

# **SUPPLEMENTARY INFORMATION**

## **FORCE FIELD DEVELOPMENT AND SIMULATIONS OF SENIOR DIALKYL SULFOXIDES**

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## Simulation Details

Saturated vapor pressure and surface tension were obtained through simulations of the vapor-liquid equilibrium (VLE). For this, additional MD systems were created based on those discussed in the manuscript, having the same number of molecules. The geometries and densities at the end of the corresponding bulk-phase simulations were used.

For saturated vapor pressure estimation, the unit MD cell size was extended up to  $10 \times 10 \times 10$  nm in all directions. The constant temperature constant volume ensemble was simulated at 300, 350, 370, and 400 K. The first 2.0 ns were disregarded as equilibration, whereas the statistical averaging was performed on the remaining 23.0 ns long trajectory. For surface tension, the unit MD cell size was extended up to 10 nm only in a single direction (perpendicular to the interface). The first 2.0 ns were disregarded as equilibration, whereas the statistical averaging was performed on the remaining 12.0 ns long trajectory. Convergence of the simulated properties was controlled by comparing the given property originated from the consequent parts of the trajectory, such as 2-7 ns; 7-12 ns, etc. All computed properties were compared to the corresponding experimental results.<sup>1-3</sup> The experimental results were extrapolated using the Antoine equation to cover the required temperature range.

## Results and Brief Comments

Saturated vapor pressures of DMSO (Figure S1) using the model of van Gunsteren and coworkers<sup>4</sup> were computed at a number of temperatures over the range 340-460 K. The experimental results are reproduced with a satisfactory accuracy, even though the model was never tuned to do that. The normal boiling point of DMSO occurs at temperature where the saturated vapor of this liquid exhibits the atmospheric pressure. The computed temperature appears ca. 20 K inferior to the experimental one, 189°C. The observed four per cents discrepancy in this property may be considered acceptable. The underestimation may occur due to a relatively small interaction cut-off distance, applied by van Gunsteren and coworkers.<sup>4</sup>

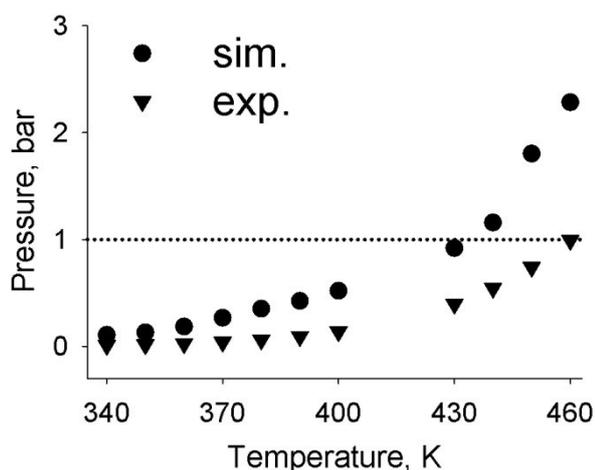


Figure S1. Saturated vapor pressure of DMSO: simulated (circles) and experimental (triangles) results.

The saturated vapor pressure of DESO (Figure S2) is also in acceptable agreement with the experiment of Markarian and coworkers.<sup>3</sup> The boiling point underestimation is ca. 15 K, whereas the boiling point itself is 175 °C. This is smaller than that of DMSO, because the added hydrophobic moieties decrease inter-molecular interaction strength. Compare with energy of cohesion discussed in the manuscript.

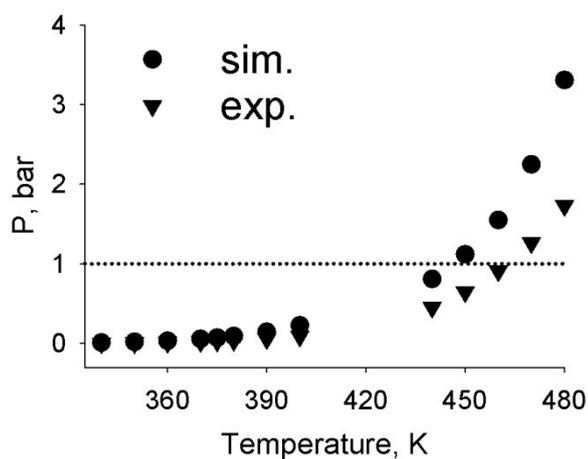


Figure S2. Saturated vapor pressure of DESO: simulated (circles) and experimental (triangles) results.

The simulated surface tension (Figure S3) is somewhat underestimated for DMSO. Unfortunately, no data for DESO were published yet. The tensions of DMSO and DESO are comparable, whereas the insignificant difference between them further decreases with temperature. Thus, surface tension of DMSO decreases faster than surface tension of DESO. Note that reproduction of the VLE properties in computer simulations remains challenging due to different polarization effects at room temperature and in the vicinity of the boiling point of most polar liquids. In the meantime, the VLE properties are directly connected to the mobility of particles in the liquid phase.

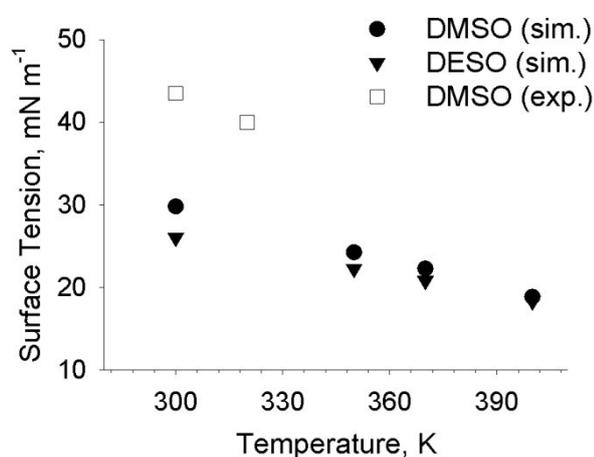


Figure S3. Simulated and experimental surface tension: DMSO (circles), DESO (triangles), DMSO experimental (squares).<sup>2</sup>

To recapitulate, the comparison of the simulated and experimental data indicates that accuracies of both of the original model (van Gunsteren and coworkers<sup>4</sup>) and the derived model are satisfactory at the room conditions and at the elevated temperature, up to normal boiling point.

## REFERENCES

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