

Dialysis of NiSO₄ in Cylindrical Cation-Exchange Membrane

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The dialysis of nickel(II) has been studied in a batch dialyzer with forced convection of the feed and stripping (sulfuric acid) solutions inside and outside the cylindrical membrane. The model of ion transport through the cation-exchange membrane has been based on the phenomenological approach. Using this model the dialysis coefficient of the membrane has been obtained by extrapolation of the overall dialysis coefficients.

Ion-exchange membranes have the good characteristic of permitting continuous separation of the ions from the aqueous solution without changing the phase. One of those separation systems based on Donnan equilibrium is the Donnan dialysis, using the driving force of driving ions which have a considerable concentration difference. One of the basic relationships in the development of theory of membrane processes is the Nernst—Planck equation describing the flow of components in electrical field. The fact that the Nernst—Planck equation only describes mutually independent fluxes through a membrane restricts its validity. A number of authors [1—12] have dealt with the description of the processes taking place in the Donnan dialysis through an ion-exchange membrane in the last years.

The model of ion transport through a cation-exchange membrane used by us adopts a phenomenological description of this process. The theoretical model has been verified by monitoring the dialysis of nickel(II) sulfate/sulfuric acid in a batch arrangement with forced convection of both feed and stripping solution inside and outside the cylindrical membrane, respectively.

For verification of the theoretical model we selected NiSO₄ because nickel salts are present as a frequent constituent of an industrial waste and then it is possible to hope for an industrial utilization of this study. Further advantage of this selection is the possibility of the spectrophotometric monitoring of the course of dialysis in the range of visible light without a necessity of the interference with the dialysis process.

Dialysis process carried out on the cylindrical membrane has some advantages in comparison with that in a batch dialyzer with a flat membrane: *a*) the ratio of a membrane surface to a volume of feed and/or

stripping solutions is much larger, which speeds up the dialysis process considerably (*ca.* 30 h in comparison with *ca.* 5 d); *b*) it is possible to watch the course of dialysis continuously, by inserting a suitable sensor into the flow of the feed or the stripping solution.

THEORETICAL

In a phenomenological description of the Donnan dialysis in a batch dialyzer it is possible to write eqn (1) for the flux of substance in the dialyzed solution

$$-dc_i/dt = Ak_N X_i/V_D \quad (1)$$

where c_i means the concentration of component i , A is the membrane area, k_N is the overall dialysis coefficient representing the reciprocal value of the resistance of membrane and both adjacent laminar layers of liquid, and V_D is the total volume of the solution dialyzed. X_i represents the driving force of the process which can be expressed as the difference between the actual concentration c_i and concentration c_i^* representing the concentration of component in the dialyzed solution which is at equilibrium with the given composition of components in the dialyzer at the given time.

$$X_i = c_i - c_i^* \quad (2)$$

The c_i^* value for a system consisting of the dialyzed solution of sulfate of a bivalent cation and stripping solution of sulfuric acid can be calculated by solving a set of balance equations for the input and stripping solutions (eqns (3.1) through (3.4)) (the balance of the metal cations and protons); the indices D and S denote the dialyzed and stripping solutions, respectively.

$$[\text{Me}^{2+}]_{\text{D}} + [\text{MeSO}_4]_{\text{D}} = n^*(\text{Me}, \text{D})/V_{\text{D}} \quad (3.1)$$

$$[\text{Me}^{2+}]_{\text{S}} + [\text{MeSO}_4]_{\text{S}} = n(\text{Me}, \text{S})/V_{\text{S}} \quad (3.2)$$

$$[\text{H}^+]_{\text{D}} + [\text{HSO}_4^-]_{\text{D}} + 2[\text{H}_2\text{SO}_4]_{\text{D}} = 2n(\text{Me}, \text{D})/V_{\text{D}} \quad (3.3)$$

$$[\text{H}^+]_{\text{S}} + [\text{HSO}_4^-]_{\text{S}} + 2[\text{H}_2\text{SO}_4]_{\text{S}} = 2(n^0(\text{H}_2\text{SO}_4)V_{\text{S}}^0 - n(\text{Me}, \text{S}))/V_{\text{S}} \quad (3.4)$$

The calculation must also take into account the protonation constant of sulfuric acid, association constants of bivalent cation sulfates [13] (eqns (4.1) through (4.3)), and the Donnan equilibrium condition (eqn (4.4))

$$K_1 = a(\text{H}^+, \text{D}) \cdot a(\text{HSO}_4^-, \text{D})/a(\text{H}_2\text{SO}_4, \text{D}) \quad (4.1)$$

$$K_2 = a(\text{H}^+, \text{D}) \cdot a(\text{SO}_4^{2-}, \text{D})/a(\text{HSO}_4^-, \text{D}) \quad (4.2)$$

$$\beta = a(\text{MeSO}_4, \text{D})/(a(\text{Me}^{2+}, \text{D}) \cdot a(\text{SO}_4^{2-}, \text{D})) \quad (4.3)$$

$$\frac{a(\text{H}^+, \text{D})}{a(\text{H}^+, \text{S})} = \sqrt{\frac{a(\text{Me}^{2+}, \text{D})}{a(\text{Me}^{2+}, \text{S})}} \quad (4.4)$$

and the conditions of the electroneutrality for both parts of the dialyzer

$$[\text{H}^+]_{\text{D}} + 2[\text{Me}^{2+}]_{\text{D}} = [\text{HSO}_4^-]_{\text{D}} + 2[\text{SO}_4^{2-}]_{\text{D}} \quad (5)$$

The equations similar to these (eqns (4.1) through (4.3) and eqn (5)) are valid for the stripping solution (index S instead of index D is used).

This system of equations is nonlinear, hence it is impossible to analytically express the c_i^* values as a function of time or of c_i concentration. The problem had to be solved by applying some of numerical methods to eqn (1). As in expressing activities the activity coefficients cannot generally be considered unity, the extended Debye—Hückel relation has been adopted for the calculation. Although this made the calculation more complicated, the obtained results were considerably more precise.

Calculation of Dialysis Coefficient

The calculation of overall dialysis coefficient starts from the differential equation (1) in which the separation of variables is carried out, the virtual equilibrium concentration c_i^* being considered to be a function of the metal cation concentration in the dialyzed solution. If volume changes of the solution during the experiment are not considered, the calculation can be speeded up by calculating c_i^* only in a few points of the interval (c_i^∞, c_i^0) and using then the approximation by a suitable analytical function, e.g. the Lagrange

polynomial.

$$\int_{c^0}^c \frac{-dc_i}{c_i - c_i^*} = A \int_0^t \frac{k_{\text{N}}}{V_{\text{D}}} dt \quad (6)$$

If the indicated integration is carried out and/or if the table of integrals at the left-hand side of the equation is calculated for all the concentrations measured and the values of this integral are plotted against time, a linear dependence results after establishing of steady state at the membrane. Therefrom it is possible to calculate the k_{N} value after subtracting the slope value.

The ratio D/l is referred to as the dialysis coefficient of membrane, K_{M} , and its reciprocal represents the mass transfer resistance in the membrane alone. However, a model of dialysis must also take into account the resistances in diffusion films at both sides of the membrane. The total mass transfer resistance is then expressed as a sum of the partial resistances

$$1/k_{\text{N}} = 1/K_{\text{M}} + 1/K_{\text{L1}} + 1/K_{\text{L2}} \quad (7)$$

where K_{L1}^{-1} and K_{L2}^{-1} are mass transfer resistances in diffusion film at one and the other sides of the membrane. The k_{N} value is denoted as overall dialysis coefficient.

A computer program called "Dialysis" has been created for the evaluation of rate of the Donnan dialysis in the system of nickel(II) sulfate and sulfuric acid: it enables the calculation of the overall dialysis coefficient in the above-mentioned way. The program was assembled in the Turbo Pascal language and it is divided into several relatively independent units corresponding to individual programmed activities.

For determining the dependence of k_{N} on the flux intensity one can start from the analogy between heat and mass transfer and presume validity of the Wilson relation [14]:

In a through-flux arrangement the turbulence can be evaluated by the Reynolds number Re , which leads to the equation

$$1/k_{\text{N}} = 1/K_{\text{M}} + \text{const.}/\text{Re}^{0.8} \quad (8)$$

where the exponent 0.8 was determined by optimization procedure in Quatro Pro program, with maximal value of the regression coefficient.

For $\text{Re} \rightarrow \infty$ then it is

$$1/k_{\text{N}} = 1/K_{\text{M}} \quad (8.1)$$

Using this condition, the experimental k_{N} values can be extrapolated according to eqn (7) for $1/\text{Re}^{0.8} \rightarrow 0$ to find the dialysis coefficient K_{M} of the membrane.

EXPERIMENTAL

The measurements were carried out on a through-

Table 1. Dependences of Overall Dialysis Coefficients upon Re in Dialysis of NiSO₄ Solutions of Various Concentrations ($c(\text{Ni}) = c(\text{H}_2\text{SO}_4)$)

$c(\text{NiSO}_4)$ mol dm ⁻³	0.025	0.030	0.040	0.050
Re _D = Re _S	$k_N \cdot 10^4$ mol s ⁻¹			
1445	2.13	2.52	2.41	2.41
1515	2.20	2.58	2.47	2.48
1572	2.26	2.63	2.51	2.52
1675	2.37	2.69	2.59	2.63
1800	2.43	2.78	2.68	2.61
2050	2.58	2.96	2.83	2.94

flux dialyzer. The dialyzed and the stripping solutions were placed in separated thermostated graduated containers. The circulation of solution was ensured by peristaltic pumps IKA 20. These pumps produce considerable shocks which could negatively influence the performance of the dialyzer. Therefore, the loop – immediately after the pump – contained a bypass with a valve in order to suppress the shocks and to enable a more precise control of flow rate. The adjusted flow rate was checked experimentally before each dialysis run.

The dialysis itself was realized through a cylindrical cation-exchange membrane Nafion 810 connected by its end to a glass thermostated tube. The concentration changes in the dialyzed solution were measured spectrophotometrically using a Spekol 11 apparatus (Zeiss, Jena) with the use of a through-flow cell placed at the outlet side of the dialyzer. Before the cell, there was a simple device (of our own design) for removing bubbles. The cell itself was a glass tube of 5 cm length and 1 cm diameter with quartz glass windows enabling measurements in the UV region of spectrum. At the inlet side, the cell contained a partition directing the potentially present bubbles outside the light beam path during passing the cell. The cell was placed in a thermostated cell holder of the spectrophotometer and its constant position was secured by a stopper. The values of light transmittance of the dialyzed solution at the wavelength of 394 nm (corresponding to the absorption maximum of nickel(II) sulfate solution) were recorded by means of a recorder. The recording was used to evaluate the time dependence of absorbance, and hence the nickel(II) ion concentration, as it is given below.

Between individual measurements, the membrane was treated so as to be in a basic form at the beginning of the next measurement. Therefore, after finishing each measurement, the whole apparatus was repeatedly rinsed with distilled water, whereafter the stripping section inclusive of the storage container was filled with 0.005 mol dm⁻³ H₂SO₄ while the dialysis section was filled with distilled water. Thus the mem-

brane was transferred to the H⁺ form. Before the next experiment, the whole apparatus had to be rinsed with distilled water and then with the new solutions to be measured on that day.

Reynolds number was calculated by means of well-known term $Re = 4V'\rho/\pi d\mu$, where the values of density and viscosity are equal for the water ($\rho = 1 \text{ kg dm}^{-3}$, $\mu = 0.001 \text{ Pa s}$), inner diameter of membrane $d = 0.003 \text{ m}$. The volumetric flow rate was measured at the beginning and end of each experiment three times.

RESULTS AND DISCUSSION

In order to verify the theoretical model the dialysis of aqueous solutions of nickel(II) sulfate at the concentrations of 0.025 mol dm⁻³, 0.03 mol dm⁻³, 0.04 mol dm⁻³, and 0.05 mol dm⁻³ was chosen. The stripping solution was always a sulfuric acid solution of the same concentration as that used for the dialyzed NiSO₄ solution in the respective run. This choice minimized the volume changes due to osmotic phenomena during the dialysis. At the same time, this choice facilitated the determination of the precise NiSO₄ concentration value in both the input and stripping solutions at the time of infinity, as it follows from the theory that this concentration must be the same in both compartments of the dialyzer [15].

The dialysis of each NiSO₄/H₂SO₄ system of the chosen equal concentrations was repeated using a different value of the volumetric flow rate (*i.e.* different value of Re number) of both the solutions. This Re number was approximately the same for the dialyzed and the stripping solutions in the individual experiments.

The evaluation of experimental data and their above-mentioned computer treatment gave the values of the overall dialysis coefficients shown in Table 1.

A similar set of experiments were carried out at the constant Re_S, *i.e.* with varying NiSO₄ and H₂SO₄ concentrations and varying volumetric flow rate of the dialyzed NiSO₄ solution but with the constant flow rate of the stripping H₂SO₄ solution.

Table 2. Values of the Dialysis Coefficients K_M and K'_M

$c(\text{NiSO}_4)/(\text{mol dm}^{-3})$	$K_M \cdot 10^5/(\text{m s}^{-1})$	$K'_M \cdot 10^5/(\text{m s}^{-1})$
0.025	10.53	11.18
0.030	9.58	9.11
0.040	9.55	10.80
0.050	12.42	11.73

Extrapolation of the overall values k_N obtained for the dialysis coefficients according to eqn (8) gave the values of dialysis coefficients K_M and K'_M presented in Table 2.

From Table 2 it is obvious that the Reynolds number in the stripping solution has no significant effect upon the value of the dialysis coefficient. For the dialysis rate, the decisive factor is the Re number of the dialyzed solution.

CONCLUSION

The model suggested makes use of the phenomenological attempt for description of the transport of ions through cation-exchange membrane. Using the above theoretical model we calculated the values of overall dialysis coefficients for nickel(II) ions from the experiments carried out. In order to eliminate their dependence upon the volumetric flow rate, we carried out an extrapolation to obtain the value of the dialysis coefficient for nickel(II) ion at the infinite flow rate of both the stripping and dialyzed solutions. Moreover, it was found that the values of the dialysis coefficient obtained in another set of measurements carried out at a constant volumetric flow rate of the stripping solution were practically identical. Hence, the decisive influence upon the transport rate of ion through the membrane in the arrangement used by us prevails on the side of the solution dialyzed.

SYMBOLS

A	membrane area [m^2]
c_i	concentration of component [mol dm^{-3}]
c_i^*	concentration equilibrium with the composi-

	tion of dialyzer at the given moment [mol dm^{-3}]
[]	actual concentration [mol dm^{-3}]
a	activity
K_1, K_2	protonation constants of sulfuric acid
β	association constant of sulfate
K_M	dialysis coefficient of membrane [m s^{-1}]
K'_M	dialysis coefficient of membrane from experiments with $\text{Re}_S = 1445$ [m s^{-1}]
k_N	overall dialysis coefficient [m s^{-1}]
l	thickness of membrane [m]
Re	Reynolds number
index D	feed solution
index S	stripping solution

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