Increased rate of solvent diffusion in a prototypical supramolecular gel measured on the picosecond timescale

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Electronic Supporting Information

Sample preparation

The gels and solvent mixtures for all measurements were prepared following the same procedure to ensure comparability. The mixed solvent was produced by individually measuring 7 parts of water and 3 parts of ethanol by volume and shaking these in a vial until complete mixing had occurred. An amount of 0.006 g (0.3% *w/v*) or 0.010 g (0.5% *w/v*) of gelator **1** was weighed accurately into a vial and 2.0 ml of the solvent mixture was added. The generated suspension was subsequently heated with a heat gun until boiling of the solvent in the tightly closed vial. Upon boiling, most of the gelator went into solution. Larger particles were dispersed by sonication and subsequently dissolved by further heating. Once a clear solution was prepared, the gels were either transferred hot into the respective pre-heated sample holders or allowed to cool in the vial for the gels to set. All gel samples were stored at room temperature for 30 minutes before measurements commenced to allow for the development of the fibrous gel network. All reference solvent samples were produced using the same heating/sonication regime and hot transfer into sample holders to account for solvent evaporation and potential change in the solvent ratio occurring in the gel samples.

Quasi-elastic neutron scattering (QENS)

QENS spectroscopy measures the inelastic interaction between the neutron radiation and the sample, during which very small energy transfers give information about the diffusion of molecules. QENS data were measured on LET (ISIS, UK)[1] at incident neutron energies of 0.74, 1.38 and 3.4 meV. Complementary experiments were carried out on the time-of-flight spectrometer IN6 at the Institut Laue-Langevin, Grenoble, France (see ESI). The reduced spectra were fitted by $R(q,\omega) \otimes S(q,\omega)$ (wherein R is the spectrometer resolution function, S is the scattering function of the sample, q the absolute value of the momentum transfer and ω

the energy transfer encountered by the scattered neutron) without imposing any q-dependence using the model established for pure water (H_2O),[2] being implemented as:

$$S(q,\omega) = a_1(q)\frac{1}{\sigma_1(q)^2 + \omega^2} + a_2(q)\frac{1}{[\sigma_1(q) + \sigma_2(q)]^2 + \omega^2} \tag{1}$$

In equation 1, $\sigma_1(q)$ and $\sigma_2(q)$ are scalar fit parameters, of which σ_1 can be associated with the apparent centre-of-mass diffusion of both the water and ethanol solvent molecules, and accounts for both rotational and translational motions, which are difficult to decouple at the elevated temperatures explored in this study.[3] The variable σ_2 can be attributed to faster motions at the limit of the accessible energy window.[2] Attempts to further extend the model to account for the different populations, namely water and ethanol separately, led to inconclusive results and unsatisfactory fits. Therefore, the single linewidth σ_1 accounts for the combined contributions from the different solvent molecules. The factor $\sigma_2 \gg \sigma_1$ accounts for an apparent background due to vibrational contributions and is disregarded in the further analysis.[2]

The resulting σ_1(q) was fitted by a jump-diffusion model[2] defining the self-diffusion coefficient D and residence time τ:

$$\sigma_1(q) = \frac{Dq^2}{1 + Dq^2\tau} \tag{2}$$

QENS experiments were carried out with the following experimental setup on two different neutron spectrometer: LET at ISIS, Didcot, UK and IN6 at the Institut Laue-Langevin, Grenoble, France.

LET: The experiments have been carried out on the cold neutron chopper spectrometer LET[1] at the pulsed neutron source of the ISIS facility at the Rutherford Appleton Laboratory. The samples were filled in double-walled cylindrical aluminium sample holders and sealed against vacuum. The samples were held in a closed-cycle cryostat inside the neutron spectrometer during the data acquisition. The temperature was controlled to better than ±0.01 K using local resistance heating on the sample holders.

The instrument setup allowed recording of data quasi-simultaneously at three different incident energies, namely 0.74, 1.38, and 3.4 meV. At the lower energies, the scattering signal is weaker due to the wavelength-dependent source flux, such that the minute differences in the scattering signal from the gels and pure solvents, respectively, can only be discerned with sufficiently small statistical errors in the data recorded at 3.4 meV. The background was measured by recording the scattering signal from an empty sample cell, but found to be negligibly weak compared to the scattering from the sample solvents and gels at 3.4 meV incident energy.

The data reduction was carried out using python scripts provided by the LET instrument team. The accessible scattering vector range was binned into equidistant q-slices with width $\Delta q = 0.1$ Å^{-1}. The spectrometer resolution function $R(q,\omega)$ was measured using vanadium foil as a sample and modelled by fitting a sum of four Gaussian functions and a constant background to the measured signal.

IN6: Time-of-flight spectra were recorded on the spectrometer IN6 at the ILL using the incident wavelength $\lambda = 5.1$ Å ($E = 3.13$ meV). The IN6 data were reduced and interpolated to a (q,ω)-grid using the lamp software provided by the ILL. The fits were carried out analogously to the LET data at 1.38 meV incident energy using equation 1 and subsequently equation 2 for the resulting linewidths. The samples on IN6 were filled in cylindrical aluminium sample holders similar (but not identical) to those employed on LET, and inserted in a liquid helium-cooled cryostat on IN6. Example spectra from IN6 and fits are depicted in Figure S2, and the fits of the jump diffusion model (equation 2) to the resulting widths $\sigma_1 =$

$\sigma_1(q)$ are plotted in Figure S3. The obtained diffusion coefficients are summarized in Table S2.

Table S1 Summary of fit results for the diffusion coefficients D and residence times τ (equation 2) for various samples and temperatures as measured by QENS on the instrument LET (ISIS neutron source, UK) and fitted using a jump diffusion model. Some samples were prepared more than once to check the reproducibility of the sample preparation. The errors denote the 95% confidence limits from the fits of equation 2. Gels were made using 7:3 (*v*/*v*) water:ethanol as the solvent with gelator **1** at different *w*/*v* percentages. Reference solvent samples were 7:3 (*v*/*v*) water:ethanol mixtures.

Sample	T [K]	D [10^{-9} m^2 s^{-1}]	2σ on D	τ [ps]	2σ on τ
Solvent	275	0.527	0.059	3.826	1.093
Gel 0.3%	275	0.604	0.043	3.026	0.597
		0.598	0.058	3.541	0.839
Gel 0.5%	275	0.576	0.061	3.512	0.943
		0.577	0.057	3.604	0.891
Solvent	285	0.741	0.049	2.307	0.453
		0.730	0.050	2.319	0.476
Gel 0.3%	285	0.872	0.050	2.078	0.334
		0.857	0.068	2.407	0.478
Gel 0.5%	285	0.824	0.062	2.268	0.470
Solvent	295	1.098	0.025	1.548	0.105
		1.115	0.068	1.674	0.281
Gel 0.3%	295	1.220	0.059	1.594	0.204
		1.206	0.065	1.818	0.232
Gel 0.5%	295	1.163	0.064	1.726	0.243
		1.144	0.056	1.761	0.223
Solvent	305	1.500	0.068	1.311	0.155
Gel 0.3%	305	1.663	0.080	1.314	0.151
Gel 0.5%	305	1.602	0.068	1.456	0.139

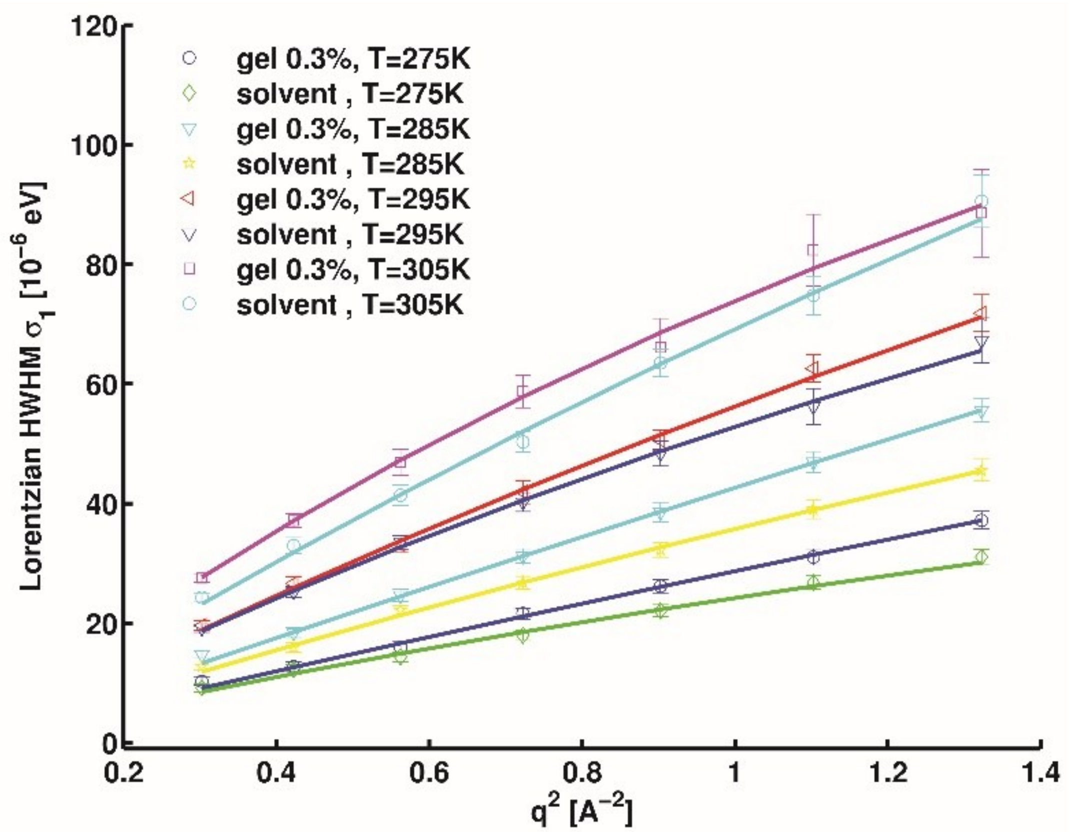

Figure S1 Lorentzian linewidth σ_1 fitted to the spectra recorded on LET using the incident neutron energy 3.4 meV corresponding to the averaged solvent centre-of-mass self-diffusion for a pure solvent and a gel, respectively, at different temperatures (symbols), and fit of the jump diffusion model (lines). Gels were made using 7:3 (*v*/*v*) water:ethanol as the solvent with gelator **1** at different *w*/*v* percentages. Reference solvent samples were 7:3 (*v*/*v*) water:ethanol mixtures.

Table S2 Summary of fit results of the spectra recorded on IN6 at 3.13 meV incidence energy for the diffusion coefficients D and residence times τ for various samples and temperatures. The errors denote the 95% confidence limits from the fits of equation 2. Gels were made using 7:3 (*v*/*v*) water:ethanol as the solvent with gelator **1** at different *w*/*v* percentages. Reference solvent samples were 7:3 (*v*/*v*) water:ethanol mixtures.

Sample	T [K]	D [10^{-9} m^2/s]	2σ on D	τ [ps]	2σ on τ
Solvent	276	0.977	0.188	3.989	0.905
Gel 0.3%	276	1.029	0.264	3.946	1.150
Solvent	295	1.306	0.140	1.635	0.347
Gel 0.3%	295	1.368	0.059	1.544	0.133
Solvent	310	1.702	0.145	0.665	0.202
Gel 0.3%	310	1.782	0.085	0.552	0.107

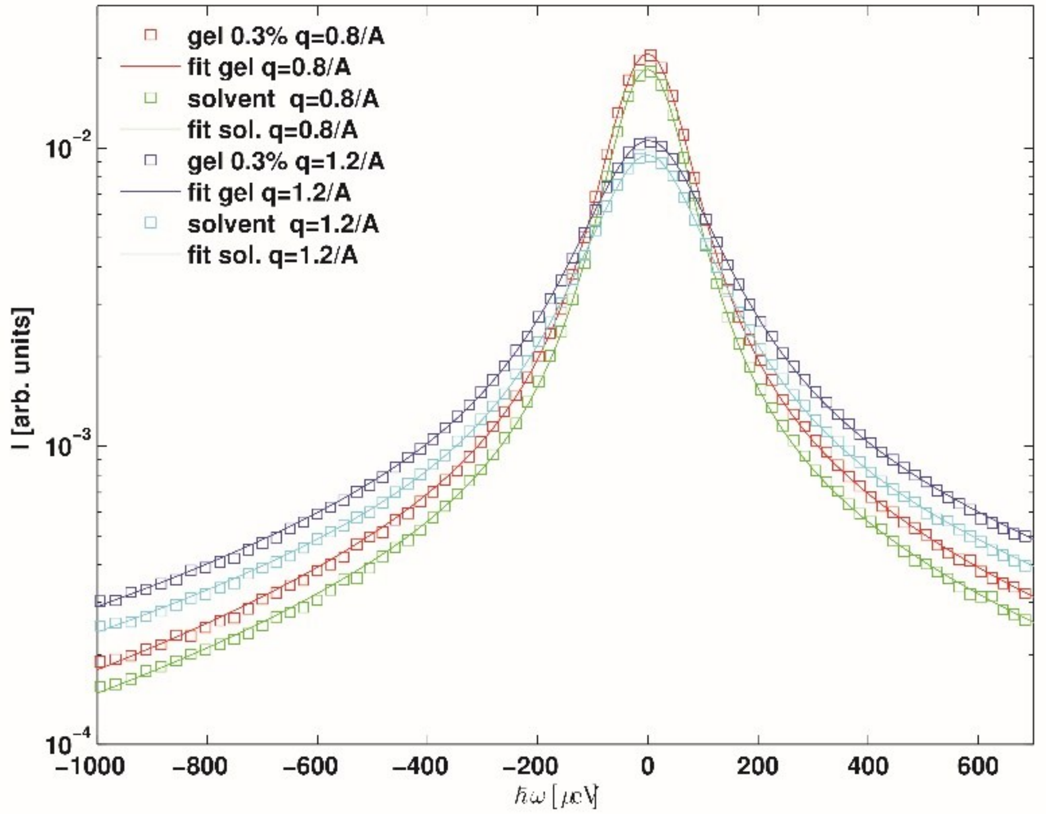

Figure S2 Example data (symbols) recorded on IN6 (ILL, France) on a supramolecular gel using a 7:3 (*v*/*v*) water:ethanol solvent with 0.3% *w*/*v* gelator **1** at $T = 295$ K, and the corresponding pure solvent, for different values of the scattering vector q using the incident neutron energy 3.13 meV. The solid lines denote fits by equation (1) (main article) convoluted with the spectrometer resolution.

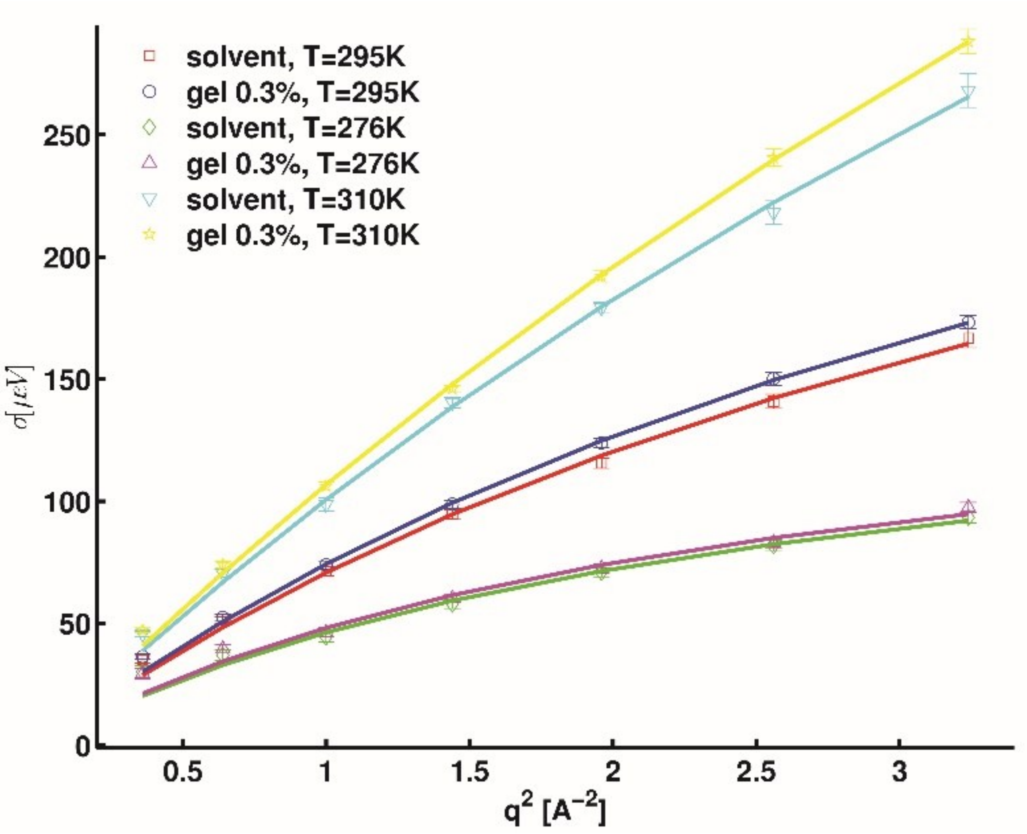

Figure S3 Lorentzian linewidth σ_1 fitted to the spectra recorded on IN6 using the incident neutron energy 3.13 meV corresponding to the averaged solvent centre-of-mass self-diffusion for a pure solvent and a gel, respectively, at different temperatures (symbols), and fit of the jump diffusion model (lines). Gels were made using 7:3 (*v*/*v*) water:ethanol as the solvent with gelator **1** at different *w*/*v* percentages. Reference solvent samples were 7:3 (*v*/*v*) water:ethanol mixtures.

Rheometry

Rheometry experiments were performed using a TA Instruments AR 2000 on a rough Peltier plate with a 25 mm rough-plate geometry and 2.5 mm gap. Gelator solutions were prepared by boiling in sealed 7 ml vials, and were immediately poured into a 25 mm diameter cylindrical glass mould on the Peltier plate. The gels were left to stand at 22 °C for 30 minutes before removing the mould and beginning the analysis.

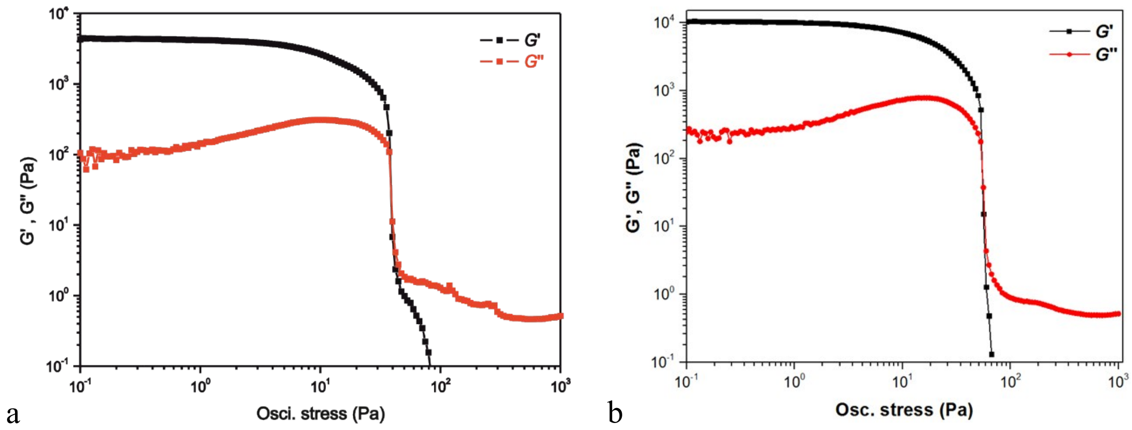

Figure S4 Stress-sweep oscillatory shear rheometry data for a gel of a) 0.3% *w/v* and b) 0.5% *w/v* gelator **1** in 7:3 *v/v* water/ethanol.

Powder X-ray diffraction

Gels for PXRD were prepared by sonicating and boiling gelator solutions in sealed 7 ml vials and leaving the materials to stand at room temperature (approximately 20 °C) for 2 h. Excess solvent was removed by applying filter paper to the gels, but samples were not otherwise dried prior to analysis. Experiments were performed at 20 °C using a PANalytical Empyrean diffractometer fitted with a copper tube operated at 40 kV and 40 mA (wavelength λ = 1.5419 Å). A 1/8° fixed divergence slit, 1/4° antiscatter slit and 10 mm mask were mounted in the primary beam path, and a Ni filter and 7.5 mm antiscatter slit in the diffracted beam. A set of 0.04 rad axial Soller slits were used in both beam paths. Detection was performed with a PIXcel (PANalytical) 1D scanning line detector with 255 active channels. Scans were conducted over a 2Θ range of 2 - 40° with a step size of 0.02626° and a scan speed of 0.0112° s^{-1}.

Scanning electron microscopy

Gels for SEM analysis were prepared by sonicating and boiling gelator solutions in sealed 7 ml vials and leaving the materials to stand at room temperature for 2 h. Samples were deposited on silicon wafers, dried in air for 6 h, and coated with 2 nm of platinum using a Cressington 328 Ultra High-resolution EM Coating System. The images were obtained using an FEI Helios NanoLab DualBeam microscope in immersion mode, with beam settings of 1.5 kV and 0.17 nA.

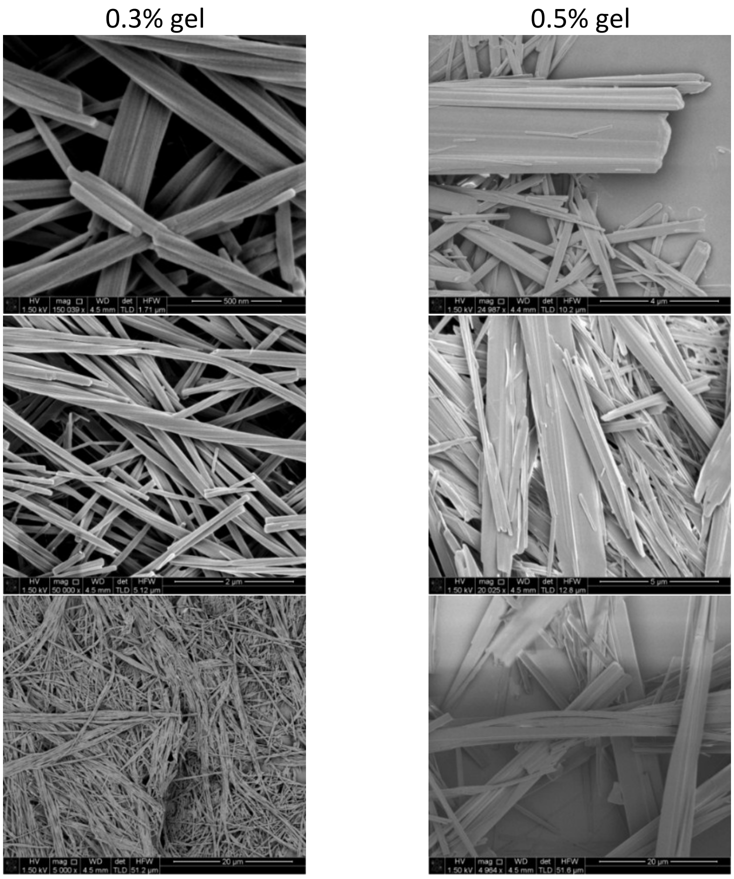

Figure S5 Scanning electron micrographs of the 0.3% gel (left column) and the 0.5% gel (right column) of gelator **1** at different magnifications. Gels were made using 7:3 (*v*/*v*) water:ethanol as the solvent

Nuclear magnetic resonance measurements

A 600 MHz Varian spectrometer equipped with an Agilent OneNMR Probe able to deliver a maximum pulsed field gradient of 62 G cm^{-1} was used to acquire ^1H Diffusion-Ordered SpectroscopY (DOSY) experiments using the Oneshot45 pulse sequence.[4] 20 gradient pulse amplitudes ranging from 9.75 to 52.65 G cm^{-1} in equal steps of gradient squared were used 4 transients, 128 dummy scans and 32768 complex data points covering 4.6 kHz were used. The diffusion-encoding pulsed gradient duration was 1.5 ms. The diffusion time was 100 ms. The gradient stabilisation delay was 2 ms. The repetition time was 4.5 s, of which 3.5 s comprised the acquisition time. The angle of the first radiofrequency pulse was changed from 90˚ to 40˚ to avoid saturating the receiver. The samples were prepared following the general procedure, but 10% of the water was exchanged for D_2O to allow the spectrometer to lock. A total of 22 experiments were run waiting 20 min between experiments. The results were analysed using mono-exponential fittings.

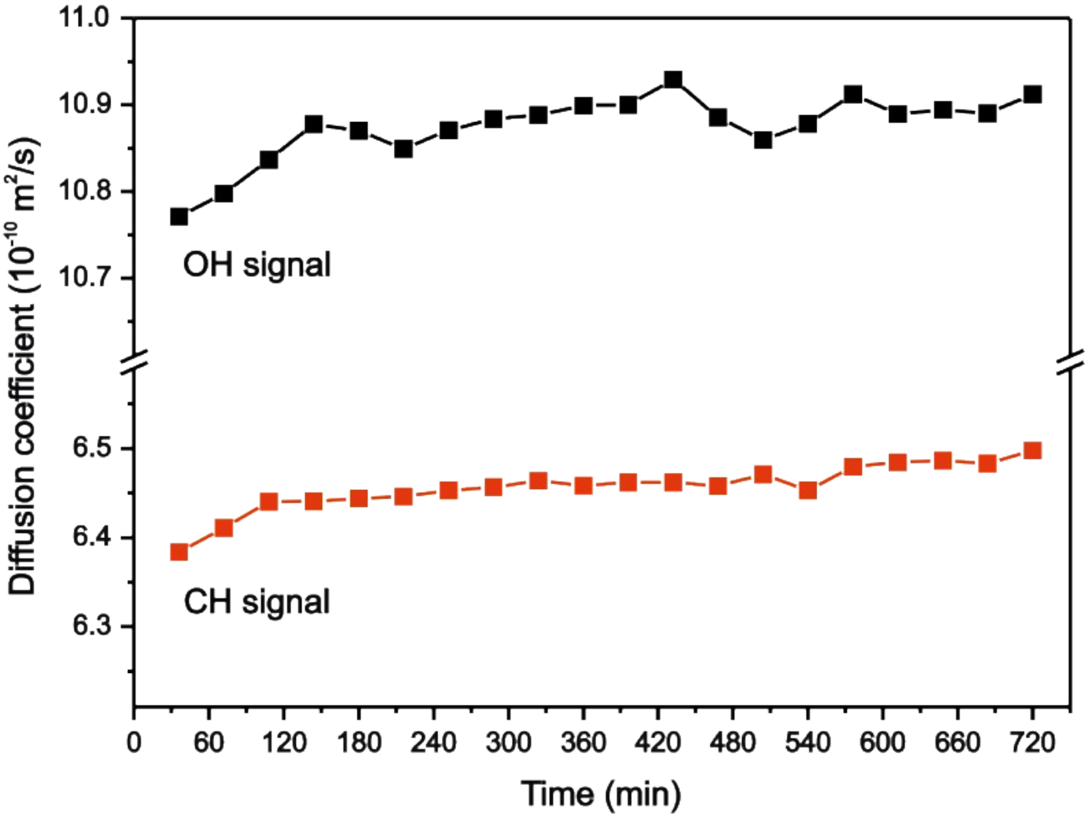

Figure S6. ^{1}H-DOSY NMR spectroscopy on the solvent mixture 7:3 (*v*/*v*) water:ethanol. The figure shows the estimated diffusion coefficients of the ethanol-CH protons (red) as well as those of the combined ethanol and water OH protons (black). The diffusion coefficients were measured periodically to be able to discard experimental errors caused by the drift of the magnetic field (shim drift).

Z-spectroscopy[5]

Z-spectra were acquired using a 600 MHz Varian spectrometer equipped with an Agilent OneNMR Probe able to deliver a maximum pulsed field gradient of 62 G cm^{-1}. 100 experiments were acquired varying the frequency of the saturation pulse to cover 50 kHz either side of the water signal. One scan per saturation frequency was collected comprising 65536 complex data points covering a spectral width of 12.6 kHz. The repetition time was 4.3 s, of which 1.3 s comprised the acquisition time and 3.0 s the saturation pulse. The saturation pulse strength ($\gamma B_1/2\pi$) was 156 Hz. A pulsed field gradient of 6 G cm^{-1} (0.5 ms) was used to eliminate any signal produced by the saturation pulse. 16 dummy scans were used. The results are shown in Figures S7 and 8.

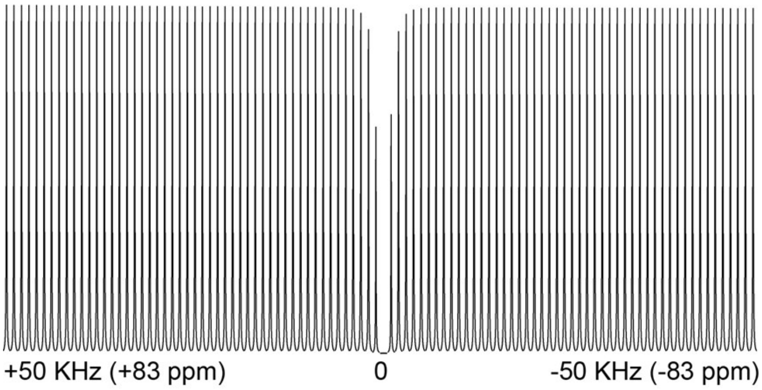

Figure S7. Z-spectroscopy spectra of ethanol in a 0.3% (*w*/*v*) gel. The figure represents the water signal versus the frequency of the saturation pulse. No indications of saturation are seen other than when the frequency of the pulse is close to the frequency of the water signal. The gel was made using 7:3 (*v*/*v*) water:ethanol as the solvent with gelator **1**.

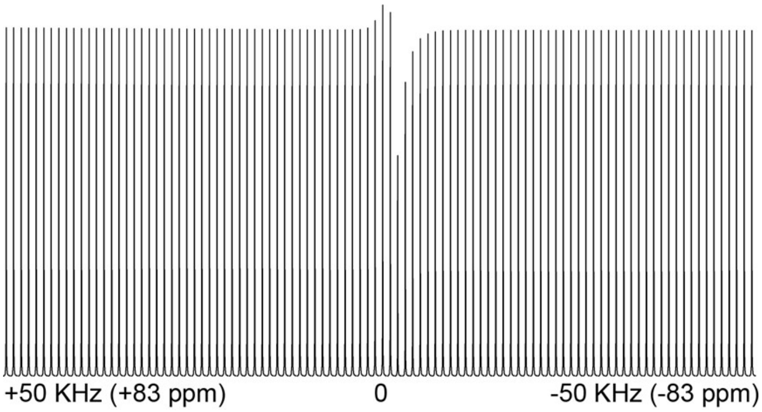

Figure S8. Z-spectroscopy spectra of ethanol in a 0.3% (*w*/*v*) gel. The figure represents the ethanol-CH_3 signal versus the frequency of the saturation pulse. No indications of saturation are seen other than when the frequency of the pulse is close to the frequency of the ethanol signal. The gel was made using 7:3 (*v*/*v*) water:ethanol as the solvent with gelator **1**.

References

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