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Mobility of small molecules in membrane materials based on copolyimide P84

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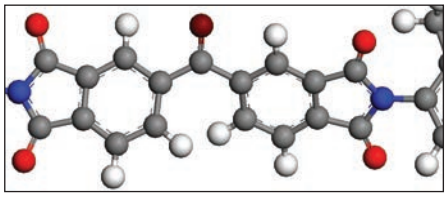
Dynamics of small molecules in copolyimide P84, which is an important membrane material for separation and purification technologies, have been analyzed using quantum chemistry and molecular dynamics methods. The most significant factors determining the membrane properties and the molecular motion of gases and liquids in the P84 membranes are both the size and dipole moment of these molecules as well as the charge state of sorption centers in the polymer.



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Polyheteroarylenes, in particular, copolyimide P84, are actively investigated due to their applications as dense polymer membrane materials with high mechanical and chemical stability, separation properties and performance characteristics.[1] P84 has been successfully applied in pervaporation, ultrafiltration and gas separation processes,[2–4] for example, in the pervaporation dehydration of alcohols.[5] Various experimental methods were proposed to improve the properties of membrane materials.[6–10]

Theoretical investigations of the mechanism of fluid permeation through membranes at the atomic/molecular level make it possible to clarify the process of fluid separation. In particular, quantum chemical methods allow one to calculate the electronic structure of a polymer and, on this basis, explain the behaviour of membrane materials in the separation processes. For example, the charge states of sorption centers in the polyimide Matrimid belonging to the class of polyheteroarylenes were explored using the density functional theory.[11] The use of generalized gradient functionals satisfactorily characterizes the relative charge states of atoms both *in vacuo* and in water.

Calculations of the diffusion of water molecules in the polyimide Matrimid, carried out by the molecular dynamics (MD) method showed the effectiveness of this approach,[12] which was used in this work to calculate the dynamic and structural properties of separated molecular penetrants in polymer P84.

First, we calculated the electronic structure of the P84 tetramer and various penetrant molecules, namely hydrogen, nitrogen, methane, ammonia, ethanol and water, by the density functional theory and estimated the charge states of all atoms. The tetramer is an optimal size of the P84 polymer model for electronic structure calculations because of the presence of interatomic interactions, which are important for sorption and the polymer network creation. Attention was focused on the oxygen and nitrogen atoms of the polymer, which represent the most significant sorption centers (Figure 1).

The electronic structure was calculated on the atomic basis DNP (ver. 4.4), including polarization, by the density functional theory with the PBE functional using the DMol^3 program of the Materials Studio software package. In accordance with the estimation of charges following the Mulliken scheme on both the polymer atoms and the penetrant molecules, cubic cells were formed for the subsequent modeling by MD. In this case, the electrostatic interaction was calculated based on the obtained charge states of atoms, while the interatomic interaction at short distances was determined by force fields, namely the universal force field (UFF)[13] and Dreiding one.[14] According to the experimental polymer density of 1.34 cm^3 g^{-1}, 10 molecules of the copolyimide P84 tetramer and 20 penetrant molecules were placed in the cubic cell.

The MD calculations were carried out using the FORCITE module of the Materials Studio package in the NVT ensemble at 298 K. The simulation duration was one ns with a step of one fs, which corresponded to one million integration steps.

The self-diffusion coefficients (SDCs) were calculated on the basis of mean-square displacements (Table1). As follows from the data obtained, the UFF more adequately describes the mobility of penetrant molecules in P84. After calculations with the Dreiding force field, anomalously overestimated values were obtained for the mobility of hydrogen and underestimated ones for ethanol. Therefore, subsequent analysis was based on the UFF calculations.

The diatomic hydrogen and nitrogen molecules, which have no dipole moment, are of the highest mobility. A slightly lower

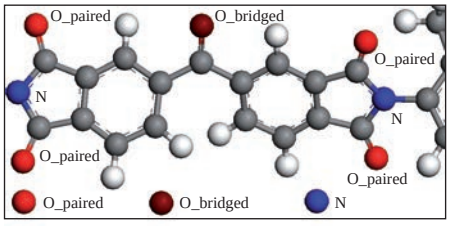

Figure 1 Sorption centers in the P84 polymer molecule. O_paired and O_bridged are designations of the oxygen atoms in different structural positions. Carbon and hydrogen atoms are shown in gray and white, respectively.

Table 1 SDCs calculated for various gases and liquids in polymer P84 at 298 K.

Penetrant	Dipole moment/ D[15]	Diameter of circumscribed sphere/Å	SDCs by UFF/ $cm^2\ s^{-1}$	SDCs by Dreiding/ $cm^2\ s^{-1}$
Ethanol	1.69	3.63	3.3788×10^{-7}	0.6244×10^{-8}
Methane	0.00	1.79	1.8704×10^{-7}	1.1980×10^{-8}
Hydrogen	0.00	0.75	1.7858×10^{-6}	1.5200×10^{-5}
Ammonia	1.47	1.62	1.1385×10^{-7}	2.0407×10^{-8}
Nitrogen	0.00	1.11	4.7518×10^{-7}	6.8143×10^{-8}
Water	1.85	1.52	3.5001×10^{-7}	5.1900×10^{-8}

Table 2 Maxima of RDFs between the penetrant molecules and the P84 sorption centers.

Penetrant	O_paired/Å	O_bridged/Å	N/Å
Ethanol	3.31	3.37	5.45
Methane	3.67	3.81	5.01
Hydrogen	3.07	6.25	4.89
Ammonia	3.43	3.27	4.87
Nitrogen	3.13	3.13	5.111
Water	3.25	3.43	5.09

mobility was observed for the polar molecules of water and ethanol. Methane and ammonia molecules have the lowest mobility. In general, the mobility of penetrant molecules is controlled by the size of a molecule (or the circumscribed sphere) and its dipole moment. The molecular size is responsible for the diffusion of nonpolar molecules.[16] The small size of a molecule without a dipole moment promotes its migration among the P84 polymer chains, while the polar molecules experience a significant effect on the charges of atoms of the sorption centers. To assess this factor, we analyzed the radial distribution functions (RDFs) between the penetrant molecules and the sorption centers.

The RDF values (Table 2) demonstrate that the oxygen atoms have the greatest effect on the penetrant molecules. These molecules come closest to the O_paired atoms and it is associated with an increase in the electrostatic effect caused by closely located atoms. The single O_bridged atom is characterized by a slightly lower RDF value. As for the nitrogen atom, it is inside the polymer chain and an access to it by penetrants is troubled by steric factors, which is reflected by the high RDF values.

Thus, the mobility of penetrants in the copolyimide P84 membrane is determined by the size and dipole moment of their molecules and by the charge states of sorption centers in the polymer chain. All these factors and data on the intermolecular interactions should be taken into account in the modeling and design of separation processes based on the copolyimide P84 membranes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.024.

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