Supporting information for "Computing solubility parameters of Deep Eutectic Solvents from Molecular Dynamics simulations"

Hirad S. Salehi[a], Mahinder Ramdin[a], Othonas A. Moultos[a], Thijs J.H. Vlugt[a,*]

[a]*Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, Leeghwaterstraat 39, 2628CB Delft, The Netherlands*

In this document, force field parameters used in our MD simulations of deep eutectic solvents (DESs) are presented. Five DESs were used in the simulations: choline chloride urea (ChClU), choline chloride glycerol (ChClG), choline chloride ethylene glycol (ChClEg), choline chloride malonic acid (ChClMa), and choline chloride oxalic acid (ChClOa). For all DESs, the parameters obtained by Doherty and Acevedo [1], based on the OPLS force field [2], were used. Additionally, the Generalized Amber Force Field (GAFF) [3] parameters by Perkins et al. [4] were used for ChClU to investigate the influence of force field on the calculations of solubility parameters and enthalpies of vaporization. Both force fields are non-polarizable and consist of bonded and non-bonded (Lennard-Jones and electrostatic) terms and model the DESs as all-atom, flexible molecules. Molecular structure and atom labels are shown in Figures S1 to S6.

*Corresponding author
Email address: t.j.h.vlugt@tudelft.nl (Thijs J.H. Vlugt)

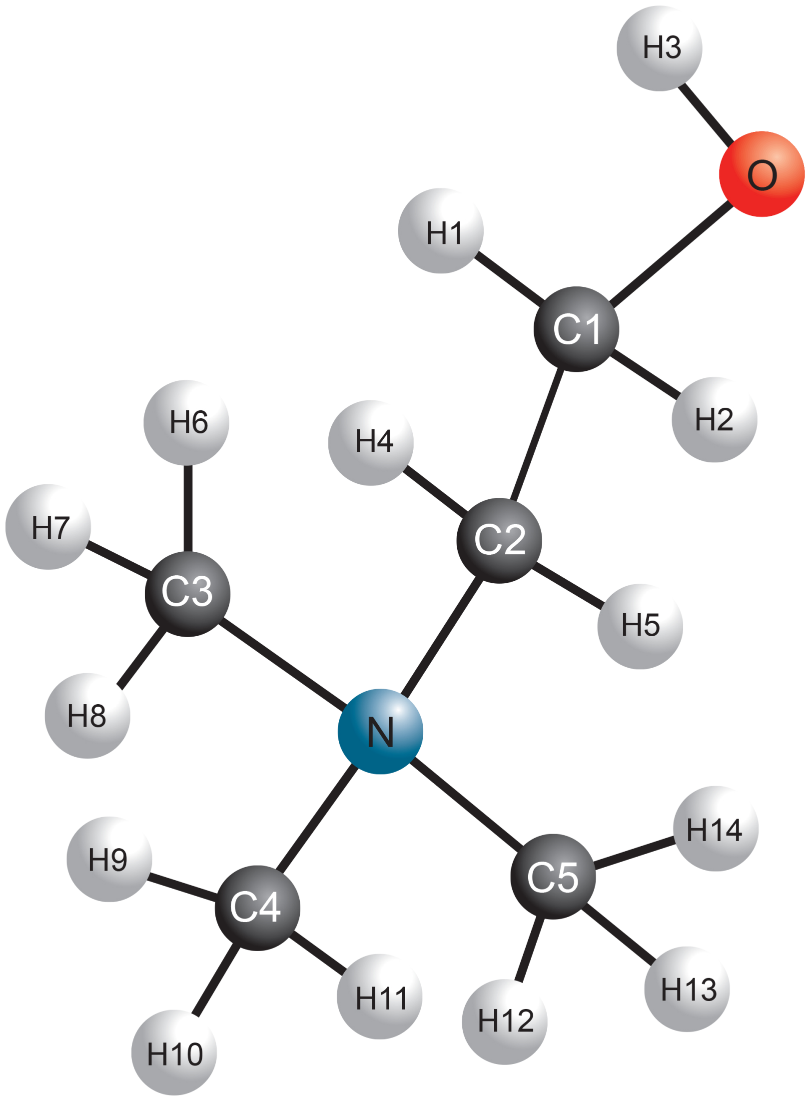

Figure S1: Choline structure and atom labels.

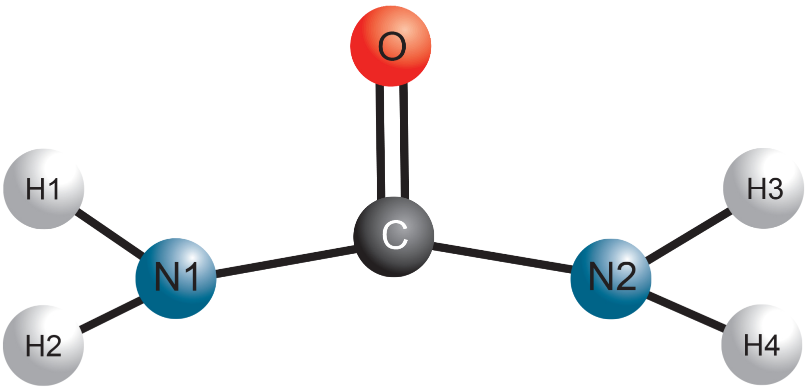

Figure S2: Urea structure and atom labels.

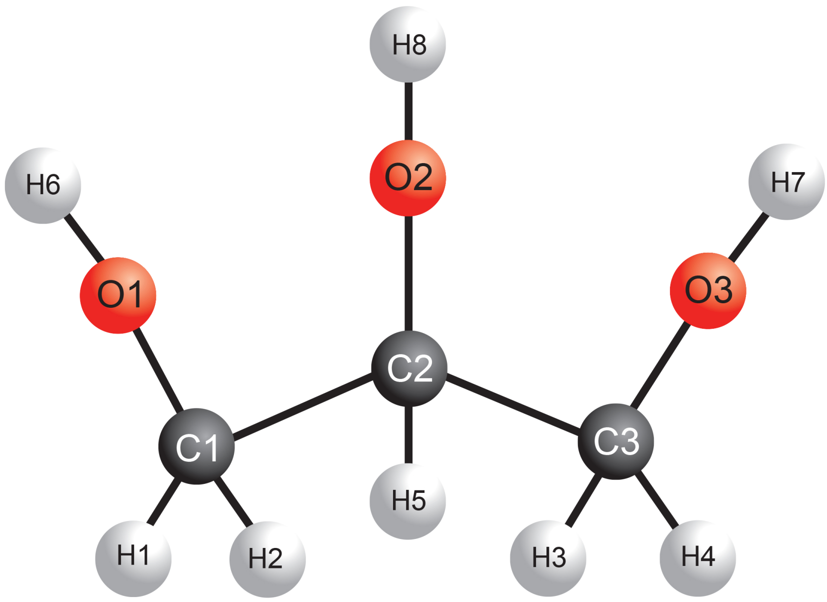

Figure S3: Glycerol structure and atom labels.

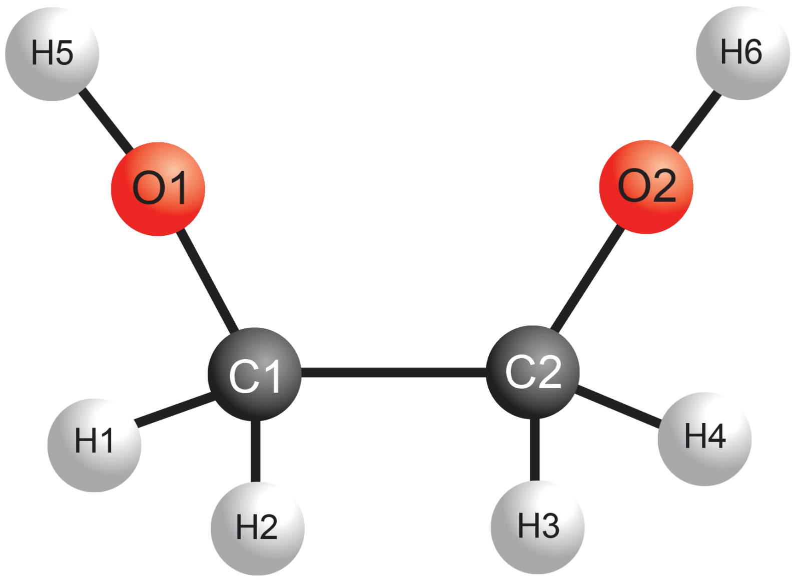

Figure S4: Etyhlene glycol structure and atom labels.

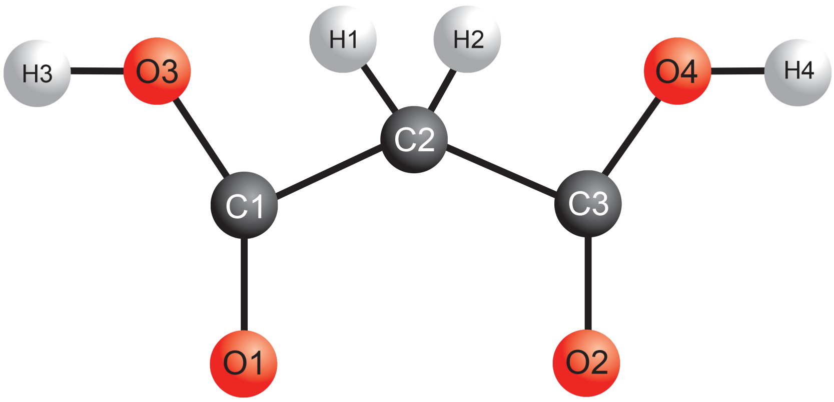

Figure S5: Malonic acid structure and atom labels.

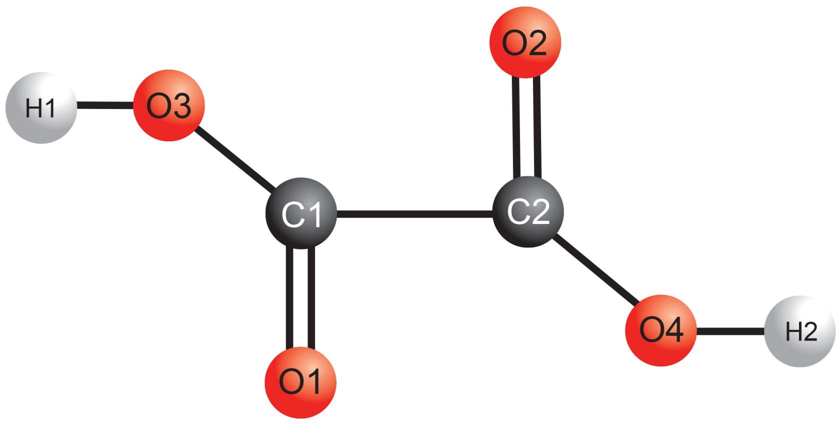

Figure S6: Oxalic acid structure and atom labels.

1. GAFF Force Field Parameters for Choline Chloride

Table S1: GAFF atom types and non-bonded parameters for choline chloride [4].

atom	atom type	partial charge	$\epsilon/(\text{kcal.mol}^{-1})$	$\sigma/(\text{Å})$
C1	CW	0.12008	0.1094	3.3997
C2	CS	-0.02576	0.1094	3.3997
$C3 - C5$	C3	-0.10736	0.1094	3.3997
$H1, H2$	H1	0.04080	0.0157	2.4714
H3	HO	0.36360	0.0010	0.1000
$H4, H5$	HX	0.08928	0.0157	1.9600
$H6 - H14$	HX	0.09544	0.0157	1.9600
N	N4	0.04016	0.1700	3.2500
O	OH	-0.49512	0.2104	3.0665
Cl	Cl	-0.80000	0.1000	4.4010

Table S2: GAFF bond parameters for choline ion [4]. The bond energy is calculated as: $E_{\mathrm{bond}}(r) = k_{\mathrm{r}}(r - r_0)^2$.

bond type	$k_{\mathrm{r}}/(\mathrm{kcal.mol^{-1}.Å^{-2}})$	$r_0/(\mathrm{Å})$
C3 – HX	338.7	1.09
C3 – N4	293.6	1.50
N4 – CS	293.6	1.50
CS – HX	338.7	1.09
CS – HX	303.1	1.54
CW – H1	335.9	1.09
CW – OH	314.1	1.43
OH – HO	369.6	0.97

Table S3: GAFF angle parameters for choline ion [4]. The angle energy is calculated as: $E_{\mathrm{angle}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	k_θ/(kcal.mol^{-1}.rad^{-2})	θ_0
HX − C3 − HX	39.04	110.7
HX − C3 − N4	49.02	107.9
C3 − N4 − CS	62.84	110.6
N4 − CS − HX	49.02	107.9
N4 − CS − CW	64.45	114.3
CS − CW − H1	46.36	110.1
CS − CW − OH	67.72	109.4
HX − CS − CW	46.02	111.7
H1 − CW − OH	50.97	109.9
CW − OH − HO	47.09	108.2
C3 − N4 − C3	62.84	110.6
HX − C3 − HX	39.04	110.7
H1 − CW − H1	39.18	109.6

Table S4: GAFF dihedral parameters for choline ion [4]. The dihedral energy is calculated as: $E_{\text{dihedral}}(\phi) = \frac{V_n}{2}[1 + \cos(n\phi - \gamma)]$.

dihedral types	$\frac{V_n}{2}$/(kcal.mol^{-1})	n	γ
H1 – CW – OH – HO	0.167	3	0
CS – CW – OH – HO	0.160	-3	0
CS – CW – OH – HO	0.250	1	0
H1 – CW – CS – HX	0.156	3	0
H1 – CW – CS – N4	0.156	3	0
OH – CW – CS – HX	0.156	3	0
OH – CW – CS – N4	0.156	3	0
CW – CS – N4 – C3	0.156	3	0
HX – CS – N4 – C3	0.156	3	0
CS – N4 – C3 – HX	0.156	3	0
C3 – N4 – C3 – HX	0.156	3	0

2. GAFF Force Field Parameters for Urea

Table S5: GAFF atom types and non-bonded parameters for urea [4].

atom	atom type	partial charge	$\epsilon/(\text{kcal.mol}^{-1})$	$\sigma/(\text{Å})$
C	C	1.0401	0.0860	3.3997
H1, H3	HZ	0.4167	0.0157	1.0691
H2, H4	HN	0.4167	0.0157	1.0691
N1, N2	N	-1.0246	0.1700	3.2500
O	O	-0.6577	0.2100	2.9599

Table S6: GAFF bond parameters for urea [4].

bond type	$k_{\mathrm{r}}/(\mathrm{kcal.mol^{-1}.\AA^{-2}})$	$r_0/(\mathrm{\AA})$
C – O	648.0	1.21
C – N	478.2	1.35
N – HN	410.2	1.01

Table S7: GAFF angle parameters for urea [4].

angle type	k_θ/(kcal.mol^{-1}.rad^{-2})	θ_0
N − C − O	75.83	122.0
C − N − HN	49.21	118.5
C − N − HZ	49.21	118.5
HN − N − HZ	39.73	117.9
N − C − N	74.80	113.4

Table S8: GAFF dihedral parameters for urea [4].

dihedral types	$\frac{V_n}{2}$/(kcal.mol^{-1})	n	γ
HN − N − C − O	2.5	-2	180
HN − N − C − O	2.0	1	0
HZ − N − C − O	2.5	-2	180
HZ − N − C − O	2.0	1	0
N − C − N − HN	2.5	2	180
N − C − N − HZ	2.5	2	180
N − N − C − O (improper)	10.5	2	180
C − HZ − N − HN (improper)	1.1	2	180

3. OPLS Force Field Parameters for Choline Chloride

Table S9: OPLS atom types and non-bonded parameters for choline chloride [1].

atom	atom type	partial charge	$\epsilon/(\text{kcal.mol}^{-1})$	$\sigma/(\text{Å})$
C1	CW	0.132	0.066	3.50
C2	CS	-0.131	0.066	3.50
$C3 - C5$	CA	-0.100	0.066	3.50
H1, H2	HW	0.034	0.030	2.20
H3	HY	0.275	0.001	0.10
H4, H5	HS	0.068	0.030	2.60
$H6 - H14$	HA	0.033	0.030	2.50
N	NA	0.791	0.170	3.25
O	OY	-0.468	0.170	3.07
Cl	Cl	-0.800	0.148	3.77

Table S10: OPLS bond parameters for choline ion [1]. The bond energy is calculated as: $E_{\mathrm{bond}}(r) = k_{\mathrm{r}}(r - r_0)^2$.

bond type	k_{r}/(kcal.mol^{-1}Å^{-2})	r_0/(Å)
HA – CA	340	1.0990
CA – NA	490	1.4980
NA – CS	490	1.5160
CS – HS	340	1.0805
CS – CW	317	1.5210
CW – HW	340	1.0850
CW – OY	450	1.3950
OY – HY	553	0.9490

Table S11: OPLS angle parameters for choline ion [1]. The angle energy is calculated as: $E_{\mathrm{angle}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	k_θ/(kcal.mol^{-1}.rad^{-2})	θ_0
HA – CA – HA	35.0	110.01
HA – CA – NA	35.0	108.90
CA – NA – CS	51.8	110.20
NA – CS – HS	35.0	106.40
NA – CS – CW	70.0	116.60
CS – CW – HW	35.0	108.30
CS – CW – OY	80.0	109.60
HS – CS – CW	35.0	109.30
HW – CW – OY	35.0	111.60
CW – OY – HY	35.0	110.90
CA – NA – CA	55.0	108.73
HS – CS – HS	35.0	108.60
HW – CW – HW	35.0	107.40

Table S12: OPLS dihedral parameters for choline ion [1]. 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/(kcal.mol^{-1})	V_2/(kcal.mol^{-1})	V_3/(kcal.mol^{-1})
CW − CS − NA − CA	0.100	0.550	0.650
CA − NA − CA − HA	0.000	0.000	0.825
CS − NA − CA − HA	0.000	0.000	0.940
HS − CS − NA − CA	0.000	1.000	0.700
OY − CW − CS − NA	-6.000	-5.000	3.200
OY − CW − CS − HS	-0.500	-2.500	0.250
HW − CW − CS − NA	-6.000	-7.000	0.750
HW − CW − CS − HS	6.000	-3.000	2.000
HY − OY − CW − CS	-0.356	-0.174	0.350
HY − OY − CW − HW	-3.000	1.000	-2.000
CS − NA − CA − CA (improper)	0.000	2.000	0.000
CA − NA − CA − CA (improper)	0.000	2.000	0.000

4. OPLS Force Field Parameters for Urea

Table S13: OPLS atom types and non-bonded parameters for urea [1].

atom	atom type	partial charge	ϵ/(kcal.mol^{-1})	σ/(Å)
C	C	0.124	0.1575	3.75
H1, H3	HC	0.276	0.0010	0.10
H2, H4	HT	0.276	0.0010	0.10
N1, N2	N	-0.453	0.2550	3.55
O	O	-0.322	0.3150	2.96

Table S14: OPLS bond parameters for urea [1].

bond type	k_r/(kcal.mol^{-1}.Å^{-2})	r_0/(Å)
O − C	570	1.229
N − C	490	1.335
HT − N	434	1.010
HC − N	434	1.010

Table S15: OPLS angle parameters for urea [1].

angle type	k_θ/(kcal.mol^{-1}.rad^{-2})	θ_0
O − C − N	80	122.9
C − N − HC	35	119.8
C − N − HT	35	119.8
N − C − N	70	114.2
HC − N − HT	35	120.0

Table S16: OPLS dihedral parameters for urea [1].

dihedral types	$V_1/(\text{kcal.mol}^{-1})$	$V_2/(\text{kcal.mol}^{-1})$	$V_3/(\text{kcal.mol}^{-1})$
HT − N − C − O	0.000	4.900	0.000
HC − N − C − O	0.000	4.900	0.000
HT − N − C − N	0.000	4.900	0.000
HC − N − C − N	0.000	4.900	0.000
HT − N − C − HC (improper)	0.000	21.000	0.000
O − C − N − N (improper)	0.000	5.000	0.000

5. OPLS Force Field Parameters for Glycerol

Table S17: OPLS atom types and non-bonded parameters for glycerol [1].

atom	atom type	partial charge	$\epsilon/(\text{kcal.mol}^{-1})$	$\sigma/(\text{Å})$
C1, C3	CB	0.16000	0.1452	3.50
C2	CM	0.14200	0.1452	3.50
H1 − H4	HC	0.06370	0.0660	2.50
H5	HZ	0.02210	0.0660	2.50
H6, H7	HO	0.03043	0.0010	0.10
H8	HM	0.29120	0.0010	0.10
O1, O3	OH	-0.54700	0.3740	3.07
O2	OM	-0.54470	0.3740	3.07

Table S18: OPLS bond parameters for glycerol [1].

bond type	$k_r/(\text{kcal.mol}^{-1}.\text{Å}^{-2})$	$r_0/(\text{Å})$
OM – CM	320	1.410
CB – CM	268	1.529
HM – OM	553	0.945
HZ – CM	340	1.090
HC – CB	340	1.090
OH – CB	320	1.410
HO – OH	553	0.945

Table S19: OPLS angle parameters for glycerol [1].

angle type	$k_\theta/(\text{kcal.mol}^{-1}.\text{rad}^{-2})$	θ_0
OM – CM – CB	50.00	108.5
CM – OM – HM	55.00	108.5
OM – CM – HZ	35.00	109.5
CM – CB – HC	37.50	110.7
CM – CB – OH	50.00	109.5
CB – OH – HO	55.00	108.5
CB – CM – CB	58.35	112.7
CB – CM – HZ	37.50	110.7
HC – CB – HC	33.00	107.8
HC – CB – OH	35.00	109.5

Table S20: OPLS dihedral parameters for glycerol [1].

dihedral types	V_1/(kcal.mol^{-1})	V_2/(kcal.mol^{-1})	V_3/(kcal.mol^{-1})
HM – OM – CM – CB	-0.356	-0.174	0.492
HZ – CM – OM – HM	0.000	0.000	0.352
HC – CB – CM – OM	0.000	0.000	0.468
OH – CB – CM – OM	12.234	0.000	0.000
HO – OH – CB – CM	-0.356	-0.174	0.492
HC – CB – CM – CB	0.000	0.000	0.300
OH – CB – CM – CB	-1.552	0.000	0.000
HC – CB – CM – HZ	0.000	0.000	0.300
OH – CB – CM – HZ	0.000	0.000	0.468
HO – OH – CB – HC	0.000	0.000	0.352

6. OPLS Force Field Parameters for Ethylene Glycol

Table S21: OPLS atom types and non-bonded parameters for ethylene glycol [1].

atom	atom type	partial charge	$\epsilon/(\text{kcal.mol}^{-1})$	$\sigma/(\text{Å})$
$\text{C1}, \text{C2}$	CG	0.116	0.1155	3.50
$\text{H1} - \text{H4}$	HG	0.048	0.0525	2.50
$\text{H5}, \text{H6}$	HO	0.348	0.0010	0.10
$\text{O1}, \text{O2}$	OG	-0.560	0.2975	3.00

Table S22: OPLS bond parameters for ethylene glycol [1].

bond type	$k_r/(\text{kcal.mol}^{-1}.\text{Å}^{-2})$	$r_0/(\text{Å})$
OG − HO	553	0.945
CG − OG	320	1.410
CG − CG	268	1.529
HG − CG	340	1.090

Table S23: OPLS angle parameters for ethylene glycol [1].

angle type	$k_\theta/(\mathrm{kcal.mol^{-1}.rad^{-2}})$	θ_0
HO – OG – CG	55.0	108.5
OG – CG – CG	50.0	108.0
OG – CG – HG	35.0	109.5
CG – CG – HG	37.5	110.7
HG – CG – HG	33.0	107.8

Table S24: OPLS dihedral parameters for ethylene glycol [1].

dihedral types	V_1/(kcal.mol^{-1})	V_2/(kcal.mol^{-1})	V_3/(kcal.mol^{-1})
OH − CG − CG − OH	3.887	-1.192	3.206
CG − CG − OH − HO	0.413	-0.754	1.028

7. OPLS Force Field Parameters for Malonic Acid

Table S25: OPLS atom types and non-bonded parameters for malonic acid [1].

atom	atom type	partial charge	$\epsilon/(\text{kcal.mol}^{-1})$	$\sigma/(\text{Å})$
C1, C3	CD	0.416	0.2625	3.75
C2	CT	-0.096	0.1650	3.50
H1, H2	HC	0.048	0.0750	2.50
H3, H4	HO	0.360	0.0010	0.10
O1, O2	OD	-0.352	0.5250	2.96
O3, O4	OH	-0.424	0.4250	3.00

Table S26: OPLS bond parameters for malonic acid [1].

bond type	$k_{\mathrm{r}}/(\mathrm{kcal.mol^{-1}.\AA^{-2}})$	$r_0/(\mathrm{\AA})$
OD – CD	570	1.229
OH – CD	450	1.364
CT – CD	317	1.522
HO – OH	553	0.945
HC – CT	340	1.090

Table S27: OPLS angle parameters for malonic acid [1].

angle type	k_θ/(kcal.mol^{-1}.rad^{-2})	θ_0
OD – CD – OH	80	121.0
OD – CD – CT	80	120.4
CD – OH – HO	35	113.0
CD – CT – CD	63	111.1
CD – CT – HC	35	109.5
CT – CD – OH	70	108.0
HC – CT – HC	33	107.8

Table S28: OPLS dihedral parameters for malonic acid [1].

dihedral types	V_1/(kcal.mol^{-1})	V_2/(kcal.mol^{-1})	V_3/(kcal.mol^{-1})
HO – OH – CD – CT	1.500	5.500	0.000
HC – CT – CD – OD	0.000	0.000	0.000
CD – CT – CD – OH	1.000	0.546	0.450
HC – CT – CD – OH	0.000	0.000	0.000
OD – CD – OH – HO	0.000	5.500	0.000
OD – CD – CT – CD	0.000	0.000	0.000
OH – CD – OD – CT (improper)	0.000	21.000	0.000

8. OPLS Force Field Parameters for Oxalic acid

Table S29: OPLS atom types and non-bonded parameters for oxalic acid [1].

atom	atom type	partial charge	$\epsilon/(\text{kcal.mol}^{-1})$	$\sigma/(\text{Å})$
C1, C2	CD	0.416	0.1575	3.75
H1, H2	HO	0.330	0.0010	0.10
O1, O2	OD	-0.352	0.3150	2.96
O3, O4	OH	-0.394	0.2550	2.92

Table S30: OPLS bond parameters for oxalic acid [1].

bond type	$k_{\mathrm{r}}/(\mathrm{kcal.mol^{-1}.\AA^{-2}})$	$r_0/(\mathrm{\AA})$
OD – CD	570	1.229
OH – CD	450	1.364
CD – CD	350	1.510
HO – OH	553	0.945

Table S31: OPLS angle parameters for oxalic acid [1].

angle type	k_θ/(kcal.mol^{-1}.rad^{-2})	θ_0
OH − CD − OD	80.00	121.00
CD − OH − HO	35.00	113.00
CD − CD − OH	70.96	118.03
CD − CD − OD	80.00	121.40

Table S32: OPLS dihedral parameters for oxalic acid [1].

dihedral types	V_1/(kcal.mol^{-1})	V_2/(kcal.mol^{-1})	V_3/(kcal.mol^{-1})
HO − OH − CD − CD	3.000	5.500	0.000
OH − CD − CD − OH	1.600	3.200	0.000
HO − OH − CD − OD	0.000	5.500	0.000
OD − CD − CD − OH	1.600	3.200	0.000
OD − CD − CD − OD	1.600	3.200	0.000
OH − CD − OD − CD (improper)	0.000	21.000	0.000

References

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