Membrane Transport of Organics. II. Permeation of Some Carboxylic Acids through Strongly Basic Polymer Membrane

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ABSTRACT: The permeability characteristics of the strongly basic polymer membrane Neosepta® AFN-7, (Tokuyama Soda) have been studied for acetic, propionic, lactic, tartaric, oxalic, and citric acid. The results were interpreted by using the model of transport in reactive membranes. The specific constants, that is, the maximum flux J_{max}, the reactivity constant K, and the permeability coefficient (P), were calculated using the experimental quasi-stationary fluxes and the equation derived as a sum of reaction–diffusion (Michaelis–Menten-type), and the solution–diffusion transport equation. The constants K and J_{max} were found to range from 0.1 to 5 dm^3 mol^{-1} and from 0.4×10^{-7} to 2.5×10^{-7} mol cm^{-2} s^{-1} depending, on the acid properties. The values of K and J_{max} were correlated with the dissociation constants $K_{dis.acid}$, and the diffusion coefficients $D_{aq.acid}$ in aqueous media, respectively. It was found that the reaction–diffusion flux is predominating for all acids, except for the lactic one, when the feed concentration is lower than 0.5 mol dm^{-3}. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2179–2190, 1999

INTRODUCTION

Some carboxylic acids of various composition and concentration are produced in advanced fermentation processes exploiting very different substrates.[1–7] Further processing of the resulting mixtures involves the recovery, separation, or active concentration of the acid of interest.[8,9] Sometimes, the imperfection of the usual methods, for example, extraction and filtration hampers the development of efficient biotechnologies or makes the quality of products lower. Among numerous separation methods that could be applied to improve fermentation technology, the membrane separation techniques seem to be the most natural, efficient, and economic. Nowadays, studies in this field deal with the application of liquid membranes[9–16] and/or polymer membranes of various composition and structure.[17–24] In this context, we reported previously[25] on the dialysis of acetic, propionic, and formic acid through the polymer membranes with sulfonic (Nafion-120) and carboxylic (Flemion) groups. The equilibrium sorption of acids into the membrane phase and their rates of permeation were found to depend mainly on $K_{diss.acid}$ determining the fraction of unionized species, which can permeate the swollen membrane polymer. As a result, transmembrane fluxes have reached relatively high values for the feed acid concentrations above $0.2M$ only. On the other hand, faster and more selective membrane processes can be expected when the membrane

Table I   Characteristics of Membrane System

Characteristics	Details
Membrane	Neosepta® AFN-7, prod. Tokuyama Soda, Japan
Properties	Strongly basic, anion permeable, reinforced
Ion-exchange capacity (mol Cl$^-$/kg)	
Dry form	3.18 (2.0–3.5)[a]
Swollen form	2.22
Water content (kg H$_2$O/kg dry Cl$^-$ form)	0.45 (0.40–0.55)
Thickness in Cl$^-$ swollen form (cm)	0.0165 (0.015–0.020)
Working area (cm^2)	3.85

		Feed Solutions	
Acid	Chemical Composition	K_{diss}	K_{OH}^{X} [b]
Acetic (AA)	CH$_3$COOH	1.75×10^{-5}	4
Propionic (PA)	CH$_3$CH$_2$COOH	1.33×10^{-5}	3
Lactic (LA)	CH$_3$CHOHCOOH	1.38×10^{-4}	
Oxalic (OA)	(COOH)$_2$	6.50×10^{-2}	72
		6.10×10^{-5}	
Tartaric (TA)	(CHOH)$_2$(COOH)$_2$	9.21×10^{-4}	
		4.31×10^{-5}	
Citric (CA)	(CH$_2$)$_2$COH(COOH)$_3$	8.60×10^{-4}	250
		1.70×10^{-5}	
		4.00×10^{-6}	

[a] Producer data.
[b] Data for strongly basic ion-exchange resin (Ender and Bosholm).[48]

exhibits an additional reactivity toward feed components. This means that instead of (or parallel to) the usual solubility (sorption)–diffusion mechanism, a specific diffusion–reaction mechanism should be involved in the membrane transport. In recent years, a number of articles were directed to investigate the membranes that contained reactive moieties, also called fixed-site carriers by analogy to liquid membranes. The examined membranes were found to transport some ionic,[26–34] gaseous,[35] and organic[36–41] substances including carboxylic acids and their anions.[42–45]

Taking the affinity of amine groups toward carboxylic acids into account, we selected the Neosepta® AFN-7 membrane with attached strongly basic functional groups as a model reactive membrane for this study. In order to obtain the experimental data sufficient to asses the influence of acid properties on transmembrane fluxes, the research was carried out with such acids as propionic, acetic, lactic, citric, tartaric, and oxalic acid. These compounds appear frequently in mixtures and should be separated from fermentation broths or effectively removed from some food products (e.g., beer, wine, juices) for their deacidification.

EXPERIMENTAL

Membrane and Reagents

The Neosepta® AFN-7 membrane is produced and commercialized by Tokuyama Soda,[46] Japan. The membrane is made by the paste method[47] and contains quaternary amine functional groups as the main active component. Some amount of 4-vinylpyridine and 2-methyl-5-vinylpyridine used for the membrane preparation leads to an additional ion-exchange capacity and some additional properties due to the presence of weakly basic ion-exchange groups.[34] Characteristics of the AFN-7 membrane measured in our laboratory are listed in Table I, together with the data of the producer[46] in parentheses. The ion-exchange capacity was determined by the standard proce-

dure. The membrane was immersed in the $1M$ KCl solution over 24 h and then carefully washed with distilled water. Thereafter, the sample was converted to its OH⁻ form by equilibrating with the $0.2M$ KOH solution and, finally, washed in distilled water to remove free electrolytes from the membrane phase. After the neutralization of membrane groups by immersing the sample in the measured volume of the $0.1M$ HCl solution, the ion exchange capacity was calculated using the following formula:

$$E_c = n_H/m_{sw} \text{ (mol g}^{-1}) \qquad (1)$$

In eq. (1), n_H denotes the number of moles of HCl, and m_{sw} denotes the mass of the membrane sample in its swollen state (Cl⁻ form). The content of water in the membrane has been determined from the mass difference of the swollen (m_{sw}) and the dried (m_d) membrane sample (Cl⁻ form, 393 K), that is,

$$W = 100(m_{sw} - m_d)/m_d \text{ (wt \%)} \qquad (2)$$

The feed solutions of concentration ranging from 1×10^{-3} to $1M$ R(COOH)$_n$ were prepared from analytical-grade reagents. The chemical composition and the dissociation constants of carboxylic acids that were used in the transport experiments are listed in Table I. Additionally, the data in the literature concerning the ion-exchange selectivity coefficients K_{OH}^{X}[48] for some acids and a conventional strongly basic ion exchanger are presented in Table I as well.

Permeability Measurements and Basic Calculations

The permeation experiments were carried out using the equipment described in details elsewhere.[25] The apparatus was composed of the permeation cell with the membrane (3.85 cm²) separating the feed (200 cm³) and strip (75 cm³) solution. Before the experiment, the membrane was equilibrated with the feed acid solution and then carefully rinsed with distilled water to remove the free acid absorbed into its internal aqueous phase. Depending on the type of experiment, the feed solution contained one of the acids, that is, acetic (AA), propionic (PA), tartaric (TA), oxalic (OA), citric (CA), lactic (LA) acid, or the mixture of propionic and acetic acid (AA–PA). Distilled water of specific conductivity lower than 3 μS (at $t = 0$) was applied in the

receiver as the stripping solution. The permeation rate was calculated after determining the concentration of the acid transported into the receiver versus time of the experiment. Each time, the concentration was evaluated by measuring the conductivity of the strip solution and thereafter converted to the concentration data by calibration procedures.

As far as the multicomponent feed solutions are concerned, the amount of transported acid was determined by the methods of capillary electrophoresis. Isotachophoreograms were recorded on a Capillary Electrophoresis Analyser EA 100 (prod. Labeco, Slovakia) equipped with conductivity detectors. The leading and terminating solutions contained L-histidine and L-histidine monohydrochloride or L-glutaminic acid, respectively. The stripping solution was sampled (0.5 cm³) during the experiment and then analyzed after dilution in the buffer of pH 5–7.5. The quantitative determinations were made using the calibration curves that relate the standard concentrations with the zone length recorded on the respective isotachoforeogram.

In order to evaluate transport rates, the quasi-stationary fluxes J (in mol cm^{-2} s^{-1}) were calculated from the following function:

$$Q(t) = Jt + \text{const (mol cm}^{-2}) \qquad (3)$$

where $Q(t)$ denotes the number of moles of the acid transported through the 1-cm² membrane area in time t. $Q(t)$ has been calculated from eq. (4), as follows:

$$Q(t) = C_{s,t}V_s A^{-1}{}_m \qquad (4)$$

The symbol $C_{s,t}$ (mol cm^{-3}) denotes the concentration of the acid in the strip solution (s) after the time t, and V_s (cm³) and A_m (cm²) denote the volume of solution and the membrane working area. All the experiments were carried out at a temperature of 298 K.

The typical experimental plots of $Q(t)$ versus t for each of the acids of $0.5–0.6M$ concentration are presented in Figure 1. It can be seen from presented curves that after a transient state (typically 1.5–3 h) the transports reached their quasi-stationary conditions represented by the linear dependence $Q(t)$ on time as required by eq. (3). Except for oxalic acid, all the transport curves are typical for these transport processes, for which a

Figure 1 Representative transport curves for the feed phase containing (■) 0.5M citric, (●) 0.5M oxalic, (▲) 0.5M tartaric, (○) 0.6M acetic, (□) 0.4M propionic, and (△) 0.6M lactic acid.

transient state occurs under an equilibrium condition for the membrane–stripping solution interface.[49] Some differences are observed for multiprotonic citric and oxalic acid; that is, citric acid always shows a very long transient period, whereas oxalic acid is characterized by a different shape of its transport curve.

RESULTS AND DISCUSSION

Transport from Single Component Solutions

From a practical point of view, it is interesting whether the fluxes differ to the degree, enabling the use of the membrane for the separation of acids. It was found herein that for the feed concentration higher than 0.1 mol dm^{-3} (see primary data in Fig. 5), the fluxes fulfill the following order:

$$J_{CA} > J_{OA} > J_{TA} > J_{AA} > J_{PA} > J_{LA} \qquad (5)$$

However, in the case of acids having biotechnological relevance, that is, LA, PA, and AA, the differences are not big and the ratio of J_{PA} or J_{LA} to J_{AA} is ~ 2 at the maximum. Comparing the order (5) with that published recently by

Zheleznov et al.[45] for the Neosepta® AMH anion exchange membrane being used in the neutralization dialysis (countertransport of carboxylic and hydroxyl anions) of similar acids, that is,

$$J_{AA} \geq J_{LA} > J_{PA} > J_{CA} > J_{OA} \qquad (6)$$

one can conclude that the interrelations between J_{AA} and J_{PA}, and J_{LA} are similar for the AFN and AMH membranes. It means that both membranes prefer the permeation of acetic acid during the simple (this work) and neutralization dialysis. From the experimental data, it can also be concluded that with increasing of the feed concentration the fluxes do not exhibit a linear relationship between J and C_{feed}. This linear relationship could be predicted from a simple model of the diffusional permeation based on I-Fick's law for diffusion. The observed curvature of plots (see curve 1 in Fig. 5) can be interpreted as a result of the transport mediating role of the reactive sites in the membrane phase. Usually, this phenomenon is observed as a typical property of liquid membranes containing a mobile carrier.[50] Nevertheless, some reactive polymer membranes were found to transport various species by the similar mechanism,[42,44] called fixed (or chained) carrier transport.[51,52]

The above considerations lead to the question of whether the transport in the AFN-7 membrane, apparently influenced by reaction phenomena, is quantitatively and qualitatively different in comparison to the conventional solubility (sorption)–diffusion membrane process. To point out these differences, in Figure 2, the results of AA and PA permeation through the strongly basic (AFN-7), strongly acidic (Nafion-120[25]), and weakly acidic (Flemion[25]) membranes are compared. The plots of normalized fluxes $J \times L_m$ versus the feed concentration show that the AFN-7 membrane is much more effective than other membranes in the transport of AA and PA from diluted solutions, that is, below the 0.2M concentration. However, the fluxes practically converge (compare AFN-7 and Nafion-120 in Fig. 2) in the region of higher concentrations. This effect can be explained as a result of the additional free diffusion of the acids through the hydrophilic polymer of the AFN-7 membrane in the system with the concentrated feed solutions. Nevertheless, the basic transport mechanism in AFN-7 remains different, which can be concluded from the Michaelis–Menten plots drawn in Figure 3.

Figure 2 Normalized fluxes of acetic and propionic acid through the strongly basic (AFN-7), the strongly acidic (Nafion-120), and the weakly acidic acid (Flemion) membrane. AFN-7: (▼) acetic acid; (▲) propionic acid. Nafion-120: (■) acetic acid; (●) propionic acid. Flemion: (□) acetic acid; (○) propionic acid.

Reaction–Diffusion Flux

Considering the membrane as an ideal and reactive carrier between two solutions, the fluxes can be quantitatively described by the Michaelis–Menten-type equation,

$$J = J_{\max} \times \frac{KC_f}{1 + KC_f} \ (\text{mol cm}^{-2}\,\text{s}^{-1}) \qquad (7)$$

where C_f is the feed concentration, and K is the characteristic constant. K can be interpreted as the overall (global) equilibrium constant of a reversible reaction between the membrane and substrates in an adjacent feed solution. The physical meaning of the K constant is given by its reciprocity $1/K$, which equals to the feed concentration at $J_{\max}/2$. On the other hand, eq. (7) can be treated as a phenomenological flux equation based on a formal analogy to a Langmuir function[47] with the empirical parameters $J_{\max}$ and K. However, using a more advanced theory and regarding the membrane transport as mediated by a carrier, mobile or fixed, $J_{\max}$ can be related to the diffusion coefficient D of a carrier or a mobile fragment of the polymer membrane, its concentration C_0, and the membrane thickness L_m, as follows:

$$J_{\max} = DC_0/L_m \ (\text{mol cm}^{-2}\,\text{s}^{-1}) \qquad (8)$$

It should be explained here that eq. (7) is only a simplified version of a more general equation describing any carrier transport. Because eq. (7) is frequently used without any proper comment, we recall its full form and underlying assumptions below. The key step for deriving eq. (7) is the form of the reversible reaction between the substrate S and the carrier C, as follows:

$$S + C \rightleftarrows CS \qquad (9)$$

The equilibrium constant for this reaction is specified above as K. The reaction system usually is treated as symmetric; that is, the K constant for reaction (9) at the feed interface is the same as the respective K constant for the reversed reaction at the stripping interface, and the diffusion coefficients of the carrier in the form of C and CS are equal. The combination of boundary conditions for diffusion processes [as determined by the equilibrium of reaction (9)] with the I-Fick's diffusion law leads[50] to the following equation for the flux of S from the feed to the stripping solution (J):

$$J = J_{\max} \times \frac{K(C_f - C_s)}{(1 + KC_f)(1 + KC_s)} \qquad (10)$$

Figure 3 Transformed Michaelis–Menten plots for the transport of acetic acid (▼, ■) and propionic (▲, ●) acid through AFN-7 (▲, ▼) and Nafion-120 (■, ●) membranes.

where C_i denote the concentration of the feed (f) or the stripping (s) solution, respectively. This equation describes the stationary flux in the membrane system when the transport processes are limited by slow diffusion phenomena. Equation (10) can be reduced to the form of eq. (7) when the concentration of solutes transported to the stripping phase is much lower than that in the feed phase, that is, $C_s \ll C_f$ and/or when $KC_s \ll 1$. Thus, the usefulness of eq. (7) in batch experiments is limited to the quasi-stationary fluxes, which can be observed at the beginning of the transport, that is, when the backward strip reaction does not influence the overall flux. The saturation fluxes J_{max} in eqs. (7) and (10) are expressed identically. However, depending on the membrane composition, the different physical meaning for diffusion coefficients should be considered. For the liquid membrane or quasi-liquid membrane transport (transport processes in solvent polymeric membranes[53]), the coefficient D denotes the diffusion coefficient of a mobile carrier in an organic membrane solvent. In the case of the polymer membranes, operating with fixed reactive groups, its meaning depends on the details of transport mechanism. Namely, in the exchange–diffusion processes (e.g., Donnan dialysis) D is defined as the interdiffusion coefficient.[52] Whereas, in the case of transports mediated by a fixed carrier, D is the diffusion coefficient of these chained membrane components, which can move in some restricted membrane areas only.

Additionally, the J_{max} of reactive polymer membranes can be interpreted using the theory developed by Cussler et al.[51] This theory distinctly classifies two limits of the membrane transport and leads to two different formulation for J_{max}. When the transport is limited by slow diffusional processes, J_{max} has the following form:

$$J_{max} = \frac{DC_0}{L_m} \times \frac{2l/l_0}{3 - l_0/l} \; (\text{mol cm}^{-2} \text{ s}^{-1}) \quad (11)$$

and, alternatively, for the processes limited by slow reaction kinetics,

$$J_{max} = \frac{KC_2^0}{L_m} \times \frac{l^3(l_0 - l)}{l_0^2} \; (\text{mol cm}^{-2} \text{ s}^{-1}) \quad (12)$$

The symbol l denotes the distance between the points of fixation of the chained membrane carrier that is mobile and active up to the distance l_0. The

Cussler's limiting equations show that for diffusion-limited phenomena, J_{max} is trivially proportional to the diffusion coefficient D and the concentration C_0, as predicted also by eq. (7). However, in the case of reaction-limited processes, the flux becomes proportional to the K constant and to the squared concentration of a carrier C_0^2.

According to the Lineweaver–Burk[54] analysis of eq. (7), the plot of $1/J$ versus $1/C_f$ should be linear when the transport is consistent with hyperbolic eq. (7). It can be seen from Figure 3 that this criterion is fulfilled in the broad range of concentrations only by the AFN-7 membrane in spite of possible contribution of free diffusion effects.

Free Diffusion

According to the solution-diffusion model of solutes transport in a hydrophilic polymer membrane, any carboxylic acid in its undissociated form can dissolve in the aqueous membrane phase and then diffuse throughout the membrane. Thus, the solution–diffusion flux J_D is dependent mainly on two parameters, such as the distribution coefficient k_d and the effective diffusion coefficient of the acid in a membrane ($\bar{D}_m$), as follows:

$$J_D = \frac{\bar{D}_m k_d}{l} (C_f - C_s) \quad (13)$$

When the feed concentration C_f is much higher that of the strip C_s, the stationary flux J_D is given by eq. (12), as follows:

$$J_D = PC_f \quad (14)$$

where P denotes the effective permeability coefficient expressed in cm s^{-1} (when C_f is in mol cm^{-3}). Equation (14) indicates the linear relationship between J_D and C_f under assumption that k_d and ($\bar{D}_m$) are not dependent on C_f. In the studied membrane system, the influence of this kind of transport can be seen as an continuous increase of total flux with an increase of the feed concentration. For example, this behavior is clearly represented by the permeation of oxalic acid through the AFN-7 membrane (see Fig. 5, OA, curve 1, above $C_f = 0.5M$).

Dual Mode Transport

Most of the experimental curves presented (in Fig. 6; curve 1) show a specific appearance typical

Figure 4 Theoretical curves for flux versus feed concentration dependence: (1) dual (1 + 2) transport mechanism; (2) reaction–diffusion (carrier) transport mechanism; (3) solution–diffusion transport mechanism. Calculated with K = 10, $P = 5 \times 10^{-6}$, and $J_{max} = 1 \times 10^{-8}$.

for the dual transport mechanism. Similar curves were frequently observed for some liquid membranes as a result of simultaneously occurring carrier and solution–diffusion transport phenomena.[55] Assuming that respective fluxes are not coupled in the membrane, one can express the total flux as a sum of reaction–diffusion (carrier) and solution–diffusion as follows:

$$J = J_R + J_D \tag{15}$$

$$J = J_{max} \frac{KC_f}{1 + KC_f} + PC_f \tag{16}$$

The characteristic theoretical curves corresponding with eqs. (7), (14), and (16) are presented in Figure 4.

Reaction–Diffusion Characteristics for Transport of Carboxylic Acids in AFN-7 Membrane

In order to evaluate the J_{max}, K, and P parameters, the experimental data were fitted with eq. (16). The first approximations for these parameters required by the fitting procedure were evaluated as follows: (1) the starting values for J_{max} and K were calculated by fitting low concentration fluxes (below $0.5M$) with eq. (7), and (2) the P value was calculated from the slope of J versus C_f curve for C_f above $0.5M$. The results of calculations are listed in Table II. The corresponding regression curves are drawn in Figure 5. These curves were then decomposed to their J_R and J_D counterparts (see Figure 5, curves 2 and 3) and the fraction of reaction–diffusion (carrier) transport was calculated and drawn as the function of C_f (curve 4). It can be concluded from Figure 5

Table II Comparison of Reaction–Diffusion Characteristics for Polymer Membranes

No.	Membrane	Transported Substance	K (dm^3 mol^{-1})	J_{max} (mol cm^{-2} s^{-1})	P (cm s^{-1})	Correlation Coefficient for Eq. (16)
1	Neosepta AFN-7 (strongly basic)	propionic acid	0.164	1.96×10^{-7}	5.36×10^{-6}	0.999
2		acetic acid	0.20	2.41×10^{-7}	1.13×10^{-5}	0.994
3		lactic acid	1.31	4.89×10^{-9}	2.31×10^{-5}	0.994
4		citric acid	2.77	6.47×10^{-8}	3.23×10^{-5}	0.999
5		tartaric acid	2.28	3.0×10^{-8}	3.32×10^{-5}	0.998
6		oxalic acid	4.58	4.11×10^{-8}	4.09×10^{-5}	0.999
7	Nafion-117 (strongly acidic)[a]	L-alanine	0.63	2.0×10^{-7}		
8		glycine	0.59	1.3×10^{-7}		
9	Laboratory made (weakly basic)[b]	chloroacetic acid	20.8	7.1×10^{-9}		
10		bromoacetic acid	41.6	1.3×10^{-8}		

[a] Data from Sikdar.[37]
[b] Data from Yoshikawa et al.[44]

Figure 5   Flux versus feed concentration dependence: (1) experimental results and eq. (16) regression curve; (2) calculated reaction–diffusion fluxes; (3) calculated solution–diffusion fluxes; (4) fraction of carrier type (reaction–diffusion) flux; PA represents propionic acid; AA, acetic acid; LA, lactic acid; CA, citric acid; TA, tartaric acid; OA, oxalic acid.

Figure 6 The dependence of reactivity constant K on the acid dissociation constant (K_d).

that, except for lactic acid, diluted ($0.5M$) carboxylic acids are transported through the AFN-7 membrane with prevailing reaction–diffusion mechanism. As it can be expected, the contribution of free diffusion becomes dominating when the membrane is contacted with the concentrated feed solutions. The different properties of lactic acid can be explained by considering the fact that the transport process of LA as mediated by an amine carrier in liquid membranes is reaction-rate-determined (with Thiele modulus $\Theta^2 < 1$).[14] Thus, it is possible that the free diffusion of LA is faster than its transport mediated by amine groups. Consequently, it is justified that the fraction of the carrier type is rather small (i.e., lower than 20%), as is seen in Figure 5.

The results of calculations suggest the correlation between the reactivity constant K and the dissociation constant $K_{dis.acid}$. This correlation (see Fig. 6) is nonlinear and shows the increase of K with the increase of dissociation ability of a carboxylic acid. This indicate that the transport mechanism involves the ion-exchange and neutralization, followed by hydrolysis processes rather than the formation of complexes between unionized acid species and the membrane functional groups.

The K constants found from our experiments vary from 0.1 to 5 dm^3 mol^{-1}. These values are comparable (see Table II) with the K constants for

glycine (0.63) and L-alanine (0.59), reported elsewhere by Sikdar,[37] for the perfluorosulfonic Nafion-117 membrane. Much higher values of K, that is, 20.8 and 41.6 dm^3 mol^{-1}, can be calculated from the data reported by Yoshikawa et al.[44] for chloro- and bromoacetic acid and the laboratory-made membrane containing vinylpirydine active groups. On the other hand, the fluxes calculated from Yoshikawa et al.[44] are lower, that is, 7×10^{-9} and 1.3×10^{-8} mol cm^{-2} s^{-1}, as compared to fluxes found in our experiments ($6 \times 10^{-8} - 3 \times 10^{-7}$ mol cm^{-2} s^{-1}). Taking into account our results and the results of Sikdar[37] (see J_{max} in Table II), one can suppose that (1) J_{max} amounting to 10^{-7} mol cm^{-2} s^{-1}, and (2) low values of K are typical for the transport of some ionizable organic species through strongly basic or strongly acidic ion-exchange membranes. The same conclusion can be drawn from the data of Zheleznov et al.,[45] who reported even lower K values ranging from 0.001 to 0.03 dm^{-3} mol for the carboxylic anions versus hydroxyl anions countertransport. Moreover, some conclusions concerning the factor that limits the transport in AFN-7 can be drawn from the actual correlation between J_{max} and reaction or diffusion constants. According to eq. (11), J_{max} should increase with the increase of the diffusion coefficient D. Conversely, in the case of reaction limited processes [eq. (12)] one can expect the increase of J_{max} with K (or $K_{dis.acid}$). The analysis of our results indicates that there is no positive correlation between J_{max} and K. The correlation can be roughly envisaged in respect to J_{max} and D after assuming that D can be related to $D_{aq.acid}$ by a tortuosity factor. Unfortunately, the plot presented in Figure 7 is not precise enough to enable a quantitative analysis of the dependence of J_{max} on $D_{aq.acid}$. This is caused by the lack of the values of $D_{aq.acid}$[56] corresponding to feed concentrations at J_{max}. As the approximation, in Figure 7, they were replaced by respective diffusion coefficients in ~ $2M$ solutions. Thus, the presented plot shows only the tendency of J_{max} to increase with $D_{aq.acid}$, and it confirms the general rule that the transport rates in polymer membranes are limited by relatively slow diffusion phenomena. In respect to the permeability coefficients (P), it is very difficult to discuss their values immediately because they are the product of distribution and diffusion coefficients, which can be interrelated in various ways. One can conclude, however, that the 10^{-5} cm s^{-1} order of P coefficients is typical for the

permeation of electrolytes through ion-exchange membranes.

Transport from Binary Solutions

The presented results indicate that the strongly basic membrane AFN-7 can be used for the separation of some carboxylic acids because of their different values of K or J_{max}. Certainly, this is justified only for these acids, which appear in mixtures after fermentation processes, for example, propionic and acetic acid. Considering the relations between properties of PA and AA, that is, $K_{AA} > K_{PA}$ (0.20 : 0.16), as well as $K_{OH}^{AA} > K_{OH}^{PA}$ (4 : 3) (see Table I), and $D_{aq.AA} > D_{aq.PA}$, one can always expect higher fluxes of acetic acid than that of propionic acid. In fact, the ratio of the limiting fluxes $J_{max,AA}/J_{max,PA}$ is 1.35; thus, it is interesting how far this ratio will change in the real competitive experiments. The results of experiments are presented in Figure 8 as the dependence of J_{PA} and J_{AA} on the concentration of the equimolar solutions of PA and AA. They prove the ability of the Neosepta AFN-7 membrane to transport preferentially acetic acid in the broad range of concentrations, that is, from 0.05 to $1M$ for each of the acids. The ratio of fluxes J_{AA}/J_{PA} attains the value of 1.4 for diluted solutions and decreases to 1.1 in the case of concentrated solutions.

Figure 7   The correlation between limiting fluxes J_{max} and aqueous diffusion coefficients $D_{aq.acid}$.

Figure 8   Fluxes in the competitive transport of ($\bigcirc$) acetic and ($\square$) propionic acid.

CONCLUDING REMARKS

Experimental data concerning the permeation of carboxylic acids through strongly basic polymer membranes can be discussed by using the dual transport model. The model describes the membrane transport as a result of the solution–diffusion and reaction–diffusion phenomena. According to the model, the transport of carboxylic acids is sufficiently characterized by three phenomenological parameters, that is, the limiting flux J_{max}, the reactivity constant K, and the permeability coefficient P. It was demonstrated that the contribution of reaction–diffusion mechanism into the overall flux depends on the concentration of feed solution. This mechanism is prevailing when the membrane is contacted with dilute carboxylic acid solution, that is, when the feed concentration does not exceed $0.5M$. With an increase in the feed concentration, the effects of reaction–diffusion phenomena are masked by prevailing permeation of the acid through the swollen gel of the anion-exchange membrane.

The correlation between J_{max} and $D_{aq.acid}$ and between K and $K_{dis.acid}$ indicate that the reaction–diffusion process (except for lactic acid) is limited by a slow diffusion of species permeating between reactive functional groups. It is possible that the diffusion step is associated with fast exchange of anions or simultaneous reactions of amine neu-

tralization and salt hydrolysis. Note that acid anions present in the feed can be exchanged with membrane counterions in the simple ion-exchange sorption process. Simultaneously, unionized acid reacts with functional groups and forms to form the salt of strong base and weak acid inside the membrane phase. This salt hydrolyses at a sufficiently high pH, especially at the stripping interface (because of the experimental condition $C_s \ll C_f$), and the acid is desorbed from the membrane phase to the receiver. The hydrolysis reaction produces also OH$^-$ ions exchanged and transported in the opposite direction according to the exchange–diffusion mechanism for anions. Both processes require the diffusion steps for the transfer of species between the mediating membrane functional groups. Chained carrier transport seems to be possible due to the presence of weakly basic pyridine groups, but as much slower, probably (see data in Table II), it is masked by faster exchange–diffusion processes.

From the practical point of view, the results presented in this article confirm the usefulness of strongly basic polymer membranes for the effective permeation of carboxylic acids from their diluted solutions. The separation effects in the competitive transports can be evaluated by comparing the characteristic constants K and $J_{\max}$ or P that can be found after permeating single acids of different concentrations.

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