Effect of temperature on the transport of solvents through PTMSP under ultra-high pressures

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Abstract. Despite a large number of studies, by now there is no any definitive explanation of the solvent transport mechanism in nanostructured polymer materials. Both convective and diffusive transport of solvents can be observed in these materials. The study of the solvents permeability at different temperatures and pressures allow the variation of the physical parameters and structure of the solvent–membrane interaction thus becoming the key factor in the understanding of the fundamental aspects of the selective transport process in nanostructured polymer membranes.

The paper presents the study of ethanol, propanol and water transport through poly [1-(trimethylsilyl)-1-propine] (PTMSP) at pressures 50-150 atm and temperature up to 90°C. The study was done by the method of pressure dynamic decay. As the temperature rises, the permeability of ethanol and propanol through PTMSP is shown to increase in proportion to decreasing viscosity that denotes a convective type of transport. As for water, the permeability change is thermo-activated that is typical for a diffusive type of transport. This difference in the transport characteristics can be related to a change in the membrane structure and energetic characteristics of the solvent–polymer interaction.

1. Introduction

Industrial-scale technologies of organic solvents nanofiltration are successfully used in food, petrochemical and chemical industry as well as for water purification systems, etc. [1,2]. Further development of nanofiltration technologies is in many aspects related to the development of new polymer membrane materials, which have to possess chemical and mechanical stability in organic solvents as well as a combination of selectivity and permeability close to those of inorganic membranes. Nowadays, a particular attention is paid to vitreous polymers with a high fraction of non-relaxed free volume. High permeability, mechanical and film-forming properties of such polymers allow a formation of high-productive membranes with thin separation layers [3, 4].

Studies of nanofiltration processes in such polymers have shown that both diffusive and convective types of solvents selective transport [5-9] are possible. However, despite a large number of studies, nowadays, there is no any uniform approach to the description of mechanisms of interaction and transport of solvents in the nanostructured materials. On the one hand, in case of solvent condensation in the micro-heterogeneous structure of polymers, areas filled with liquid appear in a membrane, through which the convective transport is possible. On the other hand, we speak about nanometer
elements of free volume, the evolved free surface of polymer defines a strong interaction between the polymer and solvent at the molecular level and in this case the diffusive transfer is more probable. Besides, the mobility of polymeric chains may cause essential changes in the membrane structure under the effect of pressure and temperature or in case of interaction with solvent.

At present, when modeling nanofiltration modes, several Darcy’s equation-based models are used [10]. The micro- and ultra-filtrations modes, the description of permeability in the nanofiltration mode considers the parameters defining the interaction of liquid and membrane material: viscosity factor $\eta$, superficial tension $\gamma$, porosity parameters, sorption value, swelling factor $SD$, etc. Nonlinear changes in transport properties are related to changes in structural characteristics of membranes under the pressure effect [11,12]. However, the temperature change has more significant effect on membrane structural parameters and solvents properties [18-22]. However, the analysis of temperature effects on membrane transport properties in the nanofiltration mode is rather fragmentary and does not allow this process to be described in a united way.

This paper studies a hydrophobic nanostructured vitreous polymer poly [1-(trimethylsilyl)-1-propine] (PTMSP). This polymer is extensively studied for the purpose of organic solvents nanofiltration [14] and membrane contactors [13]. The earlier published papers study in detail the convective transport of solvents in such PTMSP membranes. At the same time, the diffusive transport in PTMSP membranes is not considered because of different scale of flows. However, in a number of applications, for example in membrane contactors, the study of solvent diffusion mechanisms through a membrane have become urgent [ ] . This paper uses the method of pressure dynamic decay [24], of which unique sensitivity allows measuring the permeability of membranes in various ranges. This method was used to measure in a wide range of pressures and temperatures the permeability of solvents with different affinity to PTMSP; conditions of convective and diffusive transport in membranes have been determined as well.

2. Experiment

2.1 Polymers and preparation of membranes

The paper studies polymer poly [1-(trimethylsilyl)-1-propine] (PTMSP) synthetized in toluene solution using catalyst $\text{TaCl}_5$ with co-catalyst triisobutylaluminum (TIBA) [15]. The polymerization parameters $[\text{Monomer}]/[\text{Catalyst}]=50$, $[\text{Co-catalyst}]/[\text{Catalyst}]=0.3$, $[\text{Monomer}]=1 \text{ mol/l}$, $T = 25^\circ \text{C}$ ($M_w=1600000, M_w/M_n=2.9, [\eta]_{\text{toluene}}=6.9 \text{ dl/g}$). The membranes were obtained by casting 0.5-1.0%wt of the PTMSP solution in chloroform onto cellulose. The solvent was evaporated under normal conditions (atmospheric pressure, $T=20-24^\circ \text{C}$). The obtained membranes were 25±2µm thick. The PTMSP membranes characteristics defined by the helium pycnometry (Micro-Ultrapyc 1200e Quantachrome) and low-temperature absorption of nitrogen (Nova 1200e, Quantachrome) are given in Table 1. The specific area of the interior surface was calculated by the multi-pint BET and Langmuir’s methods [16].

| Properties of PTMSP | Experiment data |
|---------------------|----------------|
| Density, g/cm$^3$   | 0.9634±0.0004  |
| Surface area, m$^2$/g | 855±26 (BET) |
| Free volume, cm$^3$/g | 0.65±0.02     |

2.2 Solvents

Solvents with different affinity to PTMSP have been used: chemically pure ethanol, propanol and de-ionized water (resistance not less than 17 mega ohms). Figure 1 shows superficial tension and viscosity of the used liquids at various temperatures. Viscosity of these solvents changes non-linearly as the temperature increases [18-22]. At temperatures $\sim 20^\circ \text{C}$, viscosity of water is almost twice higher
than the one of alcohols; at temperatures ~ 90°C, the viscosity values of all liquids decrease significantly and differ by less than 10%. The water superficial tension is also essentially higher than the one of alcohols and at a temperature of 20°C the superficial tension differs by more than 3 times. Table 2 shows PTMSP swelling and sorption coefficients in these liquids [23]. It can be seen that water is practically not sorbed into PTMSP and the water affinity is much worse than the one of alcohols.

Table 2. PTMSP swelling and sorption

| Solvent    | Swelling SD=$\Delta V/V^*$ | Sorption, mol/mol |
|------------|----------------------------|-------------------|
| Water      | 0                          | <0.1              |
| Ethanol    | 0.72                       | 2.5               |
| 1-Propanol | 1.00                       | 2.5               |

2.3 Membranes permeability measurement

Permeability of solvents through PTMSP membranes were measured by the method of pressure dynamic decay (DPD) based on measuring elastic deformations of liquid in case of pressure decay [24]. Insertion of a rod into the chamber decreases the volume over the membrane and, as a result, causes compression and pressure increase in liquid. As the required pressure was provided in liquid, the rod position was fixed. Further, if liquid goes through the membrane, the amount of liquid over the membrane decreases that leads to the pressure decrease. Respectively, to define the fluid flow through the membrane, a decrease of pressure $\Delta p$ for a time period $\Delta t$ was measured. The membrane permeability factor was calculated by the formula:

$$ P_d = \frac{\chi \cdot V \cdot \Delta p \cdot \rho}{\Delta t \cdot S} \cdot \frac{d}{p} \cdot \Delta V $$

where $V$ – liquid volume over the membrane [m$^3$], $\chi$ – liquid compressibility [atm$^{-1}$], $\rho$ – liquid density [kg/m$^3$], $d$ and $S$ – thickness [m] and membrane area equal to 2.54cm$^2$. The permeability measurement accuracy depends on the liquid compressibility. Since the compressibility factors for the majority of liquids are in the range $10^{-8} – 10^{-9}$ Pa$^{-1}$, this method allows recording a change in the liquid volume over the membrane with an accuracy of 0.01% as the pressure changes by 1atm. The measurements were done at an initial pressure of 180 atm for 5 hours at the same temperature with an accuracy of ±0.5°C (temperature regulator Termeh M01).

2.3 Permeability of solvents through PTMSP

Earlier, the DPD method was used to measure the permeability of ethanol and propanol through PTMSP at pressure from 10 to 200atm and temperature of 30°C [24]. It was stated that the permeability of these solvents through PTMSP at pressure from 50 to 150atm did not practically change. Therefore, to study the temperature effect on the change in PTMSP transport characteristics, the permeability of ethanol and propanol was measured at pressure from 50 to 150 atm and at temperatures less than boiling point: from 30°C to 70°C for ethanol and from 30°C to 90°C for propanol. Diagrams of ethanol and propanol flows through PTMSP at various different are given in Fig. 1. It is seen that at a constant temperature, the flow increases linearly as the pressure rises.
The permeability coefficients of ethanol and propanol calculated by (1) are given in Fig. 2. Apparently, at a pressure of 30 atm and temperature of 30°C, the permeability values measured by the DPD method and method of a filtration in a blind cell coincide [25]. As the temperature increases, permeability coefficients increase monotonously within the whole pressure range. So, the permeability of ethanol increases more than twice, as the temperatures increase from 30 to 70°C, the permeability of propanol increases by almost 3 times, as the temperatures increase from 30 to 90°C.

Figure 3a shows a change in pressure under water flowing through PTMSP. It can be seen that at a temperature of up to 40°C, the initial pressure of about 200 atm did not change during the observation period, i.e. PTMSP is impermeable for water at such temperature and pressure. However at a temperature of 60°C and higher, there was a decrease in pressure related to the water flow through the membrane. A decrease in pressure during the first 30 minutes of measurements is related to the system relaxation and sorption processes in the membrane. The permeability values given in Fig. 3b were calculated for the pressure scaling-down area. It is seen that at a temperature of 60°C, water permeability achieves a value of \(5 \times 10^{-9} \text{ kg/m/bar-h-m}^2\), i.e. comparable with diffusion flows in other polymeric membranes. Thus, one may suppose that at temperatures from 40 to 60°C, characteristic of liquid and its affinity to polymer become such that macroscopic diffusion of water is possible. As temperature further rises from 60 to 90°C, it results in the permeability increase by almost three times.
and achieves a value of $\sim 15 \cdot 10^{-9}$ kg∙m/bar∙h∙m$^2$. If we extrapolate linearly the permeability change, then the diffusion flow appears at a temperature of about 45°C.

**Figure 3.** a) pressure change as water flows through PTMSP, b) water permeability coefficient through PTMSP

### 3. Results and discussion

In the nanofiltration mode through the nanostructured polymeric membranes, both convective and diffusion transfer of solvent [12,13,26-29] is possible. It is known that PTMSP has a non-uniform structure with areas of high and low density [32], porosity exceeds 25% and the structure of PTMSP non-relaxed free volume has bimodal distribution with the most probable diameter of "voids" of 0.66 and 1.36nm [33]. Respectively, related channels filled with liquid can occur in such free volume, through which there is a convective transfer goes and, in a general, a solvent flow through PTMSP can be described by the following equation:

$$ J = A \cdot B \cdot \Delta p $$

(2)

where $A$ – coefficient of liquid characteristics, $B$ – coefficient defined by the polymer structure parameters, $\Delta p$ – trans-membrane pressure [13]. If we consider a solvent flow through a membrane with a constant pressure, then the system temperature and interaction of liquid with polymer define coefficients $A$ and $B$. On the one hand, in case of convective transport, the flow in channels in inverse proportion to liquid viscosity $\eta(T)$. Also, in nanometer channels, the flow depends on the interfacial tension of liquid, which characterizes a slinging friction appearing because of interaction between liquid and material surface [6, 10]. As the temperature increases, the coefficient $A$ and membrane permeability have to increase non-linearly as for the majority of liquids viscosity and interfacial tension decrease when heated and therefore, the coefficient $A$ can be written down as follows:

$$ A \sim \frac{1}{\eta(T) \cdot \gamma(T)} $$

(3)

On the other hand, the mobility of polymer chains and free volume can increase both due to the temperature change and in case of solvent sorption into polymer. The structural parameter $B$ has to be as follows:

$$ B = B(\Delta p, T, \phi) $$

(4)

where $\phi$ - sorption coefficient that depends on the affinity of liquid and polymer.

There is no and definite solution for the flow in the nanofiltration mode and the type of parameters $A$ and $B$ is not unambiguously defined. However, since the temperature changes of viscosity and interfacial tension of liquids are known, then using (3) it is possible to estimate the effect of these parameters on the permeability. Figure 5 shows the experimentally defined permeability...
coefficients for ethanol and propanol normalized to the corresponding values at 30 °C as well as the
inverse values of viscosity and the interfacial tension:

\[ P_{dn} \sim \frac{P_d}{P_d(30^\circ C)}, \eta_n = \frac{\eta(T = 30^\circ C)}{\eta(T)}, \gamma_n = \frac{\gamma(T = 30^\circ C)}{\gamma(T)} \] (5)

As it can be seen from Figure 4, for ethanol (up to 45°C) and propanol (up to 65°C), the permeability
change \( P_{dn} \) coincides with the change of both viscosity \( \eta_n \) and interfacial tension \( \gamma_n \) within the error.
At higher temperatures, the change in viscosity and experimentally defined permeability coincides
within the error, while the interfacial tension change differs greatly from the permeability one.

![Figure 4](image)

**Figure 4.** Normalized coefficients of permeability through PTMSP at a pressure of 100atm; viscosity
and interfacial tension for a) ethanol and b) propanol.

This result corresponds to the model of liquid viscous flow in voids. At that, if the permeability
temperature changes are related only to liquid viscosity, then the flow will be described by the
following expression:

\[ J = \frac{B(\phi)}{\eta(T)} \cdot \Delta p \] (6)

Parameter \( B(\phi) \) contains only structural characteristics of polymer, which depend only on the
interaction of solvent with the membrane material and influence of pressure on the membrane
structure can be neglected. Earlier it was shown that in case of sorption of alcohols, PTMSP swelling
occurs and its volume increases by ~ 55% for ethanol and by ~ 110% for propanol [30]. Accounting
swelling and free volume change, the following expression was proposed for structural parameter
\( B(\phi) \):

\[ B = a \cdot \frac{V_m}{l} \cdot \frac{\phi^3}{(1 - \phi)^2} \cdot e^{\frac{1 - \gamma_{sv}}{\gamma_l}} \] (7)

where \( a \) – modeling parameter, \( \phi \) – liquid volume fraction in membrane, \( l \) – membrane thickness, \( V_m \) –
molar volume of solvent, \( \eta \) – liquid viscosity, \( \gamma_{sv} \) and \( \gamma_l \) – surface energy of polymer and solvent
[13,17]. Due to swelling resulted from solvent sorption and membrane compression under pressure,
the geometry characteristics change:
where \( \phi_0 \) and \( l_0 \) - membrane parameters without swelling, \( SD \) – swelling degree. Modeling parameter \( k \) – polymer compressibility coefficient – defines the membrane compression under pressure. As it can be seen from Figure 5, at temperatures up to 60°C for ethanol and 70°C for propanol, this model describes well the experimentally measured values of flows through PTMSP. At higher temperatures, the calculated values differ from the experimental ones.

Figure 5. Solvent flow through PTMSP at different pressures and temperatures

a) ethanol, b) propanol

If solvent sorbs badly in polymer, then the transport channels filled with liquid cannot be formed and convective transfer of liquid is impossible. However, the diffusion transfer of solvent molecules in polymer may occur as a result of the transition between stable states, of which probability is defined by the activation energy and temperature of system. At that, the diffusion flow has a pronounced threshold character as the temperature rises, for example, for water in PTMSP. As it can be seen from Figure 3, at a temperature of up to 40°C and pressure higher than 150 atm, there is no water flow through PTMSP, i.e. its size is less than the measurement sensitivity \( 0.1 \times 10^{-9} \text{kg} \cdot \text{m/bar} \cdot \text{h} \cdot \text{m}^2 \). At a temperature of 60°C, the permeability coefficient becomes \( \approx 5 \times 10^{-9} \text{kg} \cdot \text{m/bar} \cdot \text{h} \cdot \text{m}^2 \), i.e. it increases almost by two orders of magnitude in the 20°C interval. Such essential increase in the water flow corresponds to the diffusion transport by the activation mechanism and the permeability coefficient can be described by the Arrhenius equation:

\[
P = K_0 \cdot D_0 \cdot \exp \left( -\frac{E_a}{R \cdot T} \right) , \quad (9)
\]

where \( K_0 \) and \( D_0 \) – sorption and diffusion coefficients at the normalizing temperature, \( E_a \) – water activation energy, \( R \) – absolut gas constant, \( T \) – temperature. As it can be seen from Figure 6, the values of water permeability through PTMSP defined experimentally and calculated by (9) and normalized to the permeability at 60°C coincide within the error at an activation energy of \( E_a=31.1 \) kJ/mol. These activation energy values correspond to the diffusion characteristics of water in vitreous polymers. On the other hand, one may suppose that as the temperature rises and interfacial tension decreases, the sorption properties of water in PTMSP will change and the flow can be described within the convective diffusion model.
Conclusion
Flows have been measured and permeability coefficients through PTMSP of ethanol, propanol and water at temperatures from 20 to 90°C and pressure from 50 to 150 atm have been defined. Such change in pressure and temperature allows varying both structural parameters and characteristics of interaction of solvent with polymer.

Ethanol and propanol, for which sorption in PTSMP is observed, form a system of related channels, through which there is a convective diffusion of solvent. The permeability of these alcohols depends on the change in the PTMSP structural parameters under sorption and it is inverse proportion to viscosity. As for water, the thermo-activated transfer is observed at a temperature higher than 40°C. As the temperature rises, the mobility of water molecules and polymer chains increases as well as the permeability. At that, the activation energy and critical characteristics for water in PTMSP have been defined.

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