

²H NMR study of water confined in dileucine nanochannels

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Confined water demonstrates fascinating physical properties including ultrafast and frictionless diffusion [1], unexpected dielectric response [2], and chemical reactivity [3]. Peptide nanotubes represent another promising nanofluidic system, where the water behavior can be additionally tuned by the interaction with the peptide walls. Recently, efficient water diffusion and clustering was found in diphenylalanine (Phe-Phe, FF) nanotubes [4]. Here, we applied the quadrupolar solid-state nuclear magnetic resonance (NMR) spectroscopy and single crystal X-ray diffraction to analyze the structure and dynamic behavior of water confined in dileucine (Leu-Leu, LL) nanotubes.

LL dipeptide were crystalized from D₂O solution into porous crystals with 6×9 nm² rectangular channels. Water molecules grouped in two independent chains there. Half of water molecules in each chain (type 1) form hydrogen bonds with COO⁻ and NH₃⁺ groups of the peptide, whereas another half (type 2) – with COO⁻ groups only. The dynamic behavior of these chains was studied by ²H solid-state NMR. Typical ²H NMR spectrum demonstrates central lines flanked by a set of side bands modulated by the quadrupole coupling interaction. Two main central lines correspond to the observed types of water molecules. The type 1 molecules located at 10.45 ppm demonstrate the highest quadrupolar interaction with the quadrupole coupling constant (C_Q) of 201 kHz, whereas the type 2 molecules located at 6.83 ppm show C_Q of 151 kHz. The spin-spin relaxation time (T_2) is about 0.8 ns for molecules of both types meaning they can substitute each other during the diffusion. The approach from [5], allowed us to estimate self-diffusion coefficients of $9 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for type 1 and type 2 water, respectively, that are close to the value of $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ found for FF nanotubes [4].

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020 financed by national funds through the FCT/MEC (PIDDAC). NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by the Infrastructure Project 022161 (cofinanced by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC). This work has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (Grant Agreement 865974). S.K. and A.K. were supported by FCT through the project “BioPiezoSensor” (2022.03781.PTDC). Part of this work was funded by national funds (OE), through FCT in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of article 23, of the Decree-Law 57/2016, of 29 August, changed by Law 57/2017, of 19 July.

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