

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
1(1995)

**A STUDY OF INFLUENCE OF ALKALI CATIONS
ON DIALYSIS RATE OF NICKEL(II) SULFATE**

Marie HANDLÍŘOVÁ and Jaroslav MACENAUER
Department of Physical Chemistry

Received September 19, 1994

The dialysis rate of nickel(II) sulfate in a stirred batch dialyser through the cation exchange membrane Nafion 427 has been measured using aqueous solutions of alkali sulfates or sulfuric acid as a stripping solution. The influence of stirring velocity in the feed and stripping solutions on the transport rate of nickel(II) cations through the membrane has been studied. The individual values of dialysis coefficients of the membrane have been evaluated using the Wilson diagram. The time dependences of concentration of nickel(II) cations have been measured spectrophotometrically at the wavelength of 394 nm.

It has been concluded that the dialysis coefficients K_M^j ($j = H^+, K^+, Na^+, Li^+$) of the membrane depend on the character of the cation and follow the order

$$K_M^{H^+} > K_M^{K^+} > K_M^{Na^+} > K_M^{Li^+}$$

This order does not agree with the expected reverse order of the radii of cations. The change in the order of cations is connected with the hydration number of the cations.

Introduction

In the last years, the membrane processes have been the most important ones for industrial separation of a variety of components such as organic, inorganic and radioactive compounds or metal ions from their aqueous solutions. The aim of membrane processes is the separation of compounds which are present in various systems i.e. purification of solutions from undesirable admixtures or the enrichment of the desirable compounds. The transport of a solute through the membrane can be affected by different forces, such as e.g. pressure, electric potential, or chemical potential differences. Among the processes based on the last driving force the Donnan dialysis through cation exchange membranes is very important. The static or dynamic flow model was used for studies of this process by many authors¹⁻⁵ with the purpose of elucidation and quantification of its regularity. The present work deals with the dialysis of nickel(II) sulfate aqueous solution as a feed solution and alkali metal sulfates as a stripping solution in a stirred batch dialyser with a cation exchange membrane NAFION 427.

Experimental

The batch dialyser used consists of two compartments (volume 1 dm³ each), which are separated by a cation exchange membrane NAFION 427 with the active area of 62.24 cm², thickness of 0.43 mm. The dialyser was thermostated in a water bath at 25 ± 0.1 °C. The feed and stripping solutions in both the compartments were intensively stirred. The concentration changes of nickel(II) sulfate in the feed and stripping samples were measured spectrophotometrically by means of the Hewlett-Packard Spectrophotometer 8452 A at the wavelength of 394 nm. After the measurement these samples were returned into the dialyser. In order to prevent volume changes during the measurement, the initial concentrations of nickel(II) cation in the feed and alkali cation in the stripping solutions were taken equal, $c_{Ni}^o = c_{L2}^o = 0.1M$ where c_{Ni}^o and c_{L2}^o are initial concentrations in the feed and stripping compartments, respectively. The stirring velocity was 190, 540, 800 and 1038 rpm in the individual experiments. In all the cases, the feed solution was aqueous nickel(II) sulfate, the stripping solutions were aqueous solutions of lithium, sodium, and potassium sulfates or sulfuric acid.

Results

For the comparison of the influence of the nature of alkali cation on the rate of nickel(II) sulfate dialysis it was necessary to estimate the dialysis coefficients of the systems NiSO₄/Li₂SO₄, NiSO₄/Na₂SO₄, NiSO₄/K₂SO₄ and, for a more

complete insight into this problem, the $\text{NiSO}_4/\text{H}_2\text{SO}_4$ system was investigated, too. The time dependences of NiSO_4 in the feed and the stripping compartments measured at the various rates of stirring are described by the flow equations:

$$-\frac{dn_{N1}}{dt} = K_N A (c_{N1} - c_{Nr}) \quad (1)$$

$$\frac{dn_{N2}}{dt} = K_N A (c_{N1} - c_{Nr}) \quad (2)$$

where dn_{N1}/dt represents the nickel(II) cation rate of transport through the membrane from the feed to the stripping compartment and dn_{N2}/dt is the transport rate of the same cation in the opposite direction. K_N is the overall dialysis coefficient at the given rate of stirring, A is the effective membrane surface, c_{N1} and c_{N2} represent the actual concentrations of Ni(II) in the feed and stripping compartments and c_{Nr} is the equilibrium concentration of nickel(II) cation in this system. The typical dependence of the concentration of c_{N1} on time is given in Fig. 1.

The number of moles n_{N1} or n_{N2} can be expressed by the product $n_{Nj} = c_{Nj} V$ ($j = 1, 2$). Then we have

$$\frac{dn_{Ni}}{dt} = \frac{dc_j}{dt} V + c_j \frac{dV}{dt} \quad (3)$$

If the volume changes during the course of dialysis are negligible, the second term at the right-hand side of Eq.(3) is negligible. The change of the number of moles with time, dn_j/dt , can be replaced by the derivative dc_j/dt . With these simplifying assumptions we obtain the differential linear equation of the 1. order

$$-\frac{dc_{N1}}{dt} = K_N \frac{A}{V} (c_{N1} - c_{Nr}) \quad (4)$$

and after integration of Eq. (4), we obtain the expression

$$\ln \frac{c_{N1}^o - c_{Nr}}{c_{N1} - c_{Nr}} = K_N \frac{A}{V} t \quad (5)$$

Plotting the term on the left-hand side of Eq.(5) (denoted as $\ln z$ in Fig. 1) versus time gives a line with the slope $K_N A/V$. For example, this linear dependence for the dialysis system $\text{NiSO}_4/\text{K}_2\text{SO}_4$ can be seen in Fig. 1.

The equilibrium concentration of nickel(II) cations which is necessary for the evaluation of experimental data with the help of Eq. (5) can be obtained using a calculation procedure which is described in Ref.⁶ In our case, the set of non-linear algebraic equations was suggested on the basis of the equilibrium

conditions. The Donnan equilibrium condition, the dissociation constants of sulfuric acid and the stability constants of the salts, the neutrality condition in solutions on both sides of the membrane, and the balance equations for the ions transported through the membrane were taken into account. The set of these equations reads as follows:

$$\frac{X_3}{Y_3} = \left(\frac{X_1}{Y_1} \right)^{1/2} \quad (6)$$

$$\beta_1 = \frac{X_2}{X_1 X_8} \quad \beta_1 = \frac{Y_2}{Y_1 Y_8} \quad (7a,b)$$

$$\beta_2 = \frac{X_4}{X_3^2 X_8} \quad \beta_2 = \frac{Y_4}{Y_3^2 Y_8} \quad (8a,b)$$

$$K_1 = \frac{X_5 X_6}{X_7} \quad K_1 = \frac{Y_5 Y_6}{Y_7} \quad (9a,b)$$

$$K_2 = \frac{X_5 X_8}{X_6} \quad K_2 = \frac{Y_5 Y_8}{Y_6} \quad (10a,b)$$

$$2 X_1 + X_3 + X_5 = 2 X_8 + X_6 \quad (11a)$$

$$2 Y_1 + Y_3 + Y_5 = 2 Y_8 + Y_6 \quad (11b)$$

$$c_1^o V_1 = V_1 (X_2 + X_8 + X_6 + X_4 + X_7) \quad (12a)$$

$$c_2^o V_2 = V_1 (Y_2 + Y_8 + Y_6 + Y_4 + Y_7) \quad (12b)$$

$$c_{Ni}^o V_1 = V_1 (X_1 + X_2) + V_2 (Y_1 + Y_2) \quad (13a)$$

$$c_{L2}^o V_2 = V_1 (X_3 + 2 X_4) + V_2 (Y_3 + 2 Y_4) \quad (13b)$$

The symbols X and Y refer to the feed and stripping compartments $[\text{Ni}^{2+}] = X_1$ or Y_1 ; $[\text{NiSO}_4] = X_2$ or Y_2 ; $[\text{L}^+] = X_3$ or Y_3 ; $[\text{L}_2\text{SO}_4] = X_4$ or Y_4 ; $[\text{H}^+] = X_5$ or Y_5 ; $[\text{HSO}_4^-] = X_6$ or Y_6 ; $[\text{H}_2\text{SO}_4] = X_7$ or Y_7 ; $[\text{SO}_4^{2-}] = X_8$ or Y_8 . The stability constants¹³ $\beta_{Li} = 4.365$; $\beta_{Na} = 5.012$; $\beta_K = 7.079$; $\beta_{Ni} = 208.9$; $K_1 = 97.72$; $K_2 = 0.001$ at 298 K, c_1^o or c_2^o mean the total sulfate concentration in the feed or stripping compartments.

The equilibrium concentrations of Ni(II), c_{Ni} , can be estimated experimentally, too, by the analytical determination of the concentration of this ion in the feed and the stripping compartments at infinite time.

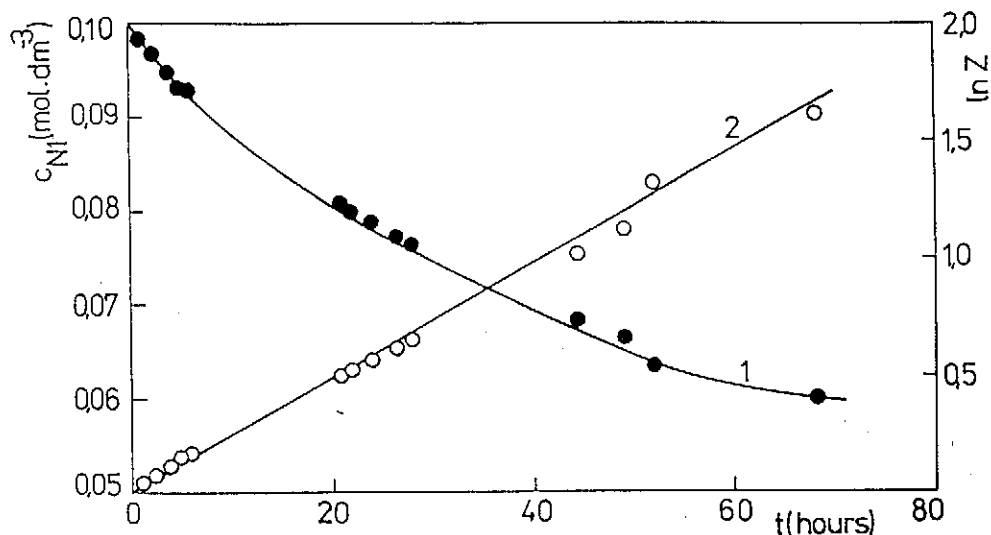


Fig. 1 The time dependence of Ni(II) concentration and its linearization in stripping compartment: $c_{Ni}^o = 0.1 \text{ M NiSO}_4$; $c_{L2}^o = 0.1 \text{ M K}_2\text{SO}_4$; $n = 1038 \text{ rpm}$; $T = 298 \text{ K}$:
 1 - c_{Ni} versus t ; 2 - $\ln \ln z$ versus t ; $z = (c_{Ni}^o - c_{Nr}) / (c_{Ni} - c_{Nr})$

For equal initial concentrations of the feed and stripping solutions, $c_{Ni}^o = c_{L2}^o$, and with the assumption that the volume changes during the course of the dialysis are negligible, the solution of Eq. (6) - (13) showed that c_{Nr} is, for all the systems studied, one half of the initial concentration of Ni(II) ions in the feed compartment, $c_{Nr} = c_{Ni}^o/2$. This result agrees well with the ion concentrations determined experimentally at the infinite time.

For all the systems, the values of overall dialysis coefficients, K_N , were calculated from the slopes of the straight lines obtained by linearization of Eq. (5) - see Table I. These coefficients depend on the flow velocity of the solution near the membrane, i.e. in fact, on the stirring rate which affects the thickness of the laminar layers on both sides of the membrane. The effect of the stripping solution used is perceptible, too. Kaufman⁷ and Wilson⁸ proposed Eq. (14) for the dependence of the value K_N on the flow rate:

$$\frac{1}{K_N} = \frac{1}{K_M} + \frac{const}{n^p} \quad (14)$$

where K_M is a dialysis coefficient independent of the stirring rate, n is the number of stirrer revolutions, and p is an empirical coefficient. The value of exponent p was determined so as to minimize the sum of squares of deviations between the reciprocal values of experimental K_N and that calculated by Eq. (14). Using an optimization procedure, we found the value of $p = 0.7$. Using Eq. (14), we estimated the values K_M by the non-linear regression analysis (see

Table I).

For a general description of the transport through the membrane we also used the Nernst-Planck equation (Eqs (15), (16)) with the assumption of ideal behaviour of all species (activity coefficients are equal to unity)

$$\dot{N}_L = -D_L \left[\frac{dc_L}{dx} + z_L c_L \frac{F}{RT} \frac{d\varphi}{dx} \right] \quad (15)$$

$$\dot{N}_{Ni} = -D_{Ni} \left[\frac{dc_{Ni}}{dx} + z_{Ni} c_{Ni} \frac{F}{RT} \frac{d\varphi}{dx} \right] \quad (16)$$

where z is a charge number and φ is a membrane potential.

Table I The overall dialysis coefficients K_N and membrane coefficients K_M : $c_{Ni}^o = c_{Li}^o = 0.1 M$; $Ni = NiSO_4$; $K_N, K_M, \text{cms}^{-1}$

Stirring rate rpm	$K_N \times 10^4$			
	Li_2SO_4	Na_2SO_4	K_2SO_4	H_2SO_4
190	4.33	5.86	6.55	12.36
540	4.46	6.54	7.20	13.04
800	4.56	7.77	8.51	14.26
1038	4.62	8.62	9.23	14.86
$K_M \times 10^4$	4.79	9.57	10.13	15.54

If the condition of electroneutrality in the membrane, the constant exchange capacity, and fixed-charge concentration of the membrane c_x are taken into account

$$z_L c_L + z_{Ni} c_{Ni} + c_x = 0 \quad (17)$$

and if we consider the both flows to be in a steady state,

$$\dot{N}_L z_L = -\dot{N}_{Ni} z_{Ni} \quad (18)$$

we obtain

$$\dot{N}_L = - \frac{D_L D_{Ni} (z_L^2 c_L + z_{Ni}^2 c_{Ni}) dc_L}{(z_L^2 c_L D_L + z_{Ni}^2 c_{Ni} D_{Ni}) dx} \quad (19)$$

By comparison of Eq. (19) with the 1st Fick law (Eq. (20))

$$\dot{N}_L = -D_{LNi} \frac{dc_L}{dx} \quad (20)$$

we obtain the interdiffusion coefficient D_{LNi}

$$D_{LNi} = \frac{D_L D_{Ni} (z_L^2 c_L + z_{Ni}^2 c_{Ni})}{z_L^2 c_L D_L + z_{Ni}^2 c_{Ni} D_{Ni}} \quad (21)$$

which is related to the dialysis coefficient K_M according to Eq. (22)

$$K_M = \frac{D_{LNi}}{d} \quad (22)$$

where D_{LNi} is the interdiffusion coefficient of alkali and nickel(II) cation and d is the membrane thickness.

The value of the individual diffusion coefficient is a function of the radius of the diffusing component according to the Einstein-Stokes equation⁹. At a constant value of the diffusion coefficient D_{Ni} , in our case, we can propose that the D_L will be inversely proportional to the radius r_L , which determines the adequate relation between K_M value and a radius of the counterion from the stripping solution in the dialysis of nickel(II) sulfate. With this assumption the values of the dialysis coefficients could follow the order



which is not fulfilled. As it can be seen from Table I, the values of the dialysis coefficients K_M obtained from the experiments follow the order

$$K_M^{H^+} > K_M^{K^+} > K_M^{Na^+} > K_M^{Li^+}$$

As the dialysis takes place in aqueous solutions it is necessary to consider the radii of the hydrated ions which penetrate the membrane. Taking into account the hydration numbers of these ions (Table II), we obtain the above-mentioned order of the dialysis coefficients.

Table II The radii¹⁰ r and the hydrate numbers¹¹ h of the ions

Ion	Li ⁺	Na ⁺	K ⁺	H ⁺
$r \times 10^{10}$, m	0.60	0.95	1.33	*
h	13.0	8.60	4.20	*

* Eigen¹² proposed the $H_3O_4^+$ structure ($H_3O \cdot 3H_2O$) in aqueous solution

From this fact we can derive a possible explanation of the order obtained for the dialysis coefficients K_M . It can be seen from Table II that the smallest hydrate number in aqueous solutions can be assigned to hydrogen having the highest dialysis coefficient. With increasing hydrate numbers of other ions in Table II the dialysis coefficients of these ions decrease (Table I). The role of the radius of the ion is negligible in this case because the radii of all these ions are very similar but hydration numbers are quite different.

Conclusion

The influence of the character of alkali metal cations on the dialysis rate of nickel sulfate has been studied. For the description of the transport rate a set of linear differential equations has been used based on the consideration that the driving force is given by the difference of the actual and equilibrium concentrations of Ni(II) ions. After solving this set we obtained an equation, which makes it possible to estimate the total dialysis coefficients from the experimental data. The overall dialysis coefficient estimated for the different flow conditions in the dialysis equipment have been studied mathematically. The value of the dialysis coefficient of the membrane Nafion 427 for alkali metal cation/nickel (II)cation systems has been estimated. A large influence of hydration number of the alkali metal cation on dialysis rate has been shown. The most extensively hydrated Li (I) cation is transported through the membrane most slowly and with the largest difficulties in spite of its very little radius as compared with the larger radii of Na and K ions.

References

1. Sandeaux J, Sandeaux R., Gavach C.: *J. Membr. Sci.* **59**, 265 (1991).
2. Schlögl R.: *Stofftransport durch Membranen*, Steinkopff, Darmstadt 1964.
3. Cwirko E.H., Carbonelli R.G.: *J. Membr. Sci.* **48**, 155 (1990).
4. Xue T., Longwell R.B., Osseo-Asare K.: *J. Membr. Sci.* **58**, 175 (1991).
5. Lake M.A., Melsheimer S.S.: *AIChE J.* **24**, 130 (1978).
6. Macenauer J, Handlířová M., Machač I.: *J. Membr. Sci.* **60**, 157 (1991).
7. Kaufmann T.G., Leonard E.F.: *AIChE J.* **14**, 110 (1968).
8. Wilson E.E.: *Trans. ASME* **37**, 47 (1915).
9. Pusch W.: *Desalination* **59**, 105 (1986).
10. Volkenštejn M.U.: *Struktura a fyzikální vlastnosti molekul*, ČSAV, Praha 1952.
11. Remy H.: *Anorganická chemie I*, Praha 1961.
12. Eigen M.: *Proc. Roy. Soc., London, Ser.A* **247**, 505 (1958).
13. Kotrlý S., Šucha L.: *Chemické rovnováhy v analytické chemii*, SNTL

Praha 1988.

Acknowledgements

This work was financially supported by the Grant Agency of the Czech Republic, Grant Project No. 104/93/2159.

Symbols

A	membrane area, cm^2
β	stability constant
c_N	nickel(II) bulk concentration, mol dm^{-3}
c_L	alkali cation bulk concentration, mol dm^{-3}
c_x	fixed-charge concentration, mol dm^{-3}
d	membrane thickness, cm
D	diffusion coefficient, $\text{cm}^2 \text{s}^{-1}$
F	Faraday constant, C m^{-1}
K	dissociation constant
K_M	membrane dialysis coefficient, cm s^{-1}
K_N	overall dialysis coefficient, cm s^{-1}
n	rotations per minute, min^{-1}
n_N	mole number of Ni(II), mol
p	empirical exponent
R	gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
T	temperature, K
t	time, s
V	volume, dm^3

Indexes

1, 2	feed or stripping compartment
o	initial
r	equilibrium