Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# The influence of like-charge attraction on the structure and dynamics of ionic liquids: NMR chemical shifts, quadrupole coupling constants, rotational correlation times and failure of Stokes-Einstein-Debye

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## Supporting Information

## SI0 Measured and calculated values in a temperature range between 315 and 406 K for IL I

| $T$ / K | $\delta^1$H / ppm | $\chi_D$ / kHz | $T_1$ / ms | $\tau_c$ / ps |
|---|---|---|---|---|
| 406 | 2,84 | 268,53 | 162,23 | 5,77 |
| 383 | 2,94 | 266,84 | 112,04 | 8,47 |
| 360 | 3,04 | 265,15 | 66,64 | 14,42 |
| 338 | 3,15 | 263,46 | 34,92 | 27,87 |
| 315 | 3,25 | 261,77 | 16,26 | 60,61 |

**Tab. 1:** Measured and calculated values for chemical shifts, $\delta^1$H, quadrupole coupling constants, $\chi_D$, deuteron relaxation times, $T_1$, and reorientational correlations times, $\tau_{OD}$, in a temperature range between 315 and 406 K for IL **I**.

## SI1 Measured and calculated values in a temperature range between 315 and 406 K for IL II

| $T$ / K | $\delta^1$H / ppm | $\chi_D$ / kHz | $T_1$ / ms | $\tau_c$ / ps |
|---|---|---|---|---|
| 406 | 2,73 | | | |
| 383 | 2,86 | 268,14 | 94,70 | 9,92 |
| 360 | 2,99 | 266,03 | 59,51 | 16,04 |
| 338 | 3,12 | 263,92 | 34,55 | 28,07 |
| 315 | 3,25 | 261,81 | 18,01 | 54,70 |

**Tab. 2:** Measured and calculated values for chemical shifts, $\delta^1$H, quadrupole coupling constants, $\chi_D$, deuteron relaxation times, $T_1$, and reorientational correlations times, $\tau_{OD}$, in a temperature range between 315 and 406 K for IL **II**.

## SI2 Measured and calculated values in a temperature range between 315 and 406 K for IL III

| $T$ / K | $\delta^1$H / ppm | $\chi_D$ / kHz | $T_1$ / ms | $\tau_c$ / ps |
|---|---|---|---|---|
| 406 | 3,52 | | | |
| 383 | 3,63 | 255,59 | 80,61 | 12,83 |
| 360 | 3,73 | 253,90 | 49,57 | 21,14 |
| 338 | 3,83 | 252,21 | 27,29 | 38,92 |
| 315 | 3,93 | 250,52 | 13,94 | 77,21 |

**Tab. 3:** Measured and calculated values for chemical shifts, $\delta^1$H, quadrupole coupling constants, $\chi_D$, deuteron relaxation times, $T_1$, and reorientational correlations times, $\tau_{OD}$, in a temperature range between 315 and 406 K for IL **III**.

## SI3 Measured and calculated values in a temperature range between 338 and 406 K for IL IV

| $T$ / K | $\delta^1$H / ppm | $\chi_D$ / kHz | $T_1$ / ms | $\tau_c$ / ps |
|---|---|---|---|---|
| 406 | 5,18 | 230,10 | 58,13 | 21,94 |
| 383 | 5,27 | 228,68 | 36,42 | 35,47 |
| 360 | 5,35 | 227,25 | 19,28 | 67,83 |
| 338 | 5,44 | 225,82 | 8,85 | 149,69 |

**Tab. 4:** Measured and calculated values for chemical shifts, $\delta^1$H, quadrupole coupling constants, $\chi_D$, deuteron relaxation times, $T_1$, and reorientational correlations times, $\tau_{OD}$, in a temperature range between 338 and 406 K for IL **IV**.

## SI4 Reorientational Dynamics from MD Simulations

We determine the reorientational dynamics by focusing the time evolution of the orientation of O-D vector in an external laboratory frame. The time-correlation function C($t$) of the second Legendre polynomial of the angle $\theta$ of the O-D vector with a fixed external axis of reference $P_2\{\cos[\theta]\} = \{3 \cos^2[\theta] - 1\}/2$ is computed according to

$$C(t) = \langle P_2\{\cos[\theta(0)]\} \cdot P_2\{\cos[\theta(t)]\}\rangle \tag{1}$$

Assuming that the electric field gradient (EFG) at the deuteron position of the O-D bond is solely determined by the surrounding electron distribution and does not depend on the local molecular environment, as well as the actual molecular conformation of the [HEMIm]$^+$ cation, and assuming that the reorientational motion is fast on the NMR timescale, the relaxation rate is directly proportional to the quadrupole coupling constant times the reorientational correlation time of the O-D bond $\tau_c$ with

$$\left(\frac{1}{T_1}\right)_D = \frac{3}{2}\pi^2\left(1 + \frac{\eta_D^2}{3}\right)\chi_D^2 \cdot \tau_c \tag{2}$$

For the case of the extreme narrowing limit, the correlation time $\tau_c$ corresponds to an integral over the correlation function C(t) with

$$\tau_c = \int_0^\infty C(t)dt \tag{3}$$

| T / K | $A_1$ | $\tau_1$ / ps | $\beta_1$ | $A_2$ | $\tau_2$ / ps |
|---|---|---|---|---|---|
| 300 | 0,734 | 12,7 | 0,321 | 0,234 | 143,6 |
| 320 | 0,781 | 6,4 | 0,325 | 0,206 | 65,2 |
| 340 | 0,798 | 3,5 | 0,347 | 0,195 | 40,8 |
| 360 | 0,814 | 2,3 | 0,369 | 0,181 | 28,0 |
| 380 | 0,831 | 1,6 | 0,382 | 0,167 | 19,8 |
| 400 | 0,843 | 1,2 | 0,394 | 0,156 | 14,7 |

**Tab. 5**: Parameters describing the time-dependent fitted reorientational correlation functions C(t) according to Eq. 4 as a function of temperature.

| T / K | $\tau_C$ / ps |
|---|---|
| 300 | 98,2 |
| 320 | 46,2 |
| 340 | 22,4 |
| 360 | 12,9 |
| 380 | 8,4 |
| 400 | 5,8 |

**Tab. 6**: Integrated correlation times $\tau_C$ for the reorientational motion of the O-D bond-vector in the $[\mathrm{HEMIm}]^+$ cation as a function of temperature *T*.

For estimating $\tau_C$, the long-time behavior of C(*t*) needs to be properly accounted for. To achieve this, we fitted the time correlation function C(*t*) to a combined mono-exponential and stretched exponential representation following

$$C(t) = A_1 \cdot e^{-\left(t/\tau_1\right)^{\beta_1}} + A_2 \cdot e^{-t/\tau_2} \tag{4}$$

leading to the following expression for the integrated correlation time:

$$\tau_c = A_1 \cdot \frac{\tau_1}{\beta_1} \Gamma\left(\beta_1^{-1}\right) + A_2 \cdot \tau_2 \tag{5}$$

Here Γ(…) is representing the Gamma function. The computed time correlation functions, as well as the fitted representations are shown in **Fig 1**. In all cases the analytical representation according to **Eq. 4** provides an excellent description of the correlation functions determined from MD-simulation. All parameters necessary for describing the fitted time correlation functions are summarized in **Tab. 6**.

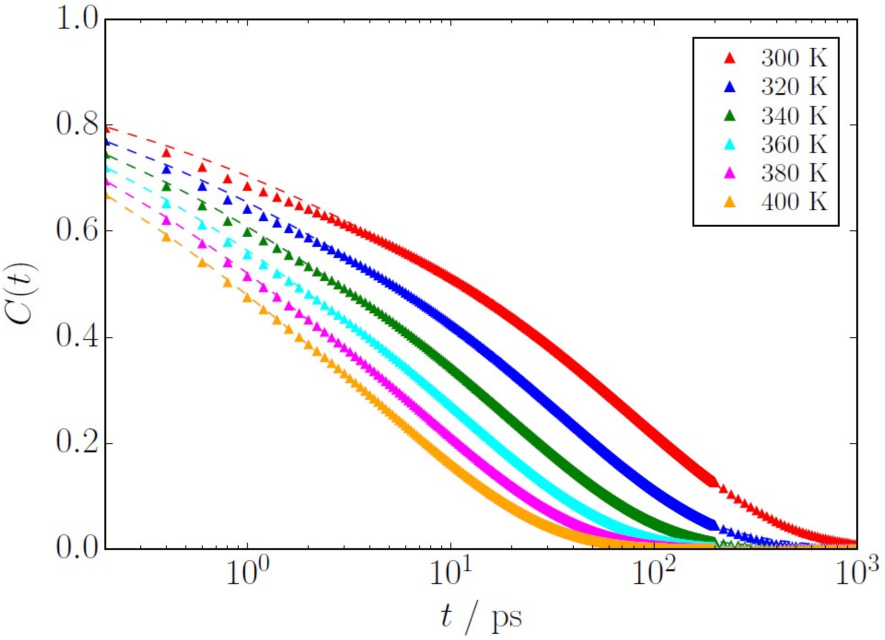

**Fig. 1:** Temperature dependence of the time correlation functions C(t) for the reorientational dynamics of the O-D vector in the [HEMIm]$^+$ cation. Symbols indicate time correlation functions computed from MD-simulation, whereas the dashed lines represent the fitted data according to **Eq. 4**.