

Membrane Transport of Organics. I. Sorption and Permeation of Carboxylic Acids in Perfluorosulfonic and Perfluorocarboxylic Polymer Membranes

ROMUALD WÓDZKI, JACEK NOWACZYK

Faculty of Chemistry, Nicolaus Copernicus University, Department of Physical Chemistry, Gagarin St. 7, 87–100 Toruń, Poland

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ABSTRACT: Experimental studies have been made on the sorption and permeation of propionic (PA), acetic (AA), and formic (FA) acid in perfluorosulfonic Nafion, and perfluorocarboxylic Flemion membranes. The sorption isotherms show the increase of distribution coefficients $K_d = C_m/C_e$ with the pK of acids, i.e., $K_{d,PA} > K_{d,AA} > K_{d,FA}$. The transmembrane fluxes (J) and permeabilities (P) change their values in the same order for $C_e < 0.1M$ and in the order $J_{PA} > J_{FA} > J_{AA}$ for higher concentrations. The differentiation of fluxes in single-component dialyses does not result in the effective separation of AA and PA during their competitive permeation through the Nafion-120 membrane. Under the same conditions, the Flemion membrane exhibits the preference toward propionic acid and transports PA and AA with the selectivity coefficient α_{AA}^{PA} equal to 1.5. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 355–362, 1997

Key words: polymer membranes; carboxylic acid; transport; sorption; separation

INTRODUCTION

Several studies have been made to utilize liquid and polymer membranes for the recovery and the separation of organic acids from fermentation broths.¹ The processes exploiting various polymer membrane techniques such as dialysis,^{2–5} electro dialysis,^{6–9} reverse osmosis,^{10–13} and nanofiltration^{12,13} were reported in the literature. The aim of this study is to develop the fundamentals for the permeation, recovery, and potential separation of organic acids by physically different membranes (made of polymer and liquid components) expected to work in hybrid multimembrane systems.¹⁴ This article focuses on the membranes made up of perfluorinated polymers that have been recognized to exhibit an exceptional

stability in various media and operating conditions.¹⁵ On the other hand, the use of these membranes in a diffusion dialysis or electro dialysis of some carboxylic acids needs the basic information concerning their permeability and sorption characteristics that determine the effective transmembrane fluxes. The effective operation of polymer membranes as selective diaphragms in the dialysis of carboxylic acids^{4,5} requires high diffusional fluxes, whereas the electro dialytic processes are efficient when “parasite” diffusional fluxes (driven by concentration gradients) are negligible. It can be expected from general properties of membranes made of ionic polymers that the sorption and permeation of weak acid electrolyte depend on the acid and polyacid (membrane) dissociation equilibria. To assess this interrelation experimentally, the uptake and the permeation of propionic (PA), acetic (AA), and formic (FA) acid through ion-exchange membranes with sulfonic (Nafion) and carboxylic (Flemion) functional groups are discussed in this article. The practical

Correspondence to: R. Wódzki.

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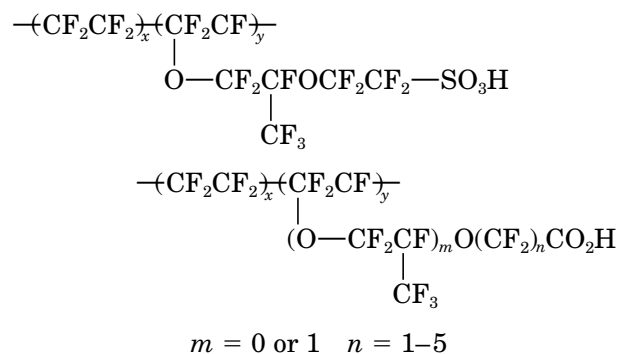
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task of these studies is related to the problem of PA recovery and separation from mixtures containing AA after the fermentation of some diary by-products.¹⁶⁻¹⁸

EXPERIMENTAL

Membranes

The perfluorosulfonic acid membrane Nafion-120 (Du Pont de Nemours, USA)¹⁹ and the perfluorocarboxylic membrane Flemion (Asahi Glass, Japan)²⁰ were used in sorption and transport experiments. The membranes are composed of a polytetrafluoroethylene backbone attached by an ether linkage to a perfluorinated side chain containing sulfonic (Nafion) or carboxylic (Flemion), acid group:



The structure of the perfluorosulfonic membrane consists of hydrophilic spherical clusters dispersed in a hydrophobic matrix of the perfluorinated polymer.²¹ Some properties of perfluorocarboxylic membranes indicate that their aqueous phase is more continuous than that of the sulfonated polymer.²² This may be represented by a more rodlike morphology for their ion-containing aqueous regions instead of spherical clusters connected by narrow channels.

The membranes were preconditioned to obtain a standard membrane material. This was made by several ion-exchanges Na^+/H^+ , and then by subsequent washing and boiling of membrane samples in deionized water for 2 h. Prior to the sorption and permeation experiments, the membranes were converted to their H^+ form by soaking in a 0.5M solution of sulfuric acid and then washed in water to remove free acid sorbed into a membrane phase. Some characteristics of the membranes found in our laboratory are listed in

Table I Properties of Nafion and Flemion Membranes

| | Nafion-120 | Flemion |
|-----------------------------------|------------------------|----------------|
| Functional group | $-\text{SO}_3\text{H}$ | $-\text{COOH}$ |
| Equivalent molecular mass | 1100 | 695 |
| Ion exchange capacity | | |
| mol H^+ /kg dry membrane | 0.85 | 1.42 |
| mol H^+ /kg swollen | | |
| membrane | 0.63 | 1.30 |
| Water content, % wt | 26.1 | 8.3 |
| Volume fraction of water in | | |
| the swollen membrane | 0.44 | 0.15 |
| Thickness in the hydrogen | | |
| form (cm) | 0.0255 | 0.0155 |

Table I. The water content was measured from the mass difference between its swollen and dried state after equilibrating the membrane with water or the acid solution. The ion-exchange capacity was determined by standard potentiometric titration.²³

Reagents

The solutions of the acids of molarity ranging from 0.001 to 0.8M were prepared using analytical grade formic acid (FA, $\text{p}K = 3.75$), acetic acid (AA, $\text{p}K = 4.75$), and propionic acid (PA, $\text{p}K = 4.87$). FA and AA were purchased from P.O.Ch. Gliwice, Poland, and PA from Ronal, Hungary.

Sorption Equilibria

The membrane sample (2.5 cm in diameter) was immersed for 24 h in 50 cm^3 of stirred acid solution. Thereafter, the membrane surface was dried with a hard filter paper, weighed, and immersed again in 30 cm^2 of deionized water for 48 h. The conductivity of the eluate had been measured until the equilibrium value was reached. The sorption and desorption cells were thermostated at $25 \pm 0.02^\circ\text{C}$. The amount of sorbed acid was then determined by using the calibration curve relating the conductivity and the concentration of standard solution. The concentration of the acid sorbed into the membrane C_m was calculated was from eq. (1):

$$C_m = C_\kappa V_e / V_m \quad (\text{mol/dm}^3 \text{ of a swollen membrane}) \quad (1)$$

where C_κ is the concentration readoff from the calibration curve, V_e is the volume of an eluate, and V_m is the volume of a membrane sample as calculated from its diameter and thickness.

Permeation Experiments

The permeation of carboxylic acids through the membranes was examined using the experimental setup, schematically presented in Figure 1. Each of the diaphragm cells was made of a Teflon tube with horizontally mounted membranes of the working area 3.85 cm^2 . The tubes were immersed in the receiving reservoirs filled with 80 cm^3 of deionized water each. The acid solution of the volume 250 cm^3 was circulated in the feed compartments by a peristaltic pump. The strip solutions were stirred at 500 rpm to minimize interfacial effects. All transport experiments were carried out at the temperature maintained at $25 \pm 0.02^\circ\text{C}$. The amount of acid transported after the time t , during single-component permeations, was calculated using eq. (2):

$$Q(t) = [(\kappa(t) - a)/b]^2 V_s / A \quad (\text{mol/cm}^2) \quad (2)$$

In eq. (2), $\kappa(t)$ denotes a conductance of the receiving solution at time t , and a and b are the parameters of the calibration curve corresponding to eq. (3):

$$\kappa = a + bC^{1/2} \quad (3)$$

V_s is the volume of receiving solution, and A is the membrane area. The flux of an acid was then calculated from the linear function $Q(t)$ vs. t , according to eq. (4):

$$Q(t) = Jt + \text{const} \quad (\text{mol/cm}^2) \quad (4)$$

where J denotes the quasi-stationary flux expressed in $\text{mol/cm}^2\text{s}$. The linearity of experimental data for eq. (4) has been checked, and J has been estimated by applying the linear regression analysis. Typically, steady-state conditions were reached after 1–2 h of the time-lag period (e.g., see Fig. 7), and lasted for over 20–30 h of the transport run. The relationship $Q(t)$ versus t has been assumed as linear, and, thus, suitable for the calculation of J , while the respective correlation coefficient was not lower than 0.99.

In the case of binary solutions containing the mixture of acetic and propionic acid, the amount

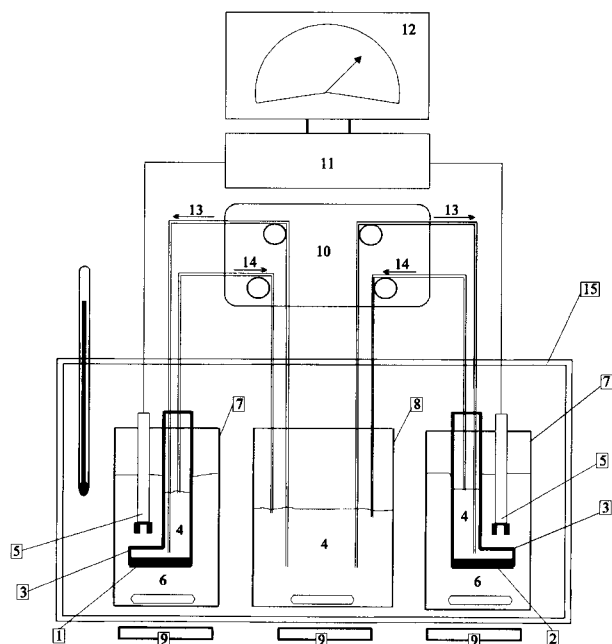


Figure 1 Scheme of experimental arrangement Nafion membrane (1), Flemion membrane (2), feed cell (3), feed acid solution (4), immersion conductivity cell (5), receiving solution (6), glass vessel (7,8), magnetic stirrer (9), peristaltic pump (10), switch (11), conductometer (12), acid input (13), acid output (14), thermostat (15).

of transported acids was determined by capillary isotachopheresis (ITP).²⁴ During the transport, the receiving solution was sampled (0.5 cm^3) and after appropriate dilution it was analyzed using a capillary electrophoretic analyser EA 100 (Labeco, Slovakia) equipped with a conductivity detector. The concentration of PA or AA was determined from a calibration curve relating the time of zone passage (through the detector) to the concentration of standard solution. The concentrations were then recalculated to $Q(t)$ and the fluxes J were estimated as the slopes of $Q(t)$ versus t dependencies.

RESULTS AND DISCUSSION

Basic Formulations

The permeation of any substance through a polymer membrane is described as a solution (sorption)-diffusion process.²⁵ The permeability coefficient (P) is then defined by the product of the effective diffusion coefficient (D_m) and the solubil-

ity constant represented by the distribution coefficient K_d :

$$P = D_m K_d \quad (\text{cm}^2 \text{ s}^{-1}) \quad (5)$$

and

$$K_d = C_m / C_e \quad (6)$$

where C_m and C_e denote the solute concentration within the membrane and in the external solution, respectively.

Some changes are introduced into the K_d formulation in the case of ion-exchange membranes composed of solid polyelectrolytes. These membranes, in contact with an electrolyte solution, reject ions of the same charge as the charge of fixed ionogenic groups. Consequently, using the Glueckauf equation describing the sorption of electrolyte in nonideal membranes,^{26,27} the distribution coefficient can be expressed by eq. (7):

$$K_d = k_G C_e^{1-Z} \quad (7)$$

where Z is the nonuniformity parameter ranging from 0 to 1 and k_G constant dependent on Z and the concentration of fixed ionogenic groups. According to eq. (7) the distribution coefficient for ionic species is concentration dependent and increases with the increase of the concentration of equilibrating solution. Additionally, the sorption of weak electrolytes becomes dependent both on their pK and the pK of membrane ionogenic groups. Thus, the membrane equilibrated with a solution of carboxylic acid can absorb considerable amounts of the acid in its dissociated and/or undissociated forms.

The separation of different solutes permeating a membrane can be expected when interrelations between the membrane and solute properties cause differentiation of fluxes. The overall separation effect is quantified by the selectivity coefficient a_B^A showing the extent of preferential transport of A species relative to B:

$$a_B^A = \frac{J_A C_{B,f}}{J_B C_{A,f}} \quad (8)$$

The criterion of separation is $a_B^A > 1$, which indicates the content of A in the strip solution (s) more favorable than that in the feed (f).

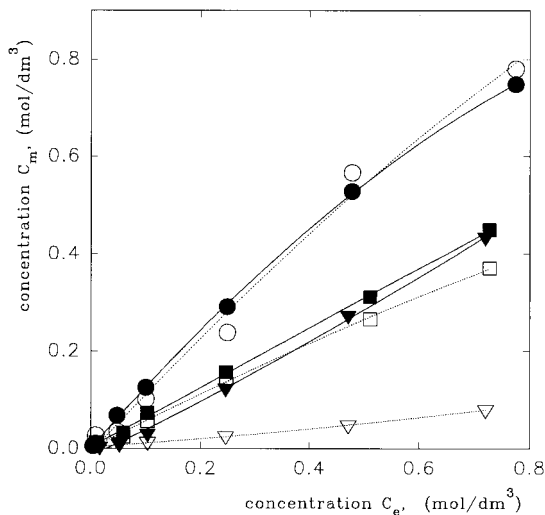


Figure 2 Sorption of acids into Nafion and Flemion membrane: propionic acid–Nafion (●), Flemion (○), acetic acid–Nafion (■), Flemion (□), formic acid–Nafion (▼), Flemion (▽).

Sorption of Carboxylic Acids

The sorption isotherms $C_m = f(C_e)$ for PA, AA, and FA are presented in Figure 2. The curves show the quantitative differences that suggest the simple relationship between distribution coefficients (see Fig. 3) and pK of sorbed acid. The values of distribution coefficients increase in homologous order $K_{d,FA} < K_{d,AA} < K_{d,PA}$, consistent with the increase of pK values. Some observed sorption phenomena are easy to explain after taking into account very high acidity and concentration of ionogenic groups (2–3M) in the internal solution of the Nafion membrane. It means that at the membrane/solution interface, carboxylic acids become undissociated and their sorption occurs as the sorption of nonionic substances, i.e., without the exclusion effects predicted by Donnan equilibria. In fact, the isotherms of PA and AA sorption into the Nafion and Flemion membranes are weakly dependent on the feed concentration and exhibit the shape observed previously for the sorption of nonionic substances by ion-exchange resins.²⁸ The amount of sorbed PA or AA into Nafion and Flemion is comparable, i.e., it does not depend on the membrane ionogenic groups and the membrane hydration. This indicates that PA and AA are partly sorbed by the perfluorinated polymer backbone. Qualitatively different results were found only for formic acid and the Nafion membrane upon which $K_{d,FA}$ depends on concentration, as predicted by eq. (7) for electrolytes.

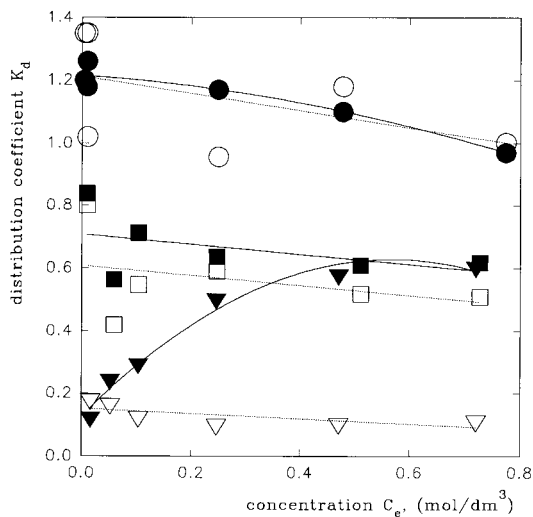


Figure 3 Distribution coefficients K_d vs. the acid concentration (C_e): propionic acid–Nafion (●), Flemion (○), acetic acid–Nafion (■), Flemion (□), formic acid–Nafion (▼), Flemion (▽).

Similar sorption phenomena have been reported by Pellegrino et al.,²⁹ who concluded that propanol and ethanol can incorporate into the fluorocarbon phase of the Nafion membrane. On the other hand, Uragami et al.³⁰ reported high distribution coefficients for PA, AA, and FA and poly(vinyl chloride)-based membranes with the same order as reported herein.

Permeation of Acids from Single-Component Solutions

The transport ability of any membrane is characterized by the relationship between the flux and the concentration of an external solution. Apart from its practical usefulness, the dependence of J on C_e allows conclusion about the possible transport mechanism. The fluxes increasing proportionally with the increase of the concentration C_e indicate the simple diffusional mechanism of the permeation according to the I-Fick law for diffusion:

$$J = P\Delta C_e \quad (\text{mol}/\text{cm}^2 \text{ s}) \quad (9)$$

If diffusing species strongly interact with ion-exchange sites or other membrane components, the relation $J(C_e)$ versus C_e is expressed by the following hyperbolic function:

$$J = J_{\text{lim}} C_e / (k_m + C_e) \quad (10)$$

where J_{lim} is the saturation flux, and k_m is a characteristic constant. According to eq. (10) the effect of flux saturation can be proved by plotting $1/J$ against $1/C_e$. This procedure yields a straight line with the slope k_m/J_{lim} and an intercept equal to $1/J_{\text{lim}}$.

The stationary fluxes of PA, AA, and FA through the Nafion and Flemion membrane are drawn in Figure 4 versus feed concentration. The presented plots show that all fluxes increase without the tendency to the saturation in the studied range of concentrations. Moreover, it is easy to verify that there is no linear dependence between $1/J$ and $1/C_e$, also for acetic acid, which was suggested elsewhere by Sikdar⁵ to obey eq. (10). This implies rather prevailing simple diffusional transport mechanism despite some deviation from linearity between the J and C_e relationship. However, this deviation can be explained by the dependence of permeability (P) or distribution (K_d) coefficient on the concentration of acid, as shown in Figures 5 and 3.

For the concentrations lower than 0.05M the fluxes of PA and AA in the Nafion membrane practically disappear, whereas the flux of FA has not been observed for the feed concentrations lower than 0.1M. In comparison, the Flemion membrane is permeable for AA and PA of the concentrations higher than 0.2M, and this membrane is impermeable for FA in the whole range of concentrations studied, i.e., up to 0.8M. The Flemion impermeability against FA is associated with the

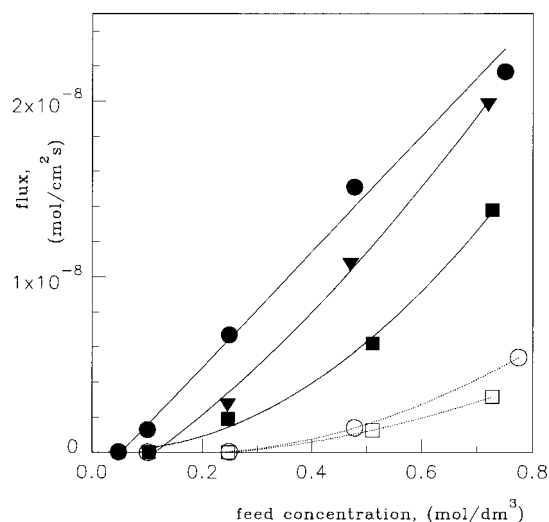


Figure 4 Flux dependence on the concentration of the feed solution C_e : propionic acid–Nafion (●), Flemion (○), acetic acid–Nafion (■), Flemion (□), formic acid–Nafion (▼).

high osmotic flow of water into the feed solution (ranging from 7.8×10^{-5} to 1.2×10^{-4} mol $\text{H}_2\text{O}/\text{cm}^2 \text{ s}$), which additionally hinders the flow of the acid from the feed to the receiver.

To compare our results with those reported by other authors, some permeability coefficients were read off from curves presented in Figure 5 by the interpolation or extrapolation to the required value of C_e . Resulting P_{PA} and P_{AA} for the Nafion-120 membrane at 0.67M and 1.64M are 7.5×10^{-7} and $\sim 1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. Thus, these values agree with the values reported by Sikdar,⁴ i.e., 7.8×10^{-7} and $1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the Nafion-117 membrane. However, a larger difference was found for formic acid, of which the permeability coefficients are of the $\sim 10^{-6}$ order of magnitude, i.e., they are much lower than these evaluated from the data of Sikdar ($\sim 10^{-5}$).

Looking for a correlation between fluxes and properties of carboxylic acids in homologous order one can conclude that the values of P form the order $P_{\text{FA}} < P_{\text{AA}} < P_{\text{PA}}$ for the Nafion membrane in the systems with diluted solution (up to 0.1M). For the concentrations higher than 0.1M this order changes to $P_{\text{AA}} < P_{\text{FA}} < P_{\text{PA}}$. This irregularity is probably caused by the higher diffusion coefficients of FA strongly influencing the product $D_{\text{FA}} \times K_{d,\text{FA}}$ (see also Fig. 5). Certainly, high distribution coefficients (found in the equilibrium experiments) suggest much higher permeability coefficients and fluxes than that measured experimentally, which are typical for the diffusion of many substances in ion-exchange membranes. To some

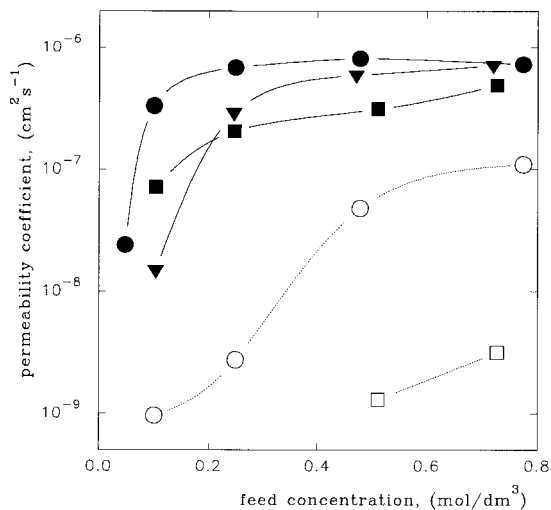


Figure 5 Permeability coefficients of propionic (●,○), acetic (■,□), and formic (▼) acid in Nafion (filled symbols) and Flemion (empty symbols) membrane.

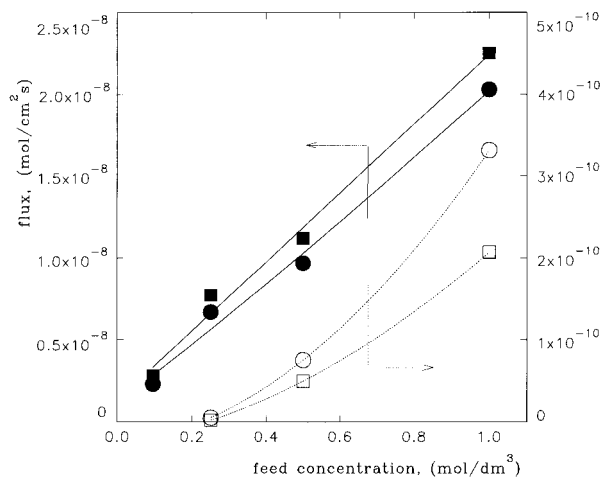


Figure 6 Flux vs. the concentration of the feed solution for competitive permeation of propionic acid (●, □) and acetic acid (■, □) through Nafion (filled symbols) and Flemion (empty symbols) membrane.

degree this result proves a dual mode sorption of acids into the membranes because only the acid sorbed into aqueous phase can diffuse freely in contrast to the one sorbed in the polymer backbone. This effect is remarkably seen in the case of propionic acid permeating the Nafion and Flemion membranes. The K_d values for both membranes are almost the same, whereas their permeability coefficients differ, in average more than 10 times. This effect is probably caused by different tortuosity factors^{31,32} for diffusion pathways due to the different structures of perfluorosulfonic and perfluorocarboxylic membranes.²²

Bicomponent Feed Solutions of PA and AA

The fermentation of some diary by-products containing lactose produces fermentation broths containing propionic acid of the concentration ranging from 0.2 to 0.6M and acetic acid of the concentration from 0.05 to 0.2M.¹⁶⁻¹⁸ For some uses these acids should be effectively separated with low costs and in the simplest possible way. Taking into consideration the fluxes of PA and AA, discussed above, this can be partly achieved by the dialysis of both acids, during their competitive permeation across the membranes. According to eq. (8), one can expect the selectivity coefficients $\alpha_{\text{AA}}^{\text{PA}}$ ranging from 1.3 to 1.9 for both the Nafion and the Flemion membrane.

The fluxes of acids found in the real competitive permeations are presented in Figure 6. These fluxes were calculated from $Q(t)$ versus t depend-

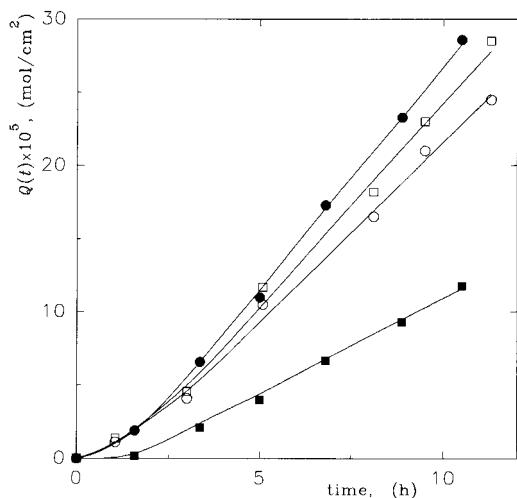


Figure 7 Representative $Q(t)$ versus t plots for competitive transport of propionic (●, ○) and acetic (■, □) acid through Nafion-120 membrane. Equimolar feed solution: 0.25M PA (○) and 0.25M AA (□); PA-enriched feed solution: 0.4M PA (●) and 0.2M AA (■).

encies represented by typical examples shown in Figure 7. The corresponding values of α_{AA}^{PA} are listed in Table II. For the Flemion membrane the selectivity coefficients amounts to 1.6 and are slightly lower than those predicted from single component permeations. Typically, the α_{AA}^{PA} values are twice as high as the ratio of the PA and AA diffusion coefficients in water. Surprisingly, the results for the Nafion membrane (see Fig. 6 and Table II) show this membrane to be nonselective in the competitive transport of AA and PA. The corresponding values of α_{AA}^{PA} listed in Table II

range from 0.83 to 0.89, apparently indicating preferential transport of acetic acid. However, these results are very close to the ratio of diffusion coefficients in water $D_{PA,aq}/D_{AA,aq}$, (0.87–0.79, Table II) and they can be considered as caused by the acids' properties only. A very small separation effect for the Nafion membrane was found only for the feed containing 0.2M solution of AA in 0.4M solution of PA as in the case of fermentation broths. For this system the selectivity coefficient is 1.12, whereas the ratio of diffusion coefficients equals 0.78.

The results evidence the effect of facilitated permeation of acetic acid at the presence of propionic acid. This can be explained by assuming the increased solubility of AA in a polymer phase due to its "plastification" by PA or alternatively by the sorption of associates formed by AA and PA in contact with the Nafion superacid.

CONCLUSION

The permeation and separation characteristics presented in this report are useful for predicting transport properties of perfluorosulfonic and perfluorocarboxylic membranes in the dialytic recovery or purification of carboxylic acids. The experiments have shown the high sorption and moderate fluxes of PA and AA in the Nafion and Flemion membranes. These properties, as related to dissociation equilibria, are consistent with increasing pK of propionic, acetic, and formic acid.

Considering the permeability coefficients

Table II Characteristics of Competitive Permeation of Propionic and Acetic Acid through Nafion and Flemion Membrane

| Concentration mol/dm ³ | | Selectivity Coefficients α_{AA}^{PA} | | | | |
|--------------------------------------|------|---|--|---------------------------|--|--|
| | | Nafion-120 | | Flemion | | Ratio of AA ³³ and PA ^{34,36} Diffusion Coefficients in Water $D_{PA,aq}/D_{AA,aq}$ |
| PA | AA | Competitive Permeation | Calculated from Single Acid Sorption and Diffusion ^a | Competitive Permeation | Calculated from Single Acid Sorption and Diffusion ^a | |
| 0.10 | 0.10 | 0.83 | 1.72 | | | 0.87 |
| 0.25 | 0.25 | 0.85 | 1.52 | 1.20 | 1.43 | 0.86 |
| 0.50 | 0.50 | 0.88 | 1.48 | 1.51 | 1.86 | 0.84 |
| 1.0 | 1.0 | 0.89 | 1.28 | 1.57 | 1.79 | 0.79 |
| 0.40 | 0.20 | 1.12 | | 1.54 | | 0.83 |

$$^a \alpha_{AA}^{PA} = \frac{D_{PA}K_{d,PA}}{D_{AA}K_{d,AA}}$$

($\sim 10^{-6}$ cm²/s), one can conclude that the technique of dialysis with the use of the Nafion membrane can be successfully adopted for recovering PA or AA from aqueous solutions of concentrations 0.1 to 1M. However, the fluxes and separation coefficients show the Nafion membrane to be nonselective in competitive dialyses, at least for the solutions of compositions studied herein. In contrast with Nafion, the Flemion membrane (despite of its lower permeability coefficients) gives a chance to gain some separation between PA and AA, which probably can be enhanced by additional adjusting pH of the feed or the strip solution.

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