**Electronic Supplementary Information**

# *N,N*-Dimethylformamide-induced phase separation of hexafluoroisopropanol–water mixtures

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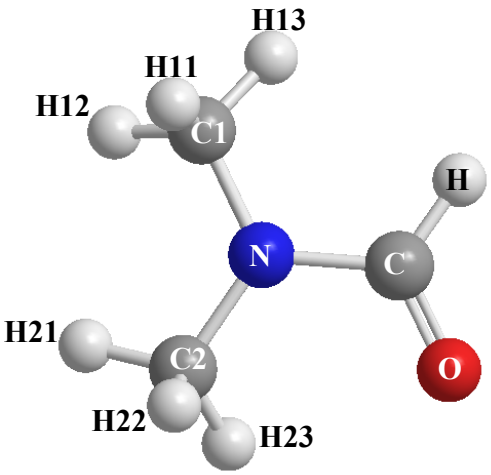
Table S1 Intramolecular atom–atom bond lengths and notation of the atoms in DMF and the potential parameters utilized for the MD simulations.

| Intramolecular Atom–Atom Bond Lengths | | |
|---|---|---|
| Molecule | Bond | $r$ / Å |
| DMF | C1–H11 | 1.090 |
| | C1–H12 | 1.090 |
| | C1–H13 | 1.090 |
| | C2–H21 | 1.090 |
| | C2–H22 | 1.090 |
| | C2–H23 | 1.090 |
| | C1–N | 1.449 |
| | C2–N | 1.449 |
| | C–N | 1.335 |
| | C–H | 1.080 |
| | C–O | 1.229 |




| Bond Angle Potentials | | | |
|---|---|---|---|
| Molecule | Angle | $K_\theta$ / kcal mol$^{-1}$ rad$^{-2}$ | $\theta_0$ / deg |
| DMF | H11–C1–H12 | 35 | 109.5 |
| | H11–C1–H13 | 35 | 109.5 |
| | H12–C1–H13 | 35 | 109.5 |
| | H21–C2–H22 | 35 | 109.5 |
| | H21–C2–H23 | 35 | 109.5 |
| | H22–C2–H23 | 35 | 109.5 |
| | H11–C1–N | 38 | 109.5 |
| | H12–C1–N | 38 | 109.5 |
| | H13–C1–N | 38 | 109.5 |

(Cont.)

| | | | |
|---|---|---|---|
| | H21–C2–N | 38 | 109.5 |
| | H22–C2–N | 38 | 109.5 |
| | H23–C2–N | 38 | 109.5 |
| | C1–N–C2 | 50 | 118.0 |
| | C1–N–C | 50 | 121.9 |
| | C2–N–C | 50 | 121.9 |
| | N–C–O | 80 | 122.9 |
| | N–C–H | 35 | 119.1 |
| | H–C–O | 80 | 122.9 |

Torsion Potentials

| Molecule | Torsion | $V_n/2$ / kcal mol$^{-1}$ | $n$ | $\phi_0$ / deg |
|---|---|---|---|---|
| DMF | H11–C1–N–C2 | 0 | 3 | 0 |
| | H12–C1–N–C2 | 0 | 3 | 0 |
| | H13–C1–N–C2 | 0 | 3 | 0 |
| | H21–C2–N–C1 | 0 | 3 | 0 |
| | H22–C2–N–C1 | 0 | 3 | 0 |
| | H23–C2–N–C1 | 0 | 3 | 0 |
| | H11–C1–N–C | 0 | 3 | 0 |
| | H12–C1–N–C | 0 | 3 | 0 |
| | H13–C1–N–C | 0 | 3 | 0 |
| | H21–C2–N–C | 0 | 3 | 0 |
| | H22–C2–N–C | 0 | 3 | 0 |
| | H23–C2–N–C | 0 | 3 | 0 |
| | C1–N–C–O | 10 | 2 | 180 |
| | C2–N–C–O | 10 | 2 | 180 |
| | C1–N–C–H | 10 | 2 | 180 |

(Cont.)

| | | | | |
|---|---|---|---|---|
| | C2–N–C–H | 10 | 2 | 180 |

van der Waals Parameters and Point Charges

| Molecule | Atom | $\sigma$ / Å | ε / kcal mol$^{-1}$ | $q$ / e |
|---|---|---|---|---|
| DMF | C1 | 3.500 | 0.066 | –0.110 |
| | C2 | 3.500 | 0.066 | –0.110 |
| | N | 3.250 | 0.170 | –0.140 |
| | C | 3.750 | 0.105 | 0.500 |
| | O | 2.960 | 0.210 | –0.500 |
| | H11 | 2.500 | 0.030 | 0.060 |
| | H12 | 2.500 | 0.030 | 0.060 |
| | H13 | 2.500 | 0.030 | 0.060 |
| | H21 | 2.500 | 0.030 | 0.060 |
| | H22 | 2.500 | 0.030 | 0.060 |
| | H23 | 2.500 | 0.030 | 0.060 |
| | H | 2.420 | 0.015 | 0.000 |