Polish J. Chem., **76**, 1637–1647 (2002)

Analysis of Membrane Selectivity in the Pressure Driven Transport in Terms of the Solution-Diffusion Models and Irreversible Thermodynamics

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(Received July 12th, 2002; revised manuscript August 7th, 2002)

A comparison of different models has been presented for the pressure driven stationary transport of the mixture of two liquids (1,2) through a membrane. The following models have been discussed: the solution-diffusion model (SD), modified solution-diffusions models (SDI and SDIY) and the "black-box" approach (BB) based on linear irreversible thermodynamics. The set of general equations describing separation factor ($SF_{1/2}$) has been derived for each model. It has been found that if $SF_{1/2}$(SD) > 1, then $SF_{1/2}$(SD) > $SF_{1/2}$(SDI) > $SF_{1/2}$(SDIY). For the moderate pressure differences (Δp = 10 bar) the SD model and its modifications (SDI, SDIY) yield $SF_{1/2}$ very close to unity and cannot describe the experimental results. Contrary to them the BB approach is able to predict the experimental $SF_{1/2}$. $SF_{1/2}$(BB) increases with the increase of coupling between fluxes, however, its upper limit is determined by the conditions of the positive entropy production and of the positive fluxes.

Key words: solution-diffusion model, irreversible thermodynamics, reverse osmosis, separation factor

The aim of this paper is to compare several models applied to the description of the transport of a mixture of non-electrolytes through a membrane in the stationary state. The following transport models have been chosen:

- solution-diffusion model (SD), based on Fick's equation [1,2];
- solution-diffusion imperfection model (SDI) and its modification by Yaroshchuk (SDIY) [3]; these models combine the fickian diffusion through the selective part of the membrane and the convection through the imperfect parts of the membrane,
- the black box approach (BB) based on irreversible thermodynamics [4].

The applicability of each model will be checked using experimental results of the separation of water-methanol mixture through the membrane Nafion 117 in the lithium form during the pressure driven transport. The parameter to be evaluated will be the selectivity factor, $SF_{1/2}$, defined as:

$$SF_{1/2} = \frac{x_{1,p}/x_{2,p}}{x_{1,f}/x_{2,f}} \overset{J_i = c_{i,p}J_v}{=} \frac{J_1/J_2}{x_{1,f}/x_{2,f}} \tag{1}$$

where $x_{i,p}$, $x_{i,f}$ denote the molar fraction of species i in the permeate, feed, respectively, J_i is its flux. For the stationary state

$$J_i = c_{i,p} J_v \tag{2}$$

where J_v is the volume flux. Thus, in (1) $x_{1,p}/x_{2,p}$ can be replaced by the flux ratio J_1/J_2. Throughout the whole paper the $x_{i,f}$ denotes the molar fraction of the species i in the feed solution at the boundary solution/membrane, not in the bulk solution (see Fig. 4). According to this, the true selectivity factor will be discussed, not the observed one.

THEORY

1. Solution-diffusion model (SD)

The solution-diffusion approach to the membrane transport is described in [1,2]. The flux of species i is given by the Fick's law:

$$J_i = -\bar{D}_i \frac{d\bar{c}_i}{dz} = -\bar{D}_i \frac{d\bar{c}_i}{d\bar{x}_i}\frac{d\bar{x}_i}{dz} \xrightarrow{J_i = \text{const}} -\frac{\hat{\bar{D}}_i^{(x)}}{l_m}(\bar{x}_{i,p} - \bar{x}_{i,f}) \tag{3}$$

Assuming that [1,2]:

1) there is a thermodynamic equilibrium at the boundary feed/membrane and membrane/permeate expressed by:

$$\mu_{i,f} = \bar{\mu}_{i,f} \quad \text{and} \quad \bar{\mu}_{i,p} = \mu_{i,p} \tag{4a,b}$$

2) the pressure inside the membrane phase is equal to the feed pressure ($\bar{p} = p_f$),

3) the partial molar volumes do not depend on the concentration and pressure ($\bar{v}_i$ = const),

the transport equation (3) can be rearranged to the following expression:

$$J_i(\text{SD}) = \frac{P_i x_{i,f}}{l_m}\left(1 - \frac{\bar{f}_{i,f}}{\bar{f}_{i,p}}\exp\left(-\frac{\bar{v}_i(\Delta p - \Delta\pi_i)}{RT}\right)\right) \tag{5}$$

where Δp, $\Delta\pi_i$ denote the differences of hydrostatic and osmotic pressures of the feed (subscript f) and permeate (subscript p):

$$\Delta p = p_f - p_p \tag{6}$$

$$\Delta\pi_i = -\frac{RT}{\bar{v}_i}\ln\left(\frac{f_{i,f}x_{i,f}}{f_{i,p}x_{i,p}}\right) \tag{7}$$

P_i is the permeability coefficient of species i:

$$P_i = \hat{\bar{D}}_i^{(x)} K_{i,f} \tag{8}$$

whereas K_i is the partition coefficient of species i:

$$K_i = \bar{x}_i/x_i = \bar{f}_i/f_i \tag{9}$$

In the case of the moderate pressure differences (*i.e.* 20 bar or less) the condition

$$(\Delta p - \Delta\pi_i)\bar{v}_i << RT \tag{10}$$

is fulfilled and then, assuming that $\bar{f}_{i,f} = \bar{f}_{i,p}$, (5) simplifies to:

$$J_i(SD) = \frac{P_i x_{i,f} \bar{v}_i}{l_m RT}(\Delta p - \Delta\pi_i) \tag{5a}$$

Substituting the transport (5a) into (1) one obtains:

$$SF_{1/2}(SD) = \frac{P_1 \bar{v}_1 (\Delta p - \Delta\pi_1)}{P_2 \bar{v}_2 (\Delta p - \Delta\pi_2)} \tag{11}$$

This equation makes possible the calculation of $SF_{1/2}$ and its comparison with the experimental $SF_{1/2}$.

2. Solution-diffusion-imperfection model (SDI)

In this model it is assumed that in the membrane two parallel transport paths exist: one according to the solution-diffusion mechanism and the other one according to the convective transport. Thus the transport (5a) should be extended as follows:

$$J_i(SDI) = J_i(SD) + J_i^{(imp)} \tag{12}$$

where

$$J_i^{(imp)} = c_{i,f} J_v^{(imp)}, \qquad J_v^{(imp)} = L_v^{(imp)} \Delta p / l_m \tag{13),(14}$$

Substituting (12), (13) into (1) we get:

$$SF_{1/2}(SDI) = \frac{J_1(SD)/x_{1,f} + J_v^{(imp)} \rho_f / (x_{1,f} M_1 + x_{2,f} M_2)}{J_2(SD)/x_{2,f} + J_v^{(imp)} \rho_f / (x_{1,f} M_1 + x_{2,f} M_2)} \tag{15}$$

where the following relation between c_i and x_i has been used:

$$c_i = \frac{x_i \rho}{x_1 M_1 + x_2 M_2} \tag{16}$$

In (16) ρ denotes the density of solution, M_i – the molar mass of component *i*.

As the imperfection terms in the numerator and denominator of (15) are the same and positive, and assuming that the part $J_i(SD)$ of $J_i(SDI)$ is positive, we can conclude that:

1) for $SF_{1/2}(SD) > 1$: $SF_{1/2}(SD) > SF_{1/2}(SDI) > 1$ (17a)
21) for $SF_{1/2}(SD) < 1$: $SF_{1/2}(SD) < SF_{1/2}(SDI) < 1$ (17b)

The SDI model has been improved by Yaroshchuk [3]. In that improved model (SDIY) the diffusion of a solute in the imperfections is additionally taken into account. Thus, instead of (13) we have (see (3) in [3]):

$$J_i^{(imp)}(SDIY) = -P_i^{(imp)}\frac{dc_i}{dz} + c_i J_v^{(imp)} \tag{18}$$

Taking into account (14), the integration of (18) yields (see (4) in [3]):

$$J_i^{(imp)}(SDIY) = b_i c_{i,f} J_v^{(imp)} = b_i J_i^{(imp)}(SDI) \tag{19}$$

where

$$b_i = \frac{1-(c_{i,p}/c_{i,f})\exp(-Pe)}{1-\exp(-Pe)} \tag{20}$$

Pe is the dimensionless Peclet number defined here as:

$$Pe = \frac{L_v^{(imp)}}{P_i^{(imp)}}\Delta p \tag{21}$$

It should be noted that Pe does not depend on the kind of the species i, because $P_1^{(imp)} = P_2^{(imp)}$. This latter relation results from the fact that $\bar{\nu}_1 J_1^{(imp)} + \bar{\nu}_2 J_2^{(imp)} = J_v^{(imp)}$ and $\bar{\nu}_1 c_1 + \bar{\nu}_2 c_2 = 1$ (assuming that $\bar{\nu}_i$ = const).

Let us discuss now the influence of the value of the coefficient b_i on SF. In our system we have for water: $c_{1,p}/c_{1,f} > 1$, whereas for methanol: $c_{2,p}/c_{2,f} < 1$. Thus, we can conclude that $b_1 < b_2$ and, consequently, that:

$$SF_{1/2}(SDIY) = \frac{J_1(SD)/x_{1,f} + b_1 J_v^{(imp)}\rho_f/(x_{1,f}M_1 + x_{2,f}M_2)}{J_2(SD)/x_{2,f} + b_2 J_v^{(imp)}\rho_f/(x_{1,f}M_1 + x_{2,f}M_2)} < SF_{1/2}(SDI) \tag{22}$$

This relation results from the fact that the SDIY model takes into account the diffusion in the imperfections which reduces the concentration differences across the membrane. Thus, we have the following sequence for the selectivity factor of the solution-diffusion model and its modifications: if $SF_{1/2}(SD) > 1$, then

$$SF_{1/2}(SD) > SF_{1/2}(SDI) > SF_{1/2}(SDIY) \tag{23}$$

3. Irreversible thermodynamics – the black box approach (BB)

According to linear irreversible thermodynamics the transport equation for a two-component mixture is as follows:

$$J_i = L_{i1}X_1 + L_{i2}X_2 \qquad i = 1, 2 \tag{24}$$

where the thermodynamic force, X_i, is given by:

$$X_i = -\frac{d\mu_i}{dz} = -RT\frac{d\ln(f_i x_i)}{dz} - \bar{\nu}_i\frac{dp}{dz} = \bar{\nu}_i\left(\frac{d\pi_i}{dz} - \frac{dp}{dz}\right) \tag{25}$$

As the L_{ik} coefficients strongly depend on the concentration (at c_i or $c_k \to 0$ they also tend to zero), we substitute them by the generalized permeability coefficients, P_{ik}, defined by:

$$P_{ii} = \frac{RTL_{ii}}{\bar{x}_i} K_i = \bar{D}_{ii}^{(x)} K_i \quad \text{and} \quad P_{ik} = \frac{RTL_{ik}}{\sqrt{\bar{x}_i \bar{x}_k}} \sqrt{K_i K_k} = \bar{D}_{ik}^{(x)} \sqrt{K_i K_k} \tag{26}$$

Thus, the transport equations (24) with the help of (25) take the form:

$$J_i = P_{ii} x_i \frac{\bar{\nu}_i}{RT} \left(\frac{d\pi_i}{dz} - \frac{dp}{dz} \right) + P_{ik} \sqrt{x_i x_k} \frac{\bar{\nu}_k}{RT} \left(\frac{d\pi_k}{dz} - \frac{dp}{dz} \right) \qquad i \neq k = 1, 2 \tag{27}$$

It should be noted that because of the condition for the positive entropy production $L_{ii}L_{kk} > L_{ik}^2$ (assuming symmetry of L_{ik}, *i.e.* $L_{ik} = L_{ki}$) [4,5] the P_{ik} coefficients, defined by (26), must also obey the analogous inequality:

$$P_{ii}P_{kk} > P_{ik}^2 \tag{28}$$

Although the P_{12} coefficient is a direct measure of coupling between the species "1" and "2", usually it is expressed by the so called degree of coupling, q, defined by [6]:

$$q = \frac{L_{12}}{\sqrt{L_{11}L_{22}}} \overset{eq.\ (26)}{=} \frac{P_{12}}{\sqrt{P_{11}P_{22}}} \tag{29}$$

According to inequality (28) q may change between –1 and 1.

To calculate $SF_{1/2}$ from (1), (27) should be integrated over the thickness of membrane. However, as we do not know neither the concentration dependence of P_{ik} nor the concentration profile across the membrane, we assume that P_{ik} are constant and rewrite (27) in the approximate form:

$$J_i = \frac{P_{ii}\hat{x}_i\bar{\nu}_i}{l_m RT}(\Delta p - \Delta\pi_i) + \frac{P_{ik}\sqrt{\hat{x}_i\hat{x}_k}\,\bar{\nu}_k}{l_m RT}(\Delta p - \Delta\pi_k) \quad i \neq k = 1, 2 \tag{27a}$$

where $\hat{x}_i$ denotes mean in the molar fraction range $x_{i,f}$, $x_{i,p}$.

Let us discuss two limiting cases ($q = 0$ and $q = 1$). In the first one, when there is no coupling ($P_{ik} = 0$ for $i \neq k$), (27a) is almost the same as (4a) of the SD model. Thus, the selectivity factors obtained from both models should be similar. In the second case ($q = 1$) from (27a) and (29) it results that the ratio of fluxes (both must be positive) do not depend on the acting forces:

$$\left(\frac{J_1}{J_2} \right)_{q=1} = \left(\frac{x_{1,p}}{x_{2,p}} \right)_{q=1} = \sqrt{\frac{P_{11}\hat{x}_1}{P_{22}\hat{x}_2}} \tag{30}$$

Thus, for $q = 1$ $x_{1,\mathrm{p}}$ and, consequently, $SF_{1/2}$ increase with the P_{11}/P_{22} ratio.

For $q < 1$ the fluxes depend on both forces – $(\Delta p - \Delta\pi_1)$ and $(\Delta p - \Delta\pi_2)$ (27a). Let us consider the case of positive $\Delta\pi_1$. For the two-component mixture it means that $\Delta\pi_2$ is negative and $SF_{1/2} > 1$. If the coupling is positive, then $\Delta\pi_1$ can exceed even Δp but J_1 can still be positive because of the positive cross-term (P_{12}, $(\Delta p - \Delta\pi_2) > 0$). The higher is the coupling, the higher can be $\Delta\pi_1$ and, consequently, $SF_{1/2}$. In the case of no coupling $\Delta\pi_1$ cannot exceed Δp, otherwise J_1 would be negative. Thus, one can conclude that $SF_{1/2}(q > 0) > SF_{1/2}(q = 0)$. This inequality is valid for the adequately small values of P_{22}/P_{11}. For higher values of P_{22}/P_{11} the species "2" will be preferentially transported through the membrane and, thus, the reversed relation will be observed, *i.e.* $SF_{1/2}(q > 0) < SF_{1/2}(q = 0)$ or $SF_{2/1}(q > 0) > SF_{2/1}(q = 0)$.

RESULTS AND DISCUSSION

The experimental results of the transport of water-methanol solutions through Nafion 117 (Li^+-form) used in this paper have been published in [7].

1. Solution-diffusion model (SD)

To calculate $SF_{1/2}$ from (10), the ratio P_1/P_2 should be estimated from an independent experiment. For our system, we have obtained this value from the pervaporation experiment [7]. According to the SD model [2], the separation factor in pervaporation is expressed as follows:

$$SF_{1/2}(\text{PV, SD}) = P_1/P_2 \tag{31}$$

Taking into account (31), the values of $SF_{1/2}$(SD) have been calculated for different values of $x_{1,f}$. The values of activity coefficients f_i, necessary for the calculation of $\Delta\pi_i$, have been taken from [8]. The experimental and calculated values of $SF_{1/2}$(SD) are presented in Tab. 1.

Table 1. Selectivity factor $SF_{1/2}$ in RO and PV processes, Nafion 117 (Li^+-form) – mixture water-methanol [7].

molar fraction of H_2O in the feed $x_{1,f}$	$SF_{1/2}$			
	RO Δp = 10 bar			PV experimental
	experimental	model SD		
		$P_1/P_2 = SF_{1/2}$(PV)	$P_1/P_2 \to \infty$	
0.1	1.390	0.996	1.009	1.480
0.5	1.085	0.998	1.020	1.891
0.9	1.076	0.998	1.096	1.992

It is seen that at the pressure difference 10 bar, as used in the experiment, $SF_{1/2}$(SD) is close to unity. To obtain the experimental value of $SF_{1/2}$, the applied pressure difference Δp should exceed 800 bar (calculated from (5) because the condition (10) for such high Δp is not fulfilled). The upper limit of $SF_{1/2}$(SD), calculated for P_1/P_2 going to infinity, exceeds the experimental value of $SF_{1/2}$ only for higher contents of water in the feed ($x_{1,f}$ = 0.9).

The comparison of $SF_{1/2}$ calculated according to the SD model ($x_{1,f}$ = 0.1, Δp = 10 bar) with $SF_{1/2}$ calculated according to the SDI model is shown in Fig. 2. $SF_{1/2}$(SDI) has been calculated for the increasing contribution of the imperfect flux to the total flux, expressed by the $J_v^{(imp)} l_m/P_1$(=0(≡SD solution), 15, 150 and 1500 cm^3/mol).

The results presented in Fig. 1 confirm our earlier conclusions regarding the relation between $SF_{1/2}$(SDI) and $SF_{1/2}$(SD) (17a,b). They are valid also for a higher water content in the feed (*i.e.* $x_{1,f}$ = 0.5 and 0.9). Because also the inequality (23) is fulfilled, the results for the SDIY approach are not shown. Thus, one can conclude that neither the diffusion-solution model nor its modifications are suitable for the description of our system or any system for which $SF_{1/2}$ is higher than $SF_{1/2}$(SD, $P_1/P_2 \to \infty$).

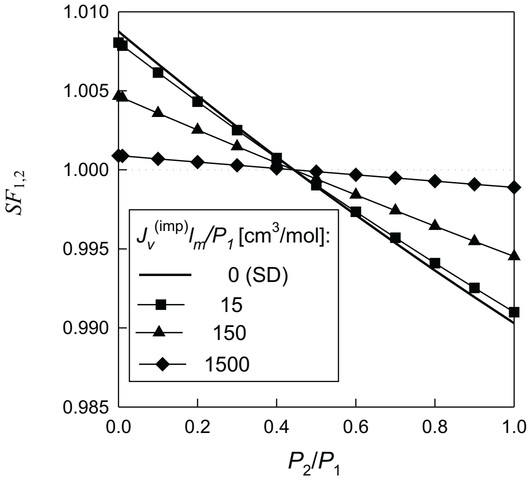

Figure 1. SDI model: $SF_{1/2}$ *vs.* P_2/P_1 for different ratios of $J_v^{(imp)}l_m/P_1 = 0$ (SD model), 15, 150 and 1500 cm^3/mol; $x_{1,f} = 0.1$, $\Delta p = 10$ bar.

2. *"black box" approach (BB)*

The calculations of $SF_{1/2}$ have been performed according to (1), (27a) and (7) for different values of the degree of coupling q. In (27a) $\hat{x}_i$ has been assumed to be the arithmetic mean $\hat{x}_i = (x_{i,f} + x_{i,p})/2$. Because of the nature of the RO process only the solutions giving the positive fluxes of both components (J_1, $J_2 > 0$) are presented.

The dependence of $SF_{1/2}$ on P_{22}/P_{11} for zero coupling is presented in Fig. 2. In that case the BB approach corresponds to the SD model (low pressure difference approximation); it is seen that the upper limit of $SF_{1/2}$(BB) (for $P_{22}/P_{11} \rightarrow 0$, $\Delta p = 10$ bar) is the

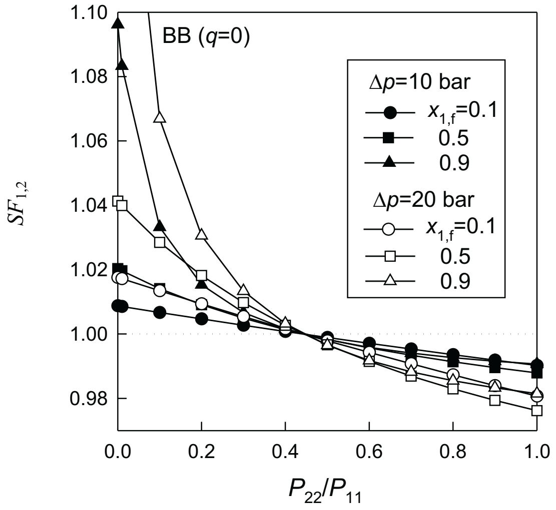

Figure 2. BB approach without coupling ($q = 0$): $SF_{1/2}$ *vs.* P_{22}/P_{11}; $x_{1,f} = 0.1$, 0.5 and 0.9; $\Delta p = 10$ and 20 bar.

same as that shown in Tab. 1. The increase of P_{22}/P_{11} diminishes $SF_{1/2}$. Regardless of the values of $x_{1,f}$ and Δp, all curves intersect at $P_{22}/P_{11} = \overline{v}_1/\overline{v}_2 \cong 0.45$; at that point $SF_{1/2}$ equals one, similarly as in the case of the SD model (Fig. 1). If $P_{22}/P_{11} < \overline{v}_1/\overline{v}_2$, then $SF_{1/2}$ increases with increasing the amount of water in the feed and with increasing pressure difference; for $P_{22}/P_{11} > \overline{v}_1/\overline{v}_2$ the higher pressure difference the stronger decrease of $SF_{1/2}$ below 1. As the pervaporation experiments (Tab. 1) yield $P_2/P_1 = SF_{1/2} > \overline{v}_1/\overline{v}_2$, one can conclude that, neglecting the coupling between the fluxes, it is not possible to explain the experimental values of $SF_{1/2}$ in RO (Tab. 1) for any value of Δp.

$SF_{1/2}$(BB) for various degrees of couplings ($q = 0, 0.9, 0.95, 0.99, 1$ and -1) is presented in Fig. 3. $SF_{1/2}$(BB) is shown only for that P_{22}/P_{11} range, for which it is higher than one. The general observation, confirming the analysis given in Theory, is that the higher degree of coupling, the higher the selectivity factor. The significant increase of $SF_{1/2}$ is obtained only at a high degree of coupling ($q > 0.9$). At the total coupling ($q = 1$) $x_{1,p}$ and, consequently, $SF_{1/2}$ increases when P_{22}/P_{11} diminishes (denoted by a thick solid line in Fig. 3, calculated on the base of (30). However, for q going to 1, but not equal 1, and the small values of P_{22}/P_{11} this increase of $SF_{1/2}$ is limited (a dotted line in Fig. 3, calculated on the base of (27a)), *i.e.* $SF_{1/2}$ ($q \to 1$) does not converge to $SF_{1/2}$ ($q = 1$). Only at higher values of P_{22}/P_{11} $SF_{1/2}$ ($q \to 1$) reaches $SF_{1/2}$ ($q = 1$). The maximum of $SF_{1/2}$ ($q \to 1$) depends on $x_{1,f}$ and Δp. For $x_{1,f} = 0.9$ and $\Delta p = 10$ bar it does not exceed 2 (Fig. 3c). Comparing with the experimental values of $SF_{1/2}$(RO) one can notice that for sufficient high values of q $SF_{1/2}$(BB) reaches $SF_{1/2}$ (experimental). Thus, using this approach the investigated system can be described quantitatively.

The characteristic feature is that the location of maximum of $SF_{1/2}$ depends on the composition of the H_2O-MeOH mixture. The lower the water content ($x_{1,f}$) the higher is the ratio P_{22}/P_{11} at which $SF_{1/2,\max}$ appears. One would expect (as in the case of the SD model or BB without coupling) that $SF_{1/2,\max}$ should appear at P_{22}/P_{11} going to zero. However, for $x_{1,f} = 0.1$ $(P_{22}/P_{11})_{\max}$ is about 5 (Fig. 3a). Only at high water content in the feed P_{22}(MeOH) becomes smaller than $P_{11}(H_2O)$. When the mole fraction of water reaches 0.9, $(P_{22}/P_{11})_{\max}$ decreases to *ca.* 0.04. Similar calculations for L_{ik} = const have shown that $SF_{1/2,\max}(L_{ik} = \text{const}) = SF_{1/2,\max}(P_{ik} = \text{const})$ and $(L_{22}/L_{11})_{\max} \neq (P_{22}/P_{11})_{\max}$.

3. Concentration polarization

As it was mentioned earlier, in the above considerations $x_{i,f}$ denotes the composition of feed solution close to the membrane, not in the bulk solution. To express $SF_{1/2}$ in terms of the composition of the bulk solution, $x_{i,f}^{(b)}$, the concentration polarization effect must be taken into account (Fig. 4).

According to the film model of concentration polarization, the concentrations of feed (*i.e.* $c_{i,f}$ and $c_{i,f}^{(b)}$) and permeate, $c_{i,p}$, are related by (32) [9]:

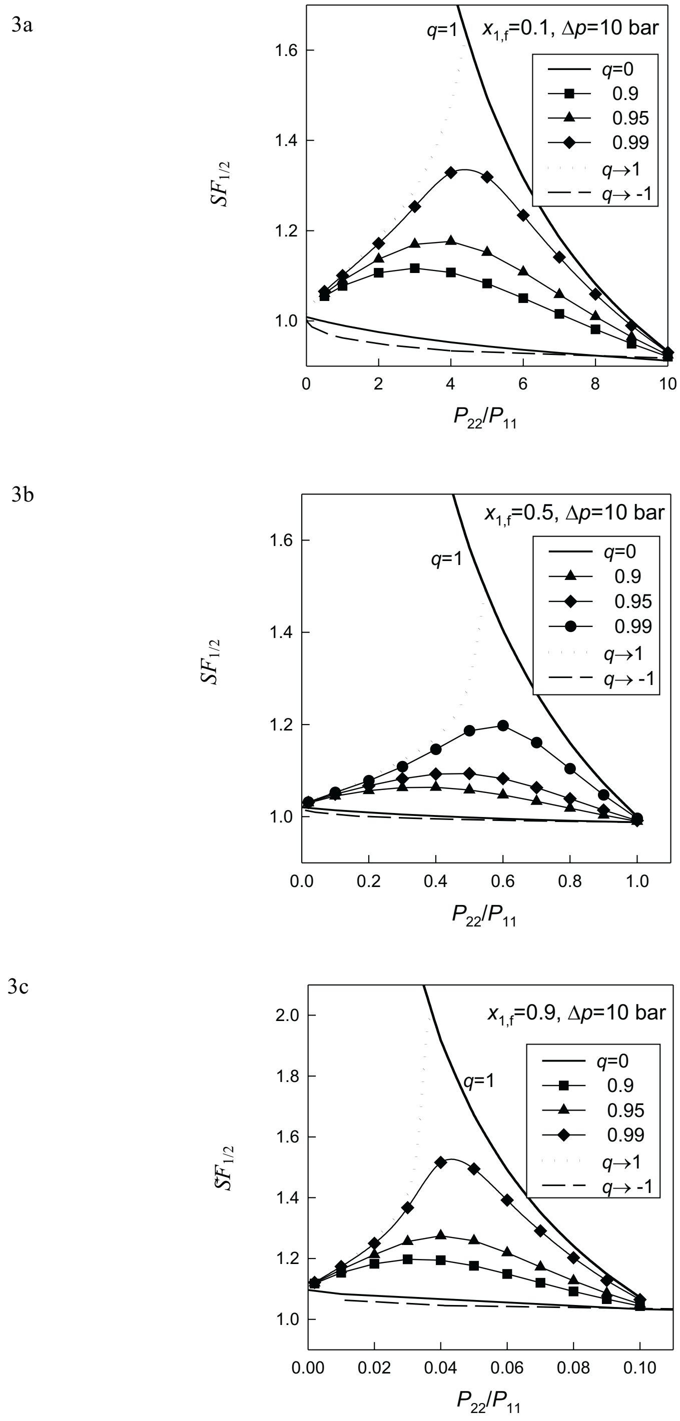

Figure 3. BB approach: $SF_{1/2}$ *vs.* P_{22}/P_{11} for different degrees of coupling q; the water content in the feed: a) $x_{1,f}$ = 0.1, b) $x_{1,f}$ = 0.5 and c) $x_{1,f}$ = 0.9; Δp = 10 bar.

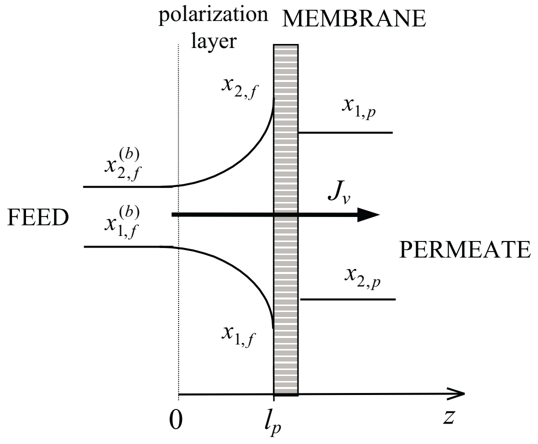

Figure 4. Concentration polarization.

$$\frac{c_{i,f} - c_{i,p}}{c_{i,f}^{(b)} - c_{i,p}} = \exp\left(\frac{J_{\mathrm{v}} l_p}{D}\right) \qquad (32)$$

J_{v} is the volume flux through the membrane, l_p is the thickness of the polarization layer, for the two-component mixture D is the mutual diffusion coefficient in the polarization layer. The mutual diffusion coefficient for MeOH-H_2O is *ca.* $1–2{\cdot}10^{-9}$ m^2/s [10], the volume flux through the Nafion 117 membrane $J_{\mathrm{v}} – 10^{-7}$ m/s, $l_p \approx 50$ μm. This yields $J_{\mathrm{v}}l_p/D \approx 0.005$. For this value of $J_{\mathrm{v}}l_p/D$ and for the maximum theoretical value of $SF_{1,2} = 2$ (at $x_1 = 0.9$) one gets $x_{1,f}^{(b)} \approx x_{1,f}$, *i.e.* the observed selectivity factor, $SF_{1/2}^{(b)}$, calculated on the base of $x_{1,f}^{(b)}$ is close to the real one, $SF_{1/2}$. The noticeable differences between $SF_{1/2}^{(b)}$ and $SF_{1/2}$ will appear at a much higher volume flux. Some exemplary calculations of $x_{1,f}/x_{1,f}^{(b)}$ and $SF_{1,2}^{(b)}/SF_{1/2}$ for $J_{\mathrm{v}}l_p/D = 0.5$, *i.e.* 100 times higher than that estimated for our system, are shown in Fig. 5. It is seen that if $SF_{1/2}$ is higher than 1, then $x_{1,f}$ at the surface of membrane decreases below $x_{1,f}$ and, consequently, the observed selectivity factor is lower than the real one ($SF_{1,2}^{(b)} < SF_{1/2}$).

CONCLUSIONS

The comparison of different models has been presented for pressure driven transport of the mixture of two liquids through a membrane in the stationary state. The following models have been discussed: the solution-diffusion model (SD), modified solution-diffusions models (SDI and SDIY) as well as the "black-box" approach (BB) based on linear irreversible thermodynamics. The set of general equations describing the separation factor, $SF_{1/2}$ has been derived. For the condition $SF_{1/2}$(SD) > 1 the following sequence has been found: $SF_{1/2}$(SD) > $SF_{1/2}$(SDI) > $SF_{1/2}$(SDIY). The BB model, with no coupling between fluxes of species 1 and 2, gives practically the same $SF_{1/2}$ as the SD model under the condition $(\Delta p - \Delta\pi_i)\bar{v}_i \ll \mathrm{RT}$, $i = 1, 2$, because of the similarity of transport equations of both models.

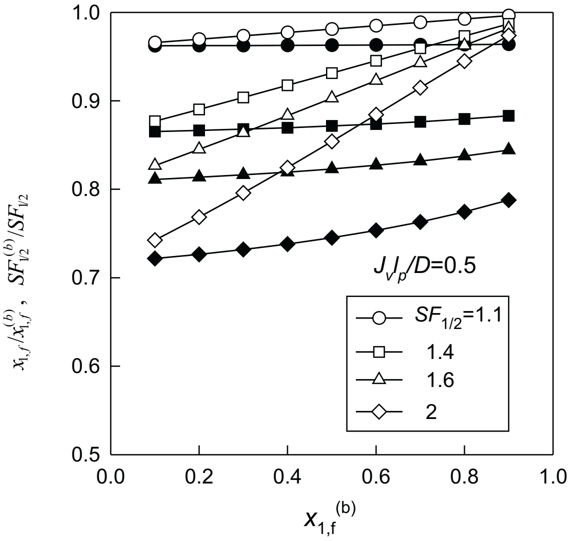

Figure 5. Concentration polarization effect on the selectivity factor: $x_{1,f}/x_{1,f}^{(b)}$ (open symbols) and $SF_{1/2}^{(b)}/SF_{1/2}$ (filled symbols) *vs.* $x_{i,f}^{(b)}$ for different values of $SF_{1/2}$; $J_v l_p/D = 0.5$.

In general, neither the SD model nor its modifications (*i.e.* SDI, SDIY) allow for the description of experimental results. For the moderate pressure differences these models yield $SF_{1/2}$ equal practically one. Even for the limiting case $P_1/P_2 \to \infty$ $SF_{1/2}$(SD) is smaller than the experimental one (excluding $x_{1,f}= 0.9$). Contrary to them the BB approach, taking into account the coupling between the transported components, is able to predict the experimental $SF_{1/2}$. At the adequate range of the P_{22}/P_{11} ratio, depending on the mixture composition, $SF_{1/2}$(BB) increases with the increase of coupling, however, it is limited by the condition of the positive entropy production and the condition of positive fluxes of both components.

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