MODELLING OF MASS TRANSPORT AND CHEMICAL REACTION IN A DIAPHRAGM

Martin SCHLEIFF[a], Günther LEFELD[a], Hermann MATSCHINER[a] and Otomar ŠPALEK[b]

[a] *Martin Luther Universität, 4020 Halle/S., G.D.R. and*
[b] *Institute of Inorganic Chemistry,*
Czechoslovak Academy of Sciences, 160 00 Prague 6, Czechoslovakia

A mathematical model was proposed for the transport of ions in a diaphragm separating an acidic and an alkaline electrolyte. Besides an approximate analytical solution, a more exact numerical one was presented. The model permits the calculation of the position of the neutralization zone in the diaphragm, rates of transport of ions, and potential in the diaphragm. The dependence of the position of the neutralization zone on the composition of both electrolytes and on the current density was calculated for two technically important cases.

Many technically important electrolytic processes can be carried out only with the use of a diaphragm which suitably restricts mass transport between the electrode spaces. The influence of the current density and electrolyte concentrations in both spaces on the rate of transport of ions in the diaphragm and thus on the yield of the electrolytic process can be calculated on the basis of certain simplifying assumptions. The formulation of the problem and the results of calculations for the case of ion transport with no chemical reaction in the diaphragm are presented in the monograph by Roušar et al.[1]. In some industrially important systems, however the assumption of no chemical reaction in the diaphragm is not fulfilled. An example is the electrolysis of alkali metal chlorides, where the strongly alkaline electrolyte is separated from the weakly acidic anolyte.

Brumlev and Buck[2] formulated the transport equations for ions in a diaphragm in which a chemical reaction takes place, but solved them numerically only for the case without chemical reaction. Caldwell et al.[3] presented the concentration distribution of H^+ and OH^- ions in a diaphragm during electrolysis of alkali metal chlorides, however they did not solve all the necessary transport equations.

The present work deals with the distribution of the potential and concentrations of ions in a diaphragm in which neutralization of the anolyte and catholyte proceeds.

Formulation of the Problem

We shall consider the concentration and potential changes in the diaphragm only in the direction normal to its surface. The transport of ions in dilute solutions can

be described by the convective diffusion equation[1,4]

$$J_i = -D_i \frac{\partial c_i}{\partial x} - c_i u_i \frac{\partial \varphi}{\partial x} + c_i v .$$ (1)

The mass balance for i-th ion can be expressed as

$$\frac{\partial c_i}{\partial t} = -\left(\frac{\partial J_i}{\partial x} + \delta_i\right) ,$$ (2)

where the term δ_i gives the rate of consumption of species i in a unit volume of the diaphragm *per* unit time. For the case of neutralization $(H^+ + OH^- \rightleftarrows H_2O)$ the rates of consumption of OH^- and H^+ ions can be expressed by the rate equations

$$\delta_1 = \delta_2 = k_1 c_1 c_2 - k_2 ,$$ (3)

the water concentration being considered constant. The ratio of both rate constants is equal to the ionic product for water

$$k_2/k_1 = c_1 c_2 = K_w .$$ (4)

In a steady state, the left side of Eq. (2) is equal to zero and the gradient of the mass flux can be expressed by the equation

$$\frac{dJ_i}{dx} = \frac{d}{dx}\left(-D_i \frac{dc_i}{dx} - c_i u_i \frac{d\varphi}{dx} + c_i v\right) = -\delta_i ,$$ (5)

where the term δ_i is for OH^- and H^+ ions given by Eqs (3) and for non-reacting ions it is equal to zero.

The concentration distribution of n ionic species in the diaphragm is thus described by a system of n ordinary differential equations of the second order. These are supplemented by the equation of electroneutrality

$$\sum_{i=1}^{n} z_i c_i = 0 .$$ (6)

The boundary conditions are the concentrations of all ions present and the potential on both sides of the diaphragm.

The object of the calculation is the concentration distribution of the ions in a steady state along the x coordinate, the magnitudes of the mass fluxes, and the current

density

$$j = F \sum_{i=1}^{n} z_i J_i .$$ (7)

Properties of the Model Equations

By comparing Eq. (5) written for OH^- and H^+ ions and using Eq. (3) it turns out that the difference of the gradients of their fluxes is equal to zero, *i.e.* that the difference of their fluxes in the diaphragm is constant. Since the neutralization reaction is very rapid $(k_1 = 10^6 \, \text{m}^3 \, \text{mol}^{-1} \, \text{s}^{-1}, \; k_2 = 10^{-2} \, \text{mol} \, \text{m}^{-3} \, \text{s}^{-1})$, an equilibrium state is established nearly everywhere in the diaphragm except for the close proximity of the neutral zone, and one of the concentrations c_1 and c_2 is negligibly low. Except for the neutral zone, one of the mass fluxes J_1 and J_2 is also nearly equal to zero. The absolute value of the mass flux of OH^- ions on the alkaline side of the diaphragm is approximately equal to that of H^+ ions on the acidic side, but their directions are opposite to each other. The neutralization reaction proceeds mainly in the close proximity of the neutral zone, in a neutralization region.

The concentration gradients of H^+ ions in the acidic part of the diaphragm and of OH^- ions in the alkaline one are considerable, since the concentrations change in these regions from the boundary values nearly to zero $(10^{-3} \, \text{mol} \, \text{m}^{-3})$ in the neutral zone. At a low electrolyte flow through the diaphragm the transport of H^+ and OH^- ions is given mainly by diffusion, and Eq. (5) for these ions can be simplified to the approximate form

$$-D_1 \frac{\text{d}^2 c_1}{\text{d}x^2} = 0 , \quad 0 \leqq x \leqq x_0$$ (8a)

$$-D_2 \frac{\text{d}^2 c_2}{\text{d}x^2} = 0 , \quad x_0 \leqq x \leqq d$$ (8b)

with the boundary conditions

$$c_1(0) = c_{1c} \quad c_1(x_0) = 0$$ (9a)

$$c_2(x_0) = 0 \quad c_2(d) = c_{2a} .$$ (9b)

Further we have the condition of equality of both fluxes

$$D_1 \frac{\text{d}c_1}{\text{d}x} = -D_2 \frac{\text{d}c_2}{\text{d}x} .$$ (10)

The above equations allow us to estimate the position of the neutral zone in the diaphragm

$$x_0 = \frac{c_{1c}D_1 d}{c_{1c}D_1 + c_{2a}D_2}.\tag{11}$$

Thus, as a first approximation, the position of the neutral zone depends on the ratio of the concentrations of OH^- and H^+ ions on both sides of the diaphragm and on the ratio of their diffusion coefficients. Equation (11) gives in many cases a good estimate of the position of the neutral zone.

Numerical Solution of Model Equations

The system of equations describing the distribution of ionic concentrations and potential in the diaphragm can only be solved numerically. Therefore, the system of Eq. (5) written for all present ionic species was solved by the finite difference method using equidistant grid. A system of nonlinear equations was obtained for the concentration and potential values at the grid points. For n ionic species in solution and N grid points, we have to calculate $(n + 1)N$ unknowns in the same number of nonlinear equations. The solution was carried out by Newton's method using Gauss' algorithm. First a grid with relatively large steps was used (only 20 grid points), in further calculations the number of grid points was doubled; the zeroth approximation of the values at the grid points was obtained by interpolation of values from the preceding calculation. When a grid of 160 points was used, the relative error of the calculated values was lower than 10^{-5} except for those in the close proximity of the neutral zone. Its thickness was estimated as 2% of the diaphragm thickness; the remaining regions of the diaphragm are practically in an equilibrium state. In comparative calculations, where the rate constant k_1 was an order of magnitude lower $(10^5 \, m^3 \, mol^{-1} \, s^{-1})$, the neutralization zone was somewhat broader, but the values in the remaining regions of the diaphragm were nearly the same. The neutralization region plays in the solution of the model equations the role of a singular point, at which the derivatives are considerably unstable. We have to deal with solving a boundary value problem with an inner interval, in which the values of the functions change abruptly, the most important result of the calculations being the position of this interval; and this can be obtained in a satisfactory manner.

The diffusion coefficients were obtained by measurement of the rate of transport of ions in a laboratory electrolyser at a zero rate of flow of electrolyte through the diaphragm. The evaluation was based on Eq. (1), known ion concentrations on both sides of the diaphragm, and measured potential drop in it[5]. The resulting values are as follows:

$$D_1 = 7{\cdot}1 \,.\, 10^{-10} \, m^2 \, s^{-1}, \quad D_2 = 1{\cdot}25 \,.\, 10^{-9} \, m^2 \, s^{-1}, \quad D_3 = 2{\cdot}6 \,.\, 10^{-10} \, m^2 \, s^{-1},$$
$$D_4 = 1{\cdot}6 \,.\, 10^{-10} \, m^2 \, s^{-1}, \quad D_5 = 1{\cdot}8 \,.\, 10^{-10} \, m^2 \, s^{-1}.$$

Ionic mobilities were calculated from the Nernst–Einstein relation

$$u_i = z_i F D_i / RT. \tag{12}$$

The calculations were carried out on an ES 104 type computer (G.D.R.) and the time of calculation of a single concentration and potential distribution in the diaphragm was about 35 s.

Transport in a Diaphragm Separating Sulphuric Acid and Sodium Hydroxide Solutions

The calculation was carried out for the case of production of hydrogen peroxide involving cathodic reduction of oxygen and anodic oxidation of sulphate ions to peroxodisulphate. The anolyte consists of H_2SO_4 and Na_2SO_4, the catholyte of Na_2SO_4 and NaOH. The pressure difference between the anolyte and catholyte is considered equal to zero, hence the convective transport is neglected.
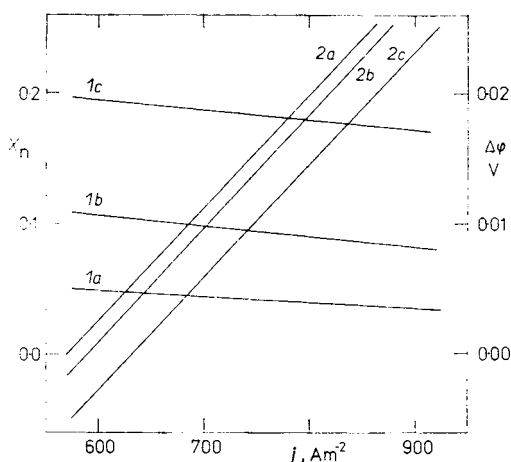
Fig. 1

Dependences of the position of the neutral zone, X_n (curves *1a—c*) and potential difference in the diaphragm, $\Delta\varphi$ (curves *2a—c*), on the current density, *j*. Catholyte: *a* $0.5M$ $Na_2SO_4 + 0.5M$ NaOH; *b* $0.5M$ $Na_2SO_4 + 1M$ NaOH; *c* $0.5M$ $Na_2SO_4 + 2M$ NaOH. Anolyte: $0.5M$ $Na_2SO_4 + 2.5M$ H_2SO_4
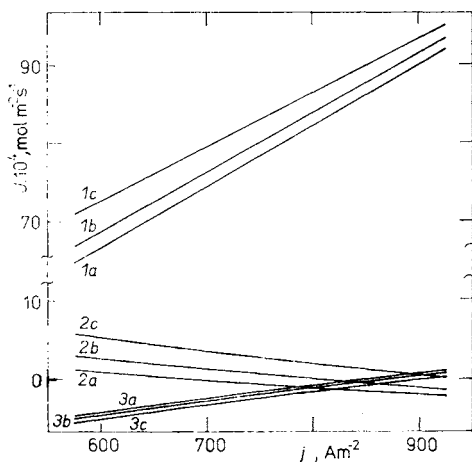
Fig. 2

Dependences of the flux, *J*, of *1* H^+ and OH^-, *2* Na^+, *3* SO_4^{2-} ions on current density, *j*. See Fig. 1 for solution composition

The calculated dependences of the coordinate of the neutralization zone and of the potential drop in the diaphragm on the current density are shown in Fig. 1, and the dependences of the ionic fluxes on the current density in Fig. 2. It can be seen from Fig. 1 that the position of the neutralization zone is shifted with increasing current density somewhat to the cathodic side. The ionic concentrations at the diaphragm surface have a greater influence, which is obvious also from the approximate equation (11); this gives nearly the same results as the numerical solution.

The fluxes of Na^+ and SO_4^{2-} ions change their direction in the given range of current densities. According to the concentrations at the diaphragm and current density, it is possible to find regions in which both fluxes have the same direction in spite of the opposite polarity of the ions. The flux of OH^- ions on the cathodic side and that of H^+ ions on the anodic side are much higher and increase with the current density. The potential drop in the diaphragm is relatively low in the given region of current densities, and below 600 A m^{-2} it acquires even negative values. The invalidity of Ohm's law is due to the existence of considerable concentration gradients in the diaphragm. In the given case, where a chemical reaction proceeds in the diaphragm, the course of the potential is not monotonous as follows from Figs 3 and 4, calculated for different composition of the electrolytes on both sides of the diaphragm. The courses of the concentrations of ions in the diaphragm are approximately linear between the surface of the diaphragm and the neutralization zone, where the concentration gradients change markedly owing to different mobilities of H^+ and OH^- ions. The numerical calculations indicate that the concentration profiles of these ions are somewhat concave, *i.e.* the gradients are higher at the neutralization zone than at the diaphragm surfaces. Also the absolute value of the potential gradient is highest in the neutralization zone. The concentration profiles in the diaphragm are independent of the effective diffusion coefficients ($i.e.$ parameters of the diaphragm), but depend on the ratio of the diffusion coefficients, especially of OH^- and H^+ ions.

Transport in a Diaphragm During Electrolysis of Alkali Chlorides

In electrolysis of alkali chlorides, a diaphragm separates the alkaline catholyte containing NaOH and NaCl from the acidic anolyte containing NaCl and HCl. The concentration of H^+ ions in the latter is only about 0.1 mol m^{-3}, *i.e.* much lower than the other concentrations and hence can be neglected in the model calculations concerning the concentration of soda lye, current efficiency, and potential drop in the diaphragm. However, in calculating the position of the neutralization zone the transport of all ion species must be considered. In alkali chloride electrolysis, the electrolyte flows through the diaphragm, hence we must take convection into account and the approximate equation (11) cannot be used to calculate the position of the neutralization zone, but we must rely on the numerical solution of the system of equations (5) and (6) instead.
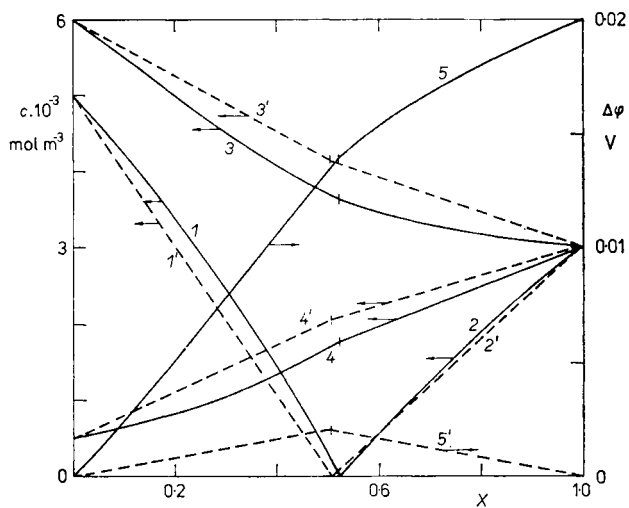
Fɪɢ. 3

Dependences of the concentration of *1* OH^-, *2* H^+, *3* Na^+, *4* SO_4^{2-} ions and *5* of the potential drop, $\Delta\varphi$, in the diaphragm on the relative distance X from the cathodic side of the diaphragm. Catholyte: $0.5M$ Na_2SO_4 + $2M$ $NaOH$. Anolyte: $1.5M$ Na_2SO_4 + $1.5M$ H_2SO_4. Total potential drop in the diaphragm 0.02 V (curves *1—5*) and 0 V (curves *1'—5'*)

Fɪɢ. 4

Dependences of ion concentrations, c, and potential drop in the diaphragm, $\Delta\varphi$, on the relative distance X from its cathodic side. Catholyte: $0.5M$ Na_2SO_4 + $5M$ $NaOH$. Anolyte and notation of the curves as in Fig. 3

The calculated dependences of the logarithm of the concentrations of OH^- and H^+ ions on the relative distance from the cathodic side of the diaphragm are shown in Fig. 5 for two rates of flow of the electrolyte through the diaphragm. The rapid pH change in the neutralization zone is typical for concentration distributions in diaphragms in the presence of a rapid chemical reaction. In Fig. 6 are shown the calculated dependences of the position of the neutralization zone on the rate of flow of electrolyte for various current densities. The concentration of NaOH indicated with the curves is a function of the rate of flow. It can be seen from the curves that for concentrations of NaOH usual in practice (around $3 \, mol \, dm^{-3}$), neutralization proceeds close at the anodic side of the diaphragm; with increasing rate of flow of electrolyte and hence with decreasing concentration of soda lye the neutralization zone is shifted deeper into the diaphragm.
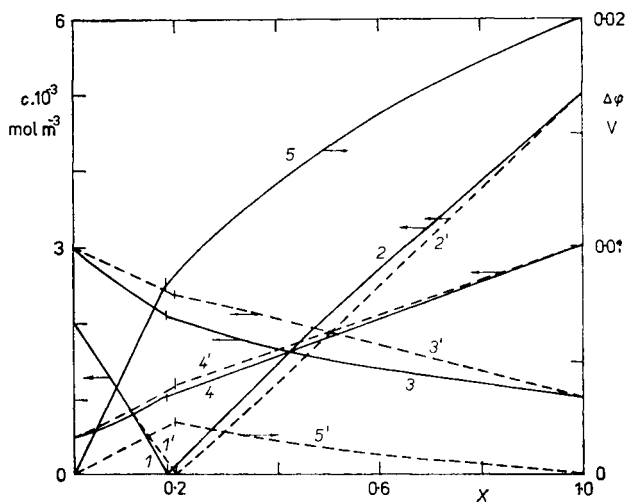
It can be concluded that our model permits the calculation of the concentration and potential distributions in a diaphragm in which neutralization takes place. Although Eq. (*1*) used in the model holds strictly only for dilute electrolytes, we assume that it may be used here to a good approximation since the diffusion coeffi-

FIG. 5

Logarithm of concentration, c, of *1* H^+ and *2* OH^- ions as function of relative distance X from the cathodic side of the diaphragm in electrolysis of alkali metal chlorides. Rate of flow of electrolyte: *a* $5·3 . 10^{-6}$; *b* $6·3 . 10^{-6} \, m \, s^{-1}$, current density $1 \, kA \, m^{-2}$

FIG. 6

Position of neutral zone, X_n, as function of the rate of flow of electrolyte, v. Current density: *1* 600; *2* 800; *3* 1 000; *4* 1 200 $A \, m^{-2}$. Molar concentration of alkali hydroxide in the catholyte is indicated with each curve

cients were obtained on the basis of Eq. (1) from measurements carried out in rather concentrated solutions.

LIST OF SYMBOLS

c_i	concentration of species i, mol m^{-3}
c_{1c}	concentration of OH$^-$ ions in the diaphragm on its cathodic side, mol m^{-3}
c_{2a}	concentration of H$^+$ ions in the diaphragm on its anodic side, mol m^{-3}
d	diaphragm thickness, m
D_i	diffusion coefficient in diaphragm, m^2 s^{-1}
F	Faraday's constant, C mol^{-1}
j	current density, A m^{-2}
J_i	flux of ions through the diaphragm, mol m^{-2} s^{-1}
k_1	neutralization rate constant, m^3 mol^{-1} s^{-1}
k_2	water dissociation rate constant, mol m^{-3} s^{-1}
K_w	ion product for water, mol^2 m^{-6}
n	number of ionic species in solution
t	time, s
u_i	ionic mobility, m^2 V^{-1} s^{-1}
v	velocity of flow of electrolyte through diaphragm, m s^{-1}
x	coordinate perpendicular to diaphragm surface, m
x_0	coordinate of neutral zone, m
X	relative distance from cathodic side of diaphragm $(= x/d)$
X_n	relative distance of neutral zone
z_i	charge number
δ_i	rate of consumption of species i per unit volume of diaphragm, mol m^{-3} s^{-1}
φ	potential in electrolyte, V
$\Delta\varphi$	potential difference in diaphragm, V

Subscript i refers to species i: 1 OH$^-$, 2 H$^+$, 3 Na$^+$, 4 SO$_4^{2-}$, and 5 Cl$^-$ ions.

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