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Evaluation of liquid transport properties of hydrophobic polymers of intrinsic microporosity by electrical resistance measurement

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ABSTRACT

In this work, the electrical resistance method was used to get an insight of the liquid transport through the polymers with excess of fractional free volume. The dense films based on the first generation of polymers of intrinsic microporosity, disubstituted polyacetylenes PMP and PTMSP, were used; water-ethanol binary mixtures allowed to adjust the affinity of the liquid phase to selected polymers continuously. In this work, the liquid-membrane interaction was considered as a stepwise occupation of accessible free volume elements within the polymer, while the appearance of continuous (pseudo)liquid channels in the polymeric matrix, so-called percolation clusters, was required for formation of hydrodynamic liquid transport. Since the appearance of such percolation clusters might dramatically change the conductivity of hydrophobic materials, it was proposed to use the electrical resistance method to investigate the evaluation of selected polymers from being a barrier (water) to being permeable (ethanol) with respect to the liquid composition. To highlight the electrical resistance of the swollen films, all water/ethanol solutions contained NaCl (0.5 g/L). The steady-state values of liquid permeation, sorption/swelling, and electrical conductivity data were considered together and discussed. The electric resistance was significantly varied for 30 μm dense films of PMP (1–1300 kΩ) and PTMSP (0.15–910 kΩ) by the adjustment of ethanol content in water. The phase shift (25– 100,000 Hz) illustrated that the behavior of PTMSP and PMP membranes changed from mainly capacitive at low ethanol concentrations to the ion conductive as higher ethanol content. The very good quantitative agreement was found between the relative change of the membrane electrical resistance and the permeability as a function of the ethanol content in the liquid phase. Consequently, electrical resistance measurements could be used as an express method to determine the membrane permeability of low permeable materials, since the time required to get steady-state results was found to be much shorter for electrical resistance measurements than for permeability measurements.

1. Introduction

The biggest membrane applications in the industry are related to different kinds of liquid-based separation processes [1,2]. In some applications such as filtration or (electro)dialysis, the membrane is supposed to be wetted by the liquid phase in order to realize the transport of solvent molecules across the membrane. In opposite, the gas-liquid contactor systems (e.g., membrane distillation) can be successfully operated on the long-term basis only if the membrane pores are filled by the gas phase despite the fact that one or two sides of the membrane are contacted with the liquid. With regard to the liquid properties, first of all, its surface tension, the same porous membrane based on, for example, poly[tetrafluorethylene] (PTFE) or poly[vinylidenefluoride] (PVDF) can be used in the gas-liquid contactors for CO_2 capture, water desalination or filtration processes [3–6]. In the case of high-pressure applications like solvent nanofiltration or gas-liquid contactor systems, the membrane top-layer is usually made of the non-porous (elastomeric polymers) or microheterogeneous (glassy polymers) materials [5,7,8].

The liquid transport across the membrane is usually determined by the filtration method using dead-end or cross-flow membrane cell. However, long-term experiments are required for characterization of barrier or semi-permeable materials due to the sensitivity of the method from about 10^{-5} kg/m^2 h bar. Recently proposed dynamic pressure decay self-calibration technique [9] allows to improve further the sensitivity from $5{\cdot}10^{-7}$ kg/m^2 h bar, but higher pressures are required for better detection of liquid transport.

At the same time, the liquid filtration process is not attributed to the phase transition like other membrane processes such as pervaporation

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or membrane distillation. Therefore, the hydrodynamic flow through the membrane can be conducted only through percolation clusters available within the membrane matrix regardless of the material nature and porous structure of selective layer. By this mean, it is expected that such transport "channels" are continuously formed through interconnected vacant sites from upstream to downstream sides of the membrane. In the case of rubbery polymers, the free volume elements appear due to the statistical fluctuation of the polymer segments, and if the size of the vacant position is comparable with the size of solvent molecules, the transport could occur within the membrane.

For the glassy polymers, interconnected free volume elements are naturally or artificially formed during the membrane preparation and are more likely fixed in time due to the more rigid structure of the matrix. In the case of glassy polymers with a high fractional free volume such as substituted polyacetylenes or PIM-1, the solvent transport through the swollen polymeric matrix is mostly determined by the fraction of pre-existing interconnected free volume elements rather than the additional free volume elements appeared upon polymer swelling [10]. For the liquids with a limited wetting capability, these polymers might be impermeable even at elevated pressures, and it becomes permeable with the increase of wetting component fraction in the binary mixture [10,11]. Such observed threshold values of sorption, swelling degree, and fractional accessible volume were explained by stepwise accommodation of free volume elements with the solvents molecules and the phenomena of percolation cluster formation. The percolation theory is widely used to describe the phenomena of formation of connected networks between randomly placed clusters or species on micro- or macroscale that enable the continuous flow or pathways from one side to another side of the objects [12–17]. For example, a percolation model was proposed to describe the adsorption and desorption process in the porous media, including the hysteresis effect [13]. Non-linear increase and certain threshold in the electrical conductivity, mechanical properties, dielectric permittivity, magnetic or gas permeability can be found when the fillers such as carbon nanotubes (CNT) or magnetic particles are introduced in the polymeric matrix [15–19]. Furthermore, the threshold concentration of CNT is a function of their geometrical characteristics, and nonlinearly decreases with increasing their aspect ratio [16,17].

The solvent clusters accommodated within vacant positions of the membrane matrix can be considered as a liquid or pseudo-liquid phase that still possesses macroscopic properties like bulk viscosity or electrical conductivity. This enables to utilize different techniques for characterization of the membrane properties. For example, the electrical properties of the different membrane sub-layers can be inferred from impedance measurements over a range of frequencies (impedance spectroscopy) [20–28]. The most used technique is the difference method in which the membrane resistance is obtained from the difference between the cell resistance measured in AC mode with and without the membrane [22–30]. For most experimental devices the current lines are normally oriented to the membrane surface and the system made up of the membrane surrounded by two identical solutions is then equivalent to an electrical circuit with serially-connected elements. Other cell configurations, with a parallel association of the membrane and the measuring solution, have been proposed to characterize membranes that are much more conductive than the measuring solution [29].

Electrical conductivity is one of the most important characteristics of ion-exchange membranes [31–34] but also measuring of electrical properties make it is possible to estimate the thickness of active layer in reverse osmosis or nanofiltration membranes [20–22,35], porosity of porous sublayers [25,26,36], monitoring of deposition (fouling) on top of the membrane [25,26,36], to get insight in the transport behavior of different charged species within the membrane [21,23] or evaluate the wetting of microporous hydrophobic membranes used in membrane contactors [27]. It should be noticed that electrical impedance spectroscopy is widely used for characterization of resistance and capacitance of active and porous sub-layers of reverse osmosis membranes [20], nanofiltration membranes [20–22,35], evaluation of (bio) fouling [25,26,36], water presence and ionic liquid loss in supported liquid membranes [37], monitoring of membrane modification with the charged species [38], wetting of porous membranes used in membrane contactors [27] and study of piezoelectric properties of porous membranes [39].

In this work, the formation of percolation clusters inside dense polymer membranes was highlighted by the determination of the membrane electrical resistance in electrolyte/water/ethanol systems. The wettability properties of the liquid phase were modified by changing the ethanol to water ratio in the different mixtures. Poly[4-methyl-2-pentyne] (PMP) and poly[1-(trimethylsilyl) − 1-propyne] (PTMSP) were selected as membrane materials since both of them were investigated for solvent nanofiltration and high-pressure gas-liquid membrane contactor applications [11,40].

2. Experimental part

2.1. Polymers and membrane formation

PTMSP was synthesized by polymerization of 1-(trimethylsilyl)–1-propyne in toluene solution using $TaCl_5$ as the catalyst with co-catalyst triisobutylaluminum (TIBA) [41]. Polymerizations were carried out under the following conditions: [Monomer]/[Catalyst] = 50, [Cocatalyst]/[Catalyst] = 0.3, $[Monomer]_0$ = 1 mol/l, T = 25 °C (M_w = $1.0{\cdot}10^6$, M_w/M_n = 2.9, $[\eta]^{25}_{toluene}$ = 6.4 dl/g). PMP was synthesized by polymerization of 4-methyl-2-pentyne in cyclohexane solution with the catalytic system $NbCl_5/Et_3SiH$ [42]. Polymerization was carried out under the following conditions: [Monomer]/[Catalyst] = 50, [Cocatalyst]/[Catalyst] = 1, $[Monomer]_0$ = 1 mol/l, T = 25 °C (M_w = $1.2{\cdot}10^6$ M_w/M_n = 2.1, $[\eta]^{25}_{cyclohexane}$ = 3.2 dl/g).

The dense PTMSP or PMP membranes were cast from solution with a polymer concentration of 0.5 wt% (solvent: chloroform) onto commercial cellophane. Then the cast film was covered with a Petri dish and left for slow evaporation for several days, followed by drying in the oven at 40 °C to constant sample weight. Further treatment of all membranes was according to the standard protocol of membrane preparation [43], which includes soaking the membrane samples in n-butanol (2 days) and aqueous ethanol solutions with stepwise decreasing of alcohol concentration from 96% to 0% (2 days) followed by drying at ambient conditions (1 day). Thicknesses of obtained membranes were 30 μm.

2.2. Electrical conductivity measurements

Membrane electrical resistance measurements were performed with the lab-made experimental device depicted in Fig. 1. The experimental setup was composed of two identical chambers of 150 mL each. The membrane, with an active surface area of 12.6 cm^2, was placed in

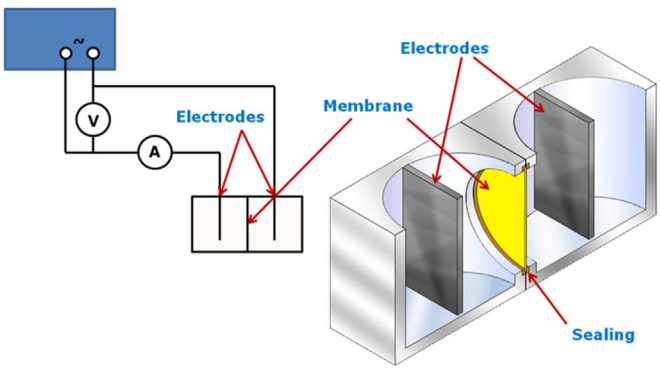

Fig. 1. Experimental setup for membrane resistance measurement.