Supporting Information for "Preferential Solvation and ion association properties in aqueous DMSO solutions"

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1 Calculation of Dielectric Spectra

All dielectric spectra have been computed following the fluctuation-based ("Green-Kubo") approach described in [1,6]. The frequency-dependent permittivity $\varepsilon(\omega)$ is calculated (in SI units) as

$$\varepsilon(\omega) = 1 + \frac{i}{\varepsilon_0 \omega} \left(\sigma(\omega) - \sigma(0) \right), \tag{1}$$

where i denotes the imaginary number, ω the angular frequency of a hypothetically applied external electric field, V is the volume of the simulation box, k_B the Boltzmann constant, T denotes temperature and $\sigma(\omega)$ is the system's frequency-dependent conductivity. The latter is computed as:

$$\sigma(\omega) = \frac{1}{3V k_B T} \int_0^\infty \langle \boldsymbol{J}_{\text{tot}}(0) \boldsymbol{J}_{\text{tot}}(t) \rangle e^{i\omega t} dt$$
$$:= \frac{1}{3V k_B T} \langle \boldsymbol{J}_{\text{tot}}(0) \boldsymbol{J}_{\text{tot}}(t) \rangle_\omega, \tag{2}$$

where $\langle \cdot \rangle$ denotes the canonical average, $\langle \cdot \rangle_\omega$ its Fourier-Laplace transform, and $\boldsymbol{J}_{\text{tot}}(t)$ is the fluctuating cumulative current

$$\boldsymbol{J}_{\text{tot}}(t) = \sum_m \sum_\alpha q_{m,\alpha} \boldsymbol{v}_{m,\alpha}(t) \tag{3}$$

summed over all molecules m consisting of atoms α with partial charges $q_{m,\alpha}$ and corresponding velocities $\boldsymbol{v}_{m,\alpha}(t)$.

Since $\boldsymbol{J}$ is additive and the Fourier-Laplace transform in eqn. (2) is linear, the contributions of different molecular species A, B in a binary system to the overall spectrum can be calculated by summing over the corresponding molecules $\{m \in A\}$, $\{m \in B\}$ individually:

$$\boldsymbol{J}_{\text{tot}}(t) = \boldsymbol{J}_A(t) + \boldsymbol{J}_B(t)$$
$$= \sum_{m \in A} \sum_\alpha q_{m,\alpha} \boldsymbol{v}_{m,\alpha}(t) + \sum_{m \in B} \sum_\beta q_{m,\beta} \boldsymbol{v}_{m,\beta}(t) \tag{4}$$

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Thus, it follows that

$$\sigma(\omega) = \frac{1}{3Vk_BT}\left[\langle \boldsymbol{J}_{\mathrm{A}}(0)\boldsymbol{J}_{\mathrm{tot}}(t)\rangle_{\omega} + \langle \boldsymbol{J}_{\mathrm{B}}(0)\boldsymbol{J}_{\mathrm{tot}}(t)\rangle_{\omega}\right]$$

$$= \frac{1}{3Vk_BT}\left[\langle \boldsymbol{J}_{\mathrm{A}}(0)\boldsymbol{J}_{\mathrm{A}}(t)\rangle_{\omega} + \langle \boldsymbol{J}_{\mathrm{B}}(0)\boldsymbol{J}_{\mathrm{B}}(t)\rangle_{\omega} + \langle \boldsymbol{J}_{\mathrm{A}}(0)\boldsymbol{J}_{\mathrm{B}}(t)\rangle_{\omega} + \langle \boldsymbol{J}_{\mathrm{B}}(0)\boldsymbol{J}_{\mathrm{A}}(t)\rangle_{\omega}\right]$$

$$= \frac{1}{3Vk_BT}\left[\langle \boldsymbol{J}_{\mathrm{A}}(0)\boldsymbol{J}_{\mathrm{A}}(t)\rangle_{\omega} + \langle \boldsymbol{J}_{\mathrm{B}}(0)\boldsymbol{J}_{\mathrm{B}}(t)\rangle_{\omega} + 2\langle \boldsymbol{J}_{\mathrm{A}}(0)\boldsymbol{J}_{\mathrm{B}}(t)\rangle_{\omega}\right]$$

$$\coloneqq \sigma_{\mathrm{AA}}(\omega) + \sigma_{\mathrm{BB}}(\omega) + 2\sigma_{\mathrm{AB}}(\omega). \tag{5}$$

The permittivity spectrum $\varepsilon(\omega)$ in eqn. (1) can be decomposed accordingly:

$$\varepsilon(\omega) = 1 + \frac{i}{\varepsilon_0\omega}\left[(\sigma_{\mathrm{AA}}(\omega) - \sigma_{\mathrm{AA}}(0)) + (\sigma_{\mathrm{BB}}(\omega) - \sigma_{\mathrm{BB}}(0)) + 2(\sigma_{\mathrm{AB}}(\omega) - \sigma_{\mathrm{AB}}(0))\right]$$

$$\coloneqq 1 + \varepsilon_{\mathrm{AA}}(\omega) + \varepsilon_{\mathrm{BB}}(\omega) + 2\varepsilon_{\mathrm{AB}}(\omega) \tag{6}$$

In the accompanying paper, the system consists of water, DMSO, and ions so that in principle, the permittivity spectrum should be decomposed into 3 contributions (or even 4, if the different ionic species are considered separately). However, the ionic contribution to the overall spectrum is insignificant and therefore neglected in the decomposition so that

$$\varepsilon(\omega) \approx 1 + \varepsilon_{\mathrm{water/water}}(\omega) + \varepsilon_{\mathrm{DMSO/DMSO}}(\omega) + 2\varepsilon_{\mathrm{water/DMSO}}(\omega). \tag{7}$$

The insignificance of ionic contributions can be inferred from the spectra shown in fig. **??**, since the spectra with (solid lines) and without ionic contributions (dashed lines) almost coincide.

1.1 Dielectric spectra: raw data

The raw data with smoothed curves for the dielectric spectra as shown in the main article are presented in Fig. 1. The raw data for the cross-correlations is depicted in Fig. 2.
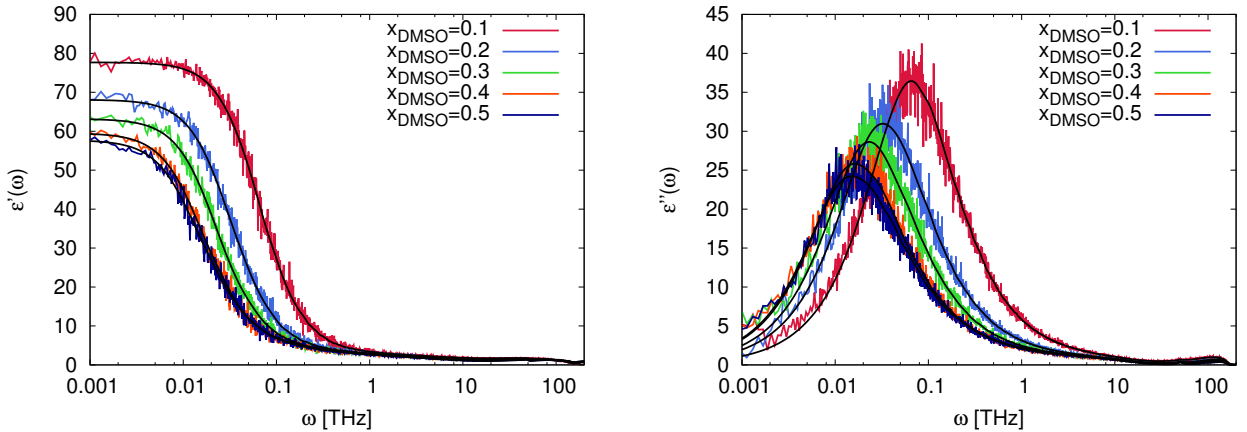

Figure 1: Left: Frequency-dependent dielectric permittivity $\epsilon'(\omega)$ for mole fractions $x_{\mathrm{DMSO}} = 0.1 - 0.5$ in presence of the ion pair. Right: Frequency-dependent dielectric loss $\epsilon''(\omega)$ for mole fractions $x_{\mathrm{DMSO}} = 0.1 - 0.5$ in presence of the ions. The solid lines represent smoothed curves as shown in the main article.
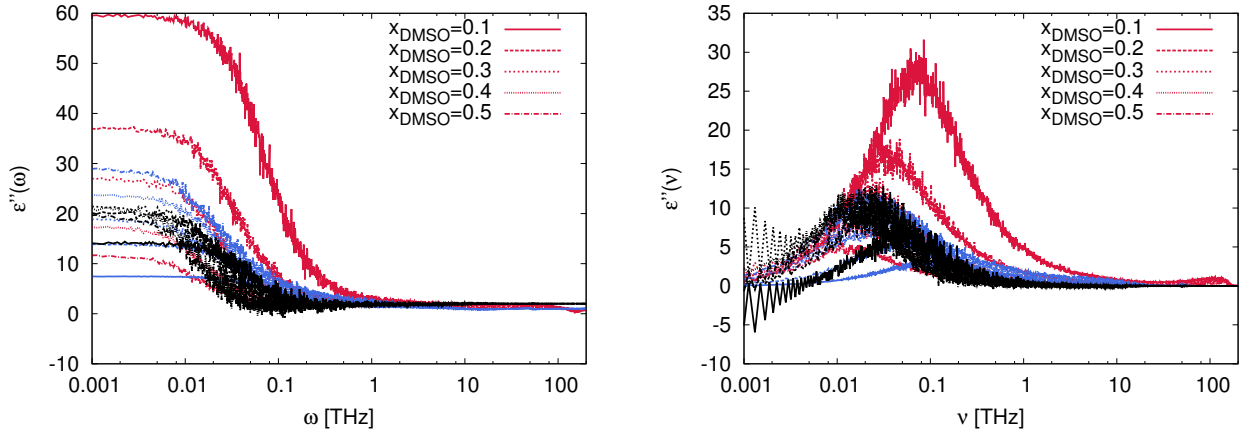
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Figure 2: Left: Contributions to the frequency-dependent dielectric permittivity $\epsilon'(\omega)$ for mole fractions $x_{\text{DMSO}} = 0.1 - 0.5$ in presence of the ion pair. The contributions of the ions can be neglected due to their low intensity. Right: Contributions to the frequency-dependent dielectric loss $\epsilon''(\omega)$ for mole fractions $x_{\text{DMSO}} = 0.1 - 0.5$ in presence of the ions. Red lines denote the results for water contributions, blue lines for DMSO and black lines represent the cross correlation contributions for water and DMSO. The contributions of the ions can be neglected due to their low intensity.

2   Calculation of Static Conductivity and Permittivity

The static conductivities $\sigma(\omega = 0)$ have been computed according to the so-called "Einstein-Helfand" method as described in [5]. This method exploits the long-term behavior of the mean square displacement (MSD) of the system's itinerant translational dipole moment $\langle \Delta M^2_{\text{trans}}(t) \rangle$:

$$\lim_{t \to \infty} \langle \Delta M^2_{\text{trans}}(t) \rangle = 2 \langle M^2_{\text{trans}} \rangle + 6 V k_B T \sigma(0) t \tag{8}$$

The MSD of the translational dipole moment is calculated by

$$\langle \Delta M^2_{\text{trans}}(t) \rangle = 2t \int_0^t \langle \boldsymbol{J}_{\text{trans}}(0) \boldsymbol{J}_{\text{trans}}(\tau) \rangle \, d\tau - 2 \int_0^t \tau \langle \boldsymbol{J}_{\text{trans}}(0) \boldsymbol{J}_{\text{trans}}(\tau) \rangle \, d\tau \,, \tag{9}$$

where $\boldsymbol{J}_{\text{trans}}(t)$ is the translational part of the cumulative current $\boldsymbol{J}_{\text{tot}}(t)$. It is defined as

$$\boldsymbol{J}_{\text{trans}}(t) = \sum_m q_m \boldsymbol{v}_{m,\text{com}} \,, \tag{10}$$

where q_m is the total charge of the m-th molecule and $\boldsymbol{v}_{m,\text{com}}$ its center of mass velocity. Once $\langle \Delta M^2_{\text{trans}}(t) \rangle$ is computed for a sufficiently long time (here, the simulation time was $t > 1 \, \mu s$), the static conductivity $\sigma(0)$ can be obtained from the slope of a linear regression of $\langle \Delta M^2_{\text{trans}}(t) \rangle$ according to eqn. (8).

For the static permittivity $\varepsilon(\omega = 0)$, a similar method is employed. Again, the MSD is computed as before, but this time for the system's *total* itinerant dipole moment:

$$\langle \Delta M^2_{\text{tot}}(t) \rangle = 2t \int_0^t \langle \boldsymbol{J}_{\text{tot}}(0) \boldsymbol{J}_{\text{tot}}(\tau) \rangle \, d\tau - 2 \int_0^t \tau \langle \boldsymbol{J}_{\text{tot}}(0) \boldsymbol{J}_{\text{tot}}(\tau) \rangle \, d\tau \tag{11}$$

Then, eqn. (8) becomes

$$\lim_{t \to \infty} \langle \Delta M^2_{\text{tot}}(t) \rangle = 2 \langle M^2_{\text{tot}} \rangle + 6 V k_B T \tilde{\sigma} t \,, \tag{12}$$

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and together with the relation (equation (26.4.3D) from reference [4] for tinfoil boundary conditions, in SI units)

$$\varepsilon(0) = 1 + \frac{\langle M_{\text{tot}}^2 \rangle}{3\varepsilon_0 V k_B T}, \tag{13}$$

the static permittivity can be obtained from the y-axis offset of a linear regression of $\langle \Delta M_{\text{tot}}^2(t) \rangle$ according to eqn. (12). It should be mentioned that the "conductivity" $\tilde{\sigma}$ in eqn. (12) cannot be used as an estimate for the true static conductivity since it contains rotational contributions.

3 System Details

In the following, we present the solution details for the systems with ions (Tab. 1) and without ions (Tab. 2). All simulations with ions include one SDS^{2-} ion and two lithium ions.

x_{DMSO}	Number of DMSO molecules	Number of water molecules	Box volume (nm × nm × nm)
0.1	150	1433	$3.94 \times 3.94 \times 3.94$
0.2	250	1002	$3.89 \times 3.89 \times 3.89$
0.3	301	793	$3.91 \times 3.91 \times 3.91$
0.4	209	340	$3.30 \times 3.30 \times 3.30$
0.5	252	273	$3.35 \times 3.35 \times 3.35$

Table 1: Number of solvent molecules for the DMSO-water mixture with ions for different mole fractions x_{DMSO} with resulting average box volumes.

x_{DMSO}	Number of DMSO molecules	Number of water molecules	Box volume (nm × nm × nm)
0.0	0	895	$3.00 \times 3.00 \times 3.00$
0.1	75	553	$2.95 \times 2.95 \times 2.95$
0.2	100	442	$2.92 \times 2.92 \times 2.92$
0.3	134	323	$2.94 \times 2.94 \times 2.94$
0.4	98	135	$2.50 \times 2.50 \times 2.50$
0.5	110	113	$2.55 \times 2.55 \times 2.55$
0.6	131	80	$2.62 \times 2.62 \times 2.62$
0.7	148	60	$2.66 \times 2.66 \times 2.66$
0.8	170	40	$2.77 \times 2.77 \times 2.77$
0.9	192	20	$2.85 \times 2.85 \times 2.85$
1.0	288	0	$3.02 \times 3.02 \times 3.02$

Table 2: Number of solvent molecules for the DMSO-water mixture without ions for different mole fractions x_{DMSO} with resulting average box volumes.

4 Hydrogen Bond Analysis

In order to study the binding properties between water and DMSO molecules, we calculated the average number of hydrogen bonds $\langle N_{HB} \rangle$ between water and water molecules and water and DMSO molecules. The corresponding data and the total number of hydrogen bonds for a single water molecule are presented in Fig. 3.
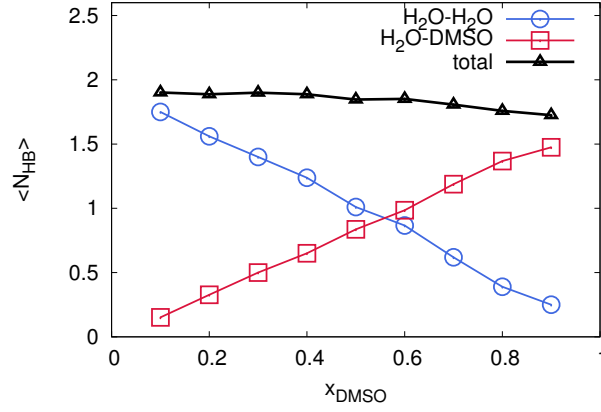
Figure 3: Average number of hydrogen bonds $\langle N_{HB} \rangle$ for a water molecule with water molecules (blue circles) and DMSO molecules (red squares). The average number of hydrogen bonds per water molecule as a sum of both contributions is denoted by black triangles. Lines represent a guide to the eyes.

The results are in perfect agreement to the findings presented in a previous publication [3]. The total number of hydrogen bonds is $\langle N_{HB} \rangle \leq 2$ for all mole fractions of DMSO. Moreover, also the crossing point at $x_{DMSO} = 0.6$ is comparable to previous results [3].

5 Mass density

The mass density for different mole fractions was also calculated and compared with experimental findings. The corresponding results are depicted in Fig. 4.
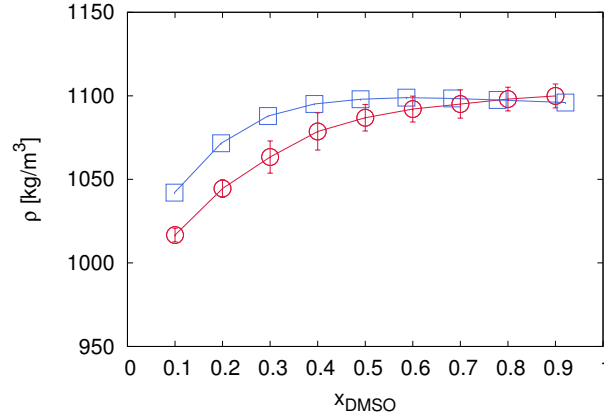

Figure 4: Simulation results (red circles) and experimental findings [2] at 298.15 K (blue squares) for the mass density at different mole fractions of DMSO. Lines serve as a guide to the eyes.

The simulation results are in qualitative agreement with experimental results measured at 298.15 K [2].

6 Water Coordination Numbers and Radial Distribution Function

In order to test the validity of our force field combination, we calculated the coordination numbers of water molecules in presence of SDS^{2-} by integration of the radial distribution function.
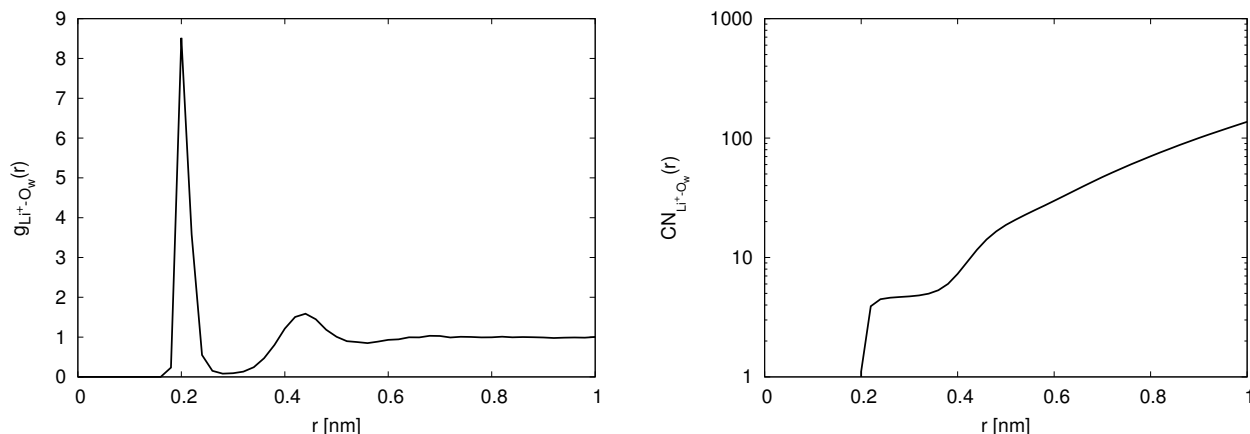

Figure 5: Left: Radial distribution function of water molecules with respect to lithium ions. The position of lithium ions and the corresponding position of oxygen atoms (water molecules) were chosen as reference. Right: Water coordination numbers around lithium ions as calculated by the integrated radial distribution function.

The corresponding results are shown in Fig. 5. One can clearly observe a well-defined first hydration shell around lithium ions within a maximum distance of 0.3 nm. The corresponding coordination number is given by 4.73 water molecules which is in good agreement with ab initio MD simulations [7], where a coordination number of 5 at $r = 0.3$ nm was found. The first maximum at 0.22 nm also coincides with ab-initio MD simulations [7].

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