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# Anionic and Cationic Hofmeister Effects Are Non-Additive for Guanidinium Salts.

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## Supporting Information

## MATERIALS

*N*-Methylacetamide (NMA >99% Sigma Aldrich) and the salts of the present study: NaBr (Sigma Aldrich), NaI (Sigma Aldrich), GdmI (Sigma Aldrich), GdmSCN (Sigma Aldrich), $MgI_2$ (Fischer GmbH), GdmCl (Sigma Aldrich), NaCl (Sigma Adrich) and KI (Sigma Aldrich) were used as received. We prepared three different series of solutions: (a) aqueous salt solutions of NaBr, NaI, GdmI, GdmSCN and $MgI_2$ at $c_{\text{salt}}$ = 0.15, 0.25, 0.75, 1.25 and 2 mol/L, (b ) ternary solutions of NMA (2 mol/L) + water + salt with increasing salt concentrations from 0.25 to 2 mol/L at increments of 0.25 mol/L and (c) quaternary solutions with mixture of NaCl + KI and GdmCl + KI at total salt concentration of $c_{\text{salt}}$ = 1.5 mol/L in aqueous NMA ($c_{\text{NMA}}$ = 2 mol/L). The composition of the salt was varied from neat NaCl/GdmCl to neat KI with the ratios $c_{\text{NaCl}} / c_{\text{KI}}$ and $c_{\text{GdmCl}} / c_{\text{KI}}$ at 90/10, 83.3/16.6, 66.6/33.3, 50/50, 33.3/66.6 16.6/83.3. To avoid uptake of moisture all samples were prepared initially in a glove box, adding weighted amounts of the solid components (salt and/or NMA) into volumetric flasks. Subsequently, we added the appropriate of Milli-Q water.

## METHODS

We measured complex permittivity spectra at three different frequency regions, using two complementary techniques:

a) For frequencies at $0.8 \leq \nu/\text{GHz} \leq 36$ and $56 \leq \nu/\text{GHz} \leq 125$ we used a frequency domain reflectometer based on an Anritsu Vector Star MS4647A, vector network analyser with an open ended coaxial probe.[1] At $0.8 \leq \nu/\text{GHz} \leq 36$ an open ended coaxial probe based on 1.85 nm coaxial connectors was used, while the higher frequency region was covered using an open ended probe based on 1mm coaxial connectors together with an external frequency converter module (Anritsu 3744 mmW module). For the calibration of the instrument we used three different calibration standards, namely: air, water and conductive silver paint (short). All measurements were performed at 23±1 °C.

b) For frequencies at $0.4 < \nu/\text{THz} < 1.6$ we used THz Time Domain Spectroscopy (TDS).[2] THz pulses of duration ~1 ps were generated in a ZnTe (110) nonlinear crystal, from pulses of a Ti:Sapphire amplified laser system (Coherent Legend Elite, USA) of 800 nm wavelength and duration of 100 fs. Using the measured frequency dependent refractive index ($\hat{n}(\nu) = n(\nu) - ik(\nu)$) obtained from the ratio of transmitted intensity spectrum through the empty cell and the cell filled with the samples, we measure the complex permittivity via $\hat{n}(\nu)^2 = \hat{\varepsilon}(\nu)$.

The thus obtained spectra for the ternary samples are shown in Figs. 1a and S1. In order to determine contributions due to the formation of rigid hydration shells around the ions (see main manuscript and eq. S1), we also measure spectra of aqueous salt solutions at $0.8 \leq \nu/\mathrm{GHz} \leq 36$ and $56 \leq \nu/\mathrm{GHz} \leq 125$. These spectra are shown in Fig. S2.

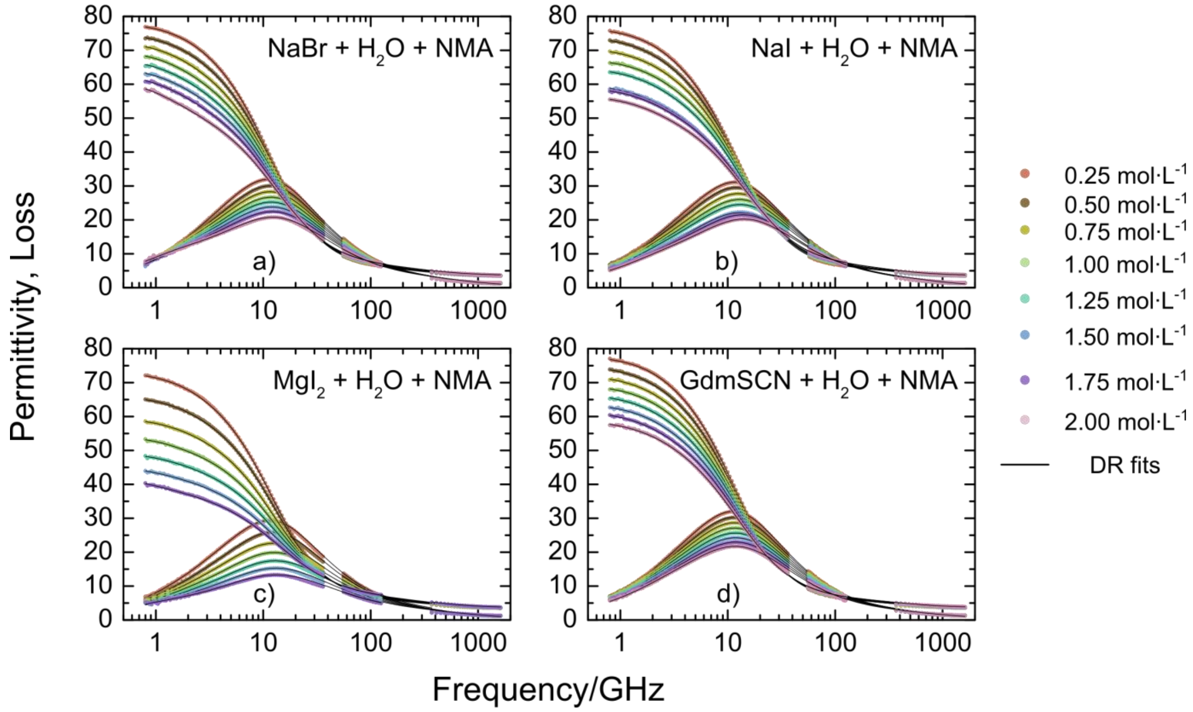

**Figure S1.** Dielectric permittivity and dielectric loss spectra for ternary mixtures of (a) NaBr, (b) NaI, (c) MgI$_2$, (d) GdmSCN, in an aqueous NMA (2 mol/L solution). The solid lines correspond to fits with eq. 1 to the data (symbols). For visual clarity the conductivity contribution has been subtracted (last term of eq. 1).

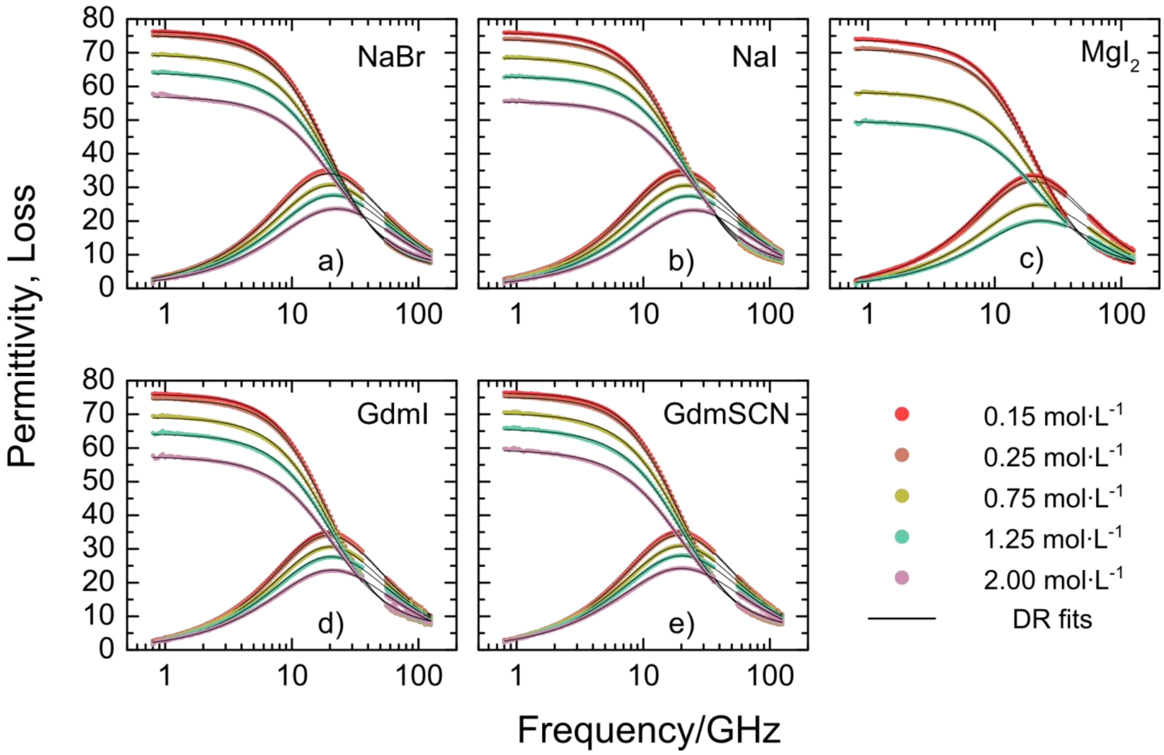

**Figure S2.** Dielectric permittivity and dielectric loss spectra of aqueous solutions with increasing of (a) NaBr, (b) NaI, (c) MgI$_2$, (d) GdmI and (e) GdmSCN. The solid line corresponds to fits of eq. S5. For visual clarity the conductivity contribution has been subtracted (last term of eq. S5).

# DATA ANALYSIS

## 1) Constrained fit of the dielectric spectra for the ternary solutions

All the dielectric spectra of the ternary solutions mentioned above were fitted with a constrained version of eq. 1, by fixing the water amplitude to the value expected for an ideal solution ($S_{\text{water}}$ in eq. 1 fixed to $S_{\text{water,exp}}$). $S_{\text{water,exp}}$ was obtained using the expected water amplitude based on the molar concentration of water ( $S_{\text{Cavell}}^{\text{water}}$ ), which we correct for kinetic depolarization ( $f_{\text{water}} \cdot S_{\text{KD}}^{\text{water}}$ ) and potentially for rigid binding of water molecules in the hydration shell of an ion ($S_{\text{hyd}}$ ):

$$S_{\text{water,exp}} = S_{\text{Cavell}}^{\text{water}} - f_{\text{water}} \cdot S_{\text{KD}}^{\text{water}} - S_{\text{hyd}} \qquad \text{(S1)}$$

The relaxation amplitude of water, was calculated for each sample using the Cavell equation,[3] which relates the amplitude with the concentration of the dipolar species, $c_{\text{water}}$ ,and their squared effective dipole moment, $\mu_{\text{eff,water}}^2$:

$$S_{\mathrm{Cavell}}^{\mathrm{water}} = \frac{\varepsilon_{\mathrm{s}}}{\varepsilon_{\mathrm{s}} + (1 - \varepsilon_{\mathrm{s}})/3} \cdot \frac{N_{\mathrm{A}} c_{\mathrm{water}}}{3 k_{\mathrm{B}} T \varepsilon_0} \cdot \mu_{\mathrm{eff,water}}^2 \tag{S2}$$

, with $\varepsilon_{\mathrm{s}}$, the static dielectric constant (i.e. $\varepsilon_{\mathrm{s}} = lim_{\nu \to 0}\, \varepsilon'(\nu)$), $N_{\mathrm{A}}$ Avogadro's constant, $k_{\mathrm{B}}$ the Boltzmann constant, $T$ the thermodynamics temperature and $\varepsilon_0$ the permittivity of free space. The value of $\mu_{\mathrm{eff,water}}$ was calculated from the dielectric spectrum of neat water[3,4] and assumed to be constant upon salt addition throughout the analysis.

Note that the depolarization due to dilution is included in this expression, as the reduction of concentration of water upon addition of salt is taken into account.

The kinetic depolarization was estimated based on the Hubbard and Onsager model:[5]

$$S_{\mathrm{KD}}^{\mathrm{water}} = f \cdot \frac{S_{\mathrm{Cavell}}^{\mathrm{water}}}{\varepsilon_{\mathrm{s}}} \cdot \frac{\tau_{\mathrm{water}}}{\varepsilon_0} \cdot \kappa \tag{S3}$$

, where $\tau_{water}$ is the relaxation time of water and $\kappa$ the sample's electrical conductivity. The term $f$ describes the friction coefficient and we assumed slip boundary conditions ($f = 2/3$) throughout the analysis.

To account for the presence of NMA and water in the samples, we assume uniform distribution of all the molecules in the sample. The total kinetic depolarization (eq. S2) was accordingly obtained by correcting the value for $S_{\mathrm{KD}}^{\mathrm{water}}$ for the volume fraction of water, $f_{water}$:

$$f_{\mathrm{water}} = \frac{V_{\mathrm{water}}}{V_{\mathrm{water}} + V_{\mathrm{NMA}}} \tag{S4}$$

Here we calculate the volume of water $V_{\mathrm{water}}$ in the sample from the mass fraction of water in the sample and take the density of pure water. The values of $V_{\mathrm{NMA}}$ were calculated based on the apparent molar volumes of NMA in water.[6]

To take the depolarization due to rigid binding of water molecules in the hydration shell of ions ($S_{\mathrm{hyd}}$) into account, we measure spectra for aqueous salt solutions (Fig. S2). We fit a relaxation model (analogue to eq. 1) with only a single, symmetrically broadened Cole-Cole relaxation ($S_{\mathrm{water}}, \tau_{water}, \alpha_{CC}$) and an Ohmic loss term to all the experimental spectra:

$$\hat{\varepsilon}(\nu) = \frac{\varepsilon_S - \varepsilon_\infty}{1 + (i 2\pi \nu \tau_{water})^{(1-\alpha_{CC})}} + \varepsilon_\infty + \frac{\kappa}{2\pi i \nu \varepsilon_0} \tag{S5}$$

The thus obtained relaxation amplitudes ($S_{\mathrm{water}}$), are shown in Fig. S3a together with what would be expected based on the water concentration and kinetic depolarization ($S_{\mathrm{Cavell}}^{\mathrm{water}} - S_{\mathrm{KD}}^{\mathrm{water}}$ ). The other parameters obtained from fitting eq. S5 to the spectra are shown in Figs. S3b & S3c.

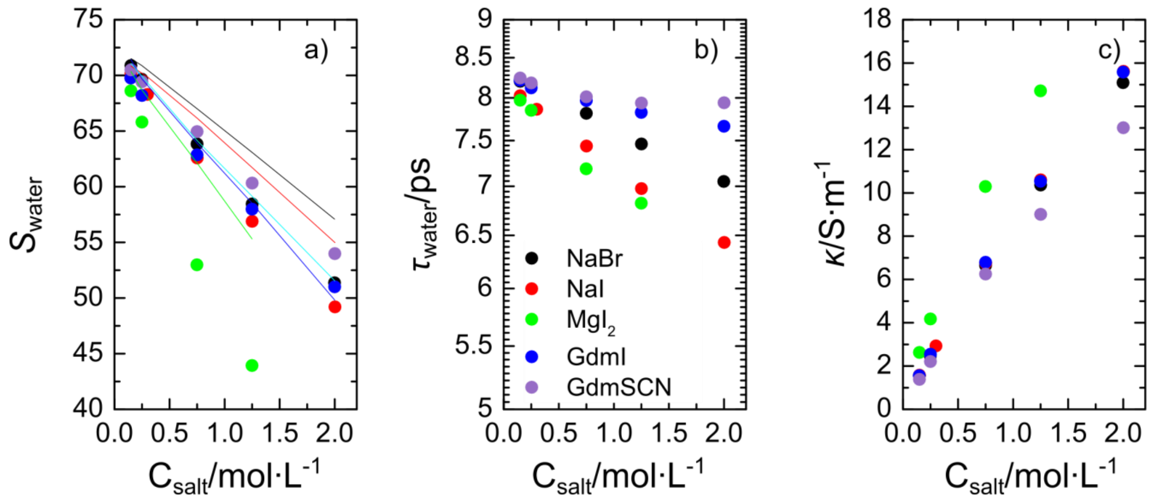

**Figure S3.** (a) Values of $S_{\mathrm{water}}$ obtained by fitting eq. S5 to the spectra of the aqueous salt solutions (symbols). The lines correspond to what would be expected based on only dilution and kinetic depolarization ($S^{\mathrm{water}}_{\mathrm{Cavell}} - S^{\mathrm{water}}_{\mathrm{KD}}$ ). The difference between $S_{\mathrm{water}}$ and $S^{\mathrm{water}}_{\mathrm{Cavell}} - S^{\mathrm{water}}_{\mathrm{KD}}$ corresponds to $S_{\mathrm{hyd}}$ (b) relaxation time, $\tau_{water}$ and (c) conductivity, $\kappa$, obtained by fitting eq. S5 to the spectra of aqueous salt solutions.

As can be seen in Fig. S3a the $S_{hyd}$ only for GdmI, $S_{\mathrm{water}} \approx S^{\mathrm{water}}_{\mathrm{Cavell}} - S^{\mathrm{water}}_{\mathrm{KD}}$, since neither Gdm$^+$ nor I$^-$ are strongly hydrated.[7,8] For all Na$^+$ and Mg$^{2+}$ salts $S_{\mathrm{water}} < S^{\mathrm{water}}_{\mathrm{Cavell}} - S^{\mathrm{water}}_{\mathrm{KD}}$ due to the formation of a hydration shell with irrotational binding of water molecules.[4,9,10] As we have already reported previously,[8] for GdmSCN we observe a minor residual amplitude $S_{\mathrm{water}} > S^{\mathrm{water}}_{\mathrm{Cavell}} - S^{\mathrm{water}}_{\mathrm{KD}}$, which increases linearly with increasing salt concentration and can be explained by a minor contribution of the non-centrosymmetric SCN$^-$ ion to the dielectric spectra.[8]

To obtain the contribution from either the hydration or the minor contribution due to SCN$^-$ we use the aqueous solutions to calculate $S_{\mathrm{hyd}}$ using eq. S1 (using $S_{\mathrm{water,exp}} = S_{\mathrm{water}}$ and $f_{\mathrm{water}} = 1$). These values for $S_{\mathrm{hyd}}$ were then used to correct for the contributions from the hydration or the minor contribution due to SCN$^-$ in analyzing the ternary (NMA containing) samples.

The fit parameters obtained by fitting the eq. 1 to the spectra are displayed in Figs. S4-S6.

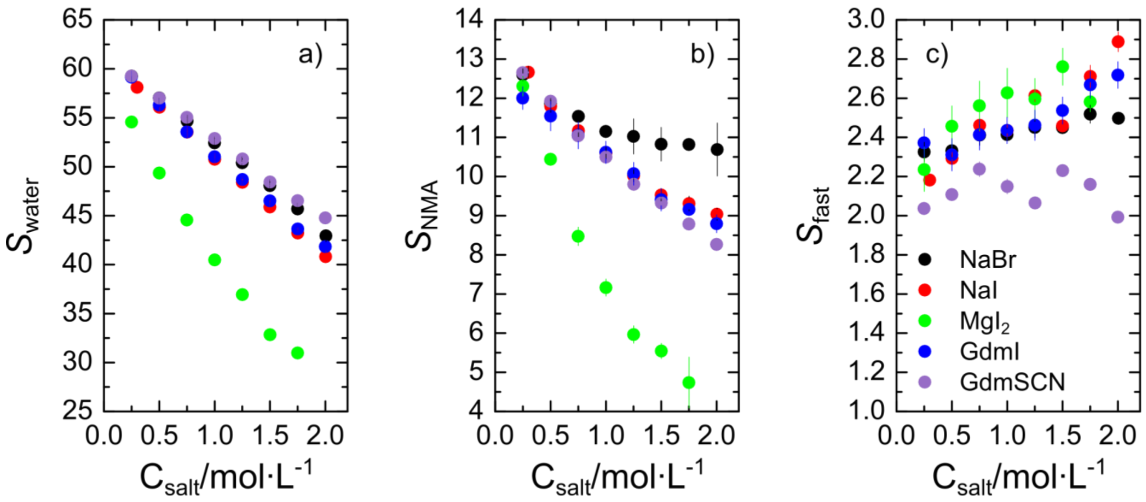

**Figure S4.** (a) Water relaxation amplitude, $S_{\mathrm{water}}$ (calculated according to eq. S1) (b) Amplitude of the NMA relaxation ($S_{NMA}$) and (c) amplitude of the fast water relaxation, $S_{\mathrm{fast}}$, as obtained from fitting the constrained eq. 1 to the experimental spectra for the ternary samples. The error bars correspond to standard deviation within six independent measurements.

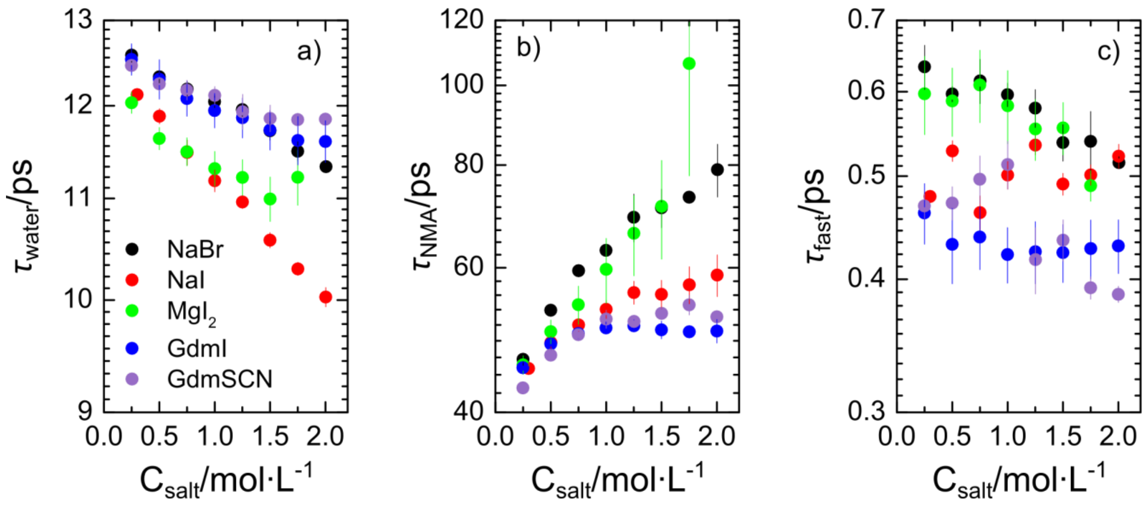

**Figure S5.** (a) The relaxation time of water, $\tau_{water}$, (b) the relaxation time of NMA, $\tau_{NMA}$ and (c) the relaxation time of the fast water mode, $\tau_{fast}$, as obtained from fitting the constrained eq. 1 to the experimental spectra for the ternary samples. The error bars correspond to the standard deviation within six independent measurements.

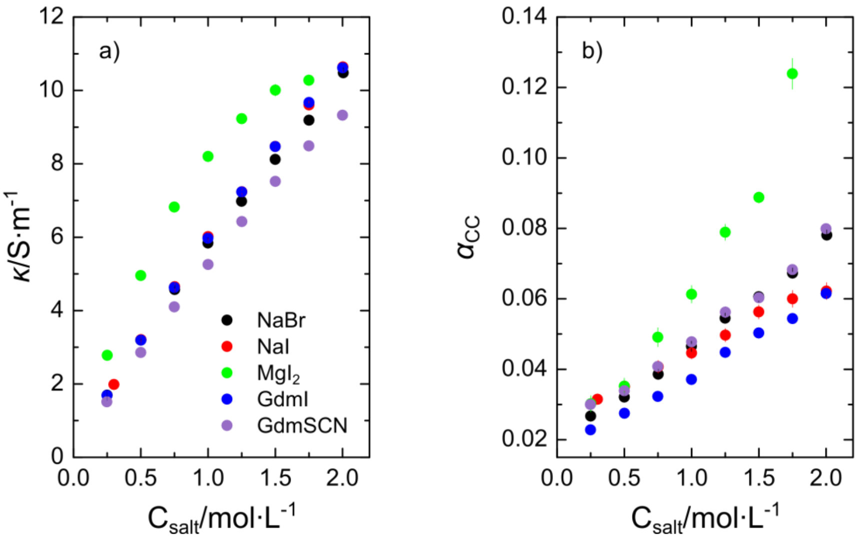

**Figure S6.** (a) Sample conductivities, $\kappa$ and (b) Cole-Cole parameter, $\alpha_{CC}$, as obtained from fitting the constrained eq. 1 to the experimental spectra for the ternary samples. The error bars correspond to the standard deviation within six independent measurements.

## 2) Quaternary solutions

For the two series of quaternary solutions (1.5 mol/L NaCl/KI and GdmCl/KI + $H_2O$ + NMA) we used the same analysis as described above. The spectra together with the fits of the constrained eq. 1 to the data are shown in Fig. S7.

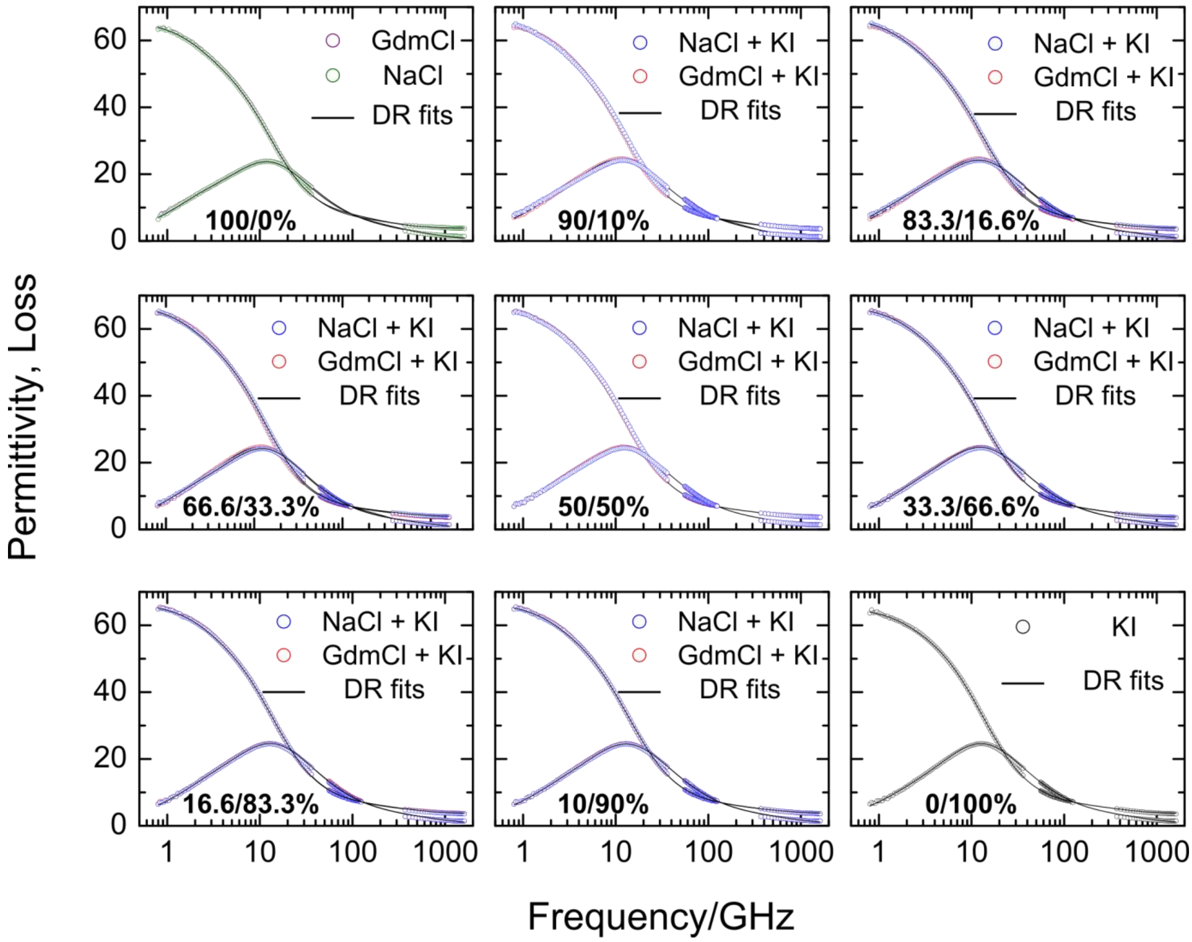

**Figure S7.** Dielectric permittivity and dielectric loss spectra for quaternary samples (Salt + $H_2O$ + NMA) at $c_{\text{salt}}$ = 1.5 mol/L. Symbols show experimental data and lines correspond to the fit using eq. 1. From panels top left to bottom right the compositions of the salt is varying gradually from neat NaCl/GdmCl to neat KI. Note that for visual clarity the conductivity contribution has been subtracted.

## 3) Calculation of the $C_{\text{NMA, free}}$

For all samples containing NMA, we relate the relaxation amplitude of NMA, $S_{\text{NMA}}$ to the corresponding concentration of effectively free NMA, $c_{\text{NMA, free}}$. Therefore we use analogue to water(eq. S2) the Cavell equation for NMA. The effective dipole moment for NMA, $\mu_{\text{eff,NMA}}$ was in line with our previous studies[8,11,12] extracted from the dielectric spectra of aqueous NMA solutions.

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