

Apparent Diffusivity of Sulfuric Acid in Anion-Exchange Membrane Neosepta-AMH

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Original scientific paper

Received: November 15, 2004

Accepted: April 1, 2005

The transport of sulfuric acid through an anion-exchange membrane Neosepta-AMH (Tokuyama Soda, Co., Inc.) has been studied. For that purpose, a two-compartment batch cell with stirrers has been used. The experiments have been carried out at various initial acid concentrations and intensity of mixing in both the compartments, the temperature being kept at a constant value of 20 °C. The time dependences of the acid concentration, which have been recorded, have enabled the calculation of apparent diffusivity of sulfuric acid. The dependence of apparent diffusivity upon its concentration has been approximated by the second degree polynomial whose coefficients have been determined with the help of the model based on the Fick's law. Using all the experimental data obtained, it has been shown that apparent diffusivity of sulfuric acid in the membrane is strongly concentration-dependent. Moreover, it has been found that diffusivity of sulfuric acid in a Neosepta-AMH membrane is much lower than that in a Neosepta-AFN membrane.

Keywords:

Anion-exchange membrane, diffusion dialysis, sulfuric acid, diffusivity

Introduction

Diffusion dialysis is a membrane process using anion-exchange membranes, which facilitate the transport of anions while cations, except hydrogen ions, are effectively rejected. The driving force of this process is not supplied from outside, hence it is impossible to control the rate of the whole process by it. In the past, diffusion dialysis found somewhat limited applications in the industrial practice, because of considerable mass transfer resistance as a consequence of high thickness of the membranes. However, development of new improved membranes of lower thickness gradually eliminated this undesirable effect.

At present, diffusion dialysis finds its largest industrial applications in the separations of acids, namely HCl, HNO₃, H₂SO₄ and HF, from their salts in acid wastewaters, e.g. wastewaters from pickling and etching.^{1,2} Another interesting applications of diffusion dialysis are separation of H₂SO₄ and glucose in the process of manufacturing glucose from wood and desalination for low-molecular-mass organic substances, such as sugars, alcohols, organic acids, low amino acids etc.³

The aim of this paper is to obtain basic data on the rate of transport of sulfuric acid through anion-exchange membrane Neosepta-AMH, as these data can be considered to be reference data for dialysis in complex systems. Although ions (i.e. H⁺,

HSO₄⁻, SO₄²⁻) are transported through this membrane, for simplicity, the transport of neutral molecules is considered here. Such an approach, which has already been used in the case of ion diffusion through ion-exchange membrane, enables the determination of apparent diffusivity of the component.⁴⁻⁶

Theory

In order to obtain basic transport characteristics of solutions in the membrane, a two-compartment cell is mostly used.^{4,7-12} If the concentration of the component A (i.e. sulfuric acid) in the compartment I is higher than that in the compartment II, then transport of the component A exists. Moreover, if the pseudo-steady state is supposed, the transport of the component A is described by the following equations

$$J_A^I = k_L^I (c_A^I - c_{Ai}^I) \quad (1)$$

$$J_{AM} = -\frac{1}{\delta_M} \int_{c_{AM}^I}^{c_{AM}^{II}} D_{AM} dc_{AM} \quad (2)$$

$$J_A^{II} = k_L^{II} (c_{Ai}^{II} - c_A^{II}) \quad (3)$$

Equations (1) and (3) describe the transport of the component A through the liquid films whose existence is supposed on both sides of the membrane. Equation (2) describes the transport of the component A through the membrane – here concen-

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tration dependent diffusivity in the membrane is considered. For simplicity, suppose that the dependence of diffusivity of the component A upon its concentration in the membrane can be approximated by a second degree polynomial

$$D_{AM} = a_0 + a_1 c_{AM} + a_2 c_{AM}^2 \quad (4)$$

Using Eq. (4), taking into account the volume changes in the cell, and with respect to the definition of molar flux ($J_A^I = J_{AM} = J_A^{II} = -\frac{1}{A} \frac{dn_A^I}{d\tau}$), Eq. (2) can be rewritten into the following form

$$\begin{aligned} \frac{dc_A^I}{d\tau} = & -\frac{A}{V^I \delta_M} \left\{ a_0 [c_{AM}^I - c_{AM}^{II}] + \right. \\ & + \frac{a_1}{2} [(c_{AM}^I)^2 - (c_{AM}^{II})^2] + \\ & \left. + \frac{a_2}{3} [(c_{AM}^I)^3 - (c_{AM}^{II})^3] \right\} - \frac{c_A^I dV^I}{V^I d\tau} \\ \tau = 0 \quad c_A^I = & c_{A0}^I \end{aligned} \quad (5)$$

A complete description of the transport of the component A through the membrane and both liquid films needs the equilibrium relations (6) to be added to Eqs (1), (3) and (5).

$$c_{AM}^j = \psi_A^j c_{Ai}^j \quad j = I, II \quad (6)$$

Equation (5) is an ordinary differential equation describing the time dependence of the concentration of the component A in the compartment I of the dialysis cell. If the time dependences of the concentration of the component A and those of the volume of liquid in the compartment I are available, then Eq. (5) can be numerically integrated and, in the connection with a suitable optimization procedure, one can obtain the coefficients a_0 , a_1 , a_2 of the polynomial (4), which quantify the dependence of diffusivity of the component A upon its concentration in the membrane. Moreover, the procedure given presumes that data on solution/membrane equilibrium and other data enabling the estimation of mass transfer coefficients in both compartments are available.

Experimental

Membrane used

In all the measurements, an anion-exchange membrane Neosepta-AMH developed and produced by Japanese firm Tokuyama Soda Co., Inc., was used. Its basic physical properties are summarized in Table 1.

Table 1 – Basic properties of NEOSEPTA-AMH membrane¹³

Exchange capacity, mekv g ⁻¹	1.3 – 1.5
Thickness, m	0.25 × 10 ^{-3*}
Water content, g H ₂ O per g of dry membrane	0.186*
Electric resistance, Ω cm ⁻²	11.0 – 13.0
Transport number	0.98 <
Area in dialysis experiments, m ²	62.2 × 10 ^{-4*}

*Measured

Solution/membrane equilibrium

In order to determine the basic transport characteristics of the solution in the membrane, it is necessary to know the data on solution/membrane equilibrium. These data can be obtained by the procedure, which is based on the saturation of the membrane with the solution with subsequent extraction of the component into water.

The anion-exchange membrane of 25 – 30 cm² surface area (the membrane was cut into 4 – 6 pieces), which was kept in 0.5 mol l⁻¹ NaCl, was rid of salt by thorough washing in water, and then saturated with concentrated sulfuric acid (approx. 2 mol l⁻¹), with the aim to replace all Cl⁻ ions by anions of acid. After this treatment and after repeated thorough washing of the membrane in distilled water, the membrane was shaken in the solution of acid of known concentration for 17 hours. Then it was carefully wiped with filter paper to remove the solution adhering to the membrane surface, and repeatedly (4×) shaken in 25 ml distilled water for 2 h. The acid concentrations in, both, solutions and the extracts obtained were determined by micro-titration with 0.1 mol l⁻¹ NaOH. All the experiments were carried out at 20 °C.

Dialysis experiments

Dialysis of sulfuric acid was investigated in a two-compartment cell with stirrers. The experimental set-up is shown in Fig. 1.

At the beginning of each experiment, compartments I and II of the cell were filled with sulfuric acid and distilled water, respectively. The experiments were carried out at various initial acid concentrations and rotational speeds of the stirrers ($n^I = n^{II}$). The initial acid concentration was in the range from 0.1 to 2.0 kmol m⁻³, while the rotational speeds of the stirrers were changed in the interval from 1.17 to 9.17 s⁻¹. The initial liquid volume in both compartments was always 1 × 10⁻³ m³. In the

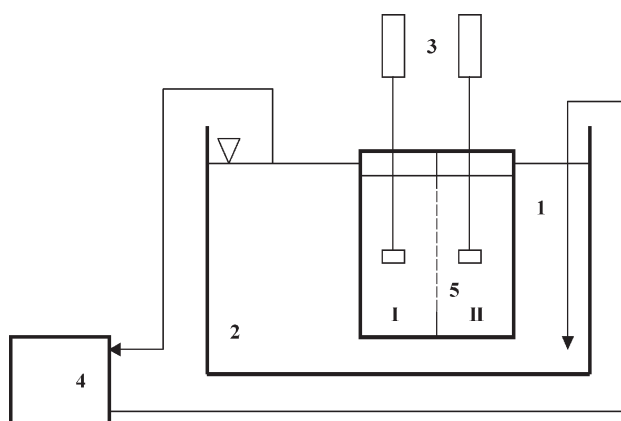


Fig. 1 – Scheme of experimental set-up: 1 – batch cell; 2 – thermostat reservoir; 3 – mixers; 4 – thermostat; 5 – membrane; I, II – compartments

course of each experiment, the acid concentration and the height of the liquid level (for the determination of the volume changes) in both compartments, were measured. The acid concentration was determined using titration with $0.1 \text{ mol l}^{-1} \text{ NaOH}$. The changes in the liquid level were measured using a modified micrometer screw with a needle. In such a way, the distance between the liquid level and the edge of the cell was measured. The duration of one experiment was dependent upon the initial acid concentration and rotational speed of stirrers – it was in the range from 96 to 101 h. The temperature was kept at a constant value of $20 \pm 0.5 \text{ }^\circ\text{C}$.

Data treatment and discussion

Solution/membrane equilibrium

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

Figure 2 shows the dependence of the 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 is always lower than that in the external solution, and throughout the concentration range investigated it increases with increasing acid concentration in the external solution. The form of this dependence is very similar to that obtained in the case of a Neosepta-AFN membrane equilibrated with the same acid.⁶ But a detailed inspection reveals that H_2SO_4 concentration in an AMH membrane is lower than that in an AFN membrane. The experimental data on solution/membrane equilibrium were approximated by the following empirical equation

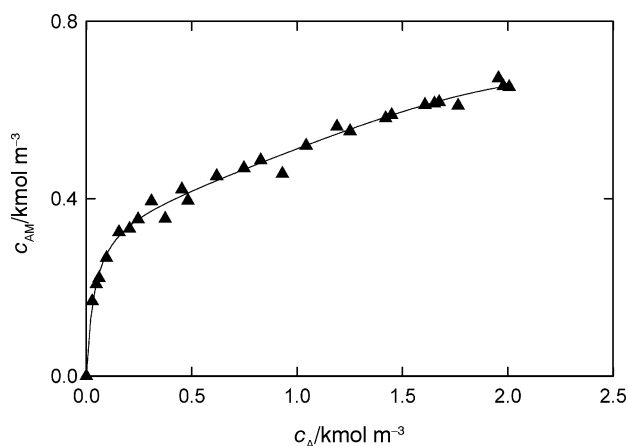


Fig. 2 – Dependence of H_2SO_4 concentration in membrane upon H_2SO_4 concentration in external solution: ▲ – experiment; — – calculated from Eq. (7)

$$c_{AM} = \frac{c_A}{p_1 + p_2 c_A + p_3 c_A^2 + p_4 c_A^3} \quad (7)$$

whose constants p_i ($i = 1, 2, \dots, 4$) were determined by a non-linear regression and they are presented in Table 2.

Table 2 – Constants in Eq. (7)

p_1	$\frac{p_2}{\text{m}^3 \text{ kmol}^{-1}}$	$\frac{p_3}{\text{m}^6 \text{ kmol}^{-2}}$	$\frac{p_4}{\text{m}^9 \text{ kmol}^{-3}}$	Range of c_A kmol m^{-3}	δ_t %
1.049×10^{-1}	2.639	-1.005	2.114×10^{-1}	0–2.0	3.29

The suitability of Eq. (7) was evaluated with the help of the mean quadratic relative error, $\delta_{\%}$, defined by Eq. (8).

$$\delta_{\%} = \sqrt{\frac{1}{m} \sum_{i=1}^m \left(\frac{c_{AM, \text{exp}}^i - c_{AM, \text{calc}}^i}{c_{AM, \text{exp}}^i} \right)^2} \cdot 100 \quad (8)$$

Dialysis experiments

During the dialysis experiments, the acid concentration in both compartments was recorded as a function of time. Typical courses of the acid concentration are shown in Fig. 3. In all the cases, dialysis of sulfuric acid proceeded in the following way: due to diffusion of H^+ , HSO_4^- and SO_4^{2-} ions through the membrane, the acid concentration in the compartment I decreased with time, while that in the compartment II increased until equilibrium, characterized by the identical acid concentrations on both sides of the membrane, was achieved.

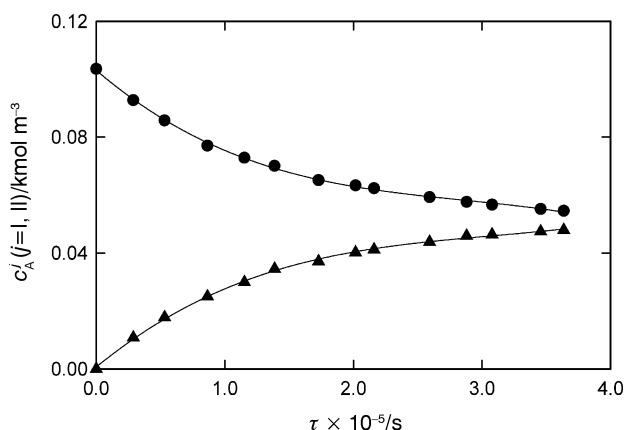


Fig. 3 – Dependence of H_2SO_4 concentration in compartment I (●) and II (▲) upon time: $n^I = n^{II} = 1.17 \text{ s}^{-1}$; $c_{A0}^I = 0.1 \text{ kmol m}^{-3}$

Fick's first law was used to treat all the dialysis experiments obtained. Its application supposes that the membrane and the acid solution inside it create a homogeneous phase. For that reason, the amount of sulfuric acid in the membrane was referred to the volume of the swollen membrane. Thus, the rate of mass transport in this membrane was evaluated in the term of apparent diffusivity of acid, which was considered to be a function of the acid concentration in the membrane – see Eq. (4). In the model used, we supposed the pseudo-steady state – $J_A^I = J_{AM} = J_A^{II}$.

The mass transfer coefficients in Eqs (1) and (3) were calculated from the equation⁶

$$Sh = C Re^{1/2} Sc^{1/3} \quad (9)$$

Modification of Eq. (9) taking into account the definition of Re number in stirring leads to the relation

$$k_L^j = C(n^j)^{1/2} (D_A^j)^{2/3} (\nu^j)^{-1/6} \quad j = I, II \quad (10)$$

The coefficients a_0 , a_1 , a_2 of the second degree polynomial (4), which approximates the dependence of apparent diffusivity of sulfuric acid upon its concentration in the membrane, were determined by the numerical integration of the basic differential eq. (5) with subsequent optimization. For this purpose, we used all time-dependencies of the acid concentration obtained experimentally at various initial acid concentrations and rotational speeds of the stirrers ($n^I = n^{II}$). The procedure used is given in detail elsewhere.⁶ The results, i.e. parameters a_0 , a_1 , a_2 and C , are presented in Table 3.

Figure 4 presents the dependence of diffusivity of sulfuric acid upon its concentration in the membrane. Here, the same dependence for the Neosepta-AFN membrane is presented, too. As can be

Table 3 – Coefficients a_i ($i = 0, 1, 2$) of polynomial (4)

$\frac{a_0}{\text{m}^2 \text{ s}^{-1}}$	$\frac{a_1}{\text{m}^5 \text{ s}^{-1} \text{ kmol}^{-1}}$	$\frac{a_2}{\text{m}^8 \text{ s}^{-1} \text{ kmol}^{-2}}$	C
4.378×10^{-19}	7.642×10^{-10}	-7.822×10^{-10}	2.47×10^2

seen from this figure, diffusivity of sulfuric acid in the AMH membrane is much lower than that in the AFN membrane – the difference between both the curves in Fig. 4 increases with increasing acid concentration. Furthermore, diffusivity of H_2SO_4 in the AFN membrane is still increasing with increasing acid concentration – in the concentration range investigated – while on the dependence $D_{AM} = f(c_{AM})$ for the AMH membrane a weak maximum at a concentration of 0.49 kmol m^{-3} can be observed. Moreover, a concentration range, in which diffusivity of the acid in the AMH membrane does not significantly change, can be identified – i.e. from 0.3 to 0.6 kmol m^{-3} .

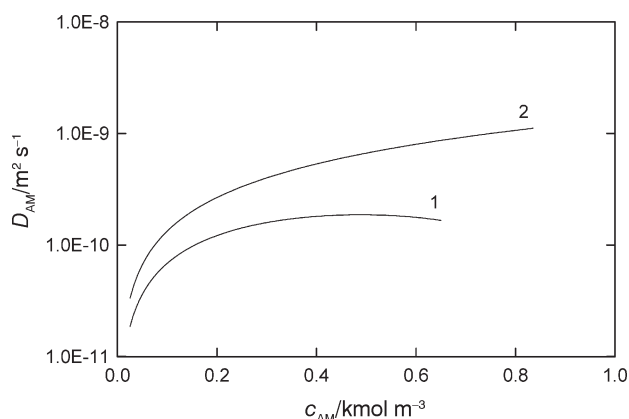


Fig. 4 – Dependence of apparent diffusivity of sulfuric acid upon its concentration in membrane: 1 – Neosepta-AMH membrane; 2 – Neosepta-AFN membrane

Conclusion

The transport of sulphuric acid through an anion-exchange membrane Neosepta-AMH was characterized by apparent diffusivity of acid in the membrane. This parameter, including its concentration dependence, was determined from the concentration-time dependencies obtained experimentally in a two-compartment batch cell. In the treatment of the basic data obtained, the model was used which describes the time-dependence of sulphuric acid concentration in the compartment with a higher acid concentration. The model developed takes into account mass transfer resistances in liquid films on both sides of the membrane and the solution/membrane equilibrium. The transport of sulphuric acid through the membrane is described by Fick's first law.

ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Education, Youth and Sports of the Czech Republic — Project No. MSM 0021627502.

Symbols

A	– surface area of membrane, m^2
a_0	– coefficient, $m^2 s^{-1}$
a_1	– coefficient, $m^5 s^{-1} kmol^{-1}$
a_2	– coefficient, $m^8 s^{-1} kmol^{-2}$
C	– constant
c	– molar concentration, $kmol m^{-3}$
D	– diffusivity, $m^2 s^{-1}$
J	– molar flux, $kmol m^{-2} s^{-1}$
k	– mass transfer coefficient, $m s^{-1}$
m	– total number of measurements
n	– rotational speed of stirrer, s^{-1}
n	– amount of substance, $kmol$
p_1	– coefficient
p_2	– coefficient, $m^3 kmol^{-1}$
p_3	– coefficient, $m^6 kmol^{-2}$
p_4	– coefficient, $m^9 kmol^{-3}$
Re	– Reynolds number
Sc	– Schmidt number
V	– volume, m^3

Greek

δ	– thickness, m
$\delta_{\%}$	– mean quadratic relative error, %
ν	– kinematic viscosity, $m^2 s^{-1}$
τ	– time, s, h
ψ	– partition coefficient

Superscripts and subscripts

A	– related to component A, i.e. sulfuric acid
calc	– calculated value
exp	– experimental value
i	– related to liquid-membrane interface
L	– related to liquid
M	– related to membrane
I, II	– related to compartments I and II
°	– initial

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