

# Transport Characteristics of Some Carboxylic Acids in the Polymeric Anion-Exchange Membrane Neosepta-AMH: Batch Experiments

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Received 6 October 2006; accepted 27 February 2007

DOI 10.1002/app.26516

Published online 3 July 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This article reports the transport of selected carboxylic acids—citric acid, oxalic acid, and tartaric acid—through an anion-exchange membrane (Neosepta-AMH) in a two-compartment dialysis cell. These basic data have been completed by measurements of the sorption isotherms. The mass-transfer rate has been quantified by the following transport characteristics: the overall dialysis coefficient, the permeability of the membrane, and the membrane mass-transfer coefficient. The sorption experiments have revealed that the Neosepta-AMH membrane exhibits the highest af-

finity to tartaric acid, whereas the lowest affinity has been found for citric acid. The analysis of the mass-transfer data has shown that the membrane is relatively permeable for oxalic acid: all three transport characteristics for oxalic acid are approximately 1 order of magnitude higher than those for citric or tartaric acid. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 909–916, 2007

**Key words:** diffusion; membranes; separation techniques

## INTRODUCTION

For many years, membrane processes based on ion-exchange polymeric membranes have been applied in the chemical, food, and pharmaceutical industries. At present, they are intensively studied, as they belong among promising separation techniques. Not only are new membranes being synthesized,<sup>1–9</sup> but new applications using commercial membranes are being investigated.<sup>10–20</sup> Even though ion-exchange membranes are used in the separation of mixtures (e.g., the separation process using anion-exchange membranes, called diffusion dialysis, is used for the efficient separation of acids from their mixtures with salts<sup>10,21–26</sup>), the basic information that must be known concerns the transport of a single component through a membrane. For that reason, permeation experiments with binary solutions are still a subject of very intensive research because the obtained results can be considered basic and reference data for the separation of complex mixtures.

Polymeric anion-exchange membranes find applications also in fermentation processes, in which mixtures containing carboxylic acids of various compositions and concentration have to be separated to obtain

the acid of interest.<sup>27–32</sup> To quantify the transport of components through a membrane, several transport characteristics can be used, such as the overall dialysis coefficient, the permeability of the membrane, and the membrane mass-transfer coefficient. All these characteristics can be obtained only experimentally. For this purpose, a two-compartment mixed cell is mostly used.<sup>5,12,13,15,19,33,34</sup>

The aim of this article is to present basic information on the transport of selected carboxylic acids through an anion-exchange membrane (Neosepta-AMH) by the use of a two-compartment cell with water as a stripping agent. These data can serve as reference data for the dialysis of complex solutions, as mentioned previously, or for neutralization dialysis.<sup>35</sup> Although the transport mechanisms of carboxylic acids inside polymeric membranes can be very complex, for simplicity, solution-diffusion transport is supposed here.

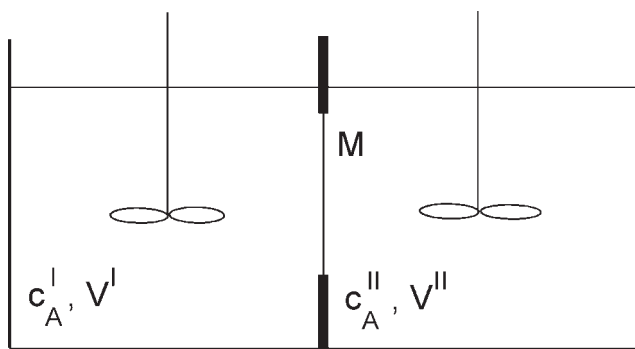
## THEORY

Figure 1 schematically shows a two-compartment mixed cell with a membrane. If the concentration of component A (carboxylic acid) in compartment I is higher than that in compartment II, then the flux of the component through the membrane exists. It can simply be calculated from the concentration and volume changes in both compartments:

$$J_A = -\frac{V^I}{A} \frac{dc_A^I}{d\tau} - \frac{c_A^I}{A} \frac{dV^I}{d\tau} = \frac{V^{II}}{A} \frac{dc_A^{II}}{d\tau} + \frac{c_A^{II}}{A} \frac{dV^{II}}{d\tau} \quad (1)$$

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Contract grant sponsor: Ministry of Education, Youth, and Sport of the Czech Republic; contract grant number: MSM 0021627502.



**Figure 1** Scheme of a two-compartment cell.

where  $J_A$  is the flux of component A ( $\text{kmol m}^{-2} \text{s}^{-1}$ ),  $V$  is the volume ( $\text{m}^3$ ),  $c$  is the molar concentration ( $\text{kmol/m}^3$ ),  $A$  is the membrane area ( $\text{m}^2$ ),  $\tau$  is the time (s), subscript  $A$  refers to component A, superscript  $I$  refers to compartment I, and superscript  $II$  refers to compartment II. Equation (1) can be rewritten as two ordinary differential equations that describe the time dependence of component A in both compartments:

$$\frac{dc_A^I}{d\tau} = -\frac{A}{V^I}J_A - \frac{c_A^I}{V^I}\frac{dV^I}{d\tau} \quad (2)$$

$$\frac{dc_A^{II}}{d\tau} = \frac{A}{V^{II}}J_A - \frac{c_A^{II}}{V^{II}}\frac{dV^{II}}{d\tau} \quad (3)$$

The initial conditions for eqs. (2) and (3) are as follows:

$$\tau = 0, c_A^I = c_{A0}^I, c_A^{II} = c_{A0}^{II} = 0 \quad (4)$$

where subscript 0 indicates the initial value. The derivation of eqs. (2) and (3) is based on the assumption that ideal mixing of the liquid in both compartments exists.

In the determination of the overall dialysis coefficient for component A ( $K_A$ ),  $J_A$  is expressed by the following relation:

$$J_A = K_A(c_A^I - c_A^{II}) \quad (5)$$

The determination of the two other characteristics is more complex than that of  $K_A$  because the mass transport in liquid films, whose existence is assumed on both sides of the membrane, must be considered (see Fig. 2). In the case of the determination of the permeability coefficient of the membrane, eqs. (6)–(8) must be added to the basic differential eqs. (2) and (3)

$$J_A^I = k_L^I(c_A^I - c_{A,if}^I) \quad (6)$$

$$J_{AM} = P_A(c_{A,if}^I - c_{A,if}^{II}) \quad (7)$$

$$J_A^{II} = k_L^{II}(c_{A,if}^{II} - c_A^{II}) \quad (8)$$

where  $k_L^I$  and  $k_L^{II}$  are the liquid mass-transfer coefficients,  $P_A$  is the permeability coefficient of the mem-

brane, subscript  $M$  denotes the membrane, and subscript  $if$  denotes the solution/membrane interface. The mass-transfer coefficient can easily be estimated with the following equation:

$$Sh = CRe^{0.5}Sc^{0.33} \quad (9)$$

where  $Sh = k_L d/D_A$  is the Sherwood number,  $Re = nd^2\rho/\mu$  is the Reynolds number,  $Sc = \mu/\rho D_A$  is the Schmidt number,  $C$  is a constant,  $n$  is the rotational speed of the stirrer ( $\text{s}^{-1}$ ),  $d$  is the diameter of the stirrer (m),  $D_A$  is the diffusivity of component A ( $\text{m}^2/\text{s}$ ),  $\mu$  is the dynamic viscosity (Pa s), and  $\rho$  is the density ( $\text{kg/m}^3$ ). Equations (6) and (8) describe the transport of component A through the liquid films, whereas eq. (7) concerns the transport through the membrane.

For the determination of the membrane mass-transfer coefficient, the equilibrium relations have to be added to eqs. (6) and (8):

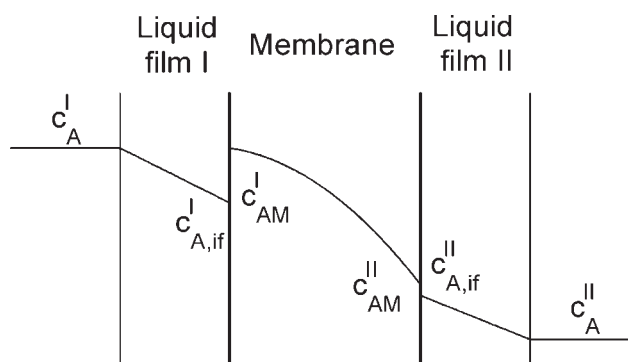
$$c_{AM}^k = \Psi_A^k c_{A,if}^k \quad k = I, II \quad (10)$$

where  $\Psi_A^k$  ( $k = I$  or  $II$ ) is the partition coefficient on both sides of the membrane. The flux of component A through the membrane is then given by the following equation:

$$J_{AM} = k_{AM}(c_{AM}^I - c_{AM}^{II}) \quad (11)$$

where  $k_{AM}$  is the membrane mass-transfer coefficient and  $c_{AM}^k$  ( $k = I$  or  $II$ ) is the concentration of component A in the membrane at both boundaries.

For simplicity, suppose the pseudo-steady state:  $J_A^I = J_{AM} = J_A^{II}$ . If the dependence of the concentrations of component A in both compartments and the volumetric changes are recorded, then it is possible to numerically solve the basic differential equations [eqs. (2) and (3)]. If this step is combined with a suitable optimizing procedure, then one can determine the basic transport characteristics mentioned previously.



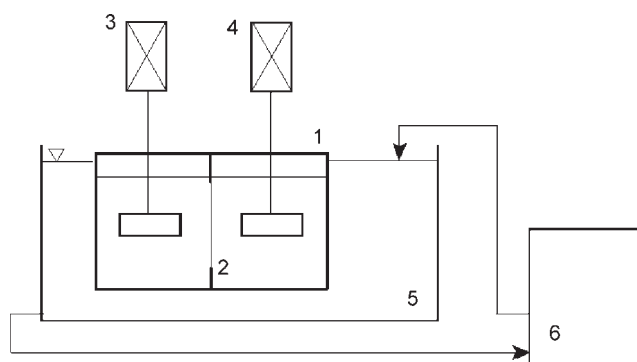
**Figure 2** Concentration profiles of component A in membrane and liquid films.

## EXPERIMENTAL

To determine the transport characteristics of a component in the membrane, a two-compartment cell with stirrers was mostly used. At the beginning of the experiment, one compartment was filled with the investigated solution, whereas the other was filled with distilled water. Afterward, the concentrations of the component in both compartments were recorded as functions of time. Moreover, the equilibrium component concentration in the membrane was also needed.

### Concentration of the carboxylic acids in the membrane

The concentration of the individual carboxylic acids in the membrane, which was equilibrated with a bulk solution of a known composition, was determined by a procedure based on the saturation of the membrane with carboxylic acid followed by an extraction of acid into water. The membrane, having a 25–30-cm<sup>2</sup> surface area (the membrane was cut into four to six pieces), which was kept in a storage solution (0.5M NaCl), was rid of salt by thorough washing in distilled water and then was repeatedly saturated with carboxylic acid of a low concentration. The aim of this step was to replace Cl<sup>-</sup> ions originally present in the membrane with anions of the studied acid. After repeated and thorough washing of the membrane in distilled water, the membrane was shaken in an acid of a known concentration for 19 h (overnight). Afterward, the membrane was carefully wiped with blotting paper to remove the solution adhering to the membrane surface and repeatedly shaken (4×) in 25 mL of distilled water. The carboxylic acid concentrations in the bulk solutions were determined by titration with a standard solution of NaOH, whereas those in the individual extracts were determined spectrophotometrically (in the ultraviolet region) after the addition of a strong acid to suppress the dissociation



**Figure 3** Experimental setup: (1) dialysis cell, (2) partition with a membrane, (3,4) stirrers with motors, (5) water bath, and (6) thermostat.

**TABLE I**  
Experimental Conditions

Acid	$M_A$ (kg/kmol)	$K_1^a$	$c_{A0}^I$ (kmol/m <sup>3</sup> )	$n^I = n^{II}$ (s <sup>-1</sup> )
Citric	192.13	$8.6 \times 10^{-4}$	0.1–1.0	1.17–9.17
Oxalic	90.03	$6.5 \times 10^{-2}$	0.1–0.8	1.17–9.17
Tartaric	150.09	$9.21 \times 10^{-4}$	0.1–1.0	1.17–9.17

<sup>a</sup> The data were taken from ref. 39.

of carboxylic acid. For that purpose, a Spectronic Helios Gamma ultraviolet–visible spectrophotometer was used. All the experiments were carried out at 25°C.

### Dialysis experiments

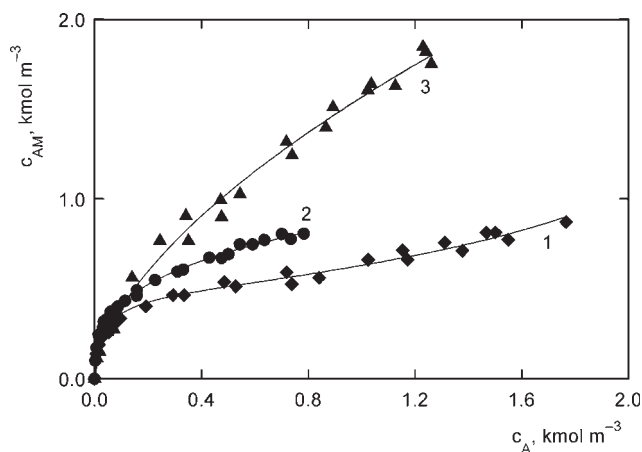
Figure 3 depicts the experimental setup used. Its main part was a dialysis cell made of Plexiglas. The inner dimensions were 0.12 m × 0.15 m × 0.16 m (length × width × height). A vertical partition, in which the membrane was fastened, divided the cell into two compartments that were approximately the same. In both compartments, the liquid was stirred with laboratory stirrers with an electronic rotation rate control. The shape and size of the stirrers were designed to ensure ideal mixing of the solution volume in both compartments of the cell. In all experiments, we used an anion-exchange membrane (Neosepta-AMH) produced by Tokuyama Soda Co., Inc. (Tokyo, Japan), whose basic properties have already been published.<sup>36,37</sup> It is a strongly basic membrane with  $-NC_7H_7^+$  functional groups.<sup>38</sup> The membrane area was 62.2 cm<sup>2</sup>.

At the beginning of each experiment, compartments I and II were filled with a carboxylic acid solution and distilled water, respectively. The initial volume of the liquid in both compartments was always 10<sup>-3</sup> m<sup>3</sup>. In the course of each experiment, the concentration of carboxylic acid and the height of the liquid levels were measured. The concentration of acid was determined by titration with a standard solution of sodium hydroxide and/or spectrophotometrically. The temperature was kept at a constant value of 25 ± 0.5°C. The experimental conditions, such as the initial acid concentration in compartment I and the range of the rotational speeds of the stirrers, are summarized in Table I.

## RESULTS AND DISCUSSION

### Concentration of carboxylic acid in the membrane

The concentration of carboxylic acid in the membrane was calculated from the amount of acid in the individual extracts (four 25-mL extracts were obtained) and the volume of the swollen membrane:



**Figure 4** Sorption isotherms of Neosepta-AMH membrane/carboxylic acid systems at 25°C: (1) citric acid, (2) oxalic acid, and (3) tartaric acid.

$$c_{AM} = \frac{25 \times 10^{-6} \sum_{j=1}^4 c_{Aj}^{\text{extract}}}{V_M} \quad (12)$$

where the superscript extract refers to the extract. In Figure 4, the sorption isotherms of the Neosepta-AMH membrane/carboxylic acid systems are presented. From this graphical presentation, it is evident that at low acid concentrations in the bulk solution (below ca. 0.2 kmol/m<sup>3</sup>), the acid concentration in the membrane sharply increases with increasing acid concentration in the bulk solution; this can be ascribed to a relatively high degree of dissociation, which exists at a low acid concentration, so that under these conditions the sorption of all the acids is facilitated. At higher acid concentrations in the bulk solution, a mild increase in the acid concentration in the membrane can be observed. Citric acid is a tricarboxylic acid, whose molar mass (see Table I) is the highest of the three acids studied, so its concentration is the lowest of all. Moreover, its dissociation constant is the lowest of all (see Table I). If only these two parameters, the molar mass and dissociation constant, were considered, then logically oxalic acid would exhibit the highest concentrations in the membrane. However, the sorption experiments have revealed that the oxalic acid concentration in the membrane is lower than that of tartaric acid, whose molar mass is somewhat higher and whose dissociation constant is much

lower. This discrepancy could be ascribed to different interactions of oxalic and tartaric acids with the membrane matrix.

For the calculation of the membrane mass-transfer coefficients, the dependences presented in Figure 4 were approximated with empirical equations [eqs. (13) and (14)], whose constants were determined by nonlinear regression (the constants are summarized in Table II). For citric acid

$$c_{AM} = \frac{c_A}{b_0 + b_1 c_A + b_2 c_A^2} \quad (13)$$

where  $b_0$ ,  $b_1$  (m<sup>3</sup>/kmol), and  $b_2$  (m<sup>6</sup>/kmol<sup>2</sup>) are constants. For oxalic and tartaric acid

$$c_{AM} = B c_A^b \quad (14)$$

where  $b$  and  $B$  (kmol<sup>1-b</sup> m<sup>3(b-1)</sup>) are constants.

### Dialysis experiments

The basic transport characteristics of the individual carboxylic acids, that is,  $K_A$ ,  $P_A$  and  $k_{AM}$ , were calculated from the time dependence of the acid concentration in both compartments (see Fig. 5).

### Overall dialysis coefficient

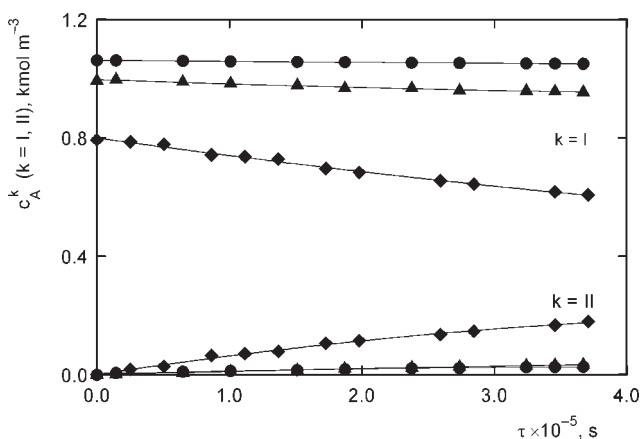
The overall dialysis coefficient was determined by the numerical integration of the set of the differential equations [eqs. (2) and (3)], in which  $J_A$  was expressed by eq. (5) with the initial conditions [eq. (4)]. For that purpose, the fourth-order Runge–Kutta method, with the integration step  $h = 3.6$  s (i.e., 0.001 h), was used. In such a way, the calculated values of the acid concentration in both compartments, that is,  $c_{A,calc}^{I,i}$  and  $c_{A,calc}^{II,i}$  were obtained and consequently used in the calculation of the objective function ( $F$ ):

$$F = \sum_{i=1}^m \left[ \left( \frac{c_{A,exp}^{I,i} - c_{A,calc}^{I,i}}{c_{A,exp}^{I,i}} \right)^2 + \left( \frac{c_{A,exp}^{II,i} - c_{A,calc}^{II,i}}{c_{A,exp}^{II,i}} \right)^2 \right] \quad (15)$$

where  $m$  is the number of experimental points in one time series, subscript exp means experimental, and subscript calc means calculated. With the Golden Sec-

**TABLE II**  
Constants of the Empirical Equations [Eqs. (13) and (14)]

Acid	$b_0$	$b_1$ (m <sup>3</sup> /kmol)	$b_2$ (m <sup>6</sup> /kmol <sup>2</sup> )	$B$ (kmol <sup>1-b</sup> m <sup>3(b-1)</sup> )	$b$
Citric	0.0743	2.091	-0.579	—	—
Oxalic	—	—	—	0.88	0.322
Tartaric	—	—	—	1.567	0.599



**Figure 5** Dependence of  $c_A^k$  ( $k = I$  or  $II$ ) on  $\tau$  at  $n^I = n^{II} = 9.17 \text{ s}^{-1}$ : ( $\blacktriangle$ ) citric acid ( $c_{A0}^I = 1.00 \text{ kmol/m}^3$ ), ( $\blacklozenge$ ) oxalic acid ( $c_{A0}^I = 0.80 \text{ kmol/m}^3$ ), and ( $\bullet$ ) tartaric acid ( $c_{A0}^I = 1.05 \text{ kmol/m}^3$ ).

tion Search, such values of  $K_A$  were searched, at which the objective function [eq. (15)] reached a minimum.

The dependences of the overall dialysis coefficient on the initial acid concentration in compartment I for the investigated carboxylic acids are illustrated in Figure 6. In all cases, the overall dialysis coefficient decreases with increasing acid concentration in compartment I at  $\tau = 0$ . The overall dialysis coefficients for tartaric acid are very close to those for citric acid. However, they are about 1 order of magnitude lower than those for oxalic acid. The Neosepta-AMH membrane is an anion-exchange membrane that has in its structure positively charged sites, so the transport of counterions through this membrane is facilitated, whereas coions (except for hydrated hydrogen ions) are effectively rejected. Of the three acids studied, oxalic acid exhibits the highest value of the dissociation constant. This fact, in combination with the relatively low molar mass of the acid, can then be a reason that this acid permeates the Neosepta-AMH membrane much more easily than citric and tartaric acids.

In the case of oxalic acid, a weak influence of the rotational speed of the stirrers on the overall dialysis coefficient has been found, and this indicates that a certain part of the mass-transfer resistance can be present in liquid films on both sides of the membrane. On the contrary, because of the scattering of  $K_A$ , no effect of the intensity of mixing on  $K_A$  for citric and tartaric acids can be identified.

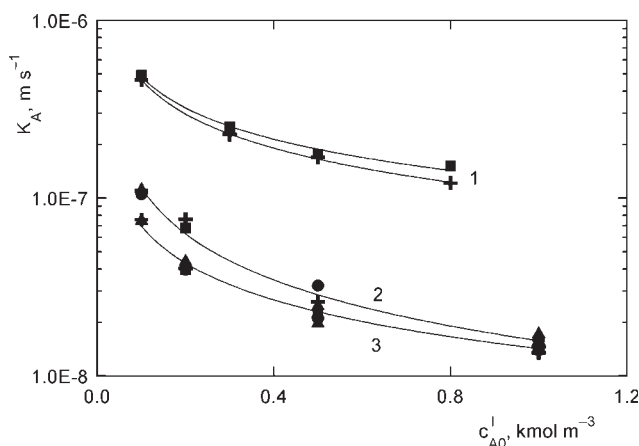
#### Permeability coefficient of the membrane

The calculation of the permeability coefficient was based on a procedure that combines the numerical integration of the basic differential equations [eqs. (2)

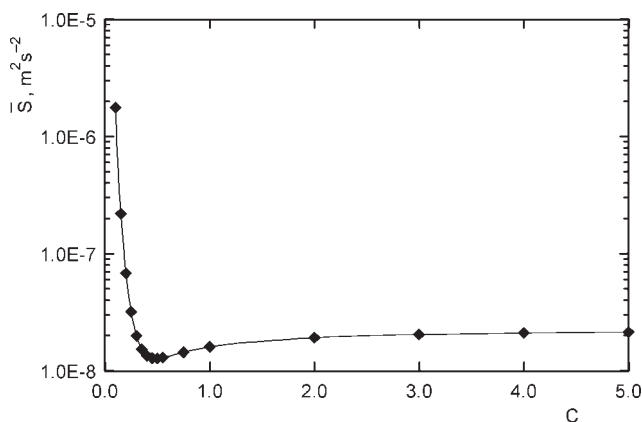
and (3)] with a suitable optimizing procedure. The procedure can be summarized as follows:

1. The initial estimation of  $P_A$  ( $P_A^{(0)} = 10^{-8} \text{ m s}^{-1}$ ) and the calculation of the derivative  $dV^k/d\tau$  ( $k = I$  or  $II$ ) from the dependence  $V^k = f(\tau)$  obtained experimentally.
2. The numerical integration of eqs. (2) and (3), in which  $J_A$  was expressed by eq. (7), with the same procedure used in the calculation of the overall dialysis coefficient. In this step, we obtained the calculated acid concentrations in both compartments at the same time as those obtained experimentally. In each integration step, it was necessary to calculate the acid concentrations in the liquid at both membrane/solution interfaces. For that purpose, the set of eqs. (6)–(8) was solved by the Newton–Raphson procedure. The physical properties of the liquid, that is, the diffusivity, dynamic viscosity, and density, that were needed in the calculation of the liquid mass-transfer coefficients from eq. (9) were taken from the literature.<sup>40,41</sup> As we did not succeed in finding the diffusivity of all carboxylic acids as a function of the concentration at 25°C, we used the diffusivity of the acid at infinite dilution.<sup>40</sup>
3. The calculation of the objective function [eq. (15)].
4. The calculation of the corrected value of  $P_A$  by a realization of one step of the optimizing procedure (the Golden Section Search was used).
5. Steps 2–4 were repeated until a minimum of the objective function was reached.

The determination of the permeability of the membrane needed the value of constant  $C$  in eq. (9). Its



**Figure 6** Dependence of  $K_A$  on  $c_{A0}^I$  for (1) oxalic acid, (2) tartaric acid, and (3) citric acid: ( $+$ )  $n^I = n^{II} = 1.17 \text{ s}^{-1}$  ( $\blacktriangle$ )  $n^I = n^{II} = 4.17 \text{ s}^{-1}$ , ( $\bullet$ )  $n^I = n^{II} = 6.17 \text{ s}^{-1}$ , and ( $\blacksquare$ )  $n^I = n^{II} = 9.17 \text{ s}^{-1}$ .



**Figure 7** Dependence of  $\bar{S}$  on constant  $C$  in eq. (9) for oxalic acid.

determination was based on considerations similar to those used in the data treatment obtained in a continuous dialyzer.<sup>42</sup> The permeability of a membrane is a membrane/solution characteristic that is independent of the intensity of mixing. This means that the values of the permeability obtained at various rotational speeds of the stirrers and at a constant initial acid concentration in compartment I must not be very different from one another. For that reason, we defined a new criterion,  $\bar{S}$ , as the sum of variances of  $P_A$  at a constant value of  $c_{A0}^I$ , which is plotted versus  $C$  in Figure 7. From this dependence, a value of  $C$  was used at which the criterion  $\bar{S}$  reached a minimum or a constant value (see refs. 37 and 42).

The values of the permeability of the membrane for the individual acids are given in Table III. Here, the values of  $P_A$  for the lower and upper limits of the concentration range investigated are presented. Moreover, the values of constant  $C$  in eq. (9) are presented here, too. Figure 8 then presents the dependence of the permeability coefficients of the membrane on the initial acid concentration in compartment I. A detailed inspection of Figures 6 and 8 reveals that in the case of oxalic acid, the dependence of  $P_A = f(c_{A0}^I)$  is identical to that of  $K_A = f(c_{A0}^I)$  at  $n^I = n^{II} = 9.17 \text{ s}^{-1}$ . This means that under these conditions (intensive mixing in both compartments), the effect of the liquid films on both sides of the membrane on the transport of oxalic acid can be neglected. The same situation can be seen in the case of citric acid. On the other

**TABLE III**  
Permeability of the Neosepta-AMH Membrane

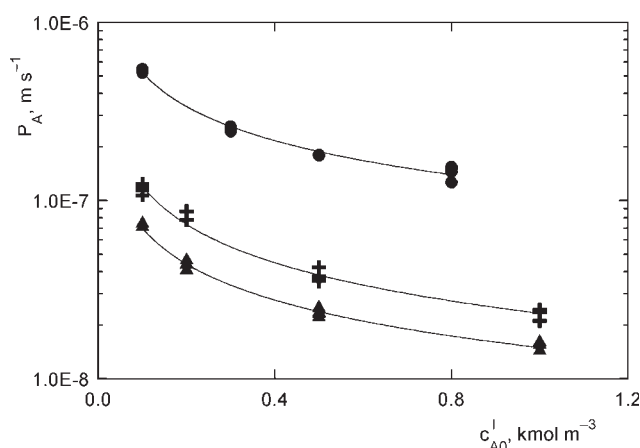
Acid	Concentration range (kmol/m <sup>3</sup> )	$C$	$P_A \times 10^7$ (m/s)
Citric	0.1–1.0	0.75	0.756–0.154
Oxalic	0.1–0.8	0.45	5.305–1.499
Tartaric	0.1–1.0	1.0	1.213–0.223

hand, the permeability coefficients of the Neosepta-AMH membrane in the medium of tartaric acid are shifted to somewhat higher values, especially at higher acid concentrations. The permeability coefficient of the membrane is proportional to the product of the solubility (i.e., the partition coefficient) and diffusivity of the component in the membrane. In all cases, the permeability coefficient decreases with increasing acid concentration. As the partition coefficient of each carboxylic acid decreases with increasing acid concentration (see Fig. 4), the diffusivity of carboxylic acid may decrease, or an increase in the diffusivity may not be able to compensate for the decrease in the partition coefficient.

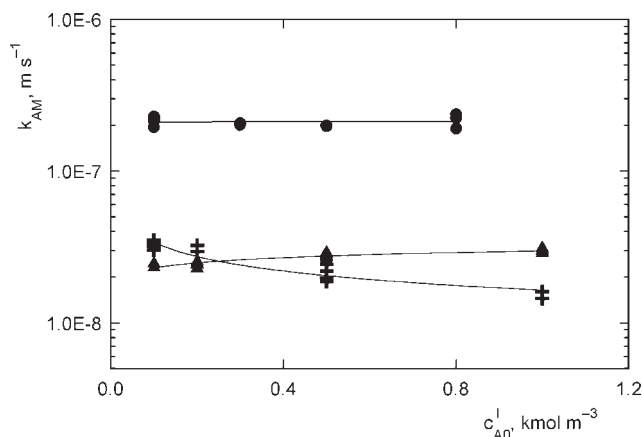
#### Membrane mass-transfer coefficient

The membrane mass-transfer coefficients were calculated with a procedure that was very similar to that used in the calculation of the permeability of the membrane. The only difference was in the calculation of the acid concentrations in the membrane on both boundaries, that is,  $c_{AM}^I$  and  $c_{AM}^{II}$ . For that purpose, eqs. (6), (8), (10), and (11) were solved; the Newton–Raphson procedure was used again. The partition coefficients  $\Psi_A^I$  and  $\Psi_A^{II}$  ( $\Psi_A = c_{AM}/c_A$ ) were calculated from eqs. (13) and (14). Constant  $C$  in eq. (9) was determined in a way similar to that given previously for the permeability coefficient.  $C$  was found to be 0.248 for citric acid, 0.671 for oxalic acid, and 1.37 for tartaric acid.

Figure 9 shows the dependence of the membrane mass-transfer coefficient on the initial acid concentration in compartment I. Similarly to the case of the permeability coefficient, the membrane mass-transfer coefficient for oxalic acid is about 1 order of magnitude higher than that for citric or tartaric acid. Moreover,  $k_{AM}$  for oxalic acid is not practically affected by the acid concentration; its mean value is  $2.12 \times 10^{-7}$



**Figure 8** Dependence of  $P_A$  on  $c_{A0}^I$ : (▲) citric acid, (●) oxalic acid, and (+) tartaric acid.



**Figure 9** Dependence of  $k_{AM}$  on  $c_{A0}^I$ : (▲) citric acid, (●) oxalic acid, and (+) tartaric acid.

m/s. The membrane mass-transfer coefficient for citric acid exhibits an increase with an increasing acid concentration, whereas  $k_{AM}$  for tartaric acid decreases with an increasing acid concentration. According to the film theory, the mass-transfer coefficient in fluids is proportional to the diffusivity of the component. Supposing the validity of this theory also in the membrane phase, we find that the dependences presented in Figure 9 reveal that the diffusivity of oxalic acid is not affected by the acid concentration. The increase in the membrane mass-transfer coefficient of citric acid can be caused by an increase in the diffusivity of citric acid in the membrane, and in the case of tartaric acid, the opposite occurs.

## CONCLUSIONS

The transport of citric, oxalic, and tartaric acids through an anion-exchange membrane (Neosepta-AMH) has been investigated. For that purpose, a two-compartment dialysis cell equipped with stirrers has been used. The transport has been quantified by the overall dialysis coefficient, the permeability of the membrane, and the membrane mass-transfer coefficient. All these transport characteristics have been determined by a procedure based on a numerical integration of the basic differential equations describing the time dependence of the acid concentration in both compartments followed by a one-dimensional optimizing procedure. Generally, the developed mathematical model takes into account the transport of acid through liquid films on both sides of the membrane.

## NOMENCLATURE

0 subscript denoting the initial value  
 (0) superscript denoting the initial estimate

$A$  membrane area (m<sup>2</sup>)  
 $A$  subscript denoting component  $A$  (carboxylic acid)  
 $b$  constant in eq. (14)  
 $B$  constant in eq. (14) (kmol<sup>1-b</sup> m<sup>3(b-1)</sup>)  
 $b_0$  constant in eq. (13)  
 $b_1$  constant in eq. (13) (m<sup>3</sup>/kmol)  
 $b_2$  constant in eq. (13) (m<sup>6</sup>/kmol<sup>2</sup>)  
 $c$  molar concentration (kmol/m<sup>3</sup>)  
 $C$  constant in eq. (9)  
 calc subscript meaning calculated  
 $d$  diameter of the stirrer (m)  
 $D$  diffusivity (m<sup>2</sup>/s)  
 exp subscript meaning experimental  
 extract superscript denoting the extract  
 $f$  general function  
 $F$  objective function  
 $h$  integration step (s)  
 $I$  superscript denoting compartment I  
 $if$  subscript denoting the solution/membrane interface  
 $II$  superscript denoting compartment II  
 $J_A$  flux (kmol m<sup>-2</sup> s<sup>-1</sup>)  
 $K$  overall dialysis coefficient (m/s)  
 $K_1$  dissociation constant  
 $k_{AM}$  membrane mass-transfer coefficient (m/s)  
 $k_L$  mass-transfer coefficient in a liquid (m/s)  
 $\mu$  dynamic viscosity (Pa s)  
 $M$  molar mass (kg/kmol)  
 $M$  subscript denoting the membrane  
 $m$  number of experimental points in one time series  
 $n$  rotational speed of the stirrer (s<sup>-1</sup>)  
 $\Psi$  partition coefficient  
 $P$  permeability of the membrane (m/s)  
 $\rho$  density (kg/m<sup>3</sup>)  
 $Re = nd^2\rho/\mu$  Reynolds number  
 $\bar{S}$  sum of variances (m<sup>2</sup>/s<sup>2</sup>)  
 $Sc = \mu/\rho D_A$  Schmidt number  
 $Sh = k_L d/D_A$  Sherwood number  
 $\tau$  time (s)  
 $V$  volume (m<sup>3</sup>)

## References

- Ohya, H.; Semenova, S.; Mizoguchi, K.; Ogihara, J.; Fukaya, S.; Suzuki, Y.; Aihara, M.; Negishi, Y. *J Appl Polym Sci* 2002, 84, 2605.
- Choi, Y. J.; Kang, M. S.; Moon, S. H. *J Appl Polym Sci* 2003, 88, 1488.
- Hu, K.; Xu, T. W.; Yang, W. H.; Fu, Y. *J Appl Polym Sci* 2004, 91, 167.
- Xu, T. W.; Yang, W. H. *J Membr Sci* 2004, 238, 123.
- Xu, T. W.; Liu, Z. M.; Yang, W. H. *J Membr Sci* 2005, 249, 183.
- Choi, Y. J.; Park, J. M.; Yeon, K. H.; Moon, S. H. *J Membr Sci* 2005, 250, 295.

7. Hu, K. Y.; Xu, T. W.; Yang, W. H.; Fu, Y. X. *J Appl Polym Sci* 2005, 98, 494.
8. Tang, B. B.; Xu, T. W.; Yang, W. H. *J Membr Sci* 2006, 268, 123.
9. Yu, H.; Xu, T. W. *J Appl Polym Sci* 2006, 100, 2238.
10. Oh, S.-J.; Moon, S.-H.; Davis, T. *J Membr Sci* 2000, 169, 95.
11. Ersoz, M.; Kara, H. *J Colloid Interface Sci* 2000, 232, 344.
12. Ersoz, M.; Gugul, I. H.; Sahin, A. *J Colloid Interface Sci* 2001, 237, 130.
13. Ersoz, M.; Cengeloglu, Y.; Kir, E.; Koyuncu, M.; Yazicigil, Z. *J Appl Polym Sci* 2001, 81, 421.
14. Cengeloglu, Y.; Kir, E.; Ersoz, M. *J Colloid Interface Sci* 2001, 244, 342.
15. Kir, E.; Cengeloglu, Y.; Ersoz, M. *Sep Sci Technol* 2003, 38, 2503.
16. Cengeloglu, Y.; Tor, A.; Esengul, K.; Ersoz, M. *Desalination* 2003, 154, 239.
17. Akgemci, E. G.; Ersoz, M.; Atalay, T. *Sep Sci Technol* 2004, 39, 165.
18. Akgemci, E. G.; Ersoz, M.; Atalay, T. *Sep Sci Technol* 2005, 40, 1899.
19. Durmaz, F.; Kara, H.; Cengeloglu, Y.; Ersoz, M. *Desalination* 2005, 177, 51.
20. Jeong, J.; Kim, M. S.; Kim, B. S.; Kim, S. K.; Kim, W. B.; Lee, J. C. *J Hazard Mater* 2005, 124, 230.
21. Kobuchi, Y.; Motomura, H.; Noma, Y.; Hanada, F. *J Membr Sci* 1986, 27, 173.
22. Lin, S. H.; Lo, M. C. *J Hazard Mater* 1998, 60, 247.
23. Xu, T. W.; Yang, W. H. *J Membr Sci* 2001, 183, 193.
24. Wódzki, R.; Szczepański, P. *Pol J Environ Stud* 2001, 10, 101.
25. Xu, T. W.; Yang, W. H. *J Membr Sci* 2003, 220, 89.
26. Xu, T. W.; Yang, W. H. *J Hazard Mater* 2004, 109, 157.
27. Timmer, J. M. K.; van der Horst, H. C.; Robbertsen, T. *J Membr Sci* 1993, 85, 205.
28. Timmer, J. M. K.; Kromkamp, J.; Robbertsen, T. *J Membr Sci* 1994, 92, 185.
29. Netke, S. A.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. *J Membr Sci* 1995, 107, 23.
30. Wódzki, R.; Nowaczyk, J. *J Appl Polym Sci* 1997, 63, 355.
31. Wódzki, R.; Nowaczyk, J. *J Appl Polym Sci* 1999, 71, 2179.
32. Wódzki, R.; Nowaczyk, J. *J Appl Polym Sci* 2001, 80, 2705.
33. Narebska, A.; Warszawski, A. *Sep Sci Technol* 1992, 27, 703.
34. Alexandrova, I.; Iordanov, G. *J Appl Polym Sci* 2005, 95, 705.
35. Zhelezov, A.; Windmüller, D. D.; Körner, S.; Böddeker, K. W. *J Membr Sci* 1998, 139, 137.
36. Körösová, M.; Palatý, Z.; Žáková, A. *Chem Biochem Eng Q* 2005, 19, 141.
37. Palatý, Z.; Žáková, A.; Prchal, P. *Desalination*, to appear.
38. Ayyildiz, H. F.; Kara, H. *Desalination* 2005, 180, 99.
39. Dobos, D. *Electrochemical Data: A Handbook for Electrochemists in Industry and Universities*; Akadémia Kiadó: Budapest, 1975.
40. Yaws, C. L. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*; Knovel: Corporation, Norwich: NY, 2003.
41. *International Critical Tables of Numeric Data, Physics, Chemistry and Technology, 1926–1930*, 1st ed.; Washburn, E. W., Ed.; Knovel: Corporation, Norwich: NY, 2003; Vol. V.
42. Palatý, Z.; Žáková, A.; Petřík, P. *Chem Eng Process* 2006, 45, 806.