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Water Diffusion through Asymmetric Polymer Membranes and Polyelectrolyte Multilayers

*Alexandr Sagidullin**, *Jochen Meier-Haack*[†], *Ulrich Scheler*[†]

* Department of Molecular Physics, Kazan State University, Kremlevskaya Str., 18,
420008 Kazan, Russian Federation, E-Mail: asagidul@ksu.ru
[†] Leibniz Institut für Polymerforschung Dresden e.V., Hohe Strasse 6,
D-01069 Dresden,Germany

1. Introduction

Modern chemical techniques of polymer synthesis and processing permit to obtain polymeric membranes with designed properties. This direction of scientific engineering and of material science needs experimental support to study the membrane properties in detail and to show which kind of membrane modifications should be used to obtain the materials with desired properties.

One of the most adequate methods for obtaining information on the structure and transport properties of natural and artificially-formed porous materials and membranes is NMR-diffusometry – pulsed field gradient NMR (PFG NMR) [1, 2]. In particular, this method permits to determine the mean pore size of materials, d, and to estimate the average life-times of liquid molecules inside the pores.

The aim of the present work is to measure the main geometrical characteristics of polymeric membranes such as the pore size and, especially, to examine some features of water self-diffusion through these membranes.

2. Experimental

Porous Poly(amide)-6 (PA-6) and polymeric polyelectrolyte multilayer of Poly(ethylene imine) and Poly(acrylic acid) (PEI/PAAc) [3] have been studied by pulsed field gradient NMR (PFG NMR). The materials have been fully filled with distilled water, to that the water molecules have played the role of probe molecules in our NMR-study. Experiments have been performed on a Bruker AVANCE 500 NMR spectrometer operating on the proton resonance frequency 500 MHz, equipped with the diffusion accessory Diff30 generating a maximum amplitude of the pulsed field gradient of $g = 12\ \mathrm{T\ m^{-1}}$ at an ambient temperature of 22ºC. The diffusion time t_d in the stimulated spin-echo diffusion measurements was varied from 100 to 900 ms.

3. Results and Discussion

The time-dependence of the lowest measured water diffusion coefficient, $D_1(t)$, has been examined for both membranes. In the time-range from 400 to 900 ms the experimental dependence $D_1(t)$ can be formally described by $D_1(t) \propto t^{-1}$. That implies that so-called restricted diffusion is observed, and the mean size of restrictions can be calculated [1]. In case of asymmetric polymer membrane PA-6 the obtained size of restrictions, $d = (4.2 \pm 0.2)\ \mu\mathrm{m}$, was in satisfying accordance with results of measurement by scanning electron microscopy; and it confirmed the adaptability of PFG NMR for the chosen polymeric membranes.

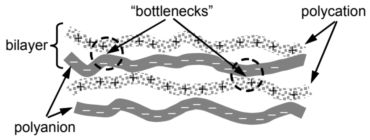

Fig. 1: Sketch of areas where the polyionic (polycationic and polyanionic) layers form peculiar "bottleneck"

Measuring the pore size of polyelectrolyte multilayers is difficult due to the difficulties associated with the preparation of the samples for electron microscopy. PFG NMR has been successfully applied to measure the mean effective size of restrictions in PEI/PAAc complexes. According to the experimental data this effective size is (5.6 ± 0.2) μm. Taking into account both the features of the membrane forming ("layer-by-layer") and basics ideas about the polyionic complexes [3], we are inclined to ascribe this size either to the mean distance between the neighboring polyionic layers or to mean distance between the areas where the polyionic layers form peculiar "bottlenecks" (see Fig. 1) restricting the free self-diffusion of water.

Molecular exchange between water molecules located inside and outside of the pores has been studied analyzing the diffusometry data. In particular, the time dependences of the relative part of the "restricted" water (with lowest D) and the evolution of the propagators were studied. It was obtained that the mean life - time of water inside pores of PA-6 is equal to 1.2 s. In contrast to PA-6, for the polyelectrolyte multilayer it was impossible to measure τ, it means that this time is much longer than the typical delay times within the PFG NMR experiment.

4. Conclusions

Investigations of the water mobility in the polymeric porous materials PA-6 and PEI/PAAc permitted to determine the mean size of restrictions in these materials. Analysis of PFG NMR data obtained for the PA-6/water system have shown that there is molecular exchange between water molecules located inside and outside of the membrane pores; the mean life-time of water in the pore is about 1.2 s. In contrast to PA-6, for multilayer complex of PEI/PAAc, it is impossible to calculate the mean life-time of water molecules inside the layers; it could mean that even if there exists molecular exchange in these membranes, it should take more time as compared with PA-6 membranes. The last result permits to assume that the multilayer polyelectrolyte membranes are able to dehydrate the liquid mixtures more efficiently than the polar polymeric membranes.

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