

## SEPARATION OF ISOMERIC XYLENES BY PERVAPORATION THROUGH CELLULOSE ESTER MEMBRANES\*

M.H.V. MULDER, F. KRUITZ and C.A. SMOLDERS

*Department of Chemical Technology, Twente University of Technology, P.O. Box 217, 7500 AE Enschede (The Netherlands)*

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### Summary

The interaction between the isomeric xylenes and different cellulose esters was investigated using solubility parameter considerations and through measurements of swelling values.

Hansen's three-dimensional solubility parameters  $\delta_d$ ,  $\delta_p$ ,  $\delta_h$  of all the components have been calculated. These values have been used to predict the interaction between polymer and penetrant. A measure for this interaction is given by  $\Delta$ , which is the distance between polymer and penetrant in the  $\delta_d$ ,  $\delta_p$ ,  $\delta_h$  space. As expected, the experimental swelling values varied in inverse proportion to the calculated  $\Delta$  values.

Pervaporation characteristics of different cellulose ester membranes were determined by measuring product rates and selectivity. The differences in membrane characteristics have been explained qualitatively in terms of the solubility parameter concept.

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### Introduction

It is well known that pervaporation can be used to separate mixtures of low molecular weight organic compounds. Contrary to other membrane processes, such as hyperfiltration and ultrafiltration, a phase transition occurs during the pervaporation process. Consequently, the energy input of the process is at least equal to the heat of vaporization of the permeating compounds. Pervaporation can be applied successfully to mixtures which are difficult to separate, such as azeotropic and isomeric mixtures.

The separation of the isomeric xylenes has been described by several authors. Michaels et al. [1] investigated the selective permeation of xylene isomers through commercially available polyethylene films. Sikonia [2] and Lee [3] studied the separation of isomeric xylenes by permeation through modified plastic films.

Separation can be achieved by differences in either solubility and/or dif-

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fusivity arising from a difference in size or shape. The solubility of the penetrant in the membrane, i.e. the interaction between polymer and penetrant, can be described qualitatively by means of solubility parameter theory. It should be emphasized, however, that there are some restrictions in using the solubility parameter theory. Only energetic contributions in the mixing process are involved and entropic effects are disregarded. Moreover, solubility parameters predict the mixing of solvents and polymers from properties of the pure substances only.

Despite these shortcomings, the solubility parameter theory is convenient to use and helpful as a first estimate of interaction phenomena.

The three-dimensional solubility parameter approach, as described by Hansen [4], has been well received, and extensive tabulations are available in the literature. Such parameters may be expected to predict feasibility of membrane materials towards permeability behaviour of organic substances. However, such a treatment still remains qualitative.

It is the purpose of this study to investigate the permeation and separation characteristics of isomeric xylenes through cellulose ester membranes. The objectives of this research are: to calculate and evaluate Hansen's solubility parameters of the cellulose esters and of the isomeric xylenes; to relate the experimental swelling results to the solubility parameters and to evaluate the solubility parameter concept in order to predict the permeation behaviour of the isomeric xylenes using cellulose ester membranes.

## Theory

The basic assumption of the solubility parameter theory is that a correlation exists between the cohesive energy density of pure substances (i.e. their potential energy per unit volume) and their mutual solubility. The solubility parameter is related to the C.E.D. as given by eqn. (1)

$$\delta = (\text{C.E.D.})^{1/2} = \left( \frac{\Delta E}{V_m} \right)^{1/2} \quad (1)$$

For miscible substances, the differences in solubility parameters are supposed to be small. Intermolecular interactions contributing to the cohesive energy of liquids can be divided into nonpolar (London dispersion forces), polar, and specific chemical forces (donor-acceptor interactions, such as hydrogen bonding).

Hansen [4] assumed that the total energy of vaporization is the sum of energies required to overcome dispersion force interactions ( $\Delta E_d$ ), polar interactions ( $\Delta E_p$ ), and to break hydrogen bonds in the liquid ( $\Delta E_h$ ).

$$\Delta E = \Delta E_d + \Delta E_p + \Delta E_h \quad (2)$$

Combining eqns. (1) and (2) gives:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

The solubility parameter can be considered to be the resultant of three components, due to dispersion forces ( $\delta_d$ ), polar forces ( $\delta_p$ ) and hydrogen bonds ( $\delta_h$ ), as has been expressed in eqn. (3).

The three components lie as vectors along orthogonal axes. The end-point of the radius vector represents the solubility parameter. This means that each solvent and each polymer can be located in a three-dimensional ( $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ ) space. The distance  $\Delta$  between the end-points of the vectors representing polymer and solvent is given in [5]:

$$\Delta = [(\delta_{d,p} - \delta_{d,s})^2 + (\delta_{p,p} - \delta_{p,s})^2 + (\delta_{h,p} - \delta_{h,s})^2]^{1/2} \quad (4)$$

where the subscripts s and p refer to solvent and polymer respectively. A schematical representation is given in Fig.1.

According to Froehling [5], a decrease in  $\Delta$  should be proportional to an increase in swelling behaviour. So interaction between polymer and penetrant will be higher if the value of  $\Delta$  decreases.

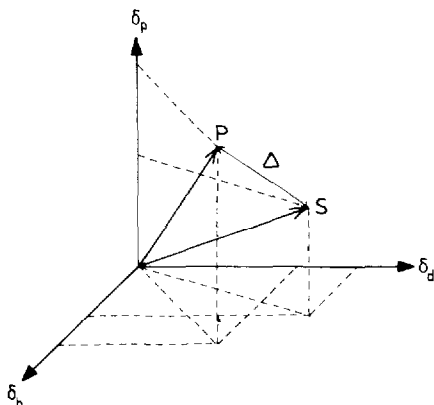


Fig.1. Schematic representation of polymer (P) and solvent (S) vectors in  $\delta_p$ ,  $\delta_d$ ,  $\delta_h$  space;  $\Delta$  is distance between end-points of vectors.

## Experimental

### Materials

Cellulose propionate was obtained from Aldrich. The other cellulose esters were obtained from Eastman Chemicals. The solvents used were of analytical grade.

### Membrane preparation

Polymer solutions were prepared by dissolving the cellulose esters in a suitable solvent (usually acetone). The membranes were prepared by casting a polymer solution on a glass plate and allowing the solvent to evaporate in a nitrogen atmosphere. The membranes obtained were completely transparent.

### Pervaporation

The pervaporation experiments were carried out in the apparatus diagrammed in Fig.2. A cross-section of the permeation cell is given in Fig.3.

The bottom disk is fitted with porous glass (10 cm in diameter), to support the membrane.

A teflon gasket is placed on the membrane before the upper part of the cell is matched. The whole unit is tightened by means of a sovirel clamp. A heating coil is placed into the upper compartment to adjust a preselected temperature and to keep the temperature of the liquid feed constant. A thermometer is placed in the cell to determine the temperature of the liquid feed. The cell is connected to two cold traps in parallel. This makes it possible to take samples at any time without interrupting the permeation run.

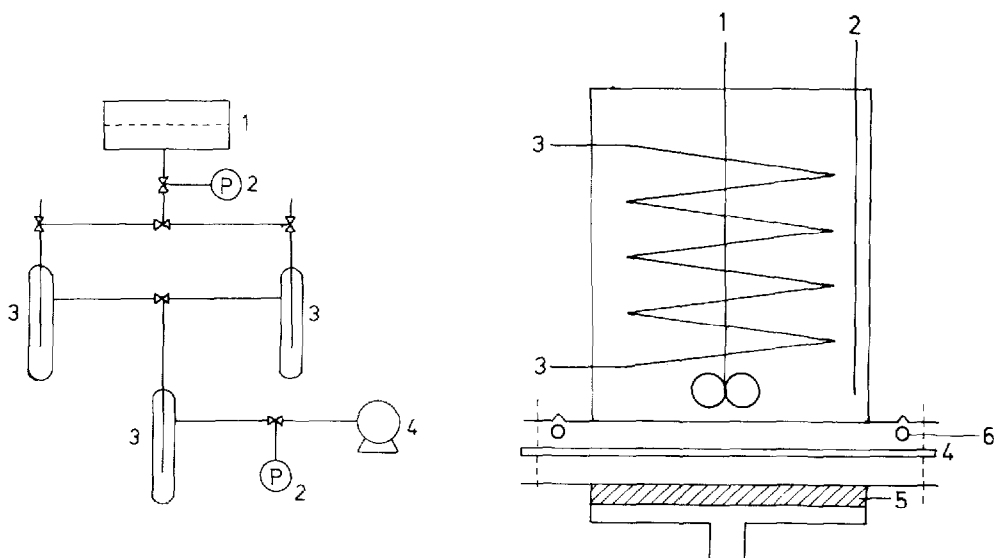


Fig.2. Schematic representation of the pervaporation apparatus. (1) permeation cell; (2) piranhi gauge; (3) cold traps; (4) vacuum pump.

Fig.3. Schematic representation of the permeation cell. (1) stirrer; (2) thermometer; (3) heating coils; (4) membrane; (5) porous glass filter; (6) teflon gasket.

Vacuum at the downstream side is maintained at a pressure of 0.1–1 mmHg (13.3–133 Pascal) by a Crompton Parkinson vacuum pump. The pressure is measured by an Edwards piranhi.

Permeation experiments were carried out for eight hours. After about three hours steady state conditions are reached. A product sample is taken at least every hour. Because conditioning history of the membrane is very important in diffusion experiments, the conditioning factors have been kept the same for all the experiments. The dry membrane was kept in contact with the liquid feed for 15 hours before the experiment was started.

### *Product analysis*

Analysis of binary solutions of para- and ortho-xylene, collected in the cold traps, were conducted on a Varian model 3700 gas chromatograph.

### *Swelling experiments*

Swelling or solubility experiments were carried out with the same membranes as used in the pervaporation experiments. Pieces of membrane were immersed in pure ortho- or para-xylene. After several periods of time, the film was taken from the liquid, carefully wiped with a tissue and weighed in a closed conical flask. This was continued until no further weight increase was observed. The solubility is expressed as a relative weight increase (g xylene/100 g dry polymer).

## Results

### *Determination of solubility parameters of isomeric xylenes*

Although extensive tabulation of three dimensional solubility parameters are available in the literature, several substances are not found in the tables. The determination of the solubility parameters is often difficult and laborious. Koenhen [6] described the determination of solubility parameters of solvents and polymers by means of correlations with physical properties. This method offers a convenient and simple way of estimating solubility parameters.

### *Determination of $\delta_d$*

The relation used to estimate  $\delta_d$  is a very simple one. The main idea is that the interaction energy between nonpolar molecules is dependent on the polarizability (London dispersion forces). The polarizability is related to the index of refraction by the Lorenz—Lorentz equation. The relation, given by Koenhen [6] to determine the dispersion component,  $\delta_d$ , is:

$$\delta_d = 9.55 n_D - 5.55 \quad (5)$$

### *Determination of $\delta_p$*

Hansen [7] calculated the polar solubility parameter, using Böttcher's relation for estimating the contribution of permanent dipoles to the cohesive energy:

$$\delta_p^2 = \frac{12108}{V_m^2} \cdot \frac{\epsilon - 1}{2\epsilon + n_D^2} \cdot (n_D^2 + 2)\mu^2 \quad (6)$$

Another, and more simple, empirical relation has been given by Koenhen [6]:

$$\delta_p = 50.1 \frac{\mu}{V_m^{3/4}} \quad (7)$$

### Determination of $\delta_h$

Determination of  $\delta_h$  is possible if the hydrogen bond energy is known. Hydrogen bonding, however, is an interaction involving a proton donor (Lewis acid) and a proton acceptor (Lewis base).

Aromatics like benzene and xylenes are weak proton acceptors. A measure for the proton acceptor power is the extent of the shift to lower frequencies of the OD infrared absorption of deuterated methyl alcohol [8, 9].

An alternative approach to determine the hydrogen bonding solubility parameter is the determination of the hydrogen bonding interaction energy of a solvent mixture. Aromatic compounds can form hydrogen bonds with chloroform. With carbon tetrachloride no hydrogen bonding occurs. The energy of mixing of aromatic solvents with chloroform and carbon tetrachloride is given in Table 1. The difference in heat of mixing of chloroform and carbon tetrachloride in the aromatic solvents (column 3 in Table 1) can be considered as the energy of that specific hydrogen bond. Because the energy of the different hydrogen bonds are known,  $\delta_h$  can be calculated using eqn. (8) [4]. The values found by Hansen [4] are also given in Table 1.

$$E_h = \delta_h^2 V_m \quad (8)$$

In our opinion the disagreement of the results given by Hansen and in this work is not very significant. We conclude here, that the method described above, using heat of mixing data, can be used to calculate  $\delta_h$  values.

TABLE 1

Heat of mixing of chloroform and carbon tetrachloride with some aromatic solvents.  $\delta_h$  is calculated by eqn. (8). Hansen's  $\delta_h$  values are given as reference.

	$\Delta H_m^*$ (J/mol) in $\text{CHCl}_3$	$\Delta H_m^*$ (J/mol) in $\text{CCl}_4$	$\Delta(\Delta H_m)$ (J/mol-H-bonding)	$\delta_h$ (eqn. (8))	$\delta_h^{\S}$ (Hansen)
Benzene	-430	115	545	1.2	1.0
Toluene	-716	- 18	698	1.3	1.1
<i>o</i> -xylene	-941	- 23	918	1.4	1.5
<i>m</i> -xylene	-894	4	898	1.3	—
<i>p</i> -xylene	-912	- 76	836	1.3	—

\*Ref [10].

†Ref [11].

§Ref [4].

### Three-component solubility parameters

The individual solubility parameters are calculated in accordance with the above given procedure. The results are given in Table 2, together with the value by Hansen [4] for *o*-xylene. The one-component solubility param-

eter can also be calculated as the square root of the cohesive energy density (eqn. (1)). These calculated values, from experimental C.E.D. data given by Allen [12], are also given in Table 2. It can be concluded that our calculated results are in agreement with the experimentally determined C.E.D. values of Allen.

TABLE 2

Three dimensional solubility parameters of the isomeric xylenes; Hansen's *o*-xylene values are given as reference, together with the  $\delta$  values calculated from Allen's CED data

	$\delta_d$	$\delta_p$	$\delta_h$	$\delta$	$\delta$ (Allen) <sup>†</sup>
<i>o</i> -xylene (Hansen)*	8.7	0.5	1.5	8.8	9.0
<i>o</i> -xylene	8.8	0.7	1.4	8.9	9.0
<i>m</i> -xylene	8.7	0.4	1.3	8.8	8.9
<i>p</i> -xylene	8.7	0	1.3	8.8	8.8

\*Ref [4].

†Ref [12].

#### *Determination of the solubility parameters of the cellulose esters*

Solubility parameters of polymers are much more difficult to determine and there is no extensive compilation.

The solubility parameter of a polymer cannot be determined directly because most polymers cannot be vaporized without decomposition. A simple and convenient method of calculating solubility parameters of polymers is by means of molar attraction constants. It is necessary, therefore, to know exactly the structural formula and the density of the polymer. According to Burrell [17], the accuracy of this method is quite good to the first decimal place. This is adequate for practical purposes.

Koehen [6] and van Krevelen [13] showed that it is possible to estimate solubility parameters of polymeric materials from molar attraction constants. There are molar attraction constants for the dispersion, polar and hydrogen bonding contributions from which the three-component solubility parameters can be calculated. The group contributions,  $F_{id}$ ,  $F_{ip}$  and  $E_{ih}$ , are given in Table 3. The values of  $\delta_d$ ,  $\delta_p$  and  $\delta_h$  for the polymers used in this work, are calculated using the following relations given by van Krevelen [13]:

$$\delta_d = \frac{\sum F_{id}}{V_{ms}} \quad (9)$$

$$\delta_p = \frac{(\sum F_{ip}^2)^{1/2}}{V_{ms}} \quad (10)$$

TABLE 3

Solubility parameter group contributions,  $F_{id}$ ,  $F_{ip}$  and  $E_{ih}$ 

Structural group	$F_{id}^*$ (cal <sup>1/2</sup> cm <sup>3/2</sup> /mol)	$F_{ip}^\dagger$ (cal <sup>1/2</sup> cm <sup>3/2</sup> /mol)	$E_{ih}^\dagger$ (cal/mol)
—CH <sub>3</sub>	201	—	—
—CH <sub>2</sub> —	139	—	—
—CH— 	51	—	—
—COO—	193	240	1674
—OH	99	244	4782
—O—	49†	196	717
ring	93†	—	—

\*Ref [6].

†Ref [13].

$$\delta_h = \left( \frac{\sum E_{ih}}{V_{ms}} \right)^{1/2} \quad (11)$$

In order to calculate reliable values, one has to know the exact structure of a polymeric segment. The necessary information to calculate the solubility parameters of commercially available cellulose esters is given in Table 4.

The ester contents have been given by the manufacturer (Eastman chemicals). From these data the degree of substitution and the segmental molar volume of the cellulose esters are calculated. From the data given in Table 4 it is possible to determine exactly the segmental structure of the different polymers and to estimate the solubility parameters by using Table 3. The result is given in Table 5.

A similar procedure to calculate  $\delta_d$  and  $\delta_h$  values of the cellulose ester has been followed by Matsuura [14], our values are slightly higher than his.

TABLE 4

Calculation of the molar segmental volume for different cellulose esters. CA = cellulose acetate, CAB = cellulose acetate butyrate, CTP = cellulose tripropionate

No.	polymer	Content (%)		Degree of substitution		Density (g/ml)	$M_s$ (g/mol)	$V_{ms}$ (ml/mol)
		acetyl	alkyl	acetyl	alkyl			
1	CA 383	38.3	—	2.31	—	1.30	259.27	199.44
2	CA 398	39.8	—	2.45	—	1.30	265.16	203.97
3	CA 432	43.2	—	2.82	—	1.29	280.71	217.60
4	CAB 171	29.5	17.0	2.04	0.71	1.25	297.69	238.15
5	CAB 272	21.0	27.0	1.49	1.16	1.25	306.14	244.91
6	CTP	—	51.0*	—	2.90	1.27	324.76	255.72

\*Ref [14].



TABLE 5

Segmental structure and solubility parameters of cellulose esters

No.	Segmental structure	$\delta_d$	$\delta_p$	$\delta_h$	$\delta$
1	$(\text{CH}_2)(\text{CH})_5(\text{O})_2(\text{OH})_{0.69}(\text{OCCH}_3)_{2.31}$	7.8	3.5	6.6	10.8
2	$(\text{CH}_2)(\text{CH})_5(\text{O})_2(\text{OH})_{0.55}(\text{OCCH}_3)_{2.45}$	7.9	3.5	6.3	10.7
3	$(\text{CH}_2)(\text{CH})_5(\text{O})_2(\text{OH})_{0.18}(\text{OCCH}_3)_{2.82}$	7.9	3.6	5.7	10.4
4	$(\text{CH}_2)(\text{CH})_5(\text{O})_2(\text{OH})_{0.25}(\text{OCCH}_3)_{2.04}(\text{OCC}_3\text{H}_7)_{0.71}$	7.9	3.2	5.5	10.1
5	$(\text{CH}_2)(\text{CH})_5(\text{O})_2(\text{OH})_{0.35}(\text{OCCH}_3)_{1.49}(\text{OCC}_3\text{H}_7)_{1.16}$	8.1	3.1	5.5	10.3
6	$(\text{CH}_2)(\text{CH})_5(\text{O})_2(\text{OH})_{0.10}(\text{OCC}_2\text{H}_5)_{2.90}$	8.4	3.1	5.1	10.3

There is a small ring (acetylated glucose unit) contribution to  $\delta_d$  which he has not taken into account.

One can compare the calculated values with experimental values. Unfortunately, there are not many experimental values of solubility parameters of polymers known. For cellulose diacetate (polymer no. 1 in Table 5), an experimental value is known ( $\delta = 10.9$ ) [18]. The agreement with the calculated value ( $\delta = 10.7$ ) is fairly good. For the other polymers used, no experimental values have been found in the literature.

Good solvents for a polymer have solubility parameters in the range of that polymer. Therefore, one can compare these solubility parameters as a first estimate. According to Gee [19], it is not quite correct to assume that the solubility parameter of the polymer is actually the midpoint of the solubility range. For cellulose triacetate, the calculated value ( $\delta = 10.4$ ) agrees well with the value of tetrachloroethane ( $\delta = 10.6$ ). Solvents for cellulose acetate butyrates ( $\delta = 10.1$ – $10.3$ ) are dioxane ( $\delta = 10.0$ ), chloroform ( $\delta = 9.3$ ), acetone ( $\delta = 9.8$ ), dichloroethane ( $\delta = 10.2$ ) and tetrachloroethane ( $\delta = 10.6$ ). (Solubility parameters of the solvents are taken from Ref. [20]).

The agreement is quite satisfactory.

#### Determination of $\Delta$

Because the solubility parameters of the different cellulose esters and the isomeric xylenes have been estimated, it is possible to calculate the distance parameter  $\Delta$ , according to eqn. (4).

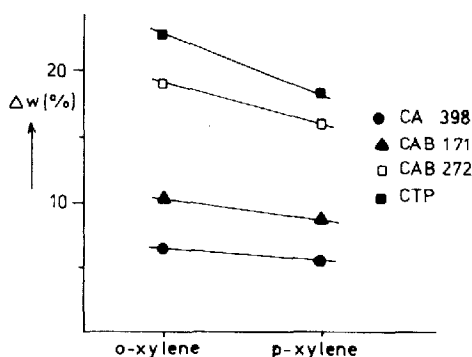
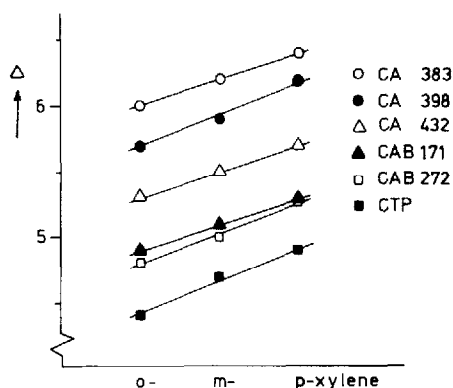
The results are given in Table 6. The results of Table 6 are also given in Fig. 4. The difference between the isomeric xylenes is small, as could be expected. The interaction between *o*-xylene and the different polymers is always larger ( $\Delta$  is smaller) than that of *p*-xylene for the same polymer. This is due to the presence of a dipole moment in *o*-xylene, whereas *p*-xylene has no dipole moment.

The polymer hydrophobicity increases from cellulose acetate (CA 383) to cellulose tripropionate (CTP). As can be seen from Fig. 4, an increase in hydrophobicity gives a decrease in the distance parameter  $\Delta$ , therefore a higher xylene solubility can be expected going from CA 383 to CTP.

TABLE 6

 $\Delta$  values of cellulose esters with regard to isomeric xylenes

No.	Polymer	<i>o</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene
1	CA 383	6.0	6.2	6.4
2	CA 398	5.7	5.9	6.2
3	CA 432	5.3	5.5	5.7
4	CAB 171	4.9	5.1	5.3
5	CAB 272	4.8	5.0	5.3
6	CTP	4.4	4.7	4.9

Fig.4. Calculated distance parameter  $\Delta$  between isomeric xylenes and cellulose esters.Fig.5. Relative weight increase (g/100 g polymer, 100%) for the cellulose esters in *o*-xylene and *p*-xylene.

### Swelling experiments

The results of the swelling experiments are given in Fig.5. No liquid uptake was observed with cellulose diacetate (CA 383) and cellulose triacetate (CA 432).

From Fig.5 it can be seen that differences in solubilities are not large, but consistently show that the solubility of *o*-xylene is always larger than that of *p*-xylene.

### Pervaporation experiments

The pervaporation results of the pure components and mixtures of *o*- and *p*-xylene through different cellulose esters are presented in Table 7 (temperature 20°C) and Table 8 (temperature 25°C). The permeation rate through cellulose diacetate (CA 398) was extremely low ( $< 10^{-3}$  cm/hr) and these results have not been considered further. With cellulose diacetate (CA 383) and cellulose triacetate (CA 432) membranes no permeability at all was observed.

TABLE 7

Pervaporation results of mixtures *o*-xylene/*p*-xylene; temperature 20° C

Membrane	Feed* (% <i>p</i> -xylene)	Rate (cm/hr) × 10 <sup>2</sup>	Δ <i>c</i> † (weight %)	α §
CTP	0	3.2	—	—
	25	4.0	5.5	1.29
	50	3.5	6.5	1.30
	75	4.8	4.7	1.31
	100	5.0	—	—
CAB 272	0	0.8	—	—
	25	0.6	2.8	1.16
	50	0.8	7.6	1.36
	75	1.1	4.9	1.33
	100	3.0	—	—
CAB 171	0	0.5	—	—
	25	1.6	5.6	1.36
	50	2.0	7.2	1.34
	75	2.3	5.9	1.43
	100	3.1	—	—

\* Weight %.

† Concentration *p*-xylene in the permeate minus concentration *p*-xylene in the feed.§ Separation factor; concentration ratio (weight %)  $y_A/y_B$  in the permeate divided by the concentration ratio  $x_A/x_B$  in the feed.

TABLE 8

Pervaporation results of mixtures *o*-xylene/*p*-xylene; temperature 25° C.

Membrane	Feed* (% <i>p</i> -xylene)	Rate (cm/hr) × 10 <sup>2</sup>	Δ <i>c</i> † (weight %)	α §
CTP	0	3.3	—	—
	25	5.0	3.1	1.22
	50	6.6	4.1	1.17
	75	9.3	4.2	1.24
	100	12.9	—	—
CAB 272	0	1.5	—	—
	25	2.1	3.4	1.25
	50	2.9	5.7	1.26
	75	4.4	4.2	1.24
	100	6.1	—	—

\* Weight %.

† Concentration *p*-xylene in the permeate minus concentration *p*-xylene in the feed.§ Separation factor; concentration ratio (weight %)  $y_A/y_B$  in the permeate divided by the concentration ratio  $x_A/x_B$  in the feed.

It is evident from the results that all polymers show higher permeation rates for *p*-xylene than for *o*-xylene. Furthermore, if the *p*-xylene concentration in the feed mixture increases, the permeation rate also increases. This is clearly illustrated in Figs.6 and 7.

On the other hand, there is no relation between selectivity and the *p*-xylene concentration in the feed. In all cases studied, a maximum in selectivity (expressed as  $\Delta c$ : the difference between the *p*-xylene concentration in permeate and feed) is observed for equimolar mixtures. The variations of the permeability with temperature show the expected behaviour: increasing the temperature gives higher permeation rates.

It is striking that results obtained with simple polymeric membranes, like the ones studied here and in the investigations of Michaels [1] are as good as the results obtained from polymers containing additives [2, 3].

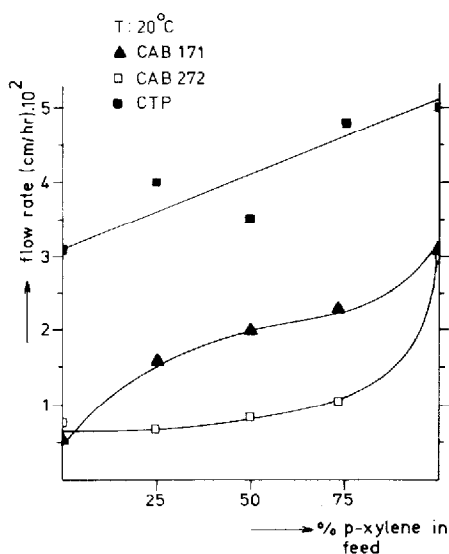


Fig. 6. Flow rate of mixture *o*-xylene/*p*-xylene (weight %) through different cellulose esters at 20°C.

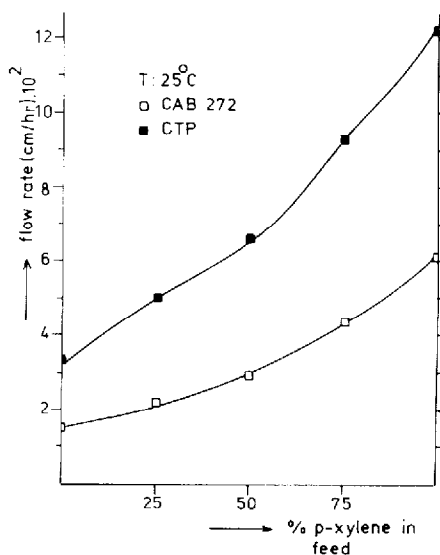


Fig. 7. Flow rate of mixture *o*-xylene/*p*-xylene (weight %) through cellulose acetate butyrate and cellulose tripropionate at 25°C.

## Discussion

Solubility measurements indicate, that for all membranes studied, the solubility of *p*-xylene is lower than that of *o*-xylene. Differences in solubility are not large but are significant. Figure 4 indicates that the calculated distance parameter  $\Delta$  between *o*-xylene and polymer is always smaller than that between *p*-xylene and polymer; thus solubility appears to be inversely proportional to  $\Delta$ . This has also been found by Froehling [5] and Broens [15]

using different polymers. An exception is cellulose triacetate (CA 432) with a  $\Delta$  value between CA 398 and CAB 171, while for this polymer no solubility was observed. The reason for this can be ascribed to the presence of crystalline material. Cellulose triacetate (CA 432) is more crystalline and small variations in crystallinity of the polymer can have large effects on the solubility of the penetrants in the polymer. Besides this exception, we can conclude from these results that the interaction between polymer and *o*-xylene is always larger ( $\Delta$  smaller, solubility larger) than that between polymer and *p*-xylene.

The affinity of a given isomer increases from cellulose diacetate (CA 383) to cellulose tripropionate (CTP). In the same order, the polymer becomes more hydrophobic as has been clearly illustrated by the solubility parameter data (Table 5).

As to the pervaporation data of the different membranes, for a given isomer the permeability increases with increasing solubility and decreasing  $\Delta$  as can be deduced from Figs. 4, 6 and 7. One is, therefore, tempted to postulate a relation between the observed permeability and the polymer-penetrant interaction. However, this relationship is not valid when comparing data for the three xylenes and each polymer. Although the affinity between *p*-xylene and a given polymer is smaller than that between *o*-xylene and polymer, the permeability is higher. These results cannot be explained in terms of molecular size, since molar volumes of the isomeric xylenes increase in the order *o*-xylene < *m*-xylene < *p*-xylene. The differences in interaction between *o*-xylene and *p*-xylene in each polymer is not large but is significant. The stronger interaction between *o*-xylene and each polymer is due to dipole forces. Therefore we assume that these dipole-dipole interactions cause an obstruction to *o*-xylene diffusion. Since *p*-xylene has no dipole moment, the interaction of this isomer and each polymer will be less strong. As a result, the permeability of *p*-xylene is higher than that of *o*-xylene.

As has been pointed out by Binning [16], besides interaction and molecular size, there is another factor which can cause a difference in permeation rate, that is a difference in shape. Michaels [1] explained the higher permeability of *p*-xylene through polyethylene by the difference between the isomers in cross-sectional area normal to the major axis. Permeability is determined by diffusivity and solubility. Despite the smaller solubility in case of *p*-xylene the diffusivity is, when compared with *o*-xylene, so large that the permeability will be larger, too. Therefore both factors, shape and interaction, are kinetic factors which will influence the diffusivity. There is, however, no relation between the solubility parameters and the kinetic factors.

As has been stated, there is no relation between selectivity and feed composition, independent whether selectivity is expressed as the separation factor or as the difference in concentration in permeate and feed. Nor is there a relation between selectivity and permeation rate. An increase in permeation rate barely effects the selectivity.

## Conclusions

We have shown that it is possible to use the solubility parameter theory in a qualitative manner to select polymers as membrane material as far as the permeability of one compound is concerned. Selectivity cannot be predicted by this  $\delta$ -parameter approach.

Solubility behaviour is found to be inversely proportional to the calculated distance  $\Delta$  in the  $\delta$ -space. Both  $\Delta$  values and solubility values are a measure for the interaction between polymer and organic solute. The results clearly indicate that, as far as one component is concerned, an increase in interaction gives an increase in permeability.

During pervaporation, a selectivity for *p*-xylene has been found in every case. This is in agreement with other investigations [1–3]. Selectivity for *p*-xylene in each polymer must be due to differences in molecular shape and solute–polymer interaction.

## List of symbols

$\delta$	Solubility parameter ( $\text{cal}^{1/2}\text{cm}^{-3/2}$ )
C.E.D.	Cohesive energy density ( $\text{cal cm}^{-3}$ )
$\Delta E$	Energy of vaporization ( $\text{cal mol}^{-1}$ )
$V_m$	Molar volume ( $\text{cm}^3 \text{mol}^{-1}$ )
$\delta_d$	Solubility parameter due to dispersion forces ( $\text{cal}^{1/2}\text{cm}^{-3/2}$ )
$\delta_p$	Solubility parameter due to polar forces ( $\text{cal}^{1/2}\text{cm}^{-3/2}$ )
$\delta_h$	Solubility parameter due to hydrogen bonding ( $\text{cal}^{1/2}\text{cm}^{-3/2}$ )
$\Delta$	Distance between polymer and solute in $\delta$ -space ( $\text{cal}^{1/2}\text{cm}^{-3/2}$ )
$\eta_D$	Index of refraction
$\epsilon$	Dielectric constant
$\mu$	Dipole moment (Debye units, D)
$F$	Molar attraction constant ( $\text{cal}^{1/2}\text{cm}^{3/2} \text{mol}^{-1}$ )
$\alpha$	Separation factor
$d$	Density ( $\text{g cm}^{-3}$ )
$M$	Molecular weight ( $\text{g mol}^{-1}$ )

## Indices

d	Dispersion
p	Polar
h	Hydrogen bonding
<i>i</i>	Component <i>i</i>
s	Segment

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