ELSEVIER

Chemical Engineering Journal 67 (1997) 191–197

Chemical Engineering Journal

Separation of higher molecular weight organic compounds by pervaporation

Renata G. Mathys *,[1], Willy Heinzelmann [2], Bernard Witholt

Institute of Biotechnology, ETH Hönggerberg, HPT, CH-8093 Zürich, Switzerland

Received 31 August 1996; revised 23 March 1997; accepted 4 April 1997

Abstract

Two-liquid phase bioconversions can be used to produce medium and long-chain 1-alkanols from the corresponding *n*-alkanes. A pervaporation process has been investigated for the separation of the product accumulated in the apolar phase of such a two-liquid fermentation system. The separation characteristics of various dense membranes towards organic mixtures (octane/1-octanol) were determined. The performance of eighteen membranes in separating 1-octanol from a large excess of octane has been tested. The different membranes showed either reasonably high selectivity (α) and low permeation rates or low selectivities and high fluxes. Minimal requirements of the pervaporation process for a desired selectivity with one and multistage pervaporations are presented. The results indicate that it should be possible to separate economically interesting organic products from higher molecular weight organic mixtures, by tailoring suitable membranes with a reasonably good selectivity and high flux for single or for multistage pervaporation systems. © 1997 Elsevier Science S.A.

Keywords: Pervaporation; Two-liquid phase fermentation; Downstream processing

1. Introduction

The separation of organic products from bioconversion systems can be tedious, depending on the chemical composition of the medium. This poses a challenge, because bioconversions are becoming increasingly interesting options for the synthesis of speciality compounds. One of the potential applications of biocatalysis is in the regio- and stereospecific oxidation of hydrocarbons, because the introduction of oxygen into inactivated organic substrates by classical chemistry remains difficult [1–3]. *Pseudomonas oleovorans* is able to oxidize a range of water–immiscible linear, branched, and cyclic alkanes and alkylbenzenes to alcohols, to oxidize alcohols to aldehydes, to demethylate branched methyl ethers, to sulfoxidate thioethers, and to epoxidize olefins [4]. As an example of such possible bioconversions, Bosetti et al. described the production of 1-alkanols from *n*-alkanes with *P. putida* (GPp11) [5], in two-liquid phase fermentations for alkanes with chain lengths from C_6 to C_{12}.

This two-liquid fermentation process is characterized by the *in situ* extraction of 1-alkanol into the apolar phase (alkane). After separation of the apolar phase from the polar phase, the product can be recovered from the organic phase. One of the industrial methods often used to separate organic liquid compounds is distillation. However, since the reaction mixture contains a large amount of alkane [95% (v/v)] with a vapor pressure higher than that of the corresponding 1-alkanol, distillation is an inefficient process for obtaining the product from an energy-saving point of view. Distillation requires that the whole feed be vaporized in order to recover a small quantity of product. Since the high-boiling-point product will have to be collected as bottom product, it will contain impurities from the fermentation medium and therefore require further purification and solvent recovery steps. Given these circumstances, other separation processes should be considered. Based on the physical and chemical constants of the components of the apolar phase and the nature of the bioprocess, pervaporation is a possible alternative. Membrane separation, particularly pervaporation, has established itself as a competitive alternative to distillation in alcohol–water separation. Economically, the process compares favorably with distillation when a relatively small amount of substance is removed, due to lower energy consumption, when an azeotrope is formed and in general, when a complex feedstock is involved. Apart from two-phase organic–water separations, the pervaporation process has also been studied

* Corresponding author.

[1] Tel. +41 1 633 3402; email: mathys@biotech.biol.ethz.ch

[2] Present address: CM-CELFA Membrantrenntechnik AG, CH-6423 Seewen-Schwyz, Switzerland.

PII S1385-8947(97)00046-6

to a lesser extent for selective and specific separation of one-phase organic liquid mixtures [6–16] [17–19]. A characteristic of membrane separations is the selective permeation by means of physical and chemical interactions such as polarity, solubility difference and hydrogen bonding between permeate and membrane. The driving force for the mass transport through the membrane is maintained by vacuum or by sweep gas on the permeate side.

The purpose of the present study was to analyze pervaporation as a possible process to separate a binary *n*-octane/1-octanol mixture. Eighteen membranes were tested and the results were compared to the fractionation of several other solvent mixtures [6,9,11,14–17].

2. Materials and methods

2.1. Model apolar phase

To test the suitability of different membranes, the apolar phase was made up from pure synthetic chemicals and consisted of 95% *n*-octane (v/v) and 5% 1-octanol (v/v).

All of the chemicals and hydrocarbons used were of the best purity available (Fluka, Buchs, Switzerland). *n*-Octane (98.5% purity) was purchased from Acros (Geel, Belgium).

2.2. Membranes

Polymer films made up of composite materials were used. Some are commercially available, but most of the composite membranes used were laboratory samples provided by CM-CELFA, Membrantrenntechnik AG, Seewen-Schwyz, Switzerland. The membranes ranged in thickness from about 1–10 μm (see Table 1).

2.3. Equipment details

The suitability of membranes was evaluated in a laboratory-scale membrane unit P-28 manufactured by CM-CELFA. Fig. 1 shows a schematic diagram of the experimental pervaporation apparatus used in this study. The apparatus consisted of a flat-sheet membrane cell with integrated feed tank made of stainless steel. The upstream feed compartment had a volume of about 500 ml, and the membrane area in contact with the feed solution was 28 cm^2. The membrane was supported on a sintered stainless steel disk. The downstream pressure was maintained at 10 mbar. Pervaporation was carried out at 80 °C. The permeate side of the cell was evacuated with a vacuum pump from Vacuubrand MZ 2C (980–2 mbar). Prior to carrying out pervaporation measurements using a new membrane, the system was conditioned for several hours using only octane. Diffusing permeate was collected in a cold trap which was immersed in liquid nitrogen. Mean values of three experiments were used in the calculation of permeation rates and selectivity. The difference between successively measured values was less than 5% (average standard deviation = 1.3).

Table 1
Summary of experimental separation parameters for 1-octanol/octane mixture

Membrane film (All membranes are composite membranes with a dense active polymer layer and a porous support)	Membrane thickness [a] (μm)	Permeation rates ($g\,m^{-2}\,h^{-1}$)	Selectivity α	Permeate composition	
				Product (% 1-octanol)	Impurity (% *n*-octane)
1. Cellulose diacetate with tensidic additives on PHN [b]	5	<1	7	86	14
2. Cellulose triacetate on PES [c]	5	<1	12	38	62
3. Poly(vinyl chloride)/poly(vinyl acetate) on PAN [d]	2	9	7	27	73
4. Polyurethane on PHN	10	4	6	24	76
5. Poly(vinyl chloride)/poly(vinyl acetate)/poly(vinyl alcohol) on PAN	2	15	5	21	79
6. Cellulose triacetate with cationic additives on PHN	5	<5	3	13	87
7. Poly(vinyl alcohol)/poly(vinyl acetate) on PAN	2	3	3	13	87
8. Poly(vinyl alcohol) on PAN	1	<2	2	9	91
9. Cellulose acetate butyrate on PES	5	<5	1	5	95
10. Polydimethylsiloxane on PAN	10	1020	<1	<5	>95
11. Polydimethylsiloxane on PES	10	730	<1	<5	>95
12. Modified polysiloxane on PAN	10	300	<1	<5	>95
13. Plasma modified fluoropolymer on PAN	1	234	<1	<5	>95
14. Modified polyphenyl on PHN	5	200	<1	<5	>95
15. Plasma modified fluoropolymer on PES	1	194	<1	<5	>95
16. Asymmetric polyacryl nitrile	<1	12	<1	<5	>95
17. Polyacryl nitrile/polyacrylic acid on PAN	2	2	<1	<5	>95
18. Modified polyacryl nitrile on PES	2	<1	<1	<5	>95

[a] Approx. thickness of active membrane layer. Porous membrane support: [b] Polyhydantoine, [c] Polyethersulfone, [d] Polyacryl nitrile.

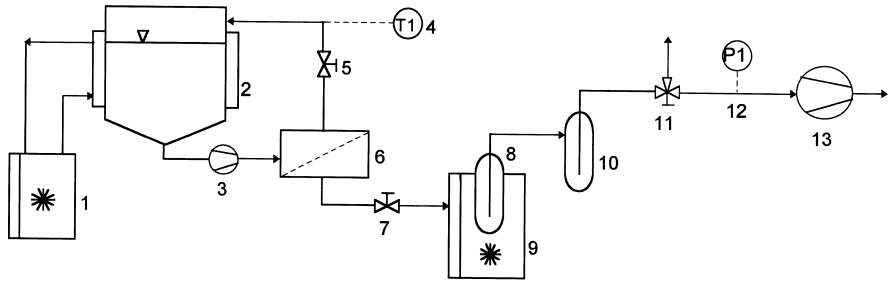

Fig. 1. Pervaporation apparatus: (1) constant temperature bath regulated by a thermostat; (2) feed tank; (3) recirculation pump; (4) thermometer Pt-100; (5) regulation valve; (6) membrane cell; (7) shut-off valve; (8) cold trap; (9) constant temperature bath regulated by a cryostat; (10) security trap; (11) vent; (12) vacuum meter; (13) vacuum pump.

2.4. Analytical procedure

To determine the permeation rate and selectivity exhibited by each membrane batch experiments were performed and the measurements were analyzed as described below. Organic phase samples were taken from the feed solution shortly before pervaporation was started. After the experiment, samples were taken from the cold trap, where the permeate was collected, and from the retentate side of the pervaporation cell. Feed mixture, retentate and permeate where weighed before and after each experiment.

Measurements of *n*-octane and 1-octanol concentrations were done using a computer-controlled capillary gas chromatograph (Fison Instruments, HRGC MEGA 2 series). Samples were prepared as follows: 1% (v/v) organic phase (directly or after freezing and thawing) was added to pure *n*-hexane with 1% (v/v) 2-octanol as internal standard. These prepared samples were analysed by split injection into a CP-SIL-5CB (25 m long with a 0.45 mm internal diameter) capillary column (supplied by Chrompack, the Netherlands) with H_2 as carrier gas, and peaks were detected with a flame ionization detector. The samples were eluted at an initial temperature of 200 °C for 2 min, followed by a linear increase of 10 °C min^{-1} to reach the final temperature of 280 °C. The compounds were quantified from the integrated GC signal by the internal standard method, using reagent grade standards.

2.5. Binary liquid permeation

If there are two components in the liquid mixture, i.e. a binary system consisting of two liquids A and B, the membrane selectivity is commonly expressed in terms of a separation factor α [7,13], defined as the concentration ratio B/A in the permeant (downstream) divided by the ratio B/A in the feed mixture (upstream):

$$\alpha_{B/A} = \frac{Y_B/Y_A}{X_B/X_A} \quad (1)$$

where X is the weight fraction in the feed (permeate) and Y the permeant weight fraction.

3. Results

The characterization of the pervaporation process with respect to permeation rate and selectivity is reported in Table 1. The values of the total mass flux (g m^{-2} h^{-1}) were measured and the selectivity (α) was calculated from Eq. (1) using the obtained experimental values. The membranes were chosen according to the following criteria:

- Organophilic (hydrophobic) pervaporation membranes are commercially available. They normally show good permeation rates for organic molecules, but at the expense of low selectivity. Such membranes, which are used on a technical scale to remove organic impurities from water, were nos. 10–12 (Table 1).
- Organo-selective membranes allow the separation of different organic molecules from each other. Not many such membranes have been described in the literature. Examples are membrane nos. 1, 2 and 6 (Table 1), which were developed for the separation of low molecular weight alcohols from ethers or esters.
- Hydrophilic (water selective) pervaporation membranes are also commercially available. They show little permeability for organic molecules. Still, two membranes, nos. 7 and 8 (Table 1), were tested.
- The other samples were membranes which, based on their composition, were expected to show some selectivity towards more polar molecules.

In all, 18 membranes were tested (Table 1; and Fig. 2 for membranes 1–9). From these we found either 1-octanol selective membranes with the correct but low selectivity (membranes 1–9) and reasonably high flux (membranes 3–5) or octane-selective membranes with the wrong selectivity (membranes 10–18) and a high flux (membranes 10–15).

4. Discussion

4.1. Suitability of pervaporation for the separation of higher molecular weight organic liquid mixtures

Octane and 1-octanol are considered higher molecular weight compounds from a diffusion point of view, based on the criterion that the driving force through a membrane

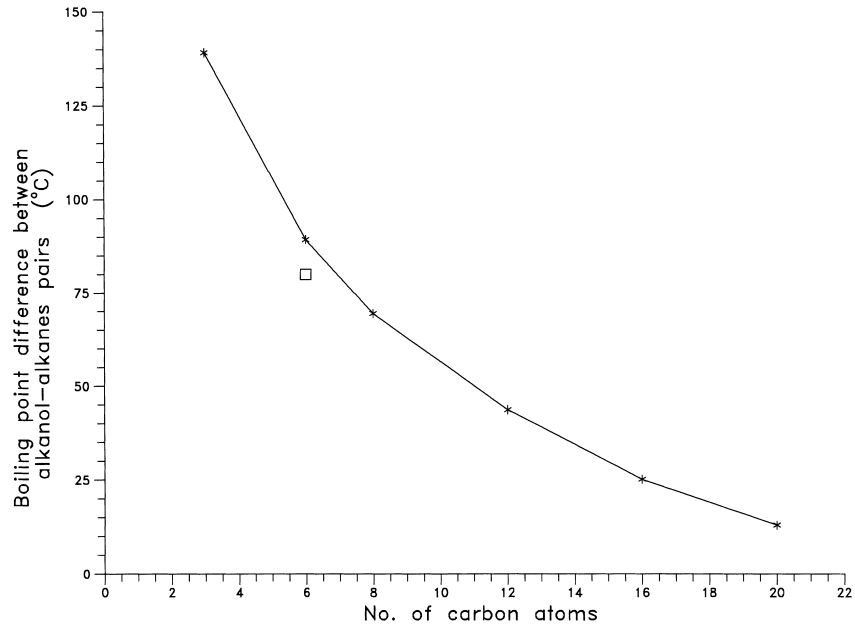

Fig. 2. Selectivity versus flux for pervaporation membranes using membranes 1 to 9 to separate 1-octanol/octane (Table 1).

decreases with increasing boiling point and therefore generally, increasing molecular weight of a compound. The permeation rate of organic mixtures, such as alkanes and alkanols depends not only on diffusion and solubility, but is also strongly dependent on partial pressure differences or consequently, boiling point differences, which decrease with increasing molecular weight (Fig. 3) for alkane–alkanol pairs with the same number of carbon atoms. Shimidzu and Okushita [15] also tried to separate a similar higher molecular weight aliphatic mixture (Fig. 3), namely cyclohexanone and cyclohexanol from cyclohexane, through a poly-(*N*-vinylpyrrolidone-co-acrylonitrile) membrane (Table 2),

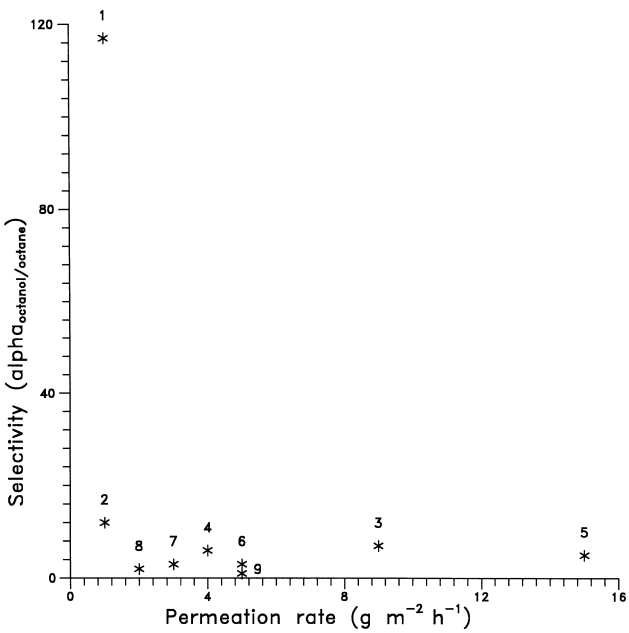

Fig. 3. Boiling point difference (at 1 atm) between homologous compounds: ∗ alkanols/alkanes with 3–20 C-atoms; □ cyclohexanol/cyclohexane.

and found a selectivity of 15 and a flux of 5 g m^{-2} h^{-1}. These results compare to the values obtained for membranes 3–5 (Table 1) in this study. Other investigators [6,9,11,14, 16,17] listed in Table 2, who tried to separate low molecular weight alkanols from higher molecular weight aliphatic compounds, reported mostly reasonably good separation results using cellulose acetate based and other membranes. Uragami et al. [9] obtained a flux of 300 g m^{-2} h^{-1} and a selectivity of <1 for the separation of *n*-heptane from *n*-propanol, an organic mixture with a boiling point difference of only 0.6 °C (Table 2). However, when increasing the heptane fraction in the feed mixture to 80%, they reported an increase in selectivity to 25 at a flux of 280 g m^{-2} h^{-1}. Sweeny and Rose [6] reported a selectivity of the ethanol separation from *n*-hexane through a cellulose acetate membrane ranging from 17 to 130, depending on temperature and membrane thickness variations. Yamaguchi et al. [16] and Steiner [17] found that the permeability and selectivity could be substantially improved when membranes were prepared with the plasma polymerization technique.

4.2. Comparison of proposed multistage performance to single stage pervaporation

In general, there is no apparent correlation between the chemical nature of the membrane film and permeation rates. Given that the desired combination of a high selectivity and acceptable flux are difficult to attain, the separation of compounds which display only subtle differences in their chemical nature, such as octane/1-octanol, perhaps require a more laborious multistage operation. A practical solution, when no suitable high selective membrane is available, may be a multistage pervaporation cascade. The product concentration can then be performed using several pervaporation stages to reach

Table 2
Organic mixtures separated by pervaporation

Binary organic feed mixture	Membrane film	Selectivity α	Permeation rates ($g\,m^{-2}\,h^{-1}$)	Membrane thickness (μm)	Operating temperature (°C)	Reference
90% cyclohexane/10% cyclohexanone + cyclohexanol	poly(*N*-vinylpyrrolidone-co-acrylonitrile)	15	5	16–22	50	[15]
90% *n*-propanol/10% heptane	nylon 12	<1	300	25	40	[9]
20% *n*-propanol/80% heptane	nylon 12	25	280	25	40	[9]
95% *n*-hexane/5% methanol	–quaternary poly(phenylene oxide)	500	550	40	25	[11]
95% *n*-hexane/5% methanol	–cellulose acetate/poly[bromo-phenylene(dimethyl)phosphonate]	90	280	40	25	[11]
95% *n*-hexane/5% methanol	–Nafion with Al^{3+} as cation	70	700	40	40	[11]
90% heptane/10% ethanol	–cellulose acetate	78	600	10	25	[14]
70% heptane/30% ethanol	–poly(hexamethylene adipamide)	63	480	10	25	[14]
n-hexane/ethanol	–cellulose acetate	17–130	–	–	–	[6]
n-hexane/ethanol	–cellophane	100	–	–	–	[6]
50% cyclohexane/50% ethanol	plasmo-graft polymerized membrane (methy acrylate and acrylamide)	190	50	5	–	[16]
95% pentane/5% methanol	plasmo-polymerized membrane (Pervap-1137)	108	2500	–	80	[17]

Table 3
Minimal requirements for 1, 2 and 3 step pervaporation

Minimal pervaporation process requirements for a desired selectivity (≈95% purity) and the necessary permeation rate	α	Permeation rate ($g\,m^{-2}\,h^{-1}$)	Product (%)	Amount of permeate ($kg\,h^{-1}$)	Required membrane area (m^2)
For octane/1-octanol pervaporation:	100 m^2 membrane for 100 kg feed (⇒6 kg product)				
1 step process	298	60	95.0	6.3	**105.0**
2 step process, 1. stage	50	135	76.1	7.88	58.4
2. stage	50	135	99.4	6.03	44.7
Total membrane area					**103.1**
3 step process, 1. stage	6	360	27.9	21.5	59.7
2. stage	6	360	69.9	8.6	23.9
3. stage	6	360	93.3	6.4	17.8
Total membrane area					**101.4**
High value product (fine chemical):	200 m^2 membrane for 100 kg feed (⇒ 6 kg product)				
1 step process	298	30	95.0	6.3	**210.0**
2 step process, 1. stage	50	66	76.1	7.88	119.4
2. stage	50	66	99.4	6.03	91.4
Total membrane area					**210.8**
3 step process, 1. stage	6	175	27.9	21.5	122.9
2. stage	6	175	69.9	8.6	49.1
3. stage	6	175	93.3	6.4	36.6
Total membrane area					**208.6**
High value product (fine chemical):	400 m^2 membrane for 100 kg feed (⇒ 6 kg product)				
1 step process	298	15	95.0	6.3	**420.0**
2 step process, 1. stage	50	33	76.1	7.88	238.8
2. stage	50	33	99.4	6.03	182.7
Total membrane area					**421.7**
3 step process, 1. stage	6	87	27.9	21.5	247.1
2. stage	6	87	69.9	8.6	98.9
3. stage	6	87	93.3	6.4	73.6
Total membrane area					**419.6**

the same required product purity. Table 3 summarizes minimal pervaporation requirement calculations for a desired selectivity, based on single and multistage pervaporations operations.

Calculations were performed based on the following assumptions: (i) The selectivity is constant over a wide range of feed composition in each step (ii) All of the product will permeate through the membrane. To achieve a desired sepa-

ration with a product purity of for example 95% (w/w), a selectivity of $\alpha = 298$ would be required, if the bioconversion in the fermentor results in the formation of about 6% product in the apolar phase pervaporation feed, i.e. for every 100 kg h^{-1} of feed mixture into the pervaporation unit, the product 1-octanol would then amount to 6 kg h^{-1}. (iii) The use of 1 m^2 of membrane area per kg h^{-1} feed to be processed is economically acceptable [20]. The resulting 1-octanol flux will then be 60 g m^{-2} h^{-1} and the required membrane area for a single step separation of about 6 kg product per hour will be 105 m^2. Given the selectivities which we have measured, a selectivity of $\alpha = 298$ with a flux of 60 g m^{-2} h^{-1} is not yet possible for 1-octanol/octane mixtures. Alternatively, if 3-stage operation is used to reach a desired purity of about 95%, a membrane with a selectivity of 6 would be acceptable, if a permeation rate of 360 g m^{-2} h^{-1} can be attained (Table 3). This is also not yet possible.

For more valuable products, such as for instance styrene epoxide or other fine chemicals which are also produced in the apolar phase of two-liquid fermentation systems [21], the downstream processing cost per m^2 of membrane area can be higher and membrane areas of 2 or 4 m^2 per kg h^{-1} of feed mixture can be utilized. The advantage of increasing the number of pervaporation steps, i.e., concentrating the product over several stages, is that the membrane can be designed for a lower selectivity (α) requiring the same total size of membrane area for the feed mixture to be processed. Fig. 4 illustrates the desired selectivity vs. permeation rates for the different calculated conditions and also includes the measured values for comparison. A comparison of the calculated results in Table 3 to the measured values in Table 1 suggests that a membrane with selectivity 5 and a permeation rate of 15 g m^{-2} h^{-1} (5) might be superior to a membrane with selectivity 117 and a permeation rate of 1 g m^{-2} h^{-1} (1) when considering a two or three stage pervaporation process. Therefore, membranes (3), (4) and (5) can be considered the best membranes identified so far.

4.3. Toward practical pervaporation processes

One way to increase permeability is by finding a suitable membrane. Another strategy is to increase the operating temperature. Due to equipment limitations, the pervaporation could only be operated at a maximum temperature of 80 °C. In principle, a flux comparable to the calculated values can be reached when increasing the operation temperature by 30–40 °C, but commercial PV membranes can only be operated up to 100 °C. Based on the Arrhenius type equation, the permeation rate increases by a factor of approximately 2 for each 10°C temperature rise [13], and it is known that the selectivity varies only slightly for temperature changes [22,23]. The dashed line in Fig. 4 gives estimated values of

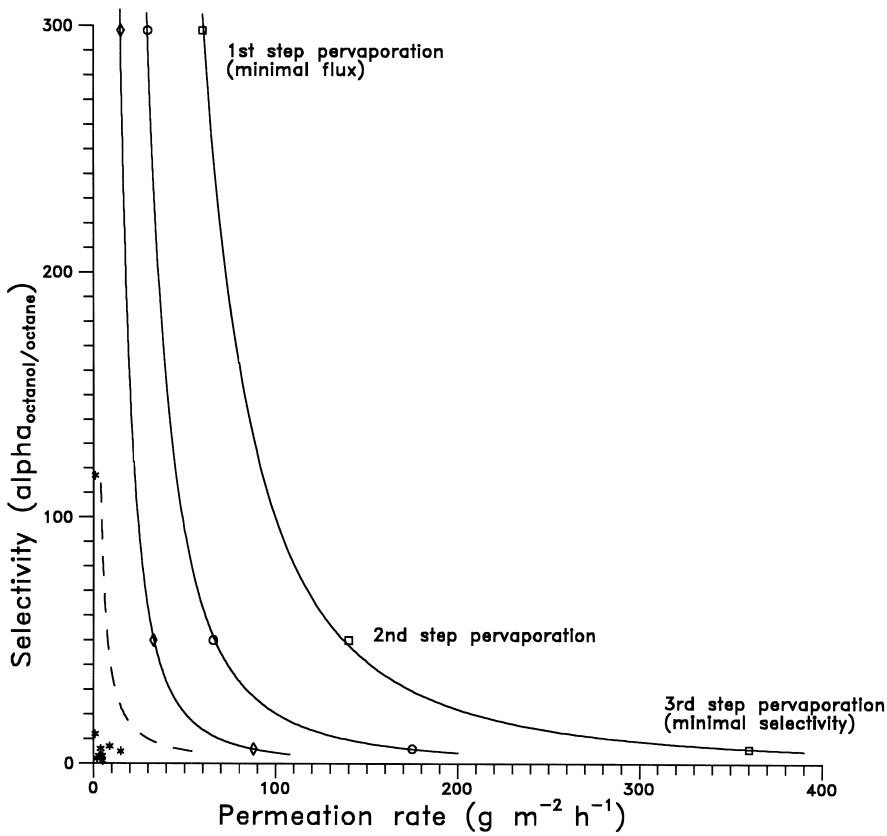

Fig. 4. Desired selectivity and permeation rates on octane–octanol mixtures for different pervaporation systems: ∗ measured data; - - -, estimated values based on measured data at 100 °C; ◇ minimal requirements for 4 m^2 membrane kg^{-1} feed; ○ minimal requirements for 2 m^2 membrane kg^{-1} feed; □ minimal requirements for 1 m^2 membrane kg^{-1} feed.

the tested membranes at 100 °C, demonstrating that the measured values (Table 1) at that operating temperature would differ by a factor of only 2 from those of a membrane requiring 4 m^2 per kg of feed processed.

5. Conclusion

It is a general rule that the flux decreases as the permselectivity of a polymeric material increases [13]. In our experiments to separate 1-octanol from *n*-octane, we saw the same phenomenon. The membranes tested showed either a high selectivity or a high flux. Nevertheless, by customizing polymer composition, it should be possible to tailor a suitable membrane with a reasonably good flux and selectivity for economically interesting organic products. Depending on the ease of separation, multistep pervaporation processes may be more feasible than single step processes.

References

[1] B. Witholt, M.-J. de Smet, J. Kingma, van J. Beilen, M. Kok, R.G. Lageveen, G. Eggink, TIBTECH 8 (1990) 46–52.
[2] B. Witholt, J. Sijtsema, M. Kok, G. Eggink, in: S. Silver, A.M. Chakrabarty, B. Iglewiski, S. Kaplan, (eds.), Pseudomonas: Biotransformations, Pathogenesis, and Evolving Biotechnology, American Society of Microbiology, Washington, DC, 1990, pp. 141–150.
[3] M.D. Lilly, J.M. Woodley, Biocatalysis, in: J. Tramper, H.C. van der Plas, P. Linko (eds.), Biocatalyst in organic synthesis, Elsevier, Amsterdam, 1985, pp. 179–192.
[4] J.B. van Beilen, J. Kingma, B. Witholt, Enzyme Microb. Technol. 16 (1994) 904–911.
[5] A. Bosetti, J. van Beilen, H. Preusting, R.G. Lageveen, B. Witholt, Enzyme Microb. Technol. 14 (1992) 702–708.
[6] R.F. Sweeny, A. Rose, Ind. Eng. Chem., Prod. Res. Devel. 4 (1965) 248–251.
[7] R.Y.M. Huang, V.J.C. Lin, J. Appl. Polym. Sci. 12 (1968) 2615–2631.
[8] H.L. Cheng, Separ. Sci. Technol. 16 (1) (1981) 25–30.
[9] T. Uragami, T. Fujisawa, M. Sugihara, 42. Separation of binary organic solvent mixtures through nylon 12 membranes, Polymer Bull. 5 (1981) 195–200.
[10] F. Suzuky, K. Onozato, J. Appl. Polym. Sci., 27 (1982) 4229–4238.
[11] I. Cabasso, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 313–319.
[12] N. Radke, H. Rödicker, Plaste Kautschuk 7 (1984) 255–257.
[13] C.E. Roger, M. Fels, N.N. Li, in: N.N. Li (ed.), Recent Development in Separation Science, vol. II, CRC Press, Cleveland, Oh, 1972, pp. 107–155.
[14] M. Laatikainen, M. Lindström, Acta Polytech. Scand. Chem. Technol. Metall. Seri. 175 (1986) 3–61.
[15] T. Shimidzu, H. Okushita, J. Membrane Sci. 39 (1988) 113–123.
[16] T. Yamaguchi, S. Nakao, S. Kimura, Ind. Eng. Chem. Res. 32 (1993) 848–853.
[17] H. Steinhauser, Chemie Technik 23 (1994) 50–53.
[18] J. Schauer, J. Appl. Polym. Sci. 53 (1994) 425–428.
[19] T.M. Aminabhavi, R.S. Khinnavar, S.B. Harbogoppad, U.S. Aithal, Q.T. Nguyen, K.C. Hansen, Journal of Membrane Scinece–Rev. Macromol. Chem. Phys. C34 (1994) 139–204.
[20] G.K.P. Kalsep, Proc. 4th Int. Conf. Pervaporation Processes Chem. Ind., Bakish Materials Corporation, New Jersey, USA, Dec. 3–7, 1989, pp. 278–296.
[21] M.G. Wubbolts, J. Hoven, B. Melgert, B. Witholt, Enzyme Microb. Technol. 16 (1994) 887–894.
[22] P.J. Hickery, C.S. Slater, Proc. 4th Int. Conf. Pervaporation Processes Chem. Ind., Bakish Materials Corporation, New Jersey, USA, Dec. 3–7, 1989, pp. 579–589.
[23] Q.T. Nguyen, A. Essamri, Z.H. Ping, J. Néel, H. Brueschke, Proc. 5th International Conf. on Pervaporation Processes in the Chem. Industry, Heidelberg, Germany, Bakish Materials Corporation, New Jersey, USA, March 11–15, 1991, pp. 67–78.