

# Supplementary Material for: “Vapor pressures and vapor phase compositions of choline chloride urea and choline chloride ethylene glycol deep eutectic solvents from molecular simulation”

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In this supplementary material, molecular structures and force field parameters, as well as additional simulation details and results, are provided for the Monte Carlo (MC) simulations of choline chloride urea (ChClU) and choline chloride ethylene glycol (ChClEg) deep eutectic solvents (DESSs). The Generalized AMBER force field (GAFF)<sup>1</sup> was used to model both DESSs. The force field parameters used in the simulations consisted of Lennard-Jones (LJ) and electrostatic non-bonded energies, as well as bonded energies including bond-bending and

torsion (dihedral) terms. All bond lengths were kept fixed, and following Ref. 2, improper torsion potentials were not taken into account.<sup>2</sup> To enhance the agreement of the simulation results with experimental data, the charges of ions (choline cation and chloride anion) were scaled in the simulations by 0.8 for ChClU, and by 0.9 for ChClEg.<sup>3,4</sup> The charges listed in this supplementary material are, however, the unscaled values (+1 for choline and -1 for chloride), and should therefore be multiplied by the proper factors when used in simulations. To prevent atomic overlaps, the values  $\epsilon/k_B = 0.5 \text{ K}$  (where  $k_B$  is the Boltzmann constant) and  $\sigma = 0.1 \text{ \AA}$  were used as the LJ parameters of unprotected hydroxyl hydrogen atoms.

The structures and atom labels of all the molecules are presented in Figures S1 to S3, and the force field parameters are listed in Tables S1 to S9. The derivations of the expressions to compute the partial pressures of the HBD and HBA components of the DESs, from the equality of liquid- and gas phase chemical potentials, are presented, based on the derivation by Kussainova et al.<sup>5</sup> The numbers of molecules and mole fractions of all DES components used in the simulations are provided in Table S10. Additional simulation results are presented in Figures S4 to S8. These include plots for the derivative of the total energy with respect to the interaction scaling parameter of choline chloride (Figure S4), the gas phase excess Gibbs energy of choline chloride in ChClU as a function of the inverse of the box size (Figure S5), the densities of the DESs as a function of composition (Figure S6), the partial pressures of choline chloride in ChClEg and ChClU as a function of composition (Figure S7), and the  $y - x$  phase diagram of ChClU (Figure S8).

## Molecular Structures

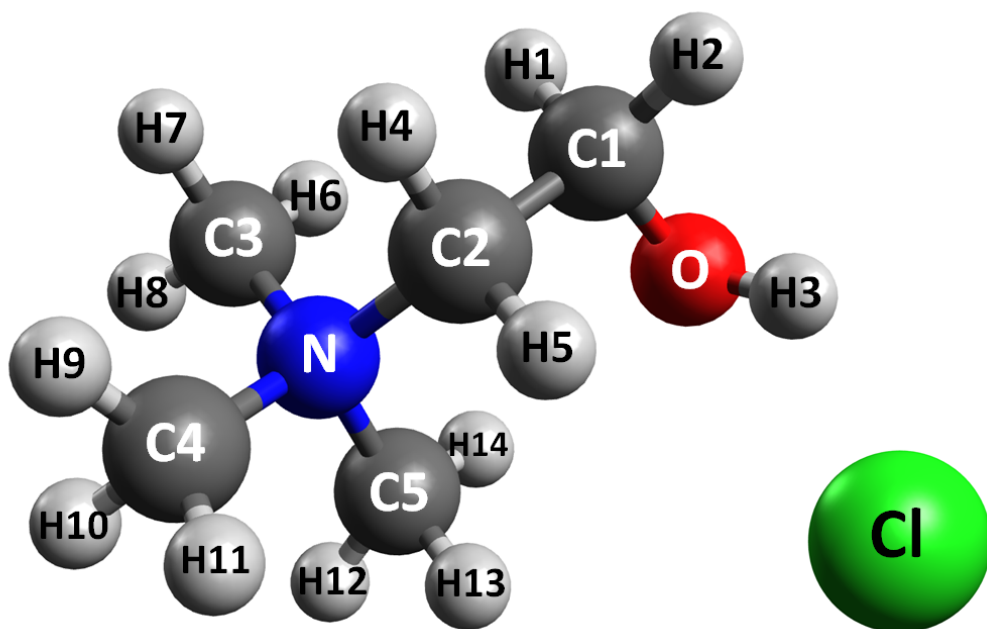


Figure S1: Structure and atom labels of choline chloride.

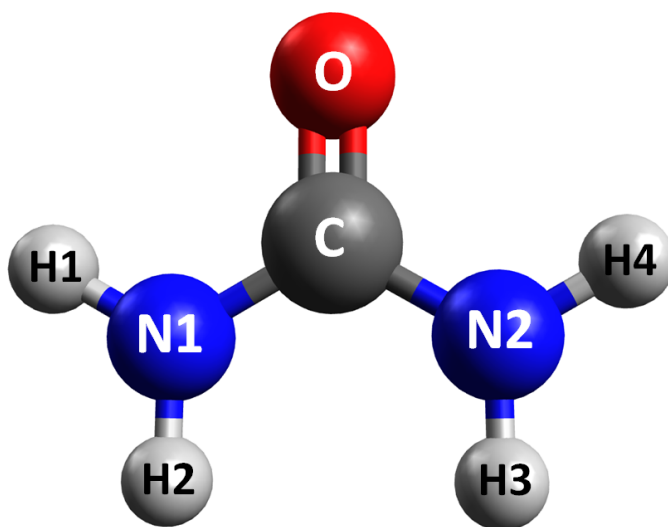
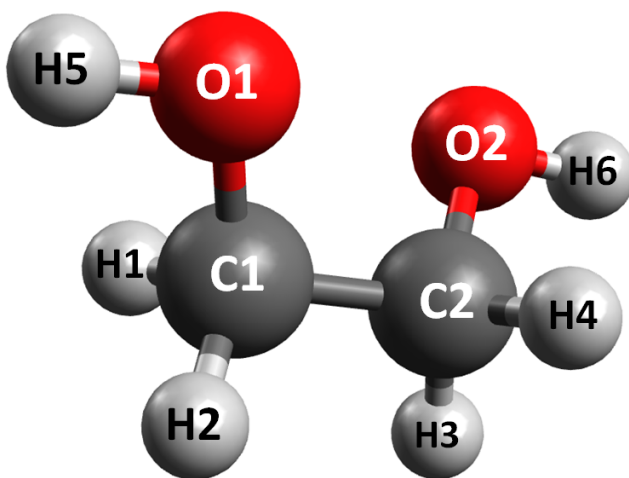


Figure S2: Structure and atom labels of urea.



**Figure S3:** Structure and atom labels of ethylene glycol.

# GAFF Force Field Parameters for Choline Chloride

**Table S1:** GAFF atom types and non-bonded parameters for choline chloride.<sup>3</sup> The listed partial charges are the unscaled charges. For ChClEg and ChClU, these charges should be multiplied by 0.9 and 0.8, respectively.<sup>3,4</sup> The atom labels are defined in Figure S1.

atom label	GAFF atom type	partial charge	$\epsilon/k_B/[K]$	$\sigma/[\text{\AA}]$
C1	cw	0.1501	55.052	3.3996
C2	cs	-0.0322	55.052	3.3996
C3-C5	c3	-0.1342	55.052	3.3996
H1,H2	h1	0.0510	7.901	2.4713
H3	ho	0.4545	0.500	0.1000
H4,H5	hx	0.1116	7.901	1.9600
H6-H14	hx	0.1193	7.901	1.9600
N	n4	0.0502	85.547	3.2500
O	oh	-0.6189	105.877	3.0664
Cl	cl	-1.0000	50.322	4.4010

**Table S2:** Bond-bending parameters for the choline cation.<sup>3</sup> The bond-bending energy is calculated as:  $E_{\text{bending}}(\theta) = k_{\theta}(\theta - \theta_0)^2$ .

GAFF angle type	$k_{\theta}/k_{\text{B}}/[\text{K}]$	$\theta_0$
hx-c3-hx	19645.692	110.7
hx-c3-n4	24667.824	107.9
c3-n4-cs	31622.318	110.6
n4-cs-hx	24667.824	107.9
n4-cs-cw	32432.502	114.3
cs-cw-h1	23329.259	110.1
cs-cw-oh	34078.030	109.4
hx-cs-cw	23158.165	111.7
h1-cw-oh	25649.102	109.9
cw-oh-ho	23696.610	108.2
c3-n4-c3	31622.318	110.6
hx-c3-hx	19645.692	110.7
h1-cw-h1	19716.143	109.6

**Table S3:** Dihedral parameters for the choline cation.<sup>3</sup> The dihedral energy is calculated as:  
 $E_{\text{dihedral}}(\phi) = \frac{V_n}{2}[1 + \cos(n\phi - \gamma)]$ .

GAFF dihedral type	$\frac{V_n}{2}/k_B/[\text{K}]$	$n$	$\gamma$
h1-cw-oh-ho	84.038	3	0
cs-cw-oh-ho	80.515	-3	0
cs-cw-oh-ho	125.805	1	0
h1-cw-cs-hx	78.502	3	0
h1-cw-cs-n4	78.502	3	0
oh-cw-cs-hx	78.502	3	0
oh-cw-cs-n4	78.502	3	0
cw-cs-n4-c3	78.502	3	0
hx-cs-n4-c3	78.502	3	0
cs-n4-c3-hx	78.502	3	0
c3-n4-c3-hx	78.502	3	0

# GAFF Force Field Parameters for Urea

**Table S4:** GAFF atom types and non-bonded parameters for urea.<sup>3</sup> The atom labels are defined in Figure S2.

atom label	GAFF atom type	partial charge	$\epsilon/k_B/[K]$	$\sigma/[\text{\AA}]$
C	c	1.0401	43.277	3.3996
H1-H4	hn	0.4167	7.901	1.0691
N1,N2	n	-1.0246	85.547	3.2500
O	o	-0.6577	105.676	2.9599



**Table S5:** Bond-bending parameters for urea.<sup>3</sup> The bond-bending energy is calculated as:  $E_{\text{bending}}(\theta) = k_{\theta}(\theta - \theta_0)^2$ .

GAFF angle type	$k_{\theta}/k_B/[\text{K}]$	$\theta_0$
n-c-o	38159.140	122.0
c-n-hn	24763.435	118.5
hn-n-hn	19992.914	117.9
n-c-n	37640.824	113.4

**Table S6:** Dihedral parameters for urea.<sup>3</sup> The dihedral energy is calculated as:  $E_{\text{dihedral}}(\phi) = \frac{V_n}{2}[1 + \cos(n\phi - \gamma)]$ .

GAFF dihedral type	$\frac{V_n}{2}/k_B/[K]$	$n$	$\gamma$
hn-n-c-o	1258.049	-2	180
hn-n-c-o	1006.439	1	0
n-c-n-hn	1258.049	2	180

# GAFF Force Field Parameters for Ethylene Glycol

**Table S7:** GAFF atom types and non-bonded parameters for ethylene glycol.<sup>4</sup> The atom labels are defined in Figure S3.

atom label	GAFF atom type	partial charge	$\epsilon/k_B/[K]$	$\sigma/[\text{\AA}]$
C1,C2	c3	0.1615	55.052	3.3996
H1-H4	h1	0.0328	7.901	2.4713
H5,H6	ho	0.4069	0.500	0.1000
O1,O2	oh	-0.6340	105.877	3.0664

**Table S8:** Bond-bending parameters for ethylene glycol.<sup>4</sup> The bond-bending energy is calculated as:  $E_{\text{bending}}(\theta) = k_{\theta}(\theta - \theta_0)^2$ .

GAFF angle type	$k_{\theta}/k_B/[\text{K}]$	$\theta_0$
ho-oh-c3	23701.642	108.2
oh-c3-c3	34067.965	109.4
oh-c3-h1	25664.199	109.9
c3-c3-h1	23349.388	110.1
h1-c3-h1	19726.208	109.6

**Table S9:** Dihedral parameters for ethylene glycol.<sup>4</sup> The dihedral energy is calculated as:  
 $E_{\text{dihedral}}(\phi) = \frac{V_n}{2} [1 + \cos(n\phi - \gamma)]$ .

GAFF dihedral type	$\frac{V_n}{2}/k_B/[\text{K}]$	$n$	$\gamma$
ho-oh-c3-h1	84.038	3	0
c3-c3-oh-ho	80.515	-3	0
h1-c3-c3-h1	78.502	3	0
oh-c3-c3-h1	125.805	1	0
oh-c3-c3-oh	72.464	-3	0
oh-c3-c3-oh	591.283	2	0

## Calculation of Vapor Pressures

In this section, derivations are presented for the partial pressures of the HBD (ethylene glycol or urea) and HBA (choline chloride) components of ChClEg and ChClU DESs, based on Kussainova et al.,<sup>5</sup> and the Supporting Information of Dawass et al.<sup>6</sup> In the derivations presented here, the vapor pressures of the DES mixtures are denoted as ‘ $P^v$ ’, and defined as

$$P^v = P_{\text{HBD}} + P_{\text{ChCl}} \quad (\text{S1})$$

in which  $P_{\text{HBD}}$  and  $P_{\text{ChCl}}$  are the partial pressures of the HBD and choline chloride (HBA) components, respectively. The mole fraction of each component  $i$  (HBD or HBA) in the gas phase is defined as:  $y_i = P_i/P^v$ . In the following derivations, it is assumed that the vapor phase of each DES is an ideal gas, composed of isolated, non-interacting molecules of the HBD component (urea or ethylene glycol), and choline chloride (HBA) ion pairs. The liquid phase of the DESs is assumed to be incompressible.

### HBD component

For the HBD component (urea or ethylene glycol), the vapor phase is assumed to be an ideal gas, composed of isolated, non-interacting molecules (zero excess Gibbs energy). The vapor phase chemical potential is therefore computed according to<sup>5</sup>

$$\mu^v(T, P^v) = \Delta_f G_{\text{HBD}}^0 + RT \ln \frac{P_{\text{HBD}}}{P^0} \quad (\text{S2})$$

where  $P^0 = 1$  bar is the reference state pressure,  $\Delta_f G_{\text{HBD}}^0$  is the Gibbs energy of formation of the HBD at  $P^0$ ,  $T$  is the absolute temperature,  $k_B$  is the Boltzmann constant, and  $P_{\text{HBD}}$  is the partial pressure of the HBD.

The liquid phase chemical potential is computed as<sup>5</sup>

$$\mu^l(T, P^v) = \Delta_f G_{\text{HBD}}^0 + RT \ln \frac{N_{\text{HBD}} k_B T}{P^0 V} + \Delta G_{\text{HBD}}^{\text{ex},l} + \bar{V}_{\text{HBD}}(P^v - P^0) \quad (\text{S3})$$

in which  $N_{\text{HBD}}$  is the number of HBD molecules in the liquid phase,  $\Delta G_{\text{HBD}}^{\text{ex},l}$  is the liquid phase excess Gibbs energy of the HBD, computed from the simulations using thermodynamic integration,  $V$  is the liquid phase volume of the DES, and  $\bar{V}_{\text{HBD}}$  is the partial molar volume of the HBD in the liquid phase. Assuming that the excess volume of the liquid phase is negligible,<sup>7</sup> the partial molar volume of the HBD can be approximated by  $V/N_{\text{HBD}}$ , in which  $V$  is the liquid phase volume of the DES. This approximation is supported by the MD simulation results of Celebi et al.<sup>7</sup> for ChClU. Although neglected here for simplicity, the excess volume can in principle be computed from the Kirkwood-Buff integrals.<sup>8</sup> Considering the low vapor pressures of the DESs compared to the value of the reference state pressure  $P^0$  (1 bar),  $P^v$  can be neglected in the last term of Equation (S3). The value of the last term of Equation (S3) is often very small compared to the other terms, and is therefore neglected (such as in the derivation by Dawass et al.<sup>6</sup>). For instance, in the simulations of ChClEg (with a molar ratio of 1:2, at 353 K) performed in the present work, the value of this term was computed as ca.  $-0.02 \text{ kJ mol}^{-1}$ , which is considerably smaller than the computed liquid phase excess Gibbs energy ( $\Delta G_{\text{HBD}}^{\text{ex},l}$ ) of ethylene glycol, i.e., ca.  $28.08 \text{ kJ mol}^{-1}$ . Although the last term of Equation (S3) is not neglected in this work, the aforementioned approximations are carried out to simplify the calculations. Considering the small value of this term, these approximations have negligible influence on the final result.

By equating the liquid and vapor phase chemical potentials from Equations (S2) and (S3), the partial pressure of the HBD component is computed according to

$$P_{\text{HBD}} = \frac{N_{\text{HBD}} k_B T}{V} \exp \left[ \frac{\Delta G_{\text{HBD}}^{\text{ex},l} - \frac{V}{N_{\text{HBD}}} P^0}{RT} \right] \quad (\text{S4})$$

It can be observed that in deriving Equation (S4), the term  $\Delta_f G_{\text{HBD}}^0$  (in Equations (S2) and (S3)) is cancelled out. Therefore, the value of this term is not required in the calculations.

As mentioned earlier, in the derivation of the final expression for  $P_{\text{HBD}}$ , the value of  $P^v$  on the right hand side of Equation (S3) was neglected due to the low vapor pressures of DESs. However, without this approximation, one would need to iteratively solve for the value of  $P_{\text{HBD}}$  when equating Equations (S2) and (S3).

## HBA component

The HBA component of both DESs studied in this work is choline chloride ('ChCl'), a salt composed of choline cation ('Ch') and chloride anion ('Cl'). It is assumed here that choline chloride appears in the vapor phase of the DESs as isolated ion pairs. The vapor phase chemical potential of choline chloride is computed according to<sup>5</sup>

$$\mu^v(T, P^v) = \Delta_f G_{\text{Ch}}^0 + \Delta_f G_{\text{Cl}}^0 + \Delta G_{\text{ChCl}}^{\text{ex},v} + 2RT \ln \frac{P_{\text{ChCl}}}{P^0} \quad (\text{S5})$$

where  $\Delta_f G_{\text{Ch}}^0$  and  $\Delta_f G_{\text{Cl}}^0$  are the Gibbs energies of formation of choline and chloride ions at the reference state pressure  $P^0 = 1 \text{ bar}$ ,  $\Delta G_{\text{ChCl}}^{\text{ex},v}$  is the excess Gibbs energy of choline chloride in the vapor phase, and  $P_{\text{ChCl}}$  is the partial pressure of choline chloride. The factor 2 on the right hand side of Equation (S5) originates from the fact that a single choline chloride molecule is composed of 2 ions. The vapor phase excess Gibbs energy of choline chloride is computed as<sup>5</sup>

$$\Delta G_{\text{ChCl}}^{\text{ex},v} = \Delta A_{NV^*T}^{\text{ex}} - RT - RT \ln \frac{V^* P^0}{k_B T} \quad (\text{S6})$$

where  $V^*$  is the volume of the gas phase simulation box, and  $\Delta A_{NV^*T}^{\text{ex}}$  is the excess Helmholtz energy of choline chloride at the (fixed) gas phase simulation volume ( $V^*$ ), computed from thermodynamic integration. The last term in Equation (S6) is a volume correction term to  $\Delta G_{\text{ChCl}}^{\text{ex},v}$ , from volume  $V^*$  to the reference state volume  $V^0 = k_B T / P^0$ . To correct for the finite size effects, the value of  $\Delta G_{\text{ChCl}}^{\text{ex},v}$  is computed at different simulation volumes  $V^*$  from Equation (S6), and the results are linearly extrapolated to infinite volume ( $V^* \rightarrow \infty$ ) by



plotting the values of  $\Delta G_{\text{ChCl}}^{\text{ex,v}}$  as a function of the inverse of the size of the simulation box.<sup>5,9</sup>

The liquid phase chemical potential of choline chloride is computed as<sup>5</sup>

$$\mu^l(T, P^v) = \Delta_f G_{\text{Ch}}^0 + \Delta_f G_{\text{Cl}}^0 + 2RT \ln \frac{N_{\text{ChCl}} k_B T}{P^0 V} + \Delta G_{\text{ChCl}}^{\text{ex,l}} + \bar{V}_{\text{ChCl}}(P^v - P^0) \quad (\text{S7})$$

in which  $N_{\text{ChCl}}$  is the number of choline chloride ion pairs (half of the total number of ions),  $\Delta G_{\text{ChCl}}^{\text{ex,l}}$  is the excess Gibbs energy of choline chloride in the liquid phase,  $V$  is the volume of the liquid phase simulation box, and  $\bar{V}_{\text{ChCl}}$  is the partial molar volume of choline chloride in the liquid phase. The factor 2 in the third term of the right hand side of Equation (S7) is due to the fact that a single choline chloride molecule consists of 2 ions. Similar to the derivation for the HBD component (Equation (S3)),  $P^v$  can be neglected in Equation (S7), and  $\bar{V}_{\text{ChCl}}$  can be approximated by  $V/N_{\text{ChCl}}$ .

By equating Equations (S5) and (S7), the partial pressure of choline chloride is computed according to

$$P_{\text{ChCl}} = \frac{N_{\text{ChCl}} k_B T}{V} \exp \left[ \frac{\Delta G_{\text{ChCl}}^{\text{ex,l}} - \Delta G_{\text{ChCl}}^{\text{ex,v}} - \frac{V}{N_{\text{ChCl}}} P^0}{2RT} \right] \quad (\text{S8})$$

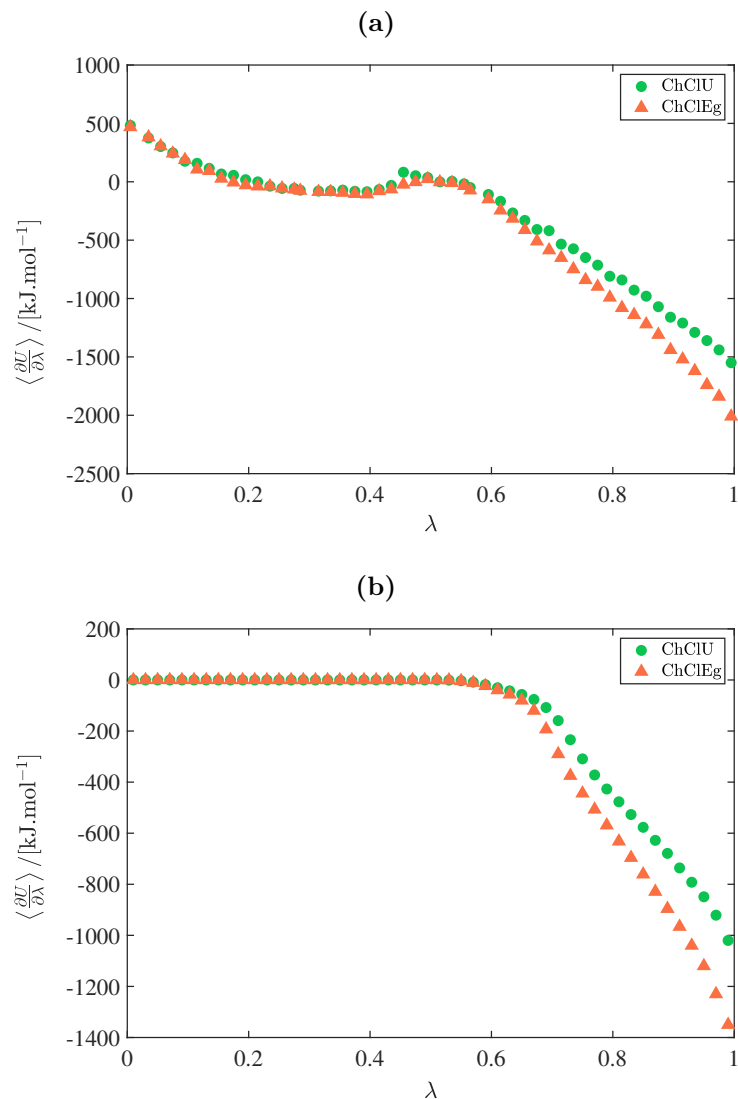
in which  $\Delta G_{\text{ChCl}}^{\text{ex,v}}$  is the extrapolated value of the vapor phase excess Gibbs energy to infinite volume. Similar to the derivation for the HBD component, by equating Equations (S5) and (S7), the terms  $\Delta_f G_{\text{Ch}}^0$  and  $\Delta_f G_{\text{Cl}}^0$  are cancelled out. As for the HBD component, the value of  $P_{\text{ChCl}}$  would need to be calculated iteratively, if one does not neglect the value of  $P^v$  on the right hand side of Equation (S7).

## Simulation Details

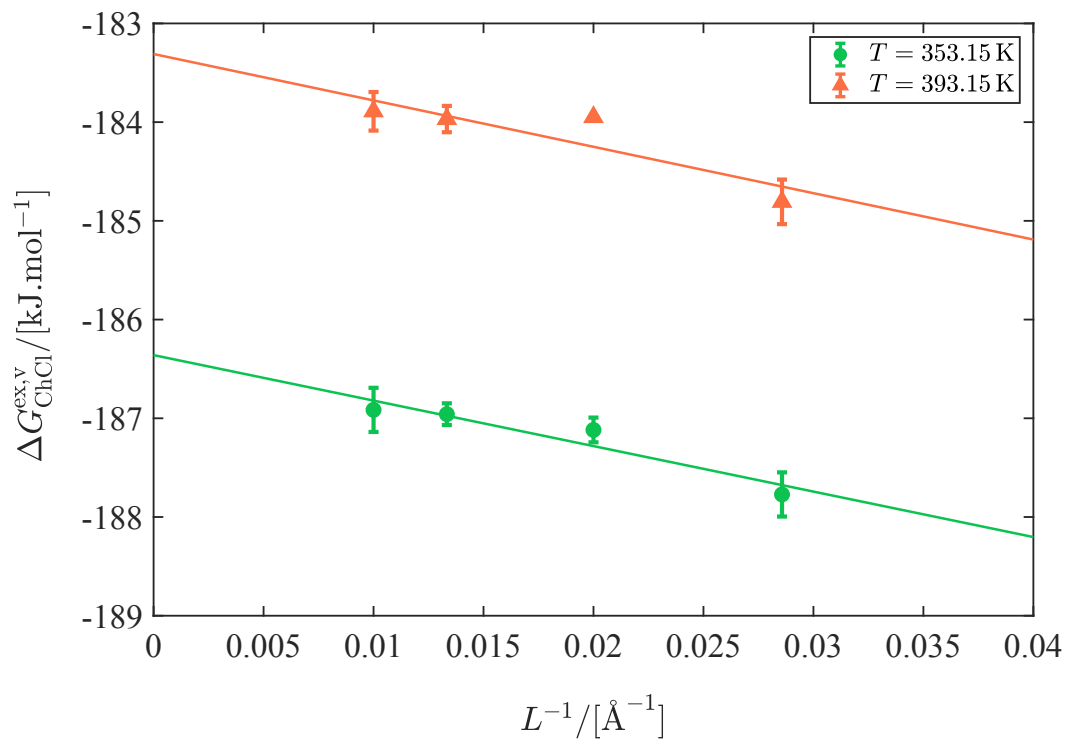
**Table S10:** The numbers of molecules  $N_i$  of each DES component  $i$  used in the simulations, at different HBA:HBD molar ratios. The DES components are: choline cation, chloride anion, and urea or ethylene glycol HBD component. The mole fractions of choline chloride (HBA component) and the HBD component (urea or ethylene glycol) are also listed, and are computed as  $x_{\text{ChCl}} = N_{\text{ChCl}}/(N_{\text{HBD}} + N_{\text{ChCl}})$ , and  $x_{\text{HBD}} = N_{\text{HBD}}/(N_{\text{HBD}} + N_{\text{ChCl}})$ , respectively, where  $N_{\text{ChCl}}$  denotes the number of choline chloride (HBA) ion pairs (half of the total number of ions of the HBA).

DES	molar ratio	$N_{\text{cation}}$	$N_{\text{anion}}$	$N_{\text{HBD}}$	$x_{\text{HBD}}$	$x_{\text{ChCl}}$
ChClU	1:1.5	60	60	90	0.60	0.40
	1:2	50	50	100	0.67	0.33
	1:3	40	40	120	0.75	0.25
ChClEg	1:1.5	60	60	90	0.60	0.40
	1:2	50	50	100	0.67	0.33
	1:3	40	40	120	0.75	0.25

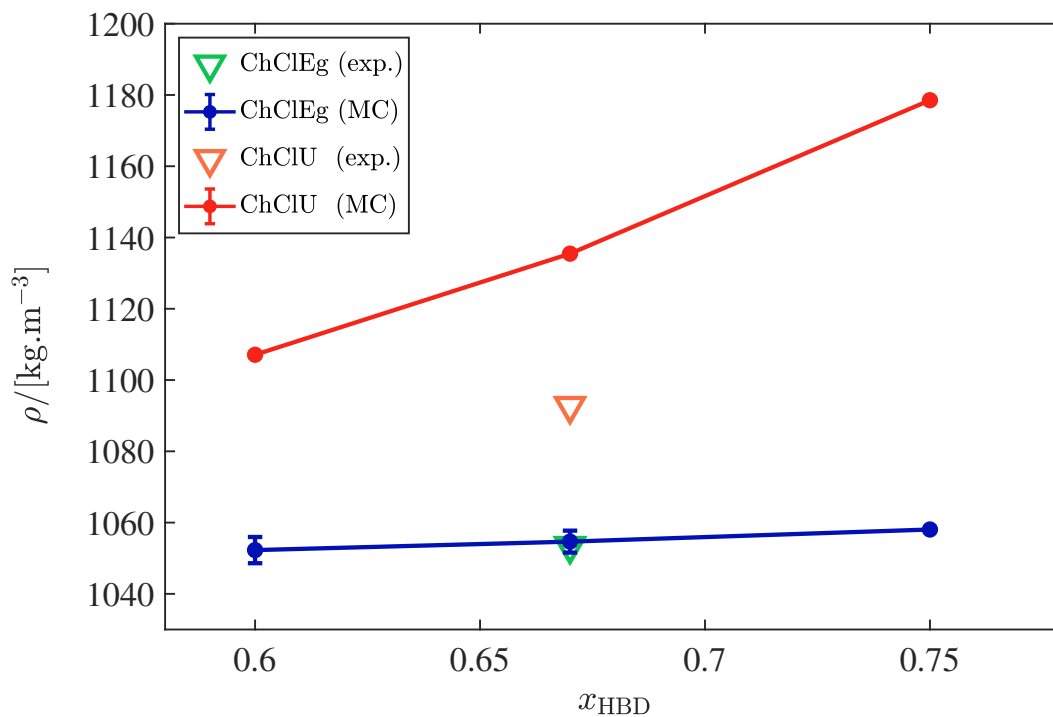
# Simulation Results



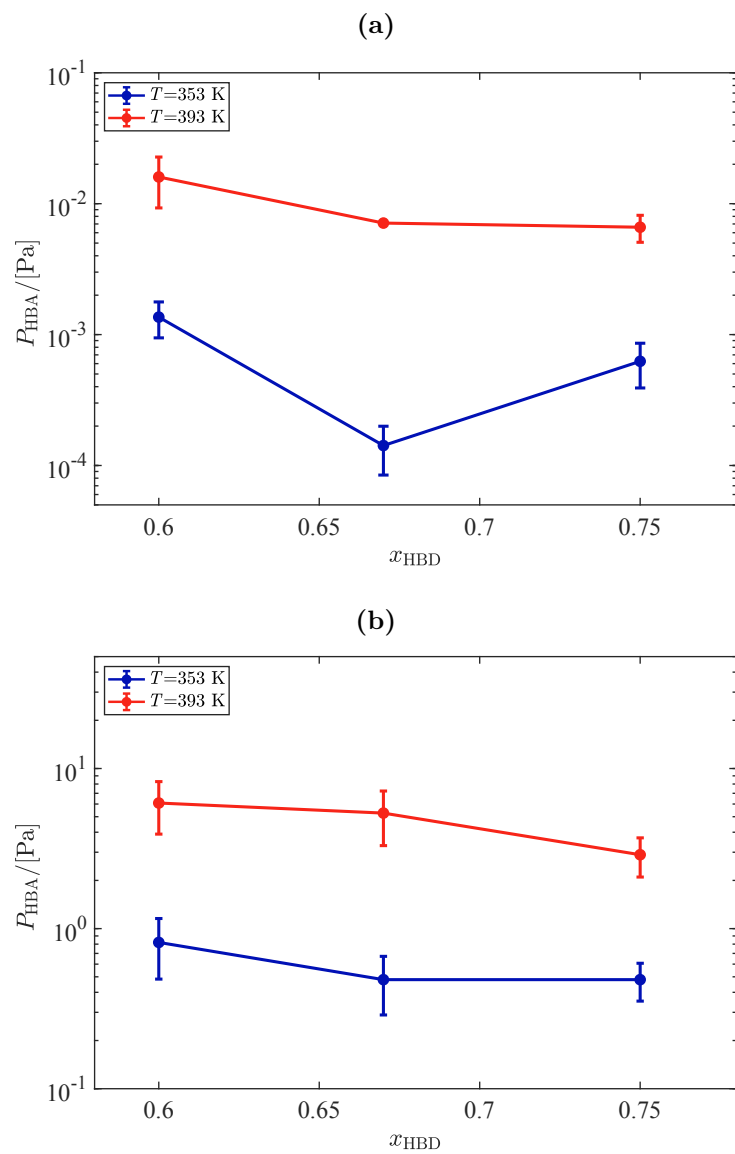
**Figure S4:** Average values of the derivative of the total energy with respect to  $\lambda$ , as a function of  $\lambda$ , for choline chloride in ChClU (at 393 K) and ChClEg (at 353 K), in (a) the liquid phase, and (b) the gas phase simulations. The differences between the gas phase values of  $\langle \frac{\partial U}{\partial \lambda} \rangle$  for choline chloride in ChClEg and ChClU, result from the different charge scaling factors used for choline chloride: 0.8 in ChClU, and 0.9 in ChClEg.



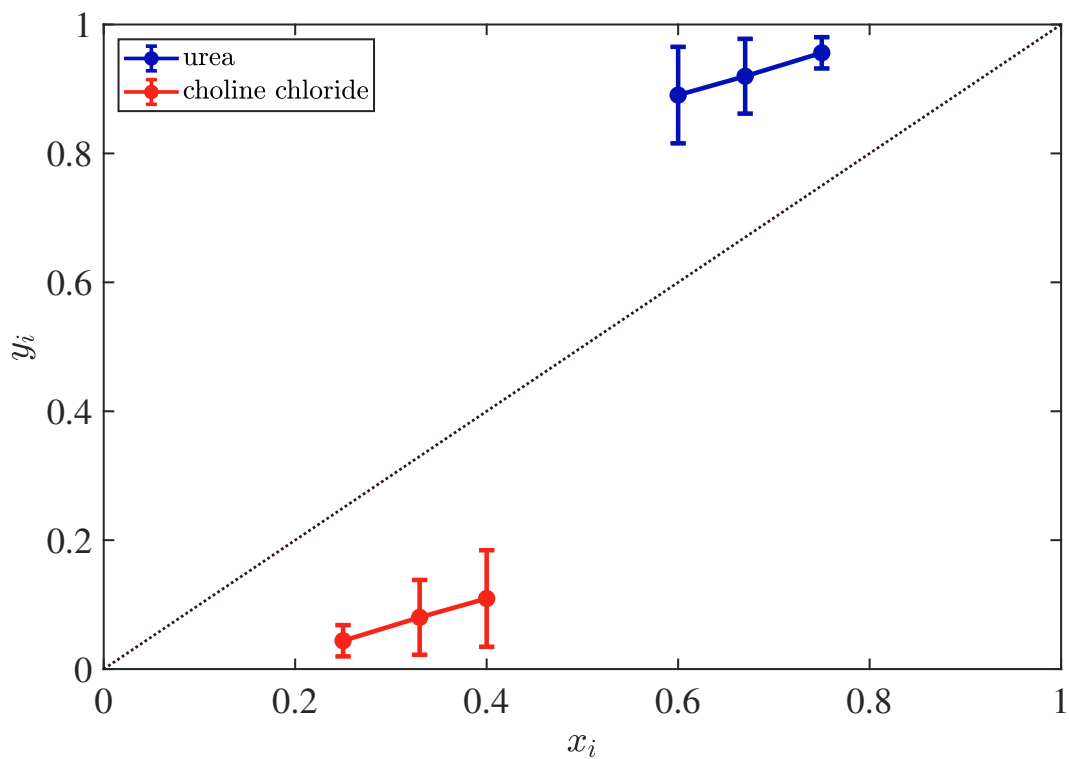
**Figure S5:** Vapor phase excess Gibbs energy of choline chloride in ChClU as a function of the inverse of the size of the simulation box ( $L = V^{1/3}$ ), at different temperatures. The solid lines depict the linear fits used for the extrapolation of the values to infinite volume.



**Figure S6:** Computed liquid densities of ChClEg (at 393 K) and ChClU (at 433 K) as a function of the liquid phase mole fraction of the HBD component (ethylene glycol or urea). The solid lines are drawn to guide the eye. The experimental values by Yadav and Pandey<sup>10</sup> (for ChClU), and Yadav et al.<sup>11</sup> (for ChClEg) are also shown for comparison.



**Figure S7:** Computed partial pressures of choline chloride (the HBA component) in (a) ChClEg, and (b) ChClIU, at various temperatures, as a function of the liquid phase mole fraction of the HBD component (ethylene glycol or urea). The solid lines are drawn to guide the eye.



**Figure S8:** Computed vapor phase mole fraction of each component  $i$  (urea or choline chloride) of ChCIU at 433 K as a function of its mole fraction in the liquid phase. The solid lines are drawn to guide the eye. The black dotted line denotes  $y_i = x_i$ .

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