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Pervaporation of Methanol/Methyl-t-Butyl Ether Mixtures Through Poly(Vinyl Alcohol)/Poly(Acrylic Acid) Blend Membranes

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Abstract: Membranes obtained by blending poly(vinyl alcohol) (PVOH) and poly(acrylic acid) (PAA) have been investigated for the separation of methanol and methyl-t-butyl ether (MTBE) liquid mixtures through a pervaporation process. Experiments were performed by contacting one side of a polymer dense film with the liquid mixture and removing the vapor on the other side with an inert gas flux, a setup for a process with sweeping gas. The blend membranes, with a COOH/OH ratio in the 0.5–2.5 range, are permeated by methanol preferentially. Higher values of flux and lower values of selectivity are observed when the methanol content in the feed increases. The ratio PAA/PVOH of the membrane influences both flux and selectivity in the same way. A maximum of both flux and selectivity is observed at a COOH/OH ratio of about 2. The swelling of membranes of different composition in the presence of different liquid composition explains the flux behavior in the pervaporation experiments. The observed membrane swelling has been explained on the basis of the solubility parameters of the components of the system.

Keywords: Pervaporation, methanol, MTBE, poly(vinyl alcohol), poly(acrylic acid), blend membranes, swelling

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INTRODUCTION

Pervaporation processes are widely considered as an alternative to conventional distillation processes for the resolution of azeotropic mixtures mainly because the membrane process only requires a partial vaporization of the feed with a significant cost and energy saving. Flux and selectivity are the critical aspects for membrane processes and research efforts are mainly devoted to search for more efficient membrane materials to improve the yield of the pervaporation process. The separation of methanol from methyl-t-butyl ether (MTBE) is an organic-organic separation whose economic importance has increased with the industrial production of octane enhancers that have substituted the lead antiknock compounds in gasoline. MTBE appears to be both a good octane enhancer and an excellent oxygenated fuel additive suitable to reformulate gasoline to meet legal requirements. It is produced by a liquid phase reaction between methanol and isobutylene, an equilibrium reaction carried out with an excess of methanol in order to improve the reaction conversion. The separation of the reaction product, a methanol-MTBE mixture, involves the formation of a minimum-boiling azeotrope (b.p. 51.6°C at 760 mmHg) with 14.3 wt.% methanol. Pervaporation processes have been proposed for this separation (1–3) also as a combined process of distillation-pervaporation (4).

Early studies in the MTBE separation by pervaporation proposed membranes based on cellulose acetate (5), nafion (6), poly(vinyl alcohol) (7), and cellulose acetate-phtalate blends (8). More recently blend membranes made of polyion complexes (9) and poly(ethylene-co-vinyl acetate) (10) have been proposed.

The transport phenomena involved in the pervaporation separation through a polymer dense membrane can be described by a solution diffusion mechanism, taking into account sorption into the polymer, diffusion through the membrane and desorption into the gas phase. For the methanol-MTBE system, higher diffusion rate for the methanol can be expected because of its lower molecular weight and its lower steric hindrance. Therefore, due to the higher solubility and the higher permeation rate through the membrane, a selective transport of methanol should be observed in hydrophilic membrane. Moreover, the separation can be improved by increasing the hydrophilic property of the membrane to improve the preferential absorption of the hydrophilic methanol. Poly(vinyl alcohol) (PVOH), which has been proposed for pervaporation separation of ethanol-water (11–13), acetic acid-water (14), and ethylene glycol/water mixture (15), appears to be a suitable membrane material for application in the methanol-MTBE separation.

The modification of the PVOH membrane structure by blending with polymers having carboxylic groups, as the poly(acrylic acid) (PAA), appears promising to enhance the performance of the membrane because of the high polarity of carboxylic groups, able to give strong interaction with methanol through hydrogen bonding. Membranes obtained by blending PVOH and PAA have been proposed for the dehydration of C_2-C_5 alcohols-water mixtures, the fused oil obtained by sugar cane fermentation (16).

The purpose of this work was to test PVOH-PAA blend membranes for the methanol-MTBE pervaporation separation with feed composition close to the azeotropic one and to assess the influence of the membrane composition on membrane performances.

EXPERIMENTAL PART

Materials and Instruments

Poly(vinyl alcohol), PVOH, MW 64000, partially and fully hydrolyzed, was a Fluka product. The methanol (ACS reagent), methyl-t-butyl ether (99.8%), and poly(acrylic acid), PAA, (DP: 28, DP: 6250) were supplied by Aldrich. All products were used as received.

The residual acetate fraction in the PVOH used for membrane manufacturing has been determined by FTIR analysis. The 1022 cm^{-1} absorption, assigned to CO, was selected as the analytical band for acetate groups determination and the 730 cm^{-1} absorbance, assigned to CH_2, was used as a reference band. By comparing the CO absorbance peak area of the membrane with that of a pure polyvinyl acetate film and a pure fully hydrolized PVOH, a 0.13 molar fraction of residual acetate groups was found in the partially hydrolized PVOH. Infrared analyses were carried out with a FTIR Ati Mattson Genesis instrument.

Thermal analysis of polymeric material was performed through DSC by a Mettler DSC 20 instrument.

Membranes

The polymers show different behavior when submitted to water dissolution: aqueous solutions of PAA or PVOH, 87% hydrolyzed, were easily obtained by stirring the polymer in pure cold water. On the contrary, the fully hydrolyzed PVOH required overnight stirring in pure water at 70°C to obtain homogeneous solutions. Dense membranes were obtained by drying the liquid films obtained by casting aqueous solutions of the polymers on flat surfaces. Pure PVOH membranes, obtained from acqueous solution 10% w/w, have been characterized by DSC analysis. The thermograms evidence an endothermal peak at about 190°C. The area of the peak, assuming a value of 32.1 J/g as heat of melting of the PVOH, allowed to evaluate a crystalline fraction of about 0.21 in the pure PVOH membrane.

Blend membranes with thickness in the 20–40 μm range were obtained by mixing, in appropriate proportion, the PVOH acqueous solution, 10% w/w, with a PAA aqueous solutions, 3% or 10% w/w and casting the resulting liquid with a calibrated wound applicator on a polycarbonate plate. The wet polymer films were allowed to dry in air at room temperature and then were peeled off and used after a further 24 h of storage in a dry environment.

Preliminary results showed different fluxes and selectivity in permeation experiments carried out with membrane just peeled off and with membrane submitted to a further drying. No variations were observed for membranes dried for more than 24 h.

Pervaporation Experiments

Pervaporation tests on MeOH-MTBE mixtures were performed using the sweeping gas technique to remove the vapors that permeated through the membrane. The experimental apparatus is reported in Fig. 1. Liquid mixtures of methanol-MTBE with a 0.1, 0.2, or 0.3 weight fraction of methanol were tested. The permeation cell was kept at 30°C, the feed was continuously circulated by means of a peristaltic pump, and the permeation side was swept with a constant, 100 Nml/min, inert gas flow (He). The permeate was analyzed by GC on a 50-m-long poly(dimethylsiloxane) coated capillary column (CP-Sil 5 CB by Chrompack). The g.c. data were collected only when a stationary state of permeation was reached. The fluxes of permeants were evaluated with reference to a standard 10 μm

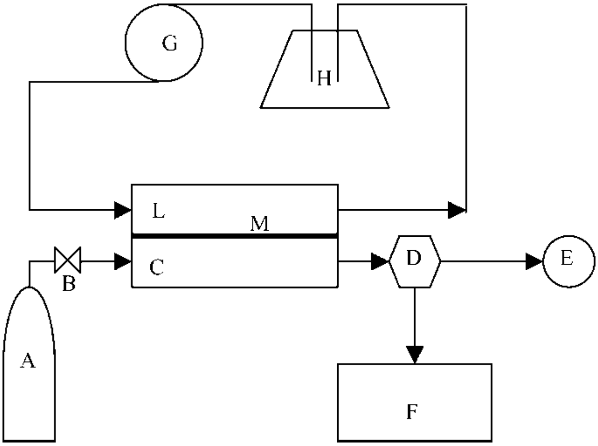

Figure 1. Scheme of the apparatus for the gas sweeping pervaporation experiments A: He bottle B: flow controller C: vapor permeate side D: six-way valve E: flow meter F: gas chromatograph G: peristaltic pump H: feed reservoir L: feed side M: polymer membrane.

thickness of the membrane and the permeation selectivity of the methanol was evaluated through the separation factor α:

$$\alpha = \frac{(C_{MeOH}/C_{MTBE})_{permeate}}{(C_{MeOH}/C_{MTBE})_{feed}}$$

RESULTS AND DISCUSSION

Preliminary pervaporation experiments were performed with pure PVOH and pure PAA membranes. Membranes made of pure PVOH shoved good selectivity for the methanol in the methanol-MTBE separation, separation factors higher than 40 were obtained in pervaporation tests, but the observed fluxes, in the order of some g m^{-2} h^{-1} for a 10 μm thick membrane, are too low to be useful for practical applications. The low fluxes should be ascribed to the high crystalline content of the PVOH membranes that reduces the volume fraction of the polymer accessible to the permeants. Moreover, the crystalline domains act as crosslinks between the amorphous chains and cause a reduction of the swelling in the presence of the liquid mixture. The two phenomena reduce the liquid uptake or, in other words, they reduce the permeant solubility in the polymer and cause a strong reduction of permeability. As a consequence, a very low flux of the permeants was observed.

On the other hand, the pure PAA membranes appear completely amorphous at the DSC analysis, but when used as free films in pervaporation experiments show a very brittle behavior, an insufficient cohesion property, and, at some extent, appear soluble in the MeOH-MTBE mixtures.

By blending PAA and PVOH, the DSC crystalline peak of PVOH cannot any longer be detected. This is an evidence of a strong interaction between the hydroxyl and the carboxyl groups that hinders the building of the regular physical structure of the PVOH. Moreover the blended films show a good stability, without loss of weight in the presence of liquid mixtures with methanol in the 0.1–0.3 weight fraction range.

Blends PVOH-PAA appear suitable materials for applications in the pervaporation process because of their mechanical properties, stability in the liquid media and high amorphous volume accessible for the sorption of permeants. The high stability of the blends should be ascribed to the physical crosslinked structure of the network formed by interaction between the hydroxylic groups of the PVOH and the carboxylic groups of the PAA.

Blends PVOH-PAA with a low content of PAA, show a performance similar to that of the pure PVOH in the methanol-MTBE separation. In Fig. 2 are reported the fluxes and selectivities observed in pervaporation experiments with different mixtures methanol-MTBE by using PVA-PAA blend membrane with a ratio COOH/OH of 0.26. As it is generally observed in the pervaporation processes, the observed fluxes and selectivity are related: by increasing the content of methanol in the feed the flux increases but, at the same time, the selectivity decreases.

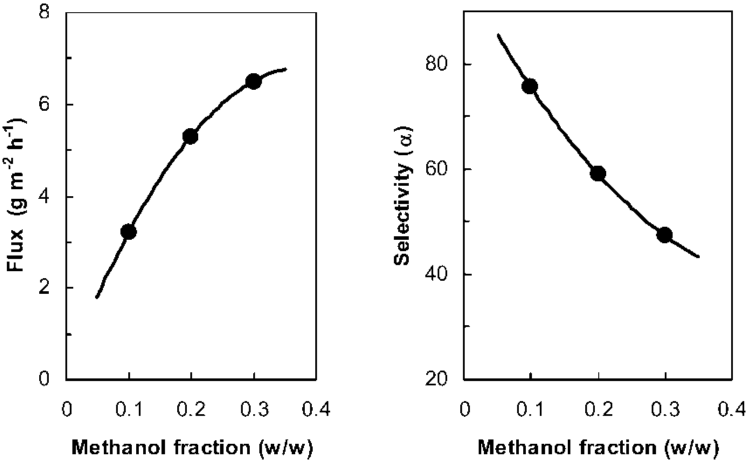

Figure 2. Total flux and methanol selectivity at different feed composition in pervaporation experiments with membrane based on blends of PAA (DP: 28) and PVA (DP:1400). Structural unit ratio in the membrane COOH/OH = 0.26.

The observed values of flux are low but it is interesting to observe that, in the tested feed composition range, the flux and the selectivity are improved when the content of PAA is increased, as can be seen in Fig. 3.

This is surprising because in pervaporation processes the flux and the selectivity show generally an opposite behavior, when the former increases the latter decreases. The observed simultaneous increase of the two parameters

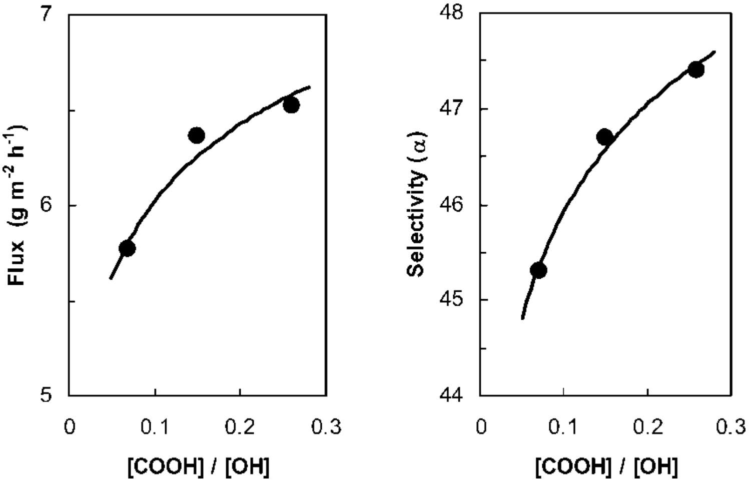

Figure 3. Flux of permeants and selectivity to methanol as a function of membrane composition. Methanol fraction in the feed: 0.3 (w/w).

with the PAA content in the membrane can be an evidence of the chemical compatibility of the methanol with the carboxylic groups that promotes the solubility of methanol in the swollen membrane.

On the basis of this behavior, the performance of the pervaporation process is expected to improve continuously when the concentration of carboxylic group in the membrane increases.

Figure 4 reports the total permeant flux for membrane having content of PAA up to 76%, w/w (CCOOH/OH = 2.3). As can be seen, the flux increases with the PAA content up to a ratio COOH/OH of about 2, then a decrease of flux can be observed. This behavior cannot be explained on the basis of the morphological structure of the membrane having different composition, because the DSC thermograms show the identical pattern for the membrane having COOH/OH ratio in the 1.0–3.0 range. Moreover, as can be seen in Fig. 5 where the fluxes of the two permeants as a function of the membrane composition are reported, the maximum of total flux is localised near the COOH/OH ratio where a maximum of methanol flux and a minimum of MTBE flux were found. A pattern of the flux like that was observed for all feeds with methanol fraction in the 0.1–0.3 range. The membranes show a maximum of separation selectivity at composition in the [COOH]/[OH] region where the flux of permeants was higher. Fig. 6 reports the high values of selectivity observed in these conditions.

The transport of permeants in the pervaporation separation through dense polymer membrane is described through the solution-diffusion mechanism that occurs in three steps: sorption of permeants on the upstream side of the membrane, diffusion through the polymer and desorption on the downstream side. Desorption cannot be considered as a step controlling the selectivity

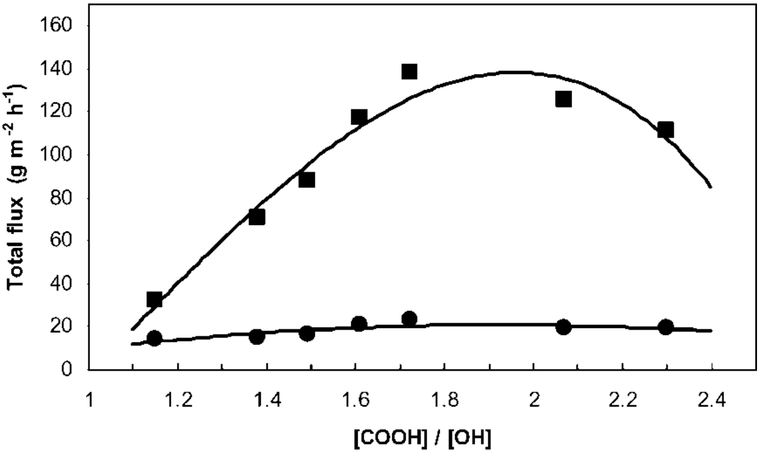

Figure 4. Total flux as a function of the membrane composition. Methanol fraction in the feed: (■) 0.2; (●) 0.1.

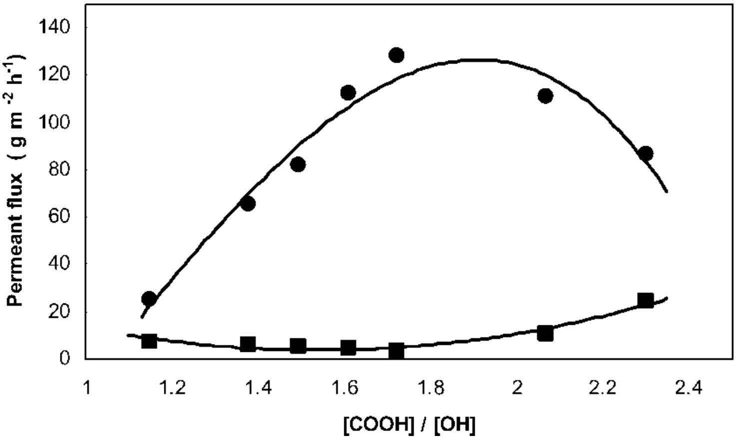

Figure 5. Flux of the permeants as a function of the membrane composition. (●) Methanol (■) MTBE. Methanol fraction in the feed: 0.2.

because the vaporization at the downstream side is not selective and it is relatively fast. The diffusion through the membrane can be slow enough to allow the assumption of the existence of a thermodynamic equilibrium between the feed and the liquid absorbed at the upstream side of the membrane. If this is the case, the selectivity and the flux are mainly controlled by the solubility of the components into the membrane.

In Fig. 7 are reported the swelling data obtained with membrane of different composition in the presence of liquid mixtures with different

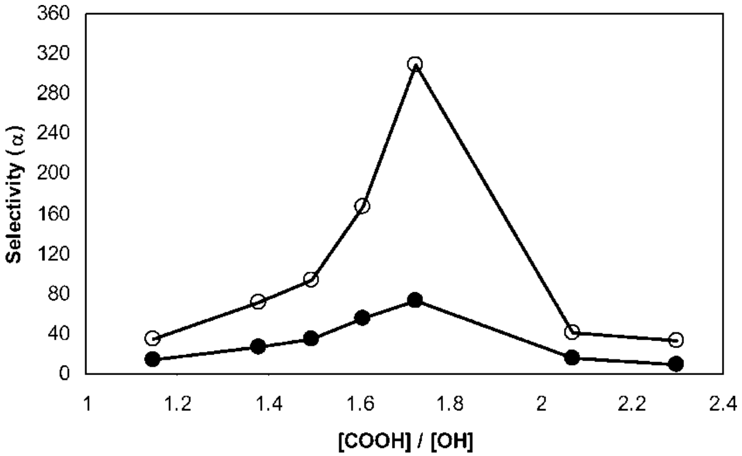

Figure 6. Methanol selectivity as a function of the membrane composition. Methanol fraction in the feed: (○) 0.1 (●) 0.3.

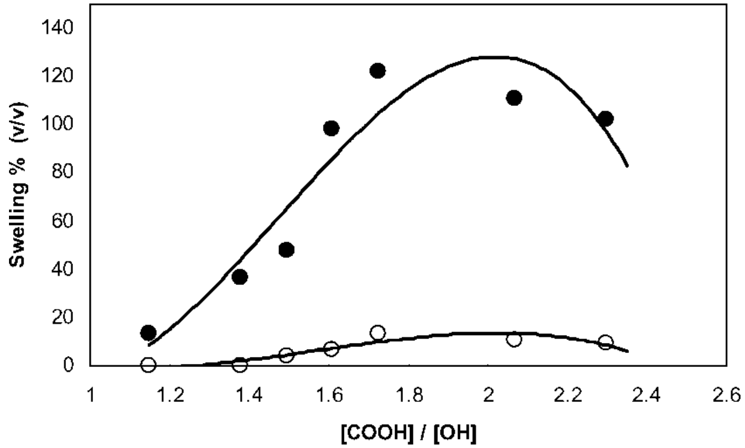

Figure 7. Membrane swelling as a function of membrane composition. Methanol fraction in the liquid: (○) 0.1 (●) 0.3.

composition. The PVOH-PAA blend membranes does not swell in the presence of pure MTBE but show a remarkable swelling when methanol is present in the liquid mixture. The swelling increases with the increase of the [COOH]/[OH] ratio with a behavior similar to that of flux and selectivity, a swelling maximum being observed at a ratio near two.

The relation between the swelling and the flux with membrane of different composition in the presence of liquid mixture in the 0.1–0.3 methanol weight fraction confirms that, in these conditions, the flux through the membrane is mainly controlled by the solubility of the permeants and by their diffusion rate that increases as the available volume for diffusion in the membrane increases.

The swelling of the membrane is controlled by the chemical structure of the polymer and of the solvent. A general rule that predicts the interaction of a polymer with a solvent states that the swelling is enhanced when the solubility parameters of polymer and solvent are close (17).

In Table 1 are reported the values of the parameters evaluated for the polymer-solvent interaction taking into account dispersion forces, δ_d, polar forces, δ_p and hydrogen bonding, δ_h, evaluated by the group contribution as suggested by Hansen (17). The last column of the table reports the solubility parameters evaluated on the basis of the three above mentioned parameters.

It is clear from Fig. 8, where these parameters are plotted, that the blend of PVOH and PAA, whose solubility parameters component is intermediate between that of the pure polymers, has higher compatibility with methanol. This evidence can be observed for all of the three components of the solubility parameter, dispersion, polar and hydrogen component. As a consequence, the selectivity in the pervaporation shown by the blend PAA-PVOH membrane is supported not only by the lower MW and steric hindrance of the methanol

Table 1. Dispersive, polar and hydrogen components of the solubility parameters, as evaluated by group contribution by Hansen method (17)

	Dispersion[a] δ_d	Polar[a] δ_p	Hydrogen[a] δ_h	Solub. param.[b] δ(a)
PVOH	16.4	14.7	24.2	32.7
PAA	20.2	9.6	15.1	27.0
MeOH	15.1	12.3	22.3	29.6
MTBE	15.3	3.42	6.32	16.9

[a] Units: $(\mathrm{J\ cm^3})^{0.5}\,\mathrm{mol}^{-1}$.

[b] $\delta^2 = (\delta_d)^2 + (\delta_p)^2 + (\delta_h)^2$.

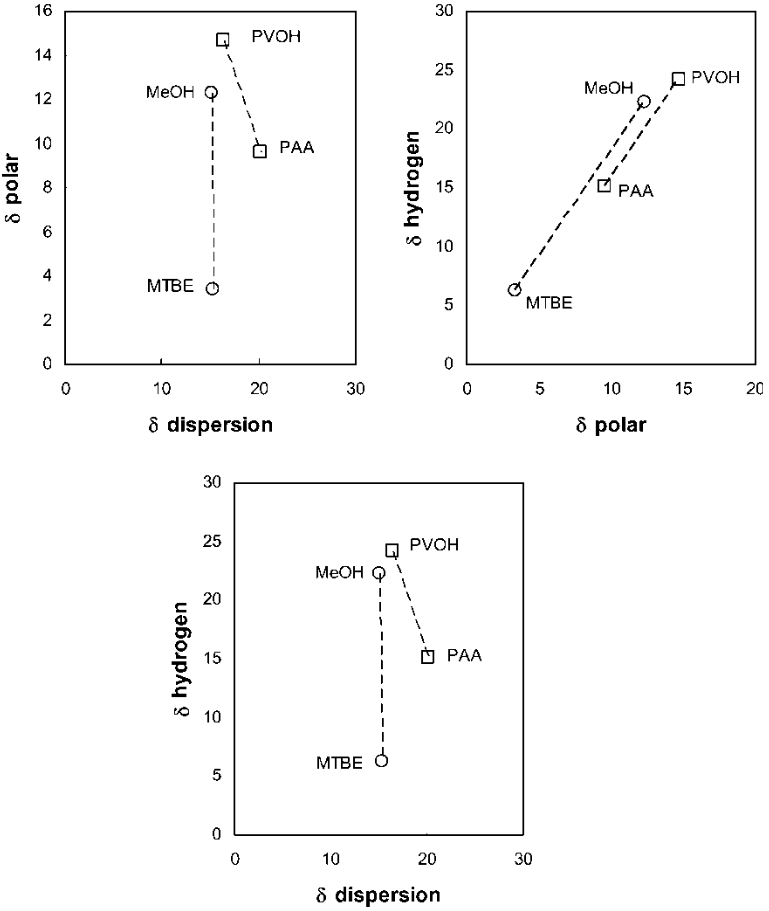

Figure 8. Dispersion, polar and hydrogen contribute to the solubility parameter of methyl-t-butyl ether (MTBE), methanol (MeOH), poly(acrylic acid) (PAA) and poly(vinyl alcohol) (PVOH).

molecule, that favor its transport by an higher diffusion rate, but also by a high compatibility, or solubility, of the methanol in the PVOH-PAA blend membrane.

Moreover, it can be observed that the solubility parameter of the methanol, $\delta = 29.6\ \mathrm{J}^{0.5}\,\mathrm{cm}^{-3/2}$, should be matched by a mixture of PAA, $\delta = 27.0\,\mathrm{J}^{0.5}\,\mathrm{cm}^{-3/2}$, and PVOH, $\delta = 32.7\,\mathrm{J}^{0.5}\,\mathrm{cm}^{-3/2}$. In other words, being the solubility parameter of methanol intermediate between that of the polymers, a blend of PAA and PVOH can have a compatibility with the methanol higher than that of the single polymer. This blend, as a consequence of the maximum interaction with methanol, has to show a maximum of the swelling in the presence of methanol. This can account for the maximum observed in the curve swelling vs. COOH/OH ratio at a value of the ratio about 2. Membranes with this composition exhibit the best performance in the separation of the mixture methanol-MTBE by pervaporation.

CONCLUSIONS

Blend membranes based on PAA and PVOH show good performances in the separation by pervaporation of methanol from mixtures methanol/MTBE. With feed composition near the azeotropic one, the selectivity and permeation rates depend on the feed composition and on the composition of the membrane. By increasing the methanol content of the feed, higher fluxes and lower selectivity were observed. By increasing the ratio [COOH]/[OH] of the membrane, higher values of both selectivity and flux were initially observed but, at values of the ratio higher than 2, flux and selectivity declined. At the maximum of the performances of the blend membrane, a selectivity to methanol of about 300 and a flux of $0.13\,\mathrm{kg\ m}^2\ \mathrm{h}^{-1}$ were observed. The swelling behavior as a function of feed composition and membrane composition is similar to the flux behavior observed in pervaporation experiments, and it can be explained on the basis of the solubility parameters of the components of the system.

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