# Supporting Information

## Surfactant-free CO$_2$-based microemulsion

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1. **Dissolution of ibuprofen in water/acetone/CO$_2$ at high pressures and constant temperature.**

The dissolution of ibuprofen in the ternary system composed of water/acetone/compressed CO$_2$ was performed in a home-made high-pressure phase analyzer, that was described before in detail.[1]. The variation of the cell volume is performed by means of a stainless-steel piston introduced into the view cell and moved by a pneumatic system (CP). In this way the volume of the cell can be varied from 50 ml to 75 ml.

Ibuprofen was chosen as a hydrophobic and CO$_2$-phobic compound. The variable volume cell was charged initially with a solution of ibuprofen in acetone. Then, water is added to the cell which provokes the precipitation of ibuprofen due to the very poor solubility of the drug in water. The masses added to the cell of the ibuprofen solution in acetone and of water are already calculated in order to keep an equimolar relationship of water and acetone and to reach 10MPa at the beginning of the experiment. The mixture is mixed for 30 min to reach thermodynamic equilibrium. At this point, the addition of CO$_2$ starts. The addition is performed at a very low flow and keeping constant the pressure (10MPa) and the temperature(308K) inside the variable volume cell, therefore increasing the volume of the cell. The addition is stopped when a single transparent homogeneous phase is observed inside the cell.

2. **Extraction of R$_{OH}$ from the acquired Raman spectra.**

Figure S1 shows the method to extract R$_{OH}$ from the acquired already baseline corrected Raman spectra. The baseline correction, which is not implemented in Figure S1, is based on a subtraction of a spline polynomial of order 4 fitted to node points, at which the mixture does not feature Raman signals. The baseline correction as well as the wavenumber positions of the node points are described elsewhere.[2]

The baseline corrected Raman spectrum of a mixture composed of water, acetone and CO$_2$ contains spectral information from all of the constituents of the mixture, which spectrally overlap. Therefore the OH stretch vibration of liquid water (this is the band we consider later for the computation of R$_{OH}$) has to be isolated from the spectrally overlapping CH stretch vibration of the acetone. To achieve an optimum "isolation" we deconvolute the Raman spectrum of the mixture into isolated contributions of the Raman signal of CO$_2$, acetone and water. The deconvolution procedure is described in detail elsewhere.[3] Here it should be mentioned, that for the deconvolution of the mixture spectrum we replace the CO$_2$ Raman signal by two Voigt profile peaks, the water OH stretch vibration of water by five Guassian peaks, the water bend vibration by two Gaussian peaks, and the acetone spectrum by the acquired raw spectrum of pure acetone. After the deconvolution procedure the contribution of acetone to the mixture spectrum can be eliminated by subtracting the corresponding weighted acetone Raman spectrum. Finally the OH stretch vibration appears isolated and is split into the low (3050-3450 cm$^{-1}$) and the high (3450-3850 cm$^{-1}$) wavenumber regions, whose integrals are the Raman intensity of the hydrogen-bonded, I$_b$, and non-hydrogen-bonded, I$_{nb}$, molecules, respectively (also see the communication).

Isolated OH stretch vibration Raman bands are shown for different mixture compositions in Figure S1. The ratio $R_{OH}$ is computed from $I_b/I_{nb}$.
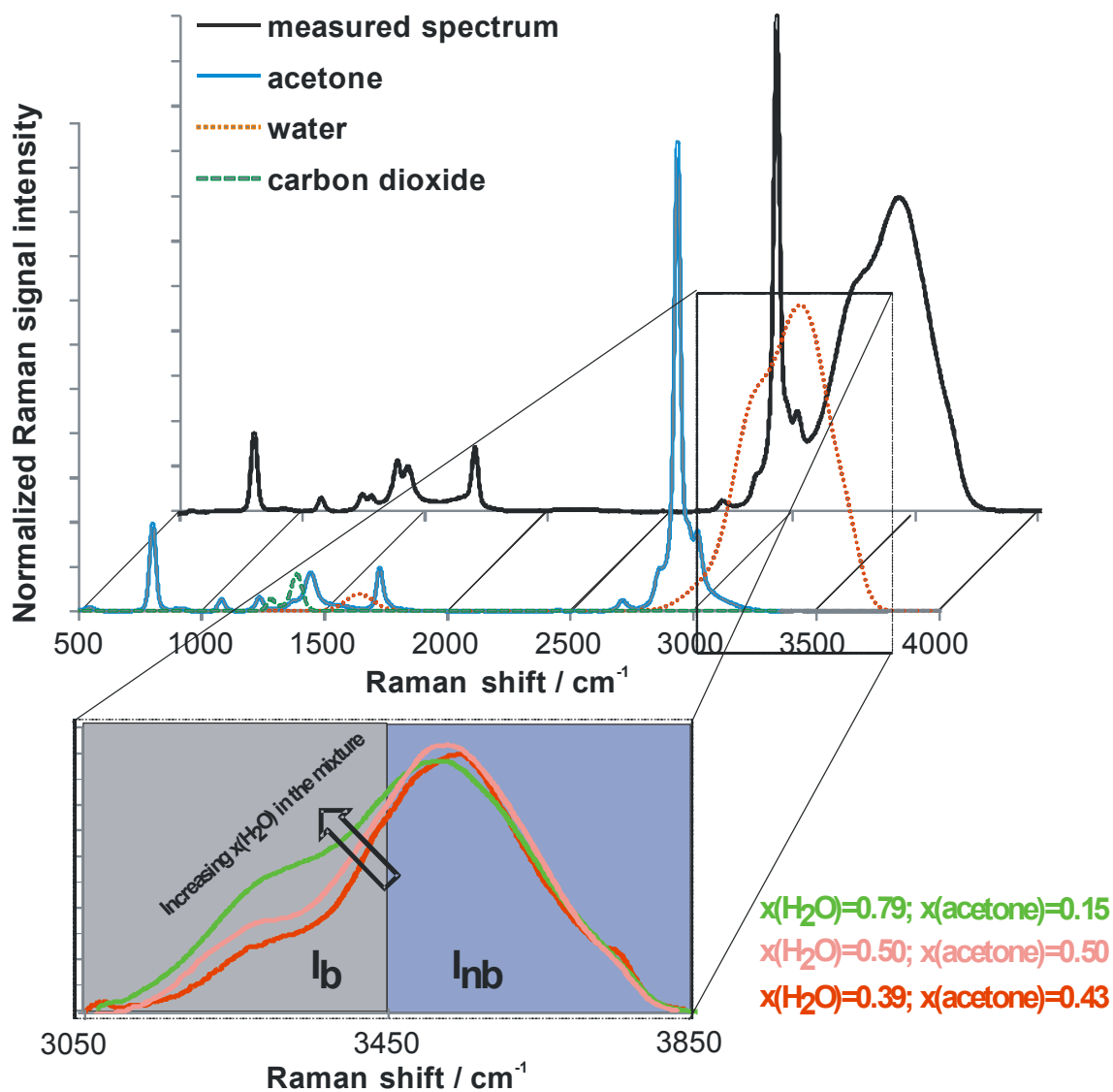


**Figure S1: Illustration how the ratio $R_{OH}$ of the non-bonded $I_{nb}$ and the bonded $I_b$ Raman signals of water are computed from the Raman spectrum of the mixture composed of water, acetone and $CO_2$.**

(1)      Temelli, F.; Córdoba, A.; Elizondo, E.; Cano-Sarabia, M.; Veciana, J.; Ventosa, N. *J. Supercrit. Fluids* **2012**, *63*, 59.

(2)      Luther, S. K.; Schuster, J. J.; Leipertz, A.; Braeuer, A. *J. Supercrit. Fluids* **2013**, *84*, 146.

(3)      Schuster, J. J.; Will, S.; Leipertz, A.; Braeuer, A. *J. Raman Spectrosc.* (Accepted for publication).