Water-Mediated Interactions Between Trimethylamine-N-Oxide and Urea

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Supporting Material

Urea - Water Mixtures

Dielectric spectra for aqueous solutions of urea ($c_{\mathrm{urea}} = 1$, 2, 3, and $4\,\mathrm{mol\,L^{-1}}$) were recorded at frequencies ranging from 100 MHz to 1.6 THz.[1,2] Three Debye type relaxations were fit to the experimental spectra (see eq 2 of the main manuscript). Experimental spectra together with the fits are depicted in Figure S1. The relaxation parameters extracted from fitting three Debye-type relaxation modes to the experimental spectra are shown in Figure S2.

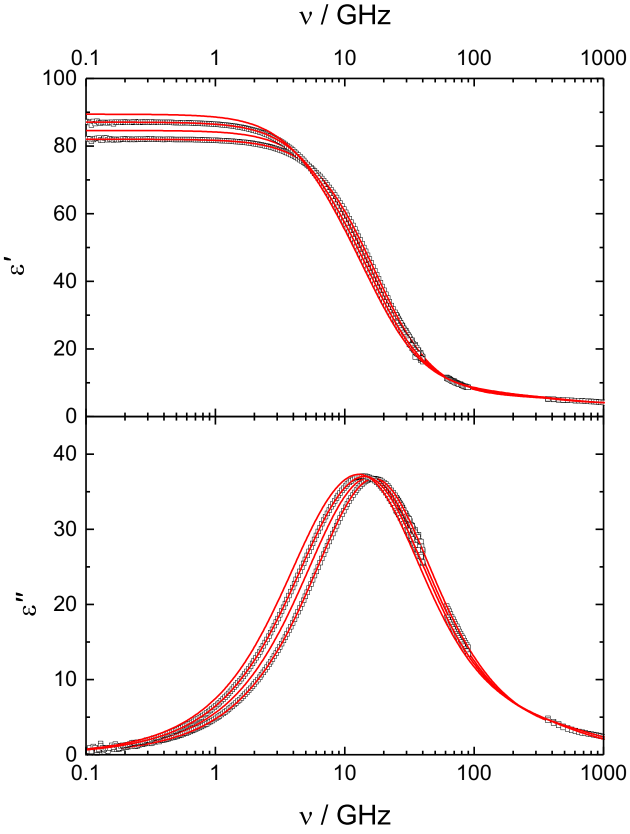

Figure S1: (**a**) Dielectric permittivity, $\varepsilon'(\nu)$, and (**b**) dielectric loss spectra, $\varepsilon''(\nu)$, for aqueous solutions of urea. Symbols correspond to experimental data whereas solid red lines show fits of three Debye modes (eq 2 of the main manuscript). For visual clarity the data are only shown for each second concentration. The arrows indicate increasing concentration of urea.

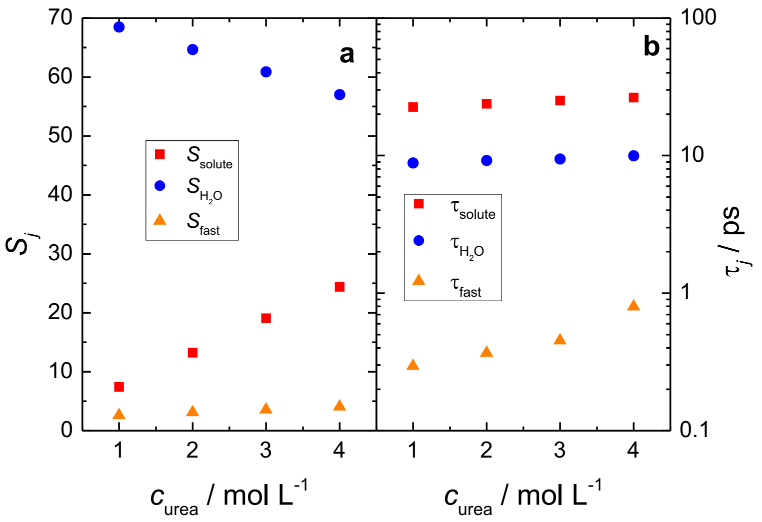

Figure S2: (**a**) Relaxation strengths, S_j, and (**b**) relaxation times, τ_j, of the solute, water, and the fast water relaxation for aqueous solutions of urea. These parameters were obtained by fitting three Debye-type relaxation modes to the experimental spectra.

Aqueous Solutions of TMAO + Urea

Equimolar TMAO + Urea Mixtures

Seven samples with equimolar concentration of TMAO and urea were studied ($c_{\text{TMAO}} = c_{\text{urea}} = 0.47$, 0.90, 1.62, 2.22, 2.73, 3.16, and $3.53\,\text{mol}\,\text{L}^{-1}$). Dielectric spectra of these samples were recorded at frequencies ranging from 100 MHz to 1.6 THz.[1,2] We fit three Debye-type relaxation modes (see eq 2 of the main manuscript) to the experimental spectra (i.e. solute, water, and fast water relaxation). The spectra together with the fits are shown in Figure 2 of the main manuscript. The parameters extracted from fitting three Debye functions to the spectra are shown in Figure S3.

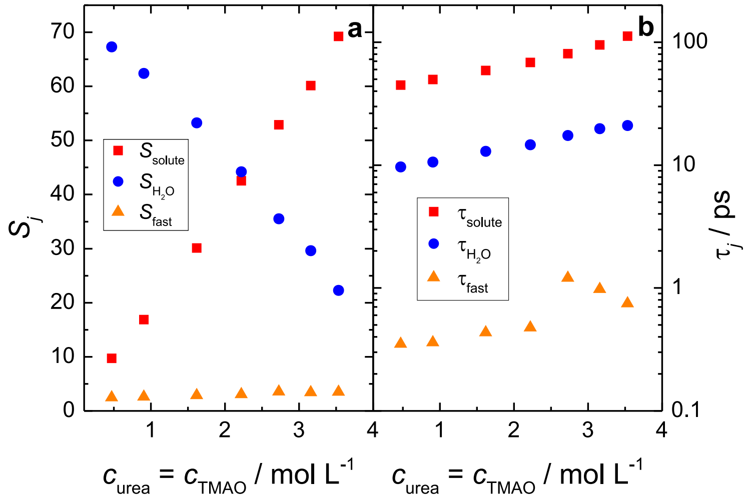

Figure S3: (**a**) Relaxation strengths, S_j, and (**b**) relaxation times, τ_j, of the solute, water, and the fast water relaxation for aqueous solutions of TMAO + urea at equimolar concentrations of both solutes. These parameters were obtained by fitting three Debye-type relaxation modes to the experimental spectra (eq 2 of the main manuscript).

Constant concentration of urea $c_{\text{urea}} = 3.53\,\text{mol}\,\text{L}^{-1}$

Six aqueous solutions of TMAO and urea were studied in this series of experiments. For all samples the concentration of urea was kept constant at $c_{\text{urea}} = 3.53\,\text{mol}\,\text{L}^{-1}$, while the concentration of TMAO was varied ($c_{\text{TMAO}} = 0.59,\ 1.18,\ 1.76,\ 2.34,\ 2.95,\ 3.53\,\text{mol}\,\text{L}^{-1}$). Dielectric spectra of these samples were recorded at frequencies ranging from 100 MHz to 70 GHz.[2] Note that for this series we do not cover frequencies at THz frequencies at which the fast water mode is centered. Thus, we fit only two Debye-type relaxation modes to the experimental spectra (i.e. the solute and the water relaxation in eq 2 of the main manuscript). The fits of this model to the experimental spectra are depicted in Figure S4. The thus extracted relaxations times and relaxation strengths are shown in Figure S5

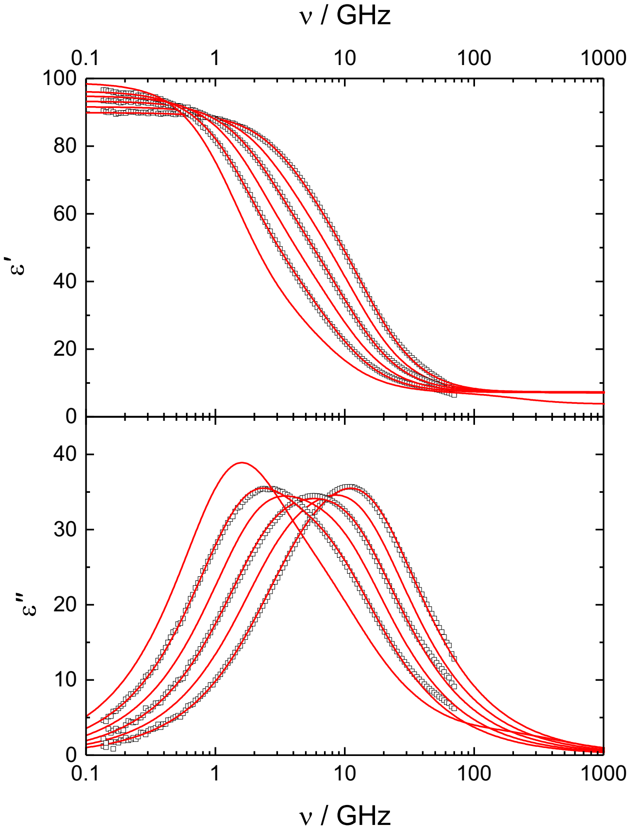

Figure S4: (**a**) Dielectric permittivity, $\varepsilon'(\nu)$, and (**b**) dielectric loss spectra, $\varepsilon''(\nu)$, for aqueous solutions of $c_{\text{urea}} = 3.53\,\text{mol}\,\text{L}^{-1}$ and variable concentration of TMAO, c_{TMAO}. Symbols correspond to experimental data whereas solid red lines show fits to two Debye modes. For visual clarity the data are only shown for each second concentration. The arrows indicate increasing concentration of TMAO.

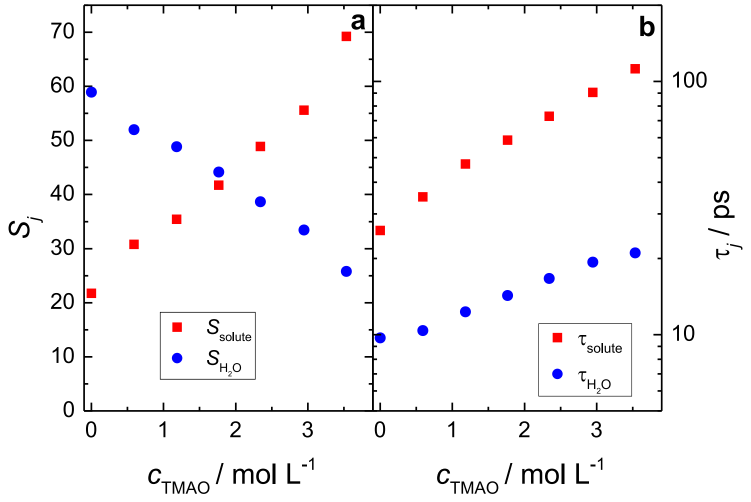

Figure S5: (**a**) Relaxation strengths, S_j, and (**b**) relaxation times, τ_j, of the solute and the water relaxation for aqueous solutions of TMAO and urea. The concentration of urea was kept constant at $c_{\text{urea}} = 3.53\,\text{mol}\,\text{L}^{-1}$, while the concentration of TMAO was varied. The parameters were obtained by fitting two Debye-type relaxation modes to the experimental spectra. Parameters for $c_{\text{TMAO}} = 0$ were interpolated from the results for aqueous solutions of urea.

Constant concentration of TMAO $c_{\text{TMAO}} = 3.53\,\text{mol}\,\text{L}^{-1}$

In a third series of ternary samples we keep the concentration of TMAO constant at $c_{\text{TMAO}} = 3.53\,\text{mol}\,\text{L}^{-1}$. Six samples were prepared with variable concentrations of urea ($c_{\text{TMAO}} = 0.59$, 1.18, 1.77, 2.35, 2.93, and $3.53\,\text{mol}\,\text{L}^{-1}$). Dielectric spectra of these samples were recorded at frequencies ranging from 100 MHz to 70 GHz. Two Debye-type relaxations were fit to the experimental spectra corresponding to the solute and the bulk water relaxations. The spectra together with the fits are shown in Figure S6. The relaxation times and relaxation strengths extracted from the fits are displayed in Figure S7.

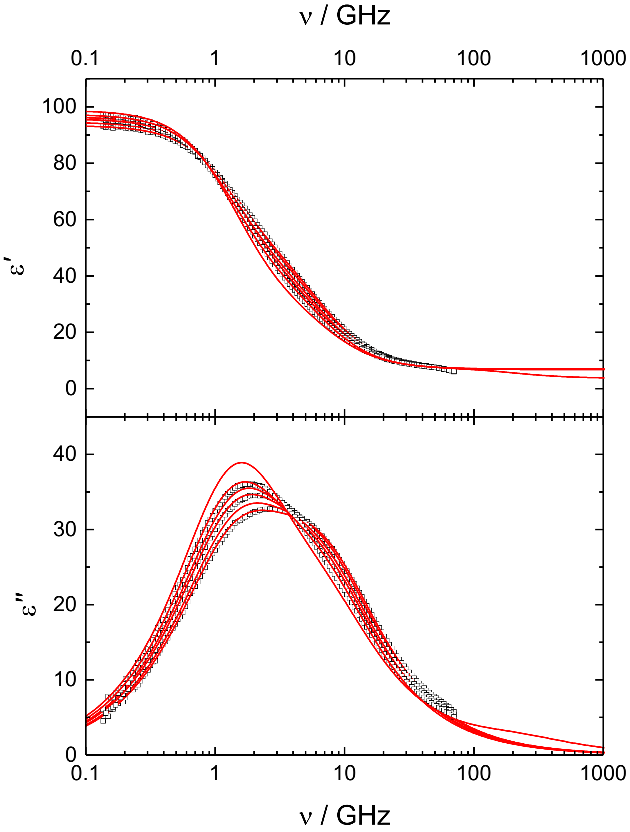

Figure S6: (**a**) Dielectric permittivity, $\varepsilon'(\nu)$, and (**b**) dielectric loss spectra, $\varepsilon''(\nu)$, for aqueous solutions of $c_{\mathrm{TMAO}} = 3.53\,\mathrm{mol\,L^{-1}}$ and variable concentration of urea, c_{urea}. Symbols correspond to experimental data whereas solid red lines show fits to two Debye modes. For visual clarity the data are only shown for each second concentration. The arrows indicate increasing concentration of urea.

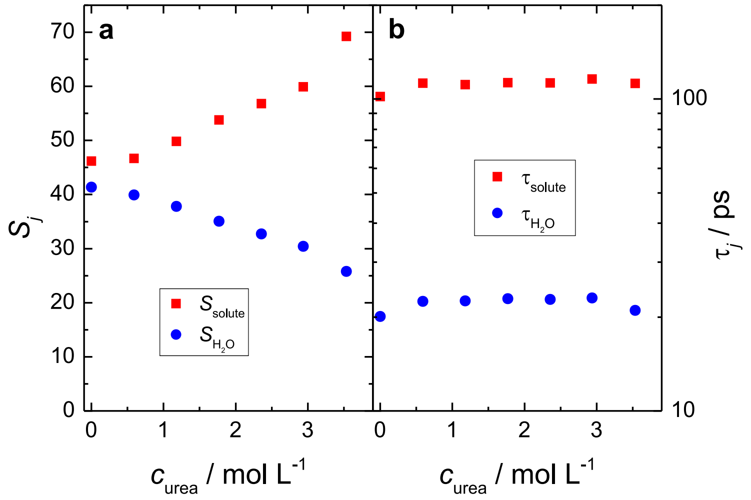

Figure S7: (**a**) Relaxation strengths, S_j, and (**b**) relaxation times, τ_j, of the solute and the water relaxation for aqueous solutions of TMAO and urea. The concentration of TMAO was kept constant at $c_{\mathrm{TMAO}} = 3.53\,\mathrm{mol\,L^{-1}}$, while the concentration of urea was varied. The parameters were obtained by fitting two Debye-type relaxation modes to the experimental spectra. Parameters for $c_{\mathrm{urea}} = 0$ were interpolated from the results for aqueous solutions of TMAO.[3]

Solute relaxation times and viscosities of ternary aqueous solutions of TMAO and urea

As indicated in the main manuscript, the solute relaxation times represent an amplitude weighted average of the rotation times for urea and TMAO·3H_2O complexes. For measurements at a fixed concentration of urea ($\mathrm{c_{urea}} = 3.5\,\mathrm{mol\,L^{-1}}$) or TMAO ($\mathrm{c_{TMAO}} = 3.5\,\mathrm{mol\,L^{-1}}$), the relative weight of both solutes contributing to the observed τ_{solute} varies with concentration. This leads to an intrinsic non-linear scaling of τ_{solute} with composition (Figure S8a) for these measurements series. Nevertheless, the observed variation of τ_{solute} is in broad accordance with the variation of the sample viscosities (dashed lines in Figure S8a). Notably, all viscosities of the ternary samples increase in a non-linear manner with increasing (co-)solute concentration (Figure S8b).

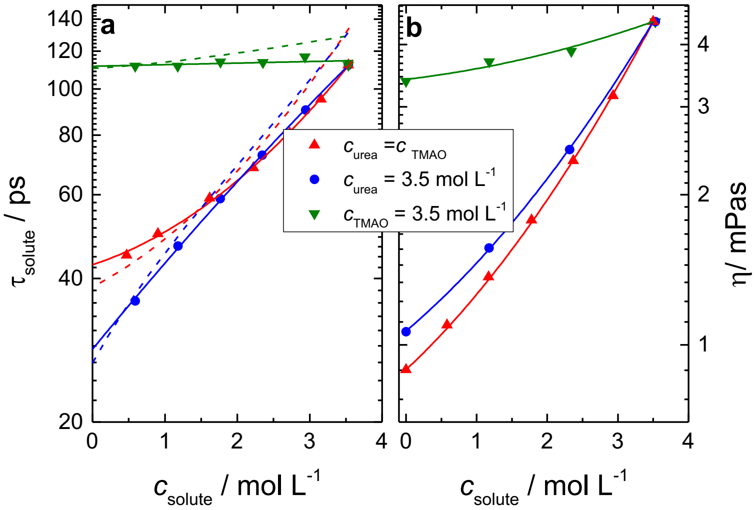

Figure S8: Solute relaxation times (**a**) and dynamic viscosities (**b**) for ternary aqueous solutions of TMAO and urea. Symbols show experimental data, solid lines are just a visual aid. Dashed lines correspond to the amplitude weighted average of the urea and TMAO relaxation times with the rotation times τ_{urea} and τ_{TMAO} taken from our studies of the binary mixtures and subsequently corrected for the increased viscosity of the sample ($\cdot\eta^{\text{ternary}}/\eta^{\text{binary}}$).

Viscosities of aqueous solutions of amphiphilic molecules

We determine the viscosities of several amphiphilic molecules co-solvated with urea and compare these to the viscosities of the ternary samples presented in the main manuscript. In Figure S9a the dynamic viscosities of solutions of TMAO, tertramethylurea (TMU), and tertiary-butanol (TBA) in water are shown. The second derivatives $\partial^2 \log(\eta)/\partial c^2$, as discussed in the main manuscript are determined to be 0.002 $\text{L}^2\,\text{mol}^{-2}$ (TMAO), -0.006 $\text{L}^2\,\text{mol}^{-2}$ (TMU), and -0.01 $\text{L}^2\,\text{mol}^{-2}$ (TBA). For equimolar mixtures of the amphiphiles with urea (Figure S9b) the second derivatives are determined to be 0.04 $\text{L}^2\,\text{mol}^{-2}$ (TMAO+urea), 0.01 $\text{L}^2\,\text{mol}^{-2}$ (TMU+urea), and -0.02 $\text{L}^2\,\text{mol}^{-2}$ (TBA+urea).

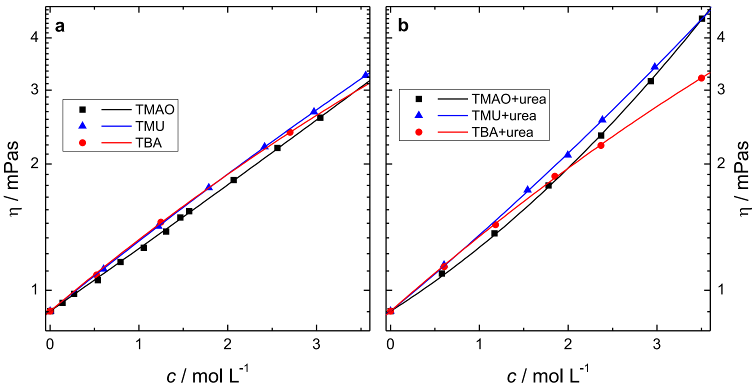

Figure S9: Dynamics viscosities, η, for solutions of TMAO, TMU, and TBA in water. Symbols show experimental data, lines show fits of a second order polynomial to $\log \eta$. Viscosities for solutions of TMAO[4] and TBA[5] were taken from the literature.

References

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