Heat and Mass Transport Resistances in Vacuum Membrane Distillation Per Drop

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Vacuum membrane distillation (VMD) is a separation process based on the use of microporous hydrophobic membranes. The membrane is located between an aqueous phase and a permeate, which is kept under vacuum at pressure values below the equilibrium vapor pressure of the feed. The liquid stream vaporizes at one side of the membrane, and the vapors diffuse through the gas phase inside the membrane pores. The process rate and performance are affected highly by the transport phenomena both in the liquid phase and through the membrane. Heat- and mass-transfer resistance in the liquid phase, as well as mass-transfer resistance through the membrane, play an important role in determining the process performance. Based on VMD experimental data for several binary aqueous mixtures containing volatile organic compounds, a simple criterion to investigate the role of each transport resistance on the separation efficiency is discussed.

Introduction

Vacuum membrane distillation (VMD) is a separation process suitable for the purification of dilute aqueous solutions. The process has been proposed for various purposes; the extraction of volatile organic compounds (VOC) from aqueous streams has been the more widely investigated application (Aptel et al., 1988; Bandini et al., 1992; Hofman et al., 1987; Lawson and Lloyd, 1996; Sarti et al., 1993). The process is particularly interesting when the aqueous mixtures contain organic compounds highly volatile with respect to water at very low concentration values. In that case, organic concentrations in the permeate streams can be obtained up to values exceeding 50 wt. %, for feed concentrations around 2 wt. % (for example, Bandini et al., 1997).

The separation technique is based on the use of microporous hydrophobic membranes, which are separating an aqueous liquid phase and a permeate kept under vacuum. The basic operation conditions are represented by permeate pressure values smaller than the equilibrium vapor pressure of the feed to prevent condensation. On the other hand, the liquid-side pressure must be maintained lower than the minimum entry value of the membrane to immobilize a liquid-vapor interface at the membrane pore entries. The process is reported in Figure 1.

In the VMD separation process, the vapor stream permeated from the membrane apparatus is condensed under vacuum; in the case of aqueous mixtures containing VOC partially miscible with water, the recovery of valuable products to a high degree of purity is possible under mild and economically attractive conditions (Bandini and Sarti, 1997).

Rather extensive studies on VMD have been published: the technical feasibility of the process has been established with reference to several organic compounds and different membrane configurations (Sarti et al., 1993; Lawson et al., 1995; Lawson and Lloyd, 1996, 1997; Bandini et al., 1997). The more relevant quantities describing the process performance and productivity are given by the separation factor and the total distillate flux, which are greatly affected by changes in the working parameters. In particular, the vacuum-side pressure and the feed-flow rate were identified as the major design variables of the process (Bandini et al., 1997).

For all the cases investigated, reducing the permeate pressure typically results in an increase in the overall permeate flux, correspondingly, a remarkable decrease in the separation factor of the process occurs. On the other hand, by increasing the downstream pressure, interestingly high values of the VOC concentration in the permeate stream can be obtained. As a general indication, when downstream pressures increase above the vapor pressure of pure water at the

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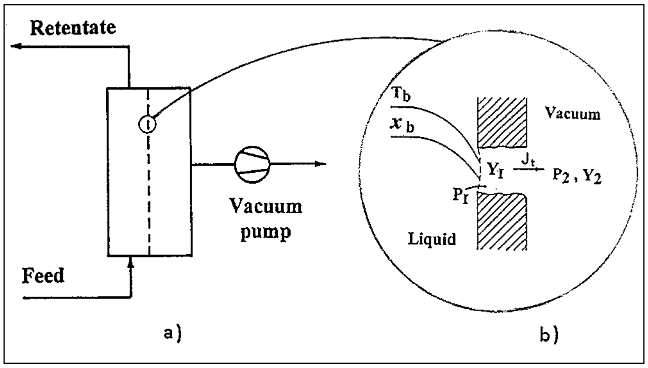


Figure 1. (a) VMD process; (b) microporous membrane.

liquid feed temperature, the permeate flux becomes increasingly richer in the VOC, thus leading to rather high vaporization factors. Such a remarkable increase in the permeate VOC concentration is paralleled by only minor decreases in the VOC permeation flux; the same behavior is observed for all the organic compounds more volatile than water.

By increasing the feed-flow rate, an appreciable increase in the permeation rate is also observed in all cases, and, in particular, the organic component flux is much more sensitive to changes in the feed-flow rate than the water flux.

At the operation conditions typical for the process, mass transfer through the membrane and the polarization effects in the liquid phase are the main physical phenomena determining the VMD performance.

VMD is characterized by the following steps: *evaporation of the liquid mixture at the L-V interface and diffusion of the vapors through the membrane pores*. To take into account the energy demanded by the evaporation of the feed taking place from the menisci located at the membrane pore entries, heat transfer towards the membrane/liquid interface must be obviously considered. As a consequence, the relevant resistances determining the process performance are associated to both heat and mass transfer through the liquid phase, as well as to the mass transfer through the membrane.

The evaporation rates of water and of the organic species are likely to be affected by the two transport resistances offered by the liquid phase with rather different sensitivities. Due to concentration and temperature polarization effects, one reasonably expects the evaporation rate of the organic component to be significantly influenced by both heat- and mass-transfer resistances in the liquid phase. For the water flux, vice versa, only temperature polarization could likely play an appreciable role in view of the high water concentration values considered.

The proper choice of the membrane to be used and of the most appropriate operating conditions to be applied are based on the evaluation of the effects produced by the various resistances on the process performance. The main objective of this present work is to perform a detailed analysis of the importance of the different transport phenomena entering the VMD process, and to obtain clear guidelines on how to improve the process performance.

Although the problem of comparing the different resistances is rather typical and well-known in chemical engineering, in the present case, however, we must compare resistances which are not dimensionally homogeneous so that the usual standard techniques cannot be applied. Schofield et al. (1987) introduced the "temperature polarization coefficient," which represents the fraction of the thermal driving force that contributes to the mass transfer driving force in membrane distillation processes. An analogous quantity was used by Bandini et al. (1992) to characterize the role of heat transfer in the liquid phase and mass transfer through the membrane in determining the evaporation rate of the VMD process. The study was performed only for aqueous solutions containing nonvolatile solutes; it is worth noting that in those cases the transmembrane flux consists of water flux only. Unfortunately, the temperature polarization coefficient is not sufficient to represent the influence of heat transfer on the distillate flux when two or more species permeate through the membrane, in that it does not allow to separate the contribution of each resistance to the flux of each component.

A general criterion to properly perform the comparison between dimensionally different resistances can be obtained by a suitable generalization of the sensitivity analysis, which was performed by Bandini et al. (1991). However, since the development of such a criterion is somewhat elaborate and the mathematic formalism might hide simple and intuitive results behind the curtain of elaborate expressions, we prefer hereafter to analyze several experimental VMD data by using a direct and simpler method which will be discussed in detail.

The role of each single resistance on the VMD performance will be apparent from the elaboration of the data through the mathematical model of the process. The extensive experimental study presented in a previous article (Bandini et al., 1997) is considered as the main source of data; the analysis is completed by also introducing model calculations for different membranes and different membrane configurations.

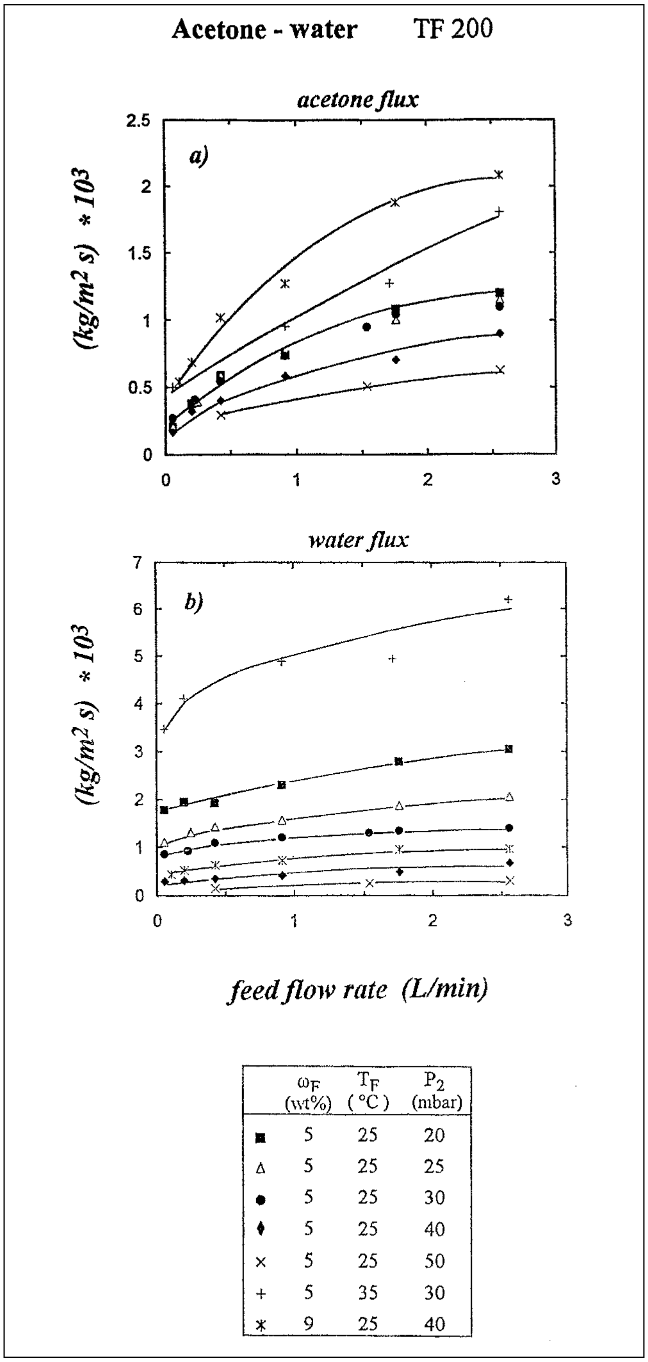
Experimental Results

The effectiveness of the transport phenomena taking place in the liquid phase is strictly connected to the fluid-dynamic conditions prevailing in the stream itself and can be experimentally investigated by properly changing the feed-flow rate.

The detailed experimental study has been presented in a previous article (Bandini et al., 1997) in which VMD experiments were performed through TF200 membranes, testing dilute binary aqueous solutions containing acetone, ethanol, isopropanol (IPA), ethylacetate (EtAc), methylacetate (MeAc), and methylterbutyl ether (MTBE).

For clarity sake, the data obtained in the VMD of dilute solutions containing acetone are reported in Figure 2 as an example. The transmembrane fluxes of water and of the organic component are separately plotted vs. the feed-flow rate in the liquid phase at various feed temperatures, compositions, and downstream pressures. For all the mixtures tested, the same qualitative behavior is observed, characterized by the following main features:

- Both the organic and water flux significantly increase with the feed-flow rate, especially so in the range of lower-flow rates;
- The influence of the feed-flow rate is much higher on the organic flux than on the water flux.



	ω_F (wt%)	T_F (°C)	P_2 (mbar)
■	5	25	20
△	5	25	25
●	5	25	30
♦	5	25	40
×	5	25	50
+	5	35	30
✳	9	25	40

Figure 2. VMD of acetone-water mixtures at various feed conditions and downstream pressures.

Acetone and water fluxes vs. the feed-flow rate.

The behavior observed clearly shows the significant importance of the transport phenomena in the liquid phase in determining the process performance; as the feed-flow rate increases, the heat- and mass-transfer resistances in the liquid phase decrease and the flux of each component increases.

On the basis of the above experimental observations, only some qualitative remarks can be made: the strong influence of the feed-flow rate on the organic flux shows that certainly the mass-transfer resistance through the membrane is not the limiting factor, since otherwise the effect of the recirculation rate would not be so significant. For water flux, on the contrary, the relatively weak influence of the recirculation rate indicates that the membrane resistance may not be negligible.

A simple criterion will be presented in the next section to analyze the contribution on the flux of each single resistance, and to determine if there is a single resistance controlling the whole process.

Analysis of Transport Resistances

Three main resistances are involved in the VMD process: in the general case, there is a mass-transfer resistance through the membrane which is in series with both the mass-transfer and the heat-transfer resistances within the liquid phase. The role of each resistance on the process is investigated from the elaboration of experimental data through the mathematical model of the process. The mathematical description of the VMD process has been discussed in detail in previous articles (Sarti et al., 1993; Bandini et al., 1997). For clarity sake, a brief summary of the relevant model equations is reported in the following.

Theory

Mass transfer through the membrane occurs essentially by a diffusive transport of vapors across the membrane, in which Knudsen diffusion is the prevailing mechanism. That has been recognized by a previous thorough experimental analysis (Sarti et al., 1993; Bandini et al., 1997) and was also confirmed by other groups (Lawson and Lloyd, 1997; Cabassud et al., 1998).

The molar flux of a permeating specie J_i is linearly related to its partial pressure difference across the membrane, as follows

$$J_i = \frac{K_m}{\sqrt{M_i}} (P_I y_{i,I} - P_2 y_{i,2}) \tag{1}$$

where K_m is the permeability coefficient ($s \cdot mol^{1/2} \cdot m^{-1} \cdot kg^{-1/2}$), which represents a quantitative measure of the membrane resistance. Remarkably, this parameter is not associated to the permeating species, but it depends only upon the membrane geometrical properties and slightly on temperature; a detailed study is reported in Bandini et al. (1997).

By taking the sum over all the components, the total molar flux J_t ($mol \cdot m^{-2} s^{-1}$) can be easily expressed as

$$J_t = \frac{K_m}{\sqrt{M}} (P_I - P_2) \tag{2}$$

where M is a suitable average molecular weight ($kg \cdot mol^{-1}$) in the permeating stream, defined as

$$\sqrt{M} = \sum_i \frac{J_i}{J_t} \sqrt{M_i} \tag{3}$$

The heat required for the interfacial evaporation is supplied by the heat flux through the liquid stream; neglecting the convective heat transfer within the gaseous phase, the heat balance across the evaporation surface gives

$$\Sigma_i J_i \lambda_i = h(T_b - T_I) \tag{4}$$

where h is the heat-transfer coefficient in the liquid phase $(\mathrm{W \cdot m^{-2} \cdot K^{-1}})$.

Mass transfer through the liquid phase can be described by the film theory model; for binary mixtures, the mole fractions in the liquid bulk $x_{i,b}$, and at the interface $x_{i,I}$, are related to the molar fluxes by the following relationship

$$\frac{J_t}{k_L c_L} = \ln \frac{x_{i,I} - J_i/J_t}{x_{i,b} - J_i/J_t} \tag{5}$$

in which k_L is the mass-transfer coefficient in the liquid phase $(\mathrm{m \cdot s^{-1}})$.

Equations 1 to 5, coupled with the relationships describing the vapor-liquid equilibrium conditions existing at the interface, embody the mathematical description of the process with reference to any cross section of the membrane. The model was already shown to adequately describe and predict the experimental behavior observed (Bandini et al., 1997).

Role of the liquid phase

Moving from the analysis of the transport phenomena in the liquid phase, the dependence of each single flux J_i and J_w on the different transport resistances is separately considered hereafter.

For each experimental run, the values of both temperature and organic mole fraction in the liquid phase at the L-V interface are calculated through the model Eqs. 1 to 5. For each case under consideration, one can thus calculate the actual driving force $\Delta P_{i,I}$ both for VOC and for water transport through the membrane; this term, appearing in the righthand side of Eq. 1, is given by

$$\Delta P_{i,I} \overset{\mathrm{def}}{\equiv} P^*_{i,I} x_{i,I} \gamma_{i,I} - P_2 y_{i,2} \tag{6}$$

where $P^*_{i,I}$ and $\gamma_{i,I}$ represent the vapor pressure and the activity coefficient of species i at the interface, respectively.

The transport resistances within the liquid phase, due to both the heat and mass transport, will be negligible for the overall process rate whenever the actual driving force calculated above $\Delta P_{i,I}$ is well approximated by the value obtained when the bulk temperature and bulk concentration are used instead of the corresponding interfacial values, prevailing at the V-L menisci, that is, when

$$\Delta P_{i,I} \approx \Delta P_{i,b} \overset{\mathrm{def}}{\equiv} P^*_{i,b}(T_b) x_{i,b} \gamma_{i,b}(x_{i,b}, T_b) - P_2 y_{i,2}$$
$$\Rightarrow \text{No resistance in the liquid phase} \tag{7}$$

Indeed, in that case the same flux is obtained either considering or neglecting the liquid-phase resistances.

It is, therefore, necessary to obtain immediately the indication whether or not the membrane offers the controlling resistance by plotting the VOC flux vs. $\Delta P_{i,b}$, as well as the water flux vs. $\Delta P_{w,b}$, and checking if a linear dependence is obtained in both cases with a slope equal to $K_m/\sqrt{M_i}$ or $K_m/\sqrt{M_w}$, respectively. In that case, according to Eq. 1, we can conclude that the transport resistances offered by the liquid phase are negligible and the process rate is controlled by the membrane resistance only. In the opposite case, we conclude that the transport resistances in the liquid phase also have to be taken into account.

Please note that, on the other hand, similar conclusions could not be drawn simply by considering (Schofield et al., 1987) the so-called temperature polarization coefficient $\vartheta = (T_b - T_I)/(T_b - T_{eb}\,[P_2, y_{i,2}])$ since the latter is an indication of the temperature profile only and does not immediately represent the influence of heat transfer on the distillate flux of one or of both species (Bandini et al., 1992).

By applying the criterion above, the same qualitative behavior is obtained for all the mixtures inspected, and, thus, only the data for acetone aqueous mixtures are explicitly reported here. For that case, water flux J_w vs. $\Delta P_{w,b}$ is shown in Figure 3a, which is not suggestive of any meaningful correlation; thus, for water transport, the resistances within the liquid phase play an important role, possibly in addition to the membrane resistance. The acetone flux is reported vs. $\Delta P_{i,b}$ in Figure 4a, which again does not indicate any general correlation so that also for acetone the liquid-phase resistances play an important role, possibly in addition to the membrane resistance.

An interesting additional result can be obtained in the analysis by considering whether both heat- and mass-transfer resistances within the liquid phase are equally important for the process rate or, alternatively, if only one of them plays a relevant role. To that extent, it is not sufficient to simply consider the temperature polarization coefficient ϑ or the corresponding concentration polarization coefficient which could be defined in an analogous way, they are representative of dimensionally different resistances, offered by different transport mechanisms which cannot be simply compared with each other based only on the temperature and concentration profiles. The proper comparison of the dimensionally different resistances can be obtained through a sensitivity analysis on the values of the species flux. Therefore, the contributions of the two resistances can be appreciated properly by testing whether the actual driving forces for the transmembrane transport, namely $\Delta P_{i,I}$ and $\Delta P_{w,I}$ are well approximated either by the values obtained by replacing T_b for the actual interfacial temperature T_I, while using the proper $x_{i,I}$ value, or, alternatively, by replacing $x_{i,b}$ for the actual interfacial mole fraction $x_{i,I}$ while using the proper interfacial temperature T_I.

In the first case, that is, when one obtains

$$\Delta P_{i,I} \approx P_i^*(T_b) x_{i,I} \gamma_i(x_{i,I}, T_b) - P_2 y_{i,2} \overset{\mathrm{def}}{\equiv} \Delta P_i(T_b, x_{i,I}) \tag{8}$$

the flux of species i, J_i, is linear vs. $\Delta P_i(T_b, x_{i,I})$ with a slope given by the membrane permeability $K_m/\sqrt{M_i}$ according to Eq. 1. In this case the so-called temperature polarization does not affect the distillate flux of species i and, thus, heat-transfer resistance, even if experimentally detectable, does not play any role for the VMD process rate; thus, the only liquid-phase resistance affecting the process is associated solely to mass transport.

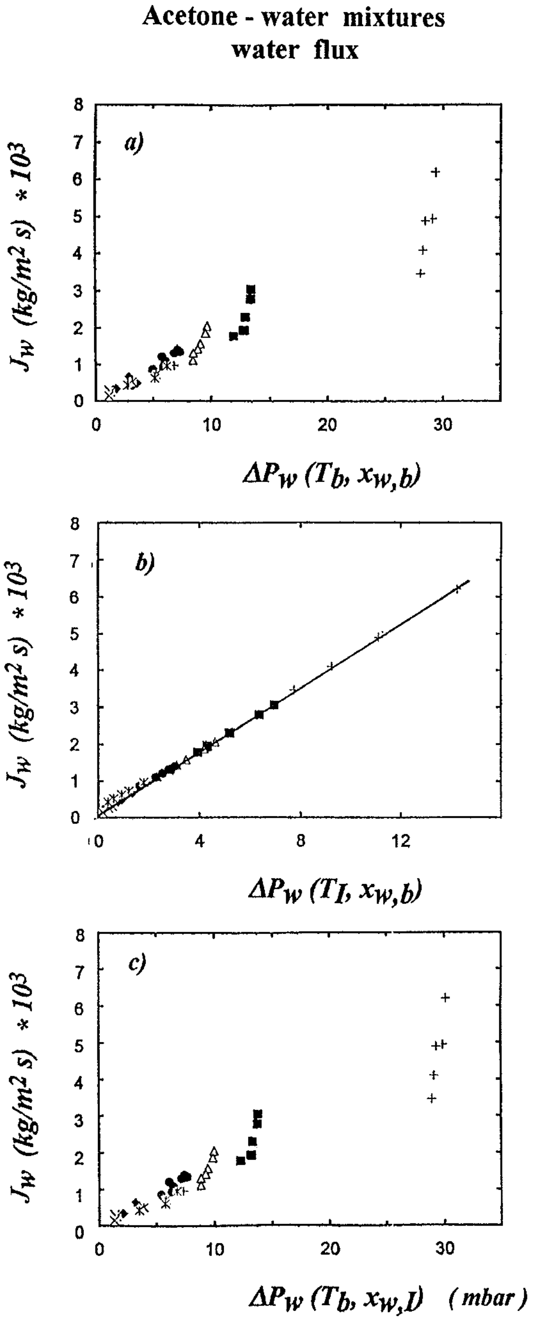


Figure 3. Water flux vs. different driving force values through the membrane.

Elaboration of the data reported in Figure 2.

In the second case, on the contrary, for the transmembrane flux driving force we have

$$\Delta P_{i,I} \approx P_i^*(T_I) x_{i,b} \gamma_i(x_{i,b}, T_I) - P_2 y_{i,2} \stackrel{\text{def}}{\equiv} \Delta P_i(T_I, x_{i,b}) \tag{9}$$

Consequently, the flux of species i, J_i, is linear vs. $\Delta P_i(T_I, x_{i,b})$, with the slope being the membrane permeability $K_m/\sqrt{M_i}$. Therefore, if this is the case, the presence of a

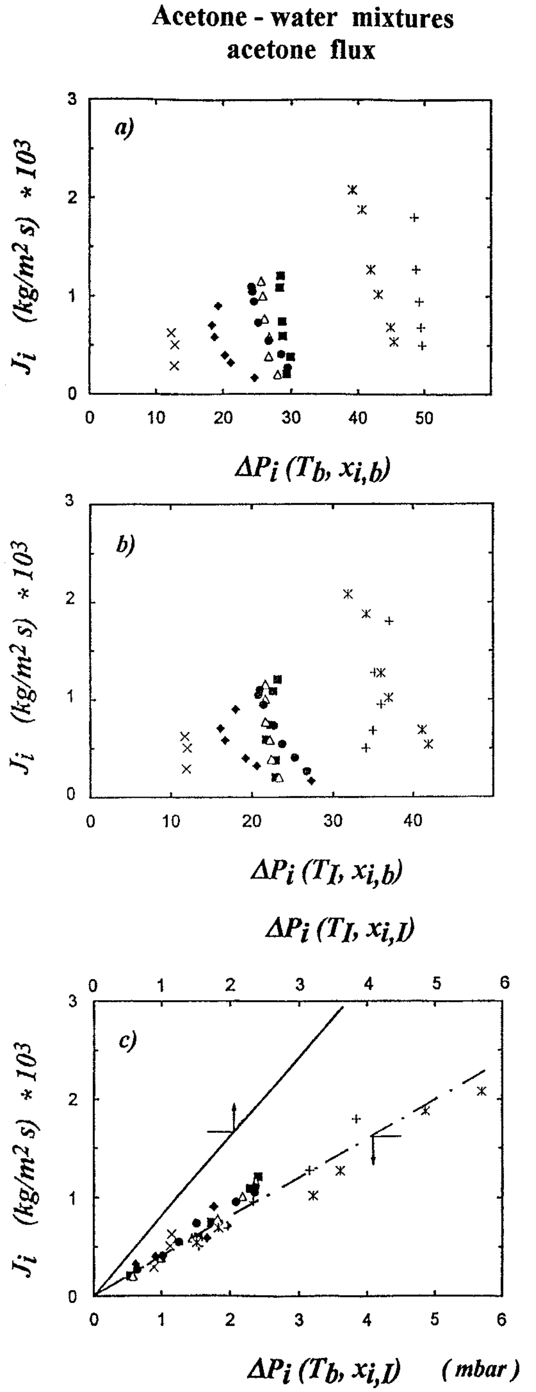


Figure 4. Acetone flux vs. different driving force values through the membrane.

Elaboration of the data reported in Figure 2.

concentration profile within the liquid phase does not appreciably alter the transmembrane flux, indicating that mass transfer within the liquid phase does not play any significant role and, finally, that heat transfer is the only liquid-phase process which contributes to the overall VMD process rate.

As suggested by the above considerations, the water flux resulting from all the operating conditions experimentally inspected was plotted vs. $\Delta P_w(T_I, x_{i,b})$ in Figure 3b and vs.

$\Delta P_w(T_b, x_{i,I})$ in Figure 3c, respectively, for acetone aqueous mixtures. While in Figure 3c no meaningful correlations are obtained, in Figure 3b the trend of all the data points is well represented by the continuous line the slope of which is indeed $K_m/\sqrt{M_w}$. It is therefore concluded that for water flux, the resistance offered by the liquid phase is embodied by the heat-transfer resistance only, whereas mass transfer within the liquid feed does not play any relevant role. The latter result is obviously consistent with the use of dilute VOC mixtures for the VMD separations.

The same conclusions are reached for the water flux obtained from all the other mixtures inspected (IPA, ethanol, EtAc, MeAc, and MTBE), as it is apparent from Figures 5a to 5e, in which J_w actually shows a linear dependence vs. $\Delta P_w(T_I, x_{i,b})$ with slopes just equal to the value $K_m/\sqrt{M_w}$, which characterizes the continuous lines.

On the other hand, a different behavior is obtained for the fluxes of the organic component. The acetone transmembrane fluxes, resulting from all the operating conditions inspected, are reported in Figures 4b and 4c vs. $\Delta P_i(T_I, x_{i,b})$ and $\Delta P_i(T_b, x_{i,I})$, respectively. In Figure 4b, the data do not show any meaningful correlation when mass-transfer resistance within the liquid phase is neglected. A good linear correlation is obtained vice versa in Figure 4c when the heat-transfer resistance is neglected and only mass transport is accounted for within the liquid; however, the slope of the dashed line which interpolates all the experimental data is approximately half the value $K_m/\sqrt{M_i}$, which would be obtained in the case of negligible heat-transfer resistance and complete mass transport control in the liquid phase (continuous line). Therefore, the conclusion is drawn that the transmembrane flux of acetone is simultaneously affected by both

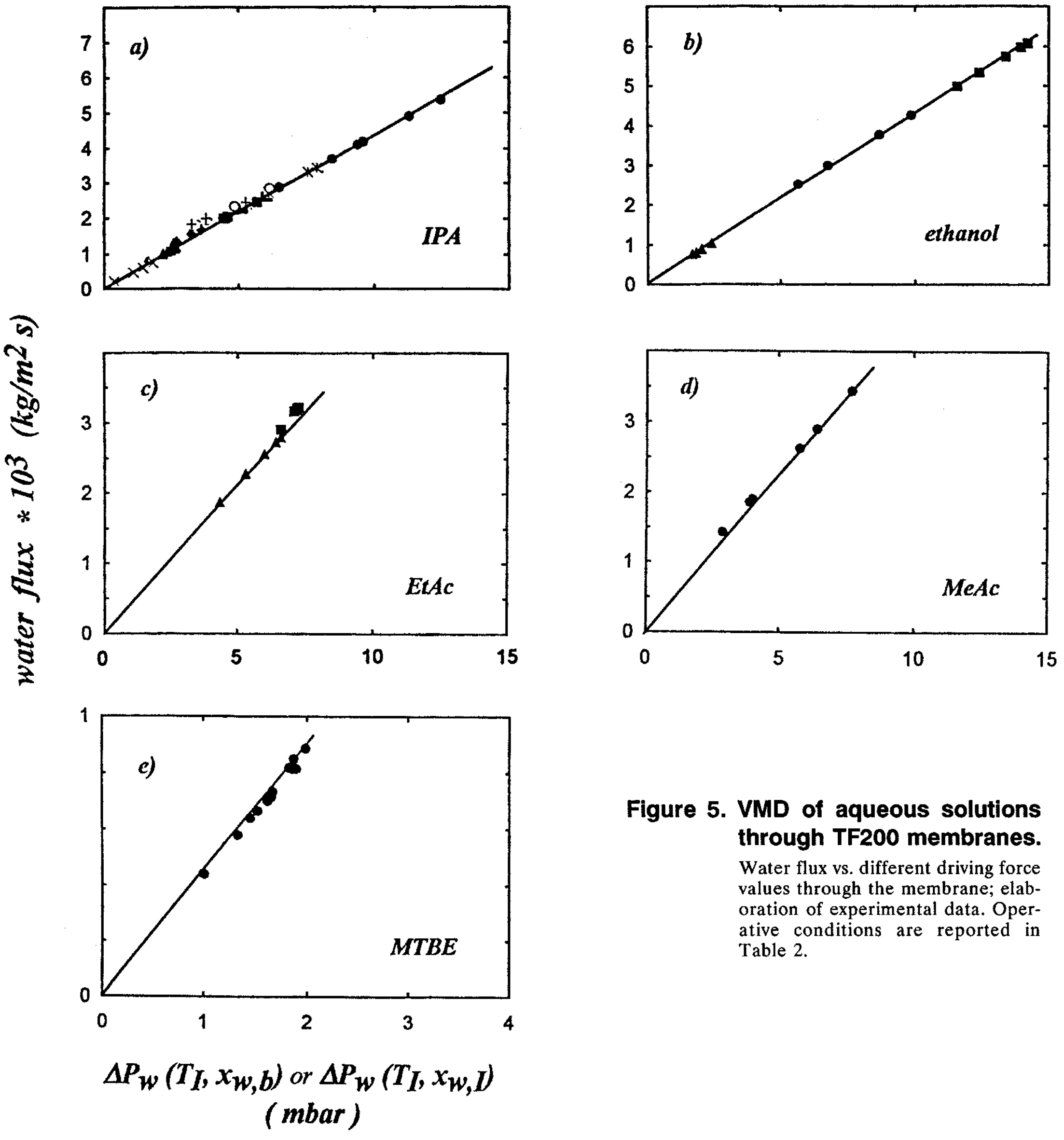


Figure 5. VMD of aqueous solutions through TF200 membranes.

Water flux vs. different driving force values through the membrane; elaboration of experimental data. Operative conditions are reported in Table 2.

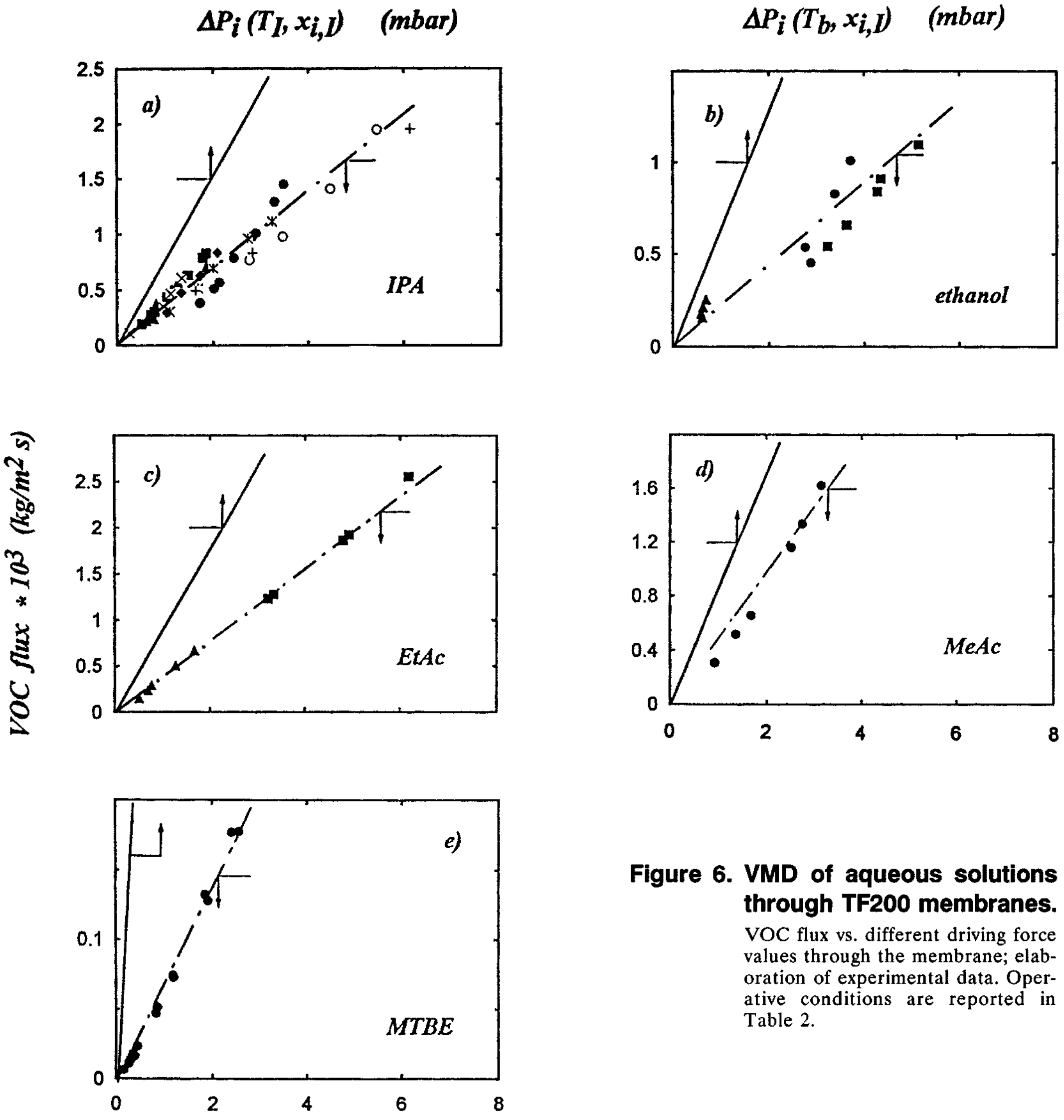


Figure 6. VMD of aqueous solutions through TF200 membranes.

VOC flux vs. different driving force values through the membrane; elaboration of experimental data. Operative conditions are reported in Table 2.

heat- and mass-transfer resistances within the liquid phase; even if the mass-transfer contribution appears to be more important, neglecting the heat-transfer resistance would lead to a large overestimation of the acetone flux.

Analogous conclusions hold also for all the other mixtures inspected (IPA, ethanol, EtAc, MeAc, and MTBE) as shown in Figures 6a to 6e, where the VOC flux is plotted vs. $\Delta P_i(T_b, x_{i,I})$. The experimental data obtained for all the operating conditions inspected for each mixture are satisfactorily interpolated by the straight dashed lines, the slope of which is always lower than the value $K_m/\sqrt{M_i}$, which would correspond to negligible heat-transfer resistance (continuous line). Therefore, both heat- and mass-transfer processes in the liquid are relevant for the transmembrane flux of the organic component in all cases. Their relative importance varies with the volatility of the organic with respect to water. More precisely, the higher the vapor pressure of the organic component is, the higher appears to be the role of heat-transfer resistance with respect to the mass-transfer resistance within the liquid phase. For instance, the slope of the line interpolating the experimental data in Figure 6 is approximately 1/6 of $K_m/\sqrt{M_i}$ in the case of MTBE, while it is 1/2 of $K_m/\sqrt{M_i}$ for acetone and is 1/1.75 for the case of MeAc.

That behavior confirms that the temperature profile within the liquid (temperature polarization) is not significant *per se*, but only to the extent to which it can significantly affect the transmembrane flux, that is, the driving force across the membrane. The latter obviously increases with the species vapor pressure at the temperature T_I. Any given variation in T_I leads to different changes in the species vapor pressure, and, thus, in the flux of the various VOCs; it is well known, on the other hand, that vapor pressure is more sensitive to temperature changes when the volatility of the organic compound is higher, consistently with the observed behavior.

As a general conclusion, we remark that the liquid phase offers resistances which determine the process rate, as well

Table 1. Selection of Commercially Available Membranes Suitable for VMD

		Avg.-Max. Pore Size (μm)	Porosity	Thickness (μm)	ID (mm)	Permeab. Coeff. at 25°C ($\mathrm{mol}^{1/2}\cdot\mathrm{s}\cdot\mathrm{m}^{-1}\cdot\mathrm{kg}^{-1/2}$)
TF200[‡]	PTFE	0.2	60%	60	Flat	3.15×10^{-5}[*]
Celgard 2400[††]	PP	0.02	38%	25	Flat	1.6×10^{-6}[†]
Celgard X-20[††]	PP	0.03–0.05	40%	25	0.4	$2.0\div2.5\times10^{-6}$[*]
Accurel Q3/2[#]	PP	0.2	75%	200	0.6	4.0×10^{-6}[†]
Accurel V8/2[#]	PP	0.2–0.65	75%	1,500	5.5	1.15×10^{-6}[**]

[*] Measured through air permeation.
[**] Measured through water vapor permeation.
[†] Predicted with tortuosity factor = 2 (Bandini et al., 1997).
[‡] From Gelman Inst. Co.
[††] From Hoechst-Celanese.
[#] From Akzo-Nobel.

as the separation factor and in particular:

(i) water flux is affected only by heat-transfer resistance within the liquid;

(ii) the flux of the organic component is affected by both heat- and mass-transfer resistances; the actual contribution of heat transfer may be different for different mixtures, and is more important for the highly volatile VOCs.

The conclusion is quite general, even if it is drawn from the elaboration of experimental data obtained only through the TF200 membranes. Since this kind of membranes is one of the most permeable membranes commercially available (see Table 1), the total fluxes measured are certainly the highest which can be achievable with the fluid-dynamic conditions considered. VMD through TF200 membranes therefore represents the case in which the heat-transfer resistance in the liquid phase is relevant and leads to high values of the temperature polarization.

Role of the membrane

The analysis is completed by comparing the membrane resistance with the transport resistances offered by the liquid phase. Based on the previous discussion, it is convenient to consider separately the effects on the flux of the organic species J_i and on the water flux J_w.

Analysis of VOC Transport Data. In the case of the VOC flux, the mass-transfer resistance through the membrane must be compared with both heat-transfer and mass-transfer resistances through the liquid phase.

For the organic component, the usual standard considerations can be followed since mass-transfer resistances are present, both in the liquid phase and in the membrane; for their comparison, it is sufficient therefore to determine whether or not the permeation across the membrane affects the distillation rate of the organic species.

To that extent, let us consider Eqs. 1 and 5 describing the mass transfer through the membrane and the mass transfer within the liquid phase, respectively. We are faced with the very usual situation in which two mass-transfer resistances are in series and can be added to give an overall mass-transfer resistance.

With reference to the organic species, Eq. 5 can be rewritten as

$$\frac{J_t}{k_L c_L} = \ln\left(1 + \frac{x_{i,b} - x_{i,I}}{J_i/J_t - x_{i,b}}\right) \tag{10}$$

In view of the low VOC concentration in the liquid stream and of the relatively high composition in the corresponding distillate, Eq. 10 can be linearized without losing numerical precision to all practical purposes; the resulting linear expression for the molar flux of the organic component is

$$J_i = k'_{Li} c_L (x_{i,b} - x_{i,I}) \tag{11}$$

in which k'_{Li} is defined as

$$k'_{Li} = \frac{k_L}{1 - \dfrac{x_{i,b}}{J_i/J_t}} \tag{12}$$

and is the mass-transfer coefficient of the ith species in the liquid phase, including also the contribution of convective transport, apparent in the denominator on the righthand side of Eq. 12. Remarkably, only in the case in which very high volatile organic compounds are processed or, alternatively, high-pressure values in the vacuum side are considered, the convective contribution does not affect appreciably the flux of the single organic species. Indeed, in that case, very high VOC compositions in the distillate are obtained with respect to the feed composition and, thus, the term $x_{i,b}/(J_i/J_t)$ is negligible with respect to unity. The mass-transfer coefficient of the organic species can therefore be predicted only on the basis of fluid-dynamic and operating conditions.

By making use of Eqs. 1 and 11, the flux of the ith species can finally be expressed as

$$J_i = \frac{K_{OV}}{\sqrt{M_i}} \left(P^*_{i,I} \gamma_{i,I} x_{i,b} - P_2 y_{i,2} \right) \tag{13}$$

in which the overall mass-transfer coefficient K_{OV} is defined as

$$\frac{1}{\dfrac{K_{OV}}{\sqrt{M_i}}} = \frac{1}{\dfrac{K_m}{\sqrt{M_i}}} + \frac{1}{\dfrac{k'_{Li} c_L}{P^*_{i,I} \gamma_{i,I}}} \tag{14}$$

The overall mass-transfer resistance of the organic species can thus be calculated once the membrane permeability and the mass-transfer coefficients in the liquid phase are available; for predictive purposes, concerning the relative extent

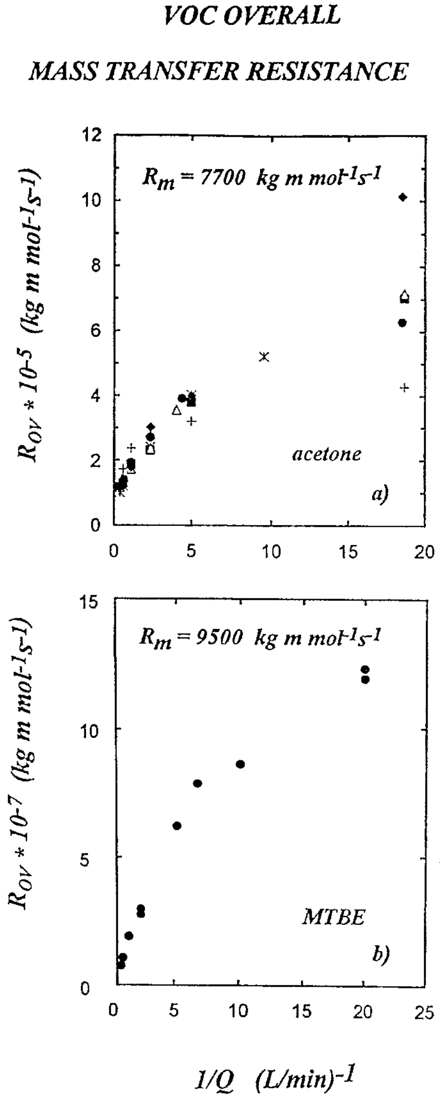


Figure 7. VMD of aqueous solutions through TF200 membranes.

VOC of overall mass-transfer resistance vs. the reciprocal of the feed-flow rate. Operative conditions are reported in Table 2.

of the mass transport resistances, the factor $P_i^*\gamma_i$ appearing in Eq. 14 could be calculated at the liquid bulk conditions.

For the experimentally investigated cases, the interfacial conditions and the mass-transfer coefficients in the liquid phase were calculated on the basis of the model Eqs. 1–5; the data were then used in order to evaluate the actual overall mass-transfer resistance of the organic species. In all the aqueous mixtures inspected, the same qualitative behavior is observed. We hereafter refer to two typical cases only for the sake of simplicity. The overall mass-transfer resistance (kg·m·mol^{-1}s^{-1}) of the organic species R_{OV}, defined as $R_{OV} = (\sqrt{Mi}/K_{OV})$, is reported in Figure 7 vs. the reciprocal of the liquid-flow rate for the VMD of acetone (Figure 7a) and MTBE (Figure 7b) aqueous mixtures, respectively. The corresponding values of the membrane resistance R_m (kg·m·mol^{-1}·s^{-1}), defined as $R_m = (\sqrt{M_i}/K_m)$, are also reported for comparison. Apparently, for both cases, the same qualitative behavior is observed: the overall mass-transfer resistance is greatly affected by the liquid-flow rate and rapidly increases as the flow rate decreases. In addition, the liquid-phase mass-transfer resistance is always largely dominant with respect to the membrane resistance. As a numerical example, it can be noted that, in the case of 5 wt. % acetone-water mixtures at 25°C and 40 mbar (Figure 7a), the ratio R_{OV}/R_m varies from 15 to 130; in the case of mixtures containing highly volatile compounds such as 0.5 wt. % MTBE-water mixtures at 25°C and 30 mbar (Figure 7b), the ratio R_{OV}/R_m varies from 800 to 13,000 in the range of the feed-flow rates inspected.

Based on the above comparison between mass-transfer resistance within the liquid phase and mass-transfer resistance in the membrane, the conclusion is drawn that, for the TF200 membranes and for all the operative conditions inspected here, the mass-transfer resistance through the membrane never controls the flux of the organic species and its contribution is always negligible.

Model Calculations of VOC Resistances. The above conclusions are also valid for several commercially available membranes. A comparison between the mass-transfer resistances of the organic component through the membrane R_m and in the liquid phase R_L is reported in Figure 8; the latter quantity is defined as

$$R_L = R_{OV} - R_m = \frac{P^*_{i,I}\gamma_{i,I}}{k'_{Li}c_L} \qquad (15)$$

Five different microporous hydrophobic membranes are considered: TF200, Celgard 2400, Celgard X-20, Accurel Q3/2, and Accurel V8/2, whose properties are reported in Table 1. The calculations are performed according to Eq. 14 for the reference case of VMD of 3 wt. % MeAc-water mixtures at 35°C. Spiral wound and shell-and-tube configurations are considered in different flow regimes for which the

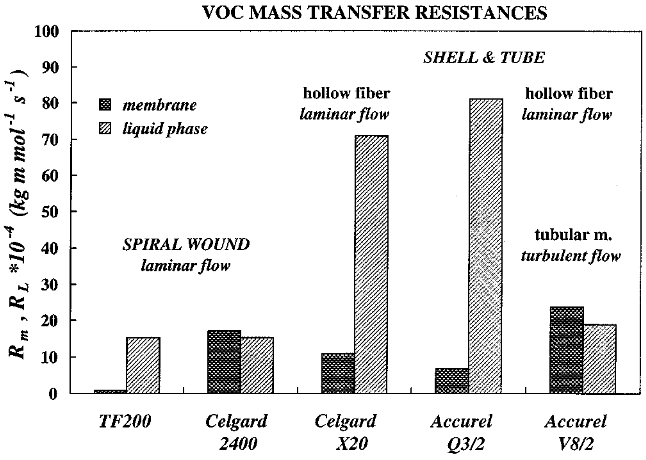


Figure 8. VMD of 3 wt. % MeAc-water mixtures at 35°C.

Comparison between the VOC mass-transfer resistance through the membrane and in the liquid phase for various membranes, different module configurations, and flow conditions.

Table 2. Operative Conditions in the VMD Experiments through TF200 Membranes at Different Feed-Flow Rates*

VOC		ω_F (wt. %)	T_F (°C)	P_2 (mbar)
IPA	■	5	25	20
	▲	5	25	30
	×	5	25	35
	●	5	35	30
	×	5	35	35
	♦	5	35	50
	○	10	35	45
	+	10	35	50
Ethanol	■	5	35	12
	●	5	35	30
	▲	3.3	25	30
EtAc	■	9	30	27
	▲	3	30	25
MeAc	●	5	35	40
MTBE	●	0.5	25	30

*Legend for Figures 5, 6, 7, and 9.

mass-transfer coefficients in the liquid phase are calculated according to the relationships reported in Table 3. For the spiral wound configuration, typical values of the hydraulic diameter and of the liquid-side velocity were taken as 1 mm and 0.5 m/s, respectively; for the shell-and-tube arrangement, modules 1 m long are considered with the liquid flowing in the tube side at 0.5 m/s and at 1.5 m/s in the laminar and turbulent flow regimes, respectively.

In Figure 8, the relative role of VOC mass-transfer resistances in the VMD process is apparent. The most relevant features which are noteworthy are the following:

(1) The spiral wound configuration allows high mass-transfer coefficients in the liquid phase, so that the overall mass-transfer resistance of the organic component is relatively low; the resistance in the liquid phase controls the organic flux when high permeability membranes such as TF200 are considered, whereas the membrane resistance prevails when lower permeability membranes are used such as Celgard 2400.

(2) Hollow fibers, such as Celgard X-20 and Accurel Q3/2 working in laminar flow conditions, show the highest overall mass-transfer resistances; the organic flux is greatly affected by the mass-transfer resistance in the liquid phase.

Table 3. Transport Correlations for Spiral Wound and Tubular Geometries

Correlation	Flow Range	Remarks
$Sh = 0.065 Re^{0.875} Sc^{0.25}$	$Re < 500$	Spiral wound configuration (Shock and Miquel, 1987) $Re = \frac{v D_h}{\nu}, \quad Sh = \frac{k_L D_h}{\mathfrak{D}}$
$Sh = 1.62 Gz_m^{1/3}$	$Gz_m > 20$	Hollow fibers; tube side; laminar flow $Sh = \frac{k_L D}{\mathfrak{D}}, \quad Gz_m = \frac{D^2 v}{\mathfrak{D} L}$ (Yang and Cussler, 1986)
$Sh = 0.023 Re^{0.8} Sc^{1/3}$	$Re > 10{,}000$ $L/D > 60$	Shell and tube. Tube side. Turbulent regime. Sieder-Tate equation

(3) The behavior of the tubular Accurel V8/2, working in turbulent flow conditions, is quite interesting: although the membrane resistance is the highest among the membranes investigated, a good overall mass-transfer resistance is observed due to a relatively low resistance in the liquid phase.

It can be observed, therefore, that low permeability membranes in turbulent regime can result in competition with higher permeability membranes which are constrained to work in laminar flow conditions because of the small fiber lumen; indeed, in view of the lower VOC mass-transfer resistances encountered in the liquid feed, higher organic fluxes can be obtained even if the membrane permeability is lower, and thus, lower membrane areas will be necessary in order to achieve a required VOC removal. However, generally, only a detailed economic evaluation of the process can finally establish which membrane and which module configuration give the best process performance.

Finally, it is interesting to observe the influence of the feed concentration on the overall mass-transfer resistance. While the membrane resistance depends slightly on the permeating species through $\sqrt{M_i}$, but greatly depends upon the geometrical properties of the membrane itself, the mass-transfer resistance in the liquid phase, on the contrary, is greatly affected by changes in the feed VOC concentration. In particular, as the feed concentration decreases, its activity coefficient γ_i increases, and thus, in view of Eq. 15, the mass-transfer resistance in the liquid phase also increases, as well as the overall mass-transfer resistance increase.

Water Flux. When the water flux J_w is considered, the liquid phase does not exhibit an appreciable mass-transfer resistance as it was observed in the previous section, so that a different procedure is needed in order to compare the resistances offered by the membrane and by the liquid feed. Indeed in this case, we have to compare the influence of mass-transfer resistance through the membrane with the effects produced on the water flux by the heat-transfer resistance in the liquid phase.

To that extent, we can define the overall polarization coefficient for the water flux η_w, as follows

$$\eta_w = \frac{\Delta P_{w,I}}{\Delta P_{w,b}} = \frac{\Delta P_w(T_I, x_{w,I})}{\Delta P_w(T_b, x_{w,b})} \qquad (16)$$

The overall polarization coefficient represents the ratio between the actual driving force for water transport across the membrane, resulting from the transport resistances in the liquid feed, and the corresponding maximum value which would be obtained when the transport resistances in the liquid phase are negligible. The coefficient η_w is essentially affected by changes in temperature, since typically $x_{w,b}$ is very close to $x_{w,I}$ in all the cases currently inspected.

Since the mass-transfer resistance in the liquid phase has negligible effects on J_w, the overall polarization coefficient η_w, defined in Eq. 16, ultimately allows the comparison of the relative influence on the transmembrane water flux of heat-transfer resistance in the liquid phase and mass-transfer resistance through the membrane.

The actual driving force for water flux can vary from a very small value, virtually zero, if the mass-transfer resistance offered by the membrane is negligible, to its maximum value, obtained when the temperature T_I at the evaporation surface is practically equal to the value T_b prevailing in the liquid bulk, that is, when the heat-transfer resistance in the liquid phase is negligible. Therefore, in terms of the overall polarization coefficient, we obtain that when $\eta_w \to 0$ and the water flux is controlled by the heat transfer in the liquid phase, whereas $\eta_w \to 1$ indicates that no appreciable resistance is offered by the liquid feed and, therefore, only mass transfer through the membrane controls the evaporation rate of water.

The overall polarization coefficients for water were calculated for each set of experimental results, and qualitatively similar behaviors were obtained in all the cases inspected. For the sake of simplicity, only the results obtained in two typical cases are explicitly reported here. Figure 9 shows the values of η_w vs. the feed-flow rate for two reference cases: VMD of acetone-water mixtures (Figure 9a) and of MeAc-water mixtures (Figure 9b), based on TF200 membranes.

Apparently, in the entire flow rate range inspected, η_w varies from 0.2 to 0.5, indicating that the heat-transfer resistance in the liquid phase prevails in determining the water flux.

In general terms one would expect a remarkable dependence of the water distillate flux on the recirculation rate, when there is a heat-transfer control within the liquid. On the other hand, under the operating conditions considered here, the heat-transfer coefficient h is not particularly sensitive to the feed-flow rate and, consequently, no major changes in the water flux are obtained; the albeit minor variations in the interfacial temperature T_I which are obtained, are responsible for the effects on the water flux shown in Figure 2.

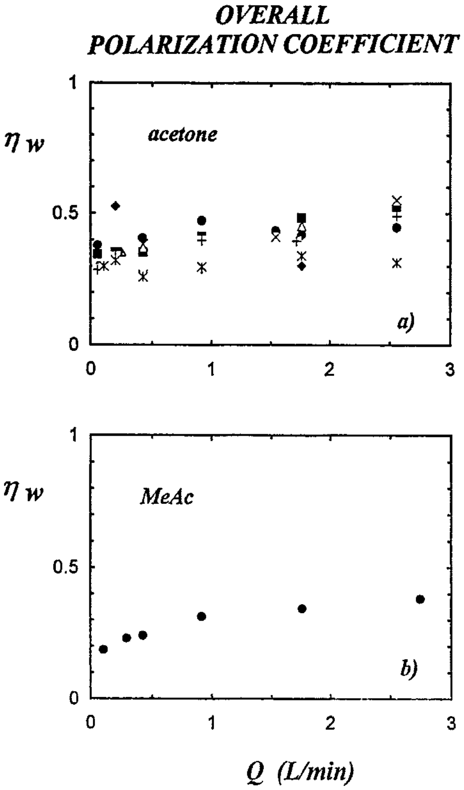


Figure 9. VMD of aqueous solutions through TF200 membranes.

Overall polarization coefficient for water vs. the feed-flow rate. Operative conditions are reported in Table 2 and Figure 2 for MeAc and acetone, respectively.

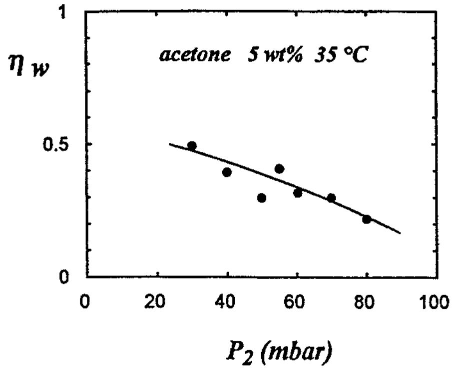


Figure 10. VMD of acetone-water mixtures through TF200 membranes.

Overall polarization coefficient for water vs. the downstream pressure. Elaboration of some experimental data from Bandini et al. (1997).

Finally, the relative role of heat- and mass-transfer resistances on the water flux is affected by the operating conditions and, particularly, by the downstream pressure. In the case of acetone-water mixtures (Figure 10) for a given feed-flow rate, η_w decreases as the downstream pressure increases, namely in the case in which lower fluxes are evaporated. The effect becomes more evident once the downstream pressure approaches the vapor pressure of pure water at the feed temperature. In this condition, the actual driving force for water is very small, and a significant percentage of changes in the water flux are associated to even minor changes in the absolute value of the interfacial temperature.

Conclusions

The separate influence of membrane permeability and of the heat- and mass-transfer resistances on the VMD performance have been thoroughly studied with the aim of recognizing the more appropriate actions affecting the separation factors and the fluxes resulting from the process. The extraction of VOCs from aqueous streams was considered as the reference case, through Teflon microporous membranes TF200.

Based on the model equations already tested in a previous work, a simple criterion was considered to test:

(1) Whether the leading resistances for the process rate are offered by the membrane or else by the transport phenomena in the liquid feed; and

(2) Whether the fluxes of water and of VOC are affected by both heat- and mass-transfer resistances in the liquid or by only one of them.

The analysis has been performed by comparing the actual driving force for the transmembrane flux of each species with the driving force, which would be present in each of the following cases: (a) the mass-transfer resistance through the liquid phase is negligible; (b) the heat-transfer resistance through the liquid feed is negligible; (c) the mass-transfer resistance offered by the membrane is dominant.

The flux of water is determined only by the heat transfer within the liquid feed and by the mass-transfer resistance offered by the membrane. That is essentially due to the low concentration range in the VOC typically of interest, which rules out for the water flux any mass-transfer resistance in the liquid phase. It has been shown, in addition, that the sensitivity of water flux to the heat-transfer rate is higher when the downstream pressure becomes closer to the vapor pressure of pure water. The latter case represents indeed an interesting operating condition, insofar as it minimizes the flux of water and leads to interestingly high VOC concentrations in the permeate side.

For all the mixtures inspected, the VOC flux is significantly affected by both heat- and mass-transfer resistances in the liquid feed, while being rather insensitive to the membrane permeability. The documented importance of mass transfer in the feed is, of course, consistent with the relatively dilute concentrations of the VOC mixtures. Interestingly, the sensitivity of the VOCs flux to the heat-transfer rate in the liquid is different from solute to solute, and increases with the volatility of the VOC considered.

The VMD performance in terms of both separation factors and transmembrane fluxes is generally affected by all the resistances encountered in the process. The separation factor is particularly sensitive to the mass transport resistance within the liquid feed and increases significantly by improving the mass-transfer rate; therefore, it is much more convenient to use membranes which allow operation in turbulent regime, even if their permeability is not so high, instead of using highly permeable membranes which are bound to operate in a laminar regime (for example, hollow fibers).

In addition, the separation factor is also affected to a smaller extent by the heat-transfer rate in view of its effects on the water flux. In particular, the separation factor of VOC vs. water decreases by increasing the heat-transfer rate in the feed; this effect is therefore in the opposite direction with respect to the mass-transfer rate. Since the fluid-dynamic regime affects both transport processes, the indication is then obtained that it is more convenient to operate with sufficiently short modules for which the temperature profile is already well developed, while the concentration profile is still in the entry region. That is particularly important when hollow fiber membranes are used with the liquid feed flowing in the lumen side.

Acknowledgments

This work was partially supported by CNR Grant 91.01756H3 and by the Italian Ministry of University and Scientific Research (MURST 60%).

Notation

c_L = molar concentration in the liquid phase, $\mathrm{mol \cdot m^{-3}}$
D = diameter, m
D_h = hydraulic diameter, m
$\mathfrak{D}$ = diffusion coefficient, $\mathrm{m^2 \cdot s^{-1}}$
k'_{Li} = mass transfer coefficient in the liquid phase defined in Eq. 12, $\mathrm{m \cdot s^{-1}}$
L = module length, m
v = fluid velocity, $\mathrm{m \cdot s^{-1}}$
K_{OV} = overall mass-transfer coefficient defined in Eq. 14, $\mathrm{s \cdot mol^{1/2} \cdot m^{-1} \cdot kg^{-1/2}}$
P = pressure, Pa
P^* = vapor pressure, Pa
Q = feed-flow rate, $\mathrm{L \cdot min^{-1}}$
$R_L = P^*_{i,I} \gamma_{i,I} / k'_{Li} c_L$ mass-transfer resistance in the liquid phase, $\mathrm{kg \cdot m \cdot mol^{-1} \cdot s^{-1}}$
y = mole fraction in the vapor phase
λ = molar latent heat of vaporization, $\mathrm{J \cdot mol^{-1}}$
θ = temperature polarization coefficient
ν = kinematic viscosity, $\mathrm{m^2 \cdot s^{-1}}$
Δ = difference
ω = mass fraction

Subscripts

2 = vacuum side
eb = boiling
i = ith component (VOC)
t = total
F = feed
I = interface

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Manuscript received Aug. 5, 1998, and revision received Mar. 22, 1999.