

Membrane Transport of Organics. III. Permeation of Some Carboxylic Acids Through Bipolar Polymer Membrane

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ABSTRACT: The permeation of acetic (AA), propionic (PA), lactic (LA), oxalic (OA), citric (CA), and tartaric (TA) acids through the bipolar ion-exchange membrane Neosepta BP-1 (Tokuyama Corp.) was studied. It was found that the fluxes (J , mol cm⁻² s⁻¹) and mass-transfer coefficients (k , cm s⁻¹) increase in the following order: CA < OA < LA < TA < PA ≤ AA. The transport processes in the Neosepta BP-1 membrane are concentration-dependent and can be described phenomenologically using I-Fick's law for diffusion. The permeation phenomena correspond to the solution–diffusion model similarly as to the permeation of carboxylic acids through strongly acidic cation-exchange membranes. However, in competitive AA–PA transport experiments, typically for strongly basic membranes, the separation ability of the BP-1 membrane with a preference toward AA was observed. The selectivity coefficients α_{PA}^{AA} calculated as the ratio of the respective mass-transfer coefficients vary in the range from 1.31 ± 0.2 to 2.1 ± 0.6 . These values depend on the feed composition and the system arrangement, which means that α_{PA}^{AA} is always higher for the system with the anion-exchange layer is in contact with a feed solution. Rather low fluxes of PA, AA, and other acids, as compared to some monopolar membranes (Neosepta AFN-7, Nafion-120, Flemion), are promising for the application of the bipolar membrane in an electrodialytic separation of carboxylic acids from their aqueous solutions or mixtures. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2705–2717, 2001

Key words: polymer membrane; bipolar; transport; separation; carboxylic acids

INTRODUCTION

Numerous methods of weak acids separation, including carboxylic acids, are based on the sorption properties of charged polymers (crosslinked polyelectrolytes) used in the form of ion-exchange resins^{1–6}, for example, chromatographic techniques.^{7–9} Similar principles of reaction–diffusion or solution–diffusion phenomena were recognized as the

source of separation effects in some membrane systems.^{10–20} On the other hand, the development of ion-exchange polymer membranes of high ionic selectivity, stability, and excellent electrochemical properties has resulted in the development of membrane electrodialysis (MED) that allows fast and effective recovery of carboxylic acids from complex mixtures containing various carboxylates, for example, acetates,^{21,22} lactates,^{23–25} propionates,²⁶ and tartates.²⁷ To improve the efficiency of MED and to facilitate the salt-to-acid conversion, there were some attempts made to use bipolar membranes (BPM)^{28–33} for this purpose including also for the separation of bioreactor products.³⁴ The main idea concerning the elec-

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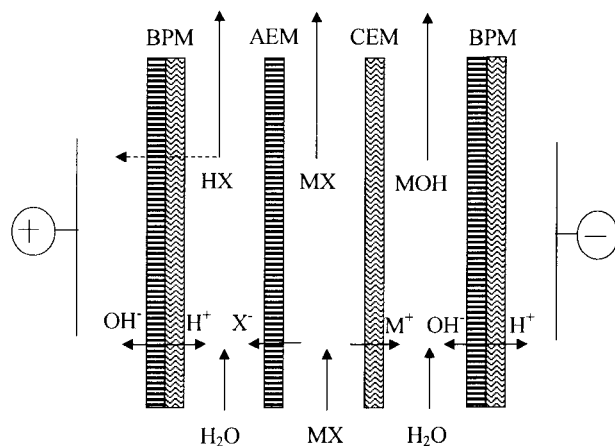


Figure 1 Scheme of electrodialytic salt-to-acid conversion with the use of BPMs. Dashed line represents possible diffusion of the weak acid (HX) through the BPM. AEM, anion-exchange membrane or layer; CEM, cation-exchange membrane or layer in the BPM.

trodialytic conversion of a carboxylate to carboxylic acid³⁵ is shown in Figure 1. The role of the BPM in this process is to split water, that is, to produce OH^- and H_3O^+ , which are to be consumed in respective compartments of the electrolysizer. The main function of the monopolar membranes, that is, the anion-exchange (AEM) and the cation-exchange membrane (CEM), in such electrochemical processes is the transportation of ions with a charge opposite to the fixed charges of the respective polyelectrolyte. As compared to these membranes, the BPM should not transport any ionic species because they are discriminated against by the opposite charged anion- and cation-exchange layer. However, in the case of weak electrolytes, such as carboxylic acids, an unfavorable diffusional flow of undissociated species (from the compartment 2 to 1, dashed line in Fig. 1) is possible. This process can lower the efficiency of acid enrichment and should be eliminated as much as possible. Thus, regarding the position of the BPM contacted by its cation-exchange layer with a concentrated acid solution, it is necessary to know how far the BPM prevents the diffusional flow of carboxylic acids.

Although the idea of the synthesis of BPMs has been known since 1950–60, the respective technology is still under development. Potential properties of the BPM were first described by Sollner et al.,³⁶ and the first membrane was synthesized by Frilette³⁷ by simple bonding of the AEMs and CEMs. It can be expected that the main physicochemical properties of polyelectrolytes forming

BPMs determine the membrane properties themselves. Consequently, the anion-exchange part of the BPM which discriminates the free permeation of cations and its cation-exchange counterpart which discriminates anions led to the unique properties which make the BPM completely impermeable for ionized species. On the other hand, another key problem is related to the nature of the transported species which can appear as ionic pairs or associates invading the membrane phase without any Donnan exclusion effects. Some other compounds like undissociated carboxylic acids can react with the polybase component of a bipolar membrane. In this context, our main task was to obtain fundamental data concerning the permeation of some carboxylic acids through BPM and their comparison with the permeability of conventional CEMs and AEMs reported elsewhere.^{19,20} Generally, in related literature, there are no suitable physicochemical data allowing reasonable prediction of the transport properties of BPMs. Thus, we believe that the results presented herein, and concerning the diffusion of carboxylic acids through a selected BPM Neosepta BP-1 (Tokuyama Corp.), can also be useful for the interpretation of transport phenomena in other membranes of comparable composition.

EXPERIMENTAL

The main goal of the experimental studies was to measure the fluxes of some carboxylic acids from their single-component solutions. These solutions were contacted alternatively with a cation- or anion-exchange layer of the BPM. Moreover, to evaluate the separation ability of the BP-1 membrane, some experiments with the feed phase containing both propionic and acetic acid were carried out.

Membrane and Reagents

The BPM used in all the experiments described herein was the Neosepta BP-1 membrane. This membrane is a development product of Tokuyama Corp. (Tokuyama City, Japan). The membrane consists of two layers made up of a strongly acidic and strongly basic polyelectrolyte. A detailed composition and procedure of preparation is unavailable. It can be expected, however, that, similarly to other Neosepta membranes, the main polymer components of the BP-1 are based on sulfonated or aminated polystyrene. The stan-

Table I Characteristics of Membrane-transport System

| Membrane | Neosepta® BP-1, product of Tokuyama Corp. (Japan) | | |
|--|---|----------------------------------|---------------------------------------|
| Composition | Bipolar: strongly basic and strongly acidic, reinforced with plastic mesh | | |
| Ion-exchange capacity ^a | Na ⁺ /Cl ⁻ | Na ⁺ /OH ⁻ | H ⁺ /Cl ⁻ |
| Cations: mol/kg(dry form) | 1.10 | 1.12 | 1.09 |
| Anions: mol/kg(dry form) | 0.17 | 0.20 | 0.18 |
| Water content (wt %) | 21.7 | 25 | 24.1 |
| Thickness (cm) | | 0.0245 | |
| Working area (cm ²) | | 3.85 | |
| Feed Solutions for Single-acid Permeation | | | |
| Acid | Chemical Composition | K_{diss} | Concentration (mol dm ⁻³) |
| AA | CH ₃ COOH | 1.75×10^{-5} | 0.05–1 |
| PA | CH ₃ CH ₂ COOH | 1.33×10^{-5} | 0.05–1 |
| LA | CH ₃ CHOHCOOH | 1.38×10^{-4} | 0.05–1 |
| OA | (COOH) ₂ | 6.50×10^{-2} | 0.05–1 |
| TA | (CHOH) ₂ (COOH) ₂ | 9.21×10^{-4} | 0.05–1 |
| CA | (CH ₂) ₂ COH(COOH) ₃ | 8.60×10^{-4} | 0.05–1 |
| Binary Feed Solutions for AA and PA Permeation | | | |
| Acid | Composition | | Concentration (mol dm ⁻³) |
| AA + PA | Equimolar solutions | | 0.05–0.8 |
| AA + PA | Mol fraction in the range 0.1–0.9 | | 0.45–0.55 |

^a Calculated in relation to the overall mass of a membrane sample.

dard characteristics of the BP-1 membrane, including its ion-exchange capacity and swelling measured in our laboratory, is given in Table I. The ion-exchange capacity of the BP-1 membrane was determined in the following way: The membrane sample (200 mg) was placed in a 0.5M NaCl solution for equilibrating. After several changes of the equilibrating solution, the membrane was carefully rinsed with distilled water to remove free electrolytes from the membrane phase. After being blotted with a hard filter paper, its thickness and weight in the swollen state were measured. The sample was then reequilibrated with a 1M HCl solution and rinsed with water to obtain the H⁺/Cl⁻ ionic form. In parallel, the second sample was prepared in the Na⁺/OH⁻ form using a NaOH solution. Thereafter, each sample was placed in a 1M sodium chloride solution (50 mL)

to exchange ions as H⁺/Na⁺ and OH⁻/Cl⁻, for the cation- and anion-exchange layers, respectively. The concentration of the removed H⁺ or OH⁻ ions was then determined by a standard potentiometric titration. The respective ion-exchange capacity was calculated using eq. (1):

$$E_c = CV/m \quad (1)$$

C (mol dm⁻³), V (dm³), and m (kg) denote the concentration of a titrant, its volume, and the mass of a membrane sample in its swollen (m_{sw}) or dried (m_{dry}) state, respectively. The ion-exchange capacity E_c refers to the overall mass of the membrane sample and does not characterize the property of the specific ion-exchange layer separately. The content of water in the BP-1

membrane was determined from the mass difference of a swollen and dried (380 K) membrane sample:

$$W = 100 \times (m_{\text{sw}} - m_{\text{dry}})/m_{\text{sw}} \quad (\%) \quad (2)$$

From the data presented in Table I, it can be seen that the content of the cation-exchange groups is about sixfold higher than that of the anion-exchange groups. Assuming that the density of the respective polymers is similar, one can conclude that the anion-exchange (basic) layer is much thinner than is the cation-exchange (acidic) layer.

Feed solutions for the membrane system are characterized in Table I. Aqueous solutions of carboxylic acids were prepared using reagent-grade chemicals. The dissociation constants of carboxylic acids and the initial concentrations in a feed are listed in Table I. To relate the experimental results to practical applications, the upper feed concentration (1M) was assumed as the mean value from the acid concentration in a real fermentation broth ($\sim 0.3M$, ref. 19) and the final acid concentration after the process of electrodiagnosis (~ 1.75 , ref. 26).

Permeation Experiments

Permeation experiments were carried out by using a transport cell (diaphragm-type cell) and the equipment was described in detail elsewhere.^{19,20} The transport cell was composed of two chambers separated by the BP-1 membrane. The feed chamber and an external reservoir contained a feed solution (250 cm³) which was circulated in the system by a peristaltic pump and PVC tubing. Another chamber (receiving chamber) contained a stripping solution (85 cm³), that is, distilled water (3 $\mu\text{S cm}^{-1}$) at zero-time or a diluted solution of the acid at $t > 0$. This solution was intensively agitated (500 rpm) by a magnetic bar. The transport cell and solutions were thermostated at 298 K.

The permeation of acids was investigated mainly by contacting a feed (f) solution with the cation-exchange (CE) layer of the BP-1 membrane, according to its position in an electrodiagnosis. In parallel, a series of experiments was made in the reversed system, that is, with a feed solution contacted with the BP-1 anion-exchange (AE) layer. Both experimental arrangements are, henceforth, marked as the (f)CE|AE(s) and (f)AE|CE(s) systems. Before the experiments, the membrane was equilibrated with a respective

feed solution. Primary experimental data resulting from the above experiments are time-dependent concentrations in the stripping solution. Fluxes of acids as dependent on the initial feed concentration were determined according to the method described in our previous articles.^{19,20} Each time, a quasi-stationary flux was calculated from the cumulative function Q versus t , examples of which are presented in the next sections. According to eq. (3), the flux J (mol cm⁻² s⁻¹) denotes the number of moles of the acid transported to the strip solution by 1 cm² of the membrane area per time unit. This quantity was calculated as the slope of the linear part of the Q versus t plot by applying a linear regression analysis:

$$Q = J \times t + \text{const} \quad (\text{mol cm}^{-2}) \quad (3)$$

All the experiments were carried out under quasi-stationary conditions, that is, the feed acid concentration was changed in the time of transport by 5–7% only. Thus, the starting and final pH of the feed were comparable and differed by ~ 0.02 of the pH unit. Any additional buffering of the feed was not applied in order to avoid possible changes in the membrane composition and properties. Because pure acid solutions of nearly constant concentrations were used, the feed pH can be immediately evaluated from the acid concentration and its pK. Consequently, the concentration dependence of the respective fluxes can be also interpreted as the dependence on the feed pH. High values of a linear correlation coefficient (r) for Q versus t dependence were assumed as the criterion for quasi-stationary transport conditions. In practice, when dealing with the system of a large volume of the feed solution, the quasi-stationary transport process can be reached after a short transient state. Obviously, to minimize the influence of an increased concentration of the strip solution ($t \geq 0$) on fluxes, the transport time was limited to about 10 h. The concentration of the strip solution was monitored in time by conductometric (single-acid solutions) or isotachophoretic (binary PA/AA solutions) measurements.

RESULTS AND DISCUSSION

Membrane fluxes (rates of permeation or rates of membrane extraction) characterize the transport efficiency of any membrane-transport system.

These quantities depend on both the composition and structure of a membrane (porous, nonporous, dense, etc.), on its nature (ionic, nonionic, reactive, etc.), and on the concentration of a penetrant. Considering the concentration dependence of membrane transport, two basic mechanisms for dense functionalized polymer membranes were recognized, that is, solution–diffusion and reaction–diffusion mechanisms. According to I-Fick's law for diffusion, a proportional increase of a flux with an increased concentration difference $\Delta C_m = C_{f,m} - C_{s,m}$, indicates a solution–diffusion sequence as the most probable transport mechanism. Note that the membrane concentrations $C_{i,m}$ ($i = \text{feed}$] or strip]) are related to the concentration of the external feed and strip solutions by their respective equilibrium distribution coefficients. In the case of nonionic substances, these coefficients are almost independent of the concentration; thus, the fluxes can be regarded as roughly proportional to the difference in concentration of the external solution constituting the phenomenological driving force for solution–diffusion processes.

Some discrepancies in the ideal flux-concentration dependence could be observed if the diffusion coefficients are strongly dependent on the concentration of a penetrant or if a membrane structure changes in contact with a concentrated feed solution because of membrane deswelling or other physicochemical phenomena. A quite different relationship between J and ΔC (or C_f when $C_f \gg C_s$) can be observed for some transports occurring according to a reaction–diffusion mechanism. In this case, the fluxes are hyperbolically dependent on the concentration of the feed solution and exhibit zero-order kinetics for high C_f values (flux saturation effect). Both types of transport were reported for a number of polymer membranes and also in the case of the systems with carboxylic acids.²⁰ In our studies on the permeation of carboxylic acids through the polymer ion-exchange membranes, it was found that solution–diffusion and reaction–diffusion mechanisms predominate in the CEMs and AEMs, respectively. Thus, the question concerning the kind of mechanism prevailing in BPMs seems to be crucial for interpreting their transport properties. To evaluate the characteristic linear dependence of J on C_f (solution–diffusion) or $1/J$ on $1/C_f$ (reaction–diffusion), the contribution of linear effects for each of the dependencies was calculated by using the squared correlation coefficient (r^2):

$$LC = 100 \times r^2, \% \quad (4)$$

LC determines the percent of linear effects in the experimental results according to the assumed linear regression function:

$$Y = a + bX \quad (5)$$

In eq. (5), $Y \equiv J$ or $1/J$ and $X \equiv C_f$ or $1/C_f$, respectively.

Transport from Single-component Solutions

Permeation in the System (f)CE/AE(s)

Typical curves illustrating the kinetics of transport through the Neosepta BP-1 membrane in the (f)CE|AE(s) system are presented in Figure 2(a–c). The results are presented as Q versus t plots, whose slopes are equivalent to the respective fluxes expressed in $\text{mol cm}^{-2} \text{h}^{-1}$. The curves in Figure 2 correspond to the transport of acetic acid (AA), citric acid (CA), and oxalic acid (OA), which represent typical but quantitatively differentiated results. Qualitatively analogous curves were observed for propionic acid (PA), lactic acid (LA), and tartaric acid (TA), meaning that after a short transient period the fluxes reached their quasi-stationary constant values represented by a linear relationship between Q and t . Some different results [see Fig. 2(c)] were obtained for CA. This acid is transported through the BP-1 membrane with a longer transient state and the slopes (fluxes) of the respective plots are significantly lower, which indicates slower transport. In the case of OA [see Fig. 2(b)], the linearity between Q and t was observed only for feed concentrations lower than $0.5M$. Above this concentration, the membrane lost its mechanical stability and the respective transport curves became irregular.

The experimental transport profiles allowed the calculation of fluxes using eq. (3). The values of calculated fluxes are drawn as a function of feed concentration in Figure (3). It can be noticed from the presented results that according to I-Fick's law for diffusion all the acids show a linear correlation between J and C_f . Moreover, the experimental data do not fulfill the reaction–diffusion model as represented by the respective hyperbolic eq. (5).

Permeation in the System (f)AE/CE(s)

Typical results for permeation of AA and TA are presented in Figure 4(a,b), respectively. The per-

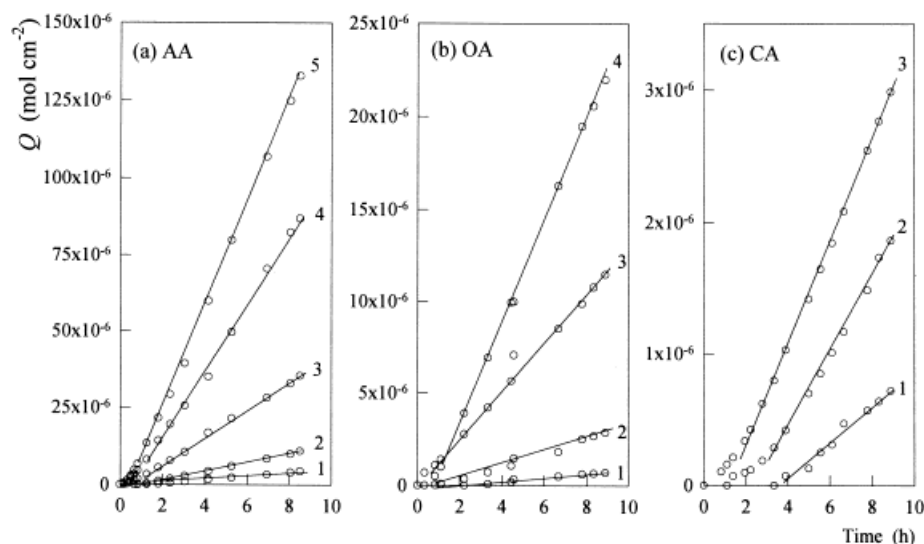


Figure 2 Representative transport curves for the BP-1 BPM with the cation-exchange layer in contact with (a) AA of the feed concentration of (1) 0.05, (2) 0.10, (3) 0.26, (4) 0.52, and (5) 0.82 mol dm⁻³; (b) OA of the feed concentration of (1) 0.05, (2) 0.10, (3) 0.25, and (4) 0.5 mol dm⁻³; (c) CA of the feed concentration of (1) 0.025, (2) 0.5, or (3) 1.0 mol dm⁻³.

meation profiles for PA, LA, and OA are similar to those presented in Figure 4. As before, CA was transported very slowly. Calculated values of quasi-stationary fluxes are drawn versus the feed

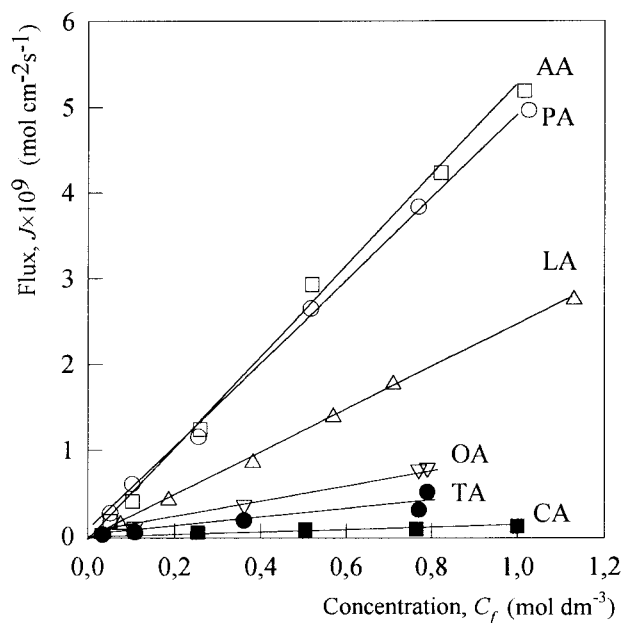


Figure 3 Flux versus feed-concentration dependence for the BP-1 BPM with the cation-exchange layer in contact with (□) AA (○) PA, (Δ) LA, (▽) OA, (●) TA, and (■) CA.

concentration in Figure 5. The comparison of plots in Figures 3 and 5 leads to the conclusion that, except for AA and PA, the fluxes found in the membrane systems (f)CE | AE(s) and (f)AE | CE(s) are similar with a tendency to achieve slightly higher values for the first configuration. It is noteworthy that in the case of monopolar membranes the transport of carboxylic acids through acidic

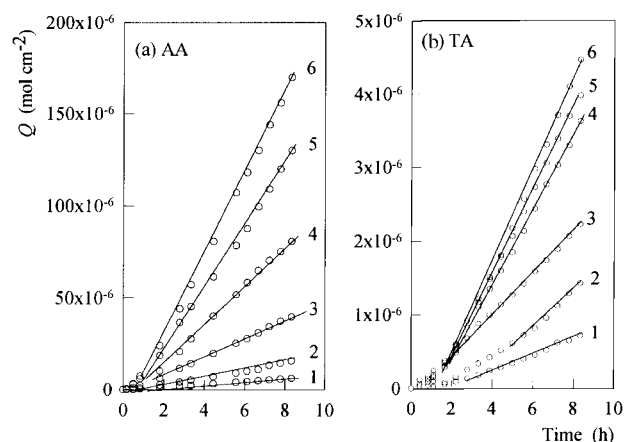


Figure 4 Representative transport curves for the BP-1 BPM with the anion-exchange layer in contact with (a) AA of the feed concentration (1) 0.05, (2) 0.10, (3) 0.26, (4) 0.52, (5) 0.82, and (6) 1.02 mol dm⁻³, and (b) TA of the feed concentration of (1) 0.05, (2) 0.10, (3) 0.25, (4) 0.51, (5) 0.75, and (6) 1.0 mol dm⁻³.

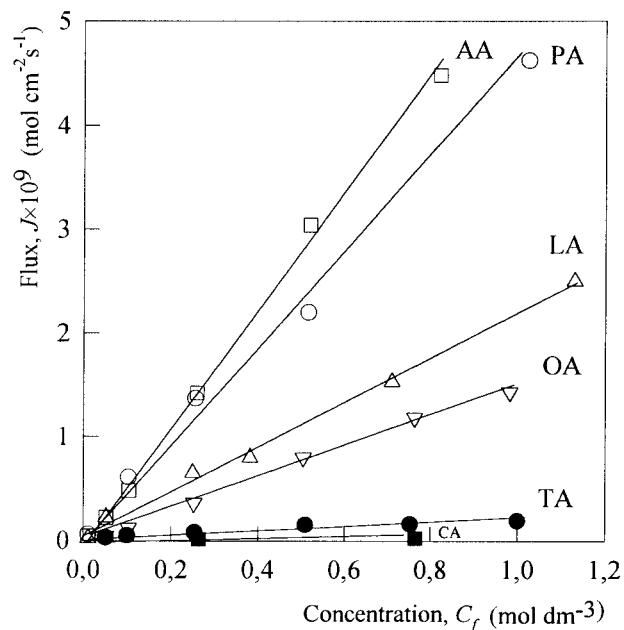


Figure 5 Flux versus feed-concentration dependence for BP-1 BPM with the anion-exchange layer in contact with (□) AA, (○) PA, (Δ) LA, (∇) OA, (●) TA, and (■) CA.

membranes is usually slower than through strongly basic membranes (see Fig. 11).

Comparison of Mass-transfer Coefficients for (f)CE|AE(s) and (f)AE|CE(s) Systems

The plots in Figures 3 and 5 indicate that, independently of the system configuration, the dependence J on C_f is almost linear. The coefficients LC calculated with eq. (5) range in the limits from 95.2 to 99.9 (see Table II, nos. 1–6). These results allow one to conclude that the nonlinear effects introduced by a reaction–diffusion process occurring in the anion-exchange layer, and probably disturbing a pure solution–diffusion mechanism, are small and unimportant for the phenomenology of the studied transport systems. Consequently, the average mass-transfer coefficients are easy to calculate from eq. (6):

$$J_{\text{lin}} = k\Delta C \quad (\text{mol cm}^{-2} \text{ s}^{-1}) \quad (6)$$

In eq. (6), k (cm s^{-1}) denotes the overall mass-transfer coefficient which can be related to the

Table II Mass-transfer Coefficients (k), Percent of Linear Effects (LC), and Selectivity ($\alpha_{\text{PA}}^{\text{AA}}$) for AA–PA Separation

| No. | Transported Substance | Transport System | | | | | |
|------------------------|---|--------------------------------|----------|----------------------------------|---------------------------------|----------|----------------------------------|
| | | (f)CE AE(s) | | | (f)AE CE(s) | | |
| | | k (cm s^{-1}) | LC (%) | $\alpha_{\text{PA}}^{\text{AA}}$ | k (cm s^{-1}) | LC (%) | $\alpha_{\text{PA}}^{\text{AA}}$ |
| Single-acid Permeation | | | | | | | |
| 1 | PA | $4.88 \pm 0.27 \times 10^{-6}$ | 99.4 | 1.08 ± 0.10 | $4.37 \pm 0.18 \times 10^{-6}$ | 99.5 | 1.32 ± 0.10 |
| 2 | AA | $5.28 \pm 0.17 \times 10^{-6}$ | 99.6 | | $5.81 \pm 0.13 \times 10^{-6}$ | 99.7 | |
| 3 | LA | $2.50 \pm 0.04 \times 10^{-6}$ | 99.9 | | $2.148 \pm 0.07 \times 10^{-6}$ | 99.6 | |
| 4 | CA | $8.70 \pm 1.40 \times 10^{-8}$ | 95.2 | | $3.02 \pm 1.007 \times 10^{-8}$ | 99.8 | |
| 5 | TA | $6.42 \pm 0.31 \times 10^{-7}$ | 99.1 | | $1.76 \pm 0.22 \times 10^{-7}$ | 98.8 | |
| 6 | OA | $1.66 \pm 0.02 \times 10^{-6}$ | 99.9 | | $1.53 \pm 0.05 \times 10^{-6}$ | 99.6 | |
| Binary Feed Solutions | | | | | | | |
| 7 | PA | $2.77 \pm 0.38 \times 10^{-6}$ | 96.3 | 1.28 ± 0.21 | $1.32 \pm 0.23 \times 10^{-6}$ | 89.3 | 1.55 ± 0.30 |
| | AA (equimolar mixtures) | $3.56 \pm 0.03 \times 10^{-6}$ | 99.9 | | $2.05 \pm 0.28 \times 10^{-6}$ | 93.1 | |
| 8 | PA | $1.27 \pm 0.08 \times 10^{-6}$ | 98.6 | 1.50 ± 0.20 | $1.61 \pm 0.15 \times 10^{-6}$ | 96.8 | 2.11 ± 0.60 |
| | AA (different molar fractions at total concentration $\sim 0.5 \text{ mol dm}^{-3}$) | $1.91 \pm 0.11 \times 10^{-6}$ | 98.6 | | $3.40 \pm 0.60 \times 10^{-6}$ | 90.6 | |

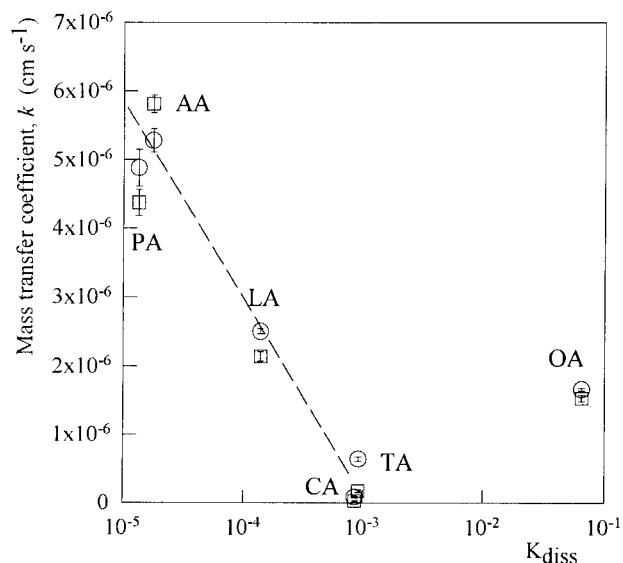


Figure 6 correlation between the mass-transfer coefficient (k) and the first dissociation constant (K_{diss}) for the system with (\circ) cation and (\square) anion-exchange layer in contact with a feed solution.

diffusion coefficient D ($\text{cm}^2 \text{s}^{-1}$), distribution coefficient K_d , and the membrane thickness, l (cm):

$$k = DK_d/l \quad (\text{cm s}^{-1}) \quad (7)$$

Under quasi-stationary conditions, with a fulfilled relation $C_f > C_s$, one can assume that $\Delta C \approx C_f$ and, thereafter,

$$J_{lin} = kC_f \quad (\text{mol cm}^{-2} \text{s}^{-1}) \quad (8)$$

According to eq. (8), the k coefficient, corresponding to the linear part of the curve J versus C_f , can be evaluated from the slope of plots presented in Figures 3 and 5:

$$k \approx 1000 \Delta J_{lin} / \Delta C_f \quad (\text{cm s}^{-1}) \quad (9)$$

Calculated k coefficients are collected in Table II. Their values are dependent on the type of acid and leads to the following sequence:

$$k_{AA} \geq k_{PA} > k_{LA} > k_{OA} > k_{TA} > k_{CA} \quad (10)$$

Further, this order can be roughly correlated with first dissociation constants. The plot presented in Figure 6 shows that this correlation is evident except for OA, the experimental data of which differ significantly from the others. There are two

reasons for this scattering: One of them is common for all acids because of some differences in their diffusion coefficients. The second reason is characteristic for OA which strongly influences the physical state of this membrane. It was observed that this acid made the membrane swollen and plasticized and, thus, more permeable. Moreover, the BPM reveals some “cameleon” properties, that is, in the case of very differentiated carboxylic acids, it exhibits the J versus K_{diss} dependence typical for the strongly acidic membrane, except for PA and AA. In this case, the membrane behaves as a strongly basic membrane. The higher affinity of the anion-exchange layer to AA and higher AA diffusion coefficients change the expected position of PA and AA in the order (10) (see Fig. 6). The strongly basic membrane Neosepta AFN-7, when compared with the BP-1, exhibits the reversed order of the J versus K_{diss} correlation for the same acids.²⁰ In general, the results found for the BPM show that the influence of the anion-exchange layer is visible but not critical for the properties of the membrane in the transport of carboxylic acids. When the feed solution is in contact with the strongly acidic layer, the degree of dissociation of acids must be diminished at the interface and the acid invades this part of the BP-1 as a neutral molecule. Thus, the weaker the acid, the easier permeation through the membrane. The remaining dissociated species are excluded from the membrane phase due to the Donnan-exclusion phenomena typical for ion-exchange resins and dilute solutions of electrolytes. These effects are visible for relatively stronger electrolytes like CA and OA. The sorption of carboxylic acids should be higher when the feed solution is contacted with the basic layer. Consequently, this should create optimum boundary conditions for the further permeation of carboxylic acid through an acidic polymer layer. Sometimes, this prediction was proved only for AA permeation (see Table II, nos. 2 and 8). Thus, the influence of the bipolar nature of the membrane studied cannot be neglected, and in some circumstances; it should be taken into account despite the fact that overall effects are rather typical for CEMs, for the BP-1 at least.

Competitive Permeation of PA and AA

The results of competitive experiments can verify the conclusions drawn from single-acid permeations as far as they concern the BP-1's ability for the separation of PA and AA. For this purpose,

the separation coefficients were calculated as the ratio of respective mass-transfer coefficients:

$$\alpha_{PA}^{AA} = \frac{\Delta J_{lin,AA} \Delta C_{PA}}{\Delta J_{lin,PA} \Delta C_{AA}} \approx \frac{\Delta J_{lin,AA} C_{f,PA}}{\Delta J_{lin,PA} C_{f,AA}} = \frac{k_{AA}}{k_{PA}} \quad (11)$$

The α_{PA}^{AA} values predicted from single-acid permeation data are 1.08 ± 0.1 and 1.32 ± 0.1 for the (f)CE|AE(s) and (f)AE|CE(s) systems, respectively. Thus, the preferential transport of AA in the presence of PA can be expected. Some typical transport curves illustrating Q versus t dependencies found for both configurations are presented in Figure 7(a,b). The presented curves correspond with the feeds containing the same content of PA and AA (molar ratio approximately 1) and the concentrations 0.1 or 0.8 mol dm⁻³. Other results fall between these curves. Without any exception, all curves are linear and allow the calculation of fluxes which are drawn in Figure 8 versus the concentration of the feed solution. The plots for the system (f)CE|AE(s) [see Fig. 8(○,□)]

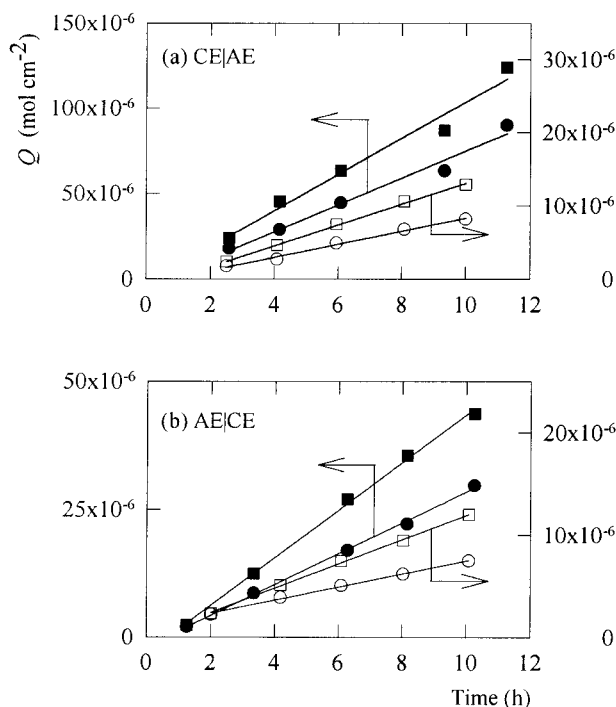


Figure 7 Competitive transport curves for the BP-1 BPM with the (a) AA cation-exchange (b) or anion-exchange layer in contact with a mixture of (■,□) AA and (●,○) PA of concentration (a) AA: (□) 0.14 and (■) 0.86 mol dm⁻³, PA: (○) 0.12 and (●) 0.81 mol dm⁻³, and (b) AA: (□) 0.15 and (●) 0.81 mol dm⁻³, PA: (○) 0.14 and (●) 0.85 mol dm⁻³.

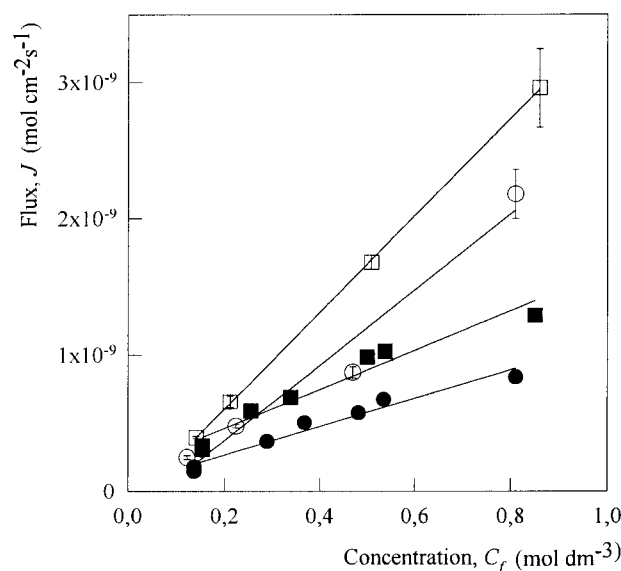


Figure 8 Flux versus feed concentration dependence for the BP-1 BPM in contact with a 1:1 mixture of (■,□) AA and (●,○) PA: (□,○) cation- or (■,●) anion-exchange layer in contact with a feed solution.

show a good linear relationship between J and C_f according to the solution-diffusion model. Thus, the k coefficients can be calculated from these plots. They are 2.8 ± 0.4 and 3.56 ± 0.03 cm s⁻¹ for PA and AA, respectively, and the selectivity for the AA transport (α_{PA}^{AA}), as calculated from the ratio of these values, is 1.28. This value is a bit higher than that predicted from single-acid permeations, that is, 1.08. The results corresponding to the (f)AE|CE(s) [see Fig. 8(●,■)] show some deviation from linearity in the case of concentrated solutions as well as rather strong scattering of data around the regression line. However, for the concentration range from 0.1 to 0.5 mol dm⁻³, this relationship can be treated as linear, and respective mass-transfer coefficients can be evaluated. The values for PA and AA are 1.27 ± 0.08 and 1.9 ± 0.1 cm s⁻¹, respectively. Thus, the selectivity coefficient is 1.69. This value is also higher than is the value of 1.32 expected from the permeation of single acids. One can remark that in the case of PA and AA the fluxes and permeability coefficients are always lower when the anion-exchange side is in contact with the feed.

Obviously, the fluxes are dependent on the concentration of the permeating species in the feed. Thus, the additional experiments with feeds of total concentration 0.5 mol dm⁻³ and different molar fractions (0.1–0.9) of the PA or AA were made. The results showing fractional flux depen-

dence versus the molar fraction of the AA in the mixture are presented in Figure 9. The curve for AA exhibits a characteristic upward curvature, which determines the separation ability of the BP-1 membrane. To evaluate the reason for this selectivity, some theoretical values of the AA fractional flux (FF_{AA}) were calculated using a simple equation derived from solution-diffusion model:

$$FF_{AA} = \frac{D_{AA,aq}k_{d,AA}C_{f,AA}}{D_{AA,aq}k_{d,AA}C_{f,AA} + D_{PA,aq}k_{d,PA}C_{f,PA}} \quad (12)$$

In eq. (12), $D_{acid,aq}$ denotes the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) of AA³⁸⁻⁴¹ or PA⁴² in aqueous media; $C_{acid,f}$, the concentration of the feed solution; and $k_{d,acid}$, the respective distribution coefficient. To evaluate the diffusional (dialytic) contribution into the separation effect, theoretical calculations were made under assumption that $k_{d,AA} = k_{d,PA}$. The resulting curve is drawn in Figure 9 as a dashed line. In comparing calculated fluxes with the experimental ones, it can be concluded that the experimentally observed preference of the BPM toward AA is much higher than that appearing from differences in the AA and PA diffusion coefficients. This can be ascribed to the presence of the anion-exchange layer giving some additional preference in the sorption of AA when compared to PA ($k_{d,AA} > k_{d,PA}$). On the

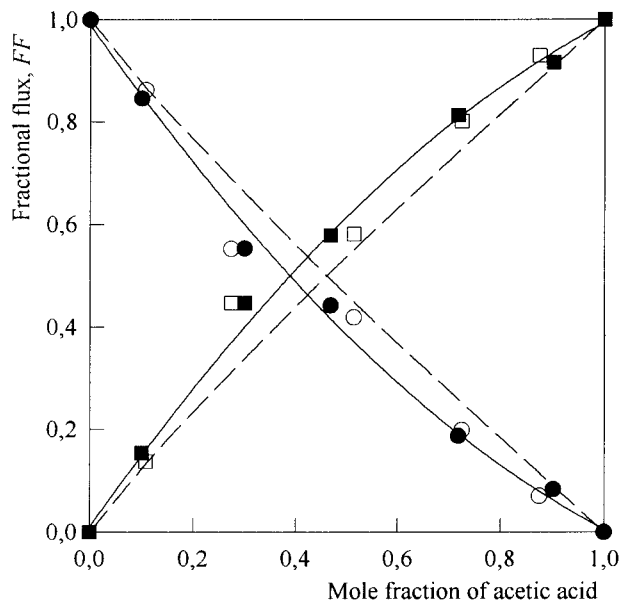


Figure 9 Fractional fluxes versus mol fraction of (■, □) AA and (●, ○) PA: (□, ○) cation- or (■, ●) anion-exchange layer in contact with a feed solution. Dashed lines calculated with eq. (12).

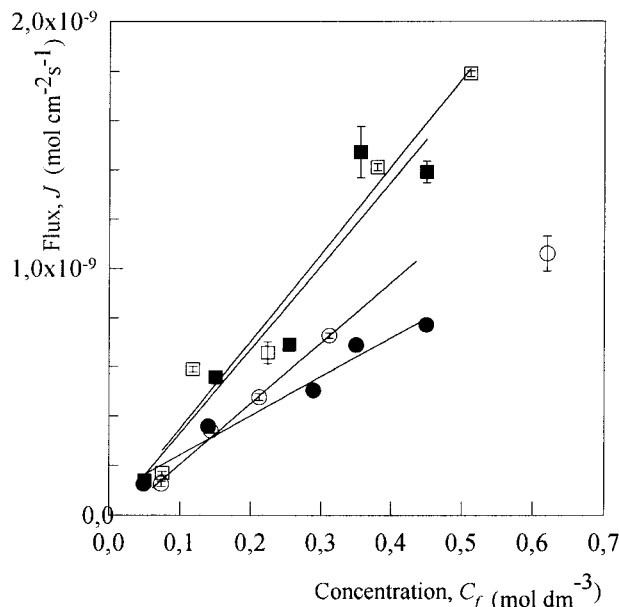


Figure 10 Flux versus feed concentration dependence for the BP-1 BPM in contact with different mixtures of (■, □) AA and (●, ○) PA: (□, ○) cation- or (■, ●) anion-exchange layer in contact with a feed solution.

other hand, the fluxes, if plotted versus the feed concentration, exhibit the linear relationships presented in Figure 10. This enabled us to calculate the respective mass-transfer and selectivity coefficients given in Table II. As expected from Figure 9, these results prove the preferential transport of AA in both studied systems. As in previous experiments, the system (f) AE|CE(s) is characterized by $k_{AA} > k_{PA}$, which can be ascribed to more exposed influence of the strongly basic layer.

In general, each selectivity calculated from the real competitive transport data differs from that predicted from the single-component permeation. It should be noted here that these quantities can be equal only exceptionally, that is, in the case when the fluxes are noncoupled and the permeation of two acids occurs as two independent and parallel processes. In the case of competition of the substrates to the transport mediating centers (e.g., basic groups in the anion-exchange part of the BP-1), the observed and predicted values are usually different. This difference is frequently observed experimentally in the case of carrier-mediated transports⁴³ and can also be predicted from detailed theoretical considerations.⁴⁴ Moreover, the competitive permeation of carboxylic acids through the polymer membranes seems even more complicated due to the possible acid-acid

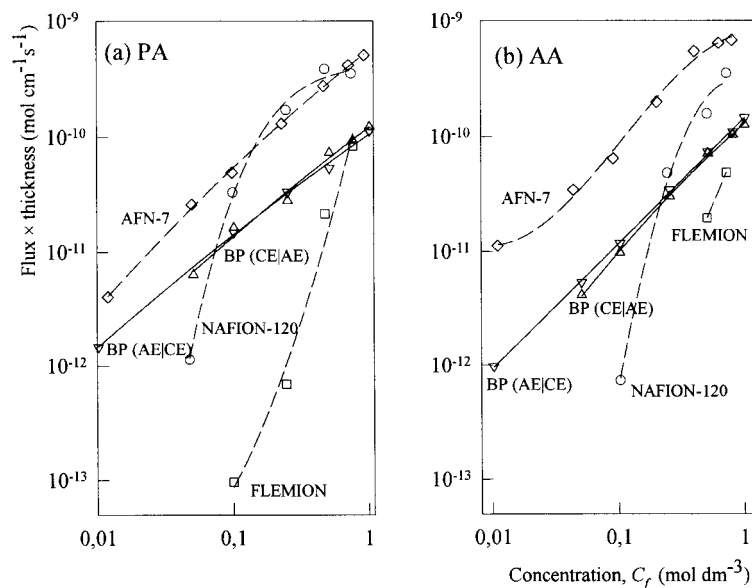


Figure 11 Normalized fluxes versus feed concentration dependence for (a) PA and (b) AA permeation through different membranes: (\diamond) strongly basic AFN-7 membrane; (\circ) strongly acidic Nafion-120 membrane; (\square) weakly acidic Flemion membrane; BP-1 BPM with (Δ) cation- or (∇) anion-exchange layer in contact with a feed solution.

interactions. It was shown by other authors⁴⁵ that the retention of one of the carboxylic acids in the feed is dependent (in various ways) on the presence of the other acid in a mixture.

Comparison of Transport Properties of CEMs, AEMs, and BPMs

It is interesting how much the transport properties of the BPM are different from other ion-exchange membranes. According to our previous studies, a comparison was made for the following membranes transporting PA and AA:

- (i) Bipolar Neosepta, BP-1 membrane (Tokuyama Corp., Japan) with strongly basic and strongly acidic functional groups,
- (ii) Strongly acidic, perfluorosulfonic acid, Nafion-120 membrane (DuPont),¹⁹
- (iii) Weakly acidic, perfluorocarboxylic acid, Flemion membrane (Asahi Glass),²⁰ and
- (iv) Strongly basic Neosepta, AFN-7 membrane (Tokuyama Corp.).²⁰

The curves illustrating the dependence of PA and AA fluxes on the concentration of the feed solution are presented in Figure 11(a,b), respectively. To obtain comparable data, the fluxes were normalized to the product $J \times l$, that is, by mul-

tipling the flux and the membrane thickness. The comparison presented in Figure 11 shows that the fluxes measured with the use of the BP-1 membranes are lower than are those observed for strongly basic and strongly acidic membranes when the feed acid concentration is higher than 0.1–0.2 mol dm⁻³. This property is very favorable from the point of view of the practical electrodialytic application described above. In the case of dilute acid solutions, the Neosepta BP-1 membrane shows average transport properties as compared to those observed for the CEM and AEM studied elsewhere.

The results reflect the differences among monopolar CEMs, AEMs, and BPMs, which were pointed out in the Introduction. As compared to these membranes, the ideal BPM should not transport at all because of the ionic Donnan exclusion of co-ions in the respective layer. However, in the case of weak electrolytes, a free diffusion of undissociated acids through the CEM and a kind of the fixed-carrier-mediated transport in the AEM layer is allowed. Some other differences can appear as a result of the differences in the swelling of membrane-forming polymers. This property determines the tortuosity factor for acid diffusion, especially in this part of the membrane-transport mechanism, which is dominated by the solution–diffusion processes, that is, the CEM

layer. The influence of the water content in a membrane as an important factor can be estimated by comparing BP-1 with a poorly swollen Flemion (carboxylic acid groups) membrane of very low permeability. Rather complex physicochemistry of transport phenomena in BPMs⁴⁶ does not allow one to indicate one controlling factor for electrolyte permeation through BP-1. Nevertheless, the data presented in Figure 11 can be used as a comparative material for other studies or for the selection of a proper membrane material for developed membrane techniques.

CONCLUSIONS

The results concerning the permeation of carboxylic acids through the bipolar BP-1 membrane proved the interrelation between their dissociation ability and membrane fluxes. Regarding the rates of permeation of AA, PA, CA, OA, LA, and TA acid, one can postulate the following order for the increase of fluxes and permeability coefficients: $CA < OA < LA < TA < PA \leq AA$. Except for OA, this sequence can be roughly correlated to the respective dissociation constant. When comparing the properties of different ion-exchange membranes, one can conclude that this behavior is similar to that observed for strongly acidic CEMs. Thus, the prevailing solution-diffusion transport mechanism of weak carboxylic acids can be postulated for the BP-1 BPM. However, the influence of the strongly basic component of the membrane can be observed in the case of the competitive permeation of AA and PA. The selectivity coefficients defined as the ratio of the mass-transfer coefficients vary in this case from 1.3 to 2.1, depending on the feed composition and the configuration of the transport system. Regarding these values, one can conclude that the PA-AA separation ability of the BP-1 membrane is similar to that observed previously for the strongly basic membrane (Neosepta AFN-7). Thus, taking into account these observations, the values of the fluxes, mass-transfer coefficients, and some transport selectivity coefficients, one can consider the BP-1 as a "cameleon" membrane, the properties of which depend on the feed composition and transport system configuration.

The results presented in this article are practically significant in the biotechnological production of carboxylic acids. Relatively low fluxes of carboxylic acids in the BP-1 membrane as compared to conventional (monopolar) CEMs and

AEMs suggest that this membrane can be considered as useful for the electro-dialytic production of carboxylic acids from their salts.

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