

Sorption of Alcohol–Toluene Mixtures in Poly(acrylic acid)–Poly(vinyl alcohol) Blend Membranes and Its Role on Pervaporation

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The overall and preferential sorption of alcohol–toluene mixtures in homogeneous blends of poly(acrylic acid) and poly(vinyl alcohol) were determined. Both the overall solubility and the equilibrium sorption selectivity were strongly dependent on the composition of the blend and of the liquid feed mixture. The swelling of the blends increased with increasing poly(acrylic acid) content and with increasing alcohol content in the liquid mixtures. Alcohols were sorbed preferentially over toluene in all cases tested. The equilibrium sorption selectivity increased with increasing poly(vinyl alcohol) content in the blends and with decreasing alcohol content in the liquid mixtures. The equilibrium sorption selectivity was predicted by a model which was derived from Flory–Huggins thermodynamics. The agreement between the predicted and the experimental results was very good. In addition, the equilibrium sorption results were compared with the pervaporation results, and this clearly shows that preferential sorption dominates the pervaporation selectivity in the systems studied.

Introduction

The separation of organic mixtures is still one of the challenging problems in membrane technology. Recently, quite a number of papers were published on the separation of polar–nonpolar mixtures, such as methanol–methyl *tert*-butyl ether, ethanol–ethyl *tert*-butyl ether, methanol–toluene, and ethanol–toluene (Park and Mulder, 1994; Doghieri et al., 1994; Jonquière et al., 1995, 1996; Sano et al., 1995; Park et al., 1995; Zhou et al., 1996; Luo et al., 1997), which is an indication of the interest in these specific separation problems. In a recent paper (Park and Mulder, 1994) it was proposed that a new type of membrane, a blend of poly(acrylic acid) (PAA) and poly(vinyl alcohol) (PVA), shows to be a very interesting material for this class of separation.

The separation by pervaporation results from the differences in the preferential sorption of the individual components of a mixture into the membrane together with the diffusion rates through the membrane. This postulation implies that both sorption and diffusion phenomena have to be considered to understand the physicochemical nature of the pervaporation-separation process.

It is impossible to investigate experimentally sorption and diffusion processes separately because they take place simultaneously. On the basis of the above consideration, however, the results of thermodynamic equilibrium sorption experiments can be used to obtain information on the sorption process during pervaporation. The sorption of a binary liquid mixture in a polymer is characterized by two parameters: (i) overall sorption and (ii) preferential sorption. The overall sorption represents the total amount of liquid inside the

polymer. The preferential sorption is a measure of the difference of the liquid composition in the binary liquid phase from that in the polymer phase.

When a polymer is in contact with a binary liquid mixture, normally one of the mixture components is preferentially sorbed into the polymer. This preferential sorption phenomenon is of special interest in the pervaporation process. Many authors have assumed an ideal additive behavior for component solubilities (Greenlaw et al., 1977; Brun et al., 1985; Rautenbach and Albrecht, 1985; Hauser et al., 1987). In this case, the amount of each component sorbed in the polymeric membrane C_i^m is assumed to be proportional to its activity a_i in the liquid mixture and the single liquid solubility $C_i^{m,0}$ in the membrane: $C_i^m = a_i C_i^{m,0}$. This equation implies that ideal preferential sorption occurs, which can be derived from pure-component sorption data. However, deviations from an ideal sorption are usually observed experimentally for the sorption of various liquid mixtures in polymers (Aptel et al., 1978; Suzuki et al., 1982; Larchet et al., 1984; Mulder et al., 1985a, Hauser et al., 1989). Furthermore, it is quite often observed that the component that is sorbed preferentially also permeates preferentially. In other words, preferential sorption is the leading factor in selective transport. A good overview of literature sources which confirm this observation has been given recently by Mulder (1991).

In this study equilibrium sorption experiments were carried out to obtain more information on the separation mechanism. The overall and preferential sorption characteristics of alcohol–toluene liquid mixtures in the poly(acrylic acid) and poly(vinyl alcohol) blend membranes were studied as a function of the blend composition and the binary liquid mixture composition as well. In addition, the equilibrium sorption results were compared with the pervaporation results to evaluate the influence of sorption on the overall pervaporation process.

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Experimental Section

Materials. Poly(acrylic acid) (PAA; $M_w = 250\,000$) and poly(vinyl alcohol) (PVA; 96% hydrolyzed, $M_w = 85\,000$ – $146\,000$) were supplied by Aldrich Chemical Co. Methyl alcohol, ethyl alcohol, and toluene (analytical grade) were purchased from Merck Co. They were used without any further purification. Water was demineralized before use.

Preparation of Polymer Films. Poly(acrylic acid) and poly(vinyl alcohol) were separately dissolved in water. The two solutions were mixed together in various proportions to obtain the proper casting solutions. Homogeneous polymer films were prepared by casting the polymer solution on a Perspex plate with a casting knife. The solvent, water, was slowly removed by evaporation under a flowing nitrogen stream at room temperature. The thickness of the resulting polymer films was about $100\ \mu\text{m}$. A homogeneous blend membrane is obtained and indicated by a single glass transition temperature (Park and Mulder, 1994).

Sorption Experiments. Strips of polymer films were first dried for 2–4 days in a flowing nitrogen atmosphere and then for 2 days in a vacuum oven at room temperature. The dried sample strip (about 1 g) was immersed in a closed bottle containing either methanol, ethanol, toluene, or a mixture of these solvents. In all cases "fresh" membrane samples were used. The bottle was placed in a thermostated bath at $30\ ^\circ\text{C}$. After the swelling equilibrium state was reached, the strip was removed from the bottle and put into a closed tube after the surface liquid was quickly removed with tissue papers. With blank samples it was demonstrated that the error due to evaporation lies within the error of the triplo experiment. In case of toluene the error is larger because the penetrant concentration is very low.

The sorbed liquid was distilled out of the sample by a laboratory vacuum apparatus described recently by Mulder et al. (1985a). The composition of the distilled sorbate was analyzed by gas chromatography equipped with a thermal conductivity detector.

The overall solubility Q is calculated from the weight of the swollen and the dry polymer sample and is expressed in units of grams of sorbed liquid per gram of dry polymer. The sorption selectivity α_S is determined from the composition of the distilled liquid and defined in the same way as the pervaporation selectivity:

$$\alpha_S = (y_1/y_2)/(x_1/x_2) \quad (1)$$

where x and y represent the concentrations in the binary liquid mixture and in the sorbed liquid, respectively. Index 1 refers to the preferentially soluble component, methanol or ethanol in this study, and index 2 refers to toluene.

Pervaporation Experiments. The pervaporation experiments were performed using the apparatus as described recently (Park and Mulder, 1994). Membranes which were immersed and swollen in the respective feed mixtures at room temperature were installed in the stainless steel pervaporation cells. The effective membrane area in each cell was $50\ \text{cm}^2$. The feed was circulated through the pervaporation cells from a feed reservoir kept at $30\ ^\circ\text{C}$ at a rate of $\sim 1\ \text{L/min}$. The pressure at the downstream side was kept below $2\ \text{mmHg}$ by a vacuum pump. The permeate was collected

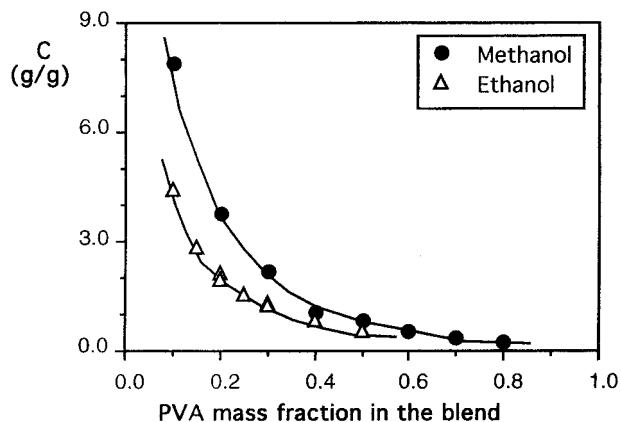


Figure 1. Pure solvent solubility of methanol and ethanol in PAA–PVA blends at various compositions at $30\ ^\circ\text{C}$.

in cold traps cooled by liquid nitrogen. The composition of the collected permeate was determined by gas chromatography equipped with a thermal conductivity detector.

The pervaporation properties are characterized by the flux J and the selectivity α_P . Fluxes were determined by measuring the weight of liquid collected in the cold traps during a certain time at steady-state conditions. The fluxes of different membranes were normalized to a membrane thickness of $20\ \mu\text{m}$, assuming a proportionality between the flux and the reciprocal membrane thickness. The pervaporation selectivity α_P is defined by

$$\alpha_P = (y_1/y_2)/(x_1/x_2) \quad (2)$$

where x and y represent the concentrations in the feed and in the permeate, respectively. Indices 1 and 2 refer to the more permeable component (methanol or ethanol in this study) and the less permeable one (toluene), respectively.

Results and Discussion

Single Liquid Sorption. The sorption results for pure methanol and ethanol in the blend membranes of poly(acrylic acid) and poly(vinyl alcohol) are given in Figure 1. From this figure it can be observed that the solubilities of both methanol and ethanol decrease strongly with increasing PVA content in the blend. This can be related to the affinity of the PAA–PVA blend toward these alcohols, which decreases with increasing PVA content.

The affinity between a polymer and a solvent can be expressed in terms of an interaction parameter. In the case of equilibrium sorption of a pure solvent in a polymer, the binary interaction parameter χ_{ip} can be calculated from the following equation, which is derived from the Flory–Rehner theory (Flory, 1953) by omitting the elastic free energy contribution:

$$\Delta\mu_1/RT = \ln(1 - \phi_p) + \phi_p + \chi_{ip}\phi_p^2 = 0 \quad (3)$$

Here, ϕ_p is the volume fraction of the polymer and can be determined from an equilibrium sorption experiment.

The calculated interaction parameters are given in Figure 2. This figure shows that the binary interaction parameters between methanol and the blend and between ethanol and the blend increase as the PVA content in the blend increases. This means that the

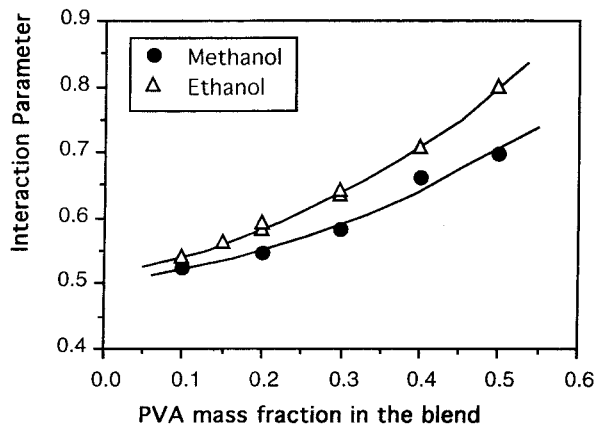


Figure 2. Interaction parameters of PAA-PVA blends at varying compositions with methanol and ethanol at 30 °C.

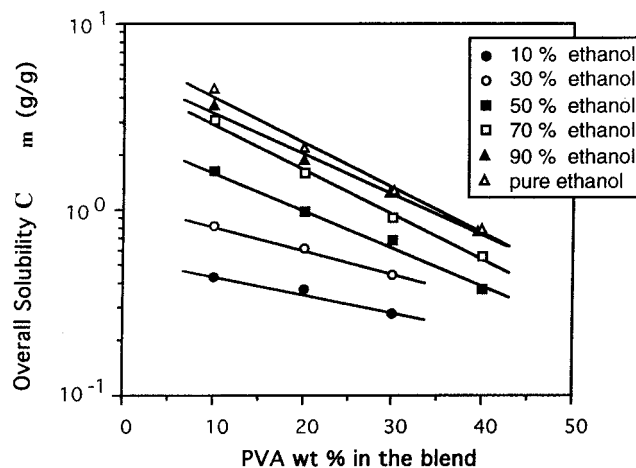


Figure 3. Effect of the blend composition on the overall solubility C of ethanol-toluene liquid mixtures in PAA-PVA blend membranes.

affinity of the blends toward both alcohols decreases. In addition, methanol shows lower interaction parameter values, and so a better affinity, than those of ethanol over the whole blend composition tested.

The decreasing affinity of the blends toward methanol and ethanol with increasing PVA content can be explained in terms of the difference in affinity of the individual polymers for these alcohols. PAA is soluble in methanol and ethanol, while PVA shows a very low solubility for these alcohols (Spitzen et al., 1987; Hauser et al., 1989). For instance, the ethanol sorption value in PVA is about 0.08 g/g of dry polymer. Since generally the properties of a two-component homogeneous blend are between those of the two component polymers being related to the composition of the blend, the overall affinity of the PAA-PVA blend for the alcohols should decrease with increasing PVA content in the blend. This was confirmed from the measurements of single liquid solubilities of methanol and ethanol: a decreasing affinity resulted in a decreasing solubility.

Contrary to the high alcohol solubility, all the tested blends showed hardly any sorption for toluene. The absolute value of toluene solubility was found to be less than 0.001 g/g of dry polymer, which is in the range of the experimental error.

Influence of the Blend Composition. The influence of the blend composition on the overall and preferential sorption was investigated over the blend composition range of PVA of 10–40 wt %. The results

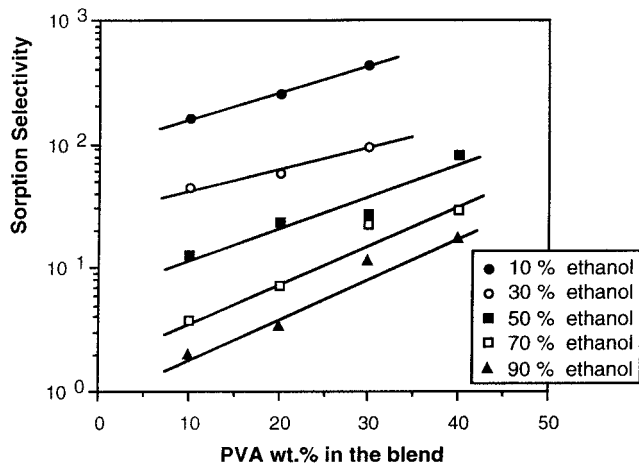


Figure 4. Effect of the blend composition on the sorption selectivity of ethanol-toluene liquid mixtures in PAA-PVA blend membranes.

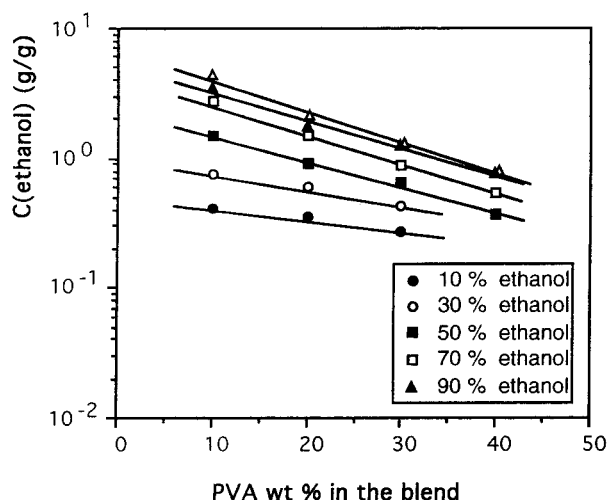


Figure 5. Component solubility of ethanol $C(\text{ethanol})$ in PAA-PVA blend membranes, as a function of the blend composition.

for ethanol-toluene liquid mixtures are presented in Figures 3 and 4.

In Figure 3 the overall solubility Q is given as a function of the blend composition. This figure shows that as the PVA content in the blend increases, the overall solubility decreases exponentially. Since the PAA-PVA blend is hardly swollen in toluene, the overall solubility behavior of the ethanol-toluene liquid mixture is to a large extent governed by the solubility characteristics of ethanol. Therefore, the decreasing overall solubility can be explained on the basis of the affinity of individual polymers for these alcoholic mixtures in a way similar to the sorption of pure ethanol.

The sorption selectivity increases gradually with increasing PVA content in the blends for all liquid mixtures with different compositions (Figure 4). This is due to a rapid decrease of the component solubility of toluene. Component solubilities of both ethanol and toluene are given in Figures 5 and 6, respectively. These figures clearly show that with increasing PVA content the component solubility of toluene decreases more rapidly than that of ethanol. For instance, in the sorption of an ethanol-toluene (1/1 by weight) mixture, a decrease from 1.42 to 0.37 g/g of dry polymer is observed for ethanol but a decrease from 0.11 to 0.005 g/g of dry polymer is observed for toluene with increasing PVA content from 10 to 40%.

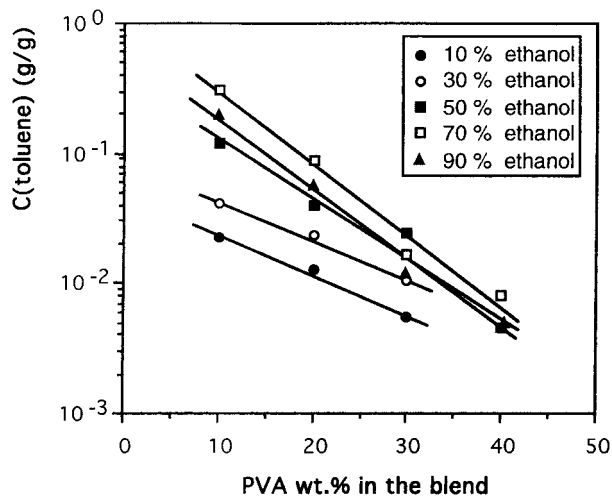


Figure 6. Component solubility of toluene $C(\text{toluene})$ in PAA-PVA blend membranes, as a function of the blend composition.

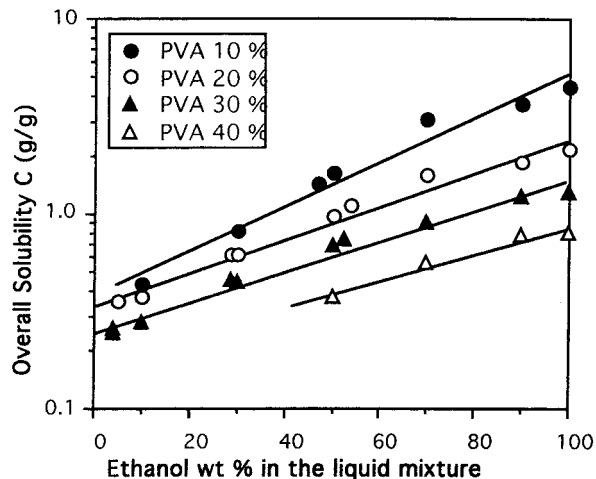


Figure 8. Overall solubility C of ethanol-toluene liquid mixtures in PAA-PVA blend membranes, as a function of liquid mixture composition.

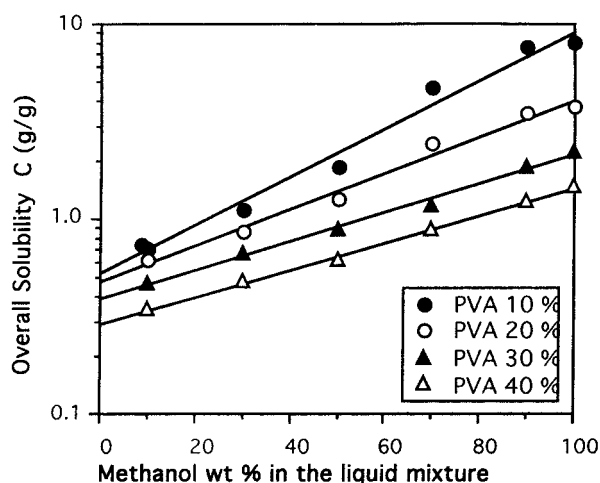


Figure 7. Overall solubility C of methanol-toluene liquid mixtures in PAA-PVA blend membranes, as a function of liquid mixture composition.

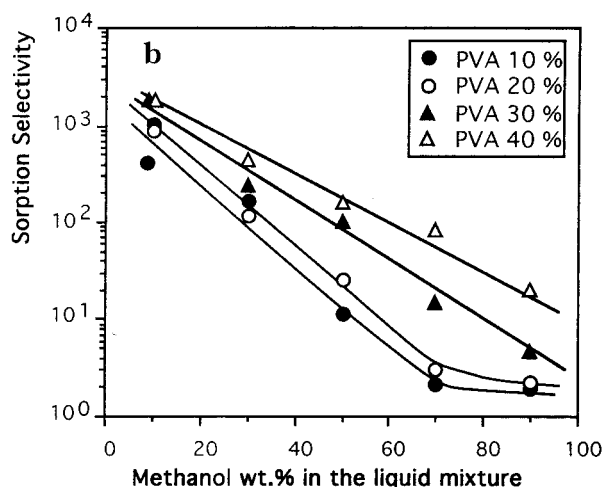
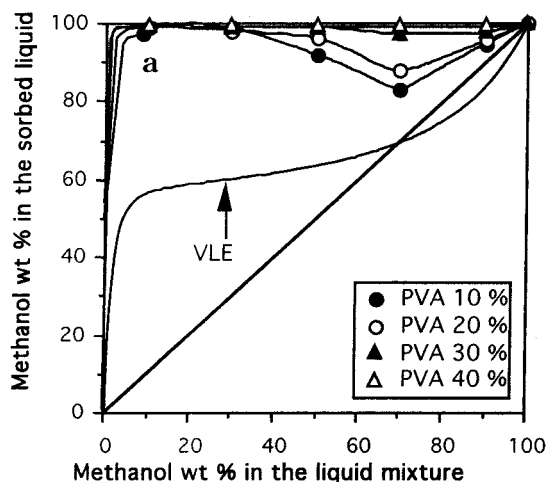


Figure 9. Composition of the sorbed liquid (a) and sorption selectivity (b) of methanol-toluene liquid mixtures in PAA-PVA blend membranes, as a function of liquid mixture composition.

Influence of the Liquid Mixture Composition. The influence of the liquid mixture composition on the sorption characteristics was investigated for methanol-toluene and ethanol-toluene liquid mixtures over the whole mixture composition range.

In Figures 7 and 8 the overall solubilities of these liquid mixtures in various PAA-PVA blends are given as a function of the liquid mixture composition, respectively. These figures show that all of the tested blends have a parallel swelling behavior for the methanol and the ethanol mixtures. The overall solubilities of both liquid mixtures increase exponentially with increasing alcohol content. This can be explained by the much better affinity of these alcohols toward the PAA-PVA blend compared to toluene. As the alcohol content in the liquid mixtures increases, the affinity of the liquid mixtures toward the blend increases and as a consequence the overall solubilities increase. In addition, the mass uptake of the methanol mixtures is about twice that of the ethanol mixtures over the whole mixture composition range. This indicates that the methanol mixtures have a higher affinity.

The influence of liquid mixture composition on the preferential sorption of both liquid mixtures is presented in Figures 9 and 10. From Figures 9a and 10a it can be seen that both alcohols are preferentially sorbed over

the whole feed composition range with alcohol concentrations of more than 80 wt % in the sorbed liquids. The equilibrium sorption selectivity values are given in Figures 9b and 10b. All tested blends show high sorption selectivities for the liquid mixtures containing small amounts of alcohol. However, the sorption selectivity decreases drastically with increasing alcohol

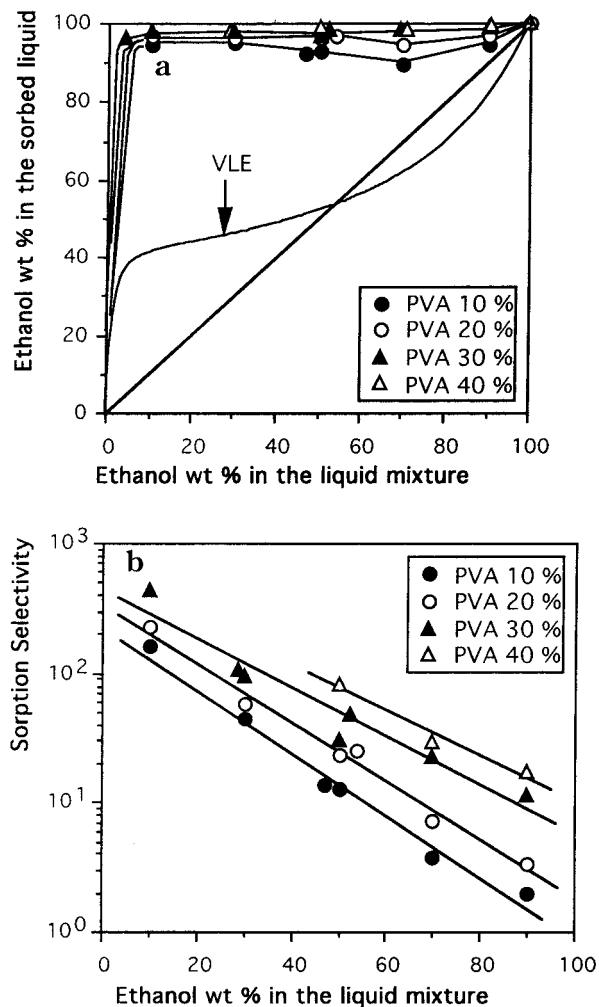


Figure 10. Composition of the sorbed liquid (a) and sorption selectivity (b) of ethanol-toluene liquid mixtures in PAA-PVA blend membranes, as a function of liquid mixture composition.

content in the liquid mixtures. At alcohol concentrations higher than 50 wt %, the sorption selectivity values of both liquid mixtures are almost equal. However, for the alcohol-lean feed compositions, the methanol mixtures show a selectivity much higher than that of the ethanol mixtures. The selectivity values for the methanol mixture at 10 wt % methanol range from 400 to 2000, while in the case of the ethanol mixture values of 200–500 are obtained for the same composition.

Prediction of the Preferential Sorption. The preferential sorption of a binary liquid mixture into a polymer membrane can be described by the following expression, which has been derived from Flory-Huggins thermodynamics (Mulder et al., 1985a):

$$\ln\left(\frac{\phi_1}{\phi_2}\right) - \ln\left(\frac{v_1}{v_2}\right) = (I-1)\ln\left(\frac{\phi_2}{v_2}\right) - g_{12}(v_2)(v_1 - v_2) + g_{12}(u_2)(\phi_1 - \phi_2) - \phi_3(\chi_{13} - I\chi_{23}) + u_1\phi_2 \frac{\partial g_{12}}{\partial u_2} - v_1 v_2 \frac{\partial g_{12}}{\partial v_2} \quad (4)$$

Indices 1 and 2 refer to the binary liquid components (taking 1 for the preferentially soluble liquid), and index 3 refers to the polymer membrane. v_i represents the volume fraction of liquid i in the binary liquid mixture.

Table 1. Physical Properties of Ethanol and Toluene

liquid	M_w	molar volume (cm ³ /mol, 25 °C)	molar volume ratio of ethanol/toluene
ethanol	46.07	58.69	0.5493
toluene	92.15	106.85	

Table 2. Solubilities of Pure Ethanol and Toluene in PAA-PVA Blend Membranes and the Calculated Interaction Parameter Values

PVA content in the blend (wt %)	density of the blend (g/cm ³)	ethanol		toluene	
		solubility (g/100 g)	χ_{13}	solubility ^a (g/100 g)	χ_{23}
10	1.404	442	0.541	0.01	7.73
				0.1	5.44
20	1.388	214	0.583	0.01	7.74
				0.1	5.45
30	1.376	128	0.634	0.01	7.75
				0.1	5.46
40	1.358	80.3	0.706	0.01	7.76
				0.1	5.47

^a Assumed values.

The volume fraction of component i in the ternary polymeric phase is denoted by ϕ_i with $\phi_1 + \phi_2 + \phi_3 = 1$. The volume fraction of liquid i of the liquid mixture in the polymeric phase is denoted by $u_i = \phi_i / (\phi_1 + \phi_2)$. I is the ratio of molar volumes of liquids 1 and 2. This equation is very useful for understanding the influence of governing factors for the preferential sorption, as discussed in the appendix.

Equation 4 was used to predict the preferential sorption of ethanol-toluene mixtures in PAA-PVA blend membranes. In this case indices 1 and 2 refer to ethanol and toluene, respectively. Their physical properties are given in Table 1. The binary interaction parameter g_{12} between ethanol and toluene at 30 °C was calculated from the Wilson equation using vapor-liquid equilibrium data taken from the literature (Gmehling et al., 1988). The dependency of g_{12} on the volume fraction of toluene was fitted to a fourth-grade polynomial relation:

$$g_{12}(x) = 1.059 - 0.997x + 9.298x^2 - 17.688x^3 + 11.459x^4 \quad (5)$$

This relation was used not only for the liquid feed but also for the sorbed liquid under the assumption that g_{12} is only dependent on the liquid composition.

The binary interaction parameters between the liquid components and the polymer, χ_{13} and χ_{23} , were assumed to be concentration-independent and were calculated from the single liquid sorption data using eq 2. The sorption values of pure ethanol in the blend membranes and the calculated χ_{13} values are given in Table 2. In this calculation the linear additivity of partial molar volumes was assumed.

Unfortunately, it was impossible to obtain very precise data of the pure toluene sorption into the blend membranes because they were extremely low: less than 0.1 g/100 g of dry membrane for all tested blends. Therefore, the values of pure toluene sorption were assumed as 0.1 and 0.01 g/100 g of dry membrane to obtain χ_{23} values. The calculated χ_{23} values are given in Table 2.

To predict the preferential sorption by eq 3, one composition value should be known. For practical reasons ϕ_3 is used, since this parameter is obtained from overall sorption measurements.

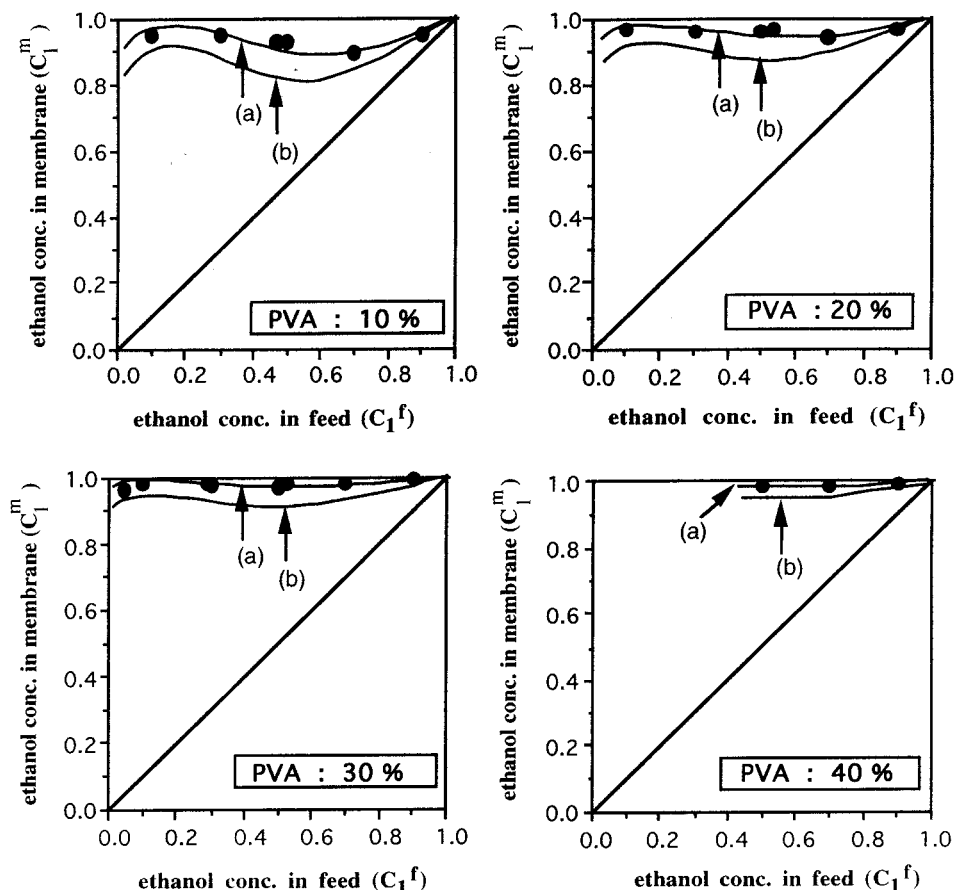


Figure 11. Ethanol concentrations in the sorbed liquid C_1^m as a function of the ethanol content in ethanol–toluene feed mixtures C_1^f for various PAA–PVA blend membranes: (●) experimentally measured and (–) predicted with assumed pure toluene solubilities of 0.01 (curve a) and 0.1 g/100 g of dry polymer (curve b).

The predicted and experimentally determined preferential sorption results are presented in Figure 11 for the blend membranes containing 10–40 wt % PVA. Here the ethanol fraction in the sorbed liquid C_1^m is plotted as a function of the ethanol fraction in the feed mixture C_1^f . When the pure toluene solubility was assumed to be 0.1 g/100 g of dry polymer, the predicted ethanol concentrations inside the membranes were lower than the experimentally measured ones in all cases tested. However, the liquid compositions in the membranes could be quantitatively predicted using a pure toluene solubility of 0.01 g/100 g of dry polymer.

Sorption versus Pervaporation. When a penetrant i diffuses through a membrane, the flux J_i is the product of the concentration C_i and the linear velocity k_i of the penetrant inside the membrane. The velocity is the product of mobility B_i and driving force. In the case of pervaporation, the driving force is a gradient in the chemical potential across the membrane, i.e., $-d\mu_i/dx$. Therefore, the following relation expresses the flux in a pervaporation process:

$$J_i = k_i C_i^m = -C_i^m B_i d\mu_i/dx \quad (6)$$

Taking ideal conditions and an empirical exponential relationship for the concentration dependence of the diffusion coefficient, eq 6 can be transformed into a Fickian equation (Mulder, 1991):

$$J_i = -D_i(C_i^m) dC_i^m/dx = -D_0 \exp(\gamma C_i^m) dC_i^m/dx \quad (7a)$$

Here, D_0 is the diffusion coefficient at zero concentration, and γ is an exponential constant.

In a vacuum pervaporation the penetrant concentration at the downstream side membrane interface can be considered to be zero. Integration of eq 7a with boundary conditions ($C_i = C_{i0}^m$ at $x = 0$ and $C_{iL}^m = 0$ at $x = L$) gives

$$J = (D_0/\gamma L)[\exp(\gamma C_{i0}^m) - 1] \quad (7b)$$

Here, L is the thickness of the membrane. From eq 7b it can be seen that the permeation rate of a penetrant is a function of the penetrant concentration in the membrane and increases with increasing penetrant concentration. In other words, the permeation rate of a penetrant is strongly dependent on the sorption ability of the penetrant into a polymer membrane.

In Figure 12, the pervaporation fluxes are plotted versus the overall sorption values for methanol–toluene and ethanol–toluene mixtures. This figure includes all of the experimental results obtained from PAA–PVA blend membranes containing 10–40 wt % PVA. Although the spreading around the curves is substantial, a relation between flux and overall solubility can be observed for both liquid mixtures. The pervaporation flux increases exponentially with the concentration of penetrants in the membrane. This may indicate a general observation in the pervaporation process that diffusivity is an exponential function of penetrant concentration in a membrane (Mulder, 1991).

In addition, a higher permeation rate of the methanol mixtures compared to that of the ethanol mixtures is

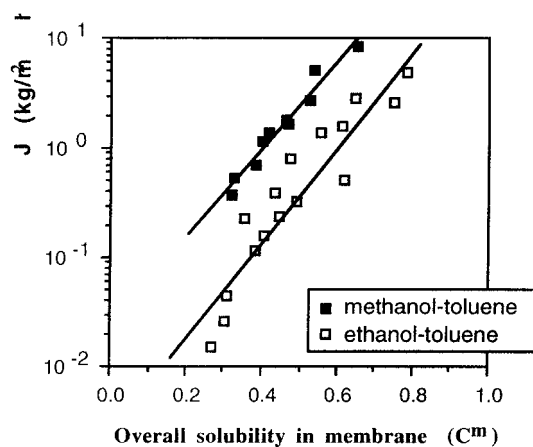


Figure 12. Relation between the pervaporation flux J and the overall equilibrium concentration C^m of the sorbed liquids in the PAA-PVA blend membranes.

observed over the whole penetrant concentration range. This might be caused by the difference in molecular size between methanol and ethanol. The flux and solubility of these alcoholic mixtures are to a large extent governed by the properties of the corresponding alcohols since the permeate and the sorbed liquid consist mainly of methanol or ethanol. Therefore, the methanol mixture can permeate faster since the molar volume of methanol is about two-thirds that of ethanol. It should be kept in mind that the penetrant concentration in the membrane is obtained from the equilibrium sorption experiments, whereas permeation is a nonequilibrium process. It is assumed that the sorption process is fast compared to the diffusion process, implying that the concentration at the feed side of the membrane interface during permeation is equal to the equilibrium concentration. This may not always be the case. Some examples are known where the penetrant concentration in the membrane at the feed side during pervaporation is lower than the equilibrium sorption value (Kim et al., 1970; Tock et al., 1974; Mulder et al., 1985b).

According to the solution-diffusion model, the pervaporation selectivity is determined by the differences in solubility and diffusivity of penetrants in a membrane. Therefore, by comparison of the pervaporation selectivity α_P and the sorption selectivity α_S , the influence of diffusion can be deduced in terms of a diffusion selectivity α_D defined by (Larchet et al., 1984; Spitzen et al., 1987).

$$\alpha_D = \alpha_P / \alpha_S \quad (9)$$

It should be realized that this equation has no quantitative meaning but serves only to compare sorption versus diffusion as a first estimate.

The diffusion selectivity value calculated in this way gives only qualitative information of the diffusion contribution to the separation in pervaporation, and no quantitative knowledge can be extracted from these values.

Tables 3 and 4 summarize the three different selectivities for methanol-toluene and ethanol-toluene mixtures, respectively, for the blend membranes containing PVA 10–40 wt %. The diffusion selectivity values calculated from eq 8 are very small and can be neglected compared to pervaporation and sorption selectivity values at least for the low alcohol feed compositions. The fact that diffusion selectivities which are

Table 3. Comparison of Pervaporation, Sorption, and Diffusion Selectivities for Methanol-Toluene Liquid Mixtures in PAA-PVA Blend Membranes

PVA in the blend (wt %)	selectivity (α)	methanol in the feed mixture (wt %)				
		10%	30%	50%	70%	90%
10	α_P	400	51			
	α_S	1038	169	11	2	2
	α_D	0.4	0.3			
20	α_P	900	69			
	α_S	873	119	25	3	2
	α_D	1.0	0.6			
30	α_P	1443	164	83	89	85
	α_S	1791	233	102	15	5
	α_D	0.8	0.7	0.8	5.9	17.0

Table 4. Comparison of Pervaporation, Sorption, and Diffusion Selectivities for Ethanol-Toluene Liquid Mixtures in PAA-PVA Blend Membranes

PVA in the blend (wt %)	selectivity (α)	ethanol in the feed mixture (wt %)				
		10%	30%	50%	70%	90%
10	α_P	344	73	22	9	10
	α_S	163	44	13	4	2
	α_D	2.1	1.7	1.7	2.3	5.0
20	α_P	723	116	42	13	19
	α_S	254	59	24	7	3
	α_D	2.8	2.0	1.8	1.9	6.3
30	α_P		180	82	15	23
	α_S	439	95	27	23	11
	α_D		1.9	3.0	0.7	2.1
40	α_P				35	43
	α_S			82	29	17
	α_D				1.2	2.5

smaller than 1 are obtained should be considered qualitatively only in comparison to the sorption selectivity, and it does not mean that the toluene diffusivity is faster.

From this comparison it can be concluded that the separation of alcohol-toluene mixtures by pervaporation is dominated by the preferential sorption, and diffusion is only of minor importance in this separation process.

Finally, sample history and relaxation phenomena are very important in separation processes where glassy polymers are used. Recently, it was shown (Park et al., 1995) that preconditioning of the film in a more interactive medium resulted initially in higher fluxes, which then gradually move to an equilibrium value. In the work presented here, preconditioning of the film prior to pervaporation took place in the testing medium.

Conclusions

From the single liquid sorption experiments it was observed that the solubility of the PAA-PVA blend membranes could be adjusted by controlling the PAA/PVA ratio in the blends. As the PVA content in the blends increases, the affinity for methanol and ethanol decreases, and thus the solubility of these alcohols decreases. The same dependency of the overall solubility on the blend composition was observed for methanol-toluene and ethanol-toluene mixtures. In addition, for both liquid mixtures the alcohols were preferentially sorbed into the blends and the sorption selectivity increased with an increasing amount of PVA.

The sorption measurements with methanol-toluene and ethanol-toluene liquid mixtures showed that the varying liquid mixture composition had a strong influence on the overall and preferential sorption. The

overall solubility in the PAA–PVA blends increased very much with increasing alcohol concentration in the liquid mixtures. In contrast, although alcohols were preferentially sorbed over the whole liquid composition range, the sorption selectivity decreased for all tested blends containing PVA of 10–40 wt %.

When the contribution of diffusion was evaluated by comparing the pervaporation selectivity with the sorption selectivity, it could be deduced that the preferential sorption dominated the pervaporation selectivity in the studied membrane–liquid mixture systems.

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Nomenclature

- a*: activity
B: mobility [(mol·m)/(N·s)]
C: concentration
D: diffusion coefficient (m²/s)
*D*₀: diffusion coefficient at zero concentration (m²/s)
g: concentration-dependent Flory–Huggins interaction parameter
J: flux [L/(m²·h)]
k: velocity (m/s)
L: membrane thickness (m)
P: permeability (m³(STP)·m/m²·s·cmHg)
Q: overall solubility (g/g)
R: gas constant [J/(mol·K)]
T: temperature (K)
u: volume fraction of liquid in the polymer phase related to penetrants only
v: volume fraction in the binary feed mixture
x: concentration in the feed
y: concentration in the permeate

Greek Letters

- α : selectivity factor
 χ : Flory–Huggins interaction parameter
 γ : plasticization constant
 ϕ : volume fraction in the ternary polymer phase

Indices

- 0: feed side of the membrane
 1: alcohol
 2: toluene
 3: polymer
D: diffusivity
i: penetrant *i*
m: membrane
p: polymer
P: permeability
S: solubility

Appendix

Thermodynamic Analysis of Preferential Sorption. On the basis of the Flory–Huggins thermodynamics of mixing, a mathematical model has been derived (Mulder et al., 1985a,b) for the description of the preferential sorption phenomena (eq 4). This equation is very useful for understanding the influence of the factors determining the preferential sorption.

Effect of Affinity of Individual Liquids toward the Membrane. The sorption of a binary liquid mixture in a polymer is to a great extent related to the

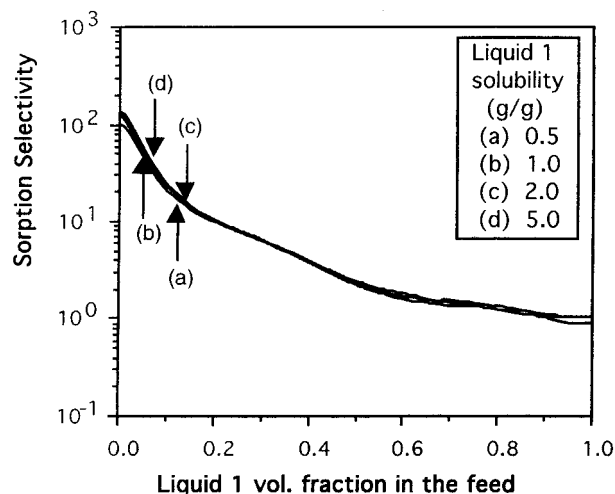


Figure 13. Influence of the pure liquid solubility of the more soluble component, liquid 1, on the sorption selectivity. The solubility of the less soluble component is kept constant at 0.05 g/g of dry polymer.

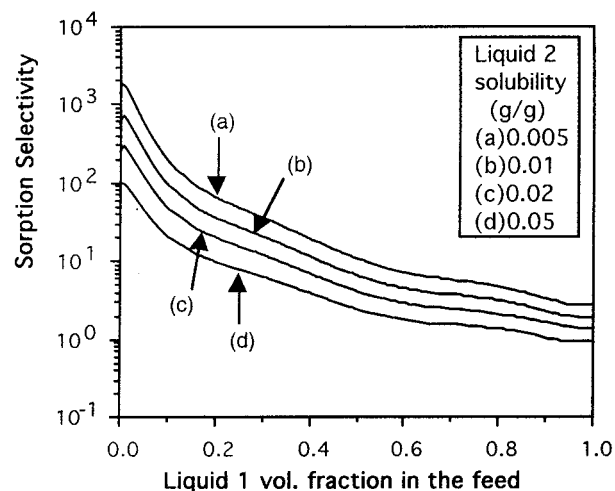


Figure 14. Influence of the pure liquid solubility of the less soluble component, liquid 2, on the sorption selectivity. The solubility of the more soluble component is kept constant at 0.5 g/g of dry polymer.

affinity of the components toward the polymer membrane. When the affinity of one liquid is varied while the affinity of the other liquid is kept constant, the preferential sorption will be changed. This effect can be demonstrated by numerical calculations using eq 4. The results are given in Figures 13 and 14. In these calculations all parameters except for the solubility were taken for an ethanol–toluene liquid mixture and a PAA–PVA (8/2 by weight) blend membrane. The overall solubility of a binary mixture was assumed to be proportional to the solubilities of single components.

In the first example the influence of the affinity of the more soluble component, liquid 1, on the preferential sorption was investigated (Figure 13). In this example, the pure liquid solubility of liquid 1 was varied from 0.5 to 5 g/g (gram of sorbed liquid per gram of dry polymer), while that of the less soluble component, liquid 2, was kept constant at 0.05 g/g. This figure shows that although the liquid 1 solubility increases by up to 1 order of magnitude, the sorption selectivity is hardly influenced. In the second example, however, the pure liquid solubility of liquid 2 was varied from 0.005 to 0.05 g/g, while that of liquid 1 was kept constant at

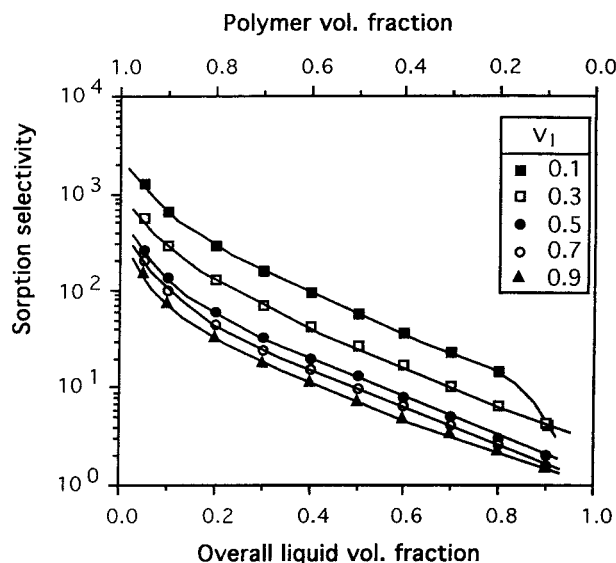


Figure 15. Influence of the polymer volume fraction on the sorption selectivity. The binary interaction parameters between the membrane and the liquid components are kept constant as $\chi_{13} = 0.58$ and $\chi_{23} = 5.45$.

0.5 g/g (Figure 14). From this figure it can be seen that an increasing solubility of the less soluble component has a much larger effect. For instance, a solubility increase from 0.005 to 0.05 g/g for liquid 2 results in a decrease in sorption selectivity of roughly 1 order of magnitude over the whole feed concentration range.

From these calculations it can be concluded that with respect to selectivity it is preferred to decrease the solubility of the less soluble component rather than to increase the solubility of the preferentially soluble component.

Overall Sorption versus Preferential Sorption.

In the sorption of a binary liquid mixture in a polymer it is quite often observed that as the overall solubility increases, the sorption selectivity decreases, or vice versa. This phenomenon can also be predicted from the same equation. In these calculations all parameters were also taken for an ethanol-toluene liquid mixture and a PAA-PVA (8/2 by weight) blend membrane, and these parameters were kept constant. Only ϕ_p , the volume fraction of the polymer membrane, was varied; the overall solubility of a liquid mixture is represented by the overall liquid volume fraction ($=1 - \phi_p$). The results are given in Figure 15. For liquid mixtures with different compositions, the sorption selectivity decreases as the overall liquid volume fraction increases. This clearly confirms a so-called "tradeoff" trend between the overall and preferential sorption. Furthermore, a similar phenomenon in permeation, i.e., a decreasing selectivity with an increasing permeability, or vice versa, can be predicted from this calculation.

The effect of cross-linking can also be verified from this result: when a membrane is cross-linked, the sorption selectivity increases with a decreasing overall solubility. Under the assumption that the interaction parameter between a solvent and a polymer membrane does not vary with cross-linking, it can be seen from the Flory-Rehner theory that the polymer volume fraction decreases with increasing cross-linking density (Spitzen, 1988).

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