

## HYDROPHOBIC MEMBRANES FOR SYSTEM MONITORING UNDERWATER GAS PIPELINES

Anna ROZICKA <sup>a</sup>, Wojciech KUJAWSKI <sup>b\*</sup>, Vittorio GUARNIERI <sup>c</sup>, Leandro LORENZELLI <sup>c</sup>, Alexey VASILIEV <sup>d</sup>, Vladimir FILIPPOV <sup>d</sup>

<sup>a</sup> MSc, PhD student; Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarina Street, Toruń, Poland

<sup>b</sup> Prof.; Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarina Street, Toruń, Poland  
E-mail address: kujawski@chem.umk.pl

<sup>c</sup> Dr.; Bruno Kessler Foundation, Via Sommarive, 18 38100 Povo di Trento, Italy

<sup>d</sup> Prof.; Russian Research Centre "Kurchatov Institute", Kurchatov sq., 1, 123182, Moscow, Russian Federation

Received: 18.06.2012; Revised: 13.09.2012; Accepted: 10.10.2012

### Abstract

The aim of this work was to prepare hydrophobic membranes as selective barriers to be applied in gas sensors. Two kinds of membranes were investigated: ceramic, modified with perfluoroalkylsilanes ( $C_6F_{13}C_2H_4Si(OEt)_3$  – C6 and  $C_{12}F_{25}C_2H_4Si(OEt)_3$  – C12) and formed from polydimethylsiloxane (PDMS). Inorganic membranes properties after modification were tested by determining the contact angle (CA). Membrane modified by C12 was more hydrophobic (CA=148°) compared with membrane modified by C6 (CA=135°). PDMS membranes of different thickness (75-195  $\mu m$ ) were formed and their properties were determined by pervaporation of water and by contact angle measurements. It was shown that water transport is inversely proportional to membrane thickness and permeability coefficient was equal to  $7.3 \cdot 10^{-15} \text{ mol m}^{-1} \text{ Pa}^{-1} \text{ s}^{-1}$ . Contact angle was equal to  $104^\circ \pm 4^\circ$ . The commercial PDMS membrane properties were tested in pervaporation of water-ethanol, water-pentane and water-hexane systems and it was found that organic compound is selectively transported through the membrane (enrichment factors were equal to 4-8, 75 and 120 for ethanol, pentane and hexane, respectively). Preferential transport of organic compounds was also discussed using Hansen's solubility parameters.

### Streszczenie

Celem pracy było otrzymanie membran hydrofobowych, przewidzianych do zastosowań w sensorach gazowych. Zbadano właściwości membran: ceramicznych, modyfikowanych powierzchniowo perfluoroalkilosiłanami: ( $C_6F_{13}C_2H_4Si(OEt)_3$  – C6 i  $C_{12}F_{25}C_2H_4Si(OEt)_3$  – C12) oraz membran uformowanych z poli(dimetylosiłoksanu) (PDMS). Właściwości membran ceramicznych po modyfikacji charakteryzowano poprzez pomiar kąta zwilżania (CA). Membrana modyfikowana roztworem C12 (CA=148°) posiadała bardziej hydrofobowe właściwości niż membrana modyfikowana C6 (CA=135°). Uformowano membrany z PDMS o różnej grubości (75-195  $\mu m$ ), oznaczono kąt zwilżania dla wody oraz określono ich właściwości perwaporacyjne w kontakcie z wodą. Wykazano, że transport wody przez membranę jest odwrotnie proporcjonalny do grubości błony, a współczynnik przepuszczalności wody wynosi  $7.3 \cdot 10^{-15} \text{ mol m}^{-1} \text{ Pa}^{-1} \text{ s}^{-1}$ . Właściwości komercyjnej membrany PDMS określono w kontakcie z mieszaninami: woda-etanol, woda-pentan i woda-heksan. Wykazano przy tym, iż składnik organiczny był selektywnie transportowany przez membranę (współczynniki wzbogacenia dla etanolu, pentanu i heksanu wyniosły odpowiednio 4-8, 75 i 120). Preferencyjny transport składników organicznych zinterpretowano również, stosując współczynniki rozpuszczalności Hansena.

**Keywords:** Ceramic membranes; PDMS membranes; Pervaporation; Contact angle; Perfluoroalkylsilanes; Surface modification.

## 1. INTRODUCTION

World economy development causes progressive increase in natural gas consumption [1], therefore it is necessary to build new transport routes for natural gas, and successively replace those already existing. One of used transport routes for natural gas are underwater pipelines. On the other hand, a growing interest of underwater pipelines systems requires development of new methods detecting gas leaks and informing about gas leaks or potential damages of pipelines.

Application of the microsensors technology enables an important improvement of characteristics of semiconductor, thermocatalytic, and infra-red optic gas sensors. In particular, it makes possible the fabrication of autonomous, wireless instruments with minimized power consumption, that can also operate at high temperatures [2].

Vasiliev et al. [3] investigated CeraMEMS chips consisting of a rigid frame made from a thin alumina film (TAF) fixed onto the frame with a glass binder. Authors used screen printing or drop deposition technique to deposit a sensing layer on top of the TAF. It was concluded that TAF membranes enable the work at temperatures up to 600°C and that the alumina micro-hotplate is more robust than a silicon chip with a thin membrane. It was also shown that the alumina-based TAF CeraMEMS platform could be successfully used for the fabrication of semiconductor and thermocatalytic gas sensors operating in a pulsing heat mode.

A methane gas sensor was prepared in Bruno Kessler Foundation (Trento, Italy). The preparation of this sensor was described in detail elsewhere [2,4]. The gas sensing properties were determined with respect to methane. Measurements were performed at temperature corresponding to the optimal gas sensitivity

(450°C). The gas sensor is capable of detecting methane at concentrations lower than 0.1 vol.% and exhibits linear response at investigated methane concentrations in the range of 0.12-2.5 vol.% [4].

The monitoring system detecting the underwater gas leaks can be constructed using such miniaturized gas sensor covered by a hydrophobic membrane. The both, modified ceramic membranes as well as the hydrophobic polymer membranes can be utilized for this purpose.

Ceramic membranes are made from inorganic oxides such as alumina, titania, zirconia or silica. These materials originally are of a hydrophilic character, what is caused by the presence of hydroxyl groups on ceramic membrane surface. Hydrophilic ceramic membrane properties can be changed into hydrophobic ones by a surface modification. The surface grafting is the most often used method for this purpose [5]. Molecules possessing the hydrophobic properties, like perfluoroalkylsiloxanes ( $C_nF_{2n+1}C_2H_4Si(OEt)_3$  – PFAS) are usually used for the surface modification.

Surface grafting by PFAS is the result of a condensation reaction between ethoxy groups of PFAS molecules and hydroxyl groups present on ceramic membrane surface (Fig. 1). Surface modification leads to the formation of PFAS monolayer on the surface and within the membrane pores. The presence of PFAS brush changes membrane properties from hydrophilic to hydrophobic ones.

Polydimethylsiloxane (PDMS) is one of the most frequently used materials for the preparation of hydrophobic membranes [6-8]. PDMS possesses a lot of advantages such as biocompatibility, flexibility and bonding ability [9]. Moreover, PDMS is resistant to UV radiation, high temperature and oxidation [10]. PDMS membranes show several advantages in a potential use: their thickness can be easi-

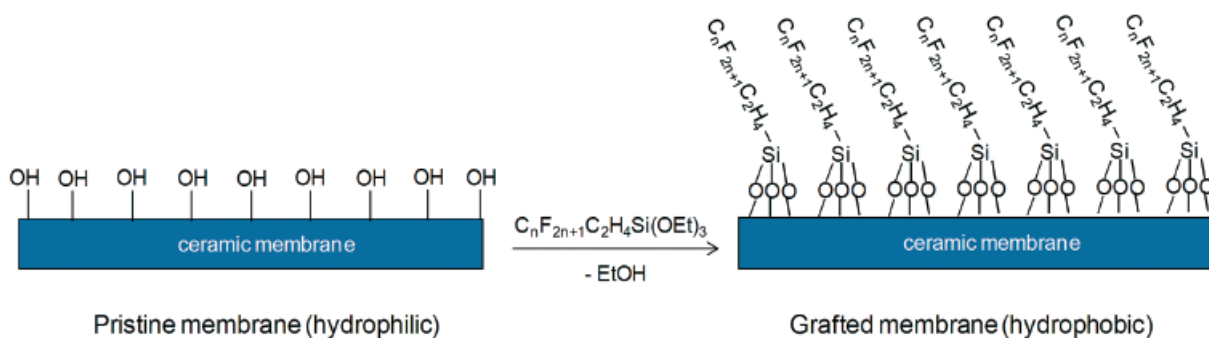


Figure 1.  
Scheme of the surface grafting of ceramics by PFAS molecules

ly controlled, a large scale preparation is uncomplicated and they are easier to be prepared in a crack-free and a pin-hole free form than ceramic or other polymeric materials [11]. PDMS based membranes are widely used in pervaporation and gas separation for the removal of organics from water, vapour and gas streams [8,12-16].

Pervaporation is a membrane separation process in which a binary or multicomponent liquid mixture is separated by partial vaporization through a membrane. The feed mixture is in direct contact with one side of the hydrophilic or hydrophobic membrane, whereas the permeate is removed in a vapour state from the opposite side into a vacuum or sweeping gas and then condensed [17,18]. Hydrophilic membranes are used in case of dehydration of solvents with small water content. This kind of membranes preferentially transport water and at the same time solvent is being dried. Inversely, in case of low solvent concentration in water, hydrophobic membranes can be used to selectively transport an organic compound [19]. Transport through dense non-porous membranes can be described using solution-diffusion model, discussed in detail elsewhere [20]. According to this transport mechanism, the component must first be partitioned and then diffuse through the solid material owing to a concentration gradient. For this reason, the separation by non-porous membrane is influenced by partition coefficient, as well as diffusivity of the component in the membrane [21].

The aim of this work was to prepare hydrophobic membranes which could be used in the underwater monitoring systems. The membrane should cover gas sensor and selectively transport organic compound to the sensor surface. Two types of surface modified ceramic membranes were prepared as well as a series of PDMS membranes of different thickness. The hydrophobic properties of these materials were determined. Transport properties of PDMS membranes were determined in contact with water and compared with properties of commercial PDMS membrane. Moreover, the selective properties of this membrane were studied by pervaporation in contact with water-ethanol, water-pentane and water-hexane mixtures.

## 2. EXPERIMENTAL

### 2.1. Materials

Planar titania membranes (cut-off 1 kDa, diameter 47 mm, total thickness 3 mm) used for this study were purchased from TAMI Industries (France).

Commercial PDMS based membrane was delivered by Pervatech (the Netherlands). This membrane is denoted thereafter as PERVATECH.

EL.LR 7660A elastomer and EL.LR 7660B curing agent were kindly provided by Wacker Chemie GmbH (Germany).

The PFAS: 1H,1H,2H,2H-perfluorooctyltriethoxysilane with molar weight ( $M_w$ ) of 510 g mol<sup>-1</sup> (further denoted as C6) and 1H,1H,2H,2H-perfluorotetradecyltriethoxysilane –  $M_w=810$  g mol<sup>-1</sup> (further denoted as C12) were purchased from SynQuest Laboratories (USA).

Ethanol, acetone, chloroform, n-pentane, n-hexane, sec-butanol, 1-propanol were purchased from POCH (Poland).

All materials were used as received.

### 2.2. Surface modification of TiO<sub>2</sub> ceramic membrane

Commercially available porous ceramic TiO<sub>2</sub> membranes were modified by C6 and C12 PFAS compounds. The 0.05 M C6 and C12 grafting solutions were prepared in chloroform. Preparation of PFAS solutions and grafting process were performed at argon atmosphere to avoid self-condensation of perfluoroalkylsilanes.

The surface modification was performed by the complete immersion of planar membranes into C6 and C12 solutions for a given period of time (1-6 hours). Each grafting stage was finished by a sequential rinse for 10 minutes in acetone, ethanol and water. Subsequently, the samples were dried for 24 h at ambient temperature and then contact angle measurements were performed.

The surface modification procedure was repeated several times for each membrane with a total grafting time equal to 37 hours.

### 2.3. Preparation of PDMS membrane

PDMS membranes of different thicknesses in the range 75 to 195  $\mu$ m were prepared using polydimethylsiloxane solution, prepared from EL.LR 7660A elastomer (denoted as component A) and EL.LR 7660B curing agent (denoted as component B). According to the supplier's information, component A was a vinyl-methyl-polysiloxane ( $M_w \cong 40\,000$ ) containing platinum based catalyst, and component B was a hydrogen functional crosslinker. The 20 wt.% solution of component A in n-hexane was prepared and subsequently component

B was added to it to adjust the A : B ratio to 10:1. The weighed amount of the solution was spread out into a mould and it was kept for 24 h at ambient temperature. In the following step, the mould with the membrane was placed in an oven at 80°C for 2 h to complete crosslinking of the membrane. The crosslinked membrane was peeled off from the mould and its thickness was measured (average of measurements in 21 points evenly distributed over the membrane area) using digital micrometer (Sylvac S 229).

## 2.4. Contact angle measurements

Contact angle is used to determine surface hydrophobic properties. According to Kwok and Neumann [22] contact angle measurements can be performed by establishing the tangent angle of a liquid drop with a solid surface as the base (Fig. 2). This is the angle determined by the mechanical equilibrium under the action of three interfacial tensions (Eq.1).

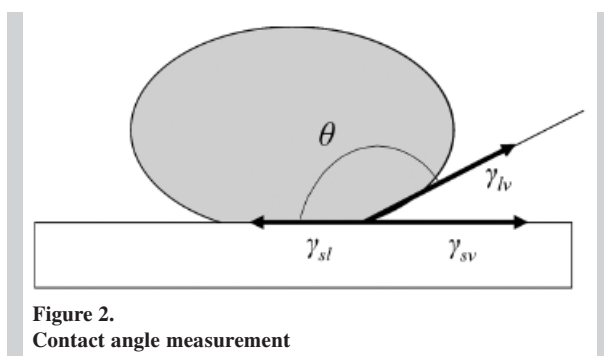


Figure 2.  
Contact angle measurement

Contact angle ( $\theta$ ) can be calculated from the Young equation [22]:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

where:

$\gamma_{lv}$ ,  $\gamma_{sv}$ ,  $\gamma_{sl}$  – surface interfacial tensions on liquid-vapour, solid-vapour and solid-liquid phase boundaries, respectively.

Contact angle measurements for water were performed on surfaces of:

- i) planar TiO<sub>2</sub> ceramic membranes modified by C6 and C12, after each grafting stage,
- ii) polydimethylsiloxane membranes.

A 0.05 mL water drop was deposited on membrane surface and pictures of the drop were taken. Subsequently, contact angle values were estimated using ImageJ software. The measurements (n=3)

were performed with an accuracy of  $\pm 2^\circ$ .

## 2.5. Pervaporation experiments

Pervaporation measurements were performed only with polymeric (PDMS) membranes using a standard laboratory set-up shown in Fig. 3 [17].

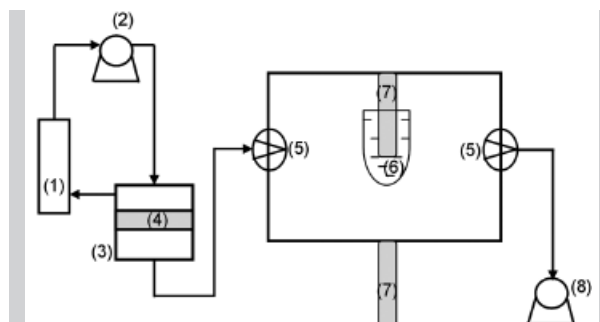


Figure 3.  
Pervaporation set-up (1) thermostated feed, (2) feed pump, (3) membrane module, (4) membrane, (5) valve, (6) liquid nitrogen, (7) permeate traps, (8) vacuum pump

PDMS membrane sample (4) was placed in a stainless steel module (3). The feed was circulated by a feed pump (2) between module (3) and feed tank (1). Vacuum pump (8) ensured low pressure on the permeate side. Permeate was collected in two permeate traps (7) cooled with liquid nitrogen (6). All pervaporation experiments were performed at 25°C.

Six polydimethylsilane membranes, with different thickness in the range 75-195  $\mu\text{m}$  and PERVATECH commercial PDMS membrane (thickness of selective layer  $d = 4 \mu\text{m}$ ) were investigated in pervaporation with deionized water as feed.

Properties of commercial PDMS membrane were also determined in pervaporation of water-ethanol (0-10 wt. %), water-pentane (0-30 ppm) and water-hexane (0-200 ppm) systems.

Concentrations of ethanol, pentane, hexane in feeds and permeates were determined using gas chromatography (GC-TCD). The analyses were carried out on Varian 3300 gas chromatograph equipped with TCD detector (injector temperature: 200°C, column temperature: 180°C, detector temperature: 220°C). A PorapakQ packed column was used (1.8 m x 2.1 mm, matrix Porapak QS 80-100 mesh (Supelco, USA)). The injection volume was 0.4  $\mu\text{L}$ , and the total GC analysis run time varied, depending on the organic component used (6-9 min.)

For water-pentane and water-hexane permeates it was necessary to add third solvent to homogenise the



two-phase samples. 1-propanol and *sec*-butanol were used for water-pentane and water-hexane mixtures, respectively. *Sec*-butanol was used instead of *n*-butanol to avoid co-elution of *n*-butanol and hexane, and hence ensure better chromatographic separation. Fluxes of water and organic components were determined by weighing the permeate collected over a given period of time.

Membrane properties, i.e. enrichment factor –  $\beta$  and permeate fluxes –  $J_i$ , were calculated from equations (2) and (3):

$$\beta = \frac{X_{i(P)}}{X_{i(F)}} \quad (2)$$

$$J_i = \frac{m_i}{t \cdot A} \quad (3)$$

where:

$X_i$  – fraction of compound  $i$  in feed ( $F$ ) and permeate ( $P$ ),

$m_i$  – mass of component  $i$  [g],

$t$  – permeation time [h],

$A$  – membrane area [m<sup>2</sup>].

### 3. RESULTS

#### 3.1. Contact angle results

Contact angle (CA) values measured for modified ceramic membranes as a function of modification time are presented in Fig. 4.

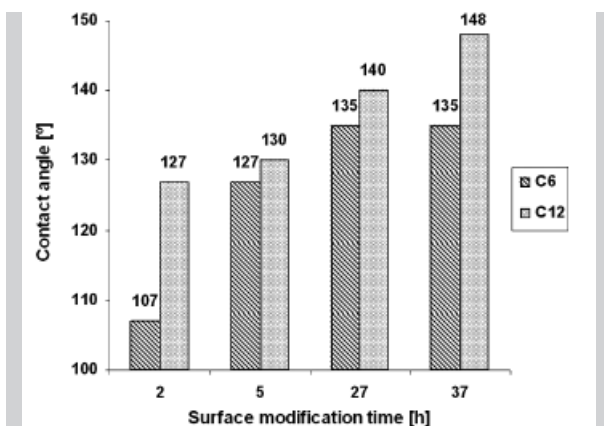


Figure 4. Evaluation of contact angle with increasing grafting time

Unmodified ceramic membrane possesses hydrophilic properties, because of the presence of

hydroxyl groups on its surface. Ceramic membrane surface modified with perfluoroalkylsilanes gained hydrophobic properties after 2 h of membrane grafting. Moreover, significant difference between contact angle values of C6 and C12 modified membranes could be noticed. For longer grafting times, contact angle for C6 modified membrane increased significantly from 107° till 127°, after 5 h of total grafting. However, contact angle did not change significantly for a longer grafting time. The highest contact angle value for C6 modified membrane was equal to 135°. On the other hand, the CA for the C12 modified membrane increased moderately from 127° (after 2h of modification) to 148° (after 37 h of modification). As it can be seen (Fig. 4) higher contact angle values were obtained for membrane grafted with C12. This is explained by a much higher hydrophobicity of C12 molecules in comparison with C6 ones, resulting from longer hydrophobic chain.

Contact angle values measured for PDMS membrane were equal to 104°±4°. This value is comparable with values obtained by Lee et al. [23] (CA=102°) and Khorasani et al. [24] (CA=105°) and proved the hydrophobicity of PDMS in contact with water.

#### 3.2. Pervaporation results

##### 3.2.1. Water transport

Water permeate flux obviously depends on the membrane thickness, because pervaporation membrane shows proportional to its thickness mass transfer resistance [21]. For higher PDMS membrane thickness, smaller fluxes are observed, because the permeation flux is inversely proportional to the membrane thickness as shown in Eq.(4).

$$J_i = P_i \frac{(p_{i,F} - p_{i,P})}{l} \quad (4)$$

where:

$J_i$  – flux of component  $i$ ,

$P_i$  – permeability coefficient of component  $i$ ,

$p_{i,F}$  – partial vapour pressure of component  $i$  on feed side,

$p_{i,P}$  – partial vapour pressure of component  $i$  on permeate side,

$l$  – membrane thickness.

The more detailed discussion of water transport across PDMS membranes is given elsewhere [4]. Obtained data were used to calculate the permeabil-

ity coefficient ( $P_w$ ) of water through PDMS membranes, applying Eq. (4). The determined value was equal to  $P_w = 7.3 \cdot 10^{-15} \text{ mol m}^{-1} \text{ Pa}^{-1} \text{ s}^{-1}$ . Kujawski et al. [25] calculated permeability coefficient for hydrophilic ion-exchange sulfonic membrane (PESS-Li<sup>+</sup>), finding the value of  $8.1 \cdot 10^{-10} \text{ mol m}^{-1} \text{ Pa}^{-1} \text{ s}^{-1}$ , which is five orders of magnitude higher than the value of  $P_w$  for PDMS membrane obtained in this work. Water is a highly hydrophilic solvent and because of that the transport of water molecules through hydrophobic PDMS membrane is so much limited.

### 3.2.2. Pervaporation of water-organics mixtures

Pervaporation experiments with Pervatech PV membrane were performed for three liquid mixtures: water-ethanol, water-pentane and water-hexane.

Pervaporation experiments were performed using water-ethanol system as a reference system [14,15]. Results of PV measurements for ethanol concentration in the range 0-10 wt.% were discussed elsewhere [4]. Ethanol is preferentially transported through the PDMS membrane, with enrichment factor  $\beta$  in the range 8-4 which decreased with increasing ethanol concentration in feed mixture.

Hydrocarbons were also selectively transported through PDMS membrane (Fig. 5). During PV of 30 ppm pentane aqueous mixture, organic compound concentration in permeate reached 2000 ppm, owing to the selective transport of pentane through the membrane. Analogous results were obtained for hexane – water system, in this case hexane concentration in permeate reached 1500 ppm, vs. 200 ppm in feed. Such a high increase of hydrocarbons concentrations is interesting from the point of view of final membrane application as a sensor cover. Average

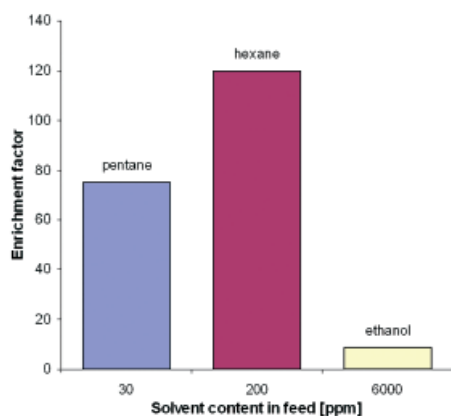


Figure 5. Enrichment factor vs. compound content in feed

enrichment factors for water-pentane and water-hexane systems calculated from Eq. (2) were equal to 75 and 120, respectively and were much higher than those calculated for water-ethanol system ( $\beta = 4 \div 8$ ), which also proved that hydrocarbons are preferentially transported through PDMS membrane.

Selective transport of organic compounds through hydrophobic membranes was additionally analysed using Hansen solubility parameters [26-28]. In this approach, a distance parameter ( $\Delta$ ) – Eq. (5) enables to quantify the similarity of two substances:

$$\Delta_{S,P} = \left[ (\delta_{d,S} - \delta_{d,P})^2 + (\delta_{p,S} - \delta_{p,P})^2 + (\delta_{h,S} - \delta_{h,P})^2 \right]^{1/2} \quad (5)$$

where:

$\Delta_{S,P}$  – distance parameter between solvent and polymer,

$\delta_d, \delta_p, \delta_h$  – Hansen solubility dispersion cohesion (d), polar cohesion (p) and hydrogen bonding (h) parameters,

S – solvent (subscript),

P – polymer (subscript).

In the case where  $\Delta$  decreases the interactions between the solvent and the polymer increase.

Table 1. Hansen solubility parameters of PDMS, chosen solvents and methane [29,30] distance parameter  $\Delta_{S,P}$  calculated values

	Hansen parameters [MPa <sup>1/2</sup> ]			$\Delta_{\text{PDMS/solvent}}$
	$\delta_d$	$\delta_p$	$\delta_h$	
PDMS	15.9	0	4.1	-
Water	15.5	16	42.3	41.4
Ethanol	15.8	8.8	19.4	17.7
Pentane	15.6	0	0	4.1
Hexane	14.9	0	0	4.2
Methane	14	0	0	4.5

Using Eq. (5) and data presented in Table 1, a distance parameter ( $\Delta$ ) was calculated. Methane and PDMS material distance parameter was also calculated, because this compound is dedicated to be selectively transported through membrane. The smallest  $\Delta$  was obtained for PDMS-pentane ( $\Delta = 4.1$ ) and because of it, this compound possesses the highest affinity to membrane material (PDMS). Slightly higher values were obtained for PDMS-hexane

( $\Delta = 4.2$ ) and PDMS-methane ( $\Delta = 4.5$ ). The highest value was calculated for PDMS-water ( $\Delta = 41.4$ ), which proved that water was not preferentially transported through hydrophobic membrane. Low distance factor values obtained for pentane and hexane were in a good agreement with the results obtained from pervaporation of water-pentane and water-hexane systems, where organic compounds were transported with high selectivity. Calculated distance parameters also explain much smaller enrichment factor received in water-ethanol system in comparison with water-pentane and water-hexane systems. Based on obtained results it can be expected that methane will be selectively transported through PDMS membrane.

#### 4. CONCLUSIONS

Ceramic membranes were modified to possess hydrophobic properties. The most hydrophobic was ceramic membrane modified with C12 molecules. It was proved that these properties are influenced by the time of modification. The highest contact angle value ( $\theta=148^\circ$ ) was obtained for ceramic membrane modified with C12 during 37 hours, whereas the highest contact angle value ( $\theta=135^\circ$ ) measured for membrane modified with C6 molecules was obtained already after 27 hours of modification.

Results obtained in pervaporation with water show that water permeate flux is inversely proportional to PDMS membrane thickness. PDMS membranes are intrinsically hydrophobic and thus compounds of similar polarity are preferentially transported through the membrane. An organic compound was selectively transported during pervaporation in water-ethanol, water-pentane and water-hexane systems (enrichment factors were equal to 4-8, 75 and 120 for ethanol, pentane and hexane, respectively). Moreover, calculated Hansen's distance parameters proved that the most preferentially transported compounds are hydrocarbons.

#### ACKNOWLEDGEMENTS

The research was supported by NATO grant ESP NRCLG 984165 "Safety and Security Monitoring System for Under-water Pipeline" 2011-2012 and CHEMO-KOP grant 53/2011 founded by a project: "CHEMO-KOP – Rozwój nowoczesnych studiów chemicznych II stopnia w Uniwersytecie Mikołaja Kopernika dla zwiększenia liczby absolwentów kierunków o szczególnym znaczeniu dla gospodarki".

#### REFERENCES

- [1] Concise Statistical Yearbook of Poland 2011, Central Statistical Office, Warsaw 2011, p.524
- [2] *Vasiliev A., Pavelko R., Gogish-Klushin S., Kharitonov D., Gogish-Klushina O., Pisiakov A., Sokolov A., Samotaev N., Guarnieri V., Zen M., Lorenzelli L.*; Sensors based on technology "nano-on-micro" for wireless instruments preventing ecological and industrial catastrophes in Sensors for Environment. Health and Security (Ed. M.-I. Baraton) 2009, p.205-227
- [3] *Vasiliev A.A., Pavelko R.G., Gogish-Klushin S., Kharitonov D., Gogish-Klushina O., Sokolov A.V., Pisiakov A.V., Samotaev N.N.*; Alumina MEMS platform for impulse semiconductor and IR optic gas sensors, Sens. Actuators, B Vol.132, 2008; p.216-223
- [4] *Rozicka A., Kujawski W., Guarnieri V., Lorenzelli L., Vasiliev A., Filippov V.*; Monitoring systems for underwater pipelines. 1. Preparation of hydrophobic membranes. Membrany i Procesy Membranowe w Ochronie Środowiska Monografie Komitetu Inżynierii Środowiska PAN, Vol.95 (Ed. K. Konieczny, I. Korus) 2012; p.191-203
- [5] *Larbot A., Gazagnes L., Krajewski S., Bukowska M., Kujawski W.*; Water desalination using ceramic membrane distillation. Desalination, Vol.168, 2004; p.367-372
- [6] *Seo J., Lee L.P.*; Effects on wettability by surfactant accumulation/depletion in bulk polydimethylsiloxane (PDMS). Sens. Actuators B, Vol.119, 2006; p.192-198
- [7] *Leger C., Lira H.L., Paterson R.*; Preparation and properties of surface modified ceramic membranes. Part II. Gas and liquid permeabilities of 5 nm alumina membranes modified by a monolayer of bound polydimethylsiloxane (PDMS) silicone oil. J. Membr. Sci., Vol.120, 1996; p.135-146
- [8] *Kujawski W., Kerres J., Roszak R.*; Application of AB-crosslinked polymers composed of styrene/isoprene-siloxane copolymers to pervaporative removal of volatile organic compounds from water. J. Membr. Sci., Vol.218, 2003; p.211-218
- [9] *Lederer T., Hilber W., Ove B.J.*; Fast thermo-pneumatic actuation of a thin PDMS membrane using a micro Peltier-element for microfluidic applications. Elektrotechnik & Informationstechnik, Vol.126, No.1/2, 2009; p.70-74
- [10] *Chruściel J., Leśniak E., Fejdyś M.*; Karbofunkcyjne silany i polisiloksany (Carbofunctional silanes and polysiloxanes). Polimery, Vol.53, 2008; p.817-829 (in Polish)
- [11] *Vankelecom I.F.K., Verduyze K.A.L., Neys P.E., Tas D.W.A., Janssen K.B.M., Knops-Gerrits P.P., Jacobs P.A.*; Novel catalytic membranes for selective reactions. Top. Catal., Vol.5, 1998; p.125-132

- [12] Peng M., Vane L.M., Liu S.X.; Recent advances in VOCs removal from water by pervaporation. *J. Hazard. Mater.*, Vol.B98, 2003; p.69-90
- [13] Panek D., Konieczny K.; Pervaporative separation of toluene from wastewaters by use of filled and unfilled poly(dimethylsiloxane) (PDMS) membranes. *Desalination*, Vol.241, 2009; p.197-200
- [14] Mohammadi T., Aroujalian A., Bakhshi A.; Pervaporation of dilute alcoholic mixtures using PDMS membrane. *Chem. Eng. Sci.*, Vol.60, 2005; p.1875-1880
- [15] Lee H.J., Cho E.J., Kim Y.G., Choi I.S., Bae H.J.; Pervaporative separation of bioethanol using a polydimethylsiloxane/polyetherimide composite hollow-fiber membrane. *Bioresour. Technol.*, Vol.109, 2012; p.110-115
- [16] W. Ji., Sikdar S.K.; Pervaporation Using Adsorbent-Filled Membranes. *Ind. Eng. Chem. Res.*, Vol.35, 1996; p.1124-1132
- [17] Kujawski W.; Application of Pervaporation and Vapor Permeation in Environmental Protection. *Polish Journal of Environmental Studies*, Vol.9, No.1, 2000; p.13-26
- [18] Kujawski W.; Pervaporation and Vapour Permeation – Separation through Nonporous Membranes. *Polish Journal of Chemical Technology*, Vol.5, No.(2), 2003; p.1-7
- [19] Chapman P.D., Oliveira T., Livingston A.G., Li K.; Membranes for the dehydration of solvents by pervaporation, *J. Membr. Sci.*, Vol.318, 2008; p.5-37
- [20] Wijmans J.G., Baker R.W.; The solution-diffusion model: a review, *J. Membr. Sci.*, Vol.107, 1995; p.1-21
- [21] Sae-Khow O., Mitra S.; Pervaporation in chemical analysis, *J. Chromatogr., A*, Vol.1217, 2010; p.2736-2746
- [22] Kwok D.Y., Neumann A.W.; Contact angle measurement and contact angle interpretation. *Adv. Colloid Interface Sci.*, Vol.81, 1999; p.167-249
- [23] Lee H.J., Cho E.J., Kim Y.G., Choi I.S., Bae H.J.; Pervaporative separation of bioethanol using a polydimethylsiloxane/polyetherimide composite hollow-fiber membrane. *Bioresour. Technol.*, Vol.109, 2012; p.110-115
- [24] Khorasani M.T., Mirzadeh H., Kermani Z.; Wettability of porous polydimethylsiloxane surface: morphology study. *Appl. Surf. Sci.*, Vol.242, 2005; p.339-345
- [25] Kujawski W., Poźniak G., Nguyen Q.T., Neel J.; Properties of Interpolymer PEES Ion-Exchange Membranes in Contact with Solvents of Different Polarity. *Sep. Sci. Technol.*, Vol.32, 1997; p.1657-1667
- [26] Sridhar S., Smitha B., Shaik A.; Pervaporation-Based Separation of Methanol/MTBE Mixtures – A Review in Separation and Purification Reviews, Vol.34, 2005; p.1-33
- [27] Shao P., Huang R.Y.M.; Polymeric membrane pervaporation. *J. Membr. Sci.*, Vol.287, 2007; p.162-179
- [28] Lipnizki F., Trägårdh G.; Modeling of Pervaporation: Models to Analyze and Predict the Mass Transport in Pervaporation. *Sep. Purif. Methods*, Vol.30, No.1, 2001; p.49-125
- [29] Hansen C.M.; Hansen Solubility Parameters: a user's handbook in CRC Press Taylor & Francis Group, Boca Raton, London, New York 2007; p.59
- [30] Alizadeh M., Abbasi F., Farahi M., Jalili K.; Silicone-Based Hydrogels Prepared by Interpenetrating Polymer Network Synthesis: Swelling Properties and Confinements Effects on the Formation Kinetics. *J. Appl. Polym. Sci.*, Vol.124, 2012; p.985-992