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# Separation of a Toluene/Ethanol Mixture by Pervaporation Using Active Carbon-Filled Polymeric Membranes

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## ABSTRACT

In order to improve the separation properties of dense polymeric membranes toward a toluene/ethanol mixture, various active carbons and two types of zeolites were introduced into a thin polymeric film in order to form a heterogeneous membrane composed of solid particles surrounded by a polymer phase. Active carbons show a high adsorption selectivity for an aromatic compound over ethanol in the low concentration range of the aromatic component. Sorption and pervaporation experiments were carried out with a toluene/ethanol mixture, and they showed no improvement in selectivity and a decrease in flux for membranes filled with active carbons. For zeolite-filled membranes, both selectivity and flux decreased. A permeability model derived for heterogeneous systems was used. It confirmed that the carbon particles have a closed porous structure, allowing no transport from one side to the other, and that the zeolites have an ethanol selective permeation behavior.

## INTRODUCTION

In order to influence separation performance, the incorporation of carbonaceous materials into a polymeric membrane has been investigated. Active carbons are widely used in adsorption processes because of their high adsorption selectivities toward certain compounds (chlorinated hydrocarbons in water; for example, Refs. 1 and 2). In addition, the molecular sieving properties can be applied in the field of gas separation [oxygen/nitrogen and carbon dioxide/methane separation by pressure swing adsorption (3, 4)]. This work was undertaken to enhance the flux and selectivity of a dense polymeric membrane by incorporation of active carbons, based on the selective properties of these materials to increase preferential sorption. From the literature it is known that the addition of silicalite-1 in silicone rubber membranes results in an increase of both flux and selectivity for alcohol in the separation of alcohol/water by pervaporation (5).

Active carbons show a high preferential adsorption selectivity for aromatic compounds in solution with alcohols, especially in the low concentration range of the aromatic compound (6–9). This behavior was experimentally observed from adsorption experiments in the liquid phase. Hence, the separation of a mixture of toluene and ethanol by pervaporation was investigated, using active carbons with various porous structures and two zeolitic adsorbents as microporous fillers. Finally, the pervaporation results are interpreted in terms of a permeability model which was derived for heterogeneous systems (10, 11).

## MATERIALS

### Active Carbons and Zeolites

A complete and detailed description of the specific characteristics of active carbons is beyond the scope of this study. In summary, active carbons are porous carbonaceous materials manufactured from various raw materials (coal, wood, polymers). Their internal porous volume and pore size are strongly dependent on the raw material used and the manufacturing process, i.e., the activation conditions. For instance, the internal surface area can reach values up to 1500 $m^2/g$ and a porous volume of 2 $cm^3/g$. Pores are found in the range of molecular dimensions (submicropores, diameter $< 1$ nm) as well as in the macroporous range (diameter $> 100$ nm). For more details, the reader should consult Refs. 12 and 13.

The active carbons used in this study were kindly supplied by CECA S.A. (France) and NORIT N.V. (The Netherlands). Table 1 gives the characteristics of the different active carbon samples used according to data given by the two manufacturers.

The active carbons available have quite different porous volumes, going from a rather macroporous structure (CP, SX Ultra) to a molecular sieving one (Cecalite, W20). Furthermore, a carbon black, Printex 60 (Degussa, Germany), was used as a nonporous reference filler with a particle size of 21 nm and a BET surface area of 115 $m^2/g$. This, for example, can be compared to a value of 1300 $m^2/g$ for the active carbon 4S.

Besides active carbons, two different zeolites were used. Zeolites are crystalline aluminosilicates whose internal structure forms a network of microvoids and pores. Pore size is typically in the molecular sieving range (<1 nm) (see Refs. 14–16). The first zeolite investigated was NaY with a Si/Al ratio of 20. This high ratio makes this zeolite less hydrophilic than the normal zeolite NaY (Si/Al = 2.7); thus the former presumably is toluene selective with respect to sorption. The pore size of this zeolite is 7.4 Å. Furthermore, silicalite-1 (UOP, USA), the pure siliceous form of zeolite ZSM-5, was also investigated because of its organophilic properties (17). This zeolite has a pore size of about 5.5 Å.

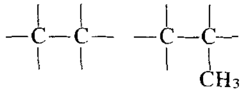
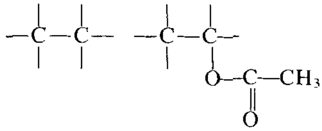
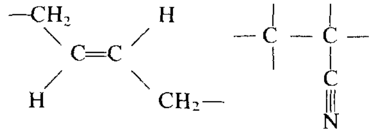
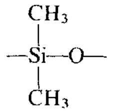
## Polymers

Active carbons are sorption selective for aromatic compound in a mixture with an alcohol, and consequently polymers have to be chosen with a selectivity for the aromatic compound as well. Hydrophobic polymers meet this requirement. Ethylene–propene rubber (Keltan 578, DSM) was used as a first choice. Furthermore, an ethylene–vinyl acetate copolymer [Elvax 150 (33% vinyl acetate), DuPont], silicone rubber [polydimethylsi-

TABLE 1
Active Carbon Characteristics (data from manufacturers)

| Active carbon | $V_{tot}$, $cm^3 \cdot g^{-1}$ | $V_{micro}$, $cm^3 \cdot g^{-1}$ | Bulk density, $g \cdot cm^{-3}$ |
|---|---|---|---|
| CP | 2.10 | 0.25 | 0.27 |
| 4S | 0.97 | — | 0.31 |
| L4S | 0.97 | — | 0.31 |
| GAC 1240 | 0.95 | 0.35 | 0.48 |
| Cecalite | 0.52 | 0.18 | 0.63 |
| SX Ultra | 1.40 | 0.39 | 0.29 |
| SA2 | 0.95 | 0.31 | 0.41 |
| W20 | 0.55 | 0.22 | 0.60 |

TABLE 2
Overview of the Polymers Investigated

| Polymer | Molecular structure | Density, g·cm$^{-3}$ |
|---|---|---|
| Ethene-propene rubber (EPDM), Keltan 578 |  | 0.86 |
| Poly(ethylene-vinyl acetate), 33% vinyl acetate (EVA), Elvax 150 |  | 0.95 |
| Nitrile butadiene rubber (NBR), 27, 34, 45% acrylonitrile, Krynac 2750, 3450, 4550 |  | 0.98 |
| Polydimethylsiloxane (PDMS), RTV 615 |  | 1.02 |

loxane (PDMS), prepared from RTV 615 A and RTV 615 B, General Electric] and a series of nitrile butadiene rubbers with various amounts of acrylonitrile (NBR, Krynac 2750, 3450, and 4550, Polysar) were investigated (27, 34, and 45 represent the acrylonitrile content based on NBR). Table 2 gives an overview of these different polymers.

## EXPERIMENTAL

### Adsorbent Preparation

### *Active Carbons*

The active carbons used had to be ground before incorporation into the polymeric matrix because particles up to 150 μm were present in the samples provided. Grinding was achieved by stirring the carbon particles with glass balls in ethanol for several weeks. This mild process resulted in particle sizes below 10 μm as observed by scanning electron microscopy. The active carbons were then activated at 150°C for 24 hours under vacuum and stored under vacuum at room temperature.

### *Zeolites*

Prior to use, the zeolite NaY was activated at 350°C for 2 hours and then kept in a vacuum oven. In the case of silicalite-1, activation was carried out at 500°C in order to calcine the organic template employed during the synthesis.

## Membrane Preparation

### *Ethylene–Propene Rubber (EPDM), Nitrile–Butadiene Rubber (NBR), and Poly(Ethylene–Vinyl Acetate) (EVA) Membranes*

The adsorbent was first stirred in the solvent (*n*-hexane for EPDM, chloroform for EVA and NBR) for 2 hours in order to break the particle clusters. The polymer was then added, and stirring was carried out until a homogeneous dispersion was obtained. Dicumylperoxide (Merck) was used as a crosslinking agent in the case of EPDM (6 wt%) and EVA (4 wt%). Dibenzoylperoxide (Merck) was used in the case of NBR (10 wt%). The solution was stirred for 2 more hours and then cast on a Teflon plate after air bubbles had been removed. Evaporation was carried out overnight under a nitrogen stream and followed by a crosslinking reaction at 155°C for 1 hour in a nitrogen atmosphere for dicumylperoxide curing and at 110°C for 45 minutes for dibenzoylperoxide. The resulting membranes were about 100 μm thick.

The solvents (analytical grade) for dissolving the polymers and the crosslinking agents were used without further purification.

### *Polydimethylsiloxane (PDMS) Membranes*

The two components of RTV 615 (prepolymer and curing agent in a 9:1 ratio) were mixed with the active carbon until a homogeneous dispersion was obtained. After removal of air bubbles, the paste obtained this way was cast on a Teflon plate. The crosslinking reaction was carried out at 80°C for 16 hours. The resulting membranes were about 100 μm thick.

## Adsorption Experiments

The characterization of porous adsorbents with respect to their sorption selectivity in the liquid phase has not yet been very well described. Often a species which does not sorb is used as a reference to calculate sorption selectivities (with zeolites as adsorbent, for example). However, in the case of active carbons, the broad pore size distribution makes the selection of a nonadsorbable component impossible. Nevertheless, it is possible to compare different adsorbents by a depletion method.

In this method a standard amount of adsorbent ($m$ = 1 g) is incorporated into a standard amount of a liquid mixture ($m_0$ = 10 g) with a certain composition which is determined by gas chromatography. After sorption equilibration (24 hours at 30°C was applied), the liquid phase is analyzed again and the change in its composition determines the depletion in the weight fraction of one of the components, $\Delta x$. Then the surface excess $m_0 \Delta x / m$ can be calculated, which allows comparisons of the different adsorbents with respect to their adsorption selectivity for a component, e.g., for toluene. The same method can be used with a polymer and a filled polymer. These experiments were carried out with 10 wt% toluene in ethanol and also with 10 wt% ethanol in toluene.

### Pervaporation Experiments

The pervaporation experiments were carried out with a mixture of toluene and ethanol (10 and 90 wt%, respectively) by using a standard setup, described elsewhere (18). The temperature of the feed mixture was kept at 30°C and the downstream pressure below 0.1 mbar. Steady-state conditions were reached after 3 hours. Then the first sample of permeate was collected in the liquid nitrogen cold trap and analyzed by gas chromatography. This was repeated over a period of 2 to 4 days in order to control the variation in time.

## RESULTS

### Adsorption by Depletion

Table 3 and Fig. 1 summarize the results obtained from the depletion method with active carbons, zeolites, and pure polymers. In Table 3 a positive sign means preferential adsorption of the minor component in the liquid mixture.

In a mixture consisting of 10 wt% toluene in ethanol, the carbons show a much larger surface excess than the organophilic zeolite silicalite-1 (Fig. 1). This is the result of the larger porous volume of the carbons. Furthermore, the effect of aluminum content in the zeolite framework can be seen in the case of zeolite NaY. For example, NaY with a Si/Al ratio of 2.7 is ethanol selective, whereas NaY with a Si/Al ratio of 20 is slightly selective for toluene.

This could be expected because the aluminum atoms in the framework bear a negative charge which is balanced by a counterion, thus making the surface more hydrophilic depending on the amount of aluminum. Hence,

TABLE 3
Adsorption Experiments by the Depletion Method; a Positive Value Indicates Preferential Sorption of the Minor Component in the Liquid Mixture; $T = 30°C$

| Adsorbent | Surface excess | |
|---|---|---|
| | Toluene 10/ethanol 90 | Toluene 90/ethanol 10 |
| CP | 20 | — |
| 4S | 14 | — |
| L4S | 13.5 | — |
| GAC 1240 | 12.7 | — |
| Cecalite | 10.4 | — |
| SX Ultra | 14 | — |
| SA2 | 12.1 | — |
| Printex 60 | 0.8 | — |
| Silicalite-1 | 0.4 | — |
| NaY Si/Al = 2.7 | −1.6 | 25.6 |
| NaY Si/Al = 10 | −0.3 | — |
| NaY Si/Al = 20 | 0.2 | 19.7 |
| EPDM | 6 | — |
| PDMS | 5.1 | — |
| EVA | 5.2 | — |

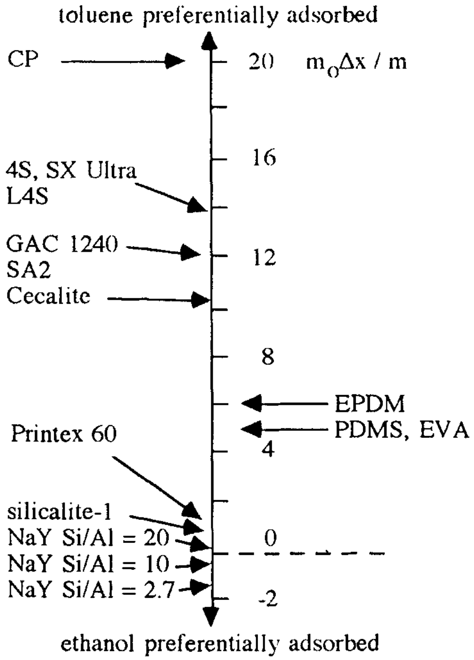


FIG. 1 Adsorption experiments by the depletion method. Surface excess obtained with 10 g feed (10 wt% toluene in ethanol) and 1 g adsorbent or polymer.

decreasing the amount of aluminum results in a less hydrophilic zeolite. The carbon black (Printex 60) does not show a very large surface excess for toluene due to its nonporous structure, i.e., adsorption can only take place on its external surface.

The polymers used in this study were also tested. The surface excess values obtained are much lower than those of the active carbons, which means that the polymers considered are less sorption selective than the active carbons (the experiments were performed with the same amounts of sorbent and liquid feed) or sorb less.

On the other hand, the hydrophobic zeolites do not seem to be selective enough to improve the separation properties of the polymers.

In Table 3 it can be seen that with a mixture of 10 wt% ethanol in toluene, the more hydrophilic zeolites NaY resulted in a large surface excess for ethanol, which means that in this concentration range they are selective for ethanol. Here, again, a larger amount of aluminum results in a more ethanol selective behavior.

## Pervaporation

The selectivity for a liquid mixture is defined as

$$\alpha_{\text{toluene/ethanol}} = \frac{\left(\dfrac{x_{\text{toluene}}}{y_{\text{ethanol}}}\right)_{\text{permeate}}}{\left(\dfrac{x_{\text{toluene}}}{y_{\text{ethanol}}}\right)_{\text{feed}}}$$

and the flux values have been normalized to a membrane thickness of 100 μm.

### Unfilled Polymers

Table 4 shows the pervaporation results obtained with the various polymers investigated.

One can see from Table 4 that PDMS and EVA are high flux polymer materials with a rather low selectivity for toluene.

The series of NBR shows a decreasing organic flux and toluene selectivity when the acrylonitrile content increases. The larger the amount of acrylonitrile, the better the chemical resistance of the polymer and the lower the overall sorption, and, consequently, a decrease of the total organic flux can be observed. On the other hand, acrylonitrile segments make the polymer matrix more hydrophilic and rigid than polybutadiene, which means that the larger the amount, the more ethanol sorption and

TABLE 4
Pervaporation Properties of Various Rubbery Polymers; Feed: Toluene/Ethanol (10/90 wt%); $T$ = 30°C

| Membrane | $\alpha_{\text{toluene/ethanol}}$ | $J_{100\mu m}$, $g \cdot m^{-2} \cdot h^{-1}$ |
|---|---|---|
| NBR 45 | 3.4 | 70 |
| NBR 34 | 4.6 | 145 |
| NBR 27 | 5.6 | 194 |
| EVA | 8.9 | 300 |
| PDMS | 13 | 800 |
| EPDM | 62 | 60 |

diffusion selective the matrix, which can explain the decrease in toluene selectivity.

EPDM is the most selective polymer investigated but shows the lowest total flux.

### Active Carbon-Filled Membranes

Figures 2 and 3 show the variation of the selectivity and flux for various active carbons incorporated into an EPDM matrix.

All these results show that the selectivity of the membrane remains mainly constant when an active carbon is incorporated into the polymeric matrix for all carbons tested. On the other hand, the total flux through the membrane is decreased drastically by the addition of these carbon particles.

Furthermore, one can see from Table 5 that polymers with different separation performances for the mixtures studied (large flux and low selectivity or low flux and high selectivity) show the same behavior upon addition of active carbon particles. The porous structure of the latter has no effect, i.e., active carbons with large pores or a carbon molecular sieve (Table 1) do not show any difference with respect to the pervaporation performance.

The results obtained with the carbon black Printex 60 are also plotted in Figs. 2 and 3. This nonporous carbonaceous material shows the same behavior as porous active carbons with respect to the pervaporation selectivity and a somewhat larger decrease of the total flux at equal volume fraction of particles in the membrane. This last phenomenon could be due to the very small particle size (20 nm) of carbon black, which results in a much larger contact surface area between the polymer and the carbon phase than with particles in the micrometer range. This may affect the

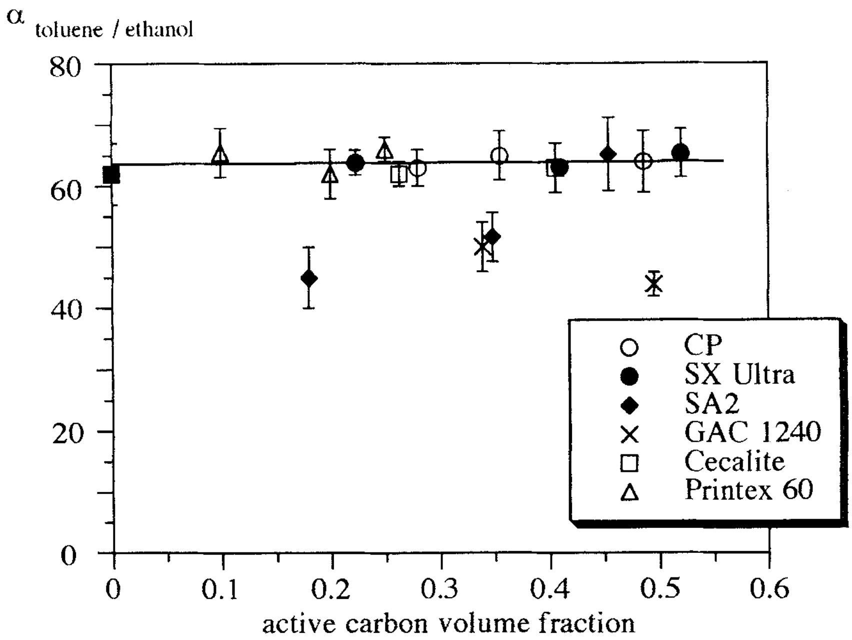


FIG. 2 Pervaporation selectivity of active carbon-filled EPDM membranes versus the volume fraction of active carbon in the membrane. Feed: toluene/ethanol (10/90 wt%); $T$ = 30°C.

TABLE 5

Effect of Active Carbons on the Pervaporation Properties of Various Polymers; Feed: Toluene/Ethanol (10/90 wt%); $T$ = 30°C

| Membrane | $\alpha_{toluene/ethanol}$ | $J_{100\mu m}$, $g \cdot m^{-2} \cdot h^{-1}$ |
|---|---|---|
| EPDM | 62 | 60 |
| EPDM + CP 48.6 vol% | 64 | 21 |
| EPDM + SX Ultra 52 vol% | 65 | 27 |
| EPDM + W20 28 vol% | 70 | 27 |
| EPDM + NaY20 31 vol% | 26 | 36 |
| EVA | 8.9 | 300 |
| EVA + CP 45 vol% | 7.9 | 225 |
| EVA + 4S 24 vol% | 9.4 | 180 |
| NBR 45 | 3.4 | 70 |
| NBR 45 + SX Ultra 44 vol% | 3.7 | 43 |
| NBR 45 + SX Ultra 55 vol% | 3.4 | 37 |
| PDMS | 13 | 800 |
| PDMS + W20 31 vol% | 14 | 570 |

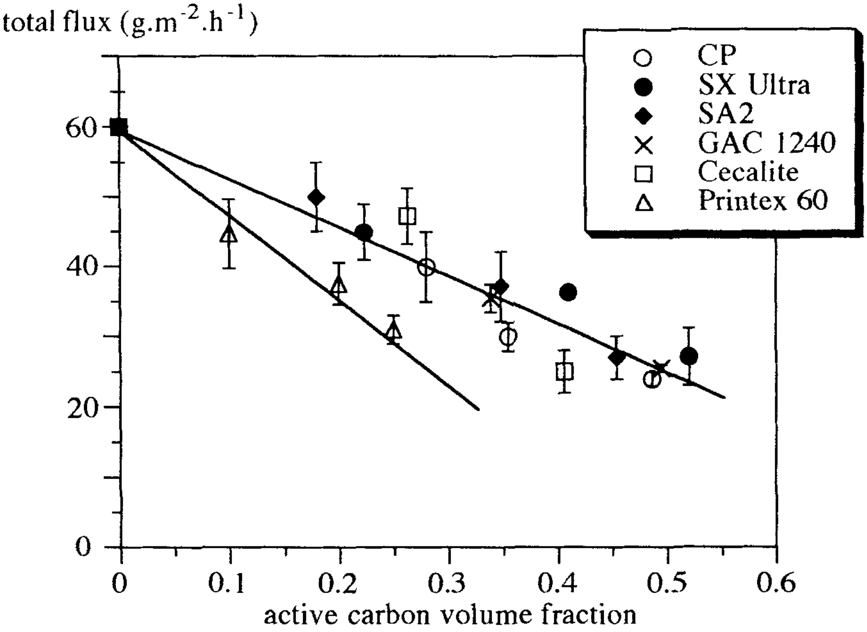


FIG. 3 Total pervaporation flux (normalized to a membrane thickness of 100 μm) through active carbon-filled EPDM membranes versus the volume fraction of active carbon in the membrane. Feed: toluene/ethanol (10/90 wt%); $T$ = 30°C.

physical crosslinking of the polymer matrix to some extent, as was described by te Hennepe (11) and Briscoe et al. (19).

### Zeolite-Filled Membranes

In Table 5 and Fig. 4, the pervaporation data obtained for the polymer EPDM, pure and with zeolites NaY (Si/Al = 20) and silicalite-1, are given. One can observe that the trend is the same as with active carbons with respect to the flux through the membrane and, in addition, a decrease of the selectivity was measured by incorporation of these zeolites into the polymer matrix. These results will be discussed in a following section.

In order to understand the transport phenomena through these filled membranes better, the results have been modeled as described in the following section.

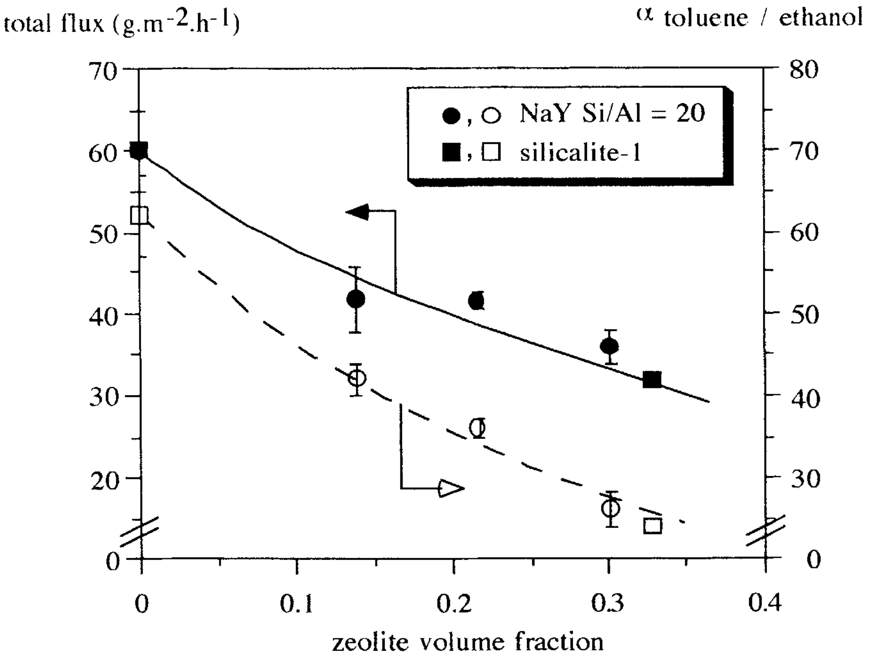


FIG. 4 Toluene/ethanol pervaporation selectivity and total pervaporation flux (normalized to a membrane thickness of 100 μm) of zeolite-filled EPDM membranes versus the volume fraction of zeolite in the membrane. Feed: toluene/ethanol (10/90 wt%); $T$ = 30°C.

## MODELING

### Development of the Model

The model used in our study was developed by te Hennepe et al. (10) for the pervaporation of alcohol/water mixtures by means of silicalite-1 filled silicone rubber membranes. Only the final equation will be given here.

However, it must be said that the geometric factor determined for silicalite-1 particles is not the same as that for active carbons. In the case of silicalite-1, the particles could be considered as cubic whereas the carbon particles used in our study do not have a very well determined shape, which makes the estimation of this parameter difficult. As a first estimate, the same value was used as for silicalite-1.

The equation for the pure component flux $J_i$, is

$$J_i = \Delta p_i \Bigg/ \left( \frac{(1 - \phi_c^{1/3})d}{P_{r,i}} + \frac{\frac{3}{2}\phi_c^{1/3}d}{P_{r,i}(1 - \phi_c) + \frac{3}{2}P_{c,i}\phi_c} \right) \tag{1}$$

in which $J_i$ = flux of pure component $i$ ($g \cdot m^{-2} \cdot h^{-1}$)

$p_i$ = partial pressure gradient of species $i$ across the membrane (mmHg)

$\phi_c$ = volume fraction of carbon in the membrane (—)

$d$ = thickness of the membrane (m)

$P_{r,i}$ = rubber permeability for component $i$ ($g \cdot m \cdot m^{-2} \cdot h^{-1} \cdot mmHg^{-1}$)

$P_{c,i}$ = carbon permeability for component $i$ ($g \cdot m \cdot m^{-2} \cdot h^{-1} \cdot mmHg^{-1}$)

$P_{r,i}$ is determined from pervaporation data with unfilled membranes. In this case, Eq. (1) is reduced to

$$J_i = \Delta p_i(P_{r,i}/d) \qquad (2)$$

The value of $\Delta p_i = (p_{i,\text{feed side}} - p_{i,\text{permeate side}})$ is calculated by assuming $p_{i,\text{permeate side}} = 0$ (vacuum at the downstream side of the membrane) and with Eq. (3) for the $p_{i,\text{feed side}}$:

$$p_{i,\text{feed side}} = c_{i,\text{feed side}} \gamma p_i^\circ \text{ (mmHg)} \qquad (3)$$

where $c_{i,\text{feed side}}$ = concentration in the liquid feed mixture (mole fraction)

$\gamma$ = activity coefficient calculated from the Margules equation

$p_i^\circ$ = calculated from the Antoine equation

The model implicitly assumes that both rubber and adsorbent permeabilities are independent of the adsorbent content of the membrane. For more details about the model, consult Refs. 10 and 18.

## RESULTS

By fitting Eq. (2) to the results obtained with pure EPDM, the following values are found:

$$P_{r,\text{toluene}} = 672.3 \times 10^{-6} \text{ g} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{mmHg}^{-1}$$

$$P_{r,\text{ethanol}} = 10.2 \times 10^{-6} \text{ g} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{mmHg}^{-1}$$

These two values are used in Eq. (1) to determine $P_{c,\text{toluene}}$ and $P_{c,\text{ethanol}}$. Two different carbons were considered: CP and SX Ultra. They were chosen because of their large porous volumes (see Table 1). The same model was also applied to the results obtained with the zeolite NaY with a Si/Al ratio of 20. The adsorbent permeability was taken as a variable to fit the calculated fluxes $J_i$ to the experimental data. The results are given in Figs. 5 to 7.

A very satisfactory agreement can be observed between the experimental data and the model fit. The fitting parameters are given in Table 6.

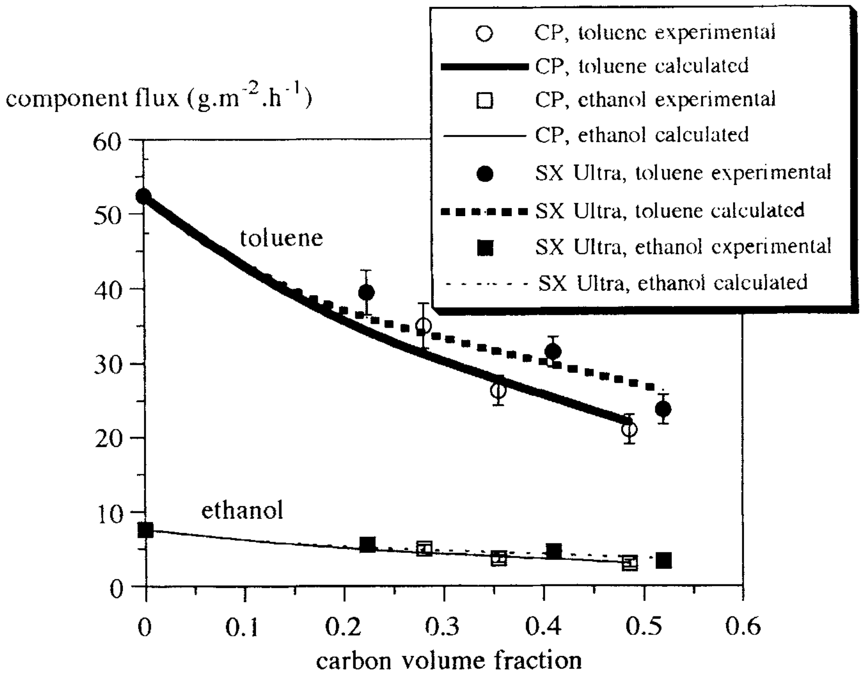


FIG. 5 Experimental and calculated component fluxes for CP and SX Ultra-filled EPDM membranes.

## DISCUSSION

The permeability values obtained confirm that the active carbon CP is essentially impermeable to toluene and ethanol in comparison with the polymer phase EPDM. In the case of SX Ultra, the permeabilities are roughly lower than those of EPDM by a factor of 4. The reason for such a behavior is the morphology of the pores inside the particles. One can imagine that if the pores are not interconnected, there is no pathway from one side of a particle to the other. Hence the sorbed molecules will not

TABLE 6
Toluene and Ethanol Permeabilities of Various Adsorbents

| Permeability coefficient | CP | SX Ultra | NaY Si/Al = 20 |
|---|---|---|---|
| $P_{i,\text{toluene}}$, g·m·m$^{-2}$·h$^{-1}$·mmHg$^{-1}$ | 27.8 × 10$^{-6}$ | 165.2 × 10$^{-6}$ | 0 |
| $P_{i,\text{ethanol}}$, g·m·m$^{-2}$·h$^{-1}$·mmHg$^{-1}$ | 0 | 2.1 × 10$^{6}$ | 29.4 × 10$^{-6}$ |

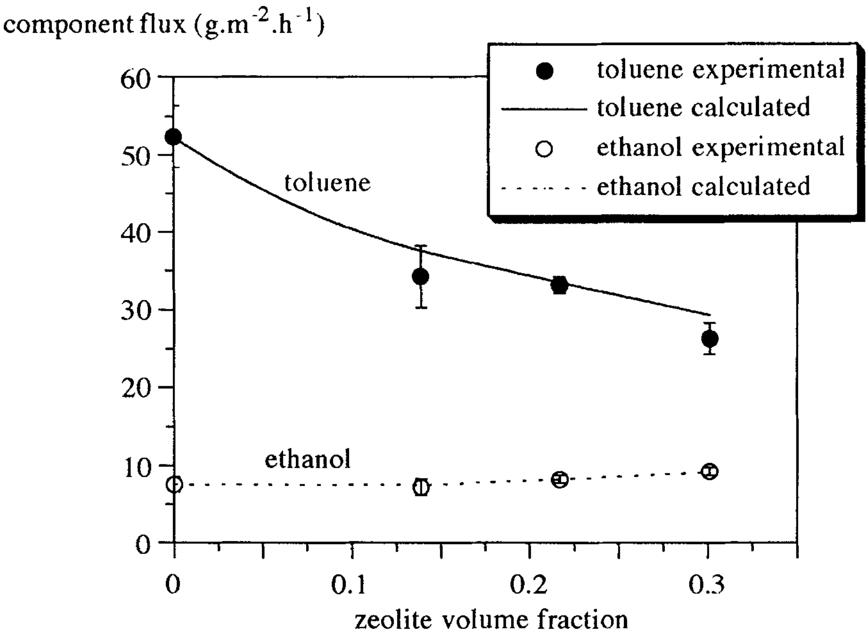


FIG. 6 Experimental and calculated component fluxes for NaY 20-filled EPDM membranes.

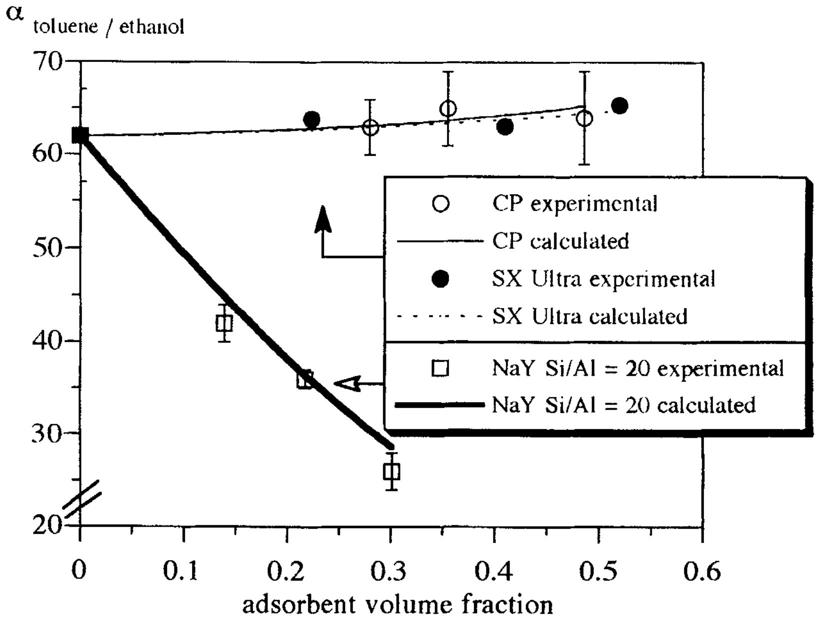


FIG. 7 Experimental and calculated selectivity for filled EPDM membranes.

diffuse out, and the particles just act like immobilizing sites for the permeant. The results suggest that SX Ultra exhibits a somewhat more interconnected structure than CP.

On the other hand, the pervaporation results obtained with the zeolite NaY with a Si/Al ratio of 20 can be explained by an ethanol selective permeation behavior, though the adsorption experiments revealed a selective character slightly in favor of toluene. A molecular sieving effect by size exclusion must then be the mechanism involved, i.e., the large toluene molecules (kinetic diameter 6.5 Å) diffuse much slower than the ethanol molecules (kinetic diameter 4.5 Å). The final result is a decrease of the toluene flux and an increase of the ethanol flux, and thus a decrease of the selectivity for toluene. For this adsorbent the porous structure is open, and this allows the molecules to diffuse from one side of the particles to the other. The same mechanism can be used to explain the experimental results obtained with silicalite-1 (Fig. 4). However, the "zeolite permeabilities" given in Table 6 should not be considered as intrinsic properties of the zeolite. They are characteristic of one zeolite in one polymer phase and in the experimental conditions of the present study (see Ref. 18 for more details).

## CONCLUSIONS

In the pervaporation of toluene/ethanol mixtures, active carbons incorporated into various polymer phases do not result in an improvement of the selectivity for toluene. Furthermore, the total flux decreases drastically with an increasing amount of active carbons, and the effect of using a variety of porous structures cannot be established. This is due to the closed pore structure of the carbons. This means that even a highly selective adsorption for toluene by the active carbon has no influence on the selectivity when used in a membrane.

The results clearly indicate that an open pore active carbon has to be used. In principle, such materials can be produced by the pyrolysis of polymers [polyvinylidene chloride for instance (20, 21)] to form a carbon molecular sieve membrane.

The effect of open pore zeolites like NaY 20 is quite different. A molecular sieving of toluene is observed in this case, whereas ethanol diffuses through the zeolite pores.

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