

Scientific report

related to the implementation of project: **Structure-dynamics-properties relationships and aging effects in nanocomposite elastomers and proton exchange membranes**
in the period January – December 2013

The objectives of year 2013

05 The development of specific NMR methods for the study of the proton self-diffusion anisotropy and anomalous diffusion for the hydrated PFSA membranes with different SiO₂ content and the PEMs polymeric network structure in the presence of deuterated water.

The decay curves of the stimulated echo function of gradient amplitude (PGSSE) corresponding to free and bound water in hydrated PFSA membrane in the presence of SiO₂ content.

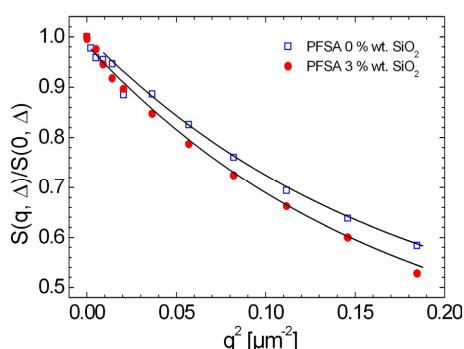


Fig. 1 The decay curves of stimulated echo function of gradient strength represented for two values of SiO₂ Content.

from 0% to 90% from the maximum gradient strength $G_{x, \max}$. Figure 1 present an example of normalized signal decay (i.e. the amplitude of stimulated echo) measured function of wave vector $q = \gamma \delta G_x$ where γ is the gyromagnetic factor of ^1H and δ is the time duration of magnetic field gradient. One can observe that, the SiO₂ filler content influence the stimulated echo decay and then the water self-diffusion processes.

Theoretical expression and corresponding numerical fitting algorithm to describe the PGSSE decay curves in the presence of diffusion, relaxation and water exchange

In the theoretical treatment of the problem related to the water self-diffusion between the PFSA

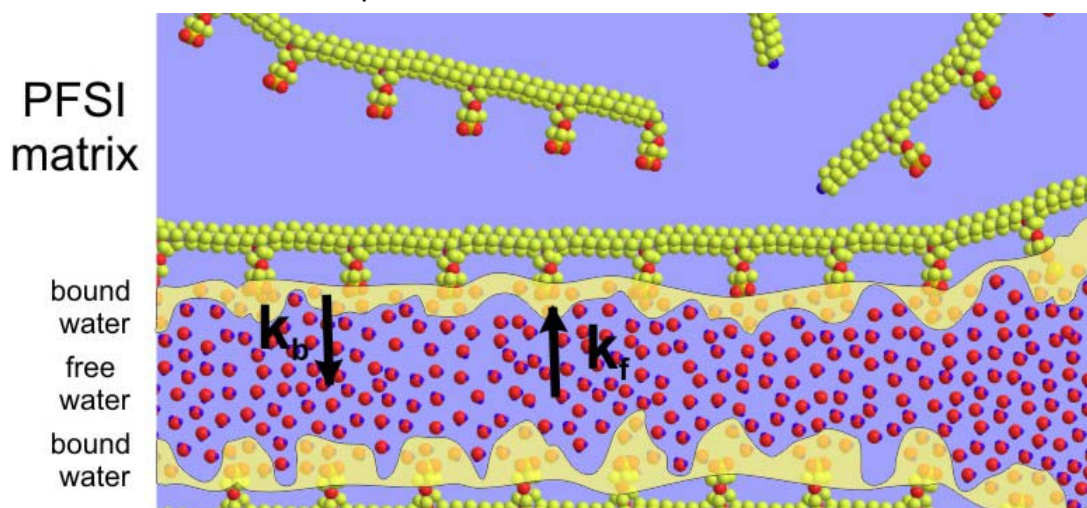


Fig. 2 Numeric simulations using ChemDraw® program of a channel inside a membrane of PFSI (PFSA) type filled with water molecules. One can observe also the free water to bounded water exchange described by exchange constants k_b and k_f .

polymeric chains channels (Fig. 2) two water pools were assumed to exist. The first one is represented by the bound water (labeled with an inferior b indices) which surround the SO_3^- functional groups and the free water (labeled with an inferior f indices) and which is capable to diffuse along the channels formed in the polymeric matrix. Between these two pools exchange processes can occur characterized by k_b the exchange rate from bound water to free water and k_f the exchange rate from free water to bound water (see the representations from Fig. 2). As an equilibrium condition, in our treatments we have to include the condition: $n_b k_b = n_f k_f$, where n_b and n_f are the proton number from bound and free water, respectively. With the assumption that the diffusion coefficient of bound water is in reality very small ($D_b \approx 0$) and then the diffusion coefficient of free water is $D_f \equiv D$, we get the signal:

$$\frac{S_f(q, \Delta)}{S_f(0, \Delta)} = \left[(a_+ - k_f - k_b - R_{1b}) \exp(-a_+ \Delta) - (a_- - k_f - k_b - R_{1b}) \exp(-a_- \Delta) \right] (a_+ - a_-)^{-1}, \quad (1)$$

and

$$\frac{S_b(q, \Delta)}{S_b(0, \Delta)} = \left[(a_+ - q^2 D - k_f - k_b - R_{1f}) \exp(-a_+ \Delta) - (a_- - q^2 D - k_f - k_b - R_{1f}) \exp(-a_- \Delta) \right] (a_+ - a_-)^{-1}. \quad (2)$$

where

$$a_{\pm} = \frac{1}{2} \left[q^2 D + k_f + k_b + R_{1f} + R_{1b} \right] \pm \frac{1}{2} \sqrt{(q^2 D + k_f - k_b + R_{1f} - R_{1b})^2 + 4k_f k_b}. \quad (3)$$

Test results of FID, Hahn echo, DQ NMR pulse sequence on PEM polymeric backbone

The dynamic properties of molecular backbone has a great influence to some extent the PEMs membranes protonic conduction properties, especially the length of the branches which contain at the end the SO_3^- functional groups which are capable to bound the water molecules. In figure 3a are presented the se FID magnetization decays, after a single radiofrequency pulse, measured for dehydrated PFSI (PFSA) membranes function of SiO_2 content. One can observe that a large rigidity is obtained at 3wt.-% SiO_2 content. We reach to the same conclusion after the analysis of Hahn echoes decay curves (Fig. 3b). For the dehydrated PFSI membranes the distance between protons is relatively large and therefore there are no dipolar interactions between ^1H ; then a double quantum filtered NMR signal cannot be registered. The polymeric backbone dynamics it was measured after the implementation of a new type of measurement based on the ^{19}F -DQ on the fluorinated polymeric membranes' backbone (see Fig. 3c).

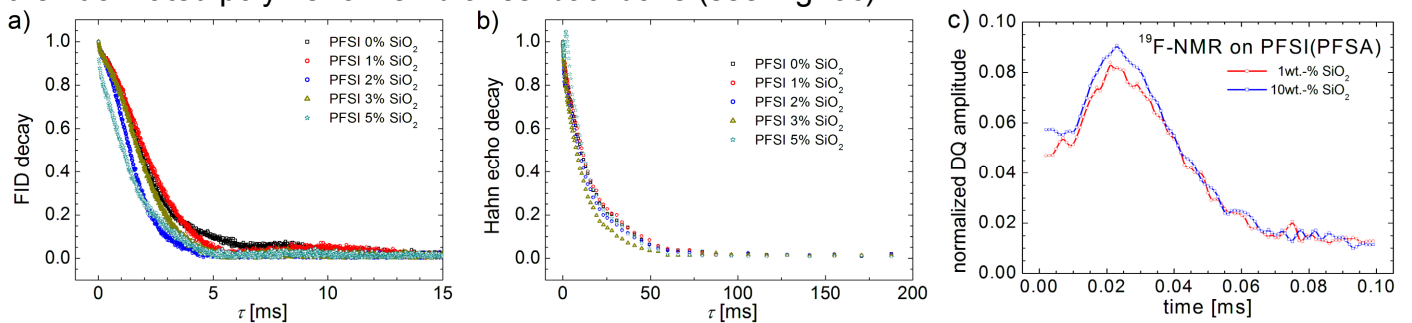


Fig. 3 Decay curves of a) FID and b) Hahn echo measured for ^1H from dry PFSI(A) membranes function of SiO_2 content; c) double-quantum build-up curves measured for ^{19}F from dry PFSI(A) membranes polymeric backbone represented for 1wt.-% and 10wt.-% SiO_2 content.

Molecular mechanics simulations of PFSA/ SiO_2 dynamics in the presence of water.

The understanding of water exchange processes cannot reach at the level of subtle details without molecular mechanics numeric simulations. In this sense the ChemDraw[®] (2010 version) simulation program was correlated with Gaussian[®] 09 program for molecular mechanics advanced simulations, molecular dynamics to get specific values of physico-chemical properties, starting from a simple model of perfluorinesulfonic acid monomers (see Fig. 4a and 4b). Then, the

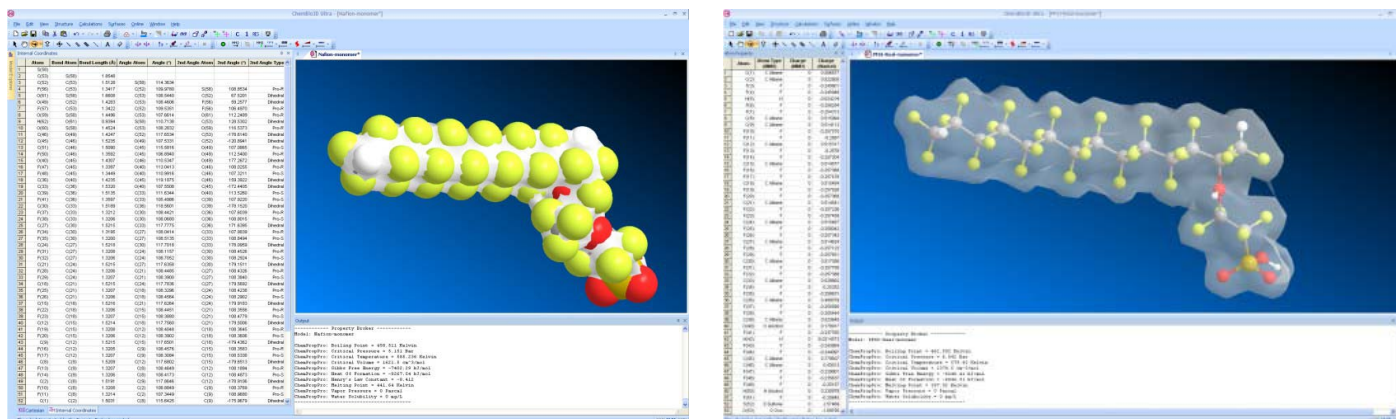


Fig. 4 Molecular mechanics simulation of a) some structural properties and b) some physical properties of PFSA (perfluorinesulfonic acid) monomer.

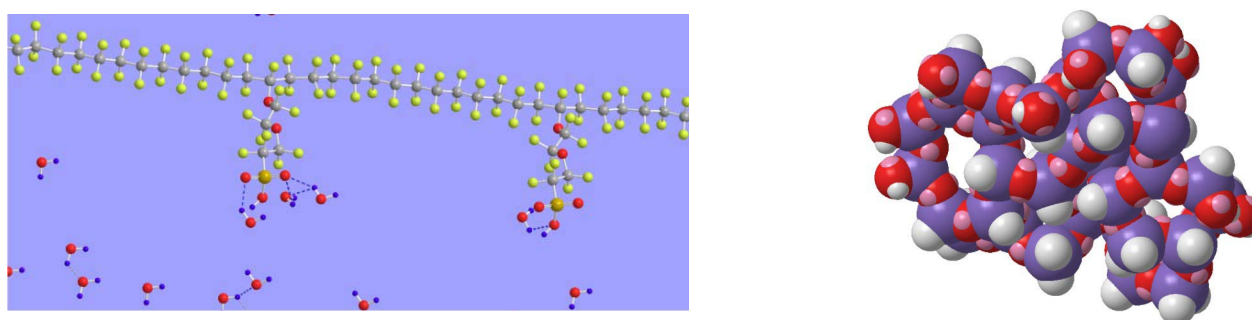


Fig. 5 a) Molecular mechanic simulations of some physical properties of a PFSA chain in the presence of water molecules and b) a possible conformation of SiO_2 cluster included in the molecular mechanics simulations of all PFSA chains.

behavior of polymeric chains was studied then in at the end we observe the results obtained for the behavior of membranes in the presence of water molecules (Fig. 5a) and of SiO_2 (Fig. 5b).

Correlation of changes in the measured parameter values with the changes in the PEM polymer network

The degree of hydration of PEMs membranes affects the dynamics of PFSA polymeric network dynamics. A sensitive measurement at the changes of PFSA polymeric backbone dynamics in interaction with hydration water molecules is those of DQ-NMR. For the first time for PFSA/ SiO_2 membranes it was implemented a pulse sequences to measure the ^{19}F -NMR DQ build-up curves function on the degree of membrane hydration. Examples of such measurement are presented in in Fig 6a. The obtained DQ curves have been analyzed using a new *Laplace-like* inversion procedure and for the first time we obtain the distribution of residual second order van Vleck moment (M_2) for such (see Fig. 6b). The values of M_2 at maximum probabilities and the full distribution were correlated with the degree of membrane hydration where the hydration water restrict the motion of PFSA polymeric network.

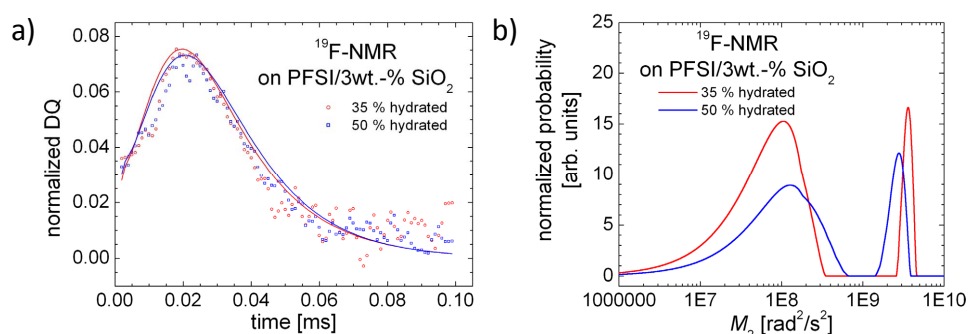


Fig. 6 a) The ^{19}F -NMR double-quantum build-up curves measured for PFSA/ SiO_2 membranes at different hydration degrees and the fits; b) the second order van Vleck moments, M_2 distributions obtained from fitting of experimental DQ curves.

O6a The development of a new tool based on the two dimensional correlation maps, 2D Laplace inversion and MONTE-CARLO simulations for the characterization of the free ↔ bound water exchange processes by the measurement of the proton exchange velocity and channel proton conduction in PFSA/SiO₂ membranes.

A numerical program based on the MONTE-CALRO concept to simulate the 2D exchange maps of water in arbitrary shape pores and channels in the presence of free ↔ bound water exchange.

A numeric program was written in C++ based on the MONTE-CARLO randomly diffusion of molecules in pores and channels of porous materials. This program has as input data a map of relaxation times as can be seen in Fig. 7c) obtained in the steps sequentially presented in Fig. 7a) -7c) starting from a simulated graphic representation, or logic conversion of some experimentally obtained images as for example from AFM or NMR imaging procedures. The program generate the randomly diffusion of molecules in pores as can be seen in Fig. 7d) and simulates 2D numeric data specific to NMR experiments as the 2D REXY T_2 – T_2 exchange maps with two (direct and indirect) encoding periods of decays under relaxation during CPMG, and an exchange time (mixing time) between them. The program can consider or not a molecular exchange during CPMG, which allows the user to simulate a real situation or to produce data to be compared with some analytical (but simplest) function which describes the molecular exchange processes via magnetization exchange.

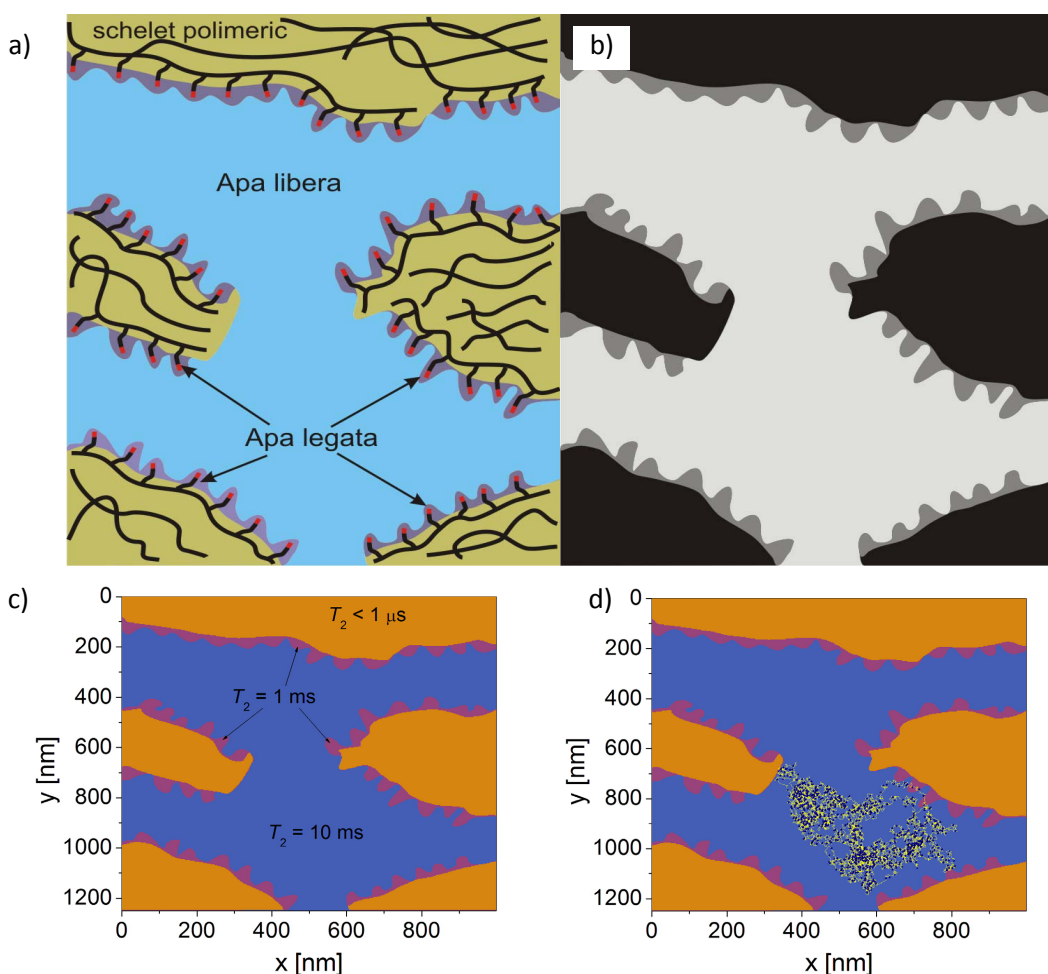


Fig. 7 a) Graphic representation of a PFSA polymeric backbone with functional branches ended with SO_3^- functional groups; b) logic representation (in grey colors) the polymeric backbone, bounded water and free water based on the representation from fig a); conversion of bit-maps from fig. b) into a map of relaxation times T_2 ; d) the use of T_2 from fig. c) to generate the MONTE-CARLO based diffusion of molecules inside pores and channels inside a PFSA mebrbranes.

The use of MONTE-CALRO numeric program as a new instrument for the simulations of 2D T_2 – T_2 exchange maps in ideal and real conditions

The MONTE-CARLO numeric program was used to simulate the 2D decay maps of CPMG- τ_m -CPMG echoes (see the red decays from Fig. 8a and 8b). The results were interpreted in the terms of water behavior inside ideal porous materials (spherical and elliptic pores) function of many characteristics of pores (dimension, shape, and connectivity/tortuosity) of water (relaxation times and diffusion coefficients) and experimental conditions (echo numbers, echo time, exchange/mixing time). The 2D maps describing the echoes decays of CPMG- τ_m -CPMG type have been analyzed using the 2D Laplace inversion transform to get the 2D T_2 – T_2 REXY exchange maps. Two such examples are presented in Fig. 8a and 8b. Moreover, for simulated maps, specific to channels from PEMs' membranes presented in Fig. 7 but rescaled (Fig. 8c) a series of simulations were performed for various semi-real conditions. Such a 2D T_2 – T_2 REXY exchange maps, where a single diffusion coefficient was considered is presented in Fig. 8d.

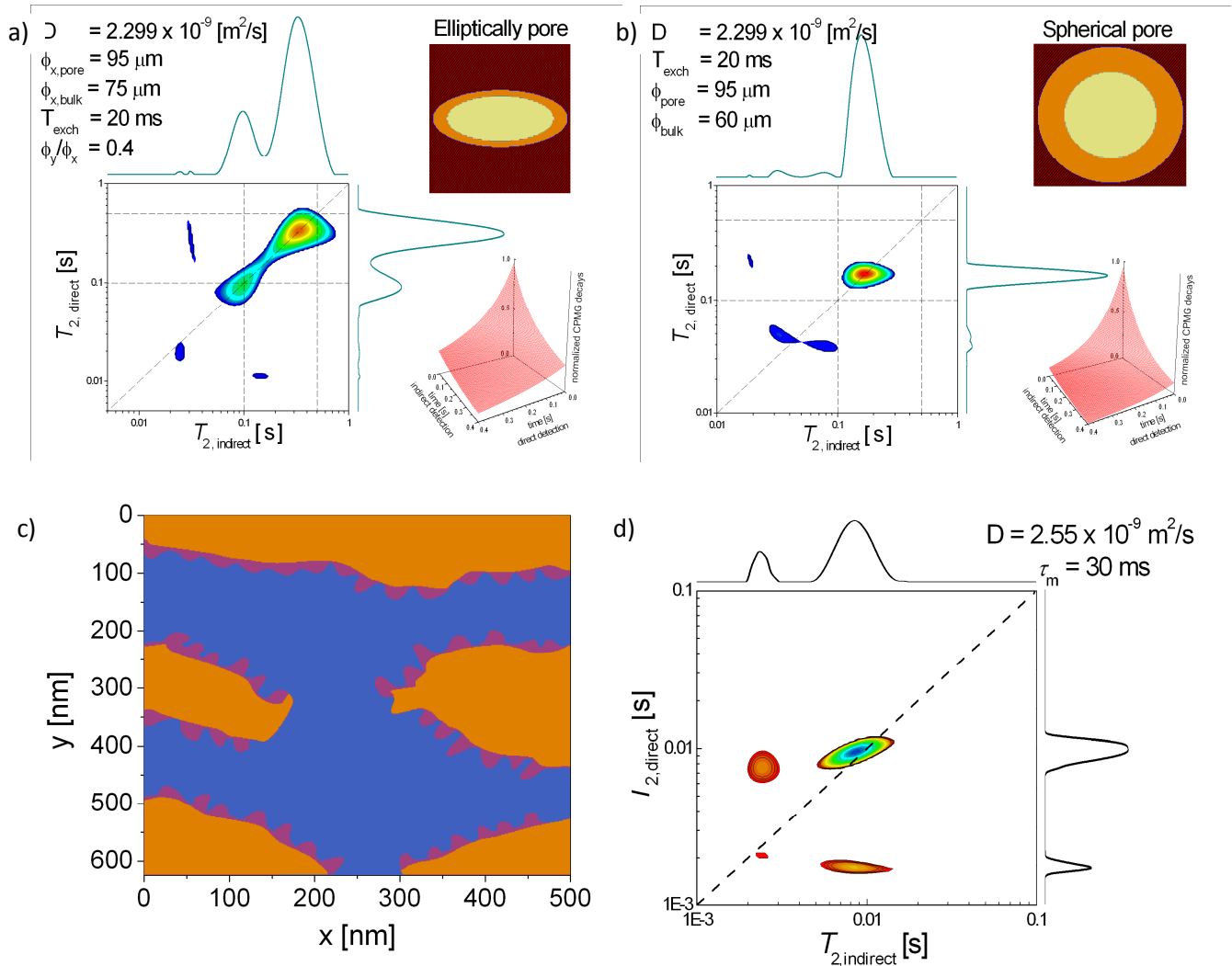


Fig. 8 MONTE-CARLO simulations of 2D T_2 - T_2 REXY exchange maps for the ideal case of a) an elliptic pore and b) spherical pore; c) a T_2 map characteristic to PEM membranes presented in Fig. 7c and rescaled and d) the T_2 - T_2 exchange map obtained for the relaxation map from Fig. 7c in ideal conditions but for real $T_{2,1}$, $T_{2,2}$ and D , τ_m values.

The dissemination of results

ISI articles

1. D. Demco; A.-M. Oros-Peusquens, L. Utu, R. Fechete, B. Blümich, N. J. Shah, Molecular dynamics parameter maps by ^1H Hahn echo and mixed-echo phase-encoding MRI, J. Magn. Reson., 227, 1–8 (2013).
2. N. Cioica, R. Fechete, C. Cota, E.M. Nagy, L. David, O. Cozar, NMR relaxation investigation of the native corn starch structure with plasticizers, J. Molec. Struct., 1044, 128–133 (2013).
3. D. Demco; Carmen Filipoi, Xiaomin Zhu, Radu Fechete, Martin Möller, Morphological Heterogeneity by Diffusional Kurtosis NMR Spectroscopy in Perfluorosulfonic Acid/SiO₂ Composite Proton-Exchange Membranes, Macromol. Chem. Phys., 214, 1345–1355 (2013)

Book

1. R. Fechete, D. Moldovan, R. Chelcea, Applications of modern NMR techniques to nanocomposite materials and biomaterials, ISBN: 978-973-662-906-8, Editura U.T.PRESS Cluj-Napoca (2013).

BDI articles

1. E. Jumate, D. Moldovan, R. Fechete, D. Manea, NMR Relaxometry Study Of Plaster Mortar With Polymer Additives, AIP Conf. Proc. 1565, 112-116 (2013).

Participation to international conferences

1. E. Jumate, D. Moldovan, R. Fechete, D. Manea, Relaxometry Study Of Plaster Mortar With Polymer Additives, Processes in Isotopes and Molecules PIM 2013, 25-27 septembrie, Cluj-Napoca, Romania (2013) - Poster.
2. R. Fechete, Applications of 1D and 2D Laplace inversion analysis, 4th Transylvanian NMR Workshop - Frontiers of Magnetic Resonance Applications to nano- and microscopically structured systems, 28-30 September, Cluj-Napoca, Romania (2013) - Oral presentation.

Date

15.10.2013

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