

DIFFUSION DIALYSIS OF SULFURIC ACID IN A BATCH CELL

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The paper deals with the diffusion dialysis of sulfuric acid into water in a batch cell with a Neosepta-AFN anionselective membrane. The transport of sulfuric acid through the membrane has been quantified with respect to the dissociation of the acid by the dialysis coefficients for HSO_4^- and SO_4^{2-} ions. These coefficients have been determined by numerical integration of the basic differential equation describing the time dependence of sulfuric acid concentration in the dialysis cell with subsequent optimization of dialysis coefficients. Moreover, the membrane permeability coefficients for HSO_4^- and SO_4^{2-} ions and nondissociated sulfuric acid have been determined by the modified method of the Wilson diagram using the data about mass transfer in liquid for the given geometrical arrangement of cell.

The diffusion dialysis adopting ionselective membranes belongs among modern separation processes. Its considerable advantage consists in slight demands for energy consumption during its application. The diffusion dialysis with anionselective membranes finds industrial applications first of all in the recuperation of inorganic acids from exhausted galvanization baths which also contain the respective salts.

Basic information about the dialysis process can be obtained from experiments carried out in a batch cell¹⁻⁴. Some results concerning the dialysis of sulfuric acid are given e.g. in refs³⁻⁵, however, the dissociation of acid is not considered here. The aim of the present work is to elucidate the transport of the dissociated forms of H_2SO_4 through anionselective membrane with respect to the fact that the data on dialysis rate in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system can be considered to be reference data for dialysis in more complex systems involving sulfuric acid and its salts.

THEORETICAL

Taking into account the volume changes of liquid, we can express the decrease of mass amount of sulfuric acid in part I of dialysis cell with higher H_2SO_4 concentration by the following equation

$$V^I(\text{d}c_A^I/\text{d}\tau) + c_A^I(\text{d}V^I/\text{d}\tau) = -K_A A(c_A^I - c_A^{II}) . \quad (I)$$

In Eq. (1) K_A stands for the dialysis coefficient which can be expressed by means of the mass transfer coefficients k_L^j ($j = \text{I, II}$) and the membrane permeability coefficient P_A

$$1/K_A = 1/k_L^{\text{I}} + 1/P_A + 1/k_L^{\text{II}} . \quad (2)$$

Hence the reciprocal value of K_A represents the total resistance against the mass transfer, and in literature the dialysis coefficient K_A is sometimes referred to as the overall one.

If a system contains sulfuric acid or sulfuric acid with its salts, the anionselective membrane will transport the HSO_4^- and SO_4^{2-} ions formed by dissociation of sulfuric acid or sulfuric acid with its salts, respectively. The decrease of mass amount of HSO_4^- and SO_4^{2-} ions in part I of cell with higher acid concentration can be expressed by Eqs (3) and (4) whose form is similar to that of Eq. (1).

$$V^{\text{I}}(d[\text{HSO}_4^-]^{\text{I}}/d\tau) + [\text{HSO}_4^-]^{\text{I}}(dV^{\text{I}}/d\tau) = -K_1 A([\text{HSO}_4^-]^{\text{I}} - [\text{HSO}_4^-]^{\text{II}}) \quad (3)$$

$$V^{\text{I}}(d[\text{SO}_4^{2-}]^{\text{I}}/d\tau) + [\text{SO}_4^{2-}]^{\text{I}}(dV^{\text{I}}/d\tau) = -K_2 A([\text{SO}_4^{2-}]^{\text{I}} - [\text{SO}_4^{2-}]^{\text{II}}) . \quad (4)$$

In Eqs (3) and (4) K_1 and K_2 are the dialysis coefficients of HSO_4^- and SO_4^{2-} ions, respectively. The data⁶ on the protonation constants in the reactions $\text{HSO}_4^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4$ and $\text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{HSO}_4^-$ show that sulfuric acid is practically completely dissociated to the first degree ($\alpha_1 = 1$), the extent of dissociation to the second degree depending on its concentration ($\alpha_2 \leq 1$). Hence, the actual concentration of HSO_4^- and SO_4^{2-} ions in both parts of the cell can be expressed by means of the total concentration of acid, c_A^j ($j = \text{I, II}$) and the dissociation degree, α_2^j ($j = \text{I, II}$).

$$[\text{HSO}_4^-]^j = (1 - \alpha_2^j)c_A^j \quad j = \text{I, II} \quad (5)$$

$$[\text{SO}_4^{2-}]^j = \alpha_2^j c_A^j \quad j = \text{I, II} \quad (6)$$

Introduction of Eqs (5) and (6) into Eqs (3) and (4) and modification with respect to the time-dependent value of dissociation degree *alpiü 7°è* give Eq. (7) expressing the relation between the dialysis coefficients K_1 and K_2 .

$$K_2 = K_1 \frac{\alpha_2^I}{1 - \alpha_2^I} \frac{\{[\text{HSO}_4^-]^I - [\text{HSO}_4^-]^{\text{II}}\}}{\{[\text{SO}_4^{2-}]^I - [\text{SO}_4^{2-}]^{\text{II}}\}} - \frac{V^I}{A} \frac{1}{1 - \alpha_2^I} \frac{c_A^I}{\{[\text{SO}_4^{2-}]^I - [\text{SO}_4^{2-}]^{\text{II}}\}} \frac{d\alpha_2^I}{d\tau} \quad (7)$$

Summation of Eqs (3) and (4) and further modification respecting the conditions $c_A^I = [\text{HSO}_4^-]^I + [\text{SO}_4^{2-}]^I$ following from Eqs (5) and (6) lead to Eq. (8).

$$\frac{dc_A^I}{d\tau} = -\frac{K_1 A}{V^I} \{[\text{HSO}_4^-]^I - [\text{HSO}_4^-]^{\text{II}}\} - \frac{K_2 A}{V^I} \{[\text{SO}_4^{2-}]^I - [\text{SO}_4^{2-}]^{\text{II}}\} - \frac{c_A^I}{V^I} \frac{dV^I}{d\tau} \quad (8)$$

With experimental data on the time dependence of sulfuric acid concentration in both parts of the cell and of the solution volume in part I at our disposal we can determine the dialysis coefficients K_1 and K_2 for HSO_4^- and SO_4^{2-} ions from Eq. (8) and adopting Eqs (5), (6), (7) and the dialysis coefficient K_A for H_2SO_4 from Eq. (1) as well. This procedure is based on numerical integration of the differential equation (8) (or (1)) with subsequent optimization procedure. The procedure given presumes the knowledge of the dissociation degree α_2^j ($j = \text{I, II}$) which is connected with the dissociation constant of the acid.

EXPERIMENTAL

Dialysis Cell

The dialysis of sulfuric acid was investigated with the help of the same experimental apparatus as that given in ref.⁷ (Fig. 1). Its main part is a dialysis cell made of organic glass. The inner dimensions were 0.12 m \times 0.15 m \times 0.16 m (length \times width \times height). A vertical partition with the dimensions of 0.15 m \times 0.16 m and 15 mm thickness divided the cell into two approximately same parts

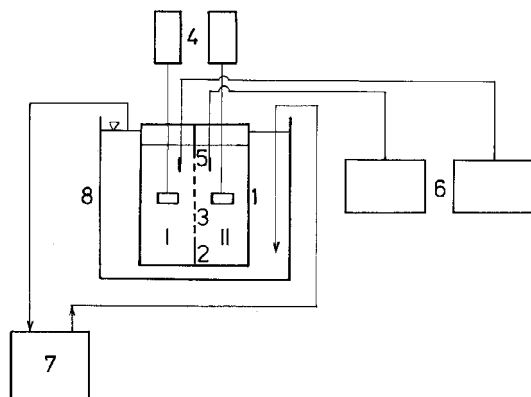


FIG. 1

Scheme of experimental apparatus: 1 dialysis cell; 2 partition; 3 membrane; 4 stirrers; 5 conductivity probes; 6 conductometers; 7 thermostat; 8 thermostated bath; I, II parts of cell

of 1.2 l volume each. In the middle of the partition there was a circular opening of 0.1 m diameter for fastening the membrane. In both parts the liquid was stirred with laboratory stirrers (four-paddle stirrers with oblique paddles – angle 65°, diameter 45 mm, height of paddles 15 mm) with rotation rate control. The shape and size of stirrers were designed to ensure “ideal” mixing of solution volumes in both parts of the cell.

In all the experiments we used the anionselective membranes Neosepta-AFN produced by the Japanese firm Tokuyama Soda Co. Ltd. The membrane area 62.2 cm², thickness 0.17 mm. The membranes were kept in 0.5 M NaCl solution and, before use, thoroughly washed with distilled water to remove the salt. After each experiment, the membranes were washed again and kept in NaCl solution for regeneration.

For the experiments, the parts I and II of the cell were filled with sulfuric acid of 0.1 kmol m⁻³ concentration and distilled water, respectively. At the beginning the volume of liquid in each compartment was 1 l, and equal level was adjusted by addition of glass beads. During the experiment the stirrer rotational speeds were the same ($n^I = n^{II}$), and at definite time intervals the changes in H₂SO₄ concentration and level height were determined to find the time dependence of volume changes at both sides of the membrane. The measurement was finished after attaining the equilibrium characterized by equal H₂SO₄ concentrations in both parts of the cell. The concentration of sulfuric acid was measured conductometrically. The changes in level height were measured from the upper edge of cell by means of a modified micrometer screw with a needle attached at the centre of the emerging piston. The time of one experiment depended on the stirrer rotational speed and varied from 32 to 49 h. The number of experimental points obtained from one experiment was 18 – 20. The temperature was kept at 20 ± 0.5 °C in all the experiments.

Beside the above mentioned ones we also carried out experiments concentrated on determination of the effect of mixing intensity upon the mass transfer in the cell. In this case the membrane was replaced by an impermeable partition covered with a layer of 2-naphthol at one side. At the beginning of experiment, the respective part of cell was filled with distilled water (1 l), and the time dependence of concentration of 2-naphthol was determined at constant stirrer rotational speed. The 2-naphthol concentration was determined by its reaction with *N*-chlorobenzenesulfonamide⁸.

Dialysis Coefficients K_1 , K_2

The dialysis coefficients K_1 , K_2 of HSO₄⁻ and SO₄²⁻ ions were determined by means of Eqs (7) and (8). In order to obtain the K_1 coefficient, the value of K_2 from Eq. (7) was introduced into Eq. (8). As it is

$$d\alpha_2^I/d\tau = (d\alpha_2^I/dc_A^I) (dc_A^I/d\tau) , \quad (9)$$

Eq. (8) can be modified to give the final form

$$\frac{dc_A^I}{d\tau} = - \frac{\frac{K_1 A}{1 - \alpha_2^I} \{ [\text{HSO}_4^-]^I - [\text{HSO}_4^-]^{II} \} + c_A^I \frac{dV^I}{d\tau}}{V^I \left\{ 1 - \frac{c_A^I}{1 - \alpha_2^I} \frac{d\alpha_2^I}{dc_A^I} \right\}} . \quad (10)$$

Similar procedure was used to obtain the differential equation (11) for determination of the dialysis coefficient K_2 .

$$\frac{dc_A^I}{d\tau} = - \frac{\frac{K_2 A}{\alpha_2^I} [\text{SO}_4^{2-}]^I - [\text{SO}_4^{2-}]^{II}] + c_A^I \frac{dV^I}{d\tau}}{V^I \left\{ 1 + \frac{c_A^I}{\alpha_2^I} \frac{d\alpha_2^I}{dc_A^I} \right\}} \quad (11)$$

The coefficients K_1 and K_2 were obtained from Eqs (10) and (11), respectively, by a procedure consisting of numerical integration of the differential equations (10) and (11) with subsequent optimization procedure. The calculation procedure for e.g. K_1 can be summarized in the following steps:

1. The calculation of value of the term $dV^I/d\tau$ from the second order polynomial approximating the time dependence of solution volume in part I of the cell.

2. The initial estimate of dialysis coefficient ($K_1^{(0)} = 2.8 \cdot 10^{-6} \text{ m s}^{-1}$).

3. Numerical integration of the differential equation (10) by the 4th order Runge-Kutta method with fixed integration step of 900 s and initial conditions of $c_A^I = c_{A0}^I$, $c_A^{II} = 0$ for $\tau = 0$. This numerical integration provides the calculated values of sulfuric acid concentration in part I, $c_{A,\text{calc}}^I$ at the time intervals of the experimental values. As the number of experimental values of H_2SO_4 concentration obtained from one measurement ($m = 18 - 20$) was smaller than that of the calculated values using the integration step of 900 s, the time coincidence of experimental and calculated values of H_2SO_4 concentrations was ensured by program. When choosing the magnitude of integration step we took into consideration the overall time of one experiment and the requirement of keeping the error of method below 1%. When solving Eq. (10), the following procedure was adopted to determine the actual concentrations of HSO_4^- ions in both parts of cell, the extent of dissociation to the second degree (α_2^I), and the derivative $d\alpha_2^I/dc_A^I$. The actual concentrations of HSO_4^- ions in both parts of the cell were determined from the overall concentration of sulfuric acid and dissociation degree α_2 (see Eq. (5)). The derivative $d\alpha_2^I/dc_A^I$ was determined numerically. The following iteration procedure was adopted to calculate the dissociation degree α_2 :

a) The initial estimate of ionic strength of solution at the given sulfuric acid concentration in part I of the cell, and/or in part II (at the beginning of calculation $J^{I,(0)} = 0.1 \text{ kmol m}^{-3}$ and $J^{II,(0)} = 0$, the ionic strength values determined in the preceding step were used for the initial estimates in the next step).

b) The calculation of dissociation constant K_{diss}^j , $j = \text{I, II}$ from the dependence $K_{\text{diss}} = f(J)$ obtained from the protonation constants of the reaction $\text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{HSO}_4^-$ published in ref.⁶. The values K_{diss}^j ($j = \text{I, II}$) were obtained by interpolating the tabulated values.

c) The calculation of dissociation degree α_2^j ($j = \text{I, II}$) from Eq. (12).

$$K_{\text{diss}}^j = ((1 + \alpha_2^j)/(1 - \alpha_2^j))\alpha_2^j c_A^j, \quad j = \text{I, II} \quad (12)$$

d) The calculation of concentrations of HSO_4^- and SO_4^{2-} ions from Eqs (5) and (6) and of H^+ ions from Eq. (13).

$$[\text{H}^+]^j = c_A^j(1 + \alpha_2^j), \quad j = \text{I, II} \quad (13)$$

e) The calculation of corrected value of ionic strength on the basis of concentrations of ions determined in the previous step

$$j^j = 0.5 ([\text{HSO}_4^-]^j + 4 [\text{SO}_4^{2-}]^j + [\text{H}^+]^j), \quad j = \text{I, II} . \quad (14)$$

f) The procedure of the points b) – e) was repeated until the relative change in ionic strength of solution was below 0.01%.

4. The calculation of sulfuric acid concentration in part II of the dialysis cell, $c_{\text{A,calc}}^{\text{II},i}$ from the mass balance

$$c_{\text{A,calc}}^{\text{I},i} V^{\text{I}} + c_{\text{A,calc}}^{\text{II},i} V^{\text{II}} = c_{\text{A0}}^{\text{I}} V_0^{\text{I}} . \quad (15)$$

5. The calculation of the objective function defined by Eq. (16).

$$F(K_1) = \sum_{i=1}^m [(c_{\text{A,exp}}^{\text{I},i} - c_{\text{A,calc}}^{\text{I},i})^2 + (c_{\text{A,exp}}^{\text{II},i} - c_{\text{A,calc}}^{\text{II},i})^2] \quad (16)$$

6. Realization of one step of the optimization procedure – obtaining of the corrected K_1 value. The optimization was carried out by means of the simplex method – the algorithm by Nelder and Mead⁹.

7. The procedure given sub 3 through 6 was repeated until reaching the minimum of the objective function (16).

The appropriateness of the procedure suggested for the calculation of dialysis coefficients K_1 and K_2 can be seen after comparison of experimental and calculated values of sulfuric acid concentration in both parts of cell in one measurement. To be more clear, the results are presented both graphically (see Fig. 2 for K_1) and numerically (see Table I for K_2). Figure 2 presents the time dependences of sulfuric acid concentrations in both parts of cell at the following conditions: $c_{\text{A},0}^{\text{I}} = 0.1 \text{ kmol m}^{-3}$, $n^{\text{I}} = n^{\text{II}} = 5.5 \text{ s}^{-1}$, $t = 20 \text{ }^\circ\text{C}$. Solid lines represent the dependences of sulfuric acid concentration calculated by the given procedure. The agreement between experimental and calculated values of

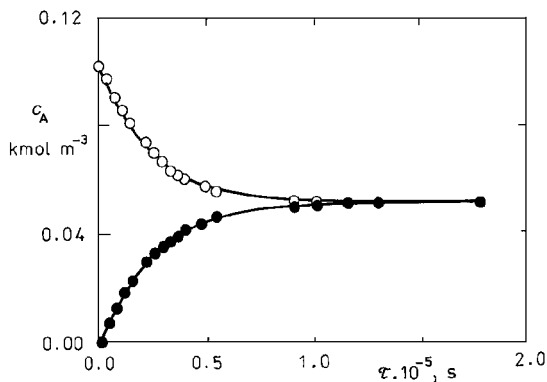


FIG. 2

Time dependence of sulfuric acid concentration in part I (○) and in part II (●) of the cell for $n^{\text{I}} = n^{\text{II}} = 5.5 \text{ s}^{-1}$, $c_{\text{A0}}^{\text{I}} = 0.1 \text{ kmol m}^{-3}$, $t = 20 \text{ }^\circ\text{C}$; — the values calculated from model (10)

H₂SO₄ concentrations indicates a good agreement between the model represented by Eq. (10) and experiment and also a good efficiency of the method for determination of K_1 .

Table I presents, beside the experimental and calculated values of H₂SO₄ concentrations in both parts, also the relative errors δ . The table is completed by the values of mean quadratic relative errors for both parts of cell. From the analysis of relative errors and mean quadratic relative errors it follows that there is a good agreement between the model (11) and experiment.

TABLE I

Comparison of experimental and calculated concentrations of H₂SO₄ using model (11) for $n^I = n^{II} = 5.5 \text{ s}^{-1}$ and $t = 20 \text{ }^\circ\text{C}$

$\tau \cdot 10^{-5}$ s	$c_{A,\text{exp}}^I$ kmol m ⁻³	$c_{A,\text{calc}}^I$ kmol m ⁻³	δ^I %	$c_{A,\text{exp}}^{II}$ kmol m ⁻³	$c_{A,\text{calc}}^{II}$ kmol m ⁻³	δ^{II} %
0.000	0.1016	0.1016	0.0	0.0000	0.0000	0.0
0.036	0.0969	0.0934	3.6	0.0073	0.0082	-12.3
0.072	0.0901	0.0872	3.2	0.0132	0.0145	-9.8
0.108	0.0852	0.0821	3.6	0.0186	0.0195	-4.8
0.144	0.0806	0.0779	3.3	0.0229	0.0237	-3.5
0.216	0.0733	0.0714	2.6	0.0296	0.0302	-2.0
0.252	0.0696	0.0689	1.0	0.0328	0.0328	0.0
0.288	0.0663	0.0667	-0.6	0.0353	0.0350	0.8
0.324	0.0630	0.0648	-2.9	0.0372	0.0369	0.8
0.360	0.0613	0.0631	-2.9	0.0390	0.0386	1.0
0.396	0.0597	0.0617	-3.4	0.0410	0.0400	2.4
0.468	0.0571	0.0593	-3.9	0.0435	0.0424	2.5
0.540	0.0553	0.0575	-4.0	0.0456	0.0442	3.1
0.900	0.0515	0.0529	-2.7	0.0497	0.0488	1.8
1.008	0.0511	0.0523	-2.3	0.0499	0.0494	1.0
1.152	0.0508	0.0518	-2.0	0.0504	0.0500	0.8
1.296	0.0505	0.0515	-2.0	0.0506	0.0503	0.2
1.764	0.0505	0.0510	-1.0	0.0506	0.0509	-0.6

Characteristics: $\bar{\delta}^I = 2.8\%$, $\bar{\delta}^{II} = 4.2\%$, $m = 18$

$$\bar{\delta}^j = \sqrt{\frac{1}{m} \sum_{i=1}^m (\delta^i)^2} \cdot 100 \quad j = \text{I, II,}$$

where

$$\delta^i = \left(c_{A,\text{exp}}^i - c_{A,\text{calc}}^i \right) / c_{A,\text{exp}}^i \cdot 100 \quad i = 1, 2, \dots, m.$$

of dialysis coefficients K_1 , K_2 , and K_A obtained from repeated experiments lie in the range of 1.8 – 7.6%, the mean error is 4.7%. From Fig. 3 it is obvious that the values of K_1 coefficient lie in the region from $2.5 \cdot 10^{-6}$ to $3.9 \cdot 10^{-6} \text{ m s}^{-1}$; the K_2 coefficients attain lower values than K_1 , lying in the range from $1.9 \cdot 10^{-6}$ to $3.0 \cdot 10^{-6} \text{ m s}^{-1}$. The values of dialysis coefficient for H_2SO_4 are close to those of K_1 – in the interval of stirrer rotational speeds investigated the values of dialysis coefficient for H_2SO_4 are lower than those for HSO_4^- ions by about $0.2 \cdot 10^{-6} \text{ m s}^{-1}$. The graphical representation in Fig. 3 also shows that all the coefficients are favourably affected by increased intensity of mixing of liquid in both parts of cell.

The coefficients K_1 , K_2 , and K_A are interrelated by Eq. (18) which can be obtained from Eqs (1), (3), and (4).

$$K_A = (K_1\{[\text{HSO}_4^-]^I - [\text{HSO}_4^-]^{II}\} + K_2\{[\text{SO}_4^{2-}]^I - [\text{SO}_4^{2-}]^{II}\})/(c_A^I - c_A^{II}) \quad (18)$$

The possibility of calculation of the dialysis coefficient K_A from Eq. (18) was verified with the use of the values obtained for the dialysis coefficients K_1 and K_2 in all the experiments realized. It was found that the coefficients K_A calculated from Eq. (18) agreed well with those calculated by the method of numerical integration of the differential equation (1) with subsequent optimization of K_A . The differences in K_A values calculated by the two procedures are small and do not exceed 0.8%.

The quantity characterizing the membrane–component system is the membrane permeability coefficient P for the given component. This coefficient is frequently determined from the modified Wilson diagram¹ which represents the dependence of reciprocal value of dialysis coefficient upon n^{-p} with the presumption of equality $k_L^I = k_L^{II}$. The extrapolation of straight lines $K_j^{-1} = f(n^{-p})$ for $j = 1, 2, A$ for an infinitely high intensity of mixing of liquid, i.e. for $n^{-p} \rightarrow 0$ ($p > 0$), when $1/k_L^I$ and $1/k_L^{II}$ are close to zero, will provide the membrane permeability coefficient for the given component (see

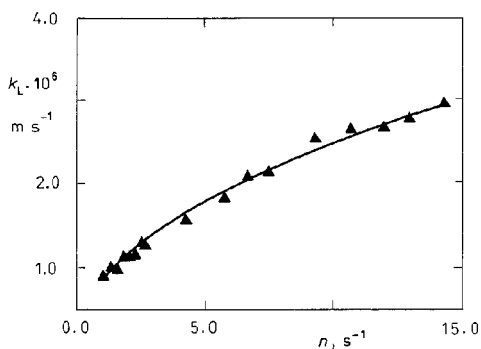


FIG. 4

The dependence of mass transfer coefficients in liquid upon stirrer rotational speeds for the system 2-naphthol–water: ▲ experiment, — calculated from correlation (20)

Eq. (2)). The value of exponent p is usually determined in such a way as to minimize the sum of squares of deviations between the reciprocal values of dialysis coefficients experimentally determined and calculated from the equation of straight line $K_j^{-1} = f(n^{-p})$ for $j = 1, 2, A$. In the present work, the membrane permeability coefficient has also been determined by means of the modified Wilson diagram. However, its construction adopts the p exponent value determined by nonlinear regression of independent data set k_L-n for the mass transfer in liquid during dissolution of 2-naphthol in water at the same experimental arrangement using the equation

$$k_L = B n^p \quad (19)$$

In the interval of stirrer rotational speeds from 1.17 to 14.33 s^{-1} the form of correlation (19) is as follows:

$$k_L = 8.24 \cdot 10^{-7} n^{0.47}, \quad (20)$$

where $[k_L] = m s^{-1}$ and $[n] = s^{-1}$.

The mean quadratic relative error for the k_L values obtained from experimental data and Eq. (17) and those calculated from Eq. (20) for a set of 17 frequencies is 4.0%. The dependence of mass transfer coefficient upon the stirrer rotational speed is presented in Fig. 4 giving the k_L vs n dependence calculated from correlation (20) as a solid line.

The modified Wilson diagrams for determination of membrane permeability coefficients for HSO_4^- and SO_4^{2-} ions and for H_2SO_4 are presented in Fig. 5. From the intercepts formed by the straight line $K_j^{-1} = f(n^{-p})$ for $j = 1, 2, A$ at the ordinate axis it was possible to determine the following values of the individual permeability coefficients: $P_1 = 4.82 \cdot 10^{-6} m s^{-1}$, $P_2 = 3.73 \cdot 10^{-6} m s^{-1}$, and $P_A = 4.60 \cdot 10^{-6} m s^{-1}$.

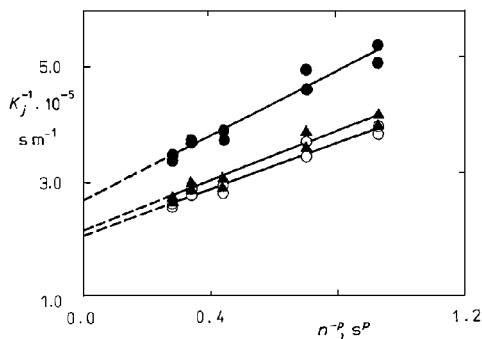


FIG. 5
Modified Wilson diagram for $p = 0.47$ for determination of membrane permeability coefficients for individual components: \circ HSO_4^- ; \bullet SO_4^{2-} ; \blacktriangle H_2SO_4 ; — fitted dependences; - - - extrapolation

Since the cited papers³⁻⁵ dealing with the dialysis of sulfuric acid do not consider the dissociation of the acid, it is impossible to compare the permeability coefficients (K_1 , K_2) with the published data. Besides, the works^{3,4} adopted different anionselective membranes, viz. Selemion DMT-1 (ref.³) and Graver Hi-Sep 70 (a membrane without ion exchanger centres⁴). The only paper allowing an at least approximate comparison of the permeability coefficient for H_2SO_4 is ref.⁵ where the same membrane was used as in the present work, viz. Neosepta-AFN. The values of P_A coefficient obtained for sulfuric acid from experiments in a continuous dialyzer⁵ are considerably affected by the acid concentration – the permeability coefficient P_A is decreased with increasing concentration of H_2SO_4 . For the lowest H_2SO_4 concentration used, i.e. 0.25 kmol m^{-3} , ref.⁵ gives the value of $P_A = 2.5 \cdot 10^{-6} \text{ m s}^{-1}$, which is lower by a factor of 2 than the P_A value obtained in the present work for the sulfuric acid concentration of 0.1 kmol m^{-3} .

CONCLUSION

Dialysis of sulfuric acid has been followed in the system of H_2SO_4 – H_2O in a batch cell with anionselective membrane. To describe the transport of sulfuric acid through the membrane, the paper suggests a model considering the dissociation of the acid. From experimental time dependences of sulfuric acid concentration in both parts of the cell and with the use of numerical integration of the basic differential equations with subsequent optimization it was possible to determine the values of dialysis coefficients for the HSO_4^- and SO_4^{2-} ions and for H_2SO_4 in nondissociated form at various rotational speeds of stirrers. Using the modified Wilson diagram and the data on the mass transfer in cell it was, furthermore, possible to determine the membrane permeability coefficients for HSO_4^- and SO_4^{2-}

$$i = 1, 2 \dots m.$$

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SYMBOLS

A	membrane area, m
B	constant in Eq. (19), m s^{p-1}
c	total concentration, kmol m^{-3}
J	ionic strength of solution, kmol m^{-3}
K_j	($j = 1, 2, A$) dialysis coefficient, m s^{-1}
K_{diss}	dissociation constant, kmol m^{-3}
k_L	mass transfer coefficient in liquid, m s^{-1}
m	number of experimental points in one measurement
n	stirrer rotational speed, s^{-1}
P	membrane permeability coefficient, m s^{-1}
p	exponent in Eq. (19), $p > 0$
t	temperature, $^{\circ}\text{C}$

V	volume, m^3
$[\]$	actual concentrations of dissociated forms of H_2SO_4 , $kmol\ m^{-3}$
α_1	dissociation extent to the first degree
α_2	dissociation extent to the second degree
δ	relative error, %
$\bar{\delta}$	mean quadratic relative error, %
τ	time, s

Indexes

A	related to sulfuric acid
B	related to 2-naphthol
calc	calculated value
exp	experimental value
0	initial
1	related to HSO_4^- ions
2	related to SO_4^{2-} ions
I	related to part I of the cell
II	related to part II of the cell
*	equilibrium

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