Supporting information for: "Computation of Gas Solubilities in Choline Chloride Urea and Choline Chloride Ethylene Glycol Deep Eutectic Solvents Using Monte Carlo Simulations"

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In this document, the molecular structure and force field parameters of the molecules used in the Monte Carlo (MC) simulations of deep eutectic solvents (DES) are presented. In our study, the solubilities of CO_2, H_2S, CH_4, CO, H_2, and N_2 gases were computed in choline chloride urea (ChClU) and choline chloride ethylene glycol (ChClEg) DESs. The force field parameters by Perkins et al. [1, 2], based on the Generalized AMBER force field (GAFF) [3], were used for both DESs. Additionally, the OPLS force field parameters [4], reported by Doherty and Acevedo [5], were used for ChClEg. The force field parameters for the DESs include bonded (bond stretching, angle bending, and dihedral), as well as electrostatic and Lennard-Jones (LJ) non-bonded terms. To improve the agreement between the simulation results and experimental data, the ionic charges were scaled by 0.8 for ChClU, and 0.9 for ChClEg, using the GAFF force field [1, 2], and by 0.8 for ChClEg using the OPLS force field [5]. The partial charges listed in this document for the ions are the unscaled values (total charge of +1 for the cation and -1 for the anion). For CO_2, CH_4 (united atom), and H_2S, the Transferable Potentials for Phase Equilibria (TraPPE) force field parameters were used [6, 7]. For CO, the three-site model by Martín-Calvo et al. [8], and for H_2, the two-site model by Cracknell [9] were used. It should be noted that all the solute gases were treated as rigid molecules and the force field parameters for these molecules only entailed non-bonded terms. LJ parameters were set as $\epsilon/k_B = 0.5\,\mathrm{K}$ (where k_B is the Boltzmann constant) and $\sigma = 0.1\,\text{Å}$ for the unprotected hydrogen atoms in hydroxyl groups, and for dummy atoms (in solute molecules) to prevent atomic overlaps in the simulations [10].

The molecular structure of the DES components (except the chloride anion) are presented in Figures S1 to S3. Furthermore, the equilibrium structures of the solute molecules (according to the used force fields) are shown in Figures S4 to S8. Dummy atoms are denoted by the label "M" in the molecular structure of the solutes. Due to the fact that a united atom TraPPE force field was used for CH_4, the structure of this molecule is excluded from the figures. Subsequently, the force field parameters for all the molecules are listed. All bond lengths were kept fixed in the simulations and thus the bond stretching potential parameters

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for the DESs are not reported here. Similarly, the parameters for improper dihedrals are excluded in this document, as improper dihedrals were not used in the simulations. The exclusion of improper dihedral and bond stretching energies from the simulations were shown in our study to not significantly affect the liquid structure and density of the pure DESs. All simulations were performed with the Brick-CFCMC software [11], developed in our group for phase/reaction equilibria calculations using the Continuous Fractional Component Monte Carlo (CFCMC) method [12].

1. Molecular Structures
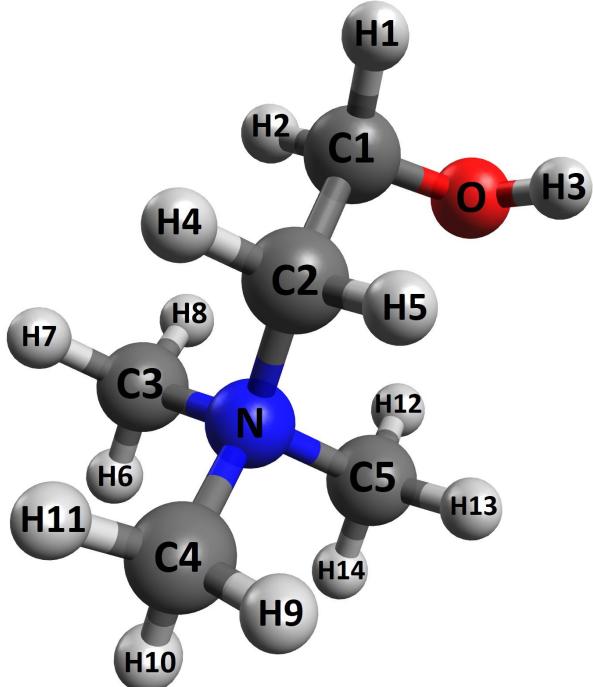

Figure S1: Choline structure and atom labels.
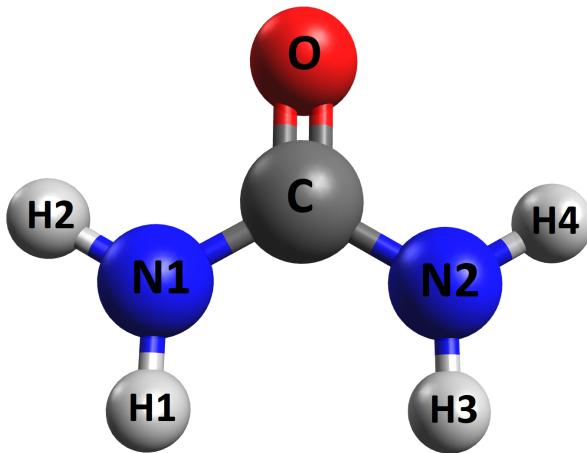
Figure S2: Urea structure and atom labels.
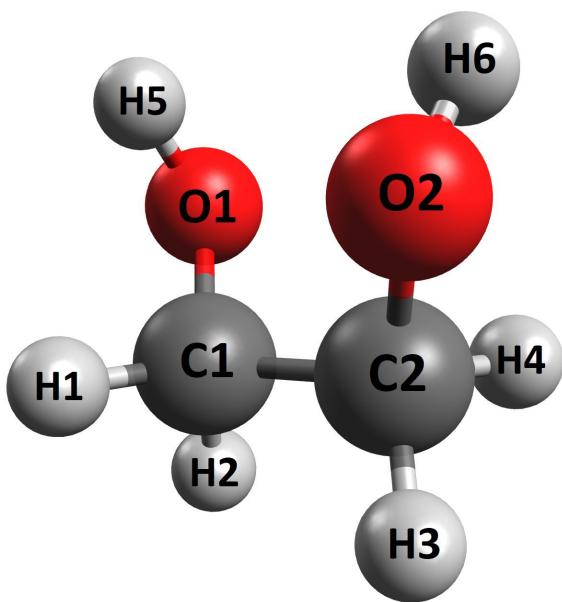
Figure S3: Ethylene glycol structure and atom labels.
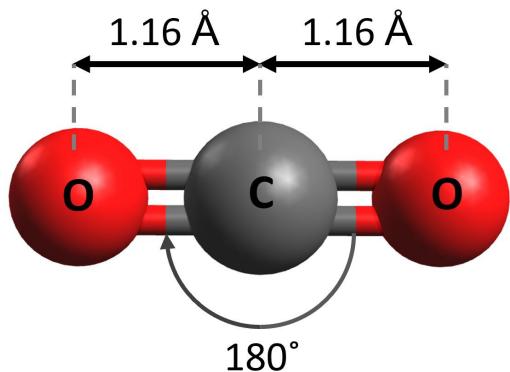

Figure S4: Carbon dioxide (CO_2) equilibrium structure [6].
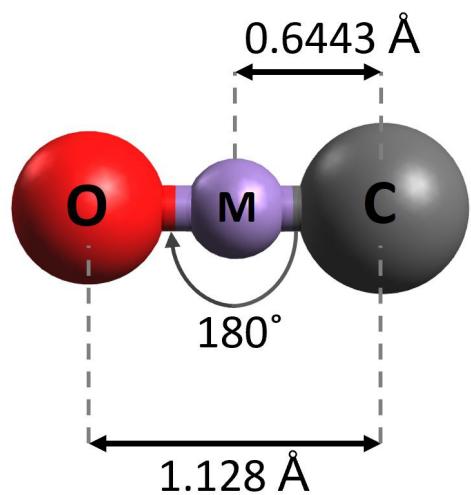
Figure S5: Carbon monoxide (CO) equilibrium structure [6].
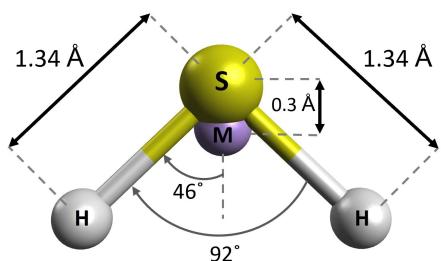
Figure S6: Hydrogen sulfide (H_2S) equilibrium structure [7].
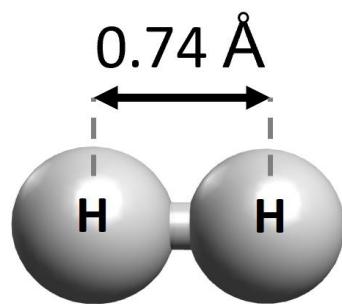
Figure S7: Hydrogen molecule (H_2) equilibrium structure [6].
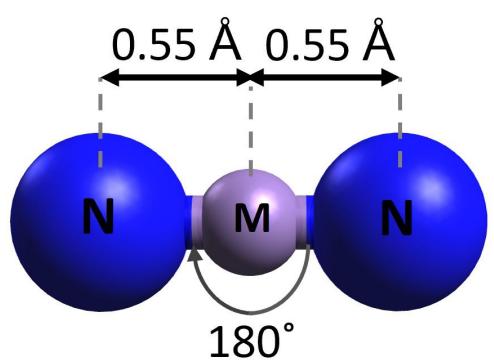
Figure S8: Nitrogen molecule (N$_2$) equilibrium structure [6].

2. GAFF Force Field Parameters for Choline Chloride

Table S1: GAFF atom types and non-bonded parameters for choline chloride [1]. The listed partial charges are the unscaled charges. For ChClEg and ChClU, these charges should be scaled by 0.9 [2] and 0.8 [1], respectively.

atom	atom type	partial charge	$\epsilon/k_\mathrm{B}/[\mathrm{K}]$	$\sigma/[\mathrm{\AA}]$
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: GAFF angle bending parameters for the choline ion [1]. The angle energy is calculated as: $E_{\mathrm{angle}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/k_{\mathrm{B}}/[\mathrm{K}]$	θ_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: GAFF dihedral parameters for the choline ion [1]. The dihedral energy is calculated as: $E_{\mathrm{dihedral}}(\phi) = \frac{V_n}{2}[1 + \cos(n\phi - \gamma)]$.

dihedral types	$\frac{V_n}{2}/k_{\mathrm{B}}/[\mathrm{K}]$	n	γ
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

3. GAFF Force Field Parameters for Urea

Table S4: GAFF atom types and non-bonded parameters for urea [1].

atom	atom type	partial charge	$\epsilon/k_{\mathrm{B}}/[\mathrm{K}]$	$\sigma/[\text{Å}]$
C	C	1.0401	43.277	3.3996
H1, H3	HZ	0.4167	7.901	1.0691
H2, 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: GAFF angle bending parameters for urea [1]. The angle energy is calculated as: $E_{\mathrm{angle}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/k_{\mathrm{B}}/[\mathrm{K}]$	θ_0
$\mathrm{N-C-O}$	38159.140	122.0
$\mathrm{C-N-HN}$	24763.435	118.5
$\mathrm{C-N-HZ}$	24763.435	118.5
$\mathrm{HN-N-HZ}$	19992.914	117.9
$\mathrm{N-C-N}$	37640.824	113.4

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

dihedral types	$\frac{V_n}{2}/k_{\text{B}}/[\text{K}]$	n	γ
HN − N − C − O	1258.049	-2	180
HN − N − C − O	1006.439	1	0
HZ − N − C − O	1258.049	-2	180
HZ − N − C − O	1006.439	1	0
N − C − N − HN	1258.049	2	180
N − C − N − HZ	1258.049	2	180

4. GAFF Force Field Parameters for Ethylene Glycol

Table S7: GAFF atom types and non-bonded parameters for ethylene glycol [2].

atom	atom type	partial charge	$\epsilon/k_\mathrm{B}/[\mathrm{K}]$	$\sigma/[\text{Å}]$
C1, C2	CG	0.1615	55.052	3.3996
H1 − H4	HG	0.0328	7.901	2.4713
H5, H6	HO	0.4069	0.500	0.1000
O1, O2	OG	-0.6340	105.877	3.0664

Table S8: GAFF angle bending parameters for ethylene glycol [2]. The angle energy is calculated as: $E_{\mathrm{angle}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/k_{\mathrm{B}}/[\mathrm{K}]$	θ_0
HO – OG – CG	23701.642	108.2
OG – CG – CG	34067.965	109.4
OG – CG – HG	25664.199	109.9
CG – CG – HG	23349.388	110.1
HG – CG – HG	19726.208	109.6

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

dihedral types	$\frac{V_n}{2}/k_{\text{B}}/[\text{K}]$	n	γ
HO − OG − CG − HG	84.038	3	0
CG − CG − OG − HO	80.515	-3	0
HG − CG − CG − HG	78.502	3	0
OG − CG − CG − HG	125.805	1	0
OG − CG − CG − OG	72.464	-3	0
OG − CG − CG − OG	591.283	2	0

5. OPLS Force Field Parameters for Choline Chloride

Table S10: OPLS atom types and non-bonded parameters for choline chloride [5]. The listed partial charges are the unscaled charges. For ChClEg, these charges should be scaled by 0.8 [5].

atom	atom type	partial charge	$\epsilon/k_{\mathrm{B}}/[\mathrm{K}]$	$\sigma/[\text{Å}]$
C1	CW	0.16500	33.212	3.50
C2	CS	-0.16375	33.212	3.50
C3 − C5	CA	-0.12500	33.212	3.50
H1, H2	HW	0.04250	15.097	2.20
H3	HY	0.34375	0.500	0.10
H4, H5	HS	0.08500	15.097	2.60
H6 − H14	HA	0.04125	15.097	2.50
N	NA	0.98875	85.547	3.25
O	OY	-0.58500	85.547	3.07
Cl	Cl	-1.00000	74.476	3.77

Table S11: OPLS angle bending parameters for the choline ion [5]. The angle energy is calculated as: $E_{\text{angle}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/k_{\text{B}}/[\text{K}]$	θ_0
HA − CA − HA	17612.685	110.01
HA − CA − NA	17612.685	108.90
CA − NA − CS	26066.774	110.20
NA − CS − HS	17612.685	106.40
NA − CS − CW	35225.370	116.60
CS − CW − HW	17612.685	108.30
CS − CW − OY	40257.566	109.60
HS − CS − CW	17612.685	109.30
HW − CW − OY	17612.685	111.60
CW − OY − HY	17612.685	110.90
CA − NA − CA	27677.07	108.73
HS − CS − HS	17612.685	108.60
HW − CW − HW	17612.685	107.40

Table S12: OPLS dihedral parameters for the choline ion [5]. The dihedral energy is calculated as: $E_{\text{dihedral}}(\phi) = \frac{1}{2}V_1[1+\cos(\phi)] + \frac{1}{2}V_2[1-\cos(2\phi)] + \frac{1}{2}V_3[1+\cos(3\phi)]$.

dihedral types	$V_1/k_{\text{B}}/[\text{K}]$	$V_2/k_{\text{B}}/[\text{K}]$	$V_3/k_{\text{B}}/[\text{K}]$
CW − CS − NA − CA	50.322	276.771	327.093
CA − NA − CA − HA	0.000	0.000	415.156
CS − NA − CA − HA	0.000	0.000	473.026
HS − CS − NA − CA	0.000	503.220	352.254
OY − CW − CS − NA	-3019.317	-2516.098	1610.303
OY − CW − CS − HS	-251.610	-1258.049	125.805
HW − CW − CS − NA	-3019.317	-3522.537	377.415
HW − CW − CS − HS	3019.317	-1509.659	1006.439
HY − OY − CW − CS	-179.146	-87.560	176.127
HY − OY − CW − HW	-1509.659	503.220	-1006.439

6. OPLS Force Field Parameters for Ethylene Glycol

Table S13: OPLS atom types and non-bonded parameters for ethylene glycol [5].

atom	atom type	partial charge	$\epsilon/k_\mathrm{B}/[\mathrm{K}]$	$\sigma/[\text{Å}]$
C1, C2	CG	0.116	58.122	3.50
H1 − H4	HG	0.048	26.419	2.50
H5, H6	HO	0.348	0.500	0.10
O1, O2	OG	-0.560	149.708	3.00

Table S14: OPLS angle bending parameters for ethylene glycol [5]. The angle energy is calculated as: $E_{\mathrm{angle}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/k_{\mathrm{B}}/[\mathrm{K}]$	θ_0
HO − OG − CG	27677.077	108.5
OG − CG − CG	25160.979	108.0
OG − CG − HG	17612.685	109.5
CG − CG − HG	18870.734	110.7
HG − CG − HG	16606.246	107.8

Table S15: OPLS dihedral parameters for ethylene glycol [5]. The dihedral energy is calculated as: $E_{\mathrm{dihedral}}(\phi) = \frac{1}{2}V_1[1 + \cos(\phi)] + \frac{1}{2}V_2[1 - \cos(2\phi)] + \frac{1}{2}V_3[1 + \cos(3\phi)]$.

dihedral types	$V_1/k_{\mathrm{B}}/[\mathrm{K}]$	$V_2/k_{\mathrm{B}}/[\mathrm{K}]$	$V_3/k_{\mathrm{B}}/[\mathrm{K}]$
OH − CG − CG − OH	1956.014	-599.838	1613.322
CG − CG − OH − HO	207.83	-379.428	517.31

7. Force Field Parameters for Solutes

Table S16: Force field parameters for solute gas molecules [6–9].

molecules	atom type	partial charge	$\epsilon/k_{\mathrm{B}}/[\mathrm{K}]$	$\sigma/[\text{Å}]$
CO_2	C	0.7000	0.0537	2.800
	O	-0.3500	0.1570	3.050
CO	C	-0.2424	0.0321	3.636
	O	-0.2744	0.1948	2.979
	M	0.5168	0.0010	0.100
CH_4	CH4	0.0000	0.2941	3.730
H_2S	S	0.0000	0.2424	3.600
	H	0.2100	0.0994	2.500
	M	-0.4200	0.0010	0.100
H_2	H	0.0000	0.0248	2.590
N_2	N	-0.4820	0.0715	3.310
	M	0.9640	0.0010	0.100

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