Russian Journal of Applied Chemistry, Vol. 77, No. 11, 2004, pp. 1877–1882. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 11, 2004, pp. 1895–1900.
Original Russian Text Copyright © 2004 by Yu. Kuznetsov, Khripunov, Kruchinina, V. Kuznetsov, Turkova, Pen'kova.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Transport Properties of Cellulose Ester Membranes for Separating Gas and Liquid Mixtures

Yu. P. Kuznetsov, A. K. Khripunov, E. V. Kruchinina, V. M. Kuznetsov,
L. D. Turkova, and A. V. Pen'kova

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia
St. Petersburg State University, St. Petersburg, Russia

Received April 29, 2004

Abstract—Mass-exchange characteristics of cellulose myristate or acetomyristate membranes in separating aqueous-organic, organic, or gas mixtures, particularly, in recovering aromatic hydrocarbons from binary mixtures with aliphatic alcohols, and also ethyl acetate from a mixture of esterification products, are studied.

There is a steady scientific and practical interest in cellulose-based membranes in recent six decades, which is caused by easy availability of cellulose raw material, and also by the possibility of directed synthesis of homologous series of various cellulose derivatives with desired physicochemical characteristics. Therefore, cellulose-based membranes with desired transport properties can be prepared as well. Microporous (diffusion) membranes are mostly formed on the basis of cellulose esters or mixed esters (diacetates, triacetates, acetobutyrates), regenerated cellulose, and chitosan [1–6]. Previously we demonstrated the possibility of using cellulose acetomyristate diffusion membranes for separating aromatic and aliphatic hydrocarbons using the pervaporation technique [7]. In this work we studied the transport properties of cellulose myristate (CM) and acetomyristate (CAM) membranes of different composition in separating gas, aqueous-organic, and organic mixtures.

EXPERIMENTAL

Cellulose myristate and acetomyristates were prepared according to the standard procedure [8]. Membranes as nonporous films of a fixed thickness were formed from chloroform solutions of the polymers on a cellophane support. The pervaporation experiments were carried out using a laboratory cell of the autonomous type (effective area of the membrane 12 cm^2) with stirring the mixtures over the membrane at a residual pressure under the membrane of 0.2 mbar. The permeate vapor (flow passed across the membrane) was condensed in a receiving vessel at the liquid nitrogen temperature and weighed, and the total flow Π (kg m^{-2} h^{-1}) was estimated. In the experiments we used binary mixtures ethanol–water, toluene–methanol, and benzene–ethanol of various compositions, and also a mixture of ethyl acetate, acetic acid, ethanol, and water. The compositions of permeates were analyzed on a refractometer or chromatographically using Porapak-Q or Reoplex columns. The partition factor α was estimated as

$$\alpha_{A/B} = (X_A/X_B)/(Y_A/Y_B),$$

where Y_A and Y_B are the concentrations of A and B in the initial binary mixture (wt %), and X_A and X_B, in the permeate (wt %).

The gas-permeability coefficient P and selectivity factor $\alpha_{A/B}$ of vapors were determined chromatographically using a column filled with 5A molecular sieve as a stationary phase at an excess pressure over the membrane of 10 mbar. The compositions of liquid permeates and gas-permeability coefficients were determined to within 5 and 10%, respectively.

To study the selectivity of CM membranes, we prepared a 1 m long chromatographic column with the CM stationary phase supported on Celite 22. The evolution of the chemical structure of cellulose esters on passing from cellulose diacetate to CM is accompanied by decreasing packing density of the polymer chains and increasing fraction of the free volume in the polymer matrix. This is caused by weakening of the network of the hydrogen bonds and disordering of the supramolecular structure, being reflected in a regular increase in the gas permeability with parallel decrease in the selectivity. These trends are illustrated

Table 1. Gas-selective characteristics of homogeneous cellulose acetomyristate membranes at 20°C

Parameter	CAM composition (acetate/myristate)		
	290/10	150/150	10/290
Permeability coefficient, barrer:*			
N_2	0.3	7.95	15.7
O_2	1.6	25.2	40.2
He	14.5	30.8	41.2
CO_2	17.5	139.3	193.5
Selectivity coefficient:			
O_2/N_2	5.3	3.2	2.55
He/N_2	42	3.9	2.6
CO_2/O_2	10.7	5.5	4.8

* 1 barrer = 1×10^{-10} cm^3 cm cm^{-2} s^{-1} cm^{-1} Hg.

Table 2. Separation of water–ethanol mixtures on cellulose acetomyristate membranes at 50°C

Parameter	CAM composition (acetate/myristate)		
	290/10	150/150	10/290
90 wt % EtOH			
Flow,* kg m^{-2} h^{-1}	5.6	1.4	1.1
H_2O in permeate, wt %	53	20	14
α_{H_2O}	10.2	2.3	1.5
50 wt % EtOH			
Flow,* kg m^{-2} h^{-1}	2.4	1.5	0.78
EtOH in permeate, wt %	20	80	85
α_{EtOH}	0.25	4.0	5.7
10 wt % EtOH			
Flow,* kg m^{-2} h^{-1}	2.8	0.48	0.36
EtOH in permeate, wt %	6	50	55
α_{EtOH}	0.6	9.1	11.1

* The flow is normalized to the membrane thickness of 10 μm.

in Table 1 with an example of CAM membranes of various compositions. The results demonstrate the opposite tendencies in the behavior of the gas-permeability coefficients *P* of the individual gases and of the selectivity factor α for various pairs of gases with increasing myristate content in the CAM membranes.

The maximal *P* values and the corresponding minimal α values were obtained for the 10/290 CAM membrane. In this case, the transport parameters approach those of the membranes based on polymers with low glass transition temperature, for example, polydimethylsiloxane [9] or cellulose diacetate plasticized with polyethylene glycol oligomers [6].

It is known that, in pervaporation separation of aqueous-organic mixtures, the direction of selective mass transfer is controlled not only by the kinetic diameter of molecules diffusing across the membrane, but also by the difference in the affinity of the components of the mixture with respect to the film-forming polymer. One of the parameters characterizing such an affinity can be the equilibrium swellability of the membrane in individual components of the mixture to be separated. This parameter with respect to water and ethanol is considerably different for cellulose diacetate and CM (6.5 and 0.3 wt %, and 10.7 and 3.7 wt %, respectively). Therefore, it was interesting to study the transport properties of CAM membranes with various acetate to myristate group ratios.

Table 2 shows the results of pervaporation separation of aqueous-ethanol solutions of various compositions. In separating the concentrated solution of ethanol, all the CAM membranes studied demonstrate dehydrating properties, even though the maximal α_{H_2O} = 10.2 is considerably lower than that of the known highly selective membranes used for dehydration [10, 11]. The tendency of α_{H_2O} to decrease in this series from 10.2 to 1.5 correlates with the increase in the hydrophobicity of the corresponding CAM membranes. At the same time, in separating more dilute solutions of ethanol with 150/150 and 10/290 CAM membranes, the direction of selective mass transfer changes for the opposite, demonstrating the tendency to increase in α_{EtOH} from 4.0 to 11.1, depending on the composition of the initial mixture and content of the myristate component in the membrane. The maximal α_{EtOH} = 11.1, obtained for 10/290 CAM membrane in separating 10 wt % EtOH–H_2O mixture, is well comparable with that of the membrane based on hydrophobic polymethylsiloxane [12]. Therefore, even higher selectivity could be expected for the CM membrane. However, its permeability with respect to both ethanol and water appeared to be very low, which is consistent with data on the equilibrium swellability of CM in these solvents, suggesting no practical interest.

The results obtained evidence the necessity in optimization of the hydrophilic–hydrophobic balance for membranes of this purpose, to attain a reasonable relation between their permeability and selectivity. Therefore, 150/150 and 10/290 CAM membranes are more suitable to concentrate ethanol from dilute aqueous solutions. It should be pointed out that, with an example of CAM membranes having a unitypical chemical structure regardless of the composition, we have demonstrated the possibility of changing the direction of selective mass transfer in separating water–ethanol mixtures.

Furthermore, it was interesting to compare the known methods for separating aqueous-organic and organic mixtures, such as rectification and distillation, with the pervaporation technique. Like distillation, in pervaporation the permeate is removed as a vapor, allowing comparative evaluation of the expediency of using this technique. In this case, we can compare the pervaporation diagrams characterizing the dependence of the permeate composition on the composition of the feed mixture with the liquid–vapor diagram of the same system.

Such a comparative analysis of the diagrams appeared to be most indicative for azeotropic systems. High efficiency of pervaporation separation in such systems was repeatedly indicated in the literature. Furthermore, there are numerous examples of industrial applications of membrane separation of azeotropic mixtures [13]. As an illustration, Fig. 1 gives the comparison of the liquid–vapor diagram [14] and the experimental data obtained for CAM membranes of various compositions in separating ethanol–water mixtures. For the CAM membranes demonstrating dehydrating and organophilic properties, the dependences of the permeate composition on the composition of the initial mixture are arranged below (Fig. 1, curve *2*) and above (curves *3* and *4*) the liquid–vapor equilibrium curve (curve *1*).

Comparative analysis of data presented in Fig. 1 shows some advantage of the 150/150 and 10/290 organophilic CAM membranes in the selectivity of separation of more dilute solutions of ethanol (Fig. 1, curves *3* and *4*) over equilibrium open evaporation. It is known from the literature [12, 15] that close arrangement of the pervaporation curves with respect to the liquid–vapor equilibrium curve is typical of a series of ethanol-selective membranes. In Fig. 1 (curve *5*) this is illustrated by an example of the membrane fabricated from Silar block copolymer, which was previously studied in separating ethanol–water mixtures over a wide composition range [16]. Our results (Fig. 1, curve *2*) also demonstrate relatively small advantage of the dehydrating 290/10 CAM membrane in the selectivity as compared to open evaporation.

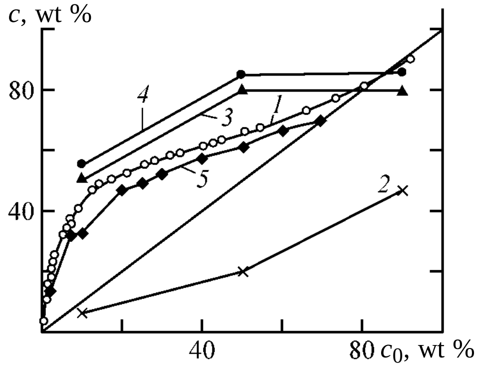

Fig. 1. Ethanol concentration *c* (*1*) in the vapor (liquid–vapor equilibrium in open evaporation) and in the permeate for membranes (*2*) 290/10 CAM, (*3*) 150/150 CAM, (*4*) 10/290 CAM, and (*5*) Silar as a function of the initial ethanol concentration c_0 in ethanol–water mixtures at 20°C.

At the same time, the advantage of pervaporation could be more pronounced just in dehydration of water–ethanol mixtures. In this case, particularly in separating ethanol-rich mixtures close in their composition to the azeotropic mixture, the selectivity of membrane separation could be higher by 2–3 orders of magnitude than that in open evaporation. This is favored by the effect of diffusion mass transfer, i.e., by smaller kinetic diameter of the water molecules. From the practical standpoint, there is a wide spectrum of polymers and membranes on their basis [11, 17, 18] demonstrating strongly different affinity for water and ethanol, with the difference being considerably larger compared to dehydrating 290/10 CAM membrane (Table 2) and also to cellulose diacetate membrane [19].

Selection of binary systems showing more promise for pervaporation separation with the CM membrane was made using inverse gas chromatography (IGC). Roberts *et al.* [20] employed this technique using chromatographic columns with different polymeric stationary phases to predict the direction of selective mass transfer across the membranes fabricated from the same polymers in separating binary liquid mixtures. As a criterion they used the retention time (retention time of a component of the mixture on the column is in inverse proportion to its flow rate across the membrane). Therefore, we determined the retention times of a series of organic solvents on the CM column. The retention time increased in the order methanol < ethanol < benzene < toluene < ethyl acetate, being 105, 116, 126, 135, and 148 s, respectively. Knowing this parameter allowed prediction of the possibility of membrane separation of mixtures of toluene (or benzene) with methanol (or ethanol) with selective mass transfer directed in favor of the aromatic component, which was confirmed in the pervapora-

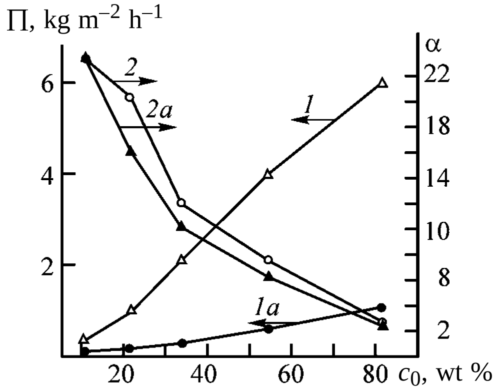

Fig. 2. (*1*, *1a*) Total flow Π and (*2*, *2a*) partition factor α in separating toluene–methanol mixture on the CM membrane as functions of the initial toluene concentration c_0 at 20°C. (*a*) For comments, see text.

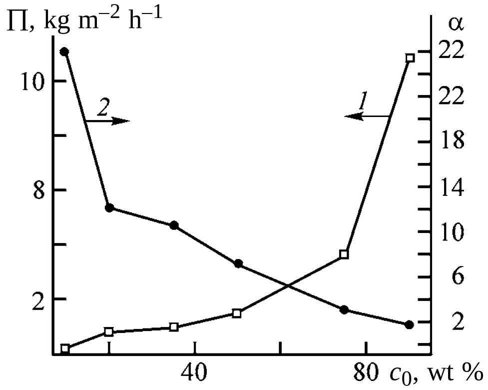

Fig. 3. (*1*) Total flow Π and (*2*) partition factor α in separating benzene–ethanol mixture on the CM membrane as functions of the initial benzene concentration c_0 at 20°C.

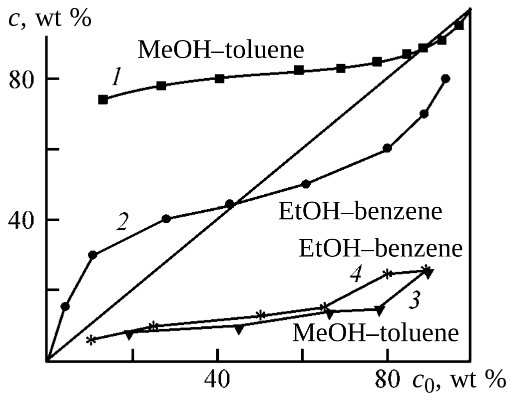

Fig. 4. (*1*, *3*) Methanol and (*2*, *4*) ethanol contents c in (*3*, *4*) permeate (CM membrane) and (*1*, *2*) vapor (liquid–vapor equilibrium in open evaporation) as functions of the initial methanol (or ethanol) concentration c_0 in mixtures with toluene and benzene, respectively, at 20°C.

tion experiments. Separation of such mixtures is of considerable scientific and practical interest, since these compounds form azeotropic systems and have similar boiling points (e.g., benzene and ethanol).

Figures 2 and 3 show the permselectivity α and total flow across the CM membrane Π as functions of the initial composition of the toluene–methanol and benzene–ethanol mixtures. As seen, over a wide concentration range, the CM membrane is selective with respect to the aromatic component of the mixture. Figure 2 demonstrates regular increase of the flow across the membrane (curve *1*) and parallel decrease in α_{toluene} (curve 2) with increasing toluene concentration in the initial mixture. Similar trend in the behavior of the transport parameters was observed also in separating the benzene–ethanol mixture (Fig. 3). It should be pointed out that, in separating the toluene–methanol mixture (Fig. 2), nearly the optimal relation between α and Π was obtained at the composition of the initial mixture close to the azeotropic composition (31 wt % toluene). For both systems, even at room temperature, 30–50 μm thick membranes allow sufficiently large flows in separating azeotropic mixtures, the attainable selectivity levels being well comparable with those of the membranes commonly used for this purpose [21].

Figure 2 (curves *1*, *2*) shows the dependences obtained in the pervaporation experiments on the same membrane with increasing toluene concentration in the initial mixture. Before passing to the next feed composition, the membrane cell was evacuated for a fixed time (10 min) to partially remove the solvents. Curves *1a* and *2a* were obtained at different evacuation time (1 h). As seen, longer drying of the membrane considerably affects the process characteristics, especially the flow Π (curve *1a*). The observed increase in the permeability at higher initial toluene concentration (Fig. 2, curve *1*) can be attributed to stepwise activation of the membrane structure at the supramolecular level with more penetrating component (toluene). Similar effect was observed previously [7] for CAM membranes in separating benzene–heptane mixtures.

In Fig. 4, the dependences of the permeate composition on the composition of the initial toluene–methanol (curve *3*) and benzene–ethanol (curve *4*) mixtures are presented along with the corresponding liquid–vapor diagrams obtained in the case of open equilibrium evaporation (curves *1*, *2*). A specific feature of pervaporation separation is that, over the entire feed composition range, the pervaporation curves are arranged considerably below the open evaporation curves, particularly, in separating the azeotropic mixtures. It should be pointed out that, in the frameworks of such comparative analysis, the pervaporation curves presented in Fig. 4 differ advantageously from those given in Fig. 2 for the system ethanol–water.

For the system toluene–methanol of the azeotropic compositions, we also studied the possibility of optimization of the transport properties with regard to the thickness of the CM membrane. The selectivity and flow across the membrane were determined at 20°C for 30-, 50-, and 690-μm thick membranes, and at 20 and 40°C for a 50-μm membrane. In each case, we determined the arbitrary production parameter as the product of $\prod$ and α. The maximal value of this parameter corresponds to the optimal relation between the flow across the membrane and the selectivity of separation. The production index appeared to be maximal for the 50-μm membrane (8.36 and 12.95 kg $\mathrm{m}^{-2}\,\mathrm{h}^{-1}$ at 20 and 40°C, respectively).

In terms of the existing concept of the pervaporation mechanism, the immediate cause of the effect of the membrane thickness is associated with the penetrant concentration gradient across the membrane. In steady-state mass transfer, the penetrant concentration decreases in the direction to the permeate side of the membrane. Therefore, the surface of the membrane at the feed side occurs in the state maximally close to the condition of equilibrium swelling with regard to the components of the mixture. In this zone, the selectivity of separation is relatively low as a result of the plasticization of the surface layers of the membrane. In deeper layers, the degree of approaching the equilibrium swelling should decrease. As a result, “drier” layers at the permeate side are plasticized to a smaller extent, and the flexibility of the polymer chains or their segments in this zone is considerably lower, which should exert a positive effect on the separation selectivity. At the same time, with all other conditions being equal, with increasing concentration of more penetrable component in the mixture, the flow across the membrane increases. In this case, the concentration gradient and the thickness of the “dry” layer decrease, negatively affecting the selective properties.

This concept gives grounds to use the term “cross-membrane selectivity gradient.” In each particular case of separation, the occurrence of such a gradient allows control of the transport characteristics of the membrane, including α. In this connection, it may be concluded that the use of the term “ideal partition factor” is incorrect with respect to pervaporation membranes as continuous nonporous films, since, with all other conditions being equal, α will increase with increasing thickness of the membrane.

To conclude, mixtures of aliphatic alcohols and aromatic hydrocarbons can be separated on pervaporation membranes in a single stage, to obtain the concentration of the aromatic component in permeate of up to 80–90 wt %. The resulting permeates can be then partitioned by, e.g., ordinary distillation. An alternative can be the use of methanol- or ethanol-selective pervaporation membranes in the second stage also. Furthermore, the IGC analysis revealed high affinity of CM for methyl acetate and ethyl acetate and low affinity for water and aliphatic alcohols. This difference could be of interest in view of the use of CM membranes in industrial processes in a series with a reactor, to shift the equilibrium of esterification and also to remove the target products from the reaction zone.

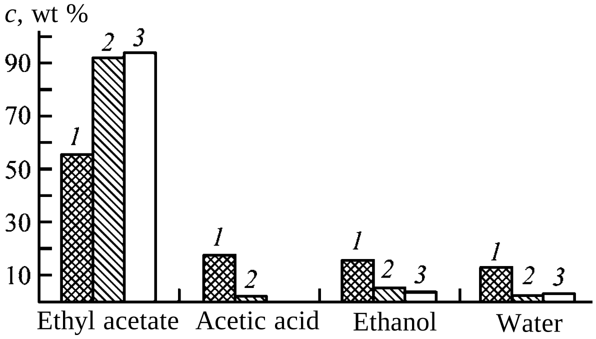

Fig. 5. Initial composition of the mixture ethyl acetate–acetic acid–ethanol–water compared to the compositions of permeates in separating the initial mixture in the pervaporation and evaporation modes with the CM membrane. (*c*) Component concentration. (*1*) Initial mixture; permeate composition: (*2*) pervaporation and (*3*) evaporation.

The histogram in Fig. 5 represents the results of separation of a four-component mixture whose composition models the esterification equilibrium realized in synthesis of ethyl acetate (55.0, 17.1, 15.4, and 12.5 wt % of ethyl acetate, acetic acid, ethanol, and water, respectively). The process was carried out at 20°C with direct contact of the simulated mixture with the surface of the CM membrane (pervaporation mode) or on a membrane in contact with vapor of this mixture (evaporation mode). In both cases, we observed considerable enrichment of permeate with ethyl acetate (from 55 to 91.6 and 93.8 wt %, respectively) with parallel significant decrease in the concentrations of acetic acid, ethanol, and water (1.5 and 0, 4.1 and 3.4, and 2.2 and 2.8 wt %, respectively). It is worth noting that the permeability of the membrane in the pervaporation and evaporation modes is considerably different (2 and 0.1 kg $\mathrm{m}^{-2}\,\mathrm{h}^{-1}$, respectively). Finally, our results are of interest in view of formation of composite CM membranes with higher permeability.

CONCLUSIONS

(1) The possibility of controlling the membrane permeability and selectivity with respect to some individual gases or their mixtures, as well as the direction of selective mass transfer in separating water–ethanol mixtures, was demonstrated with an example of cellulose acetomyristate membranes of various compositions.

(2) A comparative analysis is made of the selectivity of separation of binary organic and aqueous-alcoholic mixtures on cellulose myristate and acetomyristate membranes in the pervaporation and evaporation modes.

(3) The direction of selective mass transfer of components of organic mixtures across the cellulose myristate membrane can be predicted using the inverse gas chromatography.

(4) Cellulose myristate membranes are efficient for recovery of toluene and benzene from their mixtures with, respectively, methanol and ethanol, particularly from azeotropic mixtures.

(5) The separating properties of cellulose myristate membrane are studied with regard to a multicomponent mixture simulating the esterification equilibrium realized in synthesis of ethyl acetate. Ethyl acetate can be concentrated in permeate to 91.6–93.8 wt %.

ACKNOWLEDGMENTS

The authors are grateful to A.M. Toikka for valuable discussions. The work was financially supported by the Russian Foundation for Basic Research (project no. 03-03-32 379) and the Federal Task Program "Integration" (project B0028/1365).

REFERENCES

1. Chaudry, M.A., *J. Membrane Sci.*, 2002, vol. 206, pp. 319–332.
2. Kim, S., Lim, G., Jegal, J., and Lee, K., *J. Membrane Sci.*, 2000, vol. 174, pp. 1–15.
3. Richau, K., Schwarz, H.-H., Aptel, R., and Paul, D., *J. Membrane Sci.*, 1996, vol. 113, pp. 31–41.
4. Mochizuki, A., Amia, S., Sato, Y., *et al.*, *J. Appl. Polym. Sci.*, 1990, vol. 40, pp. 633–643.
5. Kosutic, K. and Kunst, B., *J. Appl. Polym. Sci.*, 2001, vol. 81, no. 7, pp. 1768–1775.
6. Polotskaya, G.A., Turkova, L.D., Kuznetsov, Yu.P., and Nesterov, V.V., *Vysokomol. Soedin.*, 1990, vol. 32, no. 4, pp. 1733–1738.
7. Sidorovich, A.V., Baklagina, Yu.G., Khripunov, A.K., *et al.*, *Zh. Prikl. Khim.*, 2002, vol. 75, no. 12, pp. 1733–1738.
8. Khripunov, A.K., Koz'mina, O.P., Shtennikova, I.N., and Okhrimenko, G.I., *Zh. Prikl. Khim.*, 1970, vol. 43, no. 11, pp. 2581–2583.
9. Dytnerskii, Yu.I., Kagramanov, G.G., and Storozhuk, I.P., *Zh. Vses. Khim. O–va. im. D.I. Mendeleeva*, 1987, vol. 32, no. 6, pp. 684–692.
10. Karakane, H., Tsuyomoto, M., Maeda, Z., and Honda, Z., *J. Appl. Polym. Sci.*, 1991, vol. 42, pp. 3229–3239.
11. Kuznetsov, Yu.P., Kruchinina, E.V., Nud'ga, L.A., *et al.*, *Zh. Prikl. Khim.*, 2003, vol. 76, no. 11, pp. 1857–1862.
12. Uragami, T. and Moricava, T., *J. Appl. Polym. Sci.*, 1992, vol. 44, pp. 2009–2018.
13. Baker, R.W., *Membrane Technologies and Applications*, New York: McGraw-Hill, 2000.
14. Kogan, V.B., Fridman, V.M., and Kafarov, V.V., *Ravnovesie mezhdu zhidkost'yu i parom* (Liquid–Vapor Equilibria), Moscow: Nauka, 1966.
15. Yoshikawa, M., Wano, T., and Kitao, T.J., *Membrane Sci.*, 1994, vol. 89, pp. 23–36.
16. Aksenova, E.L., Kuznetsov, V.M., Kuznetsov, Yu.P., and Toikka, A.M., *Vestn. Sankt-Peterb. Gos. Univ.*, 2000, no. 4, pp. 87–92.
17. Ohya, H., Shibata, M., Negus, Hi Y., *et al.*, *J. Membrane Sci.*, 1994, vol. 90, pp. 91–100.
18. Lenk, W. and Meer-Haask, J., *Desalination*, 2002, vol. 148, pp. 11–16.
19. Masuda, T., Tang, B., and Higashimura, T., *Polym. J.*, 1986, vol. 18, no. 7, pp. 565–567.
20. Roberts, S.L., Koval, C.A., and Nobel, R.D., *Ind. Eng. Chem. Res.*, 2000, vol. 39, pp. 1673–1682.
21. Ruckenstein, E. and Sun, F., *J. Membrane Sci.*, 1995, vol. 103, pp. 271–283.