

Pervaporation of aromatic C₈-isomers

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Abstract

A pervaporation process was applied to the separation of different mixtures of aromatic C₈-isomers using a dense homogeneous polyethylene membrane. The influence of feed temperature and downstream pressure on the flux of pure components was investigated. For mixtures, the effect of feed composition on permeation rates and separation characteristics was determined. Molar fluxes and separation factors depend on the feed composition. Coupled transport occurs and the extent of coupling depends on the difference in the permeabilities of the pure components.

The mass transport of pure components through the membrane was modelled for varying downstream pressures with diffusivities linearly dependent on the concentration of all the permeants in the membrane. On the basis of this model, molar fluxes of each component in the mixture of ethylbenzene and *p*-xylene were calculated and compared with the experimental data. The model and experimental data show good agreement.

Keywords: pervaporation; organic separations; isomer separations; polyethylene membrane; feed temperature; down stream pressure; coupled transport

Introduction

The pervaporation process attracted the interest of the scientific community in the past decades due to its inherent characteristic of producing feed-permeate compositions that are far removed from the liquid-vapor equilibrium relationship. This is a result of the selective permeation characteristics of the membrane. Extensive research was done on the separation of azeotropic mixtures like ethanol/water [1-6]. For hard to separate organic/organic mixtures with close boiling points and low relative volatilities, pervaporation is potentially very attractive.

The separation of aromatic C₈-isomers is currently achieved by distillation, crystallization or adsorption. Since these processes are complex and highly

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energy intensive, pervaporation might be an alternative process to overcome these disadvantages.

Michaels and co-workers [7] investigated the separation of xylene isomers by pervaporation with conditioned polyethylene films. Sikonia and McCandless [8] used poly(vinylfluoride) membranes containing Werner complexes for permeation experiments with xylene isomers. Cellulose acetate membranes were used by Smolders and co-workers [9] for the separation of a mixture of *p*-xylene and *o*-xylene and separation factors from 1.16 to 1.43 were achieved. McCandless and Dawns [10] presented a study that investigated a number of polymeric membrane materials for separating various binary mixtures of aromatic C₈-isomers.

In order to develop a competitive process to the existing separation techniques, one must know the influence of process parameters on separation characteristics and permeation rates. For further engineering calculations, one has to establish a model predicting the process output depending on the process parameters. Thus, the aim of this study was to investigate and model the influence of process parameters such as feed composition, downstream pressure and feed temperature on separation factors and permeation rates.

Theory

Mass transport through a nonporous polymer membrane can be described by the well-established solution-diffusion model [11]. The transport of a single component through a homogeneous membrane has been successfully modelled with Fick's first law and concentration dependent diffusivities. Customary relationships for the diffusion coefficients are linearly or exponentially dependent on the concentration of the permeant in the membrane.

$$D = D_0 (1 - \beta C) \quad (1)$$

$$D = D_0 c \quad (2)$$

$$D = D_0 \exp(\beta c) \quad (3)$$

Greenlaw and co-workers [12] have shown that, for the system hexane/heptane with a polyethylene membrane, eqns. (1) and (2) describe the dependence of permeation rates on downstream pressure very well and all the constants used have physical significance. Two phase behavior as extensively described by Sheldon and Thomson [14] is omitted here since it is not relevant to our present experimental system. With Fick's first law,

$$N = D \frac{dc}{dl} \quad (4)$$

Henry's Law, which correlates the concentration of the permeant in the membrane to the upstream and downstream activity, respectively, is given by:

$$c = sa \quad (5)$$

and using eqn. (2) for the diffusion coefficient and integrating eqn. (4), over the membrane thickness one obtains:

$$n = \frac{D_0 s^2}{2L} (a_1^2 - a_2^2) \quad (6)$$

For single component pervaporation, the upstream activity is unity

$$a_1 = 1 \quad (7)$$

and for vapor on the downstream side, the downstream activity is given by [12]:

$$a_2 = \frac{p_2}{p^0} \exp \left[-\frac{V}{RT} (p_1 - p^0) \right] \quad (8)$$

When there is liquid on the downstream side, the activity is given by [12]:

$$a_2 = \exp \left[-\frac{V}{RT} (p_1 - p_2) \right] \quad (9)$$

For small downstream pressures, $p_2 \ll p_1$, the exponential term in eqn. (8) is almost equal to unity and eqn. (6) can be written as

$$N = \frac{D_0 s^2}{2L} \left[1 - \left(\frac{p_2}{p^0} \right) \right] \quad (10)$$

For zero downstream pressure, $p_2 = 0$, the flow coefficient in eqn. (10) becomes:

$$K = 0.5 D_0 s^2 \quad (11)$$

and it can be determined by the product of the volumetric flux and the membrane thickness. Knowing the solubility of the permeant in the membrane material, the overall diffusivity can be calculated according to eqn. (11).

For binary mixtures, mass transport becomes more complex and many theories are offered in the literature [4–6, 12–14]. The extension of the above mentioned model to binary mixtures [13] takes into account the synergistic effect of the presence of a second permeant by interaction parameters in the expression for the diffusivity. The coupling of fluxes (influence on the flux of one species by the presence of the other species) can be divided into a kinetic part (diffusion) and a thermodynamic part (solution). The approach of Smolders and co-workers [4–6] treating the transport of ethanol and water through cellulose acetate membranes is based on the Flory–Huggins thermodynamics for the description of the solution part and the concentration dependent diffusion coefficients of both species for the kinetic part. Since all investigated mixtures are weakly interacting (maximum calculated activity coefficients are

in the order of 1.04), the coupling in the thermodynamic part of the solution-diffusion model is neglected for further calculations.

The extension of the above mentioned model to binary mixtures [13] takes into account the coupling of fluxes by interaction parameters in the expression for diffusivity.

$$D_i = D_{oi}(c_i + B_{ij}c_j) \quad (12)$$

$$D_j = D_{oj}(c_j + B_{ji}c_i) \quad (13)$$

It is reasonable to assume that for similar chemical components the influence on the diffusion of species i owing to the presence of species j is the same as that on the diffusion of species j due to species i , thus $B_{ij} = B_{ji} = 1$. The assumption of $B_{ij} = B_{ji}$ is still good although there exists a considerable difference in the permeabilities. Later calculations show that the diffusivities do not differ appreciably. The difference in permeabilities is mainly caused by the differences in solubility. According to Greenlaw [13], one obtains the following expression for the downstream partial pressure for the component i :

$$\frac{p_{i2}}{p_2 - p_{i2}} = \frac{M_j \rho_i D_{oi} s_i}{M_i \rho_j D_{oj} s_j} \frac{x_{i1} - (p_{i2}/p_i^0)}{(1 - x_{i1}) - [(p_2 - p_{i2})/p_j^0]} \quad (14)$$

After experimental determination of D_{oi} and D_{oj} with the above mentioned downstream pressure experiment (eqn. 11) for the pure components, eqn. (14) can be solved analytically for each component. Greenlaw [13] used this model to calculate the influence of the downstream pressure p_2 on the downstream partial pressures of the components i and j , respectively. In this study, eqn. (14) was used to model the influence of the feed composition x on the downstream partial pressures at a certain total downstream pressure p_2 . Once p_{i2} and p_{j2} are calculated one obtains the following equation after integrating eqn. (4) for each component from the liquid to the vapor side of the membrane

$$N_i L = D_{oi} \left[\frac{1}{2} (1 + b) c_i^2 + (c_{ji} - b c_{il}) c_i \right] \Big|_{c_i = c_{i2}}^{c_i = c_{i1}} \quad (15)$$

$$N_j L = D_{oj} \left[\frac{1}{2} \left(1 + \frac{1}{b} \right) c_j^2 + \left(c_{il} - \frac{1}{b} c_{jl} \right) c_j \right] \Big|_{c_j = c_{j2}}^{c_j = c_{j1}} \quad (16)$$

with

$$b = \left(\frac{N_j}{N_i} \right) \left(\frac{D_{oi}}{D_{oj}} \right) \quad (17)$$

Experimental

The pervaporation system used for the experiments is schematically shown in Fig. 1. The system consists of a heated, stirred permeation cell, an electronic

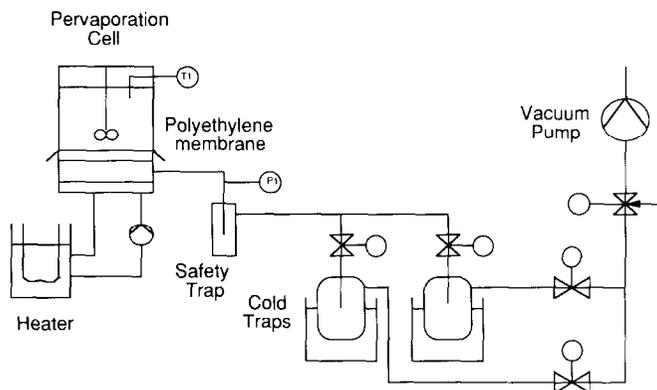


Fig. 1. Pervaporation device.

manometer, product collection traps and a vacuum pump. The membrane material used was polyethylene with a film thickness of 0.5 mil ($12.75 \mu\text{m}$). Further characteristics of the membrane material are described by Lee et al. [15].

The following binary mixtures of aromatic C_8 -isomers were experimentally analyzed: (a) ethylbenzene + *p*-xylene; (b) ethylbenzene + *m*-xylene; (c) ethylbenzene + *o*-xylene; (d) *p*-xylene + *o*-xylene. A stable feed temperature was provided by a water bath and was maintained at 25°C for all experiments, except for those which were analyzed for the effect of the feed temperature on permeation rates. For these, the whole cell was further covered with heating tape. To maintain constant fluid velocities in the permeation cell, the feed was stirred at a constant stirrer speed of 150 rpm. The vacuum pump maintained a minimum downstream pressure of 1.5 mmHg. The downstream pressure could be varied to higher pressures by opening a needle valve which was installed behind the cold traps in front of the vacuum pump.

The permeated product was condensed in the product collection traps cooled by liquid nitrogen. Permeation rates were measured by weighing the cold traps filled with product. Stable permeation rates were reached after 90 min of experimental run and for the following three hours the weight of the trap was measured each hour. Since the membrane failed after using for about two days, a new membrane was assembled in the pervaporation cell for each experimental run. The composition of the collected permeate and the final feed composition were analysed by gas chromatography.

Results

Mass transport across the membrane increases for the aromatic C_8 -isomers in the order *o*-xylene < ethylbenzene < *m*-xylene < *p*-xylene (Table 1). For the three xylene isomers, the same trend was reported by other investigators [7].

TABLE 1

Flow rates of different isomers

	<i>o</i> -xylene	ethylbenzene	<i>m</i> -xylene	<i>p</i> -xylene
Flow rate (g/hr)	0.93	1.34	1.72	2.51

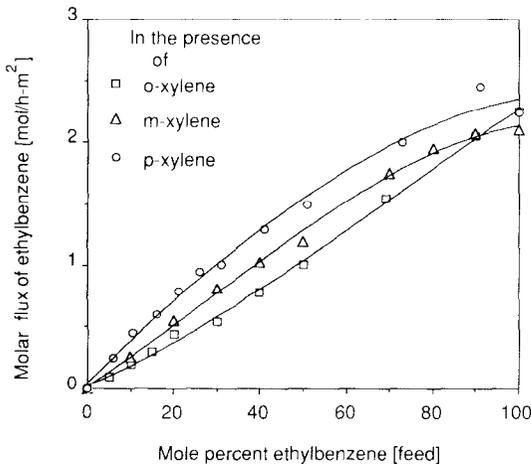


Fig. 2. Molar flux of ethylbenzene as a function of the feed composition in different mixtures.

To analyze the influence of the feed composition on permeation rates and separation factors, the upstream liquid composition of the above mentioned mixtures (a)–(d) was varied over the entire range. Generally, one could observe that the permeate mixture was enriched in that component which was the faster permeating species in the pure state.

Using concentration independent diffusion coefficients and solubility according to Henry's law, one obtains a linear relation between the feed composition and the permeation rates of the single component in a mixture. But, if transport coupling occurs, one obtains non-linear deviations. Figure 2 shows how the molar flux of ethylbenzene is affected in three different mixtures. In the presence of the much faster permeating component *p*-xylene, the transport of ethylbenzene is enhanced. A slight enhancement can also be observed for the mixture with *m*-xylene, while the transport of ethylbenzene is restricted in the presence of the slower permeating component *o*-xylene. The extent of enhancement or retardation depends on the difference in the permeation rates of pure components. Another indication for coupled transport is a concentration dependent separation factor which is shown in Fig. 3. All investigated

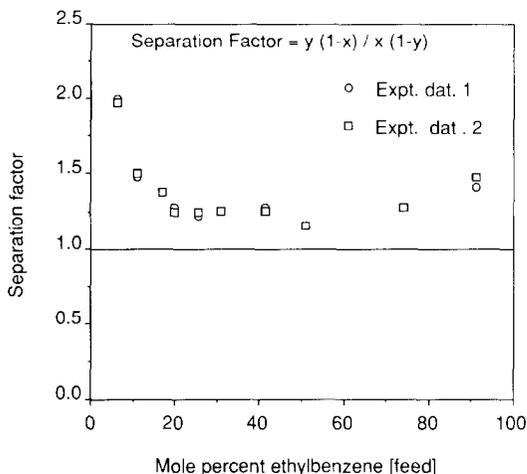


Fig. 3. Separation factor as a function of the feed composition for the mixture ethylbenzene/*p*-xylene.

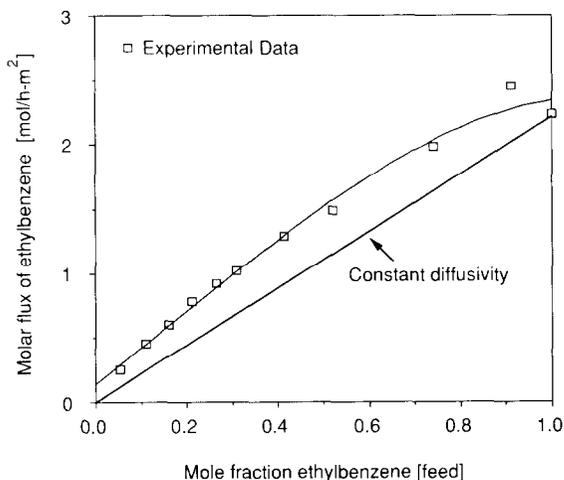


Fig. 4. Molar flux of ethylbenzene as a function of the feed composition for the mixture of ethylbenzene/*p*-xylene.

mixtures show non-linear behavior and except for small concentration of *o*-xylene in *p*-xylene (mixture d) separation factors increase towards lower concentrations while having a minimum at medium concentrations. The larger the difference between the permeation rates of pure components, the larger are the separation factors and easier is the separation between components.

A closer look at the molar flux of the faster permeating component in the mixture ethylbenzene/*p*-xylene shows another phenomenon: the transport of

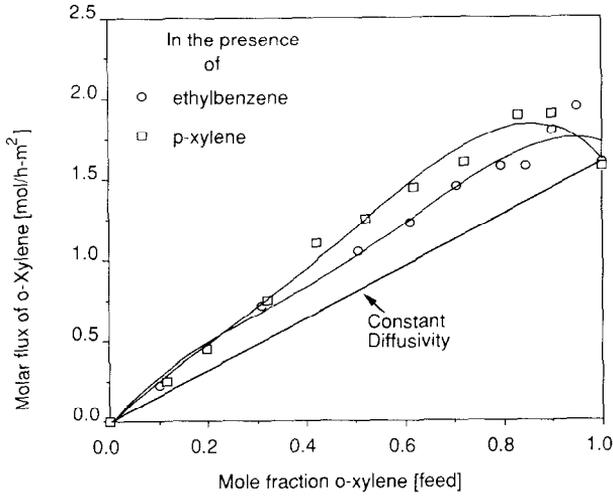


Fig. 5. Molar flux of *o*-xylene as a function of the feed composition in different mixtures.

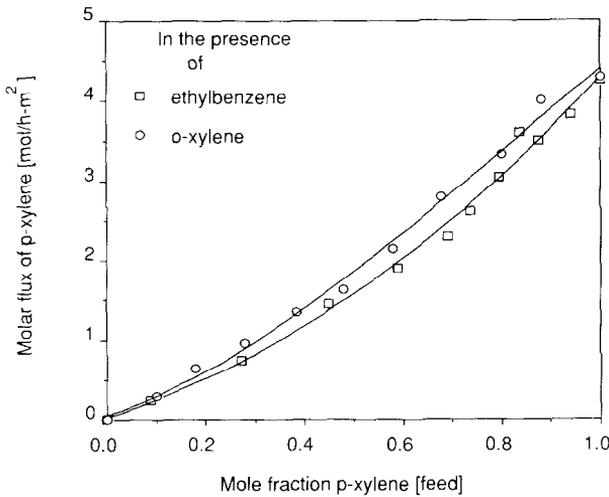


Fig. 6. Molar flux of *p*-xylene as a function of the feed composition in different mixtures.

ethylbenzene in the presence of small concentrations of *p*-xylene is even larger than that for pure ethylbenzene (Fig. 4). One observes this maximum in the molar flux of *o*-xylene, too (Fig. 5). As could be seen for ethylbenzene and *o*-xylene the extent of enhancement and even the interval of the maximum depends on the difference in permeation rates of the pure components. This cannot be stated for the retardation of the flux of *p*-xylene in the presence of the slower permeating components ethylbenzene and *o*-xylene, respectively (Fig. 6). Although one can clearly see the restriction of the movement of *p*-xylene,

there is not significant difference noticeable for the two mixtures with ethylbenzene and *o*-xylene.

Discussion

The flux dependence on downstream pressure has been modelled with concentration dependent diffusion coefficients depending exponentially or linearly on the concentration of the penetrant in the membrane, as mentioned before. Figure 7 shows the experimental data for the flux of *p*-xylene as a function of downstream pressure. The curve for the exponential model was obtained by fitting the data by the least square method. In the case of diffusivities which show a linear dependence on concentration, the flux across the membrane is given by eqn. (10). Because a downstream pressure $p_2=0$ could not be realized experimentally, the constant K was obtained by linear regression (N vs. p_2).

Figure 8 shows the molar flux of *m*-xylene vs. downstream pressure. In this graph the experimental data are only compared to the linear model. The following results were obtained with this model. All constants have a physical meaning, while for the exponential model experimental data were fitted by using an adjustable parameter (eqn. 3).

In both graphs one can see that the flux of the components strongly depends on the downstream pressure at pressures lower than the saturation pressure. In the vicinity of the saturation pressure fluxes change abruptly and become constant due to a change in the downstream activity according to eqn. (9).

The observed deviation between the model and the data might be the result of the simplifying assumptions employed in developing the model [12]. It may

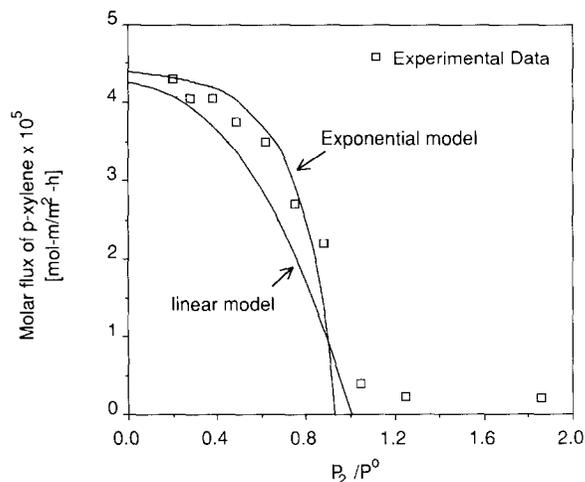


Fig. 7. Molar flux of *p*-xylene vs. downstream pressure.

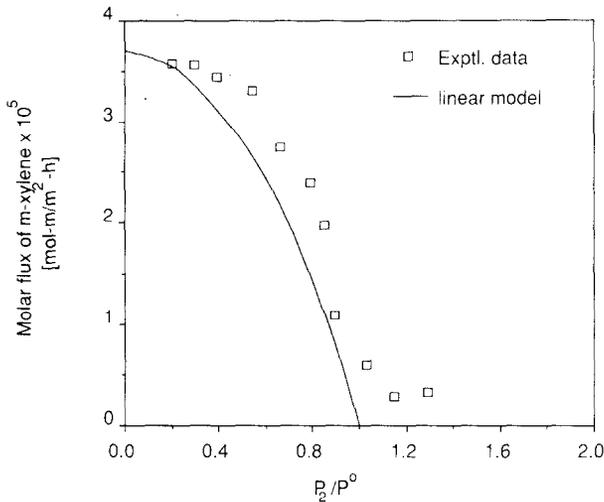


Fig. 8. Molar flux of *m*-xylene vs. downstream pressure.

also be due to the small leaks in the downstream vacuum system, the registered pressure is not strictly the partial pressure of the pure component, but the sum of the partial pressures of the component and air. Thus, the partial pressure of the organic compound is smaller than the indicated pressure. Under these conditions, the experimental data should be shifted along the x -axis closer to the theoretical curve and the gap between experiment and model would be smaller.

The effect of feed temperature on permeation rates of the pure components is shown in Fig. 9. Permeabilities depend on the temperature according to an Arrhenius type relationship. One can see that the differences in the permeabilities decrease with increasing feed temperature. Since the separation factors decrease with a decreasing difference in the permeation rates of the pure components, one can expect a more difficult separation for binary mixtures of aromatic C_8 -isomers with increasing temperature.

For the system of ethylbenzene/*p*-xylene, the model for the effect of feed composition on the permeation rates [eqns. (14)–(17)] is compared with the experimental data. Using the solubility data of Rogers [16] for ethylbenzene: $s = 0.266$ g vapor/g amorphous polymer and *p*-xylene: $s = 0.344$ g vapor/g amorphous polymer. At unit activity, one can calculate the values of K for ethylbenzene: $K = 1.08 \times 10^{-8}$ cm²/sec and *p*-xylene: $K = 1.51 \times 10^{-8}$ cm²/sec, and the diffusivities for ethylbenzene: $D_0 = 3.047 \times 10^{-7}$ cm²/sec and *p*-xylene: $D_0 = 2.559 \times 10^{-7}$ cm²/sec. With these values one is able to solve eqns. (14)–(17). Figures 10 and 11 show the molar fluxes of *p*-xylene and ethylbenzene as a function of the feed composition and compare the model with the experimental data, with the assumption that the diffusion coefficients are linearly dependent on the penetrant concentrations.

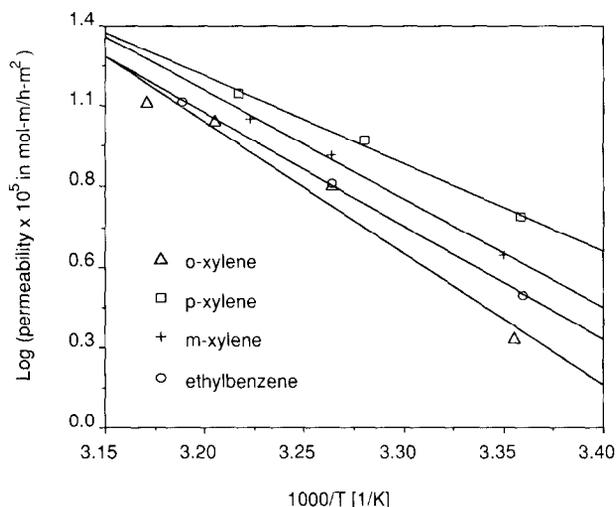


Fig. 9. Temperature dependence of permeabilities.

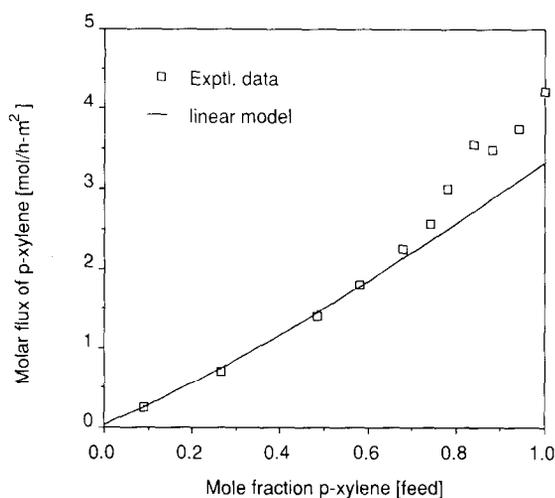


Fig. 10. Molar flux of *p*-xylene as a function of the mole fraction of *p*-xylene in the mixture of ethylbenzene and *p*-xylene.

For the molar flux of *p*-xylene, the model agrees well with the experimental data up to feed compositions of 60 mol% *p*-xylene, but with increasing concentration of *p*-xylene, the theoretical curve deviates from the experimental curve. For ethylbenzene, the theoretical curve is very close to the experimental data points. The predicted values for the flux of ethylbenzene are in general, slightly smaller than those obtained from experiments. Flux retardation for the faster component and flux enhancement for the slower one is described by the model,

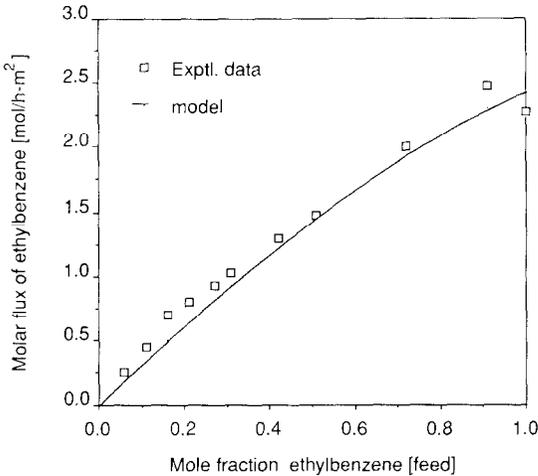


Fig. 11. Molar flux of ethylbenzene as a function of the mole fraction of ethylbenzene in the mixture of ethylbenzene and *p*-xylene.

although the existence of a maximum for the flux of ethylbenzene at low concentrations of *p*-xylene is not explained.

The model curves for the mixtures are based on the calculations carried out for the pure components. The deviation between calculated and experimental data calls for a refined model for binary mixtures. A better agreement between model and experiment might be achieved, if solubilities are not assumed to be constant. However, Figs. 10 and 11 show a good agreement between experimental data and model and the linear concentration dependent diffusion coefficient is a reasonable relation to describe mass transport through the membrane for weakly interacting systems.

Conclusions

A pervaporation process using a polyethylene membrane has been successfully applied for the separation of binary mixtures of mixed xylenes, but separation factors seem to be too small for industrial application over the whole concentration interval. At intermediate mole fractions all of the investigated mixtures show separation factors close to unity, while they increase for almost every system at lower mole fractions. This leads to the conclusion that pervaporation might economically be feasible as a purification process for already roughly separated mixed xylenes. A pervaporation device at the top of a distillation column can be suggested. Certainly, an improvement in the separation characteristics of polymeric membranes could be a step towards the industrial application of pervaporation process for the separation of aromatic C₈-isomers.

Total molar fluxes and separation factors depend on the feed composition

for all investigated mixtures. Coupled transport occurs and the extent of transport enhancement and retardation, respectively, depends on the difference in the permeabilities of the pure components. For the mixture of ethylbenzene and *p*-xylene, a model which is suggested to describe the permeation rates and separation characteristics as a function of the downstream pressure is applied to the case where the feed composition is the independent variable. Good agreement between experimental data and model is obtained. A better fit of experimental data by the model might be achieved if the solubility is assumed to be a function of the activity. This can also be expected for the experiments carried out to investigate the influence of the downstream pressure on the permeation rates of pure components.

Acknowledgements

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List of symbols

<i>a</i>	activity (—)
<i>b</i>	constant used in eqn. (17) (—)
<i>B</i>	interaction parameter (—)
<i>c</i>	concentration (g/g)
<i>D</i>	diffusion coefficient (m ² /sec)
<i>K</i>	constant used in eqn. (11) (m ³ -m/m ² -sec)
<i>l</i>	distance in the membrane (m)
<i>L</i>	membrane thickness (m)
<i>N</i>	flux (m ³ /m ² -sec)
<i>p</i>	pressure (N/m ²)
<i>p</i> ⁰	saturation pressure (N/m ²)
<i>R</i>	universal gas constant
<i>s</i>	solubility (g/g)
<i>T</i>	temperature (°K)
<i>V</i>	molar volume (m ³ /mole)
<i>x</i>	liquid mole fraction (—)
<i>y</i>	vapor mole fraction (—)

Greek symbols

α	separation factor (—)
β	constant used in eqns. (1) and (3) (—)
ρ	density (kg/m ³)

Subscripts

1	upstream side
2	downstream side

- 0 physical characteristic independent of the variable
i component *i*
j component *j*

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