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Current Efficiency and Transport Phenomena in Systems with Charged Membranes

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Abstract

The interaction between the current efficiency of electrodialytic separation with ion-exchange membranes and all the fluxes depressing selectivity, i.e., electric transport of coions, electroosmotic flow of water, diffusion, and osmosis, are described and experimentally examined. A simple method for the determination of current efficiency for any concentration difference across the membrane and current density is presented. A simple relationship between the current efficiency and the efficiency of energy conversion in the desalination process is shown.

INTRODUCTION

In this paper we present a simple definition of the current efficiency (CE) for a single ion-exchange membrane system. It allows for the estimation of CE from a determination of concentration changes in cathode and anode solutions. With the proposed definition, CE can be expressed as a simple function of different kinds of transport taking place in the system. This fact makes it possible to examine the effects of these transports on current efficiency, that is, to calculate the losses of CE due to:

- Electric transport of coions
- Electroosmotic flow of water
- Diffusion of a salt
- Osmotic transport of water

Thus, the full characteristics of a single ion-exchange membrane (cation- or anion-exchange) for separation processes like electrodialysis can be obtained.

The mathematical solution has been examined for computing the current efficiency and its losses for the systems $\text{NaCl}_{\text{aq}}/\text{Nafion 120}$ membrane and $\text{NaOH}_{\text{aq}}/\text{Nafion 120}$ membrane based on the experimental results published previously (1, 2).

CURRENT EFFICIENCY OF A MEMBRANE SYSTEM. A DEFINITION

Consider the one membrane system seen in Fig. 1. The ion-exchange membrane (M) separates two solutions of an Av_1Bv_2 electrolyte differing in concentrations. For the cation-exchange membrane (sign $\omega = -1$) the cathode is on the more concentrated side whereas for the anion-exchange membrane (sign $\omega = 1$) it is on the diluted side. The electrodes and electrode reactions do not belong to the system. They are separated from the system by ideal membranes of reverse sign to the investigated membrane.

At $t = 0$ the concentration difference across the membranes is $\Delta c^\circ = c^{\circ\prime} - c^{\circ\prime\prime}$. After passing an electric current through the membrane for time t , the concentration difference changes to $\Delta c'$. The ratio of $(\Delta c' - \Delta c^\circ)$ for the real membrane to $(\Delta c' - \Delta c^\circ)$ for the ideal membrane system ($t_2, t_w, J_s, J_w^s = 0$) is a measure of the current efficiency:

$$\text{CE} = \frac{(\Delta c' - \Delta c^\circ)}{(\Delta c' - \Delta c^\circ)_{\text{ideal}}} \quad (1)$$

Rearrangement of this formula, as shown in Appendix B, leads to the

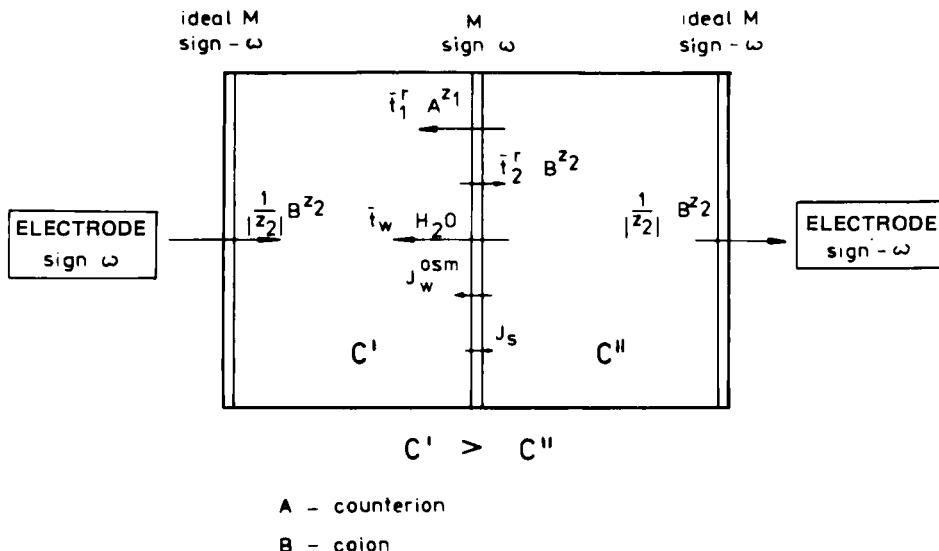


FIG. 1. Standard system for defining the current efficiency of an ion-exchange membrane in the isobaric condition ($\Delta p = 0$). The transport processes caused by the passage of 1 F of electric charge (i_1 and i_2 are the electric transport of counterions and coions, respectively; i_w is the electroosmotic transport of water) and by the concentration difference (J_s = diffusion of a salt, J_w^{osm} = osmotic flux of water) are denoted.

following equation relating the current efficiency to total counterions (J_1) and water (J_w) fluxes:

$$CE = \omega z_1 v_1 (J_1/v_1 - 0.018 \bar{n} J_w)/I \quad (2)$$

Considering that the counterions are driven by the constant electric field and the chemical potential gradient, and that the same holds for water, Eq.

(2) can be rearranged to:

$$CE = z_1 v_1 (\bar{i}_1 / v_1 - 0.018 \bar{m} \bar{i}_w - \omega (J_s - 0.018 \bar{m} J_w^{os}) F / I) \quad (3)$$

where \bar{i}_1 = reduced transport number of counterions (Eq. A2)

\bar{i}_w = transport number of water

\bar{m} = mean molality defined by Eq. (B17)

J, J_w^{os} = diffusion and osmotic fluxes

I = electric current

$\omega = \begin{cases} -1 & \text{for cation-exchange membrane} \\ +1 & \text{for anion-exchange membrane} \end{cases}$

The formula account for the fluxes that decrease current efficiency, as indicated in Eq. (3a):

$$\begin{array}{cccc} \text{electrical} & \text{electroosmotic} & \text{diffusion} & \text{osmotic flux} \\ \text{transport} & \text{transport} & \text{of a salt} & \text{of water} \\ \text{of coions} & \text{of water} & & \\ \downarrow & \downarrow & \downarrow & \downarrow \\ CE = 1 - \bar{i}_2 - z_1 v_1 0.018 \bar{m} \bar{i}_w - z_1 v_1 \omega (J_s - 0.018 \bar{m} J_w^{os}) F / I \quad (3a) \end{array}$$

With the help of the transport equations of irreversible thermodynamics and the Gibbs-Duhem equation, the diffusion and osmotic fluxes, J , and J_w^{os} , can be expressed as a function of the difference of the chemical potential of a solute, $\Delta \mu_s$ (3):

$$J_s - 0.018 \bar{m} J_w^{os} = \left[\left(\frac{J_s}{\Delta \mu_s} \right) - 0.018 \bar{m} \left(\frac{J_w^{os}}{\Delta \mu_s} \right) \right] \Delta \mu_s = f(L_{ik} \bar{m}) \Delta \mu_s \quad (4)$$

Here $f(L_{ik} \bar{m})$ represents a combination of the phenomenological conductance coefficients L_{ik} and the mean molality, \bar{m} , of a solute. Equations (3) and (4) clearly show that losses of selectivity due to osmotic and diffusion fluxes are dependent on the ratio of the chemical potential difference of solute and the current $\Delta \mu_s / I$.

DETERMINATION OF CURRENT EFFICIENCY IN A SYSTEM WITH ELECTRODE REACTIONS

Substituting the concentration changes for the system with ideal membrane, $(\Delta c' - \Delta c^\circ)_{\text{ideal}}$ (Eq. B15), and the equation

$$\Delta c' - \Delta c^\circ = \omega(\Delta c'_a - \Delta c'_c) \quad (5)$$

into Eq. (1), Eq. (6) is obtained:

$$\text{CE} = \frac{z_1 v_1 V^\circ F (\Delta c'_c - \Delta c'_a)}{2(1 - \bar{v}_s \bar{c}^\circ) I \Delta t} \quad (6)$$

where $\Delta c'_a$, $\Delta c'_c$ = concentration changes of anolyte and catholyte after time Δt

\bar{c}° = mean concentration of anolyte and catholyte at time $t = 0$, $\bar{c}^\circ = (c_a^\circ + c_c^\circ)/2$.

Equation (6) can only be applied to the standard system (Fig. 1) without any other effect but transport, i.e., without the electrode reactions. Actually, the experimentally determined variations of the concentrations of the cathodic and anodic solutions are produced by both the transport phenomena and the electrode reaction (Fig. 2).

For computing the current efficiency related to the transport phenomena only, the concentration/volume effects of the electrode reactions should be accounted for. The use of electrodes makes it necessary to correct the numerator of Eq. (6), i.e., the difference $\Delta c'_c - \Delta c'_a$. In the general form the formula for the membrane current efficiency determined in the practical system can be written as

$$\text{CE} = \frac{z_1 v_1}{2(1 - \bar{v}_s \bar{c}^\circ)} \left[\frac{F V^\circ}{I} \left(\frac{\Delta c'_c}{\Delta t} - \frac{\Delta c'_a}{\Delta t} \right)^{\text{pract}} + \text{correction} \right] \quad (7)$$

Some electrodes and the formulas for corrections are shown in Table 1. It should be noticed that the electrodes should react, producing only ions common to those in the solutions.

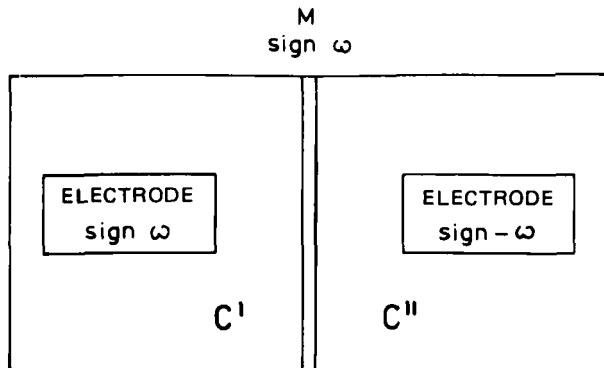


FIG. 2. Practical system. The electrode reactions belong to the system.

RELATION BETWEEN CURRENT EFFICIENCY AND EFFICIENCY OF ENERGY CONVERSION

Regarding the general formula for efficiency of energy conversion given by Kedem and Caplan (4), the efficiency of energy conversion, η_E , for the system studied here takes the form (5)

$$\eta_E = \omega \frac{J_1^w}{I} \frac{\Delta \mu_s}{\Delta E} \quad (8)$$

where $J_1^w = J_1/v_1 - 0.018mJ_w$

ΔE = is the difference of electrical potential measured with electrodes reversible to coions:

$$\Delta E = \Delta \bar{\mu}_2/z_2 F \quad (10)$$

By comparing Eq. (8) for J_1^w and Eq. (3) for the current efficiency, it can be seen that η_E can be rewritten now as the product of current efficiency and the force-to-force ratio $\Delta \mu_s/\Delta E$:

$$\eta_E = \omega \frac{1}{z_1 v_1} CE \frac{\Delta \mu_s}{\Delta E} \quad (11)$$

TABLE I
Corrections for Calculating Current Efficiency from Eq. (7) for the Different Electrode/Solution Systems and with an Ion-Exchange Membrane

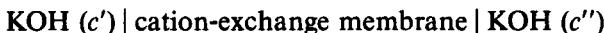
Electrode	Electrode reactions for cathode (<i>c</i>) and anode (<i>a</i>)	Correction $\Delta\bar{n}_c^{\text{cor}} = \Delta\bar{n}_a^{\text{cor}} + c_a^2\Delta V_a^{\text{cor}} - c_c^2\Delta V_c^{\text{cor}}$ for membranes	
		Cation exchange	Anion exchange ($z_2 = z$)
Ag/AgCl Solute: MeCl_2	$c: \text{AgCl} + \text{Ag} + \text{Cl}^-$ $a: \text{AgCl} - \text{Ag} - \text{Cl}^-$	$2\varepsilon^o (\bar{v}_{\text{Ag}} - \bar{v}_{\text{AgCl}})$	$-2[(1 - \varepsilon^o \bar{v}_s)/z_2 - c^o (\bar{v}_{\text{Ag}} - \bar{v}_{\text{AgCl}})]$
Platinum Solute: $\text{Me}(\text{OH})_2$	$c: \text{H}_2\text{O} + \text{OH}^- + 0.5\text{H}_2\uparrow$ $a: 0.5\text{H}_2\text{O} - \text{OH}^- + 0.25\text{O}_2\uparrow$	$-\bar{v}_w (c_c^o + 0.5c_a^o)$	$-2(1 - \varepsilon^o \bar{v}_s)/z_2 - \bar{v}_w (c_c^o + 0.5c_a^o)$
Platinum Solute: H_2SO_4	$c: \text{H}^+ + 0.5\text{H}_2\uparrow$ $a: -0.5\text{H}_2\text{O} + \text{H}^+ + 0.25\text{O}_2\uparrow$	$(1 - \varepsilon^o \bar{v}_s) + 0.5c_w^o \bar{v}_w$	$0.5c_w^o \bar{v}_w$

RESULTS AND DISCUSSION

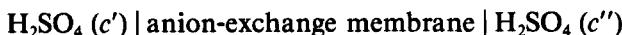
1. Determination of Current Efficiency

In order to verify Eq. (7), the determination of the CE of membrane systems with two extreme electrolytes (strong acid and strong base) has been performed.

The investigated systems:



Membrane: KESD-2 ("Galena," Poland); Nafion 315 (Du Pont de Nemours, USA).



Membrane: AESD-2a ("Galena," Poland). Temperature: 298 K. Electric current: 0.1 A. Membrane surface: 10 cm². Volume of one compartment: 140 cm³.

The membrane cell was equipped with platinum electrodes and magnetic stirrers. The changes of concentrations of cathode and anode solutions caused by passage of electric current were determined by acid-base titration. The results of the experiment are gathered in Table 2. The calculated CE shows that for the working conditions examined here ($m'/m'' = 5$, $i = 100 \text{ A/m}^2$), the investigated membranes are insufficient in separating electrolytes with mobile coions: H⁺ for the anion-exchange membrane and OH⁻ for the cation-exchange membranes.

The accuracy of the calculation of CE from Eq. (7) is limited mainly by the accuracy of determination of concentration changes. This effect can be estimated from the law of errors propagation:

$$\Delta(\text{CE}) = \frac{|z_1| v_1 F V^\circ}{2(1 - \bar{v}_s \bar{c}^\circ) I \Delta t} ((\Delta(\Delta c_a))^2 + (\Delta(\Delta c_c))^2)^{0.5} \quad (12)$$

where $\Delta(\text{CE})$, $\Delta(\Delta c_a)$, and $\Delta(\Delta c_c)$ are the standard deviations of CE, Δc_a , and Δc_c , respectively.

For the investigated systems, $\Delta(\Delta c_a)$ and $\Delta(\Delta c_c)$ equal to 0.0005 mol/dm³ give $\Delta(\text{CE}) = 0.02$.

TABLE 2
Experimental Results and the Calculated Current Efficiency (Eq. 7): $I = 0.1 \text{ A}$, $V^o = 140 \text{ cm}^3$, $T = 298 \text{ K}$

Membrane system	c_a^o	c_c^o	c_a'	c_c'	Δt (min)	Correction	CE
KESD-2 KOH	0.0702	0.4032	0.0510	0.4152	54	-0.008	0.65
Nafion 315 KOH	0.0702	0.4032	0.0512	0.4188	46	-0.008	0.84
AESD-2a H_2SO_4	0.3725	0.0702	0.0655	0.3767	45	0.003	0.45

a) NaCl - Nafion 120

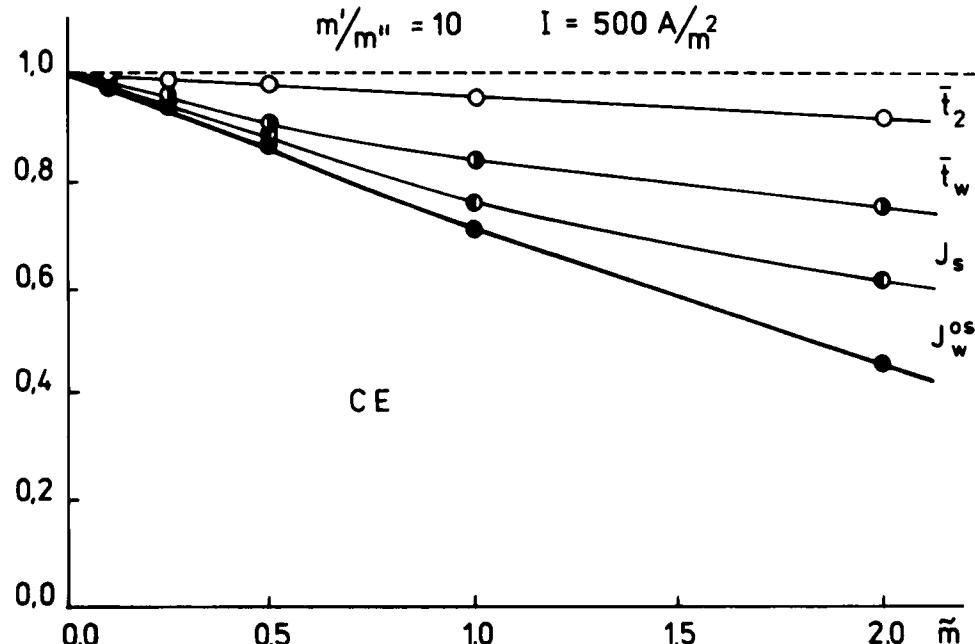
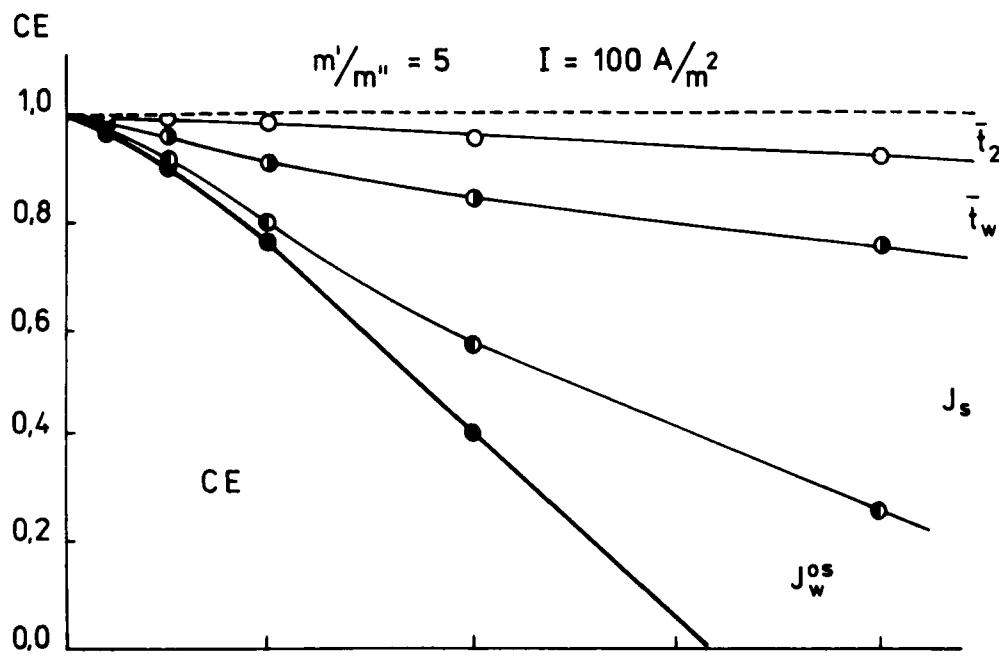
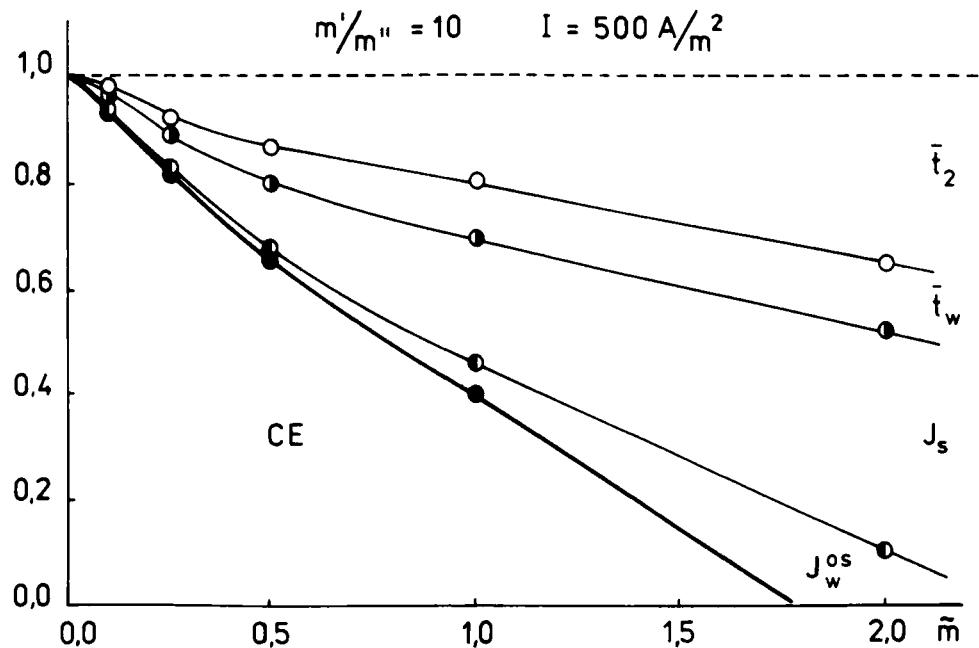
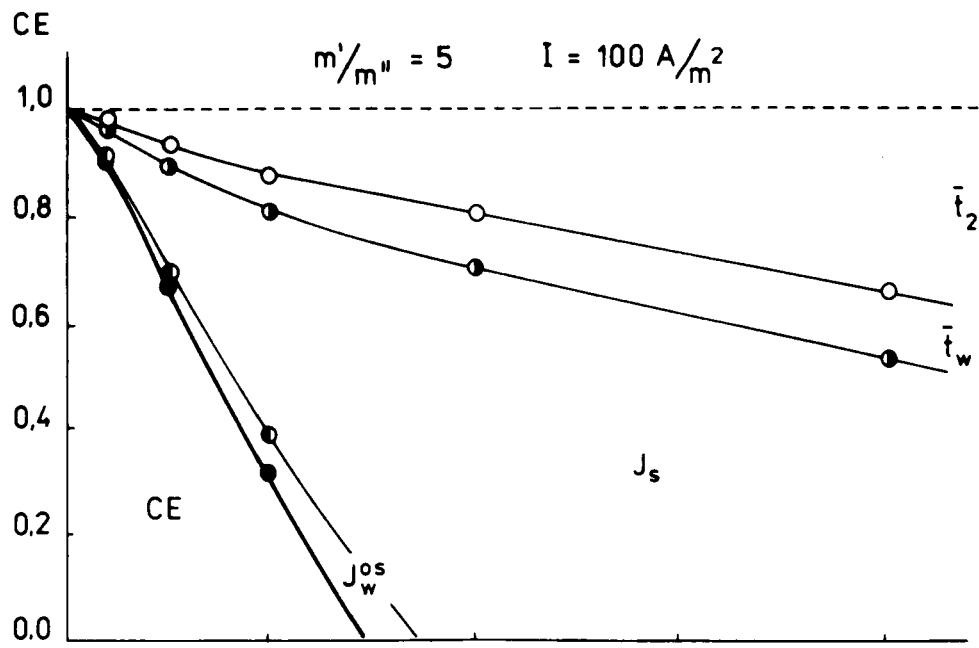


FIG. 3. Losses of the current efficiency due to imperfect selectivity of a membrane (\bar{t}_2), diffusion of a solute (J_s), and electroosmotic (\bar{t}_w) and osmotic (J_w^{os}) fluxes. $T = 298 \text{ K}$.

b) NaOH - Nafion 120



2. The Losses of Current Efficiency

To determine losses of current efficiency due to different kinds of transport (Eq. 3a), four experiments should be performed. Here we present results for the systems $\text{NaCl}_{\text{aq}}/\text{Nafion 120}$ and $\text{NaOH}_{\text{aq}}/\text{Nafion 120}$. All the experimental results used for computing CE have been published elsewhere (1, 2).

Figures 3(a) and 3(b) present the effects of the conjugated fluxes on efficiency of electric transport of counterions across the cation-exchange membrane (Nafion 120) for two different values of concentration ratio, m'/m'' , and current density, i : $m'/m'' = 5$, $i = 100 \text{ A/m}^2$, and $m'/m'' = 10$, $i = 500 \text{ A/m}^2$.

On both figures the current efficiency corresponds to the abscissa (see Eq. 3a):

$$\text{CE} = 1 - \Sigma \text{ losses}$$

and is dependent on the mean concentration \bar{m} (Eq. B17). The effects which diminish the current efficiency are:

Electric transport of coions, i.e., imperfect membrane permselectivity (\bar{t}_2)

Diffusion of a solute (\bar{J}_s)

The electroosmotic (\bar{t}_w)

Osmotic water fluxes (\bar{J}_w^{os}).

The following conclusions can be drawn from the figures.

The imperfect selectivity (\bar{t}_2), assumed to be one of the most important characteristics of a membrane, produces up to 8% (NaCl) and 35% (NaOH) of the CE losses at $\bar{m} = 2$.

Similar to \bar{t}_2 , the effect of electroosmotic flow of water (\bar{t}_w) increases with m . It plays a significant role in the system with NaCl where it diminishes CE up to 30%.

Depending on the working conditions, i.e., on the concentration ratio m'/m'' and current density, the decrease of CE due to osmotic and diffusion flows can be larger than that caused by electric transport of coions and water. This effect is especially seen in the higher mean concentrations, where the current efficiency can even be reduced to zero.

The effects of electric transport of cations and diffusional flow are larger in the system with NaOH than with NaCl due to mobile hydroxyl ions.

The solution presented (Eq. 3) can be useful in obtaining information about the membranes and the working conditions for the separation processes.

APPENDIX A

Definition of Transport Numbers

1) Transport number of ion i , t_i :

$$t_i = (z_i J_i F / I)_{\Delta c=0}, \quad i = 1, 2 \quad (\text{A1})$$

where I is the electric current, J_i is the flux of species i , z_i is its charge, and F is the Faraday constant.

2) Reduced transport number of species i (6), t_i^r :
For ions ($i = 1, 2$):

$$t_i^r = \frac{1}{z_i} t_i = \left(\frac{F J_i}{I} \right)_{\Delta c=0}$$

For water:

$$t_w^r = t_w = \left(\frac{F J_w}{I} \right)_{\Delta c=0} \quad (\text{A2})$$

APPENDIX B

1. Derivation of the Formula for the Current Efficiency (Eq. 3, Fig. 1)

At $t = 0$ the concentrations of the anode ($i = a$) and the cathode ($i = c$) solutions are

$$c_i^o = n_i^o / V^o, \quad i = a, c \quad (B1)$$

where n_i^o is the number of moles of an electrolyte in the "i" solution. The volumes of both solutions are equal and denoted by V^o . After passing the current I during time Δt , the concentrations in both compartments change to

$$c'_i = (n_i^o + \Delta n_i) / (V^o + \Delta V_i), \quad i = a, c \quad (B2)$$

where Δn_i and ΔV_i are the changes of the amount of an electrolyte and of the volume in the "i" compartment, respectively. Assuming $\Delta V_i \ll V^o$, from Eqs. (B1) and (B2) we obtain

$$\Delta c'_c - \Delta c'_a = (\Delta n_c - \Delta n_a - c_c^o \Delta V_c + c_a^o V_a) / V^o \quad (B3)$$

For the standard system (Fig. 1), the changes of ΔV_i and Δn_i are as follows.

Real membrane:

$$\begin{aligned} \Delta n_i &= z_i (\Delta n^m + \Delta n^{mid}) \\ &= z_i \omega J_i / v_i \Delta t \quad (\text{moles of } Av_1 B v_2) \end{aligned} \quad (B4)$$

$$\begin{aligned} \Delta V_i &= z_i (\Delta V^m + \Delta V^{mid}) \\ &= z_i \omega (\bar{v}_s J_s / v_1 + \bar{v}_w J_w / v_2) \Delta t, \quad i = a \text{ or } c \end{aligned} \quad (B5)$$

where $z_a = 1$, $z_c = -1$

Δn^m and ΔV^m denote changes in the amounts of ions and of volume due to the transport across the investigated membrane, respectively

$$\Delta n^m = \omega J_i \Delta t / v_i (Av_1 B v_2) + x / |z_2| (B^{z_2}) \quad (B6)$$

$$\Delta V^m = \left(\omega \bar{v}_s J_s / v_1 + \bar{v}_w J_w / v_2 + \frac{\bar{v}_2}{|z_2|} \frac{I}{F} \right) \Delta t \quad (B7)$$

Δn^{mid} and ΔV^{mid} denote analogical effects of transport across ideal membranes surrounding the investigated membrane

$$\Delta n^{mid} = -x / |z_2| (B^{z_2}) \quad (B8)$$

$$\Delta V^{mid} = - \frac{\bar{v}_2}{|z_2|} x \quad (B9)$$

$$x = I\Delta t/F \quad (B10)$$

$$J_1 = -\omega \bar{t}_1 I/F + v_1 J_s \quad (B11)$$

$$J_w = -\omega \bar{t}_w I/F + J_w^{os} \quad (B12)$$

Ideal membrane ($\bar{t}_2, \bar{t}_w, J_s, J_w^{os} = 0$):

Equations (B4) and (B5) are simplified to

$$\Delta n_i = -z_i \frac{1}{z_1 v_1} x \quad (B13)$$

$$\Delta V_i = -z_i \frac{\bar{v}_s}{z_1 v_1} x \quad (B14)$$

By substituting Eqs. (B13), (B14), and (B3) into Eq. (5), we obtain

$$(\Delta c' - \Delta \bar{c}^\circ)_{ideal} = \frac{2(1 - \bar{v}_s \bar{c}^\circ)x}{z_1 v_1 V^\circ} \quad (B15)$$

By substituting Eqs. (B4) and (B5) through Eqs. (B3) and (B15) in the formula defining the current efficiency (Eq. 1), we obtain

$$CE = \frac{z_1 v_1 F}{I} \left[\frac{J_1}{v_1} - \frac{\bar{c}^\circ \bar{v}_w}{1 - \bar{v}_s \bar{c}^\circ} J_w \right] \quad (B16)$$

By introducing Eqs. (B11) and (B12) into Eq. (B16), we finally obtain

$$CE = z_1 v_1 \left[\frac{\bar{t}_1'}{v_1} - \left(\frac{\bar{c}_s}{\bar{c}_w} \right) \bar{t}_w - \omega \left(J_s - \left(\frac{\bar{c}_s}{\bar{c}_w} \right) J_w^{os} \right) F/I \right] \quad (B16a)$$

where

$$\left(\frac{\bar{c}_s}{\bar{c}_w} \right) = \frac{\bar{v}_w \bar{c}^\circ}{1 - \bar{v}_s \bar{c}^\circ} = 0.018 \bar{m} \quad (B17)$$

$$\bar{c}^\circ = (c_a^\circ + c_k^\circ)/2 \quad (B18)$$

2. The System with Electrode Reactions

In practice, in any system there are electrodes and electrode reactions which cause additional variations in the molarities of the solutions. Consequently, the differences Δn_i^{cor} and ΔV_i^{cor} will appear:

$$\Delta n_i^{\text{mid}} = z_i \Delta n^{\text{mid}} = \Delta n_i^{\text{el}} + \Delta n_i^{\text{cor}}, \quad i = a, c \quad (\text{B19})$$

$$\Delta V_i^{\text{mid}} = z_i \Delta V^{\text{mid}} = \Delta V_i^{\text{el}} + \Delta V_i^{\text{cor}}, \quad i = a, c \quad (\text{B20})$$

where Δn_i^{el} and ΔV_i^{el} denote changes of amount of ions and volume due to electrode reactions.

By substituting Eqs. (B19) and (B20) through Eqs. (B3) and B5 into Eq. (6), we obtain

$$\text{CE} = \frac{z_1 v_1}{2(1 - \bar{v}_s c^\circ)} \left[\frac{V^\circ F}{I} \left(\frac{\Delta c'_c}{\Delta t} - \frac{\Delta c'_a}{\Delta t} \right)^{\text{pract}} \right. \\ \left. + \underbrace{\Delta \bar{n}_c^{\text{cor}} - \Delta \bar{n}_a^{\text{cor}} - c_c^\circ \Delta \bar{V}_c^{\text{cor}} + c_a^\circ \Delta \bar{V}_a^{\text{cor}}}_{\text{correction}} \right] \quad (\text{B21})$$

where

$$\Delta \bar{n}_i^{\text{cor}} = -\omega \Delta n_i^{\text{cor}}/x; \quad \Delta \bar{V}_i^{\text{cor}} = -\omega \Delta V_i^{\text{cor}}/x, \quad i = a, c$$

$\Delta \bar{n}_i^{\text{cor}}$ and $\Delta \bar{V}_i^{\text{cor}}$ for some systems are presented in Table 3. Substitution in the right-hand term of Eq. (B21) gives the corrections listed in Table 1.

Acknowledgment

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TABLE 3
 $\Delta\bar{n}_i^{\text{cor}}$ and $\Delta\bar{V}_i^{\text{cor}}$ for Different Electrode/Electrolyte/Membrane Systems (Eq. B21)

Electrode	Cation-exchange membrane		Anion-exchange membrane ($z_2 = z$)	
	$i = a$; $c: z_a = 1$; $z_c = -1$	$\Delta\bar{n}_i^{\text{cor}}$	$i = a$; $c: z_a = 1$; $z_c = -1$	$\Delta\bar{V}_i^{\text{cor}}$
Ag/AgCl Solute: MeCl _z	0	$z_i(\bar{v}_{\text{Ag}} - \bar{v}_{\text{AgCl}})$	z_i/z_2	$z_i(\bar{v}_s/z_2 + \bar{v}_{\text{Ag}} - \bar{v}_{\text{AgCl}})$
Pt Solute: Me(OH) _z	0	$c: \bar{v}_w$ $a: -0.5\bar{v}_w$	z_i/z_2	$c: -\bar{v}_s/z_2 + \bar{v}_w$ $a: \bar{v}_s/z_2 - 0.5\bar{v}_w$
Pt Solute: H ₂ SO ₄	$-z_i/2$	$c: 0.5\bar{v}_s$ $a: -0.5(\bar{v}_s - \bar{v}_w)$	0	$c: 0$ $a: 0.5\bar{v}_w$

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