Electronic Supplementary Information

Viscosity data

The rheological measurements were performed with a Physica MCR 301 from Anton Paar with a CP 25-2/TG measurement spindel. The samples were pre-heated to a target temperature of 85° and quickly applied on the rheometer. Due to strong scattering of η values around the glass/phase transition temperatures, a temperature of 85°C was chosen where the DSC results show finished transitions for every investigated sample.

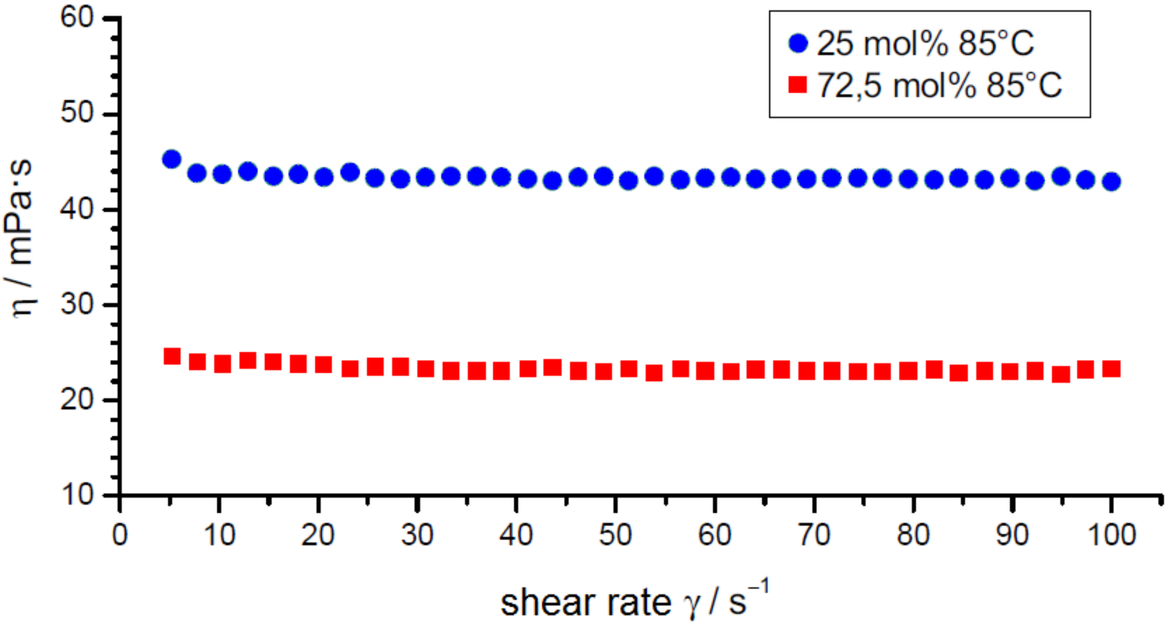


Figure S1: Viscosities for the 25 % and 72.5 % urea samples at 85°C with varying shear rate.

Radial distribution function

Radial distribution functions (RDFs) are an expression for the correlation of two particles as a function of distance and can be generated by statistical neighborhood analysis of a reference molecule and subsequent exerpting the nearest particles and their distances. Thus, a pair correlation ($g(r)$) value of 1 means that the probability of the observed particle to be found around the reference particle at the respective distance is equal to its probability at uniform particle density. In Fig. S2 it becomes clear that the hydrogen bonding between the urea NH_2-groups and the chloride is the strongest, their distance is $\sim$ 30 pm less and their pair correlation significantly higher than any of the EMIm ring hydrogen interactions.

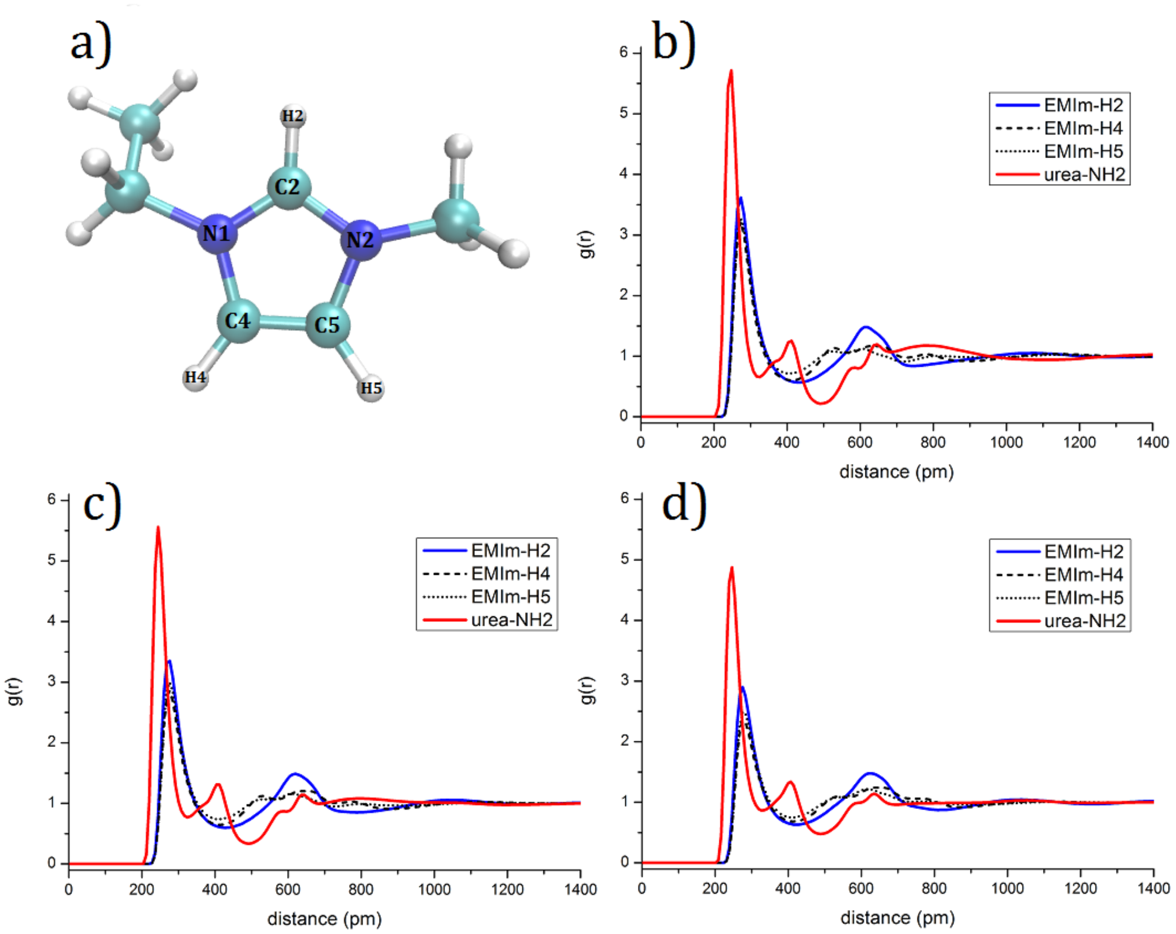


Figure S2: Radial distribution of chloride around selected atoms/group functions (see **a**) of the 25 % (**b**), 50 % (**c**), 72.5 % (**d**) urea samples.

Frémy's salt spectra

Due to its thermal instability the spin probe disodium nitrosodisulfonate (Frémy's salt) could not be used to perform EPR spectroscopy of the higher melting mixing ratios 12.5, 37.5, 62.5 and 87.5 %. The A'_{zz} progression for the 25 %, 50 % and 72.5 % urea samples are shown in Fig. S3. Note that the axes are scaled to match those of the nitroxide-based spin probes in the main article for better comparison, meaning that the absolute A'_{zz} values (especially for low temperatures) are significantly lower. Given the assumption that Frémy's salt resides in the [EMIm]-rich regions due to its charge, the different curve of the 72.5 % can be explained with the sample's distinct domain-formation.

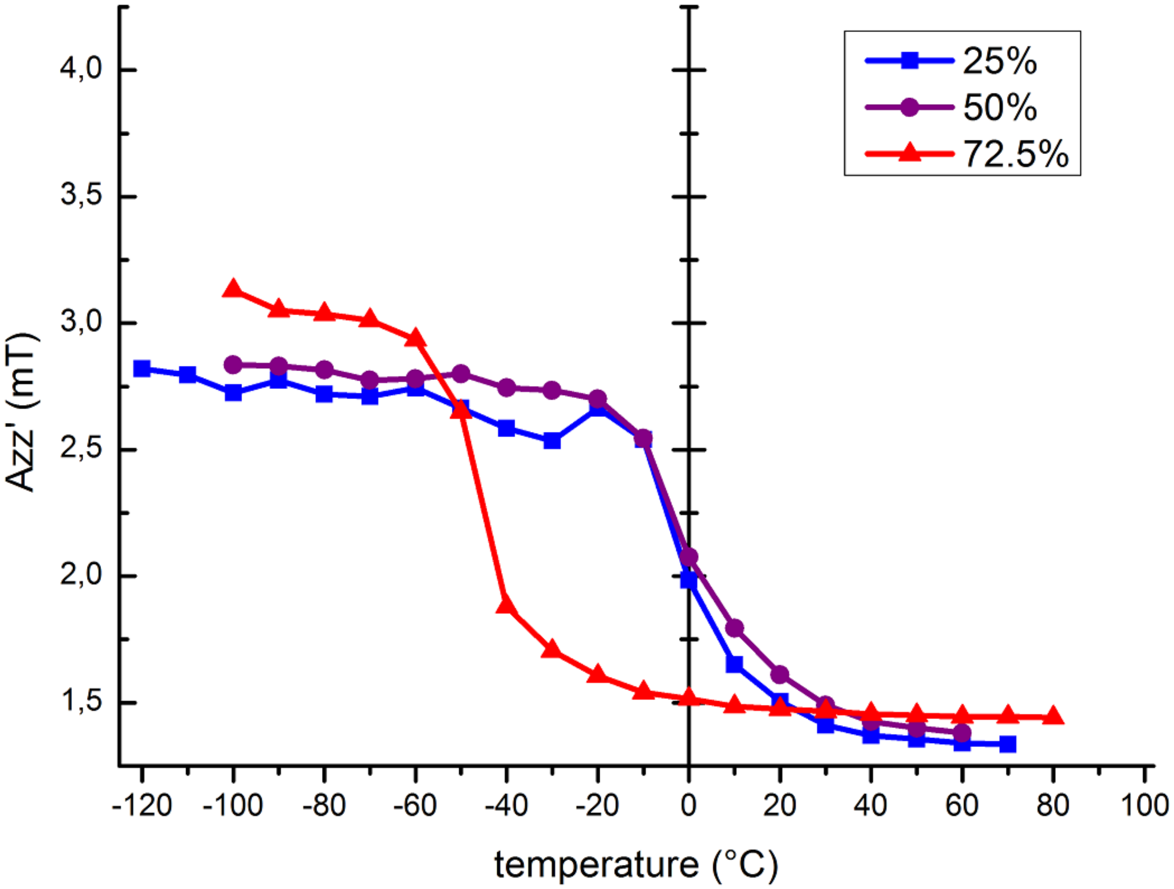


Figure S3: A'_{zz} values of Frémy's salt in all three investigated samples in the temperature range between −100 and +100 °C.

TEMPOL spectra in the 62.5 % sample

When investigating the individual CW EPR spectra, TEMPOL in the 62.5 % sample shows an anomaly between −20 and −40°C. Spectra simulation unravels the additional component to the expected rigid limit spectral species, shown in Fig. S4.

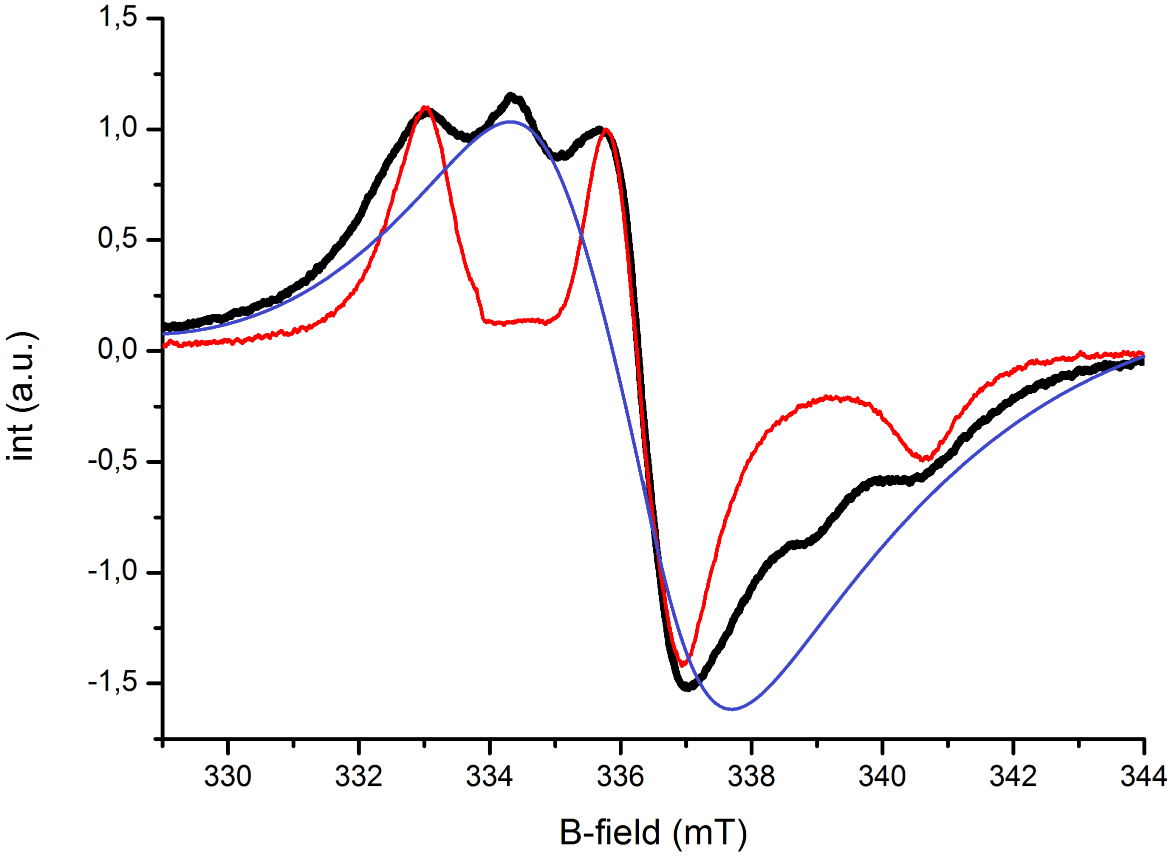
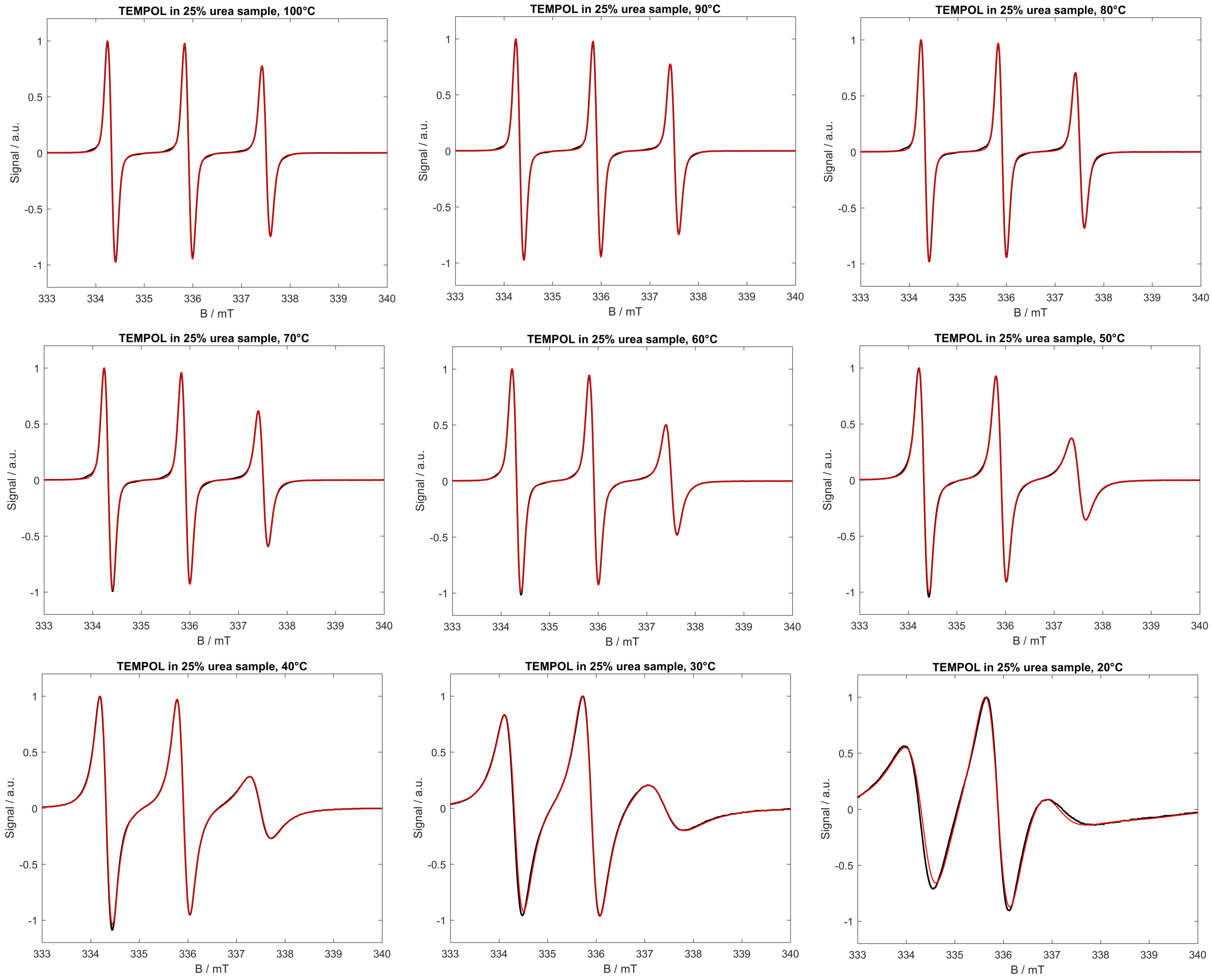


Figure S4: Individual TEMPOL-spectrum in the 62.5 % urea sample at −30° (black, thick). Assumed spectral components are a species at rigid limit (red) and a species featuring spin exchange induced dispersion (blue).

Simulated spectra

Selected spectra and their simulations with EasySpin's `chili` function for fast rotation and slow-motion regime, shown exemplarily for TEMPOL in the 25 % urea sample in the respective temperature range.



TEMPOL in 25% urea sample, 100°C

TEMPOL in 25% urea sample, 90°C

TEMPOL in 25% urea sample, 80°C

TEMPOL in 25% urea sample, 70°C

TEMPOL in 25% urea sample, 60°C

TEMPOL in 25% urea sample, 50°C

TEMPOL in 25% urea sample, 40°C

TEMPOL in 25% urea sample, 30°C

TEMPOL in 25% urea sample, 20°C

Figure S5: Experimental (black) and simulated (red) individual CW EPR spectra for TEMPOL in the 25 % urea sample at different temperatures.