Quantifying Transient Interactions between Amide Groups and the Guanidinium Cation

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Supporting Information

MATERIALS

N-Methylacetamide (NMA >99% Sigma Aldrich) and the representative salts of the Hofmeister series KCl (Riedel-de Haen), NaCl (Sigma Aldrich), MgCl₂ hexahydrate (Carl Roth GmbH) and GdmCl (Sigma Aldrich) were used as received. The hygroscopic LiCl (Sigma Aldrich) was dried for two days in vacuo at 80 °C and samples were prepared in a glove box. All samples were prepared volumetrically, by adding Milli-Q water to the weighed amount of solutes (salt and/or NMA). Aqueous salt solutions were prepared at concentrations of 0.15, 0.25, 0.75, 1.25 and 2 mol/L and ternary samples containing 2 mol/L of NMA at salt concentrations ranging from 0.25 to 2 mol/L at increments of 0.25 mol/L.

METHODS

We measured the complex permittivity spectra, $\hat{\varepsilon}(v) = \varepsilon'(v) - i\varepsilon''(v)$ of the samples, as a function of the frequency v, using two complementary methods:

- (a) At frequencies $0.8 \le v/\text{GHz} \le 36$ we use a frequency domain reflectometer based on a Anritsu Vector Star MS4647A, vector network analyser, with an open-ended coaxial probe.¹ For calibration of the instrument we used three references, air, water and conductive silver paint (short) as calibration standards. All experiments were performed at 23 ± 1 °C
- (b) For the frequency range of $0.4 \le v/\text{THz} \le 1.6$ we use THz Time Domain Spectroscopy (TDS). THz pulses of duration ~1 ps were generated in a ZnTe (110) nonlinear crystal,² from pulses of a Ti:Sapphire amplified laser system (Coherent Legend Elite, USA). The later pulses have a wavelength of 800 nm and duration of ~100 fs. The ratio of the transmission through an empty cell and a cell filled with the sample, yields the frequency dependent complex refractive index $(\hat{n}(v) = n(v) ik(v))$ as a function of the of the field frequency, v. The complex refractive index is connected to the complex permittivity via $\hat{n}(v)^2 = \hat{\varepsilon}(v)$.

All multiple reflections and transmission coefficients for all transitions (air-windowsample-window-air) were taken into account.³ We used a cylindrical near infrared quartz cell with an optical path length of 0.1 mm (Starna GmbH, Germany).

For aqueous salt solutions only measurements in the frequency range of $0.8 \le v/GHz \le 36$ were performed. The evolution of the dielectric function for all the samples is shown in Figures S1 and S2.

Dynamic viscosity, η , of selected samples were determined using a capillary Ubbelohde viscometer (ViskoSystem AVS 370, Schott Instruments, Germany) and compared to the relaxation times of NMA (Fig S4b).



Figure S1. Real and imaginary part of the dielectric function of the aqueous salt solutions with increasing salt concentration as a function of the frequency of the external field for (a) KCl, (b) NaCl, (c) LiCl, (d) $MgCl_2$ and (e) GdmCl. The solid line corresponds to fits with the model of eq S1. Note that for visual clarity the conductivity contribution has been subtracted.



Figure S2. Real and imaginary part of the dielectric function as a function of the applied field frequency for the ternary NMA+water+salt mixtures for (a) KCl, (b) NaCl, (c) LiCl and (d) MgCl₂. The solid lines correspond to fits with eq 1 (main manuscript). Note that for visual clarity the conductivity contribution has been subtracted.

DATA ANALYSIS

(a) Calculation of the total depolarization:

We fit the relaxation model described in the main manuscript (eq 1) to all ternary samples. In the case of the aqueous salt solutions the equation was reduced to:

$$\hat{\varepsilon}(\nu) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i2\pi\nu\tau_{water})^{(1-a)}} + \varepsilon_\infty + \frac{i\kappa}{2\pi\nu\varepsilon_0}$$
(S1)

In order to have similar weights on all data points across the entire frequency range we subtracted most of the conductivity prior to fitting from the raw data. The fits together with the raw data are shown in Figures S1 & S2 and Figure 1 in the main manuscript.

The total depolarization as shown in Figure 2 of the main manuscript is defined as:

$$Dep = \varepsilon_s(c_{salt}) - \varepsilon_s(c_{salt} = 0)$$
(S2)
where $\varepsilon_s = \sum S_j + \varepsilon_{\infty}$

(b) Ideal water relaxation amplitude

As shown in the main manuscript, the NMA relaxation and the water relaxation closely overlap. To reduce the number of adjustable parameters we fix the water relaxation amplitude to what would be expected for an ideal solution. The ideal amplitude of the water relaxation was assumed to correspond to the amplitude of all water molecules in solution, corrected for (ideal) kinetic depolarization and rigid binding of water in the hydration shell of the ions:

$$S_{water, exp} = S_{Cavell}^{water} - f_{water} \cdot S_{KD}^{water} - S_{hyd}$$
(S3)

The relaxation amplitude of water was obtained using the Cavell equation,⁴ which relates the molar concentration, c_{water} , to the relaxations strength, S_{Cavell}^{water} .

$$S_{Cavell}^{water} = \frac{\varepsilon_s}{\varepsilon_s + (1 - \varepsilon_s)/3} \cdot \frac{N_A c_{water}}{3k_B T \varepsilon_0} \cdot \mu_{eff,water}^2$$
(S4)

where $\mu_{eff,water}$ is the effective dipole moment⁵ of water, calculated from the dielectric spectra of neat water.^{4,6} The contribution of kinetic depolarization was calculated from the theory of Hubbard and Onsager:

$$S_{KD}^{water} = \frac{S_{Cavell}^{water}}{\varepsilon_s} \cdot \frac{\tau_{water}}{\varepsilon_0} \cdot \kappa$$
(S5)

which is based on a continuum estimation of the coupling of the rotation of the water molecules to the translation of the ions.^{7–9} Note that for the ternary solutions both the relaxation amplitude of water and of NMA are reduced due to kinetic depolarization.

To obtain the depolarization of water we multiply the depolarization with the volume fraction f_{water} assuming uniform distribution of all molecules within the sample:

$$f_{water} = \frac{V_{water}}{V_{water} + V_{NMA}}$$
(S6)

The volume of water, $V_{water'}$ was calculated from its mass and density, while for the calculation of the V_{NMA} we used the apparent molar volumes of NMA in water.¹⁰ In the cases of Na⁺, Li⁺ and Mg²⁺ an additional depolarization term (S_{hyd}) was subtracted, which accounts for irrotational binding of water molecules in the hydration shells of these cations.^{11–13} The values for S_{hyd} were obtained from the measurements of the aqueous salt solutions, where the total depolarization solely originates from S_{hyd} and S_{KD}^{water} . Note that for KCl and GdmCl S_{hyd} is zero as those cations do not bind water.^{14,15}

The parameters obtained from these fits are shown in Figures S3 and S4.

The concentration of free NMA, $c_{NMA,free}$, was obtained from S_{NMA} using eq S3 for NMA. The effective dipole moment was extracted by using the exact same approach to the NMA + water binary mixture with fixed water amplitude to obtain the amplitude of NMA. By solving eq S3 for $\mu_{eff,NMA}$ we obtain the effective dipole moment of NMA, which was assumed to be independent of added salts.



Figure S3. (a) Calculated values of the water amplitude (eq S4) as a function of increasing salt concentration. (b) Values of S_{NMA} as a function of salt concentration. (c) Fast water amplitude as a function of salt concentration. The error bars correspond to the standard deviation within six independent measurements.



Figure S4. Relaxation times obtained from fitting eq 1 (main manuscript) to the dielectric spectra as a function of salt concentration of (a) bulk water, (b) NMA and (c) fast water. The open symbols in (b) correspond to values of the dynamic viscosity measured for selected concentrations of all salts. The error bars correspond to the standard deviation within six independent measurements.

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