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PERVAPORATION, SOLUBILITY ASPECTS OF THE SOLUTION-DIFFUSION MODEL

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INTRODUCTION.

Pervaporation is a membrane process where a liquid mixture is in direct contact at one side of the membrane, the upstream side and the permeated product is removed as a vapour at the downstream side by applying a low partial pressure. This can be achieved either by creating a vacuum or by using a carrier gas (fig. 1). Pervaporation is the only membrane process where a phase transition occurs going from upstream side to downstream side.

The commercialization of the pervaporation process is under-developed compared to other membrane processes such as microfiltration, ultrafiltration or hyperfiltration. Around the sixties Binning and coworkers tried to introduce pervaporation as an industrial process but their attempts were not very successful despite intensive investigations and a number of patents [1]. The main reason for this failure was undoubtedly that permeation rate and/or selectivity were insufficient for commercial application.

Other reasons for a long incubation time of this process are:

energy consumption is relatively high compared to other membrane

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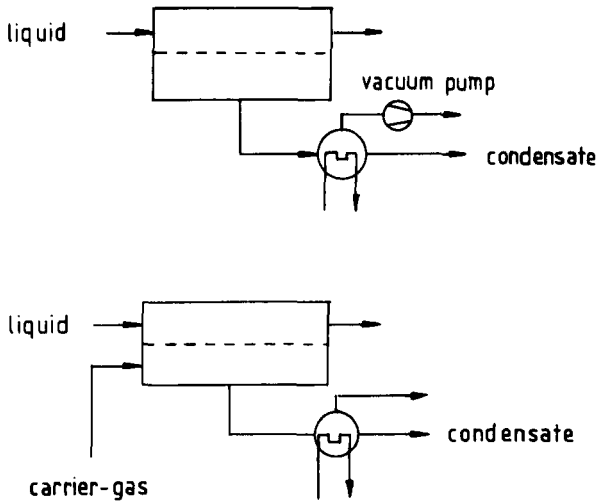

FIGURE 1. PERVAPORATION WITH DOWNSTREAM VACUUM OR A CARRIER-GAS.

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processes such as microfiltration, ultrafiltration or hyperfiltration because a phase transition occurs and the heat of vaporization has to be supplied.

- process design is difficult because of a temperature drop across the membrane and pressure losses at the downstream side.

In the last decade there has been a renewed interest in pervaporation especially in the field of ethanol-water separation. The attractiveness of this specific application is the need to produce fuels from renewable resources. Ethanol can be obtained by fermentation of biomass. **Dehydration** of ethanol can be completely or partly accomplished by pervaporation. Except for the alcohol-water separation there are a number of other potential applications. Pervaporation will especially be **competitive with other separation** techniques when the concentration of the component which has to be removed is low. Therefore the major field of application will be:

- dehydration of organic liquids containing small amounts of water (<20%).
- removal of organic contaminants such as aromatics and chlorinated hydrocarbons from waste water.
- separation of azeotropic mixtures where the azeotropic composition is not too far from one of the pure components (examples are: water/ethanol; water/i-propanol; water/t-butanol; water/-THF; water/dioxane; methanol/acetone; ethanol/hexane; propanol/-cyclohexane; etc.).

The selectivity towards a liquid mixture is expressed by the selectivity factor α.

$$\alpha_{A/B} = \frac{X_A/X_B}{Y_A/Y_B} \qquad [1]$$

where X_A and X_B are the concentrations of components A and B in the permeate and Y_A and Y_B are the concentrations in the liquid feed. The pervaporation process essentially involves a sequence of three steps:

. selective sorption into the membrane
. selective diffusion through the membrane
. desorption into a vapour phase at the downstream side.

Transport through a pervaporation membrane takes place by a solution-diffusion mechanism [2-5], i.e. the permeation rate is a function of solubility and diffusivity. Solubility is a thermodynamic property and diffusivity is a kinetic property and both affect selectivity. When two or more components are permeating through a membrane coupling will occur in general. This means that in the case of a binary mixture the flux of a component in the membrane is not only determined by the presence of the other component but also by its movement, i.e. coupling takes place in the solubility part as well as in the diffusivity part according to

$$J_i = f[S_i(c_i,c_j),D_i(c_i,c_j)] \qquad [1]$$

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S_i is the solubility of component i and D_i its diffusivity.
Many investigators made use of concentration dependent diffusion coefficients depending on the concentrations of all the components present but generally coupling in the solubility part was neglected. In most cases ideal sorption was assumed [6-8], i.e. the concentration of a component in the membrane was supposed to be directly proportional to the concentration of that component in the liquid mixture. There is much experimental evidence that in general ideal sorption does not occur [9-13]. Mostly one of the components will be sorbed preferentially, i.e. preferential or selective sorption occurs. This means that the composition of the liquid feed mixture inside the membrane is different from the composition in the liquid feed mixture in such a way that there is no linear relation between composition in the membrane and composition in the feed.
The objective of this paper is to discuss the solubility part of the solution-diffusion model in relation to selective transport. Two different types of mixtures have been investigated: a weakly interacting ('ideal') mixture, o-xylene/p-xylene and a strongly non-ideal mixture, ethanol/water.
In the first part the fundamental aspects of polymer-penetrant affinity will be described. The influence of preferential sorption on selective transport will be discussed in the second part.

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THEORY.

There are several solution theories which can describe the solubility of low molecular weight substances in polymers. Two widely used theories are i) the solubility parameter theory [14] and ii) the Flory-Huggins theory [15]. There are also more sophisticated solution theories such as the 'new' Flory theory (derived from equation-of-state relations) [16] or the fluid-lattice theory [17] which can describe polymer solution

thermodynamics more properly from a chemical-phyiscal point of view. However, there are still problems to describe the solubility behaviour quantitatively i.e. these new theories do not predict polymer-solution behaviour significantly better [18-20]. Furthermore these theories require physical and chemical data which are only available for a limited number of compounds. For describing polymer-penetrant affinity we will make use of the solubility parameter theory and of the Flory-Huggins theory.

Solubility parameter theory.

The solubility parameter theory is based on the concept of regular solutions. These are solutions having an ideal entropy of mixing and a non-ideal enthalpy of mixing.
In liquids there exist strong attractive forces between molecules and the potential energy of the molecules (relative to the molecules in the vapour phase) is called the cohesive energy. The intermolecular forces contributing to the cohesive energy can be divided into i) nonpolar interactions (dispersion or London forces), ii) polar interactions and iii) specific chemical forces such as hydrogen bonding. The cohesive energy density (CED) is defined as the ratio between cohesive energy (-E) and molar volume (V_m).

$$CED = {}^{-E}/V_m \qquad [3]$$

The cohesive energy is assumed to be equal to the total energy of vapourization. The solubility parameter (δ) is directly related to the cohesive energy density.

$$CED \equiv \delta^2 = \frac{\Delta E_{vap}}{V_m} \qquad [4]$$

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Hansen [21] assumed that the total energy of vapourization is the sum of energies required to overcome dispersion forces (ΔEd), and polar interactions (ΔEp) and to break hydrogen bonds (ΔEh).

$$\Delta E_{vap} = \Delta E_d + \Delta E_p + \Delta E_h \qquad [5]$$

Combining eqns. [4] and [5] gives

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad [6]$$

A good solvent for a certain polymer will have a solubility parameter value close to that of the polymer.
The three-component solubility parameter can be considered as a vector lying in $(\delta_d, \delta_p, \delta_h)$-space. Each solvent and each polymer can be located in this $(\delta_d, \delta_p, \delta_h)$-space being the end-point of the radius vector (see fig. 2).
Consider a given polymer (subscript p) and a penetrant (subscript s, this can be a solvent or a nonsolvent), then the distance Δ between the end-points of the radius-vectors is given by [22, 23],

$$\Delta = [(\delta_{p,s} - \delta_{p,p})^2 + (\delta_{d,s} - \delta_{d,p})^2 + (\delta_{h,s} - \delta_{h,p})^2]^{1/2} \qquad [7]$$

A schematical representation is given in fig. 2. Δ is a measure for the affinity between polymer and penetrant. When Δ decreases the affinity between polymer and penetrant will increase. When Δ approaches zero then the penetrant will be a solvent for the polymer. Table 1 gives the three-dimensional solubility parameters of

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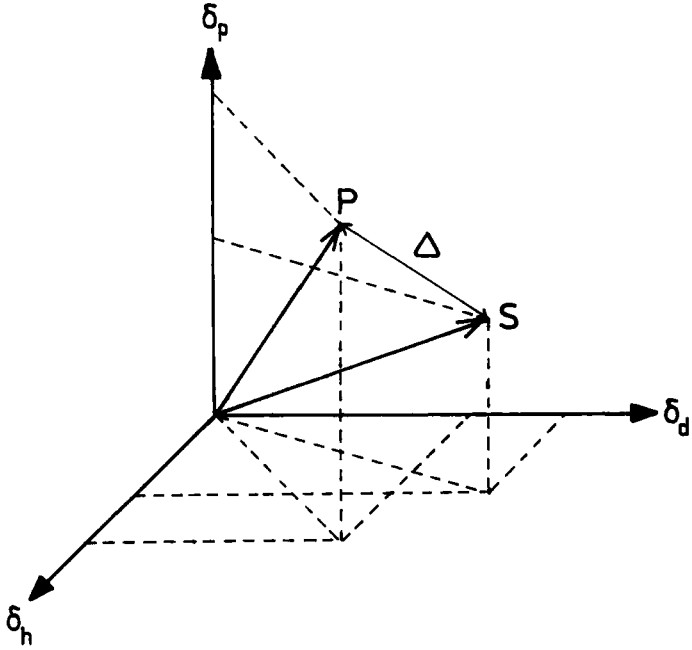

FIGURE 2. SCHEMATIC REPRESENTATION OF POLYMER (P) AND SOLVENT (S) VECTORS IN (δ_p,δ_d,δ_h)SPACE; Δ IS THE DISTANCE BETWEEN END-POINTS OF VECTORS;

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TABLE I [24]

	δ_d	δ_p	δ_h	δ
o-xylene	8.8	0.7	1.4	9.0
p-xylene	8.7	0	1.3	8.8
cellulose tripropionate	8.4	3.1	5.3	10.3

TABLE II [24]

binary system	Δ
cellulose tripropionate/o-xylene	4.4
cellulose tripropionate/p-xylene	4.9

the components of one of the systems discussed in this paper, o-xylene/p-xylene/cellulose tripropionate. The calculated values of the distance parameter Δ are given in table 2.
From table 2 it can be seen that the affinity of o-xylene to CTP is larger (the trend is small but significant) than the affinity of p-xylene to CTP. This is due to the presence of a dipole moment in o-xylene, whereas p-xylene has no dipole moment (see δ_p values in table 1).

There are some restrictions in using the solubility parameter theory. This theory accounts only for energetic contributions to the mixing process, entropic effects are disregarded. Furthermore, mixing of polymer and solvent is predicted from properties of the pure components so specific interactions between polymer and solvent occurring on mixing are not involved. At last, the theory can only be used for rather hydrophobic components and not for typically hydrophilic components, such as water and alcohols, having a high polar character or showing strong specific interactions such as hydrogen bonding. Therefore the solubility parameter approach can be used in a qualitative way only to a limited number of systems. For instance values for preferential sorption cannot be deduced from this theory as we will show later on. Nevertheless this theory is convenient to use and helpful as a first estimate of interaction phenomena. For more hydrophilic components such as water and alcohols the Flory-Huggins theory can be used.

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Flory-Huggins theory [15].

In order to calculate the entropy of mixing of solvents and polymer (long-chain) molecules Flory and Huggins used a lattice model where the segments of the polymer and the solvent molecules occupy single sites.

For a binary system consisting of polymer and solvent the Gibbs free enthalpy of mixing is given by

$$\Delta G_m = x_1 \ln v_1 + x_2 \ln v_2 + \chi_{12} x_1 v_2 \qquad [8]$$

where x and v are mole fraction and volume fraction respectively. The first two terms on the right-hand side of eqn. 8 give the ideal entropy of mixing while the last term describes the enthalpy of mixing. This last term contains a binary interaction parameter (the χ parameter) called the Flory-Huggins interaction parameter. This parameter can be considered as a free energy parameter (including both energetic and entropic contributions). It is a dimensionless quantity characterizing the difference in interaction energy of a solvent molecule immersed in pure polymer with respect to the energy of a molecule immersed in pure solvent. For solvents χ will have a value less than 0.5. When the affinity between polymer and penetrant decreases χ will increase. The binary interaction parameter of polymer and nonsolvent can be obtained from swelling or sorption measurements [11]. For the systems water/-ethanol/cellulose acetate and water/ethanol/polyacrylonitrile the binary interaction parameters are given in table 3.

From table 3 it can be seen that the affinities of ethanol and water to cellulose acetate are of the same order of magnitude with ethanol having the highest affinity. Compared to cellulose acetate polyacrylonitrile shows a different behaviour to water and ethanol. The affinity of ethanol to polyacrylonitrile is very small while the affinity of water to the same polymer is much higher.

Sorption experiments.

The overall sorption values of ethanol-water mixtures in cellulose acetate (CA), polyacrylonitrile (PAN) and polysulfone (PSf) are

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TABLE III [11]

polymer	penetrant	χ
cellulose acetate	water	1.4
cellulose acetate	ethanol	1.1
polyacrylonitrile	water	1.8
polyacrylonitrile	ethanol	4.2

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given in fig. 3. This figure clearly demonstrate the difference in thermodynamic behaviour of the three polymers to ethanol-water mixtures. Low swelling values can be observed for polyacrylonitrile and polysulfone while cellulose acetate shows much higher values. Polysulfone and polyacrylonitrile show an opposite behaviour, hardly any water sorption can be observed for polysulfone while polyacrylonitrile shows a low value for pure ethanol. The solubility of ethanol-water mixtures in cellulose acetate passes through a maximum at about 65 weight % of ethanol in the feed. Fig. 5 gives no information about the ethanol-water composition in the membrane i.e. the occurence of preferential sorption cannot be deduced from the overall sorption experiments. The overall sorption of o-xylene/p-xylene mixtures in cellulose tripropionate (CTP) is given in fig. 4. As was already concluded from the swelling experiments of the pure substances the affinity of CTP to o-xylene is larger than to p-xylene.

In order to estimate the composition of a binary liquid mixture in a membrane Krewinghaus [6] assumed a linear relationship between the concentration of a component in the membrane and the concentration outside the membrane (in the liquid feed mixture) according to

$$c_i = x_i c_i^{\circ} \qquad [9]$$

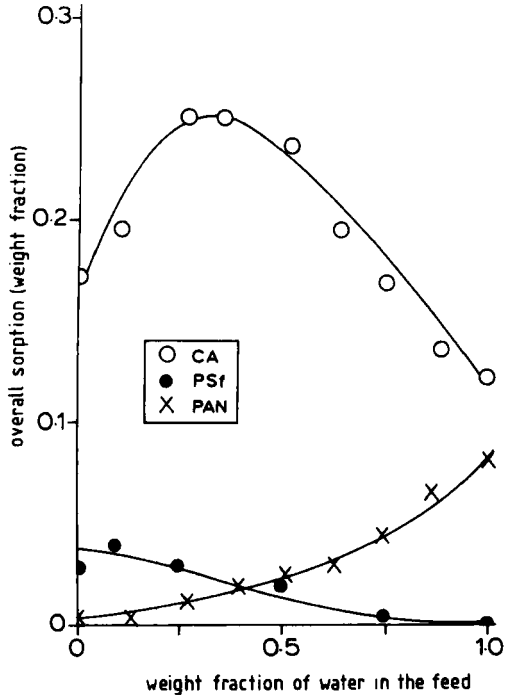

FIGURE 3. TOTAL SORPTION AS A FUNCTION OF WATER CONTENT IN WATER-ETHANOL LIQUID FEED MIXTURE FOR VARIOUS POLYMERS.

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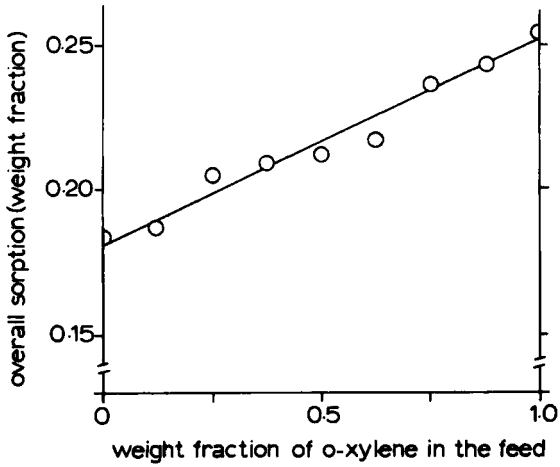

FIGURE 4. TOTAL SORPTION OF O-XYLENE/P-XYLENE IN CELLULOSE TRIPROPIONATE AS A FUNCTION OF THE O-XYLENE CONCENTRATION IN THE FEED.

where c_i is the concentration of component i in the membrane, x_i is the mole fraction of component i in the liquid feed mixture and c_i^o is the solubility of the pure component in the membrane. When eqn. [9] is applied to the results given in figs. 3 and 4 then it can be deduced that for the system water/ethanol/CA, ethanol will be sorbed preferentially over a major part of the composition range, for the system water/ethanol/PAN, water will be sorbed preferentially almost over the entire composition range and for the system o-xylene/p-xylene/CTP, o-xylene will be sorbed preferentially for o-xylene concentrations in the feed larger than 50% by weight.

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Preferential sorption versus preferential permeation.

We have now come to the main issue of this paper, the relation between preferential sorption and selective transport.
Fig. 5 gives the preferential sorption and pervaporation results of the system water/ethanol/CA as a function of the weight fraction of water in the feed.
It is obvious that both curves show the same behaviour. Water is sorbed preferentially over the entire composition range and in the pervaporation experiments a permselectivity is found for water also over the entire composition range.
The preferential sorption and pervaporation results of the system water/ethanol/PAN are given in fig. 6.
Again both curves show the same behaviour i.e. the component that is sorbed preferentially also permeates preferentially.
Polyacrylonitrile shows, compared to cellulose acetate, very high selectivities to ethanol-water mixtures.
Also for other systems it can be shown that preferential sorption is the determining factor in selective transport. Fig. 7 gives the preferential sorption and pervaporation results of the system o-xylene/p-xylene/CTP. Again it is striking that both curves show a similar behaviour. The component that is sorbed preferentially (p-xylene) permeates preferentially too.

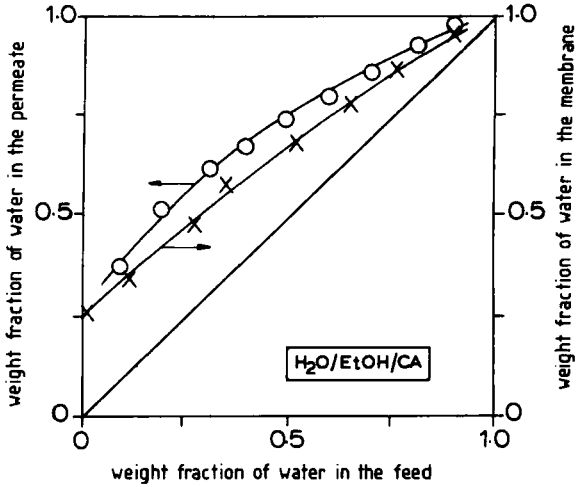

FIGURE 5. EXPERIMENTAL VALUES FOR PREFERENTIAL SORPTION AND PERVAPORATION FOR THE SYSTEM WATER/ETHANOL/CELLULOSE ACETATE AS A FUNCTION OF THE CONCENTRATION OF WATER IN THE FEED

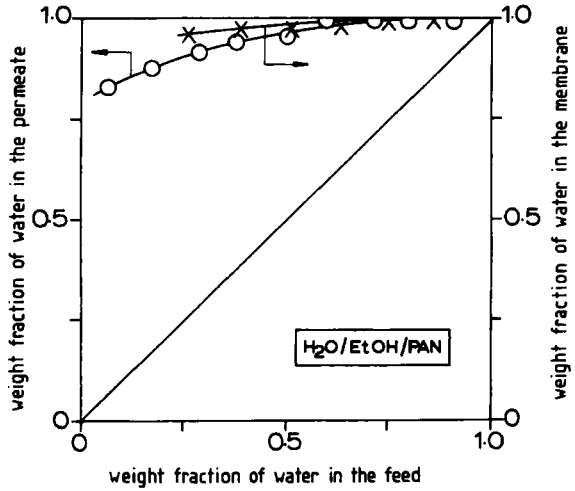

FIGURE 6. EXPERIMENTAL VALUES FOR PREFERENTIAL SORPTION AND PERVAPORATION FOR THE SYSTEM WATER/ETHANOL/POLYACRYLONITRILE AS A FUNCTION OF THE CONCENTRATION OF WATER IN THE FEED.

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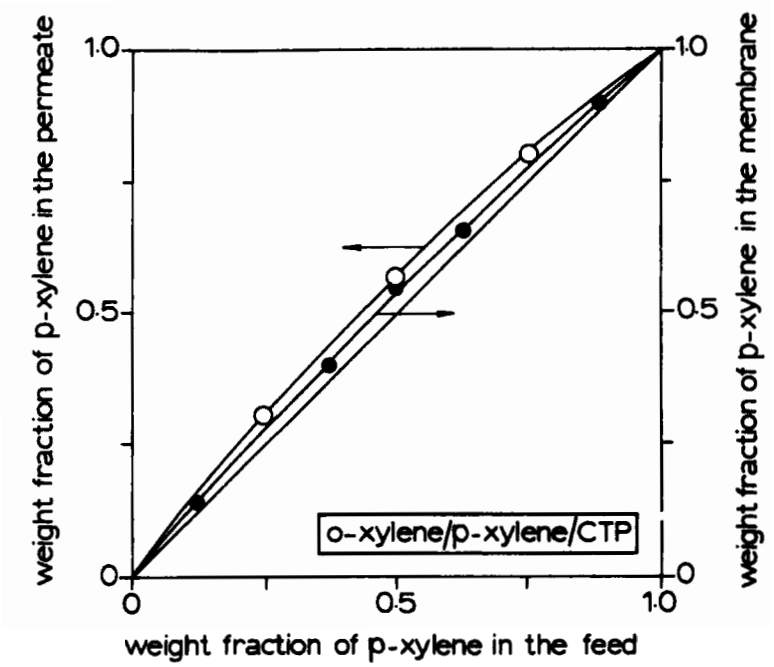

FIGURE 7. EXPERIMENTAL VALUES FOR PREFERENTIAL SORPTION AND PERVAPORATION FOR THE SYSTEM O-XYLENE/P-XYLENE/CELLULOSE TRIPROPIONATE AS A FUNCTION OF THE CONCENTRATION OF P-XYLENE IN THE FEED.

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Except for the systems described here there are a number of literature sources showing evidently that preferential sorption is the leading factor to selective transport. An overview of these literature sources is given in table 4.

For all the systems given in table 4 it was demonstrated that the component that is sorbed preferentially also permeates preferentially. Especially the results of the system ethanol/1,2-dichloroethane/PTFE-PVP are very striking [9] because an inverse in sorption selectivity results in an inverse in selective transport.

If these results are considered in terms of the solution-diffusion model where the flux of a component is a function of solubility

TABLE IV

feed mixture	type of membrane	ref.
water/ethanol	cellulose acetate	11
water/ethanol	polyacrylonitrile	11
water/ethanol	polysulfone	11
water/ethanol	polymethylmethacrylate	30
p-xylene/o-xylene	cellulose tripropionate	12
ethanol/1,2-dichloroethane	PTFE-PVP	9
ethanol/chloroform	PTFE-PVP	9
acetic acid/1,2-dichloroethane	PTFE-PVP	9
benzene/cyclohexane	poly(γ-methyl-L-glutamate)	25
water/methanol	poly(γ-methyl-L-glutamate)	25
benzene/n-heptane	poly(butadiene-acrylonitrile)	26

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(S) and diffusivity (D), this implies that the solubility part (or the ratio S_i/S_j) determines selective transport.

$$\alpha - \frac{J_i}{J_j} = f\left[\left(\frac{S_i(C_i,C_j)}{S_j(C_i,C_j)}\right),\left(\frac{D_i(C_i,C_j)}{D_j(C_i,C_j)}\right)\right] \qquad [10]$$

This does not mean that diffusivity is not important at all. The extent of permselectivity can also strongly be influenced by the ratio in diffusivities. Because multicomponent transport through (homogenous) membranes occurs generally in a coupled way the ratio of the diffusivities is difficult to estimate on forehand. For instance, if the results of the system water/ethanol/cellulose acetate are considered one can observe that sorption selectivity and permeation selectivity are almost equal (see fig. 5).

However, if the system water/ethanol/polysulfone is considered [11] a small preferential sorption for water can be observed while extremely high selectivities are obtained. This means that the effective water diffusivity in polysulfone is much larger than the ethanol diffusivity. Till now all the systems studied evidently show that in selective transport the solubility ratio dominates over the diffusivity ratio.
Another point to consider is that (preferential) sorption measurements are equilibrium experiments while permeation experiments are in fact non-equilibrium processes.

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Discussion.

Transport in pervaporation takes place according to a solution-diffusion model where both solubility and diffusivity affect selective transport. From the investigations performed by us as well as by others on the influence of preferential sorption on selective transport it has been proved experimentally that preferential sorption is the factor that determines selective transport. This was demonstrated for completely different mixtures and completely different polymeric materials.
However the extent of selectivity can be influenced by differences in diffusivities. Until now the occurrence of preferential sorption was often ignored or neglected and generally ideal sorption was assumed i.e. the concentration of a component of a liquid mixture inside the membrane was linearly related to the concentration of that component in the liquid feed mixture. There is enough experimental evidence that this approach leads to incorrect results even for systems from which it is assumed that they behave ideally. For instance for the system o-xylene/p-xylene/cellulose tripropionate, a weakly interacting system, p-xylene will be sorbed over o-xylene over the entire composition ratio; when assuming ideal sorption o-xylene would be the component that is sorbed

preferentially at high o-xylene concentrations in the feed. Therefore preferential sorption measurements are preferred over overall sorption measurements or pure component sorption measurements.
For a binary system consisting of polymer and penetrant (or permeant) the affinity can be described adequately by the solubility parameter theory in the case of hydrophobic substances while the Flory-Huggins theory can be used for polar substances too. The interaction parameters involved in these theories, δ-parameter and χ-parameter respectively, are binary parameters. In general we are interested in ternary systems consisting of a liquid feed mixture and a polymeric membrane. Because in this case coupling phenomena occur, even for weakly interacting systems, affinity or solubility in a ternary system cannot be described or predicted anymore neither by δ-parameters nor by χ-parameters only as was already shown in the experimental section. It is possible to modify the Flory-Huggins theory in such a way that ternary effects are taken into account. There are several approaches to correct for ternary effects. Pouchly [27,28] introduced a ternary interaction parameter χ_T. Another approach is to use concentration dependent interaction parameters [11,29]. In this way a better agreement can be obtained between experiment and theory.

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