Continuous Dialysis of Citric Acid: Solubility and Diffusivity in Neosepta-AMH Membrane

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The transport of citric acid through an anion-exchange membrane Neosepta-AMH in a two-compartment continuous dialyzer has been investigated. The basic data obtained were completed by the measurement of the sorption isotherm. Mass transfer rate has been quantified by diffusivity of citric acid in the membrane, which has been determined from the acid concentrations in the streams entering and leaving the dialyzer. For that purpose, a set of ordinary differential equations describing the concentrations profiles in both the compartments of the dialyzer has been numerically solved in the connection with an optimizing procedure. In the mathematical model used, mass transfer resistances in liquid films on both sides of the membrane have been taken into account. All the experiments carried out at steady state (temperature ϑ = 25 °C) revealed that first diffusivity of citric acid in the Neosepta-AMH membrane gradually increases with an increasing acid concentration until reaching a weak maximum at an acid concentration of c = 0.464 kmol m^{-3}, then it slightly decreases. In the concentration range of citric acid in the membrane from c = 0 to 0.558 kmol m^{-3}, diffusivity of acid was in the limits from D = 1.79 $\cdot$ 10^{-12} to 3.33 $\cdot$ 10^{-12} m^2 s^{-1}.

Key words:
Dialysis, continuous dialyzer, steady state mass transfer, citric acid, Neosepta-AMH membrane

Introduction

A series of carboxylic acids were produced by fermentation processes, where the mixtures obtained were processed and separated. Citric acid is one of the largest carboxylic acids produced through fermentation of glucose, molasses, or dextrase by *Aspergillus niger*. Citric acid and its salts are widely used in the food, pharmaceutical, cosmetic and chemical industries. In order to satisfy the demands of these industries, huge amounts of citric acid and its salts are required. World production of citric acid in 2004 was about 1.4 million tons, as estimated by Business Communications Co.[1] Due to a large number of applications and low prices of citric acid, its consumption continues to increase each year.

The main problem in the production of citric acid is its recovery from the fermentation broth. First, citric acid is separated from biomass by filtration or centrifugation. Then it is purified by either the lime-sulphuric acid method or liquid extraction processes, and is concentrated by multiple-effect evaporation. These separation steps complicate the process. Moreover, large quantities of the chemical are needed and large amounts of water and solid wastes are also produced.

In recent years, some methods were developed with the aim to decrease the cost of the recovery, and the formation and disposal of calcium sulphate, which is responsible for pollution problems. Membrane separation processes, which have been intensively studied for many years, seem to be very promising because of their low energy consumption due to the fact that separation is performed without changing phases.

Iglinski *et al.*[2] investigated sodium citrate conversion to citric acid by the pure electrodialysis process with a bipolar membrane. They determined the current efficiencies based on the number of moles of acid produced – both the mean and the instantaneous efficiencies were calculated. It was found that the mean efficiencies of acid and base are higher at the lowest current densities (j = 52 mA cm^{-2}) with the maximum being observed at j = 78 mA cm^{-2} for the highest initial salt concentration of c = 1.4 kmol m^{-3}. In order to overcome the disadvantages of electro-electrodialysis, Luo *et al.*[3] developed a coupled technique of two-phase electrophoresis and electro-electrodialysis named two-phase electro-electrodialysis for recovery and concentration of citric acid solution. In this technique, an organic phase of *n*-butanol was used to replace the aqueous phase as analyte and an AM-203 anion-exchange membrane as a separation medium. Citric

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acid was transferred from catholyte (aqueous phase) to anolyte (organic phase) under the action of an electric current. The experiments proved that two-phase electro-electrodialysis has the ability to overcome the electro-osmosis and osmosis of water, which increase the volume of analyte. Moreover, back diffusion caused by concentration difference can be well controlled by liquid-liquid interface. Pinacci and Radaelli[4] studied a hybrid membrane process for the recovery of citric acid from fermentation broth, which involved electrodialysis with bipolar membranes. The experiments revealed that a maximum acid/salt conversion of $X = 92$ % can be reached, thus producing a $c = 2.1 - 2.2$ kmol m^{-3} citric acid solution with a salt residual of 8 %. In the paper[5] aimed at the study of the transport of citrate ions through ion-exchange membranes, a mathematical model to represent the ion and water transport behaviour of an electrodialysis process for the concentration of citric acid under the influence of current density was developed. This model was in good agreement with the experimental data and it could be used for the prediction of the performance of electrodialysis for citric acid concentration.

The use of solvent extraction and supported liquid membrane for the separation of citric and lactic acids in aqueous solutions were studied by Juang et al.[6] Experiments were carried out as a function of the total acid concentration, the concentration ratio of the acids and the concentration of extractant (tri-n-octylamine). It was shown that the equilibrium distribution of each acid (solvent extraction) was largely affected in the presence of the other. Moreover, the competition transport of the acids in the supported liquid membrane was explained from the kinetics of solvent extraction. Juang and Chen[7] dealt with the preparation of four types of salts of tri-n-octylamine by equilibrating xylene solutions of tri-n-octylamine and aqueous solutions of nitric, hydrochloric, sulfuric, and citric acid with subsequent experimental investigation of the transport of citric acid from aqueous solutions through supported liquid membrane using these salts and pure tri-n-octylamine as mobile carriers. The stripping agent was either water or sodium carbonate solution. The experiments were performed as a function of the total tri-n-octylamine concentration and various content of the salts in the membrane phase. In contrast to the use of pure tri-n-octylamine, it was found that the amount of citric acid transported increased for all the salts in long-term tests (over 8 h). The use of supported liquid membrane to separate citric acid from the beer produced by fermentation was studied by Friesen et al.[8] The liquid membrane consisted of an organic solution composed of trilaurylamine and a long-chain alcohol dissolved in a hydrocarbon solvent that was

immobilized in a microporous polypropylene support. Using this membrane, the effects of temperature, composition, and citric concentration on the transport rate of citric acid were investigated. The experiments revealed that the highest flux of citric acid exists under the following conditions: $\vartheta = 60$ °C, trilaurylamine volume fraction of $\varphi = 38$ % in alkyl aromatic oil and $\varphi = 15$ % n-dodecanol in the membrane phase as a modifier. Citric acid was separated successfully from an aqueous solution using a hollow fiber contained liquid membrane.[9] Tri-n-octylamine diluted in various organic solvents was used as a complexing agent for facilitated transport of citric acid from an aqueous solution. Pure water and aqueous sodium hydroxide were used as stripping agents. A mathematical model of facilitated solute transport through a hollow fiber contained liquid membrane which accounts for the interfacial reversible reaction kinetics and diffusion process inherent in carrier-facilitated transport was presented. The experimental data agreed well with the theoretical predictions for permeators achieving almost complete solute recovery.

Besides the application of electrodialysis and supported liquid membranes, also transport of carboxylic acids through polymeric membranes in the absence of electric field was the object of the study.[10–12]

In order to study the transport of components through polymeric membranes, one can use two types of apparatuses – a two-compartment dialysis cell with stirrers[13–18] and continuous dialyzer.[16,19–26] In the former case, the basic transport characteristics can be calculated using the concentration-time dependences, which are recorded in each compartment of the cell. In the latter case, the dialyzer is at steady state, so that these characteristics can be calculated from the concentrations in streams entering and leaving the dialyzer. The main advantage of this apparatus is that under laboratory conditions it is possible to construct such an apparatus, some dimensions of which (preferably thickness and height) can approach those of the basic element in the industrial apparatus. The results obtained using this laboratory model can then serve for the modeling and design of larger dialysis units.

The aim of this communication is to obtain a basic transport characteristic of the citric acid – Neosepta-AMH membrane system using data obtained in a continuous dialyzer at steady state. Although the fermentation broth contains a series of components, the basic information on the transport of citric acid through the membrane must be known, as these data are considered as reference data for dialysis of complex solutions or neutralization dialysis.[27] As the dissociation degree of citric acid is low, the transport of neutral molecules of the

acid can be considered. This transport can be quantified by diffusivity of citric acid in the membrane.

Theory

Consider the balance scheme of a counter-current dialyzer with two identical compartments, whose thickness and width are δ and d, respectively – see Fig. 1. The total height of each compartment is z_T. If the concentration of citric acid (component A) in compartment I is higher than that in compartment II, then the flux of citric acid through the membrane exists. At steady state, the balance of citric acid over the differential volume, $dV = (\delta \cdot d \cdot dz)$, of compartment I is expressed by the following equation

$$S u^{I} c_{A}^{I}\big|_{z} - S u^{I} c_{A}^{I}\big|_{z+dz} - J_{A} \frac{A}{z_{T}} dz = 0 \quad (1)$$

where S is the cross-section of the compartment ($S = \delta \cdot d$), u^{I} is liquid flow rate, c_{A}^{I} is mole concentration of citric acid, J_{A} is the flux of citric acid through the membrane and A is the membrane area. Assuming constant liquid flow rate and taking into account the definition of derivation, eq. (1) can be rearranged to give eq. (2) describing the concentration profile of citric acid at steady state in compartment I

$$\frac{dc_{A}^{I}}{dz} = -\frac{1}{S u^{I}} \frac{A}{z_{T}} J_{A} \quad (2)$$

In a similar way, it is possible to derive eq. (3), which describes the dependence of the concentration of citric acid upon coordinate z in compartment II

F i g . 1 – *Balance scheme of continuous dialyzer*

$$\frac{dc_{A}^{II}}{dz} = -\frac{1}{S u^{II}} \frac{A}{z_{T}} J_{A} \quad (3)$$

Equations (2) and (3) are subject to two initial conditions

$$z = 0 \qquad c_{A}^{I} = c_{A,in}^{I} \qquad c_{A}^{II} = c_{A,out}^{II} \quad (4)$$

Note: The derivation of the differential eqs. (2) and (3) is based on the assumed existence of liquid plug flow in both compartments of the dialyzer. As proved by hydrodynamic studies,[28] this assumption is fulfilled.

The flux of citric acid can be expressed by Fick's law

$$J_{A} = -D_{AM} \frac{dc_{AM}}{dx} \quad (5)$$

Generally, diffusivity of the component is dependent upon its concentration. For simplicity, suppose that the dependence of diffusivity of citric acid upon its concentration in the membrane may be approximated by a second order polynomial

$$D_{AM} = a_0 + a_1 c_{AM} + a_2 c_{AM}^2 \quad (6)$$

The integration of eq. (5) with respect to eq. (6) leads to the following equation

$$J_{A} = \frac{1}{\delta_{M}} \left\{ a_0 [c_{AM}^{I} - c_{AM}^{II}] + \frac{a_1}{2} [(c_{AM}^{I})^2 - (c_{AM}^{II})^2] + \right. \\ \left. + \frac{a_2}{3} [(c_{AM}^{I})^3 - (c_{AM}^{II})^3] \right\} \quad (7)$$

where δ_{M} is the membrane thickness, c_{AM}^{I} and c_{AM}^{II} are the concentrations of citric acid in the membrane on both the boundaries.

The application of eq. (7) needs the concentrations c_{AM}^{I} and c_{AM}^{II}. For that purpose, it is necessary to solve mass transfer in the membrane (eq. (7)) simultaneously with that in liquid films on both the sides of the membrane (see Fig. 2), i.e.

F i g . 2 – *Concentration profiles of component in liquid films and membrane*

$$J_A = k_L^I (c_A^I - c_{Af}^I) \qquad (8)$$

$$J_A = k_L^{II} (c_{Af}^{II} - c_A^{II}) \qquad (9)$$

where k_L^I and k_L^{II} are the mass transfer coefficients, which can be estimated from eq. (10) valid for laminar flow

$$Sh = C\, Re^{0.5} Sc^{0.33} \qquad (10)$$

Finally, the equilibrium relations (11) should be added to eqs. (7) – (9).

$$c_{AM}^k = \Psi_A^k c_{Af}^k \qquad k = I, II \qquad (11)$$

If the concentrations of citric acid in the streams entering and leaving the dialyzer at $z = 0$ (i.e. $c_{A,in}^I$ and $c_{A,out}^{II}$) are known, then it is possible to integrate the set of eqs. (2) and (3), and with a suitable optimizing procedure, calculate the constants a_0, a_1 and a_2 of the polynomial (6). The set of eqs. (2) and (3) can also be integrated in the opposite direction, i.e. from $z = z_T$ to $z = 0$ – in this case, the right-hand sides of eqs. (2) and (3) are positive and the initial conditions are: $z = z_T$, $c_A^I = c_{A,out}^I$, $c_A^{II} = c_{A,in}^{II} = 0$. Furthermore, this procedure needs other data concerning mass transfer in liquid films and solution/membrane equilibria.

Experimental

Membrane used

In all the experiments, an anion-exchange membrane Neosepta-AMH was used. This polymeric, strongly basic membrane is produced by Japanese firm Tokuyama Soda Co., Inc. Its basic properties were as follows: thickness $\delta_M = 250$ μm (measured), water content 0.186 g per gram of dry membrane in Cl$^-$ form (measured) and concentration of fixed charges 1.3 – 1.5 meq. g^{-1} – see Ref.[29]

Solution/membrane equilibrium

The amount of citric acid in the membrane equilibrated with the external solution containing the same component was determined by the procedure, which is based on the saturation of the membrane with the solution with subsequent extraction of the citric acid into distilled water.

The membrane of $A = 25 - 30$ cm^2 surface area (the membrane was cut into 4 – 6 pieces), which was kept in a storage solution ($c = 0.5$ kmol m^{-3} NaCl), was rid of salt by thorough washing in distilled water, and then repeatedly saturated with $c = 0.1$ kmol m^{-3} citric acid. The aim of this pre-treatment was to replace Cl$^-$ ions originally present in the membrane by anions of acid. After repeated

thorough washing of the membrane in distilled water, the membrane was shaken in acid of known concentration for 19 hours. Then it was carefully wiped with blotting paper to remove the solution adhering to the membrane surface, and repeatedly shaken (4×) in 25 mL distilled water. The acid concentration in the external solutions and the individual extracts were determined by titration with $c = 0.1$ kmol m^{-3} NaOH and spectrophotometrically, respectively. In the latter case, samples were acidified with hydrochloric acid to suppress the dissociation of citric acid and then photometered at a wavelength of $\lambda = 210$ nm using a Spectronic Helios Gamma ultraviolet-visible Spectrophotometer. All the experiments were carried out at $\vartheta = 25$ °C.

Dialysis experiments

All the dialysis experiments were carried out using the experimental set-up, which is shown in Fig. 3. Its main part was a laboratory dialyzer with two identical compartments separated by an anion-exchange membrane, whose area was $A = 3.31 \cdot 10^{-2}$ m^2.

The height of the dialyzer was 1 m, the dimensions of each compartment were 0.92 m · 0.036 m · 0.0011 m (height · width · thickness). The constant thickness of each compartment was ensured by a net-type spacer made of PVC. The total volume of each compartment was $V = 36.4 \cdot 10^{-6}$ m^3 and the volume occupied by liquid was $V = 21.7 \cdot 10^{-6}$ m^3 – i.e. dimensionless liquid hold-up was 0.595. The
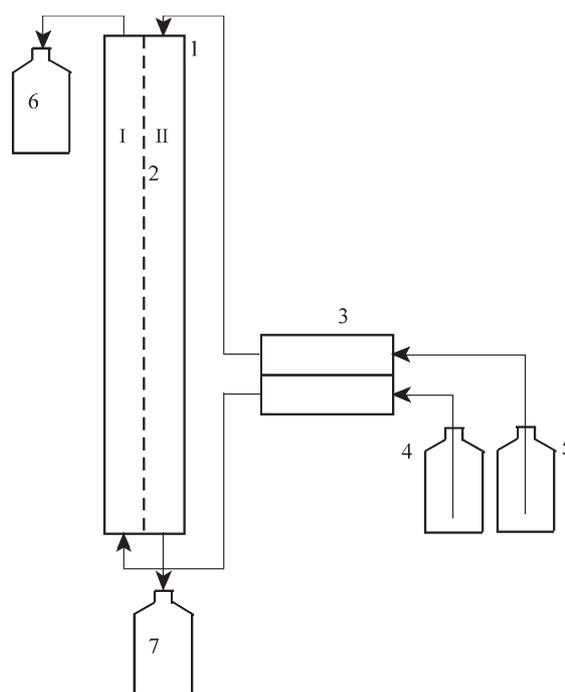
F i g . 3 – *Experimental set-up: 1 – dialyzer; 2 – membrane; 3 – peristaltic pump; 4 – feed; 5 – stripping solution (distilled water); 6 – dialyzate; 7 – diffusate; I, II – compartments*

dialyzer was placed into a box made of Plexiglas®, where the temperature was kept constant, i.e. $\vartheta = 25\ °C$.

The aqueous solution of citric acid (feed) entered the bottom of the compartment I, while distilled water (stripping agent) entered the top of the compartment II. The flow of both liquid streams was ensured by a peristaltic pump MC-MS/CA4 (Ismatec SA, Switzerland). In all the experiments, volumetric flow rate of the feed was equal to that of the stripping agent ($Q_{in}^{I} = Q_{in}^{II} = Q_{in}$). The citric acid concentration in the feed was changed from $c = 0.05$ to $0.70\ kmol\ m^{-3}$, while the volumetric flow rate, Q_{in}, was in the limits from $7 \cdot 10^{-9}$ to $23 \cdot 10^{-9}$ $m^3\ s^{-1}$ (residence time of liquid approx. $\tau = 940 - 3100\ s$). Detailed experimental conditions are summarized in Table 1. Here, also Reynolds numbers in both the compartments are given as integral mean values of Re, because properties of liquids change along the membrane.

After the steady state had been reached (time from 6 to 12 hours depending on liquid flow rate and acid concentration in the feed was necessary – as proved by preliminary experiments), three samples were taken from each stream leaving the dialyzer. At the same time, mass flow rates of both these streams were determined by weighing. Before each experiment, also mass flow rates of feed and stripping agent were measured. Using density of liquid, mass flow rate of each stream was recalculated into volumetric flow rate. The acid concentration was determined by titration with a standard NaOH solution and/or spectrophotometrically.

Data treatment and discussion

Solution/membrane equilibrium

The concentration of citric acid in the membrane was calculated from the concentration of citric acid in the individual extracts and the volume of the swollen membrane

$$c_{AM} = \frac{25 \cdot 10^{-6} \sum_{j=1}^{4} c_{Aj}^{extract}}{V_M} \tag{12}$$

Fig. 4 presents the dependence of the citric acid concentration in the membrane upon the acid concentration in the external solution. From this graphical presentation, it is evident that the acid concentration in the membrane increases with increasing acid concentration in the external solution. This dependence is very similar to that obtained in the case of sulfuric acid with the same membrane.[30] At the acid concentrations below approx. $c = 0.2$
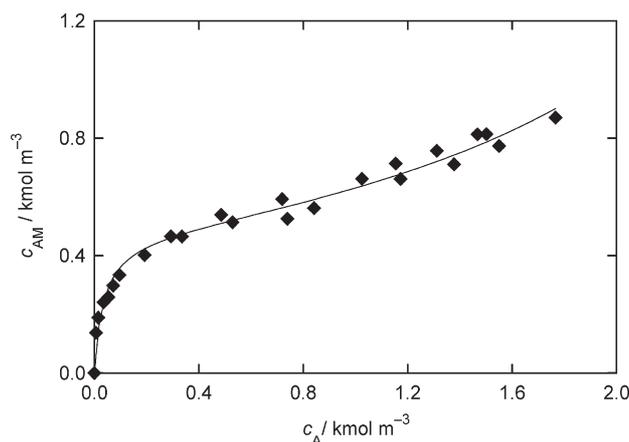
F i g . 4 – *Dependence of citric acid concentration in membrane upon that in external solution*

$kmol\ m^{-3}$ a strong increase in the acid concentration in the membrane can be seen, while at higher concentrations only a mild increase in the acid amount in the membrane exists. For the further utilization of data on solution/membrane equilibrium, the experimental data given in Fig. 4 were approximated by the following empirical equation

$$c_{AM} = \frac{c_A}{p_0 + p_1 c_A + p_2 c_A^2} \tag{13}$$

whose constants p_i ($i = 0, 1, 2$) were determined by a non-linear regression: $p_0 = 7.43 \cdot 10^{-2} \pm 2.873 \cdot 10^{-2}$, $p_1 = 2.091 \pm 0.189\ m^3\ kmol^{-1}$, $p_2 = -5.79 \cdot 10^{-1} \pm 1.27 \cdot 10^{-1}\ m^6\ kmol^{-2}$.

Dialysis experiments

The coefficients of the polynomial (6), which enables calculation of diffusivity of citric acid and its concentration dependence in the membrane, were determined by the numerical integration of the basic differential equations (2) and (3) followed by an optimizing procedure. The whole procedure may be summarized into the following steps:

1. The initial estimation of the coefficients a_0, a_1, a_2 of the polynomial (6) – because no values of diffusivity of citric acid in this membrane were known, the initial estimation was found by a trial and error method.

2. The numerical integration of the set of eqs. (2) and (3), where the flux of citric acid, J_A, is expressed by eq. (7). For that purpose, we used the Runge–Kutta 4th order method with the integration step $h = 9.209 \cdot 10^{-4}\ m$ (number of grid points in the direction z was 1000). In each integration step, it was necessary to calculate the concentration of citric acid at the solution/membrane interfaces in the membrane and both the liquid films. These concentrations were calculated from eqs. (7) – (9) and

(11) using the Newton–Raphson procedure. The physical-chemical properties of liquid (density, dynamic viscosity and diffusivity) needed in the calculation of the mass transfer coefficients were taken from literature.[31,32] The data therein given (density and dynamic viscosity) were recalculated and then fitted by the following empirical equations

$$\rho = 997.01 + 78.21c \qquad (14)$$

$$\mu = 8.974 \cdot 10^{-4} + 2.952 \cdot 10^{-4} c + 2.601 \cdot 10^{-4} c^2 \quad (15)$$

The mass transfer coefficients were determined for the mean concentrations of citric acid in the liquid films (the arithmetic mean of the boundary concentrations was used), so that these concentrations had to be corrected iteratively. As diffusivity as a function of the acid concentration at given temperature was not found, diffusivity at infinite dilution was used[32] ($D = 6.904 \cdot 10^{-10}$ m^2 s^{-1}). First, the set of eqs. (2) and (3) was integrated in the positive direction of the coordinate z, so that the calculated values of the acid concentrations at $z = z_T$ were obtained, i.e. $c_{A,out}^{I,calc}$ and $c_{A,in}^{II,calc}$. Then the integration in the opposite direction was applied. In this way, the calculated values of the acid concentrations at $z = 0$ were obtained, i.e. $c_{A,in}^{I,calc}$ and $c_{A,out}^{II,calc}$.

3. The calculation of the objective function

$$F(a_0, a_1, a_2) = \sum_{i=1}^{n} [(c_{A,out}^{I,i,calc} - c_{A,out}^{I,i,exp})^2 + (c_{A,in}^{II,i,calc})^2 +$$
$$+ (c_{A,in}^{I,i,calc} - c_{A,in}^{I,i,exp})^2 + (c_{A,out}^{II,i,calc} - c_{A,out}^{II,i,exp})^2] \qquad (16)$$

where n is the number of all the experiments carried out at various initial concentrations of citric acid and volumetric flow rates of liquid.

(Note that $c_{A,in}^{II,exp} = 0$)

4. The calculation of the corrected values of a_0, a_1 and a_2 using one step of the optimizing procedure. For that purpose, we used a simplex method – the algorithm by Nelder and Mead.

5. The steps from 2) to 4) were repeated until the minimum of the objective function (16) was reached.

The suitability of the procedure given can be judged on the basis of the comparison of the calculated and experimental values of $c_{A,in}^{I}$ and $c_{A,out}^{k}$ (k = I, II); this comparison is presented in Table 1. This table reveals good agreement between the experiment and the model represented by eqs. (2), (3) and (7) – (11). The relative errors ($\delta_{\%} = (c_A^{exp} - c_A^{calc})/c_A^{exp} \cdot 100)$) are on an acceptable level. The relative errors concerning compartment I are very small (they do not exceed 1.2 %), while those concerning compartment II are somewhat higher – in some cases they exceed 10 %.

The determination of the coefficients a_i ($i = 0$, 1, 2) of the polynomial (6) needs the constant C in eq. (10). It was estimated from the dependence of the objective function, F, upon the constant C. In the calculation of the mass transfer coefficients such value of C was used, at which the objective function reaches a constant value, $C = 0.81$. This value is somewhat higher than that found formerly in the experiments aimed at the determination of permeability of the same membrane for citric acid.[33] The coefficients a_i ($i = 0$, 1, 2) of the polynomial (6) are summarized in Table 2. The dependence of diffusivity of citric acid upon its concentration in the membrane is presented graphically in Fig. 5. Here, it may be seen that diffusivity of citric acid in the Neosepta-AMH membrane is the lowest at zero acid concentration (i.e. $D_{AM} = 1.79 \cdot 10^{-12}$ m^2 s^{-1}), and it gradually increases with an increasing acid concentration in the membrane until reaching a weak maximum at acid concentration of $c_{AM} = 0.464$ kmol m^{-3} ($D_{AM} = 3.33 \cdot 10^{-12}$ m^2 s^{-1}) – then a mild decrease may be observed. (Note: The upper concentration limit in Fig. 5 ($c_{AM} = 0.56$ kmol m^{-3}) was calculated from the sorption isotherm (13) for the highest acid concentration in the feed.)
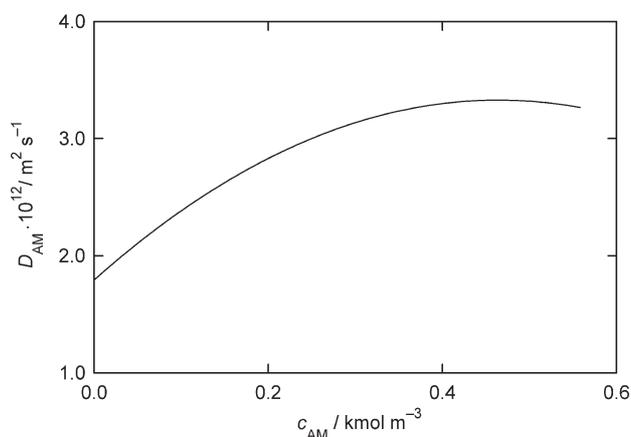
F i g . 5 – *Dependence of diffusivity of citric acid upon its concentration in membrane*

Using the coefficients a_i ($i = 0$, 1, 2) from Table 1, we calculated the concentration profiles of citric acid in both the compartments of the dialyzer. These profiles are shown in Fig. 6, from which it is evident that the acid concentration in each compartment is a linear function of the coordinate z.

Table 1 presents, beside the experimental and calculated values of citric acid concentrations, also the recovery yield and flux of citric acid. The acid recovery yield, which is a frequently used characteristic of a continuous dialysis process, was calculated from the following equation

T a b l e 1 – *Experimental conditions and results*

Exp. No	$Q_{in}^{I} \cdot 10^9$ m³ s⁻¹	$c_{A,in}^{I,exp}$ kmol m⁻³	$c_{A,in}^{I,calc}$ kmol m⁻³	$\delta_\%$ %	$c_{A,out}^{I,exp}$ kmol m⁻³	$c_{A,out}^{I,calc}$ kmol m⁻³	$\delta_\%$ %	$c_{A,in}^{II,calc}$ kmol m⁻³	$c_{A,out}^{II,exp}$ kmol m⁻³	$c_{A,out}^{II,calc}$ kmol m⁻³	$\delta_\%$ %	Re^{I}	Re^{II}	R_A %	$J_A \cdot 10^9$ kmol m⁻² s⁻¹
1	6.85	0.0500	0.0504	–0.80	0.0399	0.0397	0.50	0.0004	0.0109	0.0107	1.83	0.404	0.400	21.28	2.12
2	10.29	0.0500	0.0503	–0.60	0.0428	0.0426	0.47	0.0006	0.0080	0.0076	5.00	0.611	0.610	15.78	2.29
3	13.69	0.0500	0.0502	–0.40	0.0444	0.0441	0.68	0.0001	0.0060	0.0059	1.67	0.813	0.822	11.90	2.43
4	18.41	0.0496	0.0494	–0.40	0.0449	0.0452	–0.67	0.0006	0.0049	0.0044	10.20	1.088	1.129	10.10	2.47
5	22.74	0.0502	0.0501	–0.20	0.0463	0.0465	0.43	0.0005	0.0042	0.0037	11.90	1.348	1.389	8.45	2.53
6	7.38	0.1001	0.0996	0.50	0.0858	0.0867	–1.05	0.0014	0.0145	0.0135	6.90	0.429	0.449	14.78	2.97
7	11.37	0.1001	0.1003	–0.20	0.0909	0.0908	0.11	0.0006	0.0100	0.0096	4.00	0.671	0.677	10.05	3.22
8	15.31	0.1003	0.1008	–0.50	0.0937	0.0930	0.75	0.0002	0.0076	0.0074	2.63	0.890	0.906	7.48	3.37
9	19.00	0.1014	0.1017	–0.30	0.0957	0.0953	0.42	0.0001	0.0062	0.0061	1.61	1.109	1.127	6.07	3.46
10	22.60	0.1014	0.1013	0.10	0.0961	0.0962	–0.10	0.0001	0.0053	0.0052	1.89	1.319	1.340	5.20	3.50
11	7.14	0.3001	0.2999	0.07	0.2803	0.2807	–0.14	0.0006	0.0197	0.0193	2.03	0.389	0.432	6.63	4.16
12	10.96	0.3001	0.3029	–0.93	0.2894	0.2866	0.97	0.0003	0.0136	0.0134	1.47	0.597	0.661	4.56	4.44
13	14.63	0.3001	0.3015	–0.47	0.2911	0.2897	0.48	0.0004	0.0107	0.0104	2.80	0.796	0.880	3.56	4.56
14	19.27	0.3010	0.2998	0.40	0.2917	0.2929	–0.41	0.0004	0.0084	0.0080	4.76	1.047	1.162	2.82	4.67
15	22.89	0.3010	0.3008	0.07	0.2939	0.2942	–0.10	0.0005	0.0073	0.0068	6.85	1.249	1.380	2.42	4.72
16	7.21	0.4069	0.4074	–0.12	0.3866	0.3864	0.05	0.0011	0.0217	0.0209	3.69	0.378	0.428	5.29	4.45
17	11.0	0.4069	0.4114	–1.11	0.3969	0.3928	1.03	0.0015	0.0156	0.0144	7.69	0.576	0.659	3.80	4.69
18	14.40	0.4018	0.4035	–0.42	0.3922	0.3906	0.41	0.0006	0.0119	0.0114	4.20	0.757	0.851	2.93	4.86
19	17.94	0.4018	0.4037	–0.47	0.3904	0.3926	–0.56	0.0006	0.0099	0.0094	5.05	0.941	1.059	2.41	4.96
20	21.30	0.4018	0.4023	–0.12	0.3945	0.3940	0.13	0.0006	0.0085	0.0080	5.88	1.122	1.264	2.09	5.02
21	6.87	0.7000	0.7002	–0.03	0.6748	0.6751	–0.04	0.0012	0.0269	0.0260	3.35	0.316	0.396	3.67	5.14
22	11.15	0.6922	0.6921	0.01	0.6756	0.6759	–0.04	0.0010	0.0174	0.0166	4.60	0.518	0.663	2.49	5.48
23	14.79	0.6922	0.6890	0.46	0.6762	0.6796	–0.50	0.0017	0.0142	0.0127	10.56	0.685	0.889	2.05	5.59
24	18.61	0.6922	0.6999	1.11	0.6895	0.6819	1.10	0.0012	0.0113	0.0104	7.96	0.860	1.118	1.64	5.73
25	21.57	0.6915	0.6937	–0.32	0.6847	0.6827	0.29	0.0009	0.0099	0.0091	8.08	1.006	1.277	1.41	5.81

T a b l e 2 – *Constants of polynomial (6)*

$a_0 \cdot 10^{12}$ m² s⁻¹	$a_1 \cdot 10^{12}$ m⁵ s⁻¹ kmol⁻¹	$a_2 \cdot 10^{12}$ m⁸ s⁻¹ kmol⁻²
1.793	6.612	–7.119

$$R_A = \frac{Q_{out}^{II} \, c_{A,out}^{II}}{Q_{in}^{I} \, c_{A,in}^{I}} \cdot 100 \qquad (17)$$

An inspection of Table 1 reveals that acid recovery yield is in the limits from $R_A = 1.4$ to 21.3 % and it sharply decreases with an increasing acid concentration in the feed and volumetric flow rate. On the
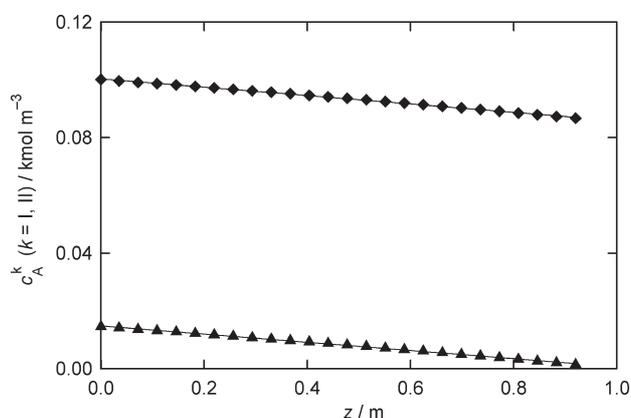
F i g . 6 – *Concentration profiles of citric acid in dialyzer for $c_{A,in}^I = 0.1$ kmol m⁻³ and $Q_{in}^I = 7.4 \cdot 10^{-9}$ m³ s⁻¹: ◆ – compartment I; ▲ – compartment II*

other hand, the flux of citric acid exhibits quite the opposite tendency – the flux increases with an increasing in both acid concentration in the feed and increasing volumetric flow rate of liquid. As the flux of citric acid changes along the coordinate z, the integral mean values of J_A are given in Table 1.

The main advantage of the dialysis process is low consumption of energy. Only energy to ensure the transport of liquids into the dialyzer is required. On the other hand, this process is very slow, because it is controlled by diffusion in the membrane phase. As it may be seen from Table 1, the flux of citric acid through the Neosepta-AMH membrane is very small, so to ensure a reasonable production of citric acid a large area of this membrane is needed. Fortunately, instead of water as a stripping agent sodium or potassium hydroxide may be used to accelerate the process. This technique called neutralization dialysis was studied only using a batch dialysis cell, see e.g. Ref.[27]

Conclusion

Dialysis of citric acid in a continuous two-compartment dialyzer with an anion-exchange membrane Neosepta-AMH was investigated. The transport of citric acid was quantified by diffusivity of acid in the membrane. This quantity, including its concentration dependence, was determined from the acid concentrations in the streams entering and leaving the dialyzer. In the treatment of the basic experimental data obtained, the model was used which describes the concentration profiles of acid in both the compartments of the dialyzer. The model developed takes into account mass transfer resistances in liquid films on both sides of the membrane and solution/membrane equilibrium. The transport of acid through the membrane was described by Fick's law.

S y m b o l s

A – membrane area, m^2

a_0 – constant in eq. (6), m^2 s^{-1}

a_1 – constant in eq. (6), m^5 s^{-1} kmol^{-1}

a_2 – constant in eq. (6), m^8 s^{-1} kmol^{-2}

C – constant in eq. (10)

c – mole concentration, kmol m^{-3}

D – diffusivity, m^2 s^{-1}

d – width of compartment, m

d_e – (= $2d\delta/(d+\delta)$) equivalent diameter of compartment, m

F – objective function, kmol^2 m^{-6}

h – integration step, m

J – mole flux, kmol m^{-2} s^{-1}

j – current density, mA cm^{-2}

k_L – liquid mass transfer coefficient, m s^{-1}

n – number of all experimental points

p_0 – constant in eq. (13)

p_1 – constant in eq. (13), m^3 kmol^{-1}

p_2 – constant in eq. (13), m^6 kmol^{-2}

Q – volumetric flow rate, m^3 s^{-1}

R_A – acid recovery yield, %

Re – (= ud_e/ν) Reynolds number

S – cross-section of compartment, m^2

Sc – (= ν/D_A) Schmidt number

Sh – (= $k_L d_e/D_A$) Sherwood number

u – liquid flow rate, m s^{-1}

V – volume, m^3

X – conversion, %

x – length coordinate, m

z – length coordinate, m

z_T – height of compartment, m

δ – thickness of compartment, m

$\delta_\%$ – relative error, %

δ_M – membrane thickness, m

λ – wave length, nm

τ – residence time, s

φ – volume fraction, %

ϑ – temperature, °C

ν – kinematic viscosity, m^2 s^{-1}

Ψ – partition coefficient

S u p e r s c r i p t s   a n d   s u b s c r i p t s

A   – referred to component A (i.e. citric acid)

calc   – calculated value

exp   – experimental value

extract   – referred to extract

f   – referred to membrane/solution interface

in   – inlet

M   – referred to membrane

out   – outlet

I, II   – referred to compartment I and II, resp.

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