Hydrogen Bond Networks in Binary Mixtures of Water and Organic Solvent SI

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1 Spectra processing

1.1 Baseline correction

The raw experimental spectra are baseline corrected by subtracting an underground spectrum from the raw experimental spectrum. The underground spectrum is generated by fitting a spline function through points in the spectrum at which the Raman signal intensity, due to the absence of Raman peaks at these positions, is known to be zero. For further details we refer to reference.¹

1.2 Isolation of the OH stretching vibration

In the baseline corrected Raman spectra $S_{\text{mix}}^{\text{EXP}}$ of binary mixtures of water and organic solvent the CH stretching vibration of the organic solvent spectrally overlaps between 3000 cm$^{-1}$ and 3200 cm$^{-1}$ with the OH stretching vibration of water or of the alcohol. Therefore, we subtract according to equations (1) and (2) the CH signal from the mixture spectra. On this purpose the
mixture spectrum $S_{\text{mix}}(\bar{v}_S)$ is represented by a modelled mixture spectrum $S_{\text{mix,mod}}(\bar{v}_S)$ that, using a partial least squares minimization, is fitted to the experimental one $S_{\text{mix}}(\bar{v}_S)$. The modelled spectrum

$$S_{\text{mix,mod}}(\bar{v}_S) = S_{\text{mod}}^{CH1,4}(\bar{v}_S) + S_{\text{mod}}^{OH1,6}(\bar{v}_S),$$

is composed of 4 pseudo Voigt profile peaks $S_{\text{mod}}^{CH1,4}$ that represent the CH Raman signal (dotted orange in Figure S1) and of six Gaussian profile peaks $S_{\text{mod}}^{OH1,6}$ (dotted blue in Figure S1) that represent the OH stretching vibration of the alcohol and water. In order to obtain the isolated OH Raman spectrum of the mixture

$$S_{\text{mix}}^{OH}(\bar{v}_S) = S_{\text{mix}}(\bar{v}_S) - S_{\text{mod}}^{CH1,4}(\bar{v}_S),$$

we subtract the modelled $S_{\text{mod}}^{CH1,4}$ CH Raman signal from the mixture spectrum $S_{\text{mix}}$.

During the fitting procedure of the modelled spectrum to the experimental spectrum each of the four pseudo Voigt profile peaks for the CH Raman signal and the six Gaussian profile peaks for the OH Raman signal have certain degrees of freedom. Their central peak position can be fitted within certain ranges (Table S1), whereas the peak height and their width have no restraints.

Table S1: List of restraints for the peak centers for the fit of the four pseudo Voigt profile peaks for the CH Raman signal and the six Gaussian profile peaks for the OH Raman signal. For acetonitrile $S_{\text{mod}}^{CH1,4}$ has been replaced by the pure Acn CH spectrum peak, without fitting a model spectrum.

| Peak | Peak center / cm$^{-1}$ Methanol | Peak center / cm$^{-1}$ Ethanol |
|------|----------------------------------|----------------------------------|
| CH1  | 2550-2650                        | 2710-2730                        |
| CH2  | 2835-2845                        | 2870-2890                        |
| CH3  | 2942-2952                        | 2920-2940                        |
| CH4  | 2950-3050                        | 2960-2980                        |
| OH1  | 3165-3250                        |                                  |
| OH2  | 3250-3300                        |                                  |
| OH3  | 3320-3450                        |                                  |
| OH4  | 3450-3560                        |                                  |
| OH5  | 3560-3700                        |                                  |
| OH6  | 3700-3500                        |                                  |

Additionally the shape of the pseudo Voigt profile peaks can be fitted by varying the fractions of Gaussian and Lorentzian shares. Due to the many fit parameters the partial least squares
optimization algorithm requires quite some computational effort. The computational effort can be reduced, if the modelled CH Raman signal $S_{\text{mod}}^{\text{CH}}$, is once fitted to the pure compound spectrum of the organic solvent, as it is shown in Figure S1, and then considered as fixed peak assemble, where all fit parameters except the intensity of the peak assemble are kept constant.

Figure S1: Raman spectra of pure methanol (a) and pure ethanol (b) at 0.4 MPa and 308 K (bold black line) with the partial least square fit of 4 pseudo Voigt profiles for the CH stretching vibration (dotted orange lines) and 6 Gaussian profiles for the OH stretching vibration (dotted blue lines). The green line shows the sum of the four pseudo Voigt profile peaks. Grey line: difference between the best fit and the pure compound spectra.

Figure S2 shows the isolated OH Raman spectra $S_{\text{mix}}^{\text{OH}}(\tilde{\nu}_S)$ of the three analyzed mixtures of water and organic solvent for mixture compositions between pure water and pure organic solvent. The up-and-down course of the spectra $S_{\text{mix}}^{\text{OH}}(\tilde{\nu}_S)$ at the left margin of the Raman-shift scale is an artifact of the subtraction of the CH-Raman signal according to equation (2) above. This range of Raman shifts is not considered for the computation of the centroid of the OH Raman signal.
**Figure S2**: Isolated OH Raman spectra of the mixture \( s_{\text{mix}}^{OH}(\bar{\nu}_S) \) for the mixtures a) water/methanol, b) water/ethanol and c) water/acetonitrile at 0.4 MPa and 308 K over the whole composition range. Pure water spectra show the largest intensity. The small black oval in (c) marks minimal negative intensity values resulting from the acetonitrile subtraction. We will discuss this at the calculation of the molar spectra where this effect becomes more visible. The mixture compositions for all Raman spectra are listed in Table S2.

1.3 Computation of molar Raman spectra

The Raman spectra \( s_{\text{mix}}^{OH}(\bar{\nu}_S) \) are converted into molar Raman spectra \( s_{\text{mix}}^{OH}(\bar{\nu}_S) \) by multiplication with the molar volume of the mixture \( v_m^{\text{mix}} \). The molar volume of each mixture

\[
v_m^{\text{mix}} = \frac{M_{\text{mix}}}{\rho_{\text{mix}}} = \frac{x_1M_1^0 + x_2M_2^0}{\rho_{\text{mix}}} \tag{4}\]

is computed from the density of the mixture \( \rho_{\text{mix}} \) which is determined with the Coriolis densitometer, the respective molar fractions \( x_i \) of the compounds in the mixture, which are known from the amounts of the compounds fed via the syringe pumps, and their molar masses \( M \). The molar Raman spectra \( s_{\text{mix}}^{OH}(\bar{\nu}_S) \) of mixtures water/organic solvent are presented in Figure S3. The centroid is computed from portion of \( s_{\text{mix}}^{OH} \) inside the blue background rectangle.
Figure S3: Molar OH Raman spectra $s^{OH}_{mix}(\tilde{v}_S)$ of the mixtures a) water/methanol, b) water/ethanol and c) water/acetonitrile at 0.4 MPa and 308 K over the whole composition range. The blue background illustrates the area from which the centroid is calculated. The small black oval in (c) marks minimal negative intensity values resulting from the acetonitrile subtraction. The mixture compositions for the all Raman spectra are listed in Table S2.

1.4 Computation of partial molar spectra

The partial molar Raman spectra of compound $i$ in the mixture with compound $j$

$$s^{OH}_{i(j)}(\tilde{v}_S) = s^{OH}_{mix}(\tilde{v}_S) + (1 - x_i) \left( \frac{\partial s^{OH}_{mix}(\tilde{v}_S)}{\partial x_i} \right)_{T,p}$$

(5)

and of compound $j$ in the mixture with compound $i$

$$s^{OH}_{j(i)}(\tilde{v}_S) = s^{OH}_{mix}(\tilde{v}_S) - x_i \left( \frac{\partial s^{OH}_{mix}(\tilde{v}_S)}{\partial x_i} \right)_{T,p}$$

(6)

are computed from the molar mixture spectra $s^{OH}_{mix}(\tilde{v}_S)$ in accordance to the computation of thermodynamic partial molar properties. In order to achieve an accurate description of the derivatives $\left( \frac{\partial s^{OH}_{mix}(\tilde{v}_S)}{\partial x_i} \right)_{T,p}$, high quality Raman spectra have to be recorded in rather small increments with respect to the composition $x_i$. 
In practice, we apply equation (5) and (6) pixel by pixel or Raman shift by Raman shift. For example, for a Raman shift of 3300 cm\(^{-1}\) the evolution of signal intensity \(s_{\text{OH}}^{\text{mix}}(3300)\) is considered as a function of the mixture composition and thereafter derived. Once this has been done for each pixel or for each Raman shift, the partial molar Raman spectrum can be reassembled for all Raman shifts.

Figure S4 shows in the upper row partial molar Raman spectra of water and in the bottom row the partial molar Raman spectra of the organic solvent.

![Graphs of partial molar OH Raman spectra](image)

Figure S4: Partial molar OH Raman spectra of the three analyzed mixtures water/methanol, water/ethanol and water/acetonitrile (left to right) at 0.4 MPa, 308 K and different water molar fractions. The upper row presents the partial molar spectra of water and the lower row the ones of the organic solvents. The blue background illustrates the area from which the centroid is calculated.

Negative intensity values within the partial molar Raman spectra are meaningful. They imply that for example the addition of acetonitrile to the mixture with water causes a reduction of the molar OH Raman spectrum \(s_{\text{mix}}^{\text{OH}}(\nu_S)\) at Raman shifts, where \(s_{\text{Acn}(W)}^{\text{OH}}(\nu_S)\) is negative and an increase where \(s_{\text{Acn}(W)}^{\text{OH}}(\nu_S)\) is positive.
## Analyzed mixture compositions and densities

Table S2: List of all investigated compositions and measured densities for the three binary mixtures W/Acn, W/MeOH and W/EtOH

| $\dot{V}_{\text{Acn}}$ / µl min⁻¹ | $\dot{V}_{W}$ / µl min⁻¹ | $x_{\text{Acn}}$ | $x_{W}$ | $\rho_{\text{mix}}^{308K}$ / kg m⁻³ | $\rho_{\text{mix}}^{318K}$ / kg m⁻³ | $\rho_{\text{mix}}^{328K}$ / kg m⁻³ |
|---------------------|---------------------|-----------------|----------|-------------------------------------|-------------------------------------|-------------------------------------|
| 0                   | 200                 | 0.00            | 1.00     | 999                                 | 998                                 | 997                                 |
| 11                  | 190                 | 0.02            | 0.98     | 990                                 | 988                                 | 990                                 |
| 22                  | 180                 | 0.04            | 0.96     | 985                                 | 980                                 | 980                                 |
| 31                  | 168                 | 0.06            | 0.94     | 977                                 | 972                                 | 968                                 |
| 41                  | 162                 | 0.08            | 0.92     | 968                                 | 963                                 | 959                                 |
| 50                  | 155                 | 0.10            | 0.90     | 957                                 | 953                                 | 951                                 |
| 58                  | 147                 | 0.12            | 0.88     | 951                                 | 946                                 | 940                                 |
| 67                  | 142                 | 0.14            | 0.86     | 944                                 | 937                                 | 935                                 |
| 72                  | 130                 | 0.16            | 0.84     | 936                                 | 929                                 | 927                                 |
| 77                  | 121                 | 0.18            | 0.82     | 927                                 | 921                                 | 918                                 |
| 84                  | 116                 | 0.20            | 0.80     | 919                                 | 914                                 | 908                                 |
| 112                 | 90                  | 0.30            | 0.70     | 887                                 | 880                                 | 874                                 |
| 128                 | 66                  | 0.40            | 0.60     | 861                                 | 853                                 | 847                                 |
| 145                 | 50                  | 0.50            | 0.50     | 838                                 | 830                                 | 823                                 |
| 161                 | 37                  | 0.60            | 0.40     | 819                                 | 811                                 | 804                                 |
| 176                 | 26                  | 0.70            | 0.30     | 803                                 | 794                                 | 787                                 |
| 186                 | 16                  | 0.80            | 0.20     | 789                                 | 780                                 | 773                                 |
| 195                 | 15                  | 0.82            | 0.18     | 786                                 | 778                                 | 771                                 |
| 200                 | 13                  | 0.84            | 0.16     | 784                                 | 775                                 | 768                                 |
| 200                 | 11                  | 0.86            | 0.14     | 781                                 | 773                                 | 766                                 |
| 170                 | 8                   | 0.88            | 0.12     | 779                                 | 771                                 | 764                                 |
| 182                 | 7                   | 0.90            | 0.10     | 777                                 | 769                                 | 762                                 |
| 210                 | 6                   | 0.92            | 0.08     | 774                                 | 766                                 | 758                                 |
| 190                 | 4                   | 0.94            | 0.06     | 773                                 | 764                                 | 756                                 |
| 230                 | 3                   | 0.96            | 0.04     | 771                                 | 762                                 | 754                                 |
| 230                 | 2                   | 0.98            | 0.02     | 769                                 | 761                                 | 753                                 |
| 200                 | 0                   | 1.00            | 0.00     | 768                                 | 759                                 | 752                                 |

| $\dot{V}_{\text{MeOH}}$ / µl min⁻¹ | $\dot{V}_{W}$ / µl min⁻¹ | $x_{\text{MeOH}}$ | $x_{W}$ | $\rho_{\text{mix}}^{308K}$ / kg m⁻³ | $\rho_{\text{mix}}^{318K}$ / kg m⁻³ | $\rho_{\text{mix}}^{328K}$ / kg m⁻³ |
|----------------------------------|---------------------|-----------------|----------|-------------------------------------|-------------------------------------|-------------------------------------|
| 0                                | 200                 | 0.00            | 1.00     | 999                                 | 998                                 | 997                                 |
| 9                                | 200                 | 0.02            | 0.98     | 991                                 | 991                                 | 990                                 |
| 18                               | 190                 | 0.04            | 0.96     | 985                                 | 985                                 | 984                                 |
| \( \dot{V}_{\text{E}} \) / µl min\(^{-1} \) | \( \dot{V}_{W} \) / µl min\(^{-1} \) | \( x_{\text{E}} \) | \( x_{W} \) | \( \rho_{\text{mix}}^{30\text{K}} \) / kg m\(^{-3} \) | \( \rho_{\text{mix}}^{31\text{K}} \) / kg m\(^{-3} \) | \( \rho_{\text{mix}}^{32\text{K}} \) / kg m\(^{-3} \) |
|---|---|---|---|---|---|---|
| 0  | 200  | 0.00 | 1.00 |    |    |    |
| 12 | 185  | 0.02 | 0.98 |    |    |    |
| 24 | 180  | 0.04 | 0.96 |    |    |    |
| 34 | 165  | 0.06 | 0.94 |    |    |    |
| 45 | 160  | 0.08 | 0.92 |    |    |    |
| 53 | 148  | 0.10 | 0.90 |    |    |    |
| 61 | 138  | 0.12 | 0.88 |    |    |    |
| 67 | 127  | 0.14 | 0.86 |    |    |    |
| 75 | 122  | 0.16 | 0.84 |    |    |    |
| 82 | 115  | 0.18 | 0.82 |    |    |    |
| 90 | 111  | 0.20 | 0.80 |    |    |    |
| 115 | 83  | 0.30 | 0.70 |    |    |    |
| 138 | 64  | 0.40 | 0.60 |    |    |    |
| 152 | 47  | 0.50 | 0.50 |    |    |    |

water / ethanol
|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 165| 34 | 0.60| 0.40| 833| 826| 821|
| 174| 23 | 0.70| 0.30| 816| 810| 805|
| 194| 15 | 0.80| 0.20| 802| 796| 790|
| 192| 13 | 0.82| 0.18| 799| 793| 788|
| 187| 11 | 0.84| 0.16| 797| 791| 785|
| 199| 10 | 0.86| 0.14| 794| 788| 782|
| 190| 8  | 0.88| 0.12| 792| 786| 780|
| 204| 7  | 0.90| 0.10| 790| 782| 778|
| 186| 5  | 0.92| 0.08| 787| 780| 775|
| 203| 4  | 0.94| 0.06| 784| 779| 772|
| 233| 3  | 0.96| 0.04| 781| 774| 770|
| 159| 1  | 0.98| 0.02| 779| 772| 768|
| 200| 0  | 1.00| 0.00| 777| 771| 766|
3 References

(1) Pelletier, M. J. Quantitative analysis using Raman spectrometry. Appl. Spectrosc. 2003, 57, 20A-42A, DOI: 10.1366/000370203321165133.

(2) Gmehling, J.; Kolbe, B.; Kleiber, M.; Rarey, J. R. Chemical thermodynamics for process simulation; Wiley-VCH-Verl.: Weinheim, 2012.