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Transport of Small Molecules through Polyphenylene Oxide Membranes Modified by Fullerene

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Abstract: Homogeneous membranes based on fullerene-polyphenylene oxide compositions containing up to 2 wt% fullerene C_{60} were prepared. The effect of fullerene addition on PPO transport properties was studied in gas separation and pervaporation processes. Permeability coefficients of H_2, O_2, N_2, CH_4, and CO_2 were measured; a correlation between gas transport properties and membrane free volume was established. Pervaporation properties were studied for the system with ethyl acetate synthesis reaction: quaternary system ethanol—acetic acid—water—ethyl acetate and some constituent binary and ternary mixtures. Pervaporation in binary systems, ethanol–water and ethyl acetate–water was considered with the use of the data on sorption capacities and interaction parameters. In pervaporation of a quaternary reacting mixture, the

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permeate containing essentially ethyl acetate was obtained. Results show that membranes with fullerene additives exhibit improved transport properties.

Keywords: Gas separation, pervaporation, homogeneous membranes, fullerene, polyphenylene oxide

INTRODUCTION

Fullerene has attracted much attention due to its unique chemical and physical properties (1, 2). Development of new materials based on fullerene for use in technology is the principal problem under investigation. Polymers provide a wide possibility of obtaining such materials. Fullerene incorporation into polymer systems leads to materials with new properties. In this case the π-electron system of the fullerene molecule is subjected to minimum transformations and retains its unique properties in the composite material, but the properties of the polymer itself are transformed. The nature of fullerene-containing polymer properties is investigated intensively (3–7).

The combination of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and fullerene C_{60} gives a donor-acceptor complex that has been studied by hydrodynamic and electrooptic methods in solution (8). The complex is not separated into components at the dilution. This indicates that the bond between PPO and C_{60} is relatively strong. Hydrodynamic studies showed that intrinsic viscosity and the asymmetry of PPO molecule decrease, that is, C_{60} molecules exert a great orienting effect on PPO chain segments. It should be noted that the hydrodynamic radius of an equivalent sphere of PPO chain in isolated state is about 50 times greater the radius of the C_{60} molecule.

The bond between PPO and C_{60} molecules detected in solutions should remain after solvent evaporation and transformation of fullerene-containing PPO into the solid state. Photoluminescence spectra showed the existence of molecular complexes in C_{60}-PPO films containing up to 2 wt% C_{60}, whereas in C_{60}-PPO films containing 4 wt% C_{60} the major part of C_{60} molecules are not bonded to PPO (9).

Polymer membranes are widely used to concentrate and purify gas and liquid mixtures in gas separation and pervaporation processes. However, there is little information on membranes based on fullerene-containing polymers (10–14). In our previous work (15) the influence of fullerenes on polystyrene transport properties in the process of air enrichment with oxygen has been studied. Fullerene-polystyrene compositions have higher O_2/N_2 selectivity than polystyrene membranes.

In the present work, transport properties of PPO membranes modified by fullerene C_{60} were studied in gas separation and pervaporation processes. In both processes, the transport of gas or liquid molecules through a nonporous membrane may be described in terms of solution-diffusion mechanism (16): Permeability = Solubility × Diffusion.

Permeability in gas separation is mainly controlled by a diffusion factor depending on the molecular size of the penetrant and also on the value and distribution of free volume in the polymer membrane. The permeability of liquid molecules in pervaporation is mainly controlled by the solubility of penetrant molecules in the polymer membrane and, thus, characterizes the polymer sorption activity. The combination of gas separation and pervaporation provides exhaustive data on the transport of small molecules in the polymer.

Pervaporation as a membrane separation process has a wide range of applications. In the present work, the effect of fullerene addition on PPO transport properties was studied in the pervaporation of the mixture with ethyl acetate synthesis reaction: $C_2H_5OH + CH_3COOH = H_2O + CH_3COO\ C_2H_5$ The shifting of the esterification equilibrium in a hybrid process involving pervaporation is one of the ways for maximizing yield of ethyl acetate. The pervaporation of constituent binary and ternary mixtures of the quaternary reacting system was also investigated.

EXPERIMENTAL

Materials

PPO with a molecular weight of 172 000 (Brno, Czech Republic) was used for the work. Fullerene extract containing >98 wt% C_{60} was purified from moisture traces by heating to 100°C in vacuum.

C_{60}-PPO compositions containing up to 2 wt% C_{60} were prepared by mixing toluene solutions of PPO and fullerene in the required quantity. The brown color appearance, when toluene solutions of colorless PPO and violet C_{60} mixed, demonstrated that C_{60} and PPO interact with complex formation.

Homogeneous C_{60}-PPO membranes of thickness ~60 μm were obtained from 5% wt C_{60}-PPO compositions in toluene by casting on a cellophane surface and drying at 40°C. C_{60}-PPO membranes were of a brown color, whose intensity depended on the quantity of C_{60} in composition.

Homogeneous PPO membranes of thickness ~60 μm were prepared by casting a 5 wt% PPO solution in toluene on cellophane and drying at 40°C.

Characterization

Density Determination

The density (ρ) of films was determined by the flotation method in a saccharose solution at 25°C.

The free volume v_f (cm^3/g) was calculated from the equation

$$v_f = v_{sp} - 1.3\ v_w \qquad (1)$$

where $v_{sp} = 1/\rho$ is the specific volume and v_w is the Van der Waals volume calculated by Bondi method (17). The C_{60} contributions to the occupied volume and to the molecular weight of PPO monomer unit were accounted for in calculating the v_w of C_{60}-PPO composition.

Contact Angle Measurements

Contact angles of liquids on PPO and C_{60}-PPO surfaces were measured by the Wilhelmy plate technique on the KRUSS installation. In the Wilhelmy plate technique the advancing (θ_a) and receding (θ_r) angles are calculated from the force exerted as the sample is immersed or withdrawn from a liquid. A computer controls the stage velocity and movements and provides the software required for calculations. Liquids under study were water ($\sigma = 72.4$ mN/m) and ethanol ($\sigma = 23.7$ mN/m).

Gas Separation Experiments

Gas permeability through membranes was determined by using a laboratory high vacuum apparatus with a static permeation cell with an effective membrane area of 5.25 cm^2 at 30°C. Gas under constant pressure higher than the atmospheric pressure was brought into the feed part of the previously evacuated apparatus. Permeability was determined from the increase of the pressure in calibrated volume of the product part. Gases under the study were H_2, O_2, N_2, CH_4, and CO_2.

Pervaporation Experiments

Pervaporation properties were measured on a laboratory cell with the effective membrane area of 14.8 cm^2 at 40°C with stirring. Downstream pressure below 30 Pa was maintained using a vacuum pump. The permeate was collected in a liquid nitrogen trap, weighed, and then analyzed by refractometry and gas chromatography. Ethanol and water were used as mixture components.

Membrane permeation flux, J (kg/m^2 h), was determined as an amount of liquid transported through the unit of the membrane area and per time unit.

The selectivity or the separation factor, α, is defined by the equation

$$\alpha = \frac{y_i/y_j}{x_i/x_j} \qquad (2)$$

where y_i and y_j are the weight fractions of components i and j in the permeate and x_i and x_j are the weight fractions of components i and j in the feed respectively.

Sorption and Swelling Experiments

Membrane films of known weight were immersed in a liquid at 20°C. After 3 days they were removed and weighted when superfluous liquid was wiped. This procedure was repeated until the weight of swelling films became constant. The degree of equilibrium swelling or sorption of liquid in polymer membrane, S (g of liquid/100 g of dry polymer), was calculated by the equation

$$S = \frac{W_s - W_d}{W_d} \cdot 100 \tag{3}$$

where W_s is the weight of a swollen membrane and W_d is the weight of a dry membrane.

RESULTS AND DISCUSSION

Physical Properties

Some physical properties of native PPO and C_{60}-PPO membranes that are useful for explaining the process of small molecules transport through these membranes were determined. First of all such properties as film density and surface tension were under consideration.

Inclusion of heterogeneous particles in polymer systems can be followed by compacting or loosening of the polymer chain structure. To elucidate the character of structural changes, the density of PPO films with different C_{60} contents was determined and the free volume was calculated. These results are given in Table 1.

In fullerene-containing samples, density increases, that is, C_{60}-PPO polymer coils become more compact. This is manifested in decreasing the free volume of C_{60}-PPO compositions and reflects molecular interaction between C_{60} and PPO with complex formation.

The contact angle is the most widespread characteristic of solid surface tension. Table 1 lists contact angles of water and ethanol on PPO and 2% wt C_{60}-PPO surfaces. PPO is a hydrophobic polymer since the maximal

Table 1. Physical properties of PPO and C_{60}-PPO membranes, 20°C

Polymer	Density, g/cm^3	Free volume, cm^3/g	Contact angle (degree) Water	Contact angle (degree) Ethanol
PPO	1.057	0.181	91.2	20.2
1 wt% C_{60}-PPO	1.093	0.150	–	–
2 wt% C_{60}-PPO	1.120	0.128	94.4	17.9

water contact angle on its surface is larger than 90°. C_{60} additives increase contact angle and hydrophobicity. In contrast, the PPO surface is well moistened in ethanol. C_{60} addition to PPO decreases contact angles of ethanol due to an enhanced affinity of ethanol for fullerene-containing membranes. These results are important for explaining the C_{60} effect on PPO sorption and pervaporation properties.

Gas Separation Properties

Polymers promising for gas separation membranes must exhibit high gas permeability and high selectivity. PPO is one of the most permeable glassy polymers with sufficiently high free volume. However, PPO exhibits relatively low selectivity in gas separation (18, 19). Attempts have already been made to modify PPO with the aim of increasing its selectivity (20–23).

The results of the PPO modification by fullerene C_{60} was estimated by measuring the permeability of H_2, O_2, N_2, CH_4, and CO_2 through both PPO and C_{60}-PPO homogeneous membranes. Table 2 lists the data on gas separation properties of these membranes, which show a decrease in permeability coefficients for all gases with increasing C_{60} content in samples. The selectivity of C_{60}-PPO membranes is higher than that of PPO. As a rule, gas transport properties are determined by the diffusion factor depending to a great extent on polymer free volume. As shown in Table 1, the addition of C_{60} to PPO leads to a decrease in the polymer free volume. This is the reason for decreasing gas permeability through C_{60}-PPO membranes. Gas permeability coefficients depend also on the kinetic size of gas molecules. Among all gases studied in this work, the permeability of large nitrogen molecules decreases to the greatest extent.

Pervaporation Properties

Pervaporation properties of membrane depend on interactions between the components of the feed solution and the polymer of the membrane. The

Table 2. Gas separation properties of PPO and C_{60}-PPO membranes, 30°C

	Permeability, barrers					Selectivity			
Membrane	H_2	O_2	N_2	CH_4	CO_2	H_2/N_2	O_2/N_2	CO_2/CH_4	CO_2/N_2
PPO	112.98	19.08	4.65	6.43	90.68	24.3	4.1	14.1	19.5
1% C_{60}-PPO	103.91	18.13	4.05	5.57	80.90	25.6	4.5	14.5	20.0
2% C_{60}-PPO	92.64	15.12	3.29	4.59	67.11	28.2	4.6	14.6	20.4

1 barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) = $0.33 \cdot 10^{-15}$ mol · m/(m^2 · s · Pa).

polymer acts as "a molecular sieve" with sorption active centers that are able to interact with the components of a liquid mixture by van der Waals, dipole-dipole, and ion-dipole forces, or hydrogen-bonding (24). The mass transport depends to a considerable extent on the affinity of the membrane polymer for components of the separating mixture (16). Quantitatively, the affinity can be expressed in terms of the Flory-Huggins interaction parameter χ which determine intermolecular forces and also characterize the solubility of a polymer in a given solvent (25). According to the Flory-Huggins theory (26) the Gibbs energy of mixing $\triangle G_m$ is given by equation:

$$\frac{\Delta G_m}{RT} = \mathrm{In}\varphi_i + \varphi_p + \chi\varphi_p^2 \tag{4}$$

where φ_i is the volume fraction of the solvent in the polymer and φ_p is the volume fraction of the polymer. The value of the dimensionless binary interaction parameter χ could be calculated from the following expression:

$$\chi = \frac{-\mathrm{In}\varphi_i - \varphi_p + \Delta G_m/RT}{\varphi_p^2} = \frac{-\mathrm{In}\varphi_i - \varphi_p}{\varphi_p^2} + \frac{\Delta G_m}{RT\varphi_p^2} \tag{5}$$

In the case of equilibrium sorption of the solvent in the polymer, the dimensionless binary interaction parameter can be estimated by Eq. 6 (see e.g. paper (27)):

$$\chi = \frac{-\mathrm{In}\varphi_i - \varphi_p}{\varphi_p^2} \tag{6}$$

that would be valid if $\triangle G_m$ is zero.

If the interaction between the polymer and the penetrant increased, the amount of penetrant inside the polymer also increases and χ decreases. In contrast, with decreasing affinity between the polymer and the penetrant, χ increases. Therefore, a lower value of χ implies higher sorption (28). More correctly the left side of equation (6) corresponds to the value

$$\chi' = \chi - \frac{\Delta G_m}{RT\varphi_p^2} \tag{7}$$

that should be valid in general case of $\triangle G_m \neq 0$.

We studied equilibrium vapor sorption of ethanol, acetic acid, water, and ethyl acetate in PPO and C_{60}-PPO homogeneous membranes. Table 3 lists data that show a better sorption capacity of fullerene-containing membranes for ester, acid, and alcohol than that of PPO membranes. Ethyl acetate exhibits the highest sorption, followed by acetic acid and ethanol. Water appears to be absolutely inert to polymers under study.

Absence of water sorption in our membranes and high sorption capacity for ethanol and ethyl acetate play an important role in pervaporation of systems involving these components, especially, in binary systems: ethyl

Table 3. Sorption capacities and parameters χ' for polymer membranes and components of esterification reaction, 20°C

	S, wt.%		Parameter χ'	
Component	PPO	2% C_{60}–PPO	PPO	2% C_{60}–PPO
Ethanol	13.0	15.0	1.45	1.34
Acetic acid	23.6	24.2	1.29	1.24
Water	0	0	–	–
Ethyl acetate	23.4	26.4	1.22	1.13

acetate—water and ethanol—water. The pervaporation of ethyl acetate–water mixtures was studied in dilute aqueous solutions containing < 7 wt% ethyl acetate. The reason is the phase separation (liquid phase splitting) of ethyl acetate–water system over a wide composition range. This mixture is homogeneous at ethyl acetate concentration below ~7 and above ~97 wt%.

Figure 1 shows that C_{60} addition to PPO increases membrane selectivity. At the same time, the addition of C_{60} only slightly changes the flux across the membranes: from 0.48 (PPO membrane) to 0.52 kg m^{-2} h^{-1} (2 wt% C_{60}-PPO membrane) in pervaporation of 7 wt% aqueous ethyl acetate. This may be a result of two opposite factors: decreasing free volume of fullerene-containing membranes, on the one hand, and increasing their swelling in ethyl acetate, on the other hand.

The pervaporation of ethanol–water mixtures by using PPO and C_{60}-PPO membranes is a rather complicated process (27). Figure 2 shows dependences of (a) ethanol content in permeate and (b) selectivity on ethanol content in feed in the pervaporation of ethanol–water mixture by using PPO and C_{60}-PPO membranes. The course of the permeate—feed concentration dependence for pervaporation differs essentially from the vapor–liquid equilibrium diagram for the ethanol–water system (Fig. 2a). In pervaporation, the permeate is enriched with water. For each composition of the feed mixture, the ethanol content in the permeate decreases with increasing C_{60} amount in membranes. Hence, the addition of C_{60} to PPO leads to the increase in selectivity of the water removal process (Fig. 2b). This fact is determined by decreasing free volume in fullerene-containing samples (Table 1) and may be a reason for the decrease in the size of transport channels in C_{60}-PPO membranes. In this case the predominant transfer of smaller water molecules is enhanced.

Figure 3 shows the dependence of specific permeation flux, $J \cdot l$, on the ethanol content in the feed in the pervaporation of the ethanol–water mixture. The total permeation flux, J, is inversely proportional to membrane thickness, l, which varied from 50 to 80 μm, and permselectivity strongly depends on it. Therefore, the product $J \cdot l$ was used for comparing the

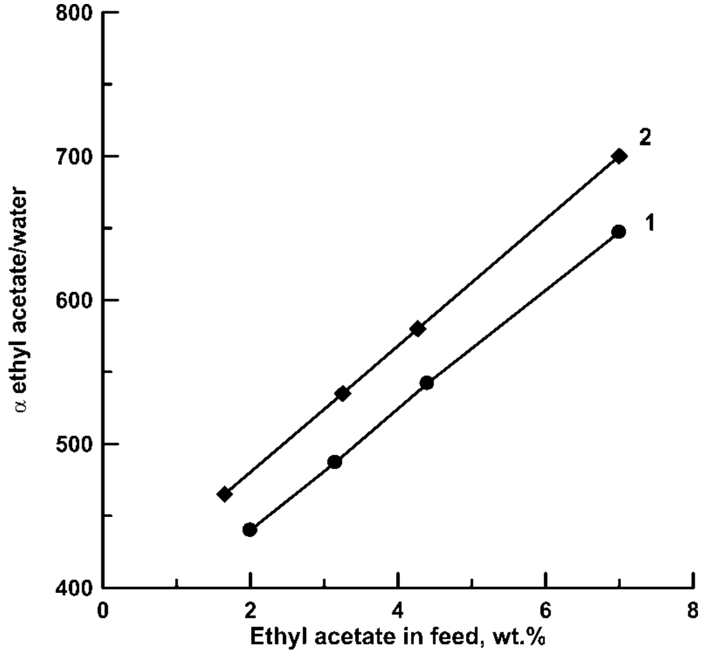

Figure 1. Dependence of separation factor, $\alpha_{\text{ethyl acetate/water}}$, on ethyl acetate content in feed for the pervaporation of water–ethyl acetate mixture through (1) PPO, (2) 2 wt% C_{60}-PPO membranes.

permeability of homogeneous membranes with different thickness, just as in (29). Figure 3 shows that C_{60} additives increase the penetrant flux across the membrane. Furthermore, permeability of membranes increases with increasing ethanol concentration in the feed, although ethanol is the less permeable component of the mixture. This fact is unusual and may be connected with sorption properties of membranes with respect to ethanol and water.

For PPO and 2 wt% C_{60}-PPO membranes, equilibrium swelling or sorption in pure liquids (ethanol and water) and in their mixtures was measured. Figure 4 shows the dependence of equilibrium sorption on ethanol concentration in the ethanol–water mixture. The sorption is absent in pure water for both PPO and 2 wt% C_{60}-PPO membranes. It could be due to the fact that PPO is a hydrophobic polymer, and its contact angle in water is greater than 90°. Addition of C_{60} increases the contact angle and hydrophobic properties of membranes.

However, ethanol is adsorbed readily and even a small amount of ethanol in aqueous solution initiates PPO swelling markedly. In this case, C_{60} additives increase the sorption capacity of membranes, which is consistent with the data of Tables 1 and 2 demonstrating that the contact angle and the

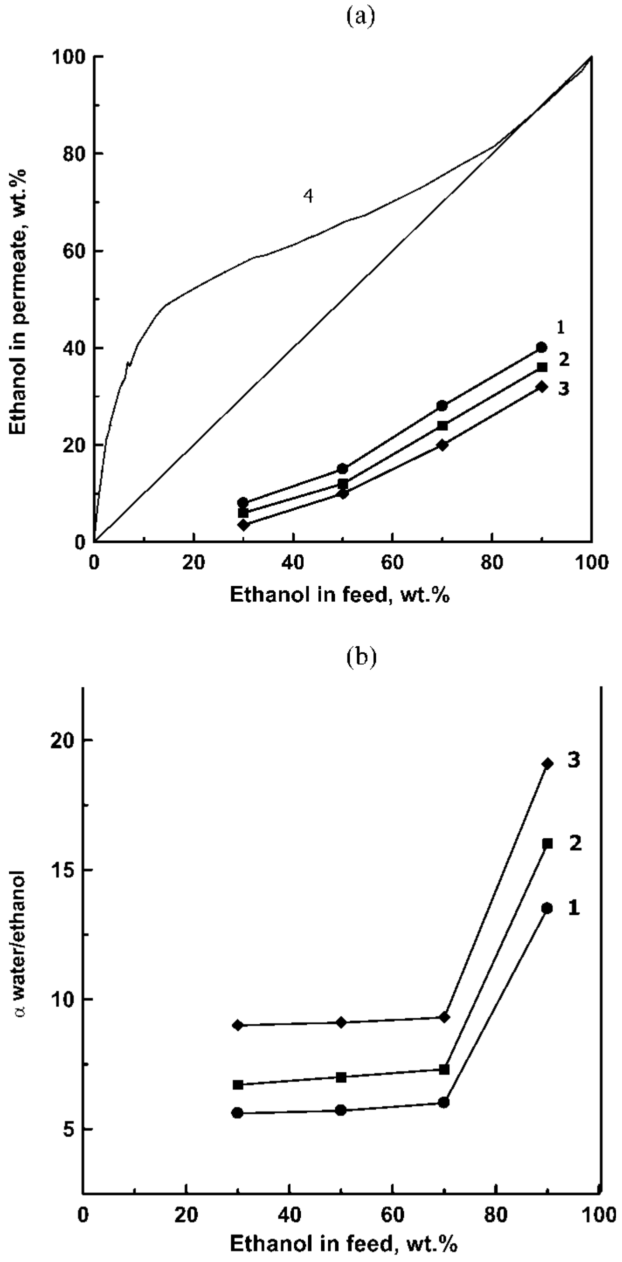

Figure 2. Dependence of (a) ethanol content in permeate and (b) separation factor, $\alpha_{water/ethanol}$, on ethanol content in feed for the pervaporation of water–ethanol mixture through (1) PPO, (2) 1 wt% C_{60}-PPO, and (3) 2 wt% C_{60}-PPO membranes. (4) Vapour–liquid equilibrium curve.

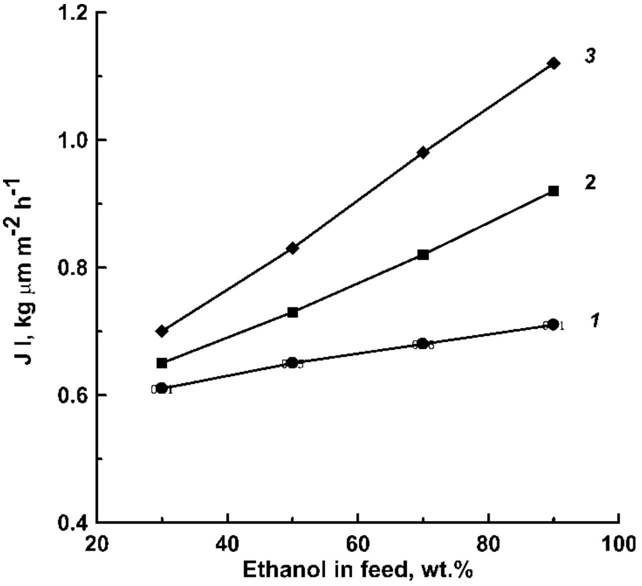

Figure 3. Dependence of permeability, $J \cdot l$, on ethanol content in feed for the pervaporation of water–ethanol mixture through (1) PPO, (2) 1 wt% C_{60}-PPO, and (3) 2 wt% C_{60}-PPO membranes.

interaction parameter of fullerene-containing membranes decrease in ethanol. This is responsible for the fact that the increase of ethanol concentration in aqueous solution leads to increasing equilibrium sorption in 2 wt% C_{60}-PPO to a greater extent than in PPO.

The mechanism of mass transfer in pervaporation of ethanol–water mixture can be presented as follows. In the initial sorption, ethanol alone takes part. Ethanol molecules interact with the PPO backbone by hydrogen-bonding and create transport channels. Owing to high affinity for ethanol, water penetrates these channels whose size is commensurable with the kinetic diameter of water molecules. Water is the more permeable component of the mixture due to the smaller size of its molecules than those of ethanol. Increasing concentration of ethanol (swelling agent) leads to the weakening of intra- and intermolecular bonds in PPO membrane and to its plasticization. This facilitates the permeability of all membranes. Transport properties are higher in C_{60}-PPO membranes.

The sorption data confirm the increase in both PPO matrix plasticization and in the number of mass-transfer channels with increasing ethanol concentration in the aqueous solution. These transformations result in increasing water permeation flux and selectivity, the tendency being more clearly pronounced for C_{60}-PPO membranes.

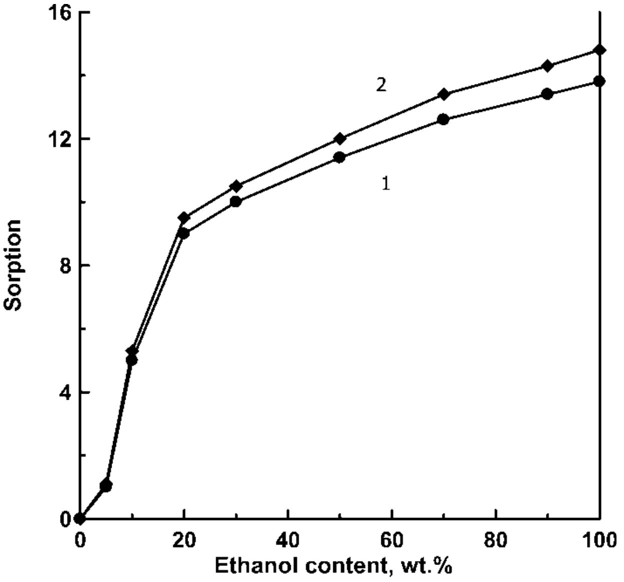

Figure 4. Dependence of equilibrium sorption on ethanol content in water–ethanol mixture for (1) PPO and (2) 2 wt% C_{60}-PPO membranes.

In pervaporation of the quaternary reacting system (with ethyl acetate synthesis reaction), the mixtures containing equal molar quantities of reagents (acetic acid and ethanol) were studied. For the composition (16.7 mol % acetic acid, 16.7 mol % ethanol, 33.3 mol % ethyl acetate, 33.3 mol % water) the permeate containing essentially ethyl acetate was obtained (Fig. 5). The feed composition is close to the chemically equilibrium state. Accordingly the shifting of chemical equilibrium in the hybrid process (reaction + pervaporation) should be significant. As a result, the ethyl acetate removal promotes shifting of the reaction equilibrium and the subsequent accelerating of esterification. Initial reagents penetrate through the membrane only slightly. Ethanol penetrates partly; acetic acid almost completely remains in the reaction mixture in spite of high value of acetic acid sorption. Similar small selectivity with respect to acetic acid has been noted in pervaporation of quaternary mixture during hybrid process of butyl acetate synthesis (30). Figure 5 shows that reaction products penetrate through our membranes by different modes, water to a little extent, furthermore, its amount decreases in comparison with the initial amount. Hence, the main component of the permeate becomes ethyl acetate. The use of membranes with C_{60} additives leads to decreasing water content and increasing ethyl acetate content in permeate.

It should be noted that the selectivity in pervaporation of the quaternary reacting mixture depends not only on binary interactions between components and the membrane polymer, but also on more complex competitive interplay

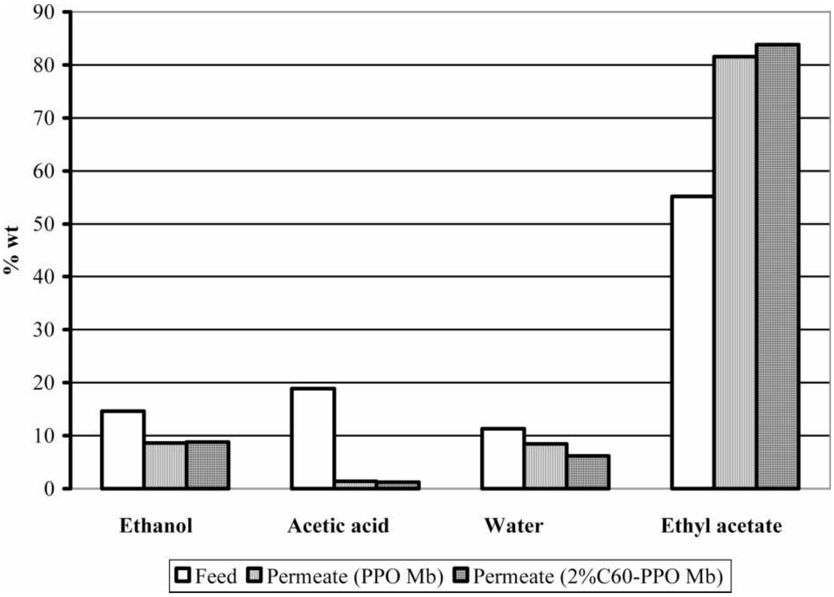

Figure 5. Content of quaternary mixture in feed and in permeate after pervaporation through PPO and 2 wt% C_{60}-PPO membranes.

between all species of the reacting system in pervaporation by using both PPO and C_{60}-PPO membranes.

CONCLUSIONS

Transport of small molecules through PPO membranes modified by fullerene C_{60} was studied in gas separation and pervaporation processes.

Permeability coefficients of H_2, O_2, N_2, CH_4, and CO_2 decrease with increasing C_{60} content in C_{60}-PPO membranes. In gas separation, selectivity of C_{60}-PPO membranes is higher than that of PPO. This is a result of interaction between C_{60} and PPO which leads to increasing polymer density and decreasing free volume of PPO membranes modified by fullerene C_{60}.

Membranes under study are effective in the separation of mixtures comprising components of ethyl acetate synthesis by esterification. In pervaporation of the quaternary mixture involving 16.7 mol % acetic acid, 16.7 mol % ethanol, 33.3 mol % ethyl acetate, 33.3 mol % water, the permeate containing essentially ethyl acetate is obtained. The use of PPO membranes modified by fullerene C_{60} leads to increasing ethyl acetate content in permeate.

In the pervaporation of ethyl acetate–water binary mixture, PPO membranes exhibit high selectivity with respect to ethyl acetate. Modification of PPO membranes by fullerene C_{60} increases the selectivity.

In the pervaporation of ethanol–water mixture, PPO membranes modified by fullerene C_{60} exhibit dehydration properties. The increasing fullerene C_{60} content in membranes leads to increase in both permeability and selectivity with respect to water.

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