

Wetting and adsorption modification in the system “Highly permeable polymer film – aqueous solution of ethanol containing organic dyes”

¹Bogdanova Yu. G. *, ¹Dolzhiikova V. D.,
²Yushkin A. A.

¹Lomonosov Moscow State University,
Moscow, Russia

²Topchiev Institute of Petrochemical
Synthesis, RAS, Moscow, Russia

*E-mail: yulibogd@yandex.ru

Regularities of wetting and adsorption modification of surfaces of continual membranes made from highly permeable glassy polymers poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and poly(4-methyl-2-pentyn) (PMP) with aqueous ethanol solutions and alcohol solutions containing organic dyes (Solvent Blue 35 and Remazol Brilliant Blue) were investigated. Isotherms of stress wetting of polymer membrane surface by ethanol solutions were found out to have maximums in the range of concentrations corresponding to the beginning of liquid sorption into the membrane and polymer swelling. Thus, the principal possibility of optimization of nanofiltration experiments by liquid wetting angle measurements on continuous polymer membrane surfaces was shown. The presence of the dye was shown not to affect PMP wetting. But in the case of PTMSP, it leads to shear of the maximum of stress wetting isotherms to the range of higher concentrations. It was found out the effectiveness of the adsorption surface modification of continuous polymer membrane surfaces by ethanol solutions containing dyes does not depend on chemical nature of the dye. At the same time, there are different trends in the energy characteristics of the membrane surface.

Keywords: wetting; polymer membrane; dye; nanofiltration of organic solvents; PTMSP; PMP.

«Аса өткізгіш полимерлік қабыршық – органикалық бояғыштары бар этанолдың сулы ерітінділері» жүйесіндегі адсорбциялық модификациялау мен жұғу

¹Богданова Ю. Г. *, ¹Должикова В. Д.,
²Юшкин А. А.

¹М.В. Ломоносов атындағы Мәскеу мемлекеттік университеті,
Мәскеу қ., Ресей

²РФА А.В. Топчиеватындағы мұнайхимиялы қсинтезі институты, Мәскеу қ., Ресей
*E-mail: yulibogd@yandex.ru

Шынытәріздес поли[1-(триметилсилил)-1-пропин] – ПТМСП және поли(4-метил-2-пентин) – ПМП аса өткізгіш полимерлерінен алынған тұтас мембрананың бетін этанолдың сулы ерітінділерімен және құрамында органикалық бояғыштары (Solvent Blue 35 және Remazol Brilliant Blue) бар этанол ерітінділерімен модификациялау және жұғу заңдылықтары зерттелді.

Этанол ерітінділерінің полимерлік мембрана бетімен жұғу кернеу изотермасында мембранаға сұйықтың сорбциялануының басталуымен полимердің ісінуіне сәйкес концентрациясында максимумдар пайда болатыны анықталды. Сонымен, тұтас полимерлік мембрана бетінде сұйықтардың жұғу бұрышымен өлшеу арқылы нанопыльтрация бойынша эксперименттерді оңтайландырудың принципіалды мүмкіндігі көрсетілді. Бояғыштардың қатысы ПМП жұғуына әсеретпейтіні, бірақ ПТМСП жағдайында жұғу кернеуі изотермасындағы максимумдарды этанолдың жоғары концентрациялары жағына ығыстыратыны көрсетілді. Құрамында бояғыш бар этанолдың сулы ерітінділерімен зерттелген тұтас полимерлік мембрананың бетін адсорбциялық модификациялау тиімділігі бояғыштардың химиялық табиғатынан тәуелсіз екені анықталды. Және бұл кезде мембрананың бетінің энергетикалық сипаттамасының өзгеруінің әртүрлі тенденцияларыда байқалады.

Түйін сөздер: жұғу; полимерлік мембрана; органикалық бояғыштардың нанопыльтрациясы; ПТМСП; ПМП.

Смачивание и адсорбционное модифицирование в системе «Пленка высокопроницаемого полимера – водные растворы этанола, содержащие органические красители»

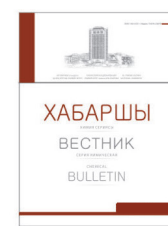
¹Богданова Ю. Г. *, ¹Должикова В. Д.,
²Юшкин А. А.

¹Московский государственный университет имени М.В. Ломоносова,
г. Москва, Россия

²Институт нефтехимического синтеза имени А.В. Топчиева Российской академии наук (ИНХС РАН), г. Москва, Россия
*E-mail: yulibogd@yandex.ru

Изучены закономерности смачивания и адсорбционного модифицирования поверхностей сплошных мембран из высокопроницаемых стеклообразных полимеров поли[1-(триметилсилил)-1-пропина] – ПТМСП и поли(4-метил-2-пентина) – ПМП водными растворами этанола и растворами этанола, содержащими органические красители (SolventBlue 35 и RemazolBrilliantBlue). Установлено, что изотермы напряжения смачивания поверхностей полимерных мембран растворами этанола имеют максимумы в области концентраций, соответствующих началу сорбции жидкости в мембрану и набуханию полимера. Таким образом, продемонстрирована принципиальная возможность оптимизации экспериментов по нанопыльтрации путем измерения краевых углов жидкостей на поверхности сплошных полимерных мембран. Показано, что присутствие красителя не влияет на смачивание ПМП, но в случае ПТМСП приводит к сдвигу максимума изотерм напряжения смачивания в сторону более высоких концентраций этанола. Обнаружено, что эффективность адсорбционного модифицирования поверхностей исследованных сплошных полимерных мембран водными растворами этанола, содержащими красители, не зависит от химической природы красителя. При этом наблюдаются различные тенденции в изменении энергетических характеристик поверхностей мембран.

Ключевые слова: смачивание; полимерная мембрана; краситель; нанопыльтрация органических растворителей; ПТМСП; ПМП.



Wetting and adsorption modification in the system “Highly permeable polymer film – aqueous solution of ethanol containing organic dyes”

¹Bogdanova Yu. G.*, ¹Dolzhihova V. D., ²Yushkin A.A.

¹Lomonosov Moscow State University, Moscow, Russia

²Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, Russia

*E-mail: yulibogd@yandex.ru

1. Introduction

Wetting is widely used in study of different processes at solid surfaces: adsorption, adhesion, chemical reaction proceeding [1]. Contact angle measurements of pure liquids at low-energy surfaces, which include most polymers, permit to determine its surface energy and “solid/liquid” interfacial energy [2], and to predict the optimal field of polymer application based on values obtained [3].

Wetting is very important in organic solvent nanofiltration (OSN), which is a pressure-driven method, permitting to separate substances with molecular weight $M = (200 - 1400)$ Da from organic liquids [4]. Due to promising applications in homogeneous catalysis, extraction processes in petrochemical, chemical, pharmaceutical, food, paint and textile industries, OSN has been intensively developed during last 15-20 years. New opportunities to achieve a high flux and appropriate separation efficiency appear due to application of glassy polymers with high fractional free volume (FFV) as membrane materials. The nanoporous structure of such polymer films is spontaneously formed during preparation of the film.

As a rule, when studying OSN, its main characteristics – flux of liquid through membrane and retention efficiency of substances dissolved in liquid – are determined. The flux is fixed using volumetric or gravimetric techniques. Different organic dyes can be used as solute for membrane testing in OSN because their concentrations in a solution can be simply determined [5]. A mass transfer of liquids and retention efficiency depend on the variety of different factors [6-8]. The aim of our study was to find parameters permitting to optimize the OSN experiments using experimental data about the wetting of continual polymer membranes with liquid systems.

Another goal was to watch whether the dye influences membrane wettability and surface tension of liquid systems, which undergo to the OSN.

2. Experimental

The objects of our study were continual membranes of highly permeable glassy polymers, synthesized in Topchiev Institute of Petrochemical Synthesis, RAS: poly[1-(trimethylsilyl)-1-propyne] (PTMSP) [9] and poly(4-methyl-2-pentyne) (PMP) [10] (Figure 1). These polymers are characterized by high FFV values: $FFV(\text{PTMSP}) = 0.33$ and $FFV(\text{PMP}) = 0.28$ and high glass transition temperature $T_g > 250^\circ\text{C}$ [11, 12].

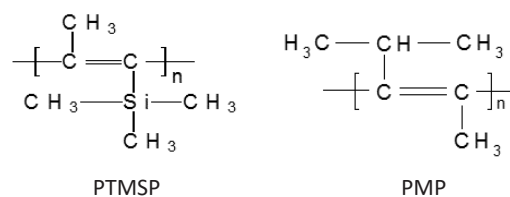


Figure 1– Structural formulae of PTMSP (left) and PMP (right) monomer chains

Dense membranes were casted from solution in chloroform with polymer concentrations of 0.5-1.0 wt.% onto a commercial cellophane. The cast film was then covered with a Petri dish and left for slow evaporation during several days, followed by drying until a constant sample weight was reached [4]. Membrane’s thickness was 20 μm . Aqueous solutions of

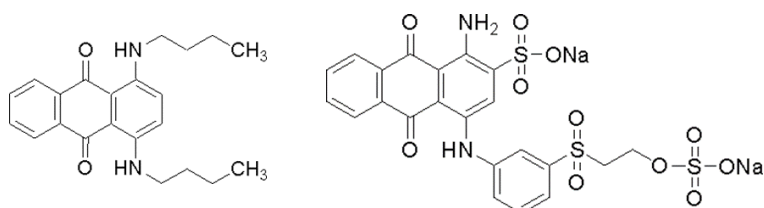


Figure 2 – Structural formulae of SB (left) and RBB (right) monomer links

ethanol were prepared by the subsequent dilution of ethanol (Extra, 96%) with distilled water. Wetting of PTMSP and PMP films with ethanol solutions and solutions containing organic dyes were investigated. Dyes (Sigma-Aldrich) were Solvent Blue 35 (SB) and Remazol Brilliant Blue (RBB) (Figure 2). Dyes concentration (C_d) in ethanol solutions was constant: $C_d(\text{SB}) = 1.0 \cdot 10^{-6}$ M and $C_d(\text{RBB}) = 4.6 \cdot 10^{-7}$ M, but ethanol concentration (C) was changed.

These dyes were selected using results of previous studies of OSN [6, 7, 13]. In the result of OSN of ethanol aqueous solutions containing dyes through PTMSP and PMP membranes, SB penetrates through membrane the most easily whereas the RBB is held almost completely. So, the bright difference in wetting behavior of solutions containing SB and RBB with respect to polymer films should be expected.

Advancing (ϑ_a) and receding (ϑ_r) contact angles of ethanol aqueous solutions, including solutions containing dyes, at the surfaces of PTMSP and PMP films were measured by sessile drop technique with an accuracy of 1 degree. Contact angles were measured at the surface of film contacting with air during its preparation. In some cases, deformation of film after deposition of the drop was observed. For this reason, reliable contact angle values were obtained not for all concentrations of ethanol solutions in the studied range (0–96%). Surface tension of ethanol solutions was determined using maximal bubble pressure method.

Due to the oil and water sensitive structure of ethanol and dyes molecules, one's adsorption at not only at the solution/air, but also at the solution/polymer interface must be taken into account when the results of wetting are analyzed. So, the alteration of PTMSP and PMP surface energy (γ_{sv}) in result of adsorption of components of solutions investigated was studied. Polymer films were placed into the studied solution for 30 min, and then they were dried during 2 h. Advancing contact angles of probe liquids – distilled

water and ethylene glycol (EG) (Aldrich, chemically purified) – were measured. The dispersive (γ_{sv}^d) and polar components (γ_{sv}^p) of polymer surface energy were calculated using Owens-Wendt-Kaelble approach [2, 14]. The accuracy of determination of γ_{sv} and its components was $1 \text{ mJ} \cdot \text{m}^{-2}$.

All measurements were performed at 20°C .

3. Results and Discussion

Ethanol possesses the surface activity at the water-air interface (Figure 3). Surface tension of dyes aqueous solutions $\gamma_{LV}(\text{RBB}) = 63.5 \text{ mJ} \cdot \text{m}^{-2}$ and $\gamma_{LV}(\text{SB}) = 59.3 \text{ mJ} \cdot \text{m}^{-2}$. In spite of surface active properties of dyes at the water-air interface, their presence in ethanol solutions did not change surface tension independently from the chemical nature of dye.

PTMSP and PMP surfaces are poorly wetted with water (Table 1). A small value of contact angle hysteresis $\Delta\vartheta = (\vartheta_a - \vartheta_r)$ at the initial polymer surfaces was observed.

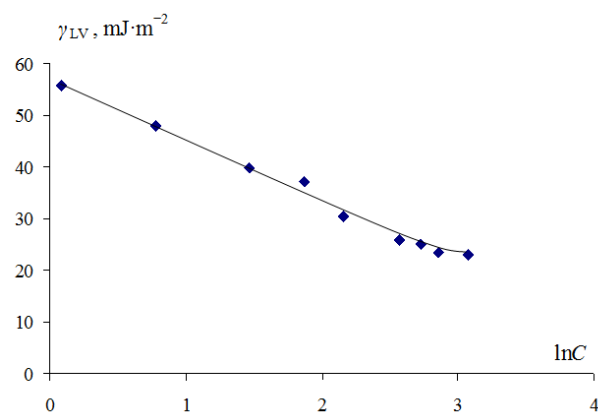


Figure 3 – The dependence of surface tension of aqueous ethanol solutions on ethanol concentration

Table 1 – Contact angles of probe liquids at the polymer surface (θ , degree), surface energy modes and surface energy (γ , $\text{mJ} \cdot \text{m}^{-2}$) of PTMSP and PMP films

Polymer	H_2O		θ_a (EG)	γ_{sv}^d	γ_{sv}^p	γ_{sv}
	θ_a	θ_r				
PTMSP	85	83	74	7	15	22
PMP	77	74	62	11	17	28

It must be expected that a wettability of PTMSP and PMP surfaces with ethanol aqueous solutions (including dyes) will be one of decisive factors which provide the mass transfer through its continual membranes. The surface energy values of initial PTMSP and PMP films correspond to those obtained earlier [15]. This is a good result because these amorphous glassy high permeable polymers are characterized by high extent of non-equilibrium state.

The ethanol concentration increase resulted in the decrease of ϑ_a and ϑ_r . The $\vartheta_a = f(C)$ dependences for both polymers are presented at Figure 4 as example; $\vartheta_r = 0$ at ethanol $C > 40\%$ in case PTMSP and at $C = 50\%$ in case of PMP.

The high contact angle hysteresis depending on ethanol concentration was observed for all systems investigated (Figure 5). It should be noted, that maximums at some of $\Delta\vartheta = f(C)$ dependences are related to sharp decrease of $\vartheta_r = f(C)$ in comparison to $\vartheta_a = f(C)$ in corresponding concentration ranges. The $\Delta\vartheta$ increase points were observed out on the increase of energetic heterogeneity of polymer surfaces [1, 16], which may be caused by the adsorption of solution components at the polymer/liquid interface. Another factor which may lead to the increase of $\Delta\vartheta$, may be changing of roughness of polymer surface due to a swelling of the polymer film contacting with a solution. The dye presence leads to the alteration of $\Delta\vartheta = f(C)$

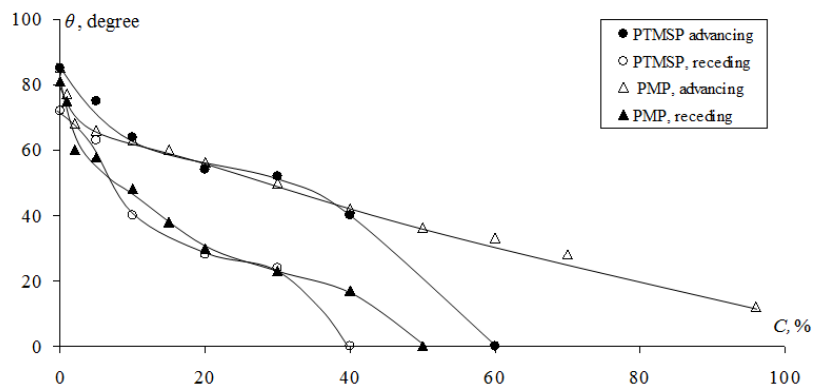


Figure 4 – Advancing (ϑ_a) and receding (ϑ_r) contact angles of ethanol aqueous solutions of different concentrations (C) at PTMSP and PMP surfaces

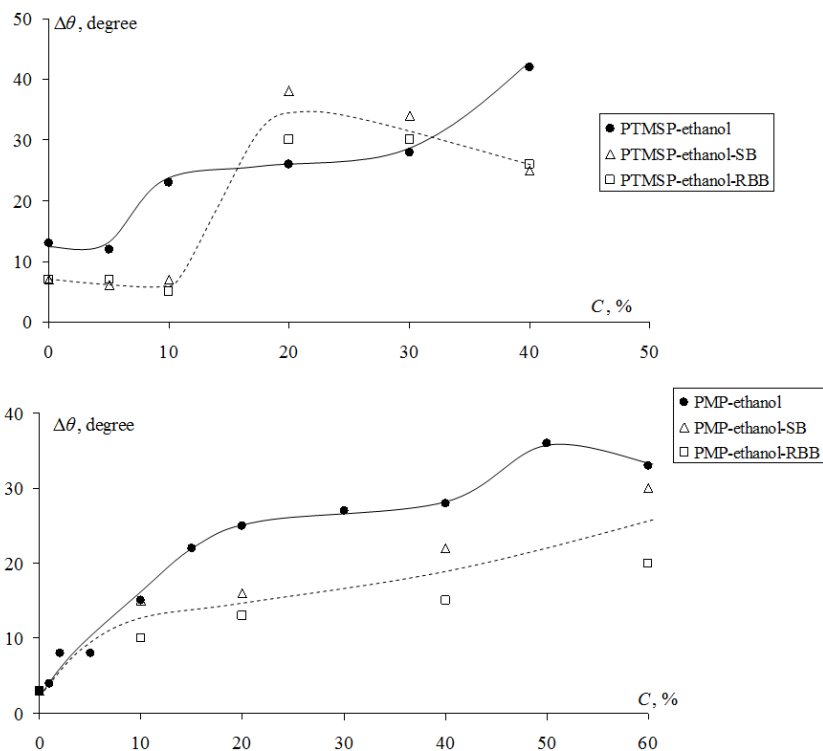


Figure 5 – Plot contact angle hysteresis at the wetting of polymer surfaces with ethanol solutions and dyes solutions in ethanol/water mixtures versus ethanol concentration

curves trends, but the dye's nature does not influence hysteresis dependences on ethanol concentration.

It is known that the permeability of water/alcohol mixtures through PTMSP and PMP continual membranes has a threshold, i.e. the liquid flux through membrane takes place at concentrations higher than the threshold concentration, which is individual for every system [4]. Threshold concentrations of ethanol are $C_t = 50\%$ for PTMSP and $C_t = 30\%$ for PMP (at pressure 30 atm) [4]. In spite of the impossibility to relate definitely ethanol threshold concentrations with $\Delta\vartheta = f(C)$ dependencies, Figure 5 illustrates high $\Delta\vartheta$ values at $C > C_t$ for both polymers.

Equilibrium contact angle value of a liquid drop at the ideal solid surface was determined by the Young equation: $\gamma_{LV} \cdot \cos\vartheta = (\gamma_{SV} - \gamma_{SL})$, where γ_{SL} is interfacial polymer/liquid energy [1]. The adsorption (Γ) of surfactants at the interfaces obeys the Gibbs equation: $\Gamma = -(C/RT) \cdot (d\gamma/dC)$, where γ – interfacial energy, C – surfactant concentration, R – universal

gas constant, T – temperature [1]. In accordance to Young equation and Gibbs adsorption equation, assuming $\gamma_{SV} = \text{const}$ [2, 14], at the high ethanol concentrations, corresponding to the formation of saturated adsorption layers at the liquid/gas and polymer/liquid interfaces (γ_{LV} and γ_{SL} are constant), $\gamma_{LV} \cdot \cos\vartheta = f(C)$ dependences must be represent rising curves with saturation. Moreover, it is known, that usually saturated adsorption layer at the solid/liquid interface is formed at lower surfactant concentration in comparison to liquid/gas interface. But the wetting strain isotherms $\gamma_{LV} \cdot \cos\vartheta = f(\ln C)$ and $\gamma_{LV} \cdot \cos\vartheta = f(\ln C)$ for polymer/ethanol solution and polymer/dye solution in ethanol-water mixtures have a not typical view with maximums; the concentration areas corresponding to maximums for ethanol solutions are $C_{\text{max}} \in (10; 20)\%$ for PTMSP and $C_{\text{max}} \in (15; 30)\%$ (Figure 6). Here we illustrate the $\gamma_{LV} \cdot \cos\vartheta = f(\ln C)$ as example due to the better simulation of nanofiltration with wetting in residing conditions.

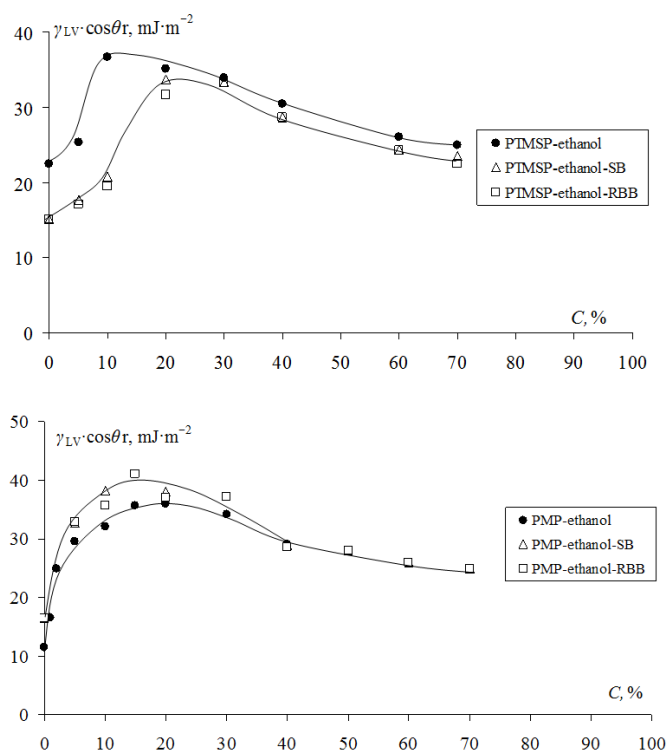


Figure 6 – Wetting strain isotherms (receding conditions) at wetting of polymers with aqueous ethanol solutions and dyes solutions in ethanol/water mixtures

Table 2 – The alteration of dispersive (γ_{SV}^d , $\text{mJ}\cdot\text{m}^{-2}$) and polar (γ_{SV}^p , $\text{mJ}\cdot\text{m}^{-2}$) modes of polymer surface energy in result of adsorption modifying

	Water		SB in water, $C = 1.0 \cdot 10^{-6} \text{M}$		RBB in water, $C = 4.6 \cdot 10^{-7} \text{M}$	
	γ_{SV}^d	γ_{SV}^p	γ_{SV}^d	γ_{SV}^p	γ_{SV}^d	γ_{SV}^p
PTMSP	6	36	12	33	5	48
PMP	6	54	24	4	18	10

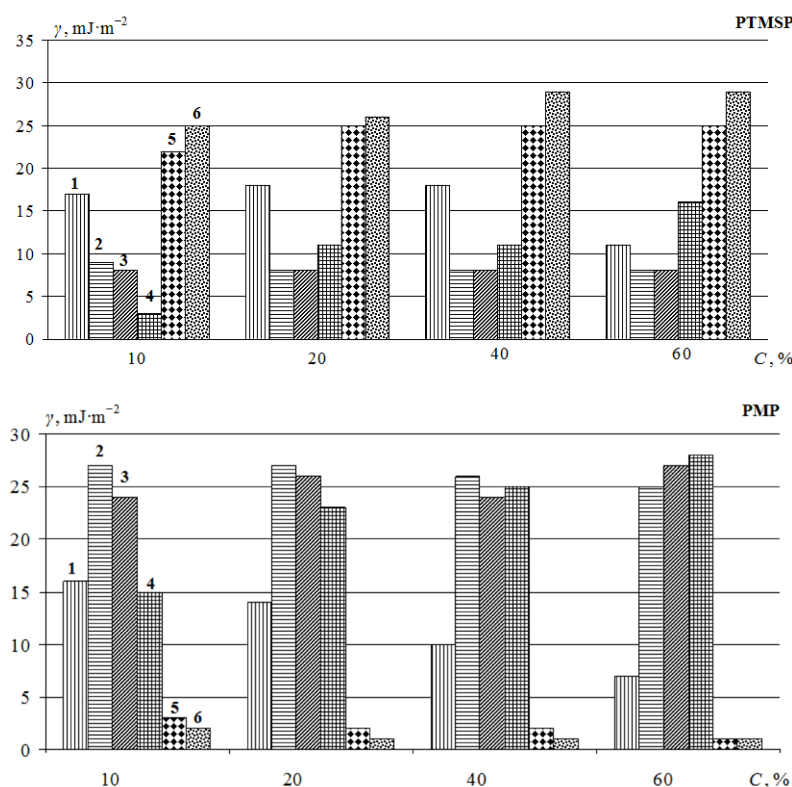


Figure 7 – The dependence of surface energy dispersive (1, 2, 3) and polar (4, 5, 6) components of PMP (top) and PTMSP (bottom), modified with ethanol solutions (1, 4) and solutions SB (2, 5) and RBB (3, 6) in ethanol-water mixtures

Analysis of changes in polymer/liquid interfacial energy $\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cdot \cos\theta_r$ showed that it is necessary to take into account changes in the surface energy of PTMSP and PMP after contact with liquid phase. Otherwise, the calculation leads to negative values of γ_{SL} that has no physical meaning. Actually, increase of the polar component of the surface energy PTMSP and PMP after contact with water (Table 2) suggests that water penetrates into the surface layer of the polymer. Thus, the not typical view of wetting strain isotherms for polymer/aqueous ethanol solution may be related to local depletion of solution with ethanol due to its sorption in membrane. The overlap of concentration ranges corresponding to maximums of wetting strain isotherms, beginning of sorption of liquid in membrane and extent of swelling increase should be mentioned (Figure 6) [4].

It was found earlier, that the interrelation between the dispersive component of polymer surface energy, its fractional free volume and gas permeability of polymer membranes exists [15]. Obtained results demonstrate the interrelation between γ_{SV}^d in Table 1 and Fig. 6, *FFV* and ethanol concentration ranges corresponding to polymer swelling and beginning of sorption in membrane of solution components obtained in [4]. The higher *FFV* is, the lower are ethanol concentrations are, which promote swelling and sorption. Of course, to maintain which component (water or ethanol) is sorbed more intensively by a membrane, the further studies must

be performed. But the obtained results are perspective for optimizing of experimental conditions (selection of polymer and alcohol concentration range) for OSN experiments.

The dye does not strongly influence the wetting strain isotherms in case of PMP, whereas in case of PTMSP dye inhibits sorption of liquid by membrane and shift of maximums of $\gamma_{LV} \cdot \cos\theta_r = f(\ln C)$ dependences in area of higher ethanol concentrations is observed (Figure 6). Obtained results show that the chemical structure of the dye does not appear at the wetting of PTMSP and PMP surfaces with aqueous ethanol solutions. Because dye presence does not influence the surface tension of alcohol solutions, its nature should not be affect an adsorption of dye at the polymer/liquid interface.

This assumption is confirmed experimentally by the determination of polymer's surface energy in result of aging of polymer films in studied solutions. The chemical structure of dye does not strongly affect γ_{LV}^d and γ_{LV}^p modes of polymer surface energy (Figure 7). This experimental fact permits to possess that during the OSN process, the dye nature appears more at the bulk of polymer film, but not at the surface level. Nevertheless, the regularities of adsorption modification of polymer surfaces with aqueous ethanol solutions containing dyes are different for PTMSP and PMP.

The modification of polymer surfaces with ethanol solutions results in the increase of the dispersive component of PTMSP surface energy (Table 2, Figure 7, column 1), but

γ_{pLV} values are lower than after aging of PTMSP film in water (Table 2, Figure 7, column 4). At ethanol concentrations $C > 40\%$ corresponding to threshold of flux of liquid through membrane, the ratio between γ_{dLV} and γ_{pLV} modes of modified PTMSP changes. In the case of PMP $\gamma_{pLV} > \gamma_{dLV}$ in range of $C \geq 20\%$ (Figure 7, columns 1, 4) and γ_{pLV} less in comparison to γ_{pLV} of PMP aged in water as well as in case of PTMSP. The dye presence in the modifying solution leads to the increase of a polar mode of surface energy of PTMSP and constant γ_{dLV} value with ethanol concentration increase (Figure 7, columns 2, 3, 5, 6). In the case of PMP, the opposite tendency in alteration of surface energy modes was observed: γ_{pLV} values of modified surface are low (Figure 7, columns 5, 6) and $\gamma_{dLV} = \text{const}$ at ethanol concentration range $C \in (10; 60)\%$, but its value is higher in comparison to the corresponding ethanol solution (Figure 7, columns 1, 2, 3).

No effect of a dye nature on these modifications with respect to polymer surfaces may be explained by a planar orientation of dyes molecules at the surface of polymer films.

4. Conclusion

Thus, correlation of wetting strain isotherms with the concentration of alcohol corresponding to the beginning of sorption of liquid in membrane and swelling of polymer was observed. Dye presence in ethanol/water mixtures does not significantly affect wetting of membranes surfaces. The dye nature does not strongly influence wetting and adsorptive modification of PMP and PTMSP surface, despite the different regularities of adsorptive modification of PMP and PTMSP surfaces were observed. Thus, the obtained results demonstrate a principal possibility of optimizing OSN experiments using more express measurements of contact angles of liquid systems at the surfaces of continual polymer membranes.

Acknowledgments

Authors acknowledge the financial support of Russian Foundation for Basic Research (Grant# 14-08-00893).

References

- 1 Adamson A.W. Physical Chemistry of Surfaces, 6th edition. – Hoboken: John Wiley and Sons, 1997.
- 2 Kloubek J. Development of methods for surface free energy determination using contact angles of liquids on solids // *Advances in Colloid and Interface Science*. – 1992. – Vol.38 – P.99-142.
- 3 Bogdanova Y.G., Dolzhikova V.D., Alentiev A.Yu., Karzov I.M. Contact angle measurements in study of polymers for creation of materials // *Journal of International Scientific Publications, Materials, Methods and Technologies*. – 2012. – Vol.6. – P.272-285.
- 4 Yushkin A., Grekhov A., Matson S., Bermeshev M., Khotimsky V., Finkelshtein E., Budd P.M., Volkov V., Vlugt T.J.H., Volkov A. Study of glassy polymers fractional accessible volume (FAV) by extended method of hydrostatic weighing: Effect of porous structure on liquid transport // *Reactive and Functional Polymers*. – 2015. – Vol.86. – P.269-281.
- 5 See Toh Y.H., Loh X., Li K., Bismarck A., Livingston A.G. In search of a standard method for the characterisation of organic solvent nanofiltration membranes // *Journal of Membrane Science*. – 2007. – Vol.291. – P.120-125.
- 6 Tsar'kov S.E., Malakhov A.O., Litvinova E.G., Volkov A.V. Nanofiltration of dye solutions through membranes based on poly(trimethylsilylpropyne) // *Petroleum Chemistry*. – 2013. – Vol.53. – P.537-545.
- 7 Tsarkov S., Khotimsky V., Budd P.M., Volkov V., Kukushkina J., Volkov A. Solvent nanofiltration through high permeability glassy polymers: Effect of polymer and solute nature // *Journal of Membrane Science*. – 2012. – Vol.423. – P.65-72.
- 8 Postel S., Spalding G., Chirnside M., Wessling M. On negative retentions in organic solvent nanofiltration // *Journal of Membrane Science*. – 2013. – Vol.447. – P.57-65.
- 9 Khotimsky V.S., Tchirkova M.V., Litvinova E.G., Rebrov A.I., Bondarenko G.N. Poly[1-(trimethylgermyl)-1-propyne] and poly[1-(trimethylsilyl)-1-propyne] with various geometries: Their synthesis and properties // *Journal of Polymer Science Part A: Polymer Chemistry*. – 2003. – Vol.41. – P.2133-2155.
- 10 Khotimsky V.S., Matson S.M., Litvinova E.G., Bondarenko G.N., Rebrov A.I. Synthesis of poly(4-methyl-2-pentyne) with various configurations of macromolecular chains // *Polymer Science*. – 2003. – Vol.45. – P. 740-746.
- 11 Hofmann D., Heuchel M., Yampolskii Yu., Khotimskii V., Shantarovich V. Free volume distributions in ultrahigh and lower free volume polymers: Comparison between molecular modeling and positron lifetime studies // *Macromolecules*. – 2012. – Vol.35. – P.2129-2140.
- 12 Morisato A., Pinnau I. Synthesis and gas permeation properties of poly(4-methyl-2-pentyne) // *Journal of Membrane Science*. – 1996. – Vol.121. – P.243-250.
- 13 Volkov A., Yushkin A., Kachula Yu., Khotimsky V., Volkov V. Application of negative retention in organic solvent nanofiltration for solutes fractionation // *Separation and Purification Technology*. – 2014. – Vol.124. – P.43-48.
- 14 Vojtechovska J., Kvitek L. Surface energy – effects of physical and chemical surface properties // *Acta Universitatis Palackianae Olomouensis Facultas Rerum Naturalium Chemica*. – 2005. – Vol.44. – P.25-48.
- 15 Bogdanova Y.G., Dolzhikova V., Filippov A. Contact angles as indicators of macromolecule packing density at polymer surface // *Proceedings of European Polymer Congress*. – Pisa, Italy, 2013. – P.3-17.
- 16 De Gen P.G. Wetting: statics and dynamics // *Advances in Physical Sciences*. – 1987. – Vol.151. – P.619-681.

References

- 1 Adamson AW (1997) *Physical Chemistry of Surfaces*, six edition. John Wiley and Sons, USA. ISBN 0-471-14873-3
- 2 Kloubek J (1992) *Adv Colloid Interfac* 38:99-142. [http://dx.doi.org/10.1016/0001-8686\(92\)80044-X](http://dx.doi.org/10.1016/0001-8686(92)80044-X)
- 3 Bogdanova YG, Dolzhikova VD, Alentiev AYu, Karzov IM (2012) *Journal of International Scientific Publications, Materials, Methods and Technologies* 6:272-285.
- 4 Yushkin A, Grekhov A, Matson S, Bermeshev M, Khotimsky V, Finkelshtein E, Budd PM, Volkov V, Vlugt TJH, Volkov A (2015) *React & Funct Polym* 86:269-281. <http://dx.doi.org/10.1016/j.reactfunctpolym.2014.06.010>
- 5 See Toh YH, Loh X., Li K, Bismarck A, Livingston AG (2007) *J Membrane Sci* 291:120-125. <http://dx.doi.org/10.1016/j.memsci.2006.12.053>
- 6 Tsar'kov SE, Malakhov AO, Litvinova EG, Volkov AV (2013) *Petrol Chem* 53:537-545. <http://dx.doi.org/10.1134/S0965544113070189>
- 7 Tsarkov S, Khotimsky V, Budd PM, Volkov V, Kukushkina J, Volkov A. (2012) *J Membrane Sci* 423-424:65-72. <http://dx.doi.org/10.1016/j.memsci.2012.07.026>
- 8 Postel S, Spalding G, Chirnside M, Wessling M (2013) *J Membrane Sci* 447:57-65. <http://dx.doi.org/10.1016/j.memsci.2013.06.009>
- 9 Khotimsky VS, Tchirkova MV, Litvinova EG, Rebrov AI, Bondarenko GN (2003) *J Polym Sci, Part A* 41:2133-2155. <http://dx.doi.org/10.1002/pola.10757>
- 10 Khotimsky VS, Matson SM, Litvinova EG, Bondarenko GN, Rebrov AI (2003) *Polym Sci Ser A+* 45:740-746.
- 11 Hofmann D, Heuchel M, Yampolskii Yu, Khotimskii V, Shantarovich V (2002) *Macromolecules* 35:2129-2140. <http://dx.doi.org/10.1021/ma011360p>
- 12 Morisato A, Pinnau I (1996) *J Membrane Sci* 121:243-250. [http://dx.doi.org/10.1016/S0376-7388\(96\)00183-4](http://dx.doi.org/10.1016/S0376-7388(96)00183-4)
- 13 Volkov A, Yushkin A, Kachula Yu, Khotimsky V, Volkov V (2014) *Sep Purif Technol* 124:43-48. <http://dx.doi.org/10.1016/j.seppur.2013.12.044>
- 14 Vojtechovska J, Kvitek L (2005) *Acta Universitatis Palackianae Olomouensis Facultas Rerum Naturalium Chemica* 44:25-48.
- 15 Bogdanova YG, Dolzhikova V, Filippov A. (2013) Contact angles as indicators of macromolecule packing density at polymer surface. *Proceedings of European Polymer Congress, Pisa, Italy*. P.3-17.
- 16 De Gen PG (1987) *Advances in Physical Sciences [Uspekhi fizicheskikh nauk]* 151:619-681. (In Russian)