# Electronic Supplementary Information

# Ionic effects on Supramolecular Hosts: Solvation and Counter-ion Binding in Polar Media

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## Quint-Viallard analysis of molar conductivity

With formal charge numbers of –4 ($Na_4TES$) respectively +4 ($TAM \cdot (HCl)_4$) for the cryptand ion the studied ionic resorcin[4]arenes can be formally regarded as unsymmetrical 1:4 respectively 4:1 electrolytes. To model the molar electrical conductivity, $\Lambda$, of solutions of unsymmetrical electrolytes Quint and Viallard (Q-V) proposed a theory based on Kohlrausch's law of independent ion migration.[1] This Q-V model can be expressed[2] by the following set of equations

$$\Lambda = \sum_{j=1}^{h} \frac{c_j |z_j| \lambda_j}{c} \tag{S1a}$$

$$\lambda_j = \lambda_j^{\infty} - S_j (I)^{1/2} + E_j I \ln I + J_{1,j} I - J_{2,j} I^{3/2} \tag{S1b}$$

$$I = \frac{\alpha}{2} \sum_j z_j^2 c_j \tag{S1c}$$

where $c_j$ represents the concentration of species $j$ with charge number $|z_j|$ at the total electrolyte concentration, $c$. The molar ionic conductivity, $\lambda_j$, is calculated with eq. (S1b) where the parameters $S_j$, $E_j$, $J_{1,j}$ and $J_{2,j}$ depend on $\lambda_j$, the distance parameter $a_j$, viscosity, $\eta$, and static permittivity, $\varepsilon$, of the solvent. The complex expressions for these parameters are given in reference 2.

Originally, the Q-V model did not consider ion association. This was included by Apelblat,[3] who coupled equations (S1a-c) with a chemical equilibrium approach

$$K_A = \frac{(1 - \alpha)}{\nu_+ \nu_- c \alpha^2} F_\gamma \tag{S2}$$

via the dissociation degree, $\alpha$, which modifies the total ionic strength, $I$, in equation (S1c). In eqn. (S2) $\nu_+$ and $\nu_-$ are the stoichiometric coefficients of the ions involved in the equilibrium and $F_\gamma$ is the quotient of their activity coefficients, $\gamma_j$, approximated in dilute solutions by the Debye-Hückel equation

$$\log \gamma_j = \frac{z_j^2 A \sqrt{I}}{1 + a_j B \sqrt{I}} \tag{S3a}$$

$$A = 1.825 \times 10^6 (\varepsilon T)^{3/2} \qquad B = 50.29 \times 10^8 (\varepsilon T)^{1/2} \tag{S3b}$$

The thus obtained data for the limiting molar conductivities, $\Lambda^{\infty}$, and association constants, $K_A^{\circ}$, are given in Table S8. The $\Lambda^{\infty}$ values from the Q-V and lcCM (Table 1 of the Main Manuscript) models differ by ~ 3% for $Na_4TES$ and ~ 6% for $TAM \cdot (HCl)_4$. This is already large but in view of the exotic electrolytes possibly acceptable. However, the association constants obtained with the Q-V approach are clearly unrealistic. With $K_A^{\circ}$ values in the range of ~140-1000 $M^{-1}$

most Q-V results are exceptionally high for aqueous solutions of salts involving $Na^+$ or $Cl^-$ ions (Table S8). Additionally, with practically no association at 278.15 and 308.15 K but values $> 140\,M^{-1}$ in between the temperature dependence for $TAM \cdot (HCl)_4$ is inconsistent.

## Estimated solute relaxation times

Rotational correlation times of possible solute species (free $Na_4TES$ respectively $TAM \cdot (HCl)_4$ and their contact (CIPs) and solvent-shared ion pairs (SIPs)) were estimated with the Stokes-Debye-Einstein equation

$$\tau_j^{rot} = \frac{3V_{\text{eff},j}\eta}{k_B T} \tag{S4}$$

where $\eta$ is the dynamic viscosity of the sample and $V_{\text{eff},j} = V_m f_\perp C$ the effective volume of the dipole, determined by its molecular volume, $V_m$, the associated geometry factor, $f_\perp$, and the hydrodynamic coupling parameter, $C$.[4] For oblate ellipsoids with semi-principal axes $a < b = c$ the geometry factor is given by

$$f_\perp = \frac{2}{3} \cdot \frac{1 - q^4}{\left(\frac{2-q^2}{\sqrt{q^2-1}}\right)\left(\arctan\sqrt{q^2-1}\right) - 1} \tag{S5}$$

where $q = b/a$.[5] For $c \to 0$ the thus obtained $\tau_j^{rot}$ values can be directly compared to experimental relaxation times, $\tau_j$.[6]

Estimates for the rotational correlation time, $\tau_{rot}$, of irregular-shaped bodies, like $TES^{4-}$ (Fig. 1 of the Main Paper) or its contact (CIP), $[NaTES]^{3-}$ (Fig. 5), or solvent-separated ion pairs (SSIP), $[TES^{4-} \cdot H_2O \cdot Na^+]^{3-}$, are very coarse as these structures only roughly resemble rotational ellipsoids. Also, their hydrodynamic coupling to bulk viscosity is unknown. Nevertheless, such values may provide a first hint for the assignment of observed relaxations. Approximating $TES^{4-}$ and $[NaTES]^{3-}$ as oblate ellipsoids with molecular volumes, $V_m$, determined by Winmostar[7] and semi-principle axes $a < b = c$ extracted with Avogadro (V 1.1.1)[8] from the MOPAC2016[9] (PM6 Hamiltonian) output yielded values of $\tau_{rot} = 1.5\,ns$ for $TES^{4-}$ and $4.8\,ns$ for $[NaTES]^{3-}$ at infinite dilution in DMSO. The corresponding values in water are $670\,ps$ for $TES^{4-}$, $474\,ps$ for $[TES^{4-} \cdot H_2O \cdot Na^+]^{3-}$, and $2.1\,ns$ for $[NaTES]^{3-}$. Thus, the relaxation times of the free anion and its ion pairs should be sufficiently different to allow their distinction in the dielectric spectrum.

On the other hand, it is also obvious that the above $\tau_{rot}$ values considerably exceed the experimental relaxation times of the solute-related modes ($\tau_1 \approx 2.2\,ns$ and $\tau_2 \approx 400\,ps$ for DMSO; $\tau_1 \approx 300\,ps$ and $\tau_2 = 60\,ps$ for water). One possible

reason besides the unknown value for the effective hydrodynamic coupling parameter, $C$, is that eqn. (S5) implies the dipole moment parallel being to the short $a$ axis of the ellipsoid. The MOPAC results suggest that this is neither true for TES$^{4-}$ nor [NaTES]$^{3-}$. Thus, one may argue that in addition to the tumbling motion of the ellipsoid involving rotation around the $b$ and $c$ axes, also the presumably faster spinning around the $a$ axis is DRS active. Although we tentatively assign mode 1 to [NaTES]$^{3-}$ contact ion pairs (CIPs) in DMSO and solvent-shared ion pairs (SSIPs) in water and mode 2 to free TES$^{4-}$ anions in both solvents, it is only fair to say that the evidence provided by the above comparison of calculated $\tau_{\text{rot}}$ values with the experimental data for $\tau_1$ and $\tau_2$ is limited.

# Supplementary Tables

Table S1: Parameters of the D+D+CD model for the dielectric spectra of Na$_4$TES solutions of concentration, $c$, in DMSO at 298.15 K: static permittivity, $\varepsilon$; amplitudes, $S_j$, and relaxation times, $\tau_j$, of the resolved modes, $j = 1 \ldots 3$; width parameter, $\beta_3$; and high-frequency permittivity, $\varepsilon_\infty$. Also included are data for density, $\rho$, and conductivity, $\kappa$, of these solutions.[a]

| $c$ | $\rho$ | $\kappa$[b] | $\varepsilon$ | $S_1$ | $\tau_1$ | $S_2$ | $\tau_2$ | $S_3$ | $\tau_3$ | $\beta_3$ | $\varepsilon_\infty$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.0000[c] | 1.095470 | 0.073 | 46.50 | | | | | 42.36 | 20.7 | 0.885 | 4.14 |
| 0.0142 | 1.100868 | 0.073 | 48.85 | 3.30 | 2080 | 0.88 | 320 | 40.75 | 20.8 | 0.879 | 3.92 |
| 0.0247 | 1.104824 | 0.102 | 49.73 | 4.53 | 2100 | 1.52 | 353 | 39.67 | 20.3 | 0.884 | 4.01 |
| 0.0519 | 1.115009 | 0.151 | 49.29 | 5.26 | 1650 | 2.38 | 321 | 37.65 | 21.1 | 0.865 | 4.00 |
| 0.0757 | 1.123791 | 0.177 | 49.71 | 6.94 | 1640 | 2.75 | 346 | 36.14 | 22.1 | 0.842 | 3.88 |
| 0.0958 | 1.131346 | 0.183 | 51.34 | 8.53 | 2420 | 3.90 | 420 | 35.36 | 23.5 | 0.809 | 3.54 |
| 0.1416 | 1.152584 | 0.165 | 51.62 | 9.08 | 3440 | 6.28 | 562 | 32.86 | 27.2 | 0.751 | 3.40 |
| 0.1846[c] | 1.173013 | 0.195 | 40.45 | | | 7.73 | 500F | 28.53 | 28.0 | 0.726 | 3.22 |

[a] Units: $c$ in M; $\rho$ in kg L$^{-1}$; $\kappa$ in S m$^{-1}$; $\tau_j$ in $10^{-12}$ s. [b] Interpolated from data of Ref. 10. [c] See Ref. 11. Parameter values followed by the letter F were not adjusted in the fitting procedure.

Table S2: Parameters of the 3D model for the dielectric spectra of aqueous Na$_4$TES solutions of concentration, $c$, at 298.15 K: static permittivity, $\varepsilon$; amplitudes, $S_j$ and relaxation times, $\tau_j$, of the resolved modes, $j = 1\ldots3$; and high-frequency permittivity, $\varepsilon_\infty$. Also included are data for density, $\rho$, and conductivity, $\kappa$.[a]

| $c$ | $\rho^b$ | $\kappa$ | $\varepsilon$ | $S_1$ | $\tau_1$ | $S_2$ | $\tau_2$ | $S_3$ | $\tau_3$ | $\varepsilon_\infty$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0000$^c$ | 0.997047 | | 78.37 | | | | | 74.85 | 8.32 | 3.52 |
| 0.0100 | 1.001444 | 0.488 | 81.90 | 4.47 | 556 | 0.57 | 60.0F | 71.01 | 8.27 | 5.85 |
| 0.0244 | 1.007969 | 1.033 | 81.38 | 5.69 | 301 | 0.87 | 60.0F | 68.80 | 8.23 | 6.03 |
| 0.0488 | 1.019547 | 1.844 | 80.56 | 6.93 | 293 | 1.94 | 60.0F | 65.42 | 8.23 | 6.26 |
| 0.0722 | 1.031324 | 2.515 | 79.27 | 6.71 | 247 | 3.77 | 60.0F | 62.44 | 8.07 | 6.36 |
| 0.0819 | 1.036412 | 2.762 | 78.80 | 7.01 | 250 | 4.32 | 60.0F | 61.14 | 7.96 | 6.32 |
| 0.1307 | 1.063694 | 3.804 | 76.54 | 7.39 | 335 | 6.02 | 60.0F | 56.80 | 8.18 | 6.33 |
| 0.1841 | 1.096924 | 4.624 | 73.39 | 6.89 | 353 | 8.18 | 60.0F | 51.71 | 8.19 | 6.61 |
| 0.2263 | 1.125676 | 5.131 | 69.14 | 5.56 | 322 | 8.36 | 60.0F | 48.07 | 8.29 | 7.16 |

[a] Units: $c$ in M; $\rho$ in kg L$^{-1}$; $\kappa$ in S m$^{-1}$; $\tau_j$ in $10^{-12}$ s. [b] Interpolated from Ref. 12. Parameter values followed by the letter F were not adjusted in the fitting procedure.

Table S3: Parameters of the 5D model for the dielectric spectra of TAM $\cdot$ (HCl)$_4$ solutions of concentration, $c$, in DMSO-Water(10.9% $w$) at 298.15 K: static permittivity, $\varepsilon$; amplitudes, $S_j$ and relaxation times, $\tau_j$, of the resolved modes, $j = 1\ldots5$; and high-frequency permittivity, $\varepsilon_\infty$. Also included are data for density, $\rho$, and conductivity, $\kappa$.[a]

| $c$ | $\rho$ | $\kappa$ | $\varepsilon$ | $S_1$ | $\tau_1$ | $S_2$ | $\tau_2$ | $S_3$ | $\tau_3$ | $S_4$ | $\tau_4$ | $S_5$ | $\tau_5$ | $\varepsilon_\infty$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.0000 | 1.098638 | 0 | 57.08 | | | | | 37.25 | 40.5 | 13.19 | 16.9 | 2.37 | 2.32 | 4.27 |
| 0.0295 | 1.104436 | 0.101 | 57.05 | 1.58 | 1650 | 0.54F | 450F | 30.53 | 47.2 | 17.31 | 20.0 | 2.91 | 2.69 | 4.19 |
| 0.0552 | 1.109257 | 0.144 | 57.08 | 2.58 | 1230 | 1.05 | 412F | 26.90 | 52.0 | 19.05 | 22.5 | 3.02 | 3.22 | 4.47 |
| 0.0852 | 1.114789 | 0.178 | 56.19 | 3.07 | 1150 | 1.67 | 387 | 25.73 | 55.5 | 17.91 | 23.5 | 3.27 | 3.66 | 4.54 |
| 0.1112 | 1.119502 | 0.196 | 55.79 | 4.44 | 1220 | 2.10 | 194 | 25.83 | 56.6 | 15.50 | 22.8 | 3.29 | 3.85 | 4.62 |
| 0.1374 | 1.124153 | 0.207 | 55.27 | 4.99 | 1290 | 2.65 | 223 | 24.73 | 60.0 | 14.93 | 23.4 | 3.29 | 3.89 | 4.67 |
| 0.1727 | 1.130475 | 0.215 | 53.92 | 5.18 | 1250 | 3.53 | 230 | 24.14 | 63.5 | 13.09 | 23.4 | 3.24 | 4.02 | 4.74 |

[a] Units: $c$ in M; $\rho$ in kg L$^{-1}$; $\kappa$ in S m$^{-1}$; $\tau_j$ in $10^{-12}$ s. Parameter values followed by the letter F were not adjusted in the fitting procedure.

Table S4: Molar electrical conductivity, $\Lambda$, of aqueous solutions of Na$_4$TES at temperatures $T$.[a]

| $10^3 m$ | $\Lambda$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | $T$ =278.15 | $T$ =283.15 | $T$ =288.15 | $T$ =293.15 | $T$ =298.15 | $T$ =303.15 | $T$ =308.15 |
| 0.04051 | 295.1 | 341.4 | 397.6 | 449.3 | 503.4 | 559.6 | 618.7 |
| 0.08309 | 295.4 | 341.4 | 390.0 | 441.1 | 494.3 | 549.6 | 606.4 |
| 0.16472 | 290.0 | 334.1 | 381.8 | 432.6 | 486.7 | 539.3 | 595.2 |
| 0.20445 | 287.7 | 331.5 | 378.3 | 427.5 | 479.0 | 532.8 | 587.3 |
| 0.24705 | 284.4 | 328.8 | 375.6 | 424.6 | 475.8 | 529.0 | 583.9 |
| 0.28748 | 282.1 | 326.4 | 372.9 | 421.4 | 472.1 | 524.9 | 579.0 |
| 0.32725 | 281.0 | 324.8 | 370.9 | 419.3 | 470.2 | 522.9 | 577.0 |
| 0.40726 | 277.6 | 320.8 | 366.3 | 414.3 | 464.1 | 516.2 | 570.0 |
| 1.23481 | 255.3 | 299.0 | 340.5 | 384.6 | 431.6 | 479.8 | 568.4 |
| 2.14952 | 245.6 | 283.5 | 323.9 | 366.6 | 411.5 | 458.3 | 530.5 |
| 2.93682 | 230.1 | 266.3 | 304.5 | 344.7 | 387.0 | 431.2 | 506.5 |
| 3.61978 | 220.8 | 255.5 | 291.9 | 330.4 | 370.6 | 412.5 | 476.7 |
| 4.18862 | 216.7 | 250.7 | 286.6 | 324.4 | 364.0 | 405.0 | 455.5 |
| 4.87160 | 208.8 | 241.6 | 276.1 | 312.5 | 350.7 | 390.1 | 447.2 |
| 5.54371 | 204.8 | 236.8 | 270.5 | 306.1 | 343.6 | 382.4 | 430.5 |
| 6.08865 | 201.4 | 233.2 | 266.7 | 302.0 | 339.0 | 377.5 | 422.3 |
| 6.75745 | 197.0 | 228.0 | 260.8 | 295.2 | 331.4 | 369.0 | 416.9 |

[a] Units: $m$ in mol kg$^{-1}$; $\Lambda$ in S cm$^2$ mol$^{-1}$; $T$ in K.

Table S5: Molar electrical conductivity, $\Lambda$, of $Na_4TES$ solutions in DMSO at temperatures $T$.[a]

| $10^3 m$ | $\Lambda$ | | | |
| --- | --- | --- | --- | --- |
| | $T=293.15$ | $T=298.15$ | $T=303.15$ | $T=308.15$ |
| 0.44103 | 72.0 | 80.3 | 89.0 | 97.8 |
| 1.03141 | 67.9 | 75.7 | 83.9 | 92.3 |
| 1.76357 | 61.2 | 68.3 | 75.6 | 83.2 |
| 2.25817 | 58.7 | 65.5 | 72.6 | 79.9 |
| 2.80300 | 56.1 | 62.6 | 69.4 | 76.4 |
| 3.45386 | 53.5 | 59.7 | 66.2 | 72.9 |
| 3.91858 | 52.3 | 58.3 | 64.7 | 71.2 |
| 4.40452 | 50.9 | 56.9 | 63.0 | 69.4 |
| 4.89774 | 49.9 | 55.6 | 61.7 | 67.9 |
| 5.38144 | 48.8 | 54.5 | 60.4 | 66.6 |
| 5.84393 | 48.2 | 53.9 | 59.7 | 65.8 |
| 6.32897 | 47.4 | 52.9 | 58.7 | 64.6 |
| 6.79298 | 46.6 | 52.1 | 57.8 | 63.6 |
| 7.25651 | 46.2 | 51.6 | 57.2 | 63.0 |
| 7.62350 | 45.7 | 51.1 | 56.7 | 62.4 |

[a] Units: $m$ in mol kg$^{-1}$; $\Lambda$ in S cm$^2$ mol$^{-1}$; $T$ in K.

Table S6: Molar electrical conductivity, $\Lambda$, of aqueous solutions of $TAM \cdot (HCl)_4$ at temperatures $T$.[a]

| $10^3 m$ | $\Lambda$ | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | $T=278.15$ | $T=283.15$ | $T=288.15$ | $T=293.15$ | $T=298.15$ | $T=303.15$ | $T=308.15$ |
| 2.14298 | 372.9 | 423.9 | 476.7 | 531.2 | 587.5 | 644.9 | 704.5 |
| 2.96417 | 364.0 | 413.7 | 464.9 | 517.8 | 572.2 | 627.9 | 686.0 |
| 3.89899 | 355.4 | 403.6 | 453.5 | 504.3 | 560.1 | 611.8 | 667.9 |
| 4.86213 | 349.8 | 397.4 | 446.5 | 497.0 | 549.0 | 602.2 | 657.3 |
| 5.75270 | 344.7 | 391.6 | 440.2 | 490.8 | 542.1 | 594.6 | 648.9 |
| 6.59003 | 340.2 | 386.4 | 434.0 | 483.0 | 533.3 | 584.9 | 638.4 |
| 7.42781 | 337.3 | 383.0 | 430.2 | 478.7 | 528.7 | 579.6 | 632.3 |
| 8.19092 | 335.2 | 380.1 | 426.7 | 474.7 | 524.3 | 574.9 | 626.9 |
| 8.80957 | 331.7 | 376.7 | 423.0 | 470.5 | 519.5 | 569.5 | 621.7 |

[a] Units: $m$ in mol kg$^{-1}$; $\Lambda$ in S cm$^2$ mol$^{-1}$; $T$ in K.

Table S7: Molar electrical conductivity, $\Lambda$, of $\text{TAM} \cdot (\text{HCl})_4$ solutions in DMSO at temperatures $T$.[a]

| $10^3 m$ | $\Lambda$ | | | |
|---|---|---|---|---|
| | $T = 293.15$ | $T = 298.15$ | $T = 303.15$ | $T = 308.15$ |
| 0.51783 | 95.1 | 105.4 | 116.3 | 127.6 |
| 1.09710 | 78.4 | 86.9 | 95.7 | 104.9 |
| 1.65674 | 70.4 | 78.0 | 85.8 | 93.8 |
| 2.21573 | 65.1 | 72.0 | 79.1 | 86.5 |
| 2.73586 | 61.5 | 68.0 | 74.7 | 81.7 |
| 3.28961 | 58.3 | 64.4 | 70.7 | 77.3 |
| 3.87559 | 55.5 | 61.3 | 67.3 | 73.5 |
| 4.42547 | 53.7 | 59.4 | 65.1 | 71.2 |
| 4.97921 | 52.0 | 57.5 | 63.0 | 68.8 |
| 5.54985 | 50.3 | 55.5 | 61.0 | 66.6 |
| 6.09307 | 48.8 | 53.9 | 59.2 | 64.7 |
| 6.57973 | 47.7 | 52.6 | 57.8 | 63.1 |
| 6.99118 | 47.8 | 52.8 | 58.0 | 63.4 |
| 7.10856 | 48.0 | 53.0 | 58.3 | 63.7 |

[a] Units: $m$ in mol kg$^{-1}$; $\Lambda$ in S cm$^2$ mol$^{-1}$; $T$ in K.

Table S8: Limiting molar conductivities, $\Lambda^\infty$, and association constants, $K_A^\circ$, of aqueous solutions of $TAM \cdot (HCl)_4$ and $Na_4TES$ at temperature, $T$, obtained from fitting $\Lambda$ with the Quint-Viallard model (eqs. S1-S3).[a]

| $T$ | $\Lambda^\infty$ | $K_A^\circ$ |
|---|---|---|
| $TAM \cdot (HCl)_4$ | | |
| 278.15 | 421.5 | 0.01 |
| 283.15 | 475.9 | 141.7 |
| 288.15 | 532.5 | 263.5 |
| 293.15 | 589.6 | 417.1 |
| 298.15 | 651.9 | 504.3 |
| 303.15 | 715.3 | 496.3 |
| 308.15 | 802.1 | 1.0 |
| $Na_4TES$ | | |
| 278.15 | 306.9 | 709.0 |
| 283.15 | 354.7 | 816.4 |
| 288.15 | 406.7 | 757.1 |
| 293.15 | 459.9 | 808.2 |
| 298.15 | 515.8 | 872.6 |
| 303.15 | 573.3 | 952.5 |
| 308.15 | 633.0 | 1039.4 |

[a] Units: $\Lambda^\infty$ in $S \cdot cm^2 \cdot mol^{-1}$; $K_A^\circ$ in $M^{-1}$; $T$ in K.

Table S9: Limiting molar ionic conductivities, $\lambda_i^\infty$, of cations ($i = +$) and cations ($i = -$) of TAM $\cdot$ (HCl)$_4$ and Na$_4$TES as function of temperature, $T$, in water and DMSO.

| | TAM $\cdot$ (HCl)$_4$ | | Na$_4$TES | |
|---|---|---|---|---|
| $T$ | $\lambda_+^\infty$ | $\lambda_-^\infty$ | $\lambda_+^\infty$ | $\lambda_-^\infty$ |
| | water | | | |
| 278.15 | 203.3 | 47.4$^c$ | 30.3$^c$ | 175.5 |
| 283.15 | 230.3 | 54.2$^c$ | 34.9$^c$ | 203.3 |
| 288.15 | 258.0 | 61.3$^c$ | 39.8$^c$ | 233.7 |
| 293.15 | 286.3 | 68.7$^c$ | 44.9$^c$ | 264.6 |
| 298.15 | 316.9 | 76.3$^c$ | 50.2$^c$ | 297.0 |
| 303.15 | 345.8 | 84.1$^c$ | 55.8$^c$ | 330.1 |
| 308.15 | 377.5 | 92.2$^c$ | 61.6$^c$ | 364.2 |
| | DMSO | | | |
| 293.15 | 23.7 | 22.7$^b$ | 12.5$^d$ | 30.0 |
| 298.15 | 30.9 | 24.1$^b$ | 14.2$^d$ | 32.6 |
| 303.15 | 38.5 | 25.6$^b$ | 15.9$^d$ | 35.5 |
| 308.15 | 46.5 | 27.3$^b$ | 17.5$^d$ | 38.6 |

$^a$ Units: $\lambda_i^\infty$ in S cm$^2$ mol$^{-1}$; $T$ in K. $^b$ Interpolated from data of Ref. 13. $^c$ Taken from Ref. 14. $^d$ Interpolated from data of Ref. 15.

# Supplementary figures
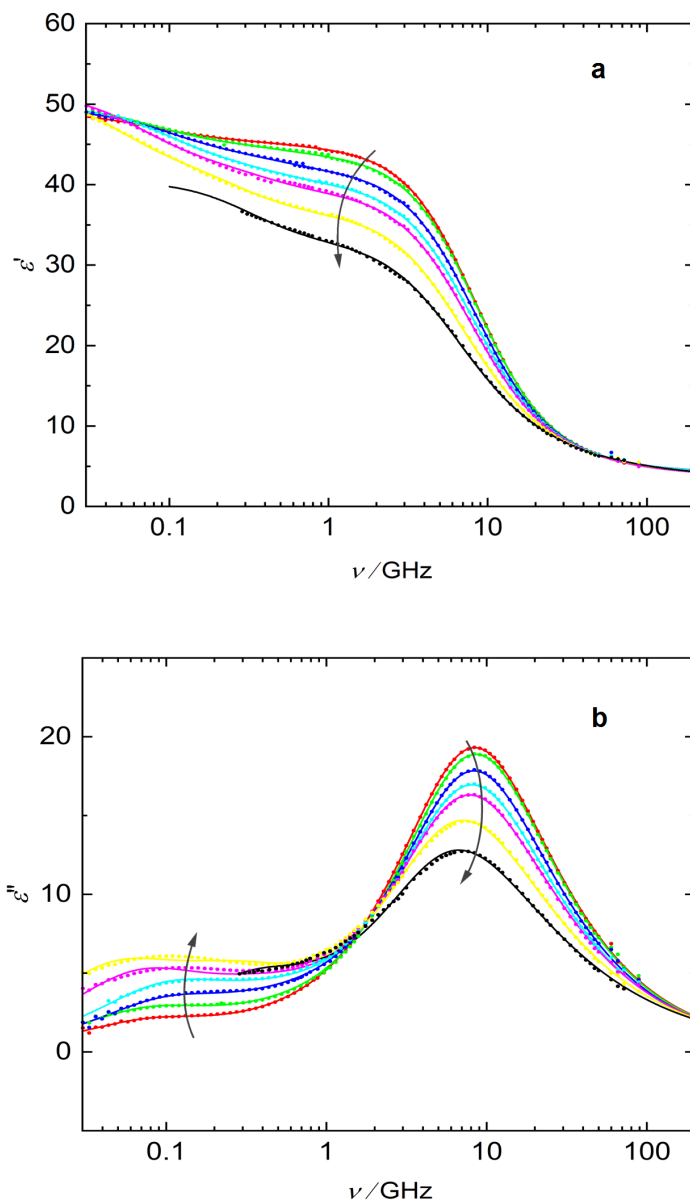
Figure S1: Spectra (symbols) of (a) relative permittivity, $\varepsilon'(\nu)$, and (b) dielectric loss, $\varepsilon''(\nu)$, and associated fits with the D+D+CD model (lines) of $Na_4TES$ in DMSO. Arrows indicate increasing concentration, $c$/M = 0, 0.0142, 0.0247, 0.0519, 0.0757, 0.0958, 0.1416, 0.1846; for clarity not all data points are shown.
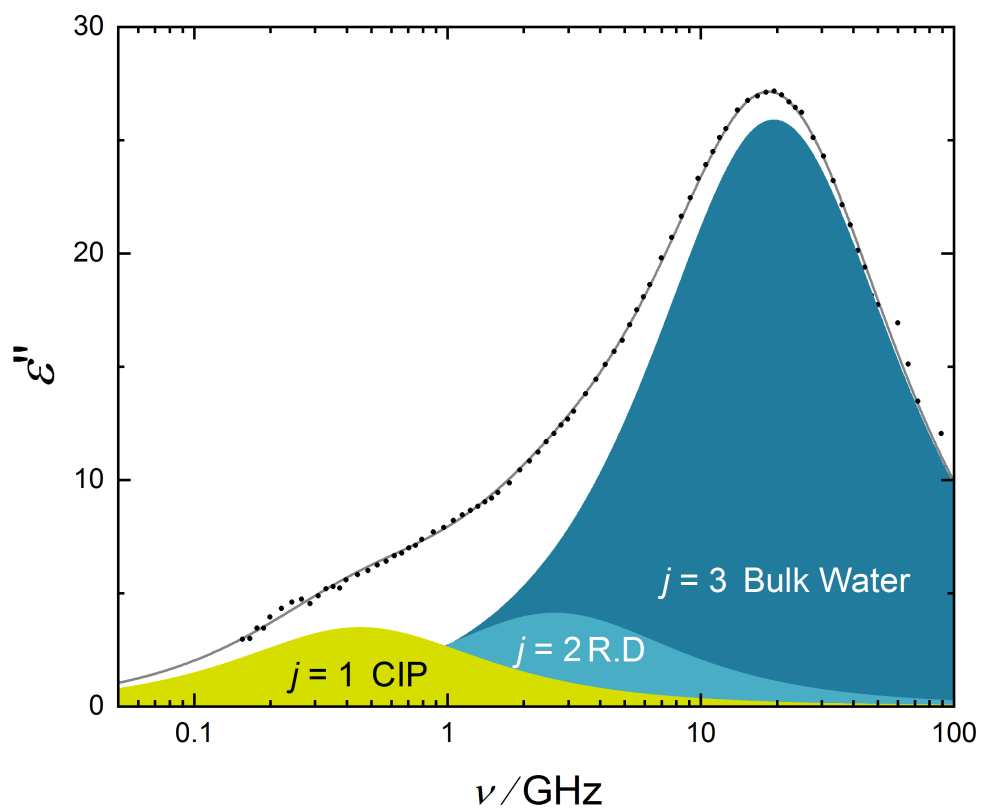
Figure S2: Dielectric loss spectrum, $\varepsilon''(\nu)$, of $c = 0.1841\,$M aqueous Na$_4$TES at 298.15 K. Experimental data (●) where fitted with the 3D Model (red line). The shaded areas indicate the contributions of the resolved modes, $j = 1 \ldots 3$.
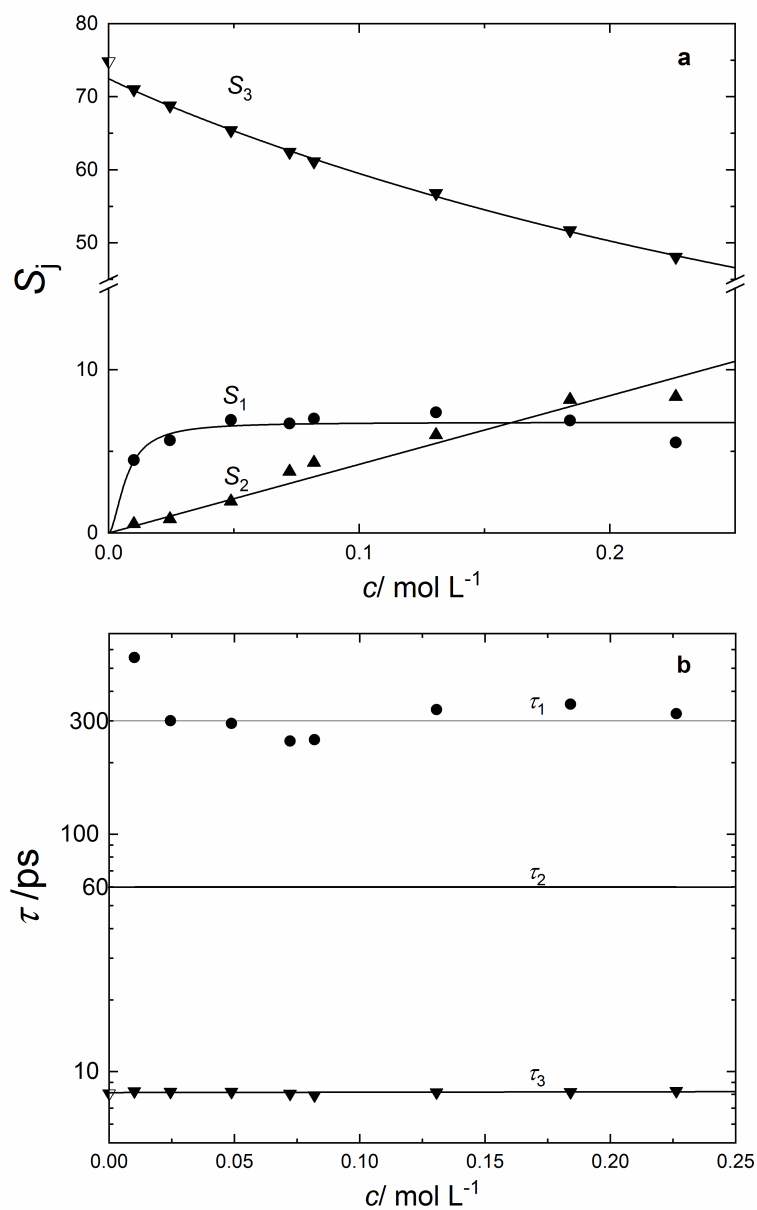
Figure S3: (a) Resolved amplitudes, $S_j$, and (b) relaxation times, $\tau_j$, as a function of Na$_4$TES concentration, $c$, in water at 298.15 K. In the final fit the relaxation time of mode $j = 2$ was fixed to $\tau_2 = 60$ ps for all $c$ to minimize the scatter of the resulting amplitudes. Lines are for eye guidance. Half-filled symbols correspond to pure water.

S15
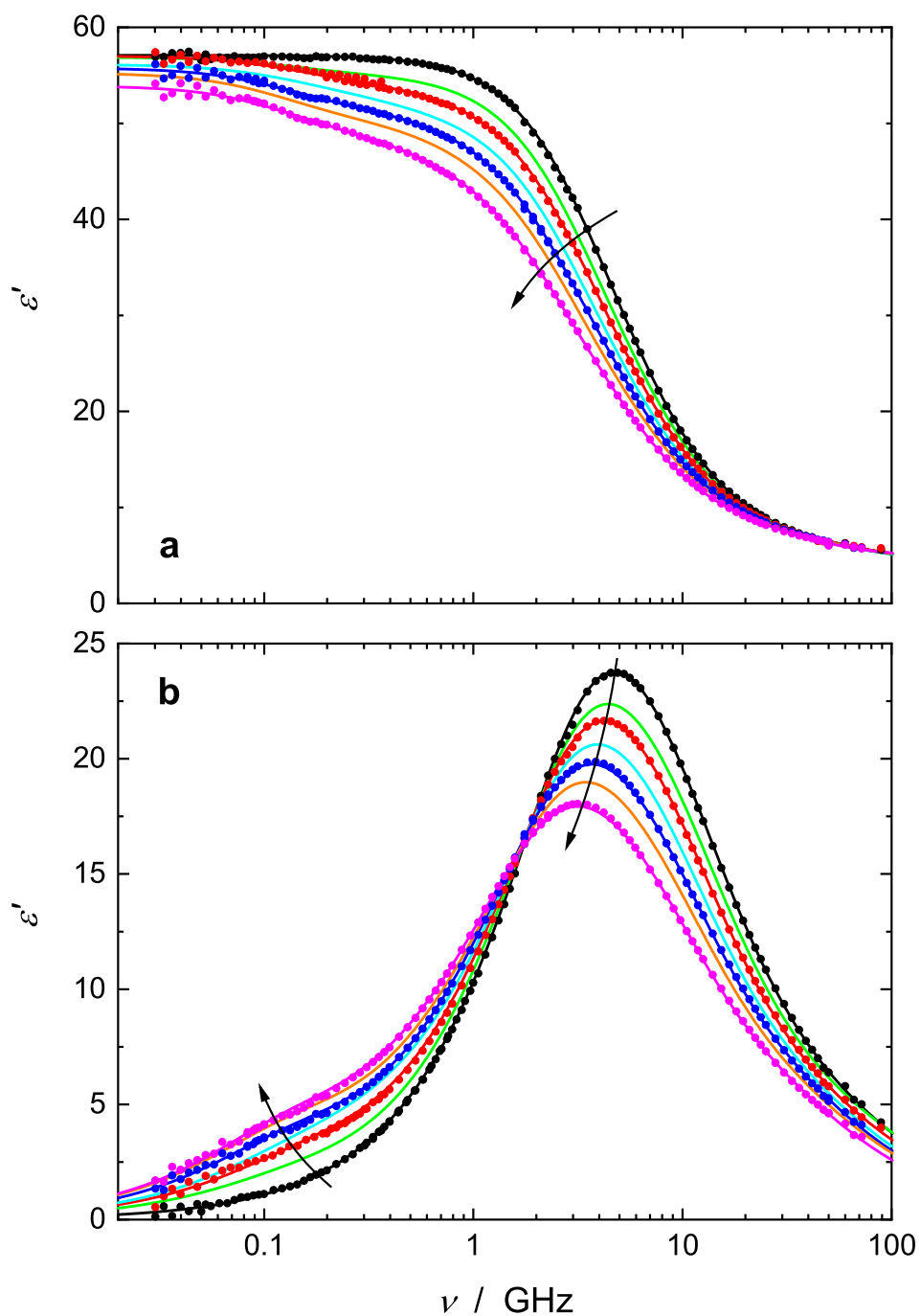
Figure S4: Spectra (symbols) of (a) relative permittivity, $\varepsilon'(\nu)$, and (b) dielectric loss, $\varepsilon''(\nu)$, of TAM·(HCl)$_4$ in DMSO-Water(10.9% $w$) and associated fits with the 5D model (lines). Arrows indicate increasing concentration, $c$/M = 0, 0.0295, 0.0552, 0.0852, 0.1112, 0.1374, 0.1727; for clarity not all data points are shown.
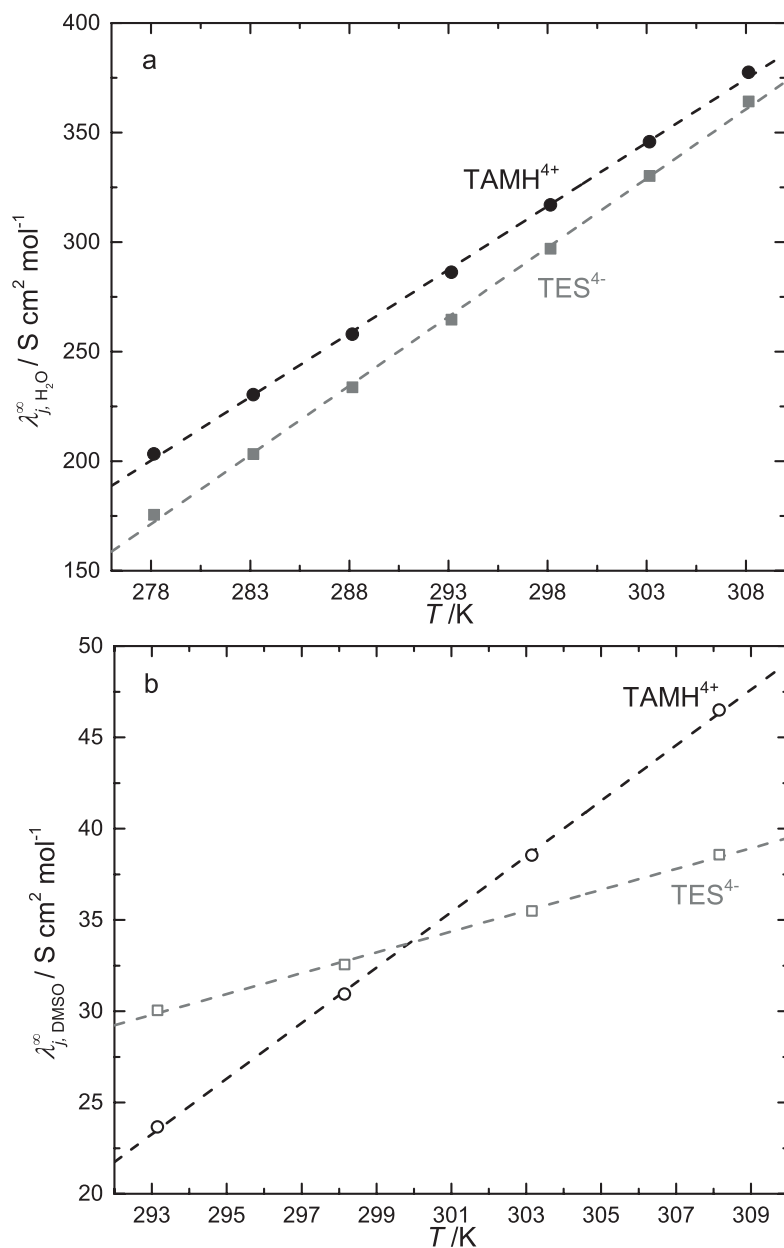
Figure S5: Molar ionic conductivities of solutions of $Na_4TES$ (squares) and $TAM \cdot (HCl)_4$ (circles) in water (a) and DMSO (b) as a function of Temperature, $T$. Dashed lines represent linear fits.

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