Electronic Supporting Information for "Solvation Dynamics of an Ionic Probe in Choline Chloride-Based Deep Eutectic Solvents"
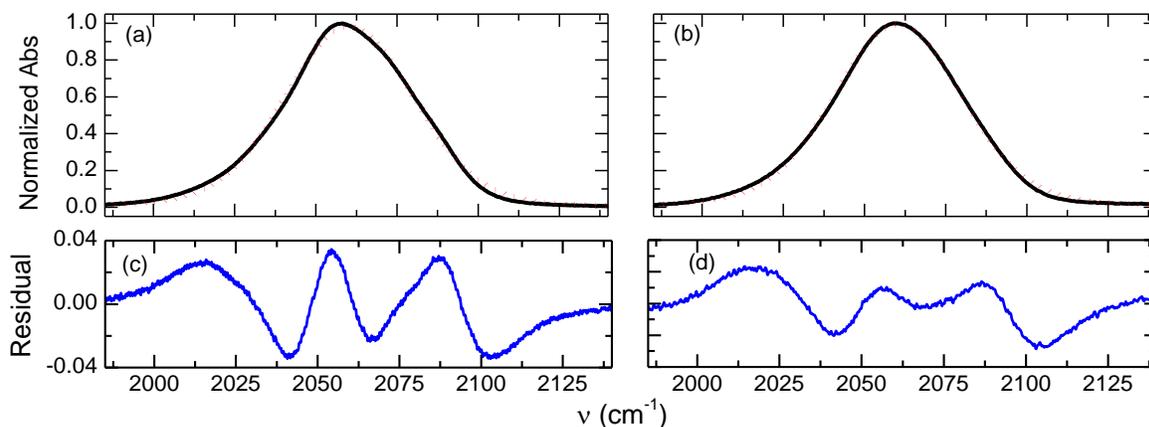
Modelling of FTIR Data

Figure S1. Modelling of thiocyanate nitrile stretch band in (a) ethylene glycol and (b) glycerol with a single Voigt profile. Data is shown as black solid lines and modelling is represented by red dashed lines. The model line does not correctly model the measured data, as can be seen by the residuals from the fit shown in (c) and (d) for ethylene glycol and glycerol, respectively. This indicates that the thiocyanate stretch of the probe ion in the ethylene glycol and glycerol cannot be modelled with a single Voigt profile.

Nitrile Stretch Mode of the Thiocyanate Ion

Figure S2. The nitrile stretch mode of the thiocyanate ion is localized mainly on the carbon (grey) and nitrogen (blue).

Table S1. Displacement vectors for the nitrile stretch of the thiocyanate ion.

	X	Y	Z
C	0.00	0.00	0.80
N	0.00	0.00	-0.61
S	0.00	0.00	-0.03

2DIR Fitting Parameters of Azide Ion Probe in DES EG and DES G

Table S2. Fitting parameters used to model the FFCF of the azide ion stretch mode in DES EG, EG, DES G, and G. The decorrelation times are very similar for the azide probe in each environment.

	A_1	τ_1 / ps	y0
DES EG	0.16±0.01	1.6±0.3	0.66±0.01
EG	0.29±0.01	1.9±0.3	0.44±0.01
DES G	0.10±0.01	1.5±0.3	0.75±0.01
G	0.10±0.01	1.4±0.4	0.73±0.01

Vibrational Lifetimes of the Thiocyanate Nitrile Stretch

Table S3. Vibrational population relaxation times, T_{10}, for the thiocyanate probe in both molecular solvents and in each DES. The T_{10} times are very similar for all three DES.

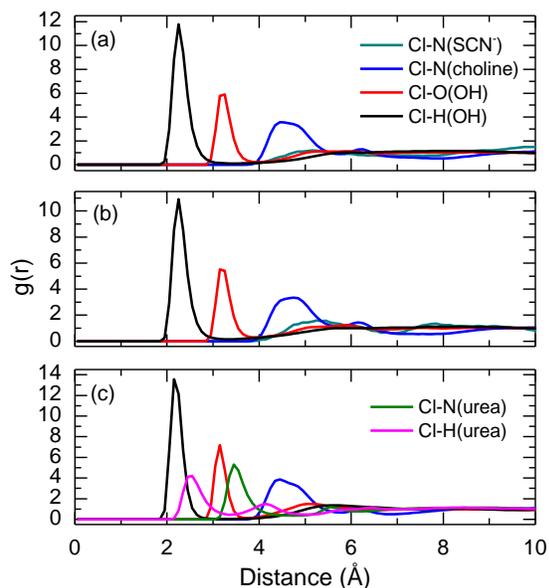|	T_{10} / ps
EG	6.6±0.1
G	8.4±0.1
DES EG	16.2±0.8
DES G	17.6±0.9
DES U	17.4±0.2

Radial Distribution Functions of Chloride Ion

Figure S3. Radial distribution functions (RDFs) of the chloride ion in (a) DES EG, (b) DES G, and (c) DES U. RDFs of the chloride ion show that SCN⁻ and Cl⁻ occupy approximately the same space in the DES solutions.

Time Autocorrelation Functions of the Number of Choline Ions in the Thiocyanate Solvation Shell from Molecular Dynamics (MD) Simulations
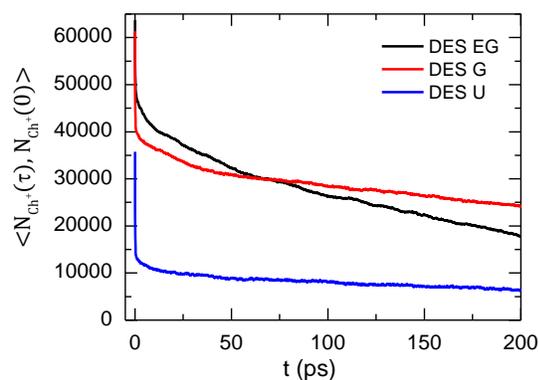

Figure S4. Time autocorrelation functions of the number of choline ions (N_{Ch^+}) in the first solvation shell of the thiocyanate ion, $C(t) = \langle N_{Ch^+}(\tau), N_{Ch^+}(0) \rangle$, obtained from MD simulations for DES EG, DES G, and DES U.

Table S4. Amplitudes and time constants from modelling the time autocorrelation function of the number of choline ions in the SCN⁻ first solvation shell as a tri-exponential decay.

	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3 / ps
DES EG	1.64E4±3E2	0.24±0.01	7.44E3±5E1	17.5±0.3	3.864E4±5E1	268±1
DES G	2.12E4±2E2	0.13±0.01	6.90E3±4E1	17.2±0.2	3.310E4±3E1	657±2
DES U	2.25E4±1E2	0.12±0.01	3.14E3±3E1	10.0±0.2	1.001E4±1E1	458±2

Time Autocorrelation Functions of the Frequency Fluctuations due to the Change in Average CN Distance from MD Simulations

Due to the symmetry of the SCN⁻ ion, it is not straight forward to calculate the FFCF from current maps. However, it has been show by Cho and co-workers that the distance between the carbon and nitrogen atoms (d_{CN}) of the SCN⁻ ion are linearly correlated to the frequency fluctuations in clusters of water under equilibrium conditions.[1] While MD simulations only produce d_{CN} values that are not at equilibrium, the average of d_{CN} over enough oscillation periods should provide $< d_{CN} >$ since the dynamics of the environment is slower (τ_{fast} ~5 ps) than the 15 fs period of oscillation of the CN. Thus, a window average over 150 fs of 10 CN oscillation periods are used to described the "equilibrium value" of the d_{CN} as function of time from which is derived the approximate FFCF of the thiocyanate ion.
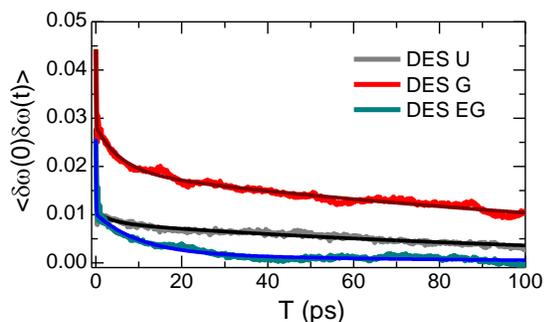

Figure S5. Time autocorrelation function of the frequency fluctuations ($\langle \delta\omega(0), \delta\omega(t) \rangle$) obtained from d_{CN} averaged over 150 fs steps of MD simulations for DES U, DES G, and DES EG.

Table S5. Amplitude and time constants from modeling the time autocorrelation function of the frequency fluctuations as a tri-exponential decay.

	A_1	τ_1 / ps	A_2	τ_2 / ps	A_3	τ_3 / ps
DES EG	0.016±0.001	0.06±0.01	0.0083±0.0002	10.3±0.6	0.0019±0.0002	80±13
DES G	0.016±0.001	0.06±0.01	0.0092±0.0002	5.8±0.3	0.0190±0.0001	166±3
DES U	0.017±0.001	0.10±0.01	0.0022±0.0002	3.8±0.6	0.0083±0.0001	119±2

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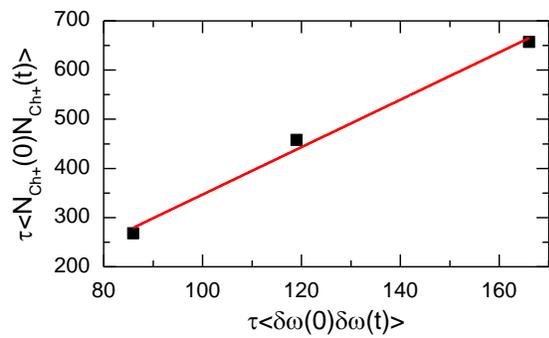Figure S6. Correlation between time scales of diffusion of choline ion and FFCF from the average distance between nitrogen and carbon of SCN^- ion (R^2=0.98).

1.   H. Lee, J.-H. Choi and M. Cho, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12658-12669.