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**DIALYSIS OF NICKEL SULFATE
WITH SIMULTANEOUS MONITORING
OF CHANGES OF SOLUTIONS DIALYZED**

Marie HANDLÍŘOVÁ¹ and Pavel ČIČMANEC
Department of Physical Chemistry, University of Pardubice,
CZ-532 10 Pardubice

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The paper deals with dialysis of aqueous solutions of nickel sulfate against aqueous sulfuric acid through a cation-selective membrane NEOSEPTA CM-2 in batch arrangement. The concentration changes of both dialyzed and stripping solutions were monitored spectrophotometrically during the dialysis. At the same time, also the volume changes of both solutions were measured; these changes are due to the osmotic flow of water through the membrane caused by different concentrations of ions in the two solutions dialyzed. The experimental data were evaluated on the basis of a mathematical model based on phenomenological description of the process. Extrapolation from the dependence of total dialysis coefficients on stirring rate of both solutions gave the permeability coefficient of the membrane for the given system of NiSO₄/H₂SO₄.

¹ To whom correspondence should be addressed.

Introduction

Membrane separation methods have been studied recently by a number of authors because they belong among modern, little energy demanding and environment friendly techniques needed in processing and recuperation of industrial wastes. A number of authors have paid attention to Donnan dialysis whose driving force lies in concentration gradient. When the entering and stripping solutions have different concentrations, the dialysis is accompanied to a varying extent by osmotic flow of solvent (water) through the membrane. For instance, Narebska et al. [1] found that the main driving force in transport of NaCl solution through the perfluorinated membrane Nafion, which hinders the flow of chloride anions through the membrane, does not lie in their interaction with the negative charge of polymeric membrane matrix but in their interaction with water. A mathematical description of osmotic phenomena was also given by Cwirko and Carbonelli [2]. They compared the data modelled with the experimental ones published by Ng and Snyder [3], a good agreement being achieved. Fabiani, Scibona, and Scupa [4], who optically monitored the movements of menisci in calibrated pipettes, developed an interesting method enabling to monitor volume changes during electro dialysis. Similar methods for measuring volume changes in dialysis of KCl, NaCl, and LiCl were also adopted by Tasaka et al. [5], whereas Ktari and Auclair [6] followed the volume changes due to osmosis by weighing the solutions dialyzed. Also other authors [7] developed a special apparatus for precise weighing for their experiments dealing with mass transport through membrane. Rebois [8] determined transport numbers in dialysis through cellulose cation- and anion-exchange membranes, taking into account also the osmotic flows of water due to different concentrations of the electrolytes. Palatý [9] considered the volume changes when dealing with the transport of sulfuric acid through the anion membrane NEOSEPTA-AFN. The present study forms a continuation of Palatý's work. Among other authors dealing with osmotic flow during membrane separations are Hahn [10] and Okada et al [11].

The present paper solves the problem of Donnan dialysis at non-isochoric conditions by means of a phenomenological description of this process. A practical verification of the theoretical model was carried out by monitoring the dialysis of nickel sulfate against aqueous solution of sulfuric acid in a batch dialyzer with flat membrane.

Theoretical

When describing the Donnan dialysis phenomenologically, we can express the flow of Ni^{2+} ions through membrane by Eq. (1)

$$-\frac{dn_{\text{Ni}}}{Vdt} = \frac{A}{V} k_N X_i \quad (1)$$

where n_{Ni} is number of moles of Ni^{2+} , A means the surface area of membrane, k_N stands for overall dialysis coefficient of membrane, whose reciprocal value represents the mass transfer resistance of membrane and its adjacent liquid films. Symbol X_i is the driving force of process which can be expressed as the difference between the actual concentration $c_{\text{Ni}^{2+}}$ and virtual concentration $c_{\text{Ni}^{2+}}^*$ of the ion in equilibrium with the composition of both dialyzed solutions at any time interval [9]

$$X_i = c_{\text{Ni}^{2+}} - c_{\text{Ni}^{2+}}^* \quad (2)$$

The $c_{\text{Ni}^{2+}}^*$ value can be calculated from a system of equations [12] describing balances (of Ni^{2+} and H^+ ions) in solutions on both sides of the membrane, the subscripts D and S being used for the dialyzed and stripping solutions, respectively.

$$[\text{Ni}^{2+}]_D + [\text{NiSO}_4]_D = \frac{n_{\text{Ni},D}^*}{V_D} \quad (3)$$

$$[\text{Ni}^{2+}]_S + [\text{NiSO}_4]_S = \frac{n_{\text{Ni},S}}{V_S} \quad (4)$$

$$[\text{H}^+] + [\text{HSO}_4^-]_D + 2[\text{H}_2\text{SO}_4]_D = \frac{2n_{\text{Ni},D}}{V_D} \quad (5)$$

$$[\text{H}^+] + [\text{HSO}_4^-]_S + 2[\text{H}_2\text{SO}_4]_S = \frac{2(n_{\text{H}_2\text{SO}_4}^0 V_S^0 - n_{\text{Ni},S})}{V_S} \quad (6)$$

The calculation must also take into account the protonisation constant of sulfuric acid, stability constant of nickel sulfate [13], and the Donnan condition of equilibrium on the membrane (Eqs (7) through (13)).

$$K_1 = \frac{a_{\text{H}^+,D} a_{\text{HSO}_4^-,D}}{a_{\text{H}_2\text{SO}_4,D}} \quad (7)$$

$$K_1 = \frac{a_{\text{H}^+,S} a_{\text{HSO}_4^-,S}}{a_{\text{H}_2\text{SO}_4,S}} \quad (8)$$

$$K_2 = \frac{a_{\text{H}^+,D} a_{\text{SO}_4^{2-},D}}{a_{\text{HSO}_4^-,D}} \quad (9)$$

$$K_2 = \frac{a_{\text{H}^+,S} a_{\text{SO}_4^{2-},S}}{a_{\text{HSO}_4^-,S}} \quad (10)$$

$$\beta = \frac{a_{\text{NiSO}_4,D}}{a_{\text{Ni}^{2+},D} a_{\text{SO}_4^{2-},D}} \quad (11)$$

$$\beta = \frac{a_{\text{NiSO}_4,S}}{a_{\text{Ni}^{2+},S} a_{\text{SO}_4^{2-},S}} \quad (12)$$

Where $K_1 = 97.72$; $K_2 = 0.001$; $\beta = 208.9$ at 298 K at the standard concentration $c^0 = 1 \text{ mol l}^{-3}$.

$$\frac{a_{\text{H}^+,D}}{a_{\text{H}^+,S}} = \sqrt{\frac{a_{\text{Ni}^{2+},D}}{a_{\text{Ni}^{2+},S}}} \quad (13)$$

And the neutrality condition for both parts of dialyzer

$$[\text{H}^+]_D + 2[\text{Ni}^{2+}]_D = [\text{HSO}_4^-]_D + 2[\text{SO}_4^{2-}]_D \quad (14)$$

$$[\text{H}^+]_S + 2[\text{Ni}^{2+}]_S = [\text{HSO}_4^-]_S + 2[\text{SO}_4^{2-}]_S \quad (15)$$

This system of equations is non-linear, hence the n_{Ni}^* value, which is a function of real concentration $c_{\text{Ni}^{2+}}$ and time, cannot be expressed explicitly but must be solved numerically. The activities of ions appearing in the individual equations were calculated from the Debye-Hückel relationship.

Equation (1), which was used for calculation of the overall dialysis

coefficient, must be modified into the form which also contains the volume changes of system due to osmotic phenomena during dialysis

$$\int_{n_{Ni}^0}^{n_{Ni}} \frac{-dn_{Ni}}{n_{Ni} - n_{Ni}^*} = A \int_0^t \frac{k_N}{V_D} dt \quad (16)$$

This differential equation, which describes the time dependence of nickel concentration, can be numerically integrated provided the initial conditions, i.e. those for $t = 0$ and $n_{Ni} = n_{Ni}^0$, are known; in connection with a suitable optimization procedure it is then possible to determine the value of overall dialysis coefficient, k_N .

The overall dialysis coefficient, k_N , given in Eq. (1) is connected with the membrane permeability coefficient by the relationship

$$\frac{1}{k_N} = \frac{1}{K_M} + \frac{1}{K_{L1}} + \frac{1}{K_{L2}} \quad (17)$$

where K_M represents the membrane permeability coefficient proper, and K_{L1}^{-1} and K_{L2}^{-1} are resistances against ion transport in the Nernst diffusion layers in the respective sides of membrane. Their values decrease with increasing stirring (and, hence, flow) rates on both sides of the membrane. The dependence of k_N on flow intensity can be described quantitatively by means of the Wilson relationship [14]:

$$\frac{1}{k_N} = \frac{1}{K_M} + \frac{\text{konst.}}{n^p} \quad (18)$$

where n is number of revolutions of stirrer, and p is the exponent determined experimentally for the case of linear dependence of k_N^{-1} on n^{-p} . Extrapolation of this linear dependence to infinite stirring rate will give the permeability coefficient, k_M , as the intercept.

Experimental

The theoretical considerations were verified by dialysing nickel sulfate solution against stripping sulfuric acid solution in a batch dialyzer.

The apparatus consisted of two cells of 1 dm³ volume each, separated by a

diaphragm formed by NEOSEPTA-CM2 membrane with the active surface area of 62.64 cm^2 , the electric resistance of $2 - 3 \text{ } \Omega \text{ cm}^{-2}$, and the thickness of 0.15 mm ; the water content in membrane was 0.35 g per g of dry membrane. These physical characteristics given by the manufacturer were verified experimentally. The whole dialyzer was placed in a bath kept at $25 \pm 0.1 \text{ }^\circ\text{C}$. The concentration changes in the course of dialysis were monitored spectrophotometrically in both the solutions, using a Hewlett-Packard apparatus at the wavelength of 394 nm . The solutions in both cells were always stirred at the same rate, the rate being varied ($300, 500, 600,$ and 960 rpm) to obtain the dependence of dialysis coefficient on rate of stirring.

The volume changes of the solutions in dialyzer were measured, after trying several methods, by means of estimating the surface level height with a micrometric screw and subsequent calculation of volume from a calibration equation. The accuracy of measurements was sufficient (ca 1 ml) within a broad range of volume changes.

Results and Discussion

The theoretical relationships were verified by means of measurements of dialysis of nickel sulfate, whose concentration always was 0.1 mol l^{-1} , with stripping solutions of sulfuric acid, whose concentrations in the individual sets of experiments were $1.0, 0.5, 0.1,$ and 0.05 mol l^{-1} .

The dialysis of each $\text{NiSO}_4/\text{H}_2\text{SO}_4$ system was repeated with different stirring rates (always equal in both solutions): $300, 500, 600,$ and 960 rpm .

After evaluating the experimental data we assembled a computer program "Dialýza" for processing the data in the way described in Theoretical. The overall dialysis coefficients obtained are presented in Table I.

Extrapolation of these overall dialysis constants according to Eq. (18) using the exponent $p = 1.2$ gave the membrane permeability coefficient K_M (Table II).

Tab. I Overall dialysis coefficient k_N

Stirring rate, rpm	H_2SO_4 concentration, mol l^{-1}				
	1.0	0.5	0.1	0.05	0.01
$k_N \times 10^6, \text{ m s}^{-1}$					
300	0.570	0.791	0.266	0.202	0.140
500	1.17	0.978	0.268	0.277	0.085
600	1.30	1.07	0.499	0.350	0.090
960	1.34	1.00	0.493	0.350	0.154

The value of exponent p was determined by the way of trial and error: it was chosen from the interval of 0.1 – 1.5, and the respective theoretical course of dependence according to Eq. (18) was examined for the best fit with the experimental data by means of the regression coefficient.

Tab. II Permeability coefficient K_M

$c_{\text{H}_2\text{SO}_4}$, mol l ⁻¹	1.00	0.50	0.10	0.05	0.01
$K_M \times 10^7$, m s ⁻¹	10.50	12.30	7.02	7.42	5.92

It turned out that above a certain stirring rate the dialysis rate is affected by stirring only little, the difference between overall dialysis coefficients at 600 and 960 rpm being within experimental error. An exception is the experiments carried out with 0.01 M H₂SO₄, where the dialysis is slow and the effect of stirring is significant at all the rpm values examined. It can also be presumed that at the lowest stirring rate, where the dialysis is very slow too, the effect of osmotic flow becomes more significant, especially so at higher concentrations of the stripping solution, due to which the dialysis is slowed down even more.

Conclusion

We studied the membrane dialysis of 0.1 M NiSO₄ solution in a batch dialyzer against sulfuric acid of different concentrations, taking into account the volume changes of both solutions due to osmotic flow at different concentrations of dialyzed and stripping solutions. The evaluation of data gave the values of the membrane permeability constant for the NiSO₄/H₂SO₄ system; although these values obtained with different concentrations somewhat differ, they, nevertheless, provide a more accurate value of dialysis rate than that ignoring the osmotic flow.

Symbols

A	membrane area, m ²
a	activity
c_i	concentration of the component, mol l ⁻¹
c_i^*	concentration equilibrium with the composition of the dialyzer at given moment, mol l ⁻¹
D	diffusivity coefficient, m ² s ⁻¹
K_{L1}, K_{L2}	mass transfer coefficients in diffusion films, m s ⁻¹
K_M	coefficient of permeability, m s ⁻¹

K_N	overall dialysis coefficient, m s^{-1}
K_1, K_2	protonation constants of sulfuric acid
l	thickness of membrane, m
n	mole number, mol
n	stirring velocity, min^{-1}
t	time, s
V	volume, l
β	stability constant of sulphate
[]	actual concentration, mol l^{-1}

Indexes

D	referred to feed solution
S	referred to stripping solution

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