A Force Field for the Solubility of Cellulose in DMSO/Ionic Liquids

Supporting Information

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1 Force Field Parameter

In this section, the optimized force field parameters for DMSO in pure and aqueous [EMIm][OAc] are shown. The atom type nomenclature can be found in Figure S-1 and the atom classes in Table S-1. The force field is based on the potential equation of the OPLS–AA force field: [1–3]

$$
\begin{aligned}
U(r^N) = & \sum_{i \in \text{bonds}} k_{l,i}(l_i - l_{i,0})^2 + \sum_{i \in \text{angles}} k_{\theta,i}(\theta_i - \theta_{i,0})^2 \\
& + \sum_{i \in \text{dihedrals}} \left[\frac{V_{i,1}}{2}[1 + \cos(\phi_i)] + \frac{V_{i,2}}{2}[1 - \cos(2\phi_i)] \right. \\
& \left. + \frac{V_{i,3}}{2}[1 + \cos(3\phi_i)] + \frac{V_{i,4}}{2}[1 - \cos(4\phi_i)] \right] \\
& + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left[4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} \right] f_{ij}
\end{aligned}
\tag{1}
$$

$$
\epsilon_{i,j} = \sqrt{\epsilon_i \, \epsilon_j}, \qquad \sigma_{i,j} = \sqrt{\sigma_i \, \sigma_j} \, . \tag{2}
$$

The non-bonded interactions are tabulated in Table S-2 and the bonded ones in Tables S-3, S-4, and S-5 in comparison to the literature force field OPLS–AA. [1–3] The force constants *(see Table S-3 and S-4)* and torsion parameters *(see Table S-5)* do not include the factor 1/2.

The non-bonded interactions between the atomic neighbours 1–2 and 1–3 were not considered. The 1–4 interactions were scaled with the factor $f_{ij} = 0.5$. The Lennard-Jones interactions were calculated with the geometric mixing rules *(see Eq. 2)*. For the Coulomb interactions, the PPPM long-range Coulomb solver (as implemented in LAMMPS) [4] was applied. The cutoff radius of the Coulomb and Lennard-Jones interactions was set to 800 pm.

For [EMIm][OAc], the force field BILFF [5] and for water TIP4P-EW [6] (with fixed bonds and angles) was applied without any modifications. The total charge of the ions was set to ±0.82.

Since no force field parameters for the protons of DMSO are defined in the literature force field OPLS–AA [1–3], the partial charges resulted from the charge neutrality of the molecule together with the defined charges for the other atoms O, S and C. For the Lennard-Jones parameters of the protons, the given values of a CH_2/CH_3 substitute in the proximity of electron-withdrawing atomic groups were adopted.

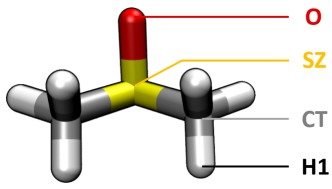

Figure S-1: Nomenclature of atom types in BILFF.

Table S-1: Nomenclature of atom types and atom classes of DMSO. The atom types are used for the non-bonded interactions *(see Table S-2)*. The atom classes are used for the bonded interactions *(see Tab. S-3, S-4, S-5)*.

Atom Type	Atom Class
O	O
S	SZ
CT	CT
H1	H1

Table S-2: Optimized atomic partial charges q and Lennard-Jones parameters σ and ϵ of DMSO.

Atom Type	BILFF			Literature[1–3]		
	q	σ / Å	ϵ / kJ mol^{-1}	q	σ / Å	ϵ / kJ mol^{-1}
O	−0.474	2.93	1.172	−0.420	2.93	1.172
S	0.136	3.30	1.653	0.130	3.56	1.653
CT	−0.029	3.30	0.276	−0.035	3.50	0.276
H1	0.066	2.38	0.126	0.060	2.50	0.126

Table S-3: Optimized bond equilibrium lengths l_0 and force constants k_l of DMSO.

Bond	BILFF		Literature[1–3]	
	l_0 / Å	k_l / kJ mol^{-1} Å^{-2}	l_0 / Å	k_l / kJ mol^{-1} Å^{-2}
O–SZ	1.533	3664.3	1.530	2928.8
SZ–CT	1.843	1269.8	1.790	1422.6
CT–H1	1.100	2621.6	1.090	1422.6

Table S-4: Optimized angle equilibrium values θ_0 and force constants k_θ of DMSO.

Angle	BILFF		Literature[1–3]	
	θ_0 / Deg	k_θ / kJ mol^{-1} rad^{-2}	θ_0 / Deg	k_θ / kJ mol^{-1} rad^{-2}
SZ–CT–H1	109.5	333.3	109.5	146.4
H1–CT–H1	107.8	507.9	107.8	138.1
CT–SZ–CT	96.0	510.4	96.0	259.4
CT–SZ–O	107.0	562.9	107.0	309.6

Table S-5: Optimized torsional coefficients V_n of DMSO.

Torsion Angle	BILFF				Literature[1–3]			
	V_1 kJ mol^{-1}	V_2 kJ mol^{-1}	V_3 kJ mol^{-1}	V_4 kJ mol^{-1}	V_1 kJ mol^{-1}	V_2 kJ mol^{-1}	V_3 kJ mol^{-1}	V_4 kJ mol^{-1}
CT–SZ–CT–H1	6.4434	−6.1924	5.7739	−3.1798	0.0000	0.0000	0.0000	0.0000
H1–CT–SZ–O	6.4434	−6.1924	5.7739	−3.1798	0.0000	0.0000	0.0000	0.0000

2 Comparison of the Partial Charges of DMSO With Literature Data

In Tab. S-6, a comparison of the atomic charges of DMSO in BILFF and various literature force fields is presented. These force fields employ different approaches to parameter optimization and utilize different calculation methods for potential energy.

BILFF is based on the OPLS–AA force field.[1–3] The atomic charges are represented in columns 2 and 3, respectively. The force fields from Ref. 7 and 8 are compatible with the functional form of AMBER.[9] On the other hand, the force fields from Ref. 10 and Ref. 11 are based on GROMOS.[12] These two force fields are classified as united-atom model force fields, while the other ones are all-atom force fields. Therefore, a row for the methyl group has been added to the atom types in the table. Since the charges in BILFF are derived from the OPLS values[1–3] (columns 2 and 3), the values are quite similar.

When comparing the charges of oxygen and sulfur, the values in BILFF exhibit also a similarity to the charges in the united atom force fields of Geerke et. al.[10] and Bordat et. al.[11] (columns 6 and 7), while the force fields based on AMBER[9] show higher partial charges (column 4 and 5).

It is important to note that these force fields were developed with a focus on different properties. The force fields by Geerke et. al.,[10] Bordat et. al.,[11] and Fox et. al.,[7] for example, aimed to accurately describe thermodynamic properties. The first one was optimized specifically for aqueous DMSO, while the other two were optimized for pure DMSO. On the other hand, the force field of Strader et. al.[8] aimed to reproduce both the structural and thermodynamic properties of aqueous DMSO. In the case of BILFF, the focus was on reproducing the hydrogen bonding behavior of DMSO in the ionic liquid [EMIm][OAc] in the presence and absence of water. Therefore, it is not surprising that the atomic charges in BILFF differ from those in the other all-atom force fields, which are specialized in capturing thermodynamic properties.

Table S-6: Comparison of the partial charges of DMSO in BILFF and different literature force fields.

Atom Type	BILFF	OPLS–AA[1–3]	Fox et. al.[7]	Strader et. al.[8]	Geerke et. al.[10]	Bordat et. al.[11]
O	−0.474 00	−0.420 00	−0.520 50	−0.556 00	−0.447 53	−0.436 74
S	0.136 00	0.130 00	0.315 50	0.312 00	0.127 53	0.116 74
CT	−0.029 00	−0.035 00	−0.324 40	−0.148 00	–	–
H1	0.066 00	0.060 00	0.142 30	0.090 00	–	–
CH_3	–	–	–	–	0.160 00	0.160 00

3 Additional Distribution Functions

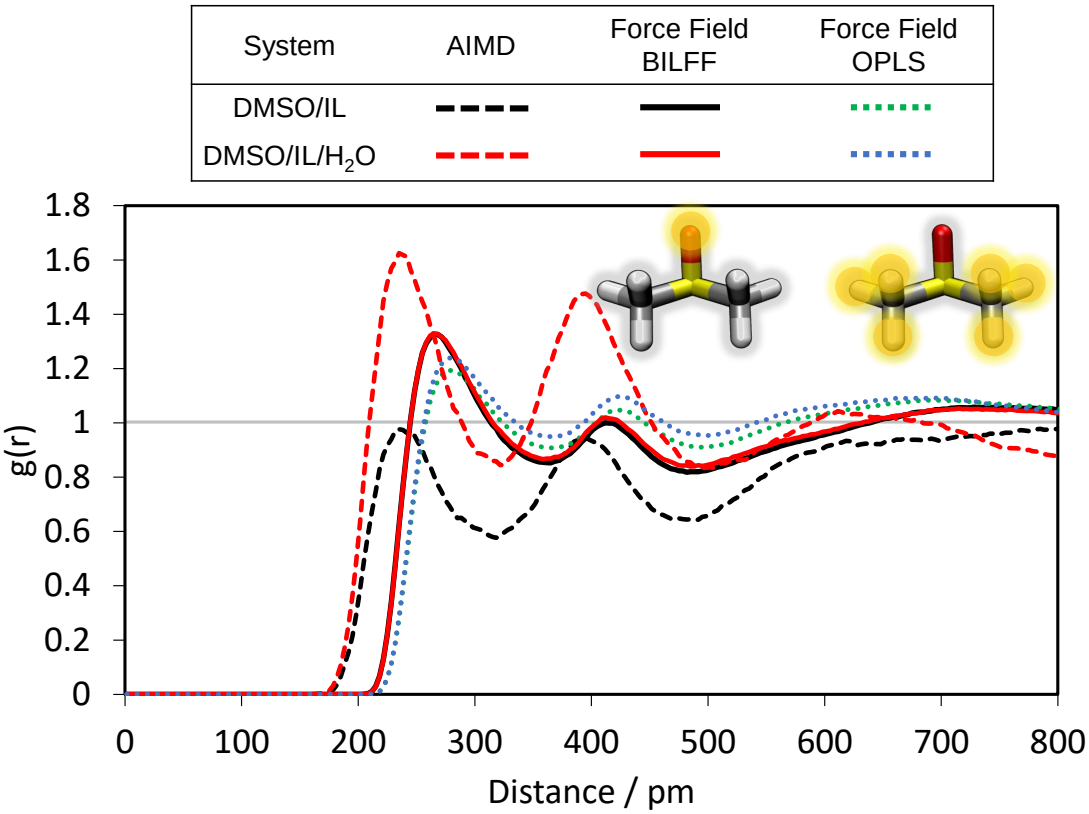

Figure S-2: Comparison of the RDFs between the reference AIMD and a force field MD simulation with the OPLS–AA force field[1–3] and BILFF between the oxygen atom and protons of DMSO.

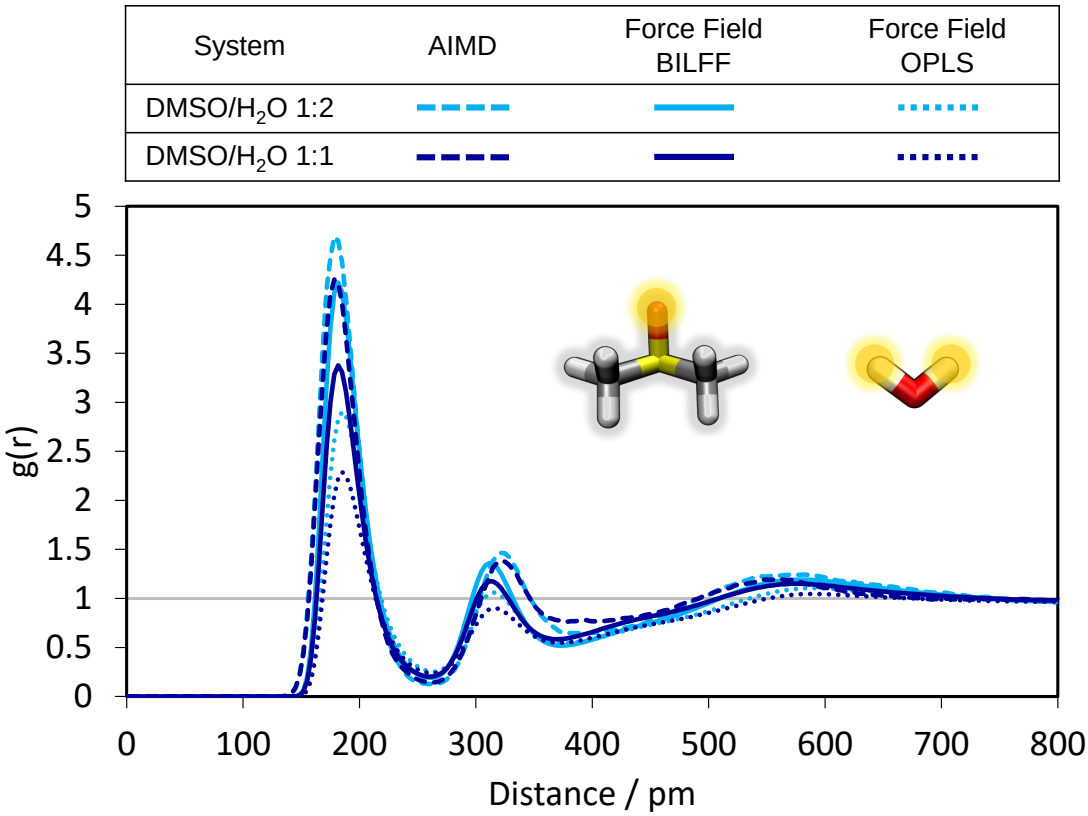

Figure S-3: Comparison of the RDFs between the DMSO oxygen and the water protons at two different DMSO/water mixing ratios (particle number ratio 1:2 and 1:1) calculated from the reference AIMD and force field MD simulations with the OPLS–AA force field[1–3] and BILFF.

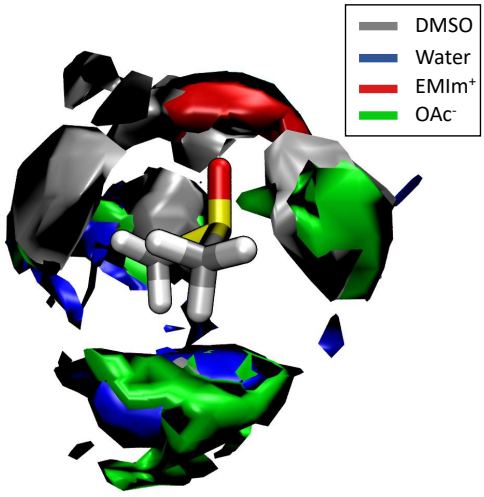

Figure S-4: Spatial distribution function (SDF) of the arrangement of molecules around DMSO with protons and oxygen atoms of DMSO (gray, oxygen: $6\,\mathrm{nm}^{-3}$; proton: $4\,\mathrm{nm}^{-3}$) and water (blue, $5\,\mathrm{nm}^{-3}$), the ring protons of $[\mathrm{EMIm}]^+$ (red, $7\,\mathrm{nm}^{-3}$) and the oxygen atom of acetate (green, $7\,\mathrm{nm}^{-3}$) in the DMSO–IL–H_2O system calculated from the reference AIMD simulation.

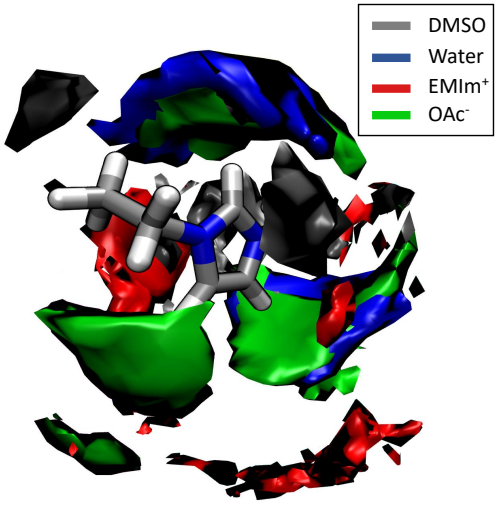

Figure S-5: Spatial distribution function (SDF) of the arrangement of molecules around $[\mathrm{EMIm}]^+$ with the protons and oxygen atoms of DMSO (gray, oxygen: $5\,\mathrm{nm}^{-3}$; proton: $3\,\mathrm{nm}^{-3}$) and water (blue, $6\,\mathrm{nm}^{-3}$), the ring center of $[\mathrm{EMIm}]^+$ (red, $9\,\mathrm{nm}^{-3}$) and the oxygen atom of acetate (green, $10\,\mathrm{nm}^{-3}$) in the DMSO–IL–H_2O system calculated from the reference AIMD simulation.

4 Lifetime of Additional Hydrogen Bonds

The calculation of the hydrogen bond lifetimes from the main text was based on specified angle and distance criteria. These were determined on the basis of occurring maxima in underlying combined distance–angle distribution functions and are listed in Tab. S-8. The same calculation criteria were used for all simulations.

Table S-7: Angle and distance criteria of the different hydrogen bonds for the calculation of the hydrogen bond lifetime.

Hydrogen Bond	Atom Distance	Angle
(DMSO)H–O(DMSO)	0–310 pm	90°–180°
([EMIm])H–O(DMSO)	0–280 pm	110°–180°
([EMIm])H–O([OAc])	0–260 pm	112°–180°
([EMIm])H–O(H_2O)	0–260 pm	120°–180°
(H_2O)H–O(DMSO)	0–250 pm	145°–180°
(H_2O)H–O([OAc])	0–180 pm	165°–180°

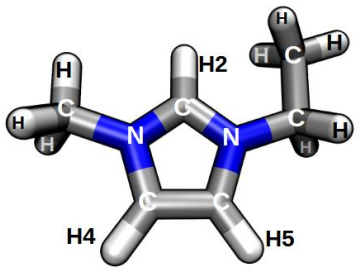

Figure S-6: Nomenclature of $[EMIm]^+$ in BILFF[5].

Table S-8: Overview of the lifetime τ of hydrogen bonds in the AIMD and the force field MD using BILFF at different temperatures. Lifetimes in ps. Please note that large lifetimes (> 100 ps) for the AIMD simulation are not reliable.

Temp.	Intermittent		Continuous	
	τ(AIMD)	τ(FFMD)	τ(AIMD)	τ(FFMD)
	DMSO/[EMIm][OAc]			
([EMIm])H2–O([OAc])				
350 K	772.3	380.17	7.79	8.24
450 K	79.44	63.89	2.57	3.19
([EMIm])H4–O([OAc])				
350 K	230.11	–	1.80	2.59
450 K	34.16	–	0.98	1.36
([EMIm])H5–O([OAc])				
350 K	173.34	–	1.64	2.38
450 K	41.01	–	1.14	1.28
([EMIm])H2–O(DMSO)				
350 K	33.93	47.06	1.14	3.11
450 K	10.50	10.34	1.08	1.57
([EMIm])H4–O(DMSO)				
350 K	42.38	54.44	2.05	2.07
450 K	–	9.80	0.96	1.13
([EMIm])H5–O(DMSO)				
350 K	71.92	62.16	2.30	2.30
450 K	456.52	10.81	0.79	1.21
	DMSO/[EMIm][OAc]/H_2O			
([EMIm])H2–O([OAc])				
350 K	185.05	307.861	5.03	6.56
450 K	59.38	52.59	2.03	2.79
([EMIm])H4–O([OAc])				
350 K	212.65	–	1.89	2.23
450 K	–	25.68	1.125	1.22
([EMIm])H5–O([OAc])				
350 K	114.44	–	1.47	2.07
450 K	–	24.71	0.78	1.16
([EMIm])H2–O(DMSO)				
350 K	44.64	48.69	2.67	3.05
450 K	4.77	9.41	0.59	1.52
([EMIm])H4–O(DMSO)				
350 K	46.80	53.04	1.78	1.97
450 K	–	8.90	0.80	1.10
([EMIm])H5–O(DMSO)				
350 K	635.37	57.24	2.01	2.20
450 K	18.10	10.11	1.14	1.18
([EMIm])H2–O(H_2O)				
350 K	67.34	80.96	0.95	1.14
450 K	21.30	10.69	0.53	0.71
([EMIm])H4–O(H_2O)				
350 K	26.75	54.77	0.55	0.77
450 K	16.43	6.50	0.35	0.50
([EMIm])H5–O(H_2O)				
350 K	11.89	54.37	0.57	0.84
450 K	3.81	6.52	0.38	0.52

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