Electronic Supplementary Information

Probing the balance of attraction and repulsion in binary mixtures of dimethyl sulfoxide and n-alcohols

Andrew Ellis,a Florian M. Zehentbauer,a Johannes Kieferab*

Sa School of Engineering, University of Aberdeen, Aberdeen, Scotland, UK
SbErlangen Graduate School in Advanced Optical Technologies, University Erlangen-Nuremberg, Germany

*E-mail: j.kiefer@abdn.ac.uk

This document provides additional information and experimental data (Raman and IR). In particular the molecular interactions between DMSO and the alcohols are discussed in more detail. Raman spectra were recorded in a 90 degree arrangement with a 532-nm diode laser as excitation source and an imaging spectrograph (entrance slit 200 µm, 1200-lines/mm grating, focal length 163 mm) equipped with an EM-CCD camera (Andor) as detector. The spectral range 900 to 3900 cm⁻¹ was recorded. Raw Raman data were processed to remove spikes and baselines were corrected using a Matlab code based on that kindly provided by Schulze et al.¹

Spectral Assignments
The experimental data are taken in context as a change in molecular structure between the binary mixtures and the pure liquids. Therefore it is important to have an idea of the molecular structure in the pure liquids to take as a baseline. In pure liquid phase, alcohols associate with strong hydrogen bonding interactions between hydroxyl groups to form a mixture of cyclic and chain structures.² The molecular superstructure of pure DMSO was the subject of a number of publications, which propose two different models for the conformation.³⁻⁵ The first of the two prevailing theories as to how these dipoles arrange themselves in the pure liquid is that the molecules form anti-parallel dimers. The second model is a ‘head to tail’ chain or cyclic alignment of the DMSO dipoles. The IR and Raman spectra of the pure liquid compounds are displayed in Fig. S1. The peaks were assigned to specific molecular vibrations with reference to a number of sources.⁶⁻¹⁰ In this work, we focus on four characteristic peaks: the OH stretching and the CO torsion of the alcohol compounds, and the CSC stretching and CH stretching in DMSO. The frequencies of these vibrations observed in the pure liquids are summarized in Table S1.

Table S1: Peak Assignments (ν = stretching, τ = torsion)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Propanol</th>
<th>Butanol</th>
<th>Pentanol</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>νOH (IR)</td>
<td>3316 cm⁻¹</td>
<td>3312 cm⁻¹</td>
<td>3315 cm⁻¹</td>
<td>-</td>
</tr>
<tr>
<td>τCO (IR)</td>
<td>635 cm⁻¹</td>
<td>640 cm⁻¹</td>
<td>642 cm⁻¹</td>
<td>-</td>
</tr>
<tr>
<td>νCSCasym (IR)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>698 cm⁻¹</td>
</tr>
<tr>
<td>νCH₃sym (Raman)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2959 cm⁻¹</td>
</tr>
</tbody>
</table>

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Figure S1: Pure Raman (black) and IR (red) spectra of a) DMSO; b) Propan-1-ol; c) Butan-1-ol; d) Pentan-1-ol.

**Solvent-induced frequency shifts**

Figures S2 and S3 display the full IR and excess IR spectra, respectively, of the mixtures in order to provide additional information. The peaks of interest are indicated by arrows. The excess IR spectra were obtained using the method described in the literature.\(^{11,12}\) The excess IR absorbance contains information about changes in the dipole moment due to non-idealities in the mixtures. Negative values indicate a dipole moment lower than it would be in an ideal mixture, and positive values analogously.

The solvent induced frequency shifts of the four characteristic vibrations - the alcohol OH stretching and CO torsion as well as the DMSO CSC asymmetric stretching and symmetric CH\(_3\) stretching - are displayed in Fig. S4. The y-axes show the difference of the peak center frequency in the mixture and its value in the pure liquid. Hence, positive values mean a blue-shift and negative ones a red-shift, or in other words a strengthened and weakened covalent bond, respectively.
Figure S2: Infrared spectra of the mixtures: a) DMSO/propanol, b) DMSO/butanol, c) DMSO/pentanol. The arrows indicate the individual peaks analyzed with respect to frequency shifts.
Figure S3: Excess infrared spectra of the mixtures: a) DMSO/propanol, b) DMSO/butanol, c) DMSO/pentanol.
Propanol/DMSO

The OH stretching vibration gives a strong, broad peak in the IR spectra with a pure frequency of around 3316 cm\(^{-1}\). Over the concentration range from \(x_{\text{DMSO}}=0\) to \(x_{\text{DMSO}}=0.5\), this vibration is observed to linearly blue-shift by 75 cm\(^{-1}\). This blue-shift is indicative of a strengthening of the O-H bond, which in turn reflects a decrease in the strength of the intermolecular hydrogen bonding. It is clear that despite this phenomenon, a HB between DMSO and propanol does exist – the maximum OH central peak frequency observed experimentally was around 3395 cm\(^{-1}\), which is still a significant red-shift compared to the predicted non-hydrogen-bonded vOH frequency of 3675 cm\(^{-1}\).

The OH peak shift slows and stops around \(x_{\text{DMSO}}=0.5\), and at mole fractions above \(x_{\text{DMSO}}=0.5\), the OH stretching vibration is stable at its blue-shifted frequency.

The CO torsional vibration gives another broad IR peak, of medium intensity at a pure central peak frequency of 635 cm\(^{-1}\). A linear red-shifting of 20 cm\(^{-1}\) is seen from \(x_{\text{DMSO}}=0\) to \(x_{\text{DMSO}}=0.3\), which indicates an increase in the rotational freedom about the C-O bond. The CO peak red-shift then slows to a stop around \(x=0.4\), and the peak frequency begins to increase back towards the pure frequency. This suggests that the moieties either side of the C-O bond are beginning to be more spatially fixed by some new configuration as DMSO concentration increases through equimolar. As the DMSO concentration increases towards pure, the CO peak settles at a new frequency about 15 cm\(^{-1}\) below the pure around \(x_{\text{DMSO}}=0.7\).

The clear peak shifts observable in the DMSO spectra were provided by the CSC and CH stretching vibrations. The CSC stretching frequencies are seen in the IR spectra, but not in Raman spectra, as the pure frequencies are around 700 cm\(^{-1}\) which is below the minimum wavenumber measured in our Raman experiment (we note that we have studied the CSC vibrations in the Raman spectrum of...
DMSO mixtures with water, methanol, and ethanol in a previous work\(^1\). They are visible as two mid intensity peaks – the higher frequency peak is the asymmetric and the lower frequency the symmetric stretching vibration. As both show virtually identical behavior we only consider the asymmetric band in the following. The asymmetric CSC stretching peak is observed at a steady maximum blue-shift of 6 cm\(^{-1}\) at \(x_{\text{DMSO}}=0.3\). Between \(x_{\text{DMSO}}=0.3\) and \(x_{\text{DMSO}}=0.7\), the blue-shift linearly decreases almost to the pure peak frequency. Above \(x_{\text{DMSO}}=0.7\), the peak frequency decreases slowly towards the pure frequency.

The DMSO CH\(_3\) symmetric stretching vibration gives a strong Raman peak at a pure frequency of 2959 cm\(^{-1}\). Across the concentration range, the peak shows steady blue shifting with increasing alcohol concentration until it stops at a maximum blue-shift of 5 cm\(^{-1}\) when \(x_{\text{DMSO}}=0.15\).

**Butanol/DMSO**

The butanol OH stretching peak is strong and broad in the IR, with a pure frequency of 3312 cm\(^{-1}\). Again, it shows a linear blue-shifting, which slows and stops around \(x_{\text{DMSO}}=0.5\), though its final stable frequency is only blue-shifted by 73 cm\(^{-1}\).

The CO torsional peak can be clearly identified as the broad peak in the IR spectra with a pure frequency of 640 cm\(^{-1}\). It shows a linear red-shifting from \(x_{\text{DMSO}}=0\) to \(x_{\text{DMSO}}=0.25\), at which point the frequency shift slows until it reaches an extreme value at a red-shift of 23 cm\(^{-1}\) and a mole fraction of \(x_{\text{DMSO}}=0.4\). With increasing DMSO concentration, the peak frequency increases again from this plateau until it reaches a new stable frequency at a red-shift of 13 cm\(^{-1}\) at \(x_{\text{DMSO}}=0.8\).

The asymmetric CSC stretching peak is at a steady maximum blue-shift of 6 cm\(^{-1}\) at \(x_{\text{DMSO}}\leq 0.25\). From \(x_{\text{DMSO}}=0.25\) and \(x_{\text{DMSO}}=0.7\), the blue-shift linearly decreases to just over 0. Above \(x_{\text{DMSO}}=0.7\), the small remaining blue-shift diminishes.

Across the concentration range, the DMSO CH\(_3\) symmetric peak shows linear blue-shifting with increasing alcohol concentration to a maximum blue-shift of 4.5 cm\(^{-1}\) at \(x_{\text{DMSO}}=0.1\), after which point there is no further change in peak frequency.

**Pentanol/DMSO**

The pentanol OH stretching peak in the IR is strong and broad, and has a pure frequency of 3315 cm\(^{-1}\). The peak shows a linear blue-shifting, which reaches saturation around \(x_{\text{DMSO}}=0.5\), and which gives a final stable frequency blue-shifted by 72 cm\(^{-1}\).

The CO torsional peak is the broad peak in the IR spectra at a pure frequency of 642 cm\(^{-1}\). It is linearly red-shifted between \(x_{\text{DMSO}}=0\) and \(x_{\text{DMSO}}=0.25\), at which point it levels off at a maximum red-shift of 26 cm\(^{-1}\) at a mole fraction of \(x_{\text{DMSO}}=0.4\). As DMSO concentration increases through equimolar, the peak frequency increases towards a new stable frequency at a red-shift of 11 cm\(^{-1}\) at \(x_{\text{DMSO}}=0.8\).

The asymmetric CSC stretching peak frequency is at a constant blue-shift of 6 cm\(^{-1}\) at \(x_{\text{DMSO}}\leq 0.2\). From \(x_{\text{DMSO}}=0.25\) to \(x_{\text{DMSO}}=0.7\), the blue-shift linearly decreases until the frequency is almost the same as the pure peak frequency. Above \(x_{\text{DMSO}}=0.7\), the frequency shifts slowly to that of the pure peak.

From \(x_{\text{DMSO}}=1\) to \(x_{\text{DMSO}}=0.1\), the CH\(_3\) peak blue-shifts with increasing alcohol concentration in a fairly linear manner to a maximum blue-shift of 6 cm\(^{-1}\) at \(x_{\text{DMSO}}<0.1\). At \(x_{\text{DMSO}}<0.1\), the peak frequency remains constant at its maximum.

**Discussion**

All of the systems show very similar behavior with only subtle differences, so the first suggestion that can be made is that the three systems all interact in a similar manner.

The observed blue-shifting of the OH stretching vibration upon DMSO addition can be accounted to the formation of HBs between the DMSO oxygen and the hydroxyl hydrogen. That the molecules associate as 1:1 dimers in equimolar solution is suggested by the observed saturation of the OH shift around \(x_{\text{DMSO}}=0.5\) in all of the systems. In other words, when alcohol is added incrementally to DMSO, each alcohol molecule forms a HB to a DMSO sulfoxide moiety until an equimolar mixture is reached. With further alcohol addition the DMSO-alcohol dimers are then solvated in an alcohol phase.

Clearly the formation of these new hydrogen bonds between the DMSO sulfoxide and alcohol hydroxyl groups is not the only significant interaction affecting the molecular vibrations. At low DMSO concentrations, when the DMSO oxygen is saturated with HBs, changes in the DMSO vibrations are still observed. The CH\(_3\) and CSC vibrations are blue-shifted from their frequency at
The stability of the CSC peak at high DMSO concentration suggests that some configuration may be causing resistance to changes in both the CO and the CSC vibrations at high DMSO concentration. The OH peak frequency remains more or less constant across the range from $x_{\text{DMSO}}=0.5$ to $x_{\text{DMSO}}=1$, so it can be concluded that this stabilization is not caused by a change in the DMSO-alcohol hydrogen bonding. Instead it is proposed that the stabilization of the CO and CSC peaks is caused by polar interactions. If polar interaction arise between $O_A$ and the positive center about S, the hydroxyl group will once again be fixed to some extent from both sides, limiting its movement and increasing the resistance to rotation.

What causes the stabilization of the peak frequency though? One of the models proposed for the pure structure of DMSO is parallel dipole alignment – head to tail chains forming linear or cyclic structures. Let us suppose that these chains do exist, and when an alcohol molecule is added to pure DMSO, it substitutes into the chain - forming an $O_D\cdot\cdot\cdot H_A-O_A$ hydrogen bond on one side; and a polar interaction between $O_A$ and the S atom of a free DMSO molecule on the other. As more alcohol molecules are added, they too will fit into a similar position in the superstructure until some critical concentration at which point the structure changes, which explains the stability of the CO peak at high DMSO concentrations. At the critical alcohol concentration, the alcohol molecules will disrupt the superstructure to the extent that chains start to fragment, and the molecules may begin to form 2:1 trimers of alcohol molecules engaged in hydrogen bonding and oxygen to sulfur polar interactions. Beyond $x_{\text{DMSO}}=0.66$, these structures would begin to be replaced by 1:1 hydrogen bonded dimers like those that exist in the equimolar mixture. This progression from chains to trimers to dimers would explain the observed red-shift with increasing alcohol concentration between $x_{\text{DMSO}}=0.8$ and $x_{\text{DMSO}}=0.4$.

From the DMSO perspective, substituting a DMSO for an alcohol molecule in the chain does not cause a major difference in electron density distribution in the DMSO molecules. Those DMSO molecules involved in the HB will lose electron density through $O_D$ while those involved in polar interactions will achieve an increase of electron density at S, much as they do in the pure structure. Therefore, if the alcohol substitutes into linear and cyclic chain structures, the charge redistribution effects of the HBs on the DMSO molecules will be minimized until there is a re-ordering of the superstructure. This can therefore explain the stability of the CSC peak at high DMSO concentration in terms of this model.

References