New Insights into Pervaporation Mass Transport under Increasing Downstream Pressure Conditions: Critical Role of Inert Gas Entrance

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The influence of the total downstream pressure on the pervaporation flux of a pure compound through a dense polymer membrane has been the subject to controversial debates recently. Experimental arguments in favor of either the solution—diffusion model or the newly proposed pore-flow model are alternatively reported on different systems. To critically reexamine this debate, an experimental study under controlled downstream conditions has been performed for pure methanol and pure 2-propanol pervaporation through a poly(dimethylsiloxane) film, the latter having been previously reported to follow pore-flow model predictions. It is shown that a rational analysis of the effects of the downstream pressure on the results can be achieved according to the classical solution—diffusion model, provided that the influence of air leaks in the installation is properly taken into account. Based on this observation, the implications of an inert gas contribution, generally speaking, on pervaporation operation are discussed.

Introduction

Pervaporation is a membrane separation technique that has received considerable attention recently from both the fundamental and applied points of view. As in any separation process making use of dense polymers, pervaporation mass transport is most often described according to the so-called solution—diffusion model, considered as a cornerstone in this field. A number of experimental verifications of this model have been already accumulated, usually based on the confirmation of its predictions (such as those summarized by Lee⁴) when membrane boundary conditions are changed either on the upper or lower side.

Nevertheless, studies dealing specifically with the influence of downstream pressure on pervaporation fluxes are exceptions from this point of view and still remain somewhat controversial. An alternative transport model⁵ (the so-called pore-flow approach), which postulates a situation that is completely different from the solution-diffusion model, has been proposed recently for that specific purpose. In fact, similarly to a two-film model sketched earlier,6 the pore-flow hypothesis postulates that two different layers coexist within the membrane when pervaporation is effective: a swollen layer on the upper side, where the compound is assumed to flow in liquid form according to Darcy's equation, and a dry zone on the downstream side, where vapor only is assumed to flow according to a surfaceflow mechanism. An important feature of this picture is that it predicts that the pervaporation flux of a pure compound reaches a plateau value different from zero, even when the compound vapor pressure is exerted on the downstream side of the membrane. Such a peculiarity is striking from the thermodynamic point of view

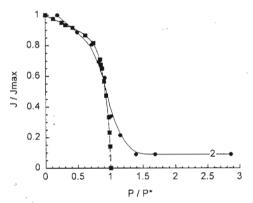


Figure 1. Influence of downstream pressure (x axis) on purecompound pervaporation relative flux (y axis). Typical patterns of previously reported experimental results consistent with the solution—diffusion model¹² (heptane/natural rubber, curve 1) and the pore-flow model⁷ (2-propanol/PDMS, curve 2).

and cannot be accounted for by a homogeneous matrix assumption. This observation has occasionally been reported experimentally for a few systems⁷⁻¹⁰ and remains a key argument in favor of the pore-flow model.

A completely different situation was described by earlier studies, which reported that pervaporation fluxes of pure compounds vanish when their vapor pressure is attained on the downstream side. ¹¹ A typical example concerns the pioneering work performed by Paul and Paciotti ¹² on hydrocarbon transport through elastomers, confirmed by other later studies. In that case, a pressure increase on the upper side (a reverse-osmosis-type situation) and a pressure decrease on the downstream side (a pervaporation-type situation), leading to drastic mass flux changes, are correctly described according to solution—diffusion model predictions, together with a zero flux value at the saturated pressure of the compound.

The somewhat controversial situation described above is summarized in Figure 1, which shows the typical pattern for each of the two models. A brief review of

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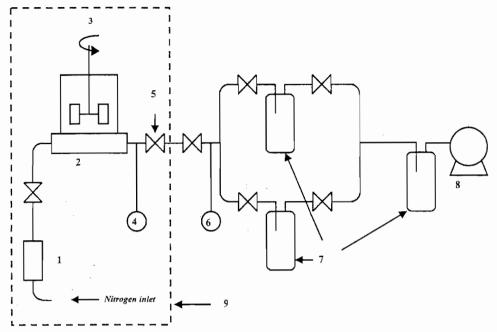


Figure 2. Overall experimental setup: (1) nitrogen mass flowmeter; (2) membrane module; (3) feed reservoir; (4) downstream manometer; (5) high-sensitivity pressure valve; (6) vacuum pump manometer; (7) cold traps; (8) vacuum pump; (9) controlled-temperature oven.

studies performed in this field does not lead to a systematic criterion (membrane structure, liquid permeant, active layer type, etc.) that could act as an explanatory factor for either of the two mechanisms. This situation complicates the analysis and has practical implications as it makes the transposition of laboratory results to industrial situations uncertain. In fact, industrial pervaporation units usually work under downstream pressure conditions in the range of 1000-5000 Pa because of the technical difficulty of achieving a lower vacuum on a large scale. What is more, pervaporation laboratory studies are most often reported under vacuum conditions ranging between 1 and 100 Pa. For this reason, the direct applicability of laboratory pervaporation results to industrial situations is frequently questioned but rarely considered.

The situation described above calls for a rational understanding of the role of downstream pressure in pervaporation, for both the fundamental and applied aspects. We report herein an experimental attempt to fill that gap, as well as an interpretation of some of the early results. As in the strategy developed earlier by Paul and Paciotti, a dense polymer film without a microporous support layer has been used to remove capillary interference (such as that potentially obtainable by thin-layer composite membranes supported on an ultrafiltration medium). Furthermore, although a great amount of data in the literature concerns the permeation of binary mixtures, thus complicating greatly the transport analysis, ¹³ we initially focused on purecompound pervaporation experiments.

Finally, a key point was to choose an experimental system that had already been reported to be in agreement with the pore-flow model and to test it under controlled conditions. We will point out the crucial role of inert gas flow, which results inevitably from air leaks (e.g., on the vacuum side) in any installation, and show how this essentially uncontrolled parameter can explain apparently contradictory results. Surprisingly, such a key characteristic of vacuum techniques as the leak level is never specified in experimental studies dedicated to

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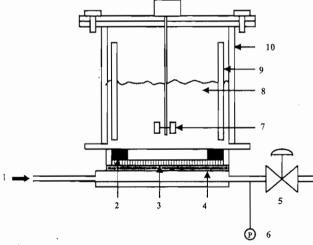


Figure 3. Detailed view of the pervaporation cell: (1) dry nitrogen inlet connection; (2) Viton O-ring; (3) membrane; (4) stainless steel sintered support; (5) high-sensitivity pressure valve; (6) downstream manometer; (7) impeller; (8) feed reservoir (liquid); (9) baffles; (10) double-walled vessel thermostated with an external oil circulation.

pervaporation and has never been systematically investigated.

Materials and Methods

The lab-scale setup used for the experiments is shown in Figure 2 and consists of a stainless steel permeation cell with an effective membrane area of $78.5~{\rm cm^2}$, installed inside a controlled-temperature oven in order to ensure constant-temperature conditions around the cell (except for the cold trap located outside the incubator). The cell, represented in Figure 3, is a cylindrical double-walled vessel that can be thermostated by external oil circulation ($\pm 0.1~{\rm ^{\circ}C}$). The height of the downstream chamber is sufficient (around 1 cm) for the axial pressure drop under operating conditions to be considered negligible (the same argument does not hold, for instance, for studies performed on hollow-fiber modules).



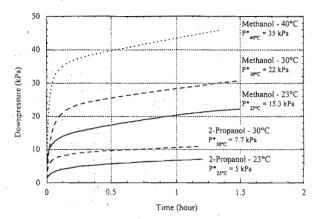


Figure 4. Total downstream pressure increase versus time for methanol and 2-propanol pervaporation, obtained after the connection to the vacuum pump was closed for different temperature conditions. The air leak level of the installation has been estimated from the slope of the curve in the linear part for long-time conditions.

On the permeate side, a vacuum pump (Alcatel 1012A) provides the necessary driving force (lowest downstream pressure of around 15 Pa). The total downstream pressure is monitored by a precision manometer (Edwards EMV 251, precision of ± 100 Pa) and can be tuned to a constant value with a high-sensitivity pressure valve, recommended for controlled vacuum-level applications (Balzers UDV 040). This choice is of importance as passive pressure control can be achieved without the need for either a temperature change or an inert gas entrance. In fact, previously reported experimental setups make use of a modification of the coldtrap temperature14 or a tunable bypass valve connected to the atmosphere on the upstream part of the vacuum pump¹⁵ for the same purpose. Permeate fluxes were obtained by gravimetric determinations of the compound mass collected in the cold trap after a certain amount of time. A minimum of three flux measurements were performed for each set of operating conditions, and they showed good reproducibility (discrepancies below 5%).

The determination of the average leak level of the installation (under operating conditions entitled "lowleak experiments" hereafter in this paper) was achieved under static vacuum conditions (after the connection valve to the vacuum pump, # 5 in Figure 2, was closed and the downstream pressure increase versus time was monitored). An example of the raw results obtained for several conditions is shown in Figure 4. A typical pattern with two different zones is obtained. It can be postulated that the influx of permeated compound is the major contribution to the first zone (i.e., up to a pressure value in the vicinity of the compound vapor pressure), followed by a linear increase for longer time values, assumed to result essentially from air leaks. Data analysis carried out according to this hypothetical mechanism leads to reproducible leak values in the range of $(1-5) \times 10^{-7}$ mol s⁻¹ for 2-propanol and methanol. The discrepancies between leak levels from one set of conditions to another remain unclear at this stage and are likely to depend on numerous parameters such as the permeated compound vapor pressure, the swelling effect exerted on the membrane, or the solubility of gases in the feed liquid. Even though leak levels have never been mentioned in studies dealing with pervaporation, we know by experience that the figure mentioned above is rather low and corresponds to an

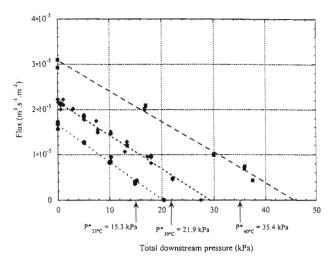


Figure 5. Downstream pressure influence on the isothermal pervaporation flux of methanol through PDMS under low-leak conditions: ●, 23 °C; ♦, 30 °C; ■, 40 °C; Arrows indicate methanolsaturated vapor pressure for the different temperature values.

installation in which welded connections are maximized and fittings are minimized. To our knowledge, a standard pervaporation unit operated under the same procedure can show leak values 1-3 orders of magnitude higher than this figure. Nevertheless, the leak level can hardly be mastered below a certain critical value, and the exact origin (sealing and/or dissolved gas extraction) cannot be specified further.

In the second part of this work, so-called "controlledleak experiments" were performed. In that case, a dry nitrogen gas flux, generated by a mass flowmeter (Brooks 5850TR) connected to a gas bottle (shown in Figure 2), was swept on the downstream side of the permeation cell.

The membrane used throughout the study was a dense poly(dimethylsiloxane) (PDMS) film, 125 μ m thick, of the filled type (ca. 30% silica by weight) purchased from Sigma Medical (Silastic from Dow Corning). It was mounted between a stainless steel plate sintered support (purchased from Poral, France) on the downstream face and a Viton O-ring on the upstream side. The pure compounds studied (methanol and 2-propanol) were of analysis grade.

Results and Discussion

Downstream Pressure Influence under Low-Leak Conditions. A first set of experiments was performed without any nitrogen flow, the only air input being obviously the leak level discussed above (Figure 4). Under these conditions, methanol shows a typical linear decrease pattern for the different temperature conditions (Figure 5). This suggests that permeability is constant for this system, in agreement with studies reported earlier. 16 The permeate flux vanishes at a downstream pressure value in the vicinity of the methanol vapor pressure (indicated by an arrow in Figure 5). Deviations of the total downstream pressure extrapolated to zero flux from the saturated vapor pressure increase with temperature. This could possibly be linked to the increased leak level with temperature experimentally observed in Figure 4. The methanol-PDMS system, however, shows an almost ideal behavior, according to the solution-diffusion model.4 Permeability (P) is constant for that particular case and can

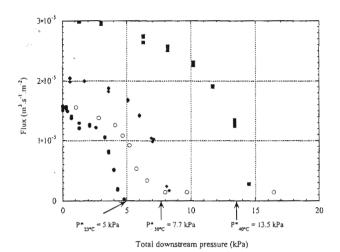


Figure 6. Downstream pressure influence on the isothermal pervaporation flux of 2-propanol through PDMS under low leak conditions: ●, 23 °C; ◆, 30 °C; ■, 40 °C; ○, previously reported data⁷ (23 °C). Data from Yoshikawa⁷ are represented at the same maximum flux level in order to facilitate comparison. Arrows indicate 2-propanol-saturated vapor pressure for the different temperature values.

easily be determined from the permeation flux (J) through

$$P_{i} = \frac{zJ_{i}}{(p'_{i} - p''_{i})} \tag{1}$$

where $(p_i' - p_i'')$ stands for the solvent vapor pressure difference across the membrane and z is the membrane thickness.

A slightly different behavior is obtained for 2-propanol under the same operating conditions (Figure 6). A nonlinear decrease is observed, which would correspond to a pressure-dependent permeability according to the solution-diffusion model. Whereas such a general pattern is in qualitative agreement with previously reported results in favor of the pore-flow model, a large discrepancy is obtained from the quantitative point of view. Results obtained in the vicinity of and above the 2-propanol vapor pressure (indicated by an arrow in Figure 6) differ considerably from those reported earlier at the same temperature. Basically, this can be attributed to differences in terms of either the permeation system (membrane type) or the installation characteristics. Taking into account the large differences of air leak levels that can possibly exist between two pervaporation installations, we have systematically investigated in a second step the deliberate addition of a controlled inert gas into the system to simulate a variable leak level.

Downstream Pressure Influence under Controlled-Leak Conditions. Results obtained on the same experimental systems with a low nitrogen flow rate sweeping the downstream side of the membrane are shown in Figure 7 for methanol and 2-propanol. The different initial slopes for each case (i.e., with or without a fixed nitrogen flow) are not surprising and simply reflect the increasing contribution in terms of dilution of the inert gas to the total downstream pressure (which always remains controlled at a fixed value). The constant permeability of the methanol—PDMS system induces a translation effect in the curve patterns when a gas inflow is superimposed. Under the same conditions, the inconstancy of the 2-propanol—PDMS system

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induces a nonlinear dependency for low pressure values and a linear tail for higher pressure values. This type of pattern is close to that previously reported for numerous systems in support of pore-flow model validation. Thus, it appears at this stage that the combination of a variable permeability and an inert gas leak, even at a very low level for the latter (i.e., less than 10⁻⁶ mol s-1, a typical leak level for a laboratory-scale pervaporation unit), can possibly generate flux decrease patterns that resemble pore-flow model predictions. More specifically, the criterion of a nonvanishing pervaporation flux at the vapor pressure of the pure compound, discussed in the introductory part of this paper, is obviously simple to achieve by taking into account an inert gas contribution but keeping the solution-diffusion model framework. A quantitative development based on the grounds expressed above has been explored and is presented below.

Data Interpretation and Solution—Diffusion Model Validation. The starting point of the analysis considers two different inlets, assumed to mix in the downstream chamber of the pervaporation cell. For the sake of simplicity, the latter is supposed to satisfy the completely stirred regime, with constant temperature and constant pressure conditions. On the basis of this picture, a mass balance under a stationary regime can be performed. Considering the solution—diffusion model, the permeated compound mass flux can be expressed as

$$Q = JA = \frac{P_i A}{z} \Delta p = \frac{P_i A(p' - yp'')}{z} \tag{2}$$

where y is the mole fraction of permeated compound in the downstream chamber, which is given by

$$y = \frac{Q}{Q + Q'} \tag{3}$$

In the above equation, Q' corresponds to the fixed leak contribution and Δp to the partial pressure difference through the membrane. Rearrangement of eqs 2 and 3 leads to an easy-to-handle expression relating the total downstream pressure (p'') to the pervaporation flux (J)

$$p'' = -\frac{z}{P_i}J + \frac{Q'p'}{A} \cdot \frac{1}{J} + p' - \frac{zQ'}{P_iA}$$
 (4)

Figure 8 shows the good agreement between the experimental data obtained for methanol and the simulation curves based on eq 4. With the knowledge of the gas inlet flow rate (low-leak or nitrogen-income conditions), the experimental data can be fitted to eq 4 in order to obtain a permeability value of 24 000 Barrer for methanol [1 Barrer = 7.5×10^{-18} m³ (STP) m/(m² s Pa)]. It can be seen that even a very low air flow (such as 10^{-6} mol s⁻¹) significantly affects the shape of the curve (fluxes versus downstream pressure), especially for high downstream pressure values. This sensitivity toward a parameter that has been virtually ignored up to now is remarkable.

Figure 8 also shows the small incidence of the leak level of the experimental setup used for this study under low-leak conditions (estimated at around 10^{-7} mol s⁻¹, as stated in the Materials and Methods section) on the flux curve.

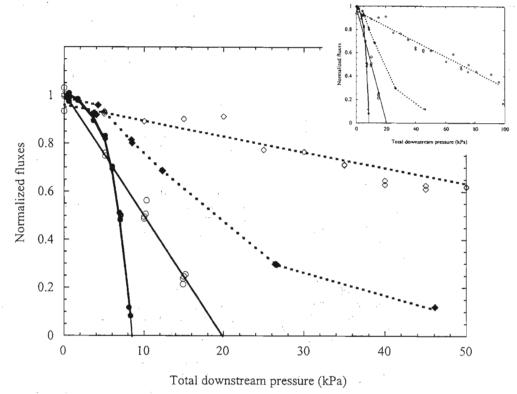


Figure 7. Downstream pressure influence on pervaporation flux of methanol (at 23 °C) and 2-propanol (at 30 °C) under controlled-leak conditions. O, methanol under low-leak conditions; O, methanol under nitrogen flow rate of 1.6 × 10⁻⁵ mol s⁻¹; O, 2-propanol under low-leak conditions; ♦, 2-propanol under nitrogen flow rate of 10⁻⁶ mol s⁻¹.

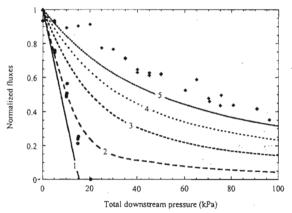


Figure 8. Experimental data and corresponding simulation results (according to eq 4) of downstream pressure influence for methanol flux at 23 °C. For simulations, the methanol permeability has been fixed at 24000 Barrer, and the inert gas flow rate has been used as an adjustable parameter: •, experimental data for low-leak conditions; , experimental data under nitrogen flow rate of 1.6×10^{-5} mol s⁻¹; simulations for nitrogen flow rates of (1) 10^{-7} , (2) 10^{-6} , (3) 5×10^{-6} , (4) 10^{-5} , and (5) 1.6×10^{-5}

Constant permeability conditions were considered for the methanol computations. A variable permeability situation was taken into account for the 2-propanol case study, shown in Figure 9. A permeability variation law, determined from the experimental data shown in Figure 6, was used for the simulation. Figure 9 shows clearly how an increased inert gas contribution can gradually shift the curve from a classical solution-diffusion result to a pore-flow-type pattern. We conclude at this stage that the peculiarities in favor of the pore-flow model (curved shape of the permeation flux and high downstream pressure tail) can be equally well represented by a classical solution-diffusion expression with an

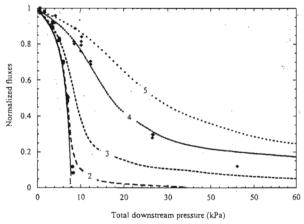


Figure 9. Experimental data and corresponding simulation results (according to eq 4) of downstream pressure influence for 2-propanol flux at 30 °C. For simulations, the 2-propanol permeability has been considered as pressure-dependent, and the inert gas flow rate has been used as an adjustable parameter: •, experimental data for low-leak conditions; ♦, experimental data for a nitrogen flow rate of 10^{-6} mol s⁻¹; simulations for nitrogen flow rates of (1) 0, (2) 10^{-7} , (3) 10^{-6} , (4) 5 × 10^{-6} , and (5) 10^{-5} $mol s^{-1}$.

inert gas contribution (eq 4). Thus, conflicting experimental data for the permeability behavior of pure compounds through dense polymers can be tentatively reconciled provided that the role of air leaks is properly taken into account.

A simplistic assumption has been postulated in the above approach: the inert gas flow rate is constant. Although this is obviously consistent with the experimental protocol used for this study (the inert gas flow rate is controlled by a mass flowmeter), it is unlikely to hold for a classical pervaporation installation. In that case, a variable leak level, more representative of the

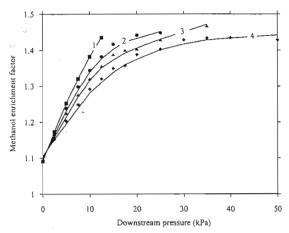


Figure 10. Simulation of the influence of total downstream pressure and air leaks on methanol enrichment factor for the separation of an equimolar methanol/2-propanol mixture at 30 °C through a PDMS membrane (thickness = 125 μm , area = 78.5 \times 10⁻⁴ m²) by pervaporation (according to eq set 6). Methanol and 2-propanol permeabilities have been fixed at 35 000 and 83 000 Barrer, respectively. The methanol enrichment factor corresponds to the methanol mole fraction in the permeate/methanol mole fraction in feed. The numbers on the curves refer to inert gas flow rate used for simulation as follows: (1) 0, (2) 2 \times 10⁻⁴, (3) 4 \times 10⁻⁴, and (4) 8 \times 10⁻⁴ mol s⁻¹.

real situation and related to the total downstream pressure through

$$Q' = k(p_{\text{atm}} - p'') \tag{5}$$

can be easily implemented within the model.

Extension to Binary Mixture Pervaporation. The general framework presented above can easily be extended to binary mixture pervaporation under variable downstream pressure conditions. Nevertheless, a simple analytical expression can no longer be derived in that case, and a numerical resolution of the following nonlinear algebraic system becomes necessary:

$$Q_{1} = J_{1}A = \frac{P_{1}A}{z}(p'_{1} - y_{1}p'')$$

$$Q_{2} = J_{2}A = \frac{P_{2}A}{z}(p'_{2} - y_{2}p'')$$

$$y_{1} = \frac{Q_{1}}{Q_{1} + Q_{2} + Q'}$$

$$y_{2} = \frac{Q_{2}}{Q_{1} + Q_{2} + Q'}$$
(6)

where 1 and 2 stand for the two compounds in the feed liquid, Q' is the leak level, and y is the downstream side mole fraction. It should be noted that the above approach does not take into account any effects of coupling between the two permeants. The implications of air leaks on partial fluxes and selectivity variations when downstream pressure is modified have been simulated for illustrative purposes based on the above set of equations. Figure 10 shows the pervaporation enrichment variation for the separation of an equimolar methanol—2-propanol vapor mixture (corresponding to a 0.26 methanol mole fraction in the liquid feed) under various leak levels. The interplay between the inert gas and total downstream pressure on the effective selectivity is noticeable. On the basis of this result, reproduc-

ibility in terms of partial fluxes and selectivity can be predicted to be difficult to achieve between two different pervaporation units working with the same binary mixtures.

Obviously, the leak values used in the upper range for simulation purposes on Figure 10 are more consistent with a sweeping gas situation. Such a strategy, based on the deliberate application of an inert gas flow on the downstream side, is often proposed as an alternative pervaporation operation in order to avoid the use of a vacuum.¹⁷ For the case study shown in Figure 10, an increased enrichment toward methanol is observed for higher downstream pressure values. This observation simply reflects the fact that, because the membrane is selective for 2-propanol, the contribution of the membrane to the separation achieved diminishes as the driving force decreases.

For the system used for simulation purposes, the addition of an inert gas sweep is detrimental to selectivity because a shift toward lower values appears under constant downstream pressure conditions (Figure 10). Nevertheless, a higher permeate flux is obtained under the same conditions. These predictions are in agreement with experimental results obtained for ethanol removal from water by sweeping gas pervaporation,17 where separation selectivity increased with decreasing gas velocity. Thus, the simplistic approach sketched in the set of equations 6 seems to be equally useful in order to gain insights into sweeping gas pervaporation operation. Obviously, the possible development of a relationship between the inert gas flux and the optimum selectivity/ flux is very attractive. Applications for azeotrope separations, based on the deliberate addition of an inert gas, could also be explored. Nevertheless, the attainment of these objectives demands a systematic case study of the numerical resolution of eq 6, which is beyond the scope of this paper.

Conclusion

The aim of this work was to investigate the apparent paradox concerning the effect of downstream pressure on pure-compound pervaporation. It has been shown that the influence of leaks in an installation is of crucial importance as soon as the downstream pressure is increased. Depending on the leak level (likely to vary over several orders of magnitude from one design to another), experimental results obtained on the same system can be considered to be in agreement with the solution-diffusion model (low-leak situation) or typical of pore-flow predictions (increased-leak situation). Based on the solution-diffusion model, a simple data analysis has been proposed, which enables the various situations to be quantitatively described, as well as the influence of leaks on the overall permeation behavior to be easily predicted. The resulting expression can be useful whatever the source of inert gas in the operation.

Several general conclusions can be drawn from this study:

For a given setup, the exact origin of the downstream pressure variation has to be clearly identified as soon as nonvanishing pressure is applied at the downstream side of a membrane used for pervaporation purposes. For the same downstream pressure value, opposite effects depending on the leak level contribution can affect fluxes and selectivity and lead to misunderstanding.

The leak level of an installation should be imperatively determined and specified in any attempt to

determine pure-compound permeability from variable downstream pressure conditions. Should this determination be difficult, an analytical system giving the relative pressure of the compound in the downstream compartment should be used in order to assess the leak level from the transitory pressure increase, similarly to the strategy proposed in this work (Figure 4). In any case, the assumption of negligible air leaks (and the corresponding theoretical equality between total downstream pressure and permeated compound pressure) should be clearly validated and not postulated a priori. Although this guideline might look obvious and has been occasionally suspected to explain discrepancies,8 we have unambiguously shown the sensitivity of such an effect on flux performances.

The same guidelines should be adopted even for binary mixtures separation to prevent conflicting reports. Significant differences in terms of fluxes and selectivity have been shown to appear when different leak conditions prevail. This statement holds particularly for units working in a rather high downstream pressure range (i.e., industrial units). To our knowledge, this recommendation does not reflect current practice up to now.

Any pervaporation operation, even with a perfect (i.e., leak-free) installation, is subject to dissolved gas extraction from the feed liquid to the vacuum compartment. This particularly concerns industrial applications, for which degassing is seldom applied on the feed stream prior to membrane treatment or for liquid feeds containing a significant level of dissolved gases (e.g., fermentation broth). A simple calculation shows that the leak level determined in our installation could equally well correspond to the extraction of gases dissolved in the feed liquid through the membrane, provided that the feed stream remains saturated by air gases (PDMS is known to be extremely permeable to gases). This should be kept in mind as a potential source of inert gas, particularly for studies making use of thin membranes. The dissolved gas renewal potential on the feed stream (such as direct contact to atmosphere in the ceiling of a feed reservoir or use of a recirculation loop) might also generate discrepancies from one installation to another. For that purpose, the maximal tolerable inlet gas flow rate for a negligible diluting effect at a given downstream pressure can be calculated. Equation 4 applies equally well in that case.

The importance of inert gas leaks brought into relief in this paper does not mean the pore-flow model is systematically inadequate for pervaporation transport. The situation postulated by this model could apply for composite-supported membranes, for which a surfaceflow contribution can possibly take place in the microporous support. The influence of upstream pressure on pervaporation fluxes, another topic for which predictions between the solution-diffusion and pore-flow models disagree, could also be considered in order to evaluate the more adequate of these two models. Nevertheless, the results and model presented in this work clearly reestablish the validity of the solution-diffusion model as soon as a single homogeneous dense polymer layer represents the major mass transfer resistance in per-

vaporation operation.

Notation

 $A = \text{membrane area } (m^2)$

D = cell diameter (m)

 $J_i = \text{flux of component } i \text{ (m}^3 \text{ s}^{-1} \text{ m}^{-2})$

k = constant value

p' = vapor pressure on upstream side (Pa)

p'' =pressure on downstream side (Pa)

 $p^* =$ saturated vapor pressure (Pa)

 P_i = permeability of component i (m³ m s⁻¹ m⁻² Pa⁻¹)

 $Q = \text{permeate compound flow rate } (m^3 \text{ s}^{-1})$ Q' = nitrogen (or air leak) flow rate (m³ s⁻¹)

= mole fraction of permeated compound in the downstream compartment

Subscripts

atm = related to atmospheric value.

1 Barrer = $7.5 \times 10^{-18} \text{ m}^3 \text{ (STP) m/(m}^2 \text{ s Pa)}$

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