S6})$$

**Table S18.** Diffusivity Data for Absorption and Desorption of Water in  $[\text{C}_2\text{C}_1\text{im}][\text{BF}_4]$  determined using Equation 17

Sorption	$T^a$ (K)	RH <sup>a</sup> (%)	$D$ ( $\times 10^{-11}$ $\text{m}^2/\text{s}$ )	$C_s, \text{meas}^a$ (mol%)	$C_s, \text{calc}^b$ (mol%)	$C_0, \text{meas}^a$ (mol%)	$C_0, \text{calc}^b$ (mol%)	$S^c$ (mol%)	$n^c$
Abs.	298.15	10.67	$9.7 \pm 0.1$	8.4	8.5	2.7	2.7	0.1	1092
Abs.	298.15	50.67	$5.6 \pm 0.1$	40.4	40.4	25.8	25.8	0.2	2261
Des.	298.15	50.67	$4.1 \pm 0.2$	40.4	39.5	59.7	62.4	1.3	1016
Abs.	298.15	70.67	$2.9 \pm 0.1$	59.4	59.2	41.9	39.2	0.4	4262
Abs.	303.15	10.67	$13.1 \pm 0.1$	9.2	9.2	2.7	2.7	0.1	966
Abs.	303.15	50.67	$7.4 \pm 0.2$	41.9	41.8	27.3	24.9	0.2	1830
Des.	303.15	50.67	$4.3 \pm 0.3$	41.7	40.7	62.8	65.6	1.6	994
Abs.	303.15	70.67	$3.2 \pm 0.1$	60.6	60.5	51.0	49.6	0.3	4919

<sup>a</sup> The measured uncertainties are:  $T = \pm 0.01 \text{ K}$ ; % RH =  $\pm 1 \%$ ;  $C_s$  and  $C_0 < \pm 0.1 \text{ mol}\%$ .

<sup>b</sup> The average uncertainties determined by the error of regression are:  $C_s = \pm 0.1 \text{ mol}\%$ ;  $C_0 = \pm 0.1 \text{ mol}\%$ .

<sup>c</sup>  $S$  is the standard error of regression for the 1D Diffusion equation and represents the error for the overall fit.  $n$  is the number of data points fitted.

**Table S19.** Diffusivity Data for Absorption and Desorption of Water in [C<sub>4</sub>C<sub>1</sub>im][OAc] determined using Equation 17

Sorption	T <sup>a</sup> (K)	RH <sup>a</sup> (%)	D (x 10 <sup>-11</sup> m <sup>2</sup> /s)	C <sub>s, meas</sub> <sup>a</sup> (mol%)	C <sub>s, calc</sub> <sup>b</sup> (mol%)	C <sub>0, meas</sub> <sup>a</sup> (mol%)	C <sub>0, calc</sub> <sup>b</sup> (mol%)	S <sup>c</sup> (mol%)	n <sup>c</sup>
Abs.	294.85	5.67	0.98 ± 0.1	59.4	59.4	38.6	33.0	0.8	3399
Abs.	294.85	15.67	1.4 ± 0.1	71.6	71.6	66.7	66.1	0.7	46
Des.	294.85	15.67	1.6 ± 0.1	71.6	71.6	74.9	75.4	0.3	997
Abs.	294.85	25.67	1.7 ± 0.1	77.8	77.8	75.2	74.7	0.8	3477
Abs.	303.15	5.67	1.7 ± 0.1	60.9	61.0	45.0	41.6	0.7	422
Abs.	303.15	15.67	2.6 ± 0.1	71.8	71.9	64.5	63.1	0.6	361
Des.	303.15	15.67	2.5 ± 0.1	72.1	72.0	72.1	76.3	0.6	1241
Abs.	303.15	25.67	2.8 ± 0.1	78.1	78.0	74.1	73.4	0.4	421
Abs.	315.15	5.67	4.0 ± 0.1	59.2	59.1	41.4	37.3	0.6	1640
Abs.	315.15	15.67	4.7 ± 0.1	71.2	71.2	66.6	65.9	0.4	541
Des.	315.15	15.67	5.2 ± 0.1	71.2	71.1	74.5	75.0	0.3	999
Abs.	315.15	25.67	5.2 ± 0.1	77.4	77.4	74.7	74.3	0.3	611

<sup>a</sup> The measured uncertainties are:  $T = \pm 0.01$  K; % RH =  $\pm 1$  %;  $C_s$  and  $C_0 < \pm 0.1$  mol%.

<sup>b</sup> The average uncertainties determined by the error of regression are:  $C_s = \pm 0.1$  mol%;  $C_0 = \pm 0.1$  mol%.

<sup>c</sup> S is the standard error of regression for the 1D Diffusion equation and represents the error for the overall fit. n is the number of data points fitted.

**Table S 20.** Diffusivity Data for Absorption and Desorption of Water in [C<sub>4</sub>C<sub>1</sub>im][Cl] determined using Equation 17

Sorption	T <sup>a</sup> (K)	RH <sup>a</sup> (%)	D (x 10 <sup>-11</sup> m <sup>2</sup> /s)	C <sub>s</sub> , meas <sup>a</sup> (mol%)	C <sub>s</sub> , calc <sup>b</sup> (mol%)	C <sub>0</sub> , meas <sup>a</sup> (mol%)	C <sub>0</sub> , calc <sup>b</sup> (mol%)	S <sup>c</sup> (mol%)	n <sup>c</sup>
Abs.	283.15	5.66	0.49 ± 0.1	50.6	50.8	37.9	35.4	0.4	1038
Abs.	283.15	15.66	0.80 ± 0.1	62.9	63.1	58.0	57.3	0.3	1961
Abs.	283.15	25.66	0.97 ± 0.1	70.1	70.1	66.8	66.2	0.2	1429
Abs.	295.15	5.67	1.0 ± 0.1	49.6	49.9	38.0	36.2	0.3	1597
Abs.	295.15	15.67	2.0 ± 0.1	61.9	62.0	57.2	56.4	0.2	1838
Des.	295.15	15.67	2.2 ± 0.1	61.9	61.9	69.0	69.9	0.4	994
Abs.	295.15	25.67	2.1 ± 0.1	69.3	69.3	66.1	65.5	0.2	1900
Abs.	303.15	5.66	1.8 ± 0.1	49.1	49.0	37.2	35.3	0.3	1544
Abs.	303.15	15.66	3.2 ± 0.1	61.7	61.7	56.7	56.0	0.2	1190
Des.	303.15	15.66	3.6 ± 0.1	61.6	61.6	68.8	69.7	0.4	993
Abs.	303.15	25.66	3.5 ± 0.1	69.0	69.1	65.8	65.3	0.2	1111

<sup>a</sup> The measured uncertainties are:  $T = \pm 0.01$  K; % RH =  $\pm 1$  %;  $C_s$  and  $C_0 < \pm 0.1$  mol%.

<sup>b</sup> The average uncertainties determined by the error of regression are:  $C_s = \pm 0.1$  mol%;  $C_0 = \pm 0.1$  mol%.

<sup>c</sup> S is the standard error of regression for the 1D Diffusion equation and represents the error for the overall fit. n is the number of data points fitted.



## **References**

- (1) Shiflett, M. B.; Yokozeki, A. Liquid-Liquid Equilibria in Binary Mixtures of 1,3-Propanediol + Ionic Liquids [Bmim][PF 6], [Bmim][BF 4], and [Emim][BF 4]. *J. Chem. Eng. Data* **2007**, *52*, 1302–1306.
- (2) Safarov, J.; Geppert-Rybczy Nska, M.; Kul, I.; Hassel, E. Thermophysical Properties of 1-Butyl-3-Methylimidazolium Acetate over a Wide Range of Temperatures and Pressures. *Fluid Phase Equilib.* **2014**, *383*, 144–155.
- (3) Li, H.; Zhao, G.; Liu, F.; Zhang, S. Physicochemical Characterization of MFm--Based Ammonium Ionic Liquids. *J. Chem. Eng. Data* **2013**, *58*, 1505–1515.
- (4) Lu, Y.; Ma, W.; Hu, R.; Dai, X.; Pan, Y. Ionic Liquid-Based Microwave-Assisted Extraction of Phenolic Alkaloids from the Medicinal Plant *Nelumbo Nucifera Gaertn.* *J. Chromatogr. A* **2008**, *1208*, 42–46.
- (5) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation. *Green Chem.* **2001**, *3*, 156–164.
- (6) Kumar, B.; Singh, T.; Rao, K. S.; Pal, A.; Kumar, A. Thermodynamic and Spectroscopic Studies on Binary Mixtures of Imidazolium Ionic Liquids in Ethylene Glycol. *J. Chem. Thermodyn.* **2012**, *44*, 121–127.
- (7) Kavitha, T.; Vasantha, T.; Venkatesu, P.; Rama Devi, R. S. S.; Hofman, T. Thermophysical Properties for the Mixed Solvents of N-Methyl-2-Pyrrolidone with Some of the Imidazolium-Based Ionic Liquids. *J. Mol. Liq.* **2014**, *198*, 11–20.
- (8) He, R. H.; Long, B. W.; Lu, Y. Z.; Meng, H.; Li, C. X. Solubility of Hydrogen Chloride in Three 1-Alkyl-3-Methylimidazolium Chloride Ionic Liquids in the Pressure Range (0 to 100) KPa and Temperature Range (298.15 to 363.15) K. *J. Chem. Eng. Data* **2012**, *57*, 2936–2941.
- (9) Takamuku, T.; Kyoshoin, Y.; Shimomura, T.; Kittaka, S.; Yamaguchi, T. Effect of Water on Structure of Hydrophilic Imidazolium-Based Ionic Liquid. *J. Phys. Chem. B* **2009**, *113*, 10817–10824.
- (10) Yasaka, Y.; Wakai, C.; Matubayasi, N.; Nakahara, M. Rotational Dynamics of Water and Benzene Controlled by Anion Field in Ionic Liquids: 1-Butyl-3-Methylimidazolium Chloride and Hexafluorophosphate. *J. Chem. Phys.* **2007**, *127*, 214509.
- (11) Ueno, M.; Ueyama, S.; Hashimoto, S.; Tsuchihashi, N.; Ibuki, K. Pressure and Temperature Effects on the Molecular Rotation in Acetonitrile-Water Mixtures. *J. Solution Chem.* **2004**, *33*, 827–846.