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

Supplementary Information

Effect of nitroxide spin probes on transport properties in Nafion membranes

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Here, additional figures are provided that are either referred to in the corresponding paper (SAXS data, Figure S2, and ILT analysis of spin probes solutions, Figure S3) or give additional information to the presented results. Figure S1 shows the trend of the relaxation times as a function of the molecular mobility for an ideal liquid system and refers mainly to the discussion in section 3.3. Figure S4 shows additional FFC data acquired for a spin probe concentration of 3% and concentration comparisons of the FFC curves for the various spin probes that are discussed in section 3.5. Furthermore, the origin of the second relaxation component observed for the D-4AT samples in section 3.4 is discussed.

Figures

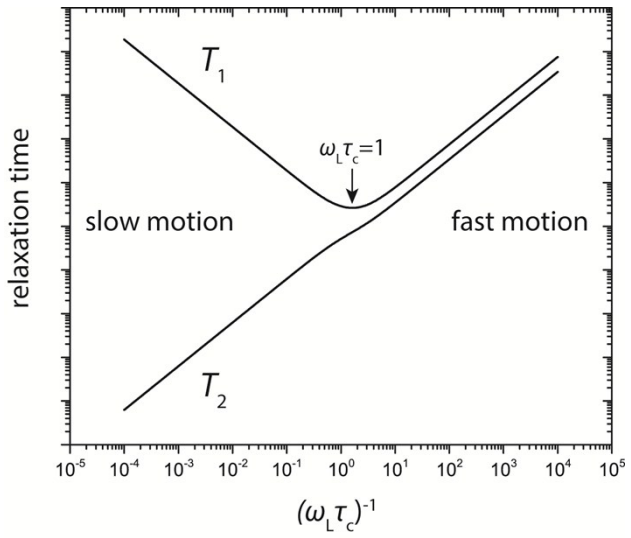

Figure S1. General trend of T_1 and T_2 relaxation time constants as a function of the correlation time τ_c or the Larmor frequency ω_L [1].

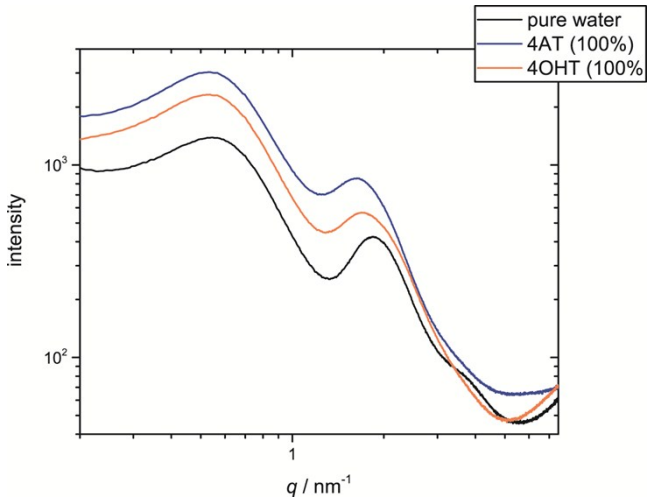

Figure S2: Small angle x-ray diffraction patterns of neat Nafion and Nafion containing TEMPO probes as recorded under ambient conditions (low water content). The principal features are preserved, but the broadening of the ionomer peak indicates a less distinct hydrophobic/hydrophilic separation.

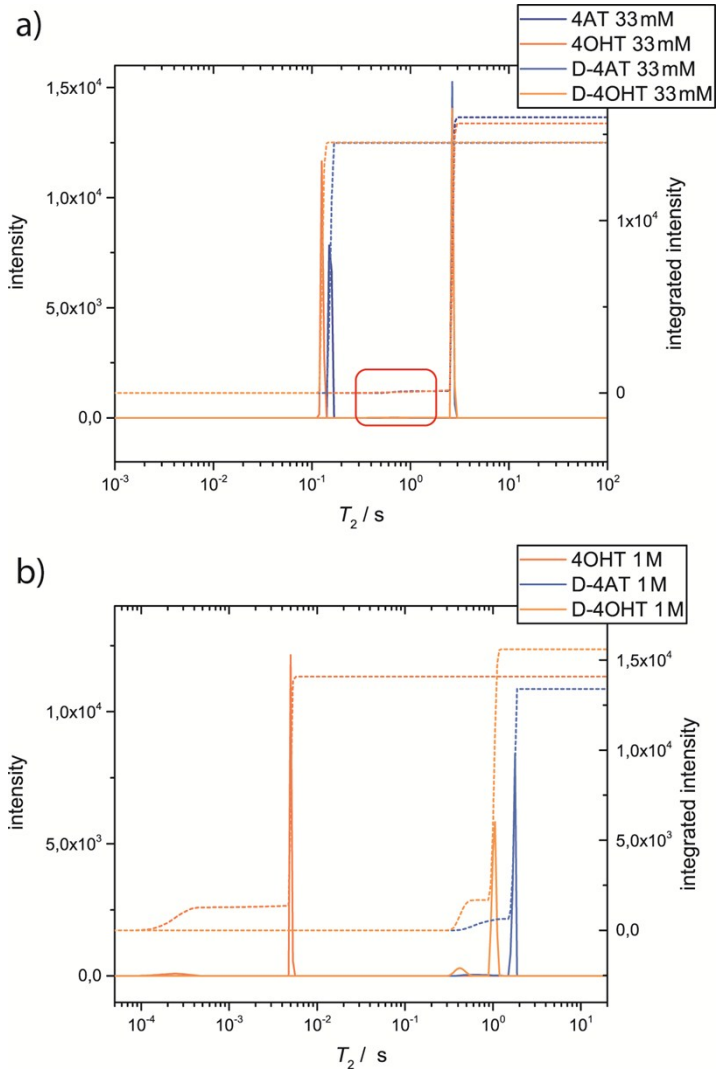

Figure S3. T_2 inverse Laplace analysis of CPMG experiments of aqueous paramagnetic and diamagnetic spin probe solutions at a) 33 mM and b) 1 M. The solid line shows the actual inversion and the dashed line the cumulated peak integral. Whereas a second component is clearly visible for the 1 M solutions, there is also a very subtle second component in the 33 mM solutions of diamagnetic spin probes highlighted by the red box. The CPMG measurements were acquired at 300 MHz with 2048 echoes and 8 scans. The echo time t_E was 8 ms, except for the 1 M 4OHT sample, where t_E was set to 1 ms.

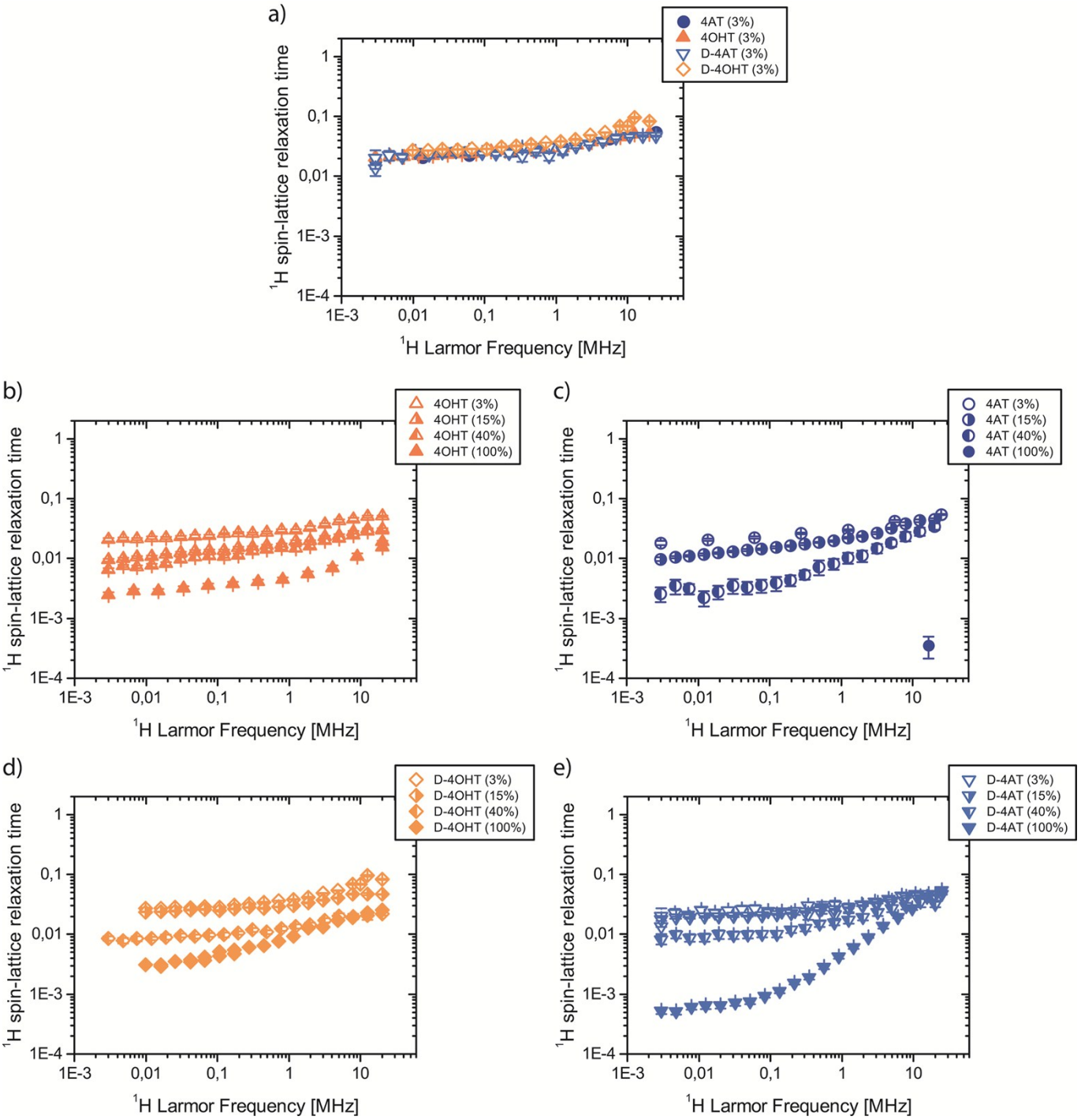

Figure S4: FFC T_1-relaxation measurements of water inside Nafion membranes with different types and concentrations of spin probes present. b) Measurements at spin probe concentration of 3% sulfonate group loading. c-e) Comparison of NMRD curves at 3%,15%,40% and 100% sulfonate group loading for b) 4AT, c) 4OHT, d) D-4AT, and e) D-4OHT. The data was acquired and analyzed as described in section 2.2 of the corresponding paper.

Discussion of the origin of the second relaxation component of D-4AT

In the presence of D-4OHT two distinct T_2 components have been observed (Figure 5 of the paper). We suggest that the additional, shorter T_2 component (~200 µs), may originate from the ^{1}H of the spin probes themselves. Hence, to shed further light on the origin of this species, a Laplace analysis of CPMG experiments with pure spin probe solutions (4AT, 4OHT, D-4AT, D-4OHT at 33 mM - original soaking solution - and 4OHT, D-4AT, D-4OHT at 1 M -

roughly matching the concentration in in a fully hydrated spin probe Nafion system (section 2.1)) were carried out (Figure S3), showing that a second T_2 component at 1 M spin probe concentration is clearly detectable, and that its T_2 is about 5-fold shorter for the diamagnetic and 10-fold shorter for the paramagnetic probes than the T_2 values of the water protons. Even for a lower concentration of spin probes (33 mM) a second weak and broad component is detectable for the diamagnetic spin probes at a same relative shift of a factor of 5 compared to the original water signal (Figure S3 a). In the Nafion measurements (Figure 5) the second, shorter component of the D-4OHT samples is around two orders of magnitude shorter and its intensity increases with spin probe concentration. This intensity scaling roughly matches the amount of spin probes ^{1}H present in the Nafion membrane: In a fully swollen state, there are approximately 14 water molecules per sulfonate group present, resulting in a ratio of 19 spin probe protons to 28 water protons for the 100% D-4OHT sample, ~8/28 for the 40% and ~3/28 for the 15% loaded samples. In our case these numbers may be higher as the hydration of the membrane is reduced by the presence of the spin probes (Figure 4). Concluding these observations, it is plausible that the second, short T_2 component observed for the D-4OHT samples originates from the spin probe itself. The signal intensity of this component matches roughly the amount of the spin probe's ^{1}H number, and the additional shift in T_2 relaxation time (Figure 5 b-d) by 1.5 orders of magnitude of the imbibed spin probes compared to the pure spin probe in solution (Figure S3) is probably due to further relaxation mechanisms caused by the confined environment in the Nafion membrane. For the diamagnetic D-4AT sample, the ^{1}H signal of the spin probe is not seen, possibly due to its strong association with the membrane surface, leading to a stronger immobilization and a shortening of its T_2 beyond the detection limit, which is approximately limited by the echo time. Notably, there is also a second fast relaxing component visible for the 100% 4OHT sample. In this case it remains questionable if this signal originates from the spin probes too, since there is no additional signal observed for the 15% and 40% OHT samples, or whether this is a measurement artifact as the echotime of the measurement is only about a factor of two shorter than the relaxation time of this second component.

Literature

1 N. Bloembergen, E. M. Purcell and R. V. Pound, Relaxation effects in nuclear magnetic resonance absorption, *Phys. Rev.*, 1948, **73**, 679–712.