

ADVANCES IN MEMBRANE PHENOMENA AND PROCESSES

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Anna NAREBSKA, Stanisław KOTER*

FROM THEORY TO PRACTICE. TRANSPORT PHENOMENA IN WORKING MEMBRANE SYSTEMS

The assistance of irreversible thermodynamics (IT) to the quantitative evaluation of the working membrane systems, useful in practice, has been proved. Basing on IT, the permselectivity of membrane in a working unit, called *dynamic* (S_d), has been defined and the equation for computing S_d in relation to degree of desalination and current density has been derived. It has been also shown that S_d is useful for searching for the most economical range of current density and desalination level in the electro dialysis unit.

LIST OF SYMBOLS

- c — concentration (mol/dm^3),
- E — electromotive force (V),
- F — Faraday constant,
- I — electric current density (A/m^2),
- J_i — flux of the species i ($\text{mol}/\text{m}^2/\text{s}$),
- J_p — volume flux (m/s),
- L_{ik} — conductance coefficients ($\text{mol}^2/\text{J}/\text{m}^2/\text{s}$),
- m — external molality,
- S — selectivity,
- t_i — transport number of the species i ,
- η_E — efficiency of energy conversion,
- η_{1E} — main component of the efficiency of energy conversion,
- η_{we} — loss of the efficiency of energy conversion due to transport of water,
- η_m, η_s, η_w — coefficients in Eq. (3) accounting for the current leakage, nonideal permselectivity of membrane, and transport of water, respectively,
- k — conductivity of a membrane ($\text{ohm}^{-1}/\text{m}^2$),
- μ_i — chemical potential of the species i (J/mol),
- ν_i — number of ions i released per molecule of salt,
- ξ — current efficiency,
- Φ — dissipation function ($\text{J}/\text{m}^2/\text{s}$).

*Institute of Chemistry, Nicolaus Copernicus University, Toruń, Poland.

1. INTRODUCTION

It happens quite frequently that when discussing related phenomena, theoreticians and practitioners speak their own languages, using mathematics for theory and experiments for the practical evaluation of the systems, but the effect of the theory on practice is still limited. With regards to membrane processes, irreversible thermodynamics of transport phenomena (IT) seems to be one of such theories.

STAVERMAN, SPIEGLER, and SCHLÖGL published their papers in the fifties [1]–[3] and in the sixties KATCHALSKY, KEDEM, CAPLAN, and MEARES [4]–[13] formulated the most general and still precise theory of the irreversible thermodynamics of membrane processes. In the seventies this theory was rather sporadically [14]–[16] and up to now the effects of IT on understanding the membrane phenomena seem to be far below its potential.

To some extent the language used by the thermodynamicists might be responsible for this state of affairs. Being focussed on the problem of energy, IT describes membrane phenomena in terms of transport coefficients representing the energy needed for or dissipated by the permeation of a species. They are the conductance ($\text{mol}^2\text{J}^{-1}\text{m}^{-1}\text{s}^{-1}$), resistance (J m s mol^{-2}), and friction ($\text{J s m}^{-2}\text{mol}^{-1}$) coefficients. Some other limitations in making IT popular may come from the large number of experiments which have to be performed prior to computing the coefficients. However, finding the transport coefficients cannot be the only task of this theory.

The aim of this paper is to show the assistance offered by irreversible thermodynamics to the quantitative evaluation of a working membrane system which is useful in practice and is based on the everyday standardization procedure for membranes.

Because of the authors' experience in the area, ion-exchange membranes applied to electric separation techniques, such as electrodialysis, and to electrochemical reactors have been chosen for discussion [19]–[27]. Prior to the discussion it is desirable, however, to recall briefly the phenomena occurring in systems containing ion-exchange membranes and to explain more precisely *why* and *what for* irreversible thermodynamics will be used.

2. WHY IRREVERSIBLE THERMODYNAMICS IS USED?

When discussing membrane processes it is essential to differentiate between the properties of a membrane in a dynamic system (working unit) and in static ones, i.e., between a system *with* and *without* flows. The concentration of charged groups within the membrane, the Donnan sorption of solutes, and the membrane swelling are the main properties examined in the case of a membrane equilibrated with an aqueous electrolyte solution (static system). Membrane conductance and the transport numbers of counterions are other properties usually measured. They are not enough, however, to evaluate the properties of membranes when installed in a working unit.

The main problem for any theory describing the phenomena within dynamic membrane systems consists in the fact that it should account for the various forces. These are the gradients of the chemical potentials of solute and solvent, pressure, temperature, and electric field which produce the direct and coupled flows of all the permeants present. The effects of coupling re-

sult from the interactions among the mobile species and between them and the polymer matrix.

The nature of the forces and fluxes can be exemplified by taking an ion-exchange membrane separating two aqueous electrolytes of different molarities as the electrochemical unit. In such a system, the constant electric field E imposed on the chemical potential differences of the solute and solvent ($\Delta\mu_s$, $\Delta\mu_w$) generates the transport phenomena drawn schematically in Fig. 1. In this system:

- The main transport, driven by the energy supplied IE , is the electric transport of counterions in the uphill direction of concentration, i.e., towards the more concentrated side. Due to the imperfect selectivity of synthetic membranes, some amount of coions may flow in the direction opposite to the counterions. This is the main, but not the only, transport process in the system.
- Since the flowing counterions impart momentum to the water molecules, they generate the electroosmotic flux of water.
- The gradient of the chemical potential of water produces an osmotic flux, directed usually towards the more concentrated side.
- The chemical potential gradient of the solute generates a diffusional flux of permeants (ions) towards the dilute side, particularly noticeable when the solutions are concentrated.

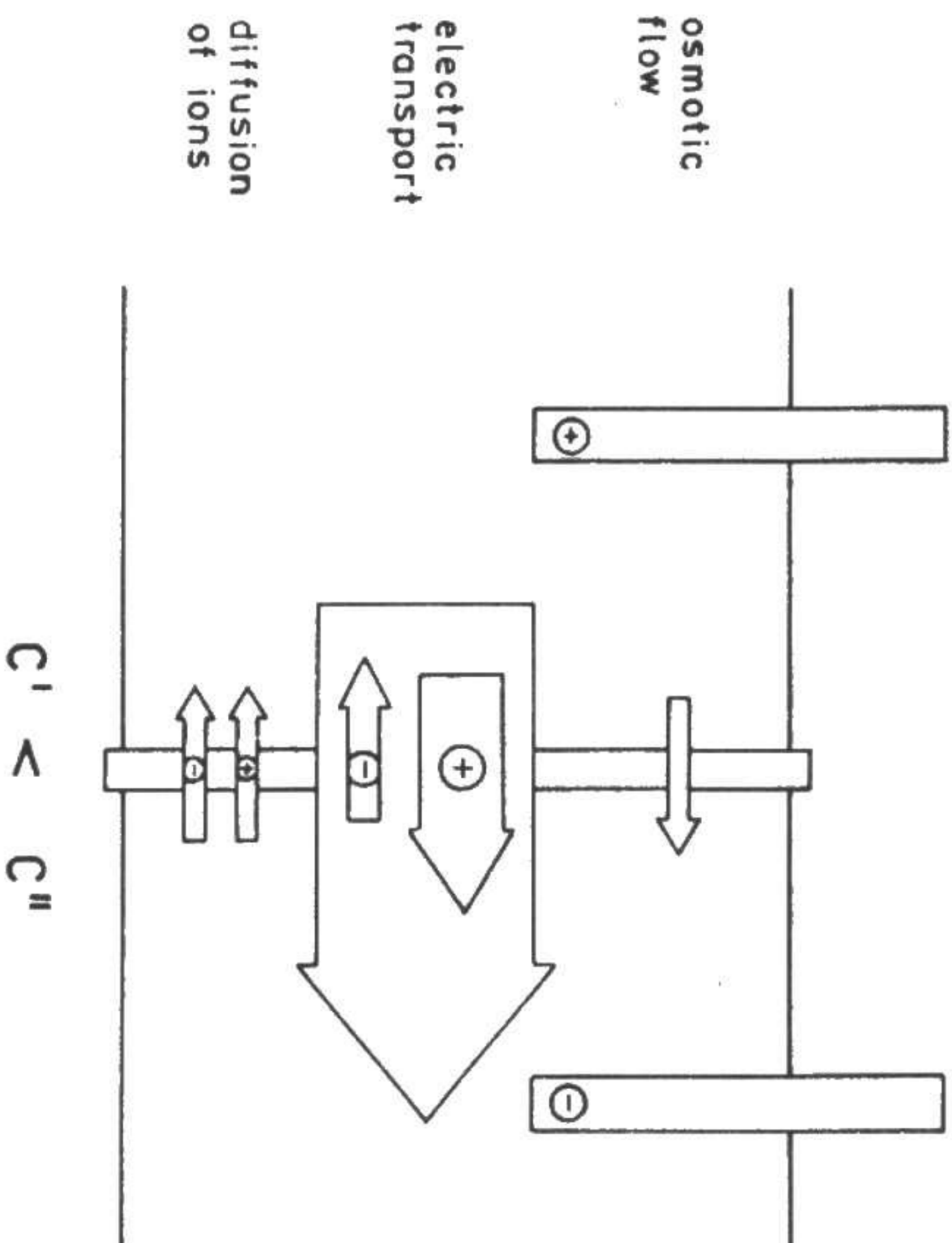


Fig. 1. Transport phenomena in an ion-exchange membrane system caused by the electric current and concentration difference

All the fluxes are related to the properties of the membrane as well as to the value of the electric field and the chemical potential gradients. Due to direct and cross interactions between flowing permeants, they can accelerate or hinder one another, thus changing the net fluxes of ions and affecting the permselectivity.

To understand the importance of the effects brought about by the flux of water, one should realize that any ion-exchange membrane resembles an aqueous gel with the molar ratio of charged polymer groups to water as low as 0.05–0.08 (i.e., one group per 15–20 molecules of water), and the resistance of a membrane to the transport of water is much less than that for the transport of ions:

$$r_w : r_{\text{Na}^+} : r_{\text{Cl}^-} = 1 : 10^2 : 10^3.$$

As a result, the transport of water by volume could be many times greater than that of counterions (Tab. 1).

Table 1
Transport phenomena in the systems Nafion 120
membrane/aqueous electrolytes; $\bar{m} = 1$, $T = 298$ K

Fluxes per unit forces	NaCl	NaOH
	$(\times 10^{-10} \text{ mol}^2/\text{m}^2/\text{N/s})$	
Electric flux of counterions (Na^+)	1.75	1.55
Electroosmotic flux of water	12.2	10.5
Osmotic flux of water	2.4	1.4
Diffusional flux of a solute	0.1	0.32

Up to now the only theory which has succeeded in accounting for the complexity of the system is irreversible thermodynamics.

As stated before the main purpose of this paper is to show how IT can help in combining the theory with simple experiments and assessing the extent salt/water separation per unit of energy.

In all the formulae derived here, the phenomenological transport equations relating the fluxes of permeants to the corresponding forces should be treated as the starting point, i.e., if we consider the cases (i) and (ii), namely

$$\begin{array}{ll} \text{Fluxes} & \text{forces} \\ \text{(i) theoretical set} & J_1, J_2, J_w \quad \Delta\tilde{\mu}_1, \Delta\tilde{\mu}_2, \Delta\mu_w \\ \text{(ii) more practical set} & J_1, J_w, I \quad \Delta\mu_s, \Delta\mu_w, E, \end{array}$$

the equation

$$J_i = L_{i1} \Delta\tilde{\mu}_1 + L_{i2} \Delta\tilde{\mu}_2 + L_{iw} \Delta\mu_w, \quad i = 1, 2, w \quad (1)$$

can be converted to:

$$J_i = L_{i1} \Delta\mu_s + L_{iw} \Delta\mu_w + L_{iE} E, \quad i = 1, w, E \quad (2)$$

where the L_{ik} are the conductance coefficients. The subscripts 1, 2, w, and s denote counterion, cation, water, and solute (i.e., neutral combination of anions and cations), respectively.

To present the main idea of the paper, mathematical expressions will be transferred to an appendix and only the main equations will be presented and discussed.

Finally, two simplifications imposed on any reasoning based on IT should be recalled. In the first of them it is said that the Nernst layers adhering to membrane surface are treated as a part of the membrane. The second is the assumption of linearity in the flux versus force relations. Nonlinear irreversible thermodynamics still undergoes development.

3. A COMMENT ON THE STANDARD METHODS OF EXAMINING MEMBRANES AND MEMBRANE UNITS

A number of methods and characteristics could be used to examine the properties of a membrane itself and the separation processes or units. The current efficiency ξ of a membrane system, which is affected by the permselectivity of the membrane, the transport of water, and current leakage, can be taken as one, important characteristics of a membrane separation process [17]:

$$\xi = n \eta_s \eta_w \eta_m \quad (3)$$

Assuming one membrane ($n = 1$) and 1:1 electrolyte in contact with a cation exchange membrane, one gets:

$$\eta_s \eta_w = \bar{t}_1 - 0.018 \bar{m} t_w \quad (4)$$

where \bar{t}_1 denotes the transport number of the counterions, \bar{t}_w means the transport number of water, and \bar{m} is the mean molarity of the separated electrolyte solutions. Equation (4) demonstrates the importance of determining \bar{t}_1 , \bar{t}_w .

In laboratories, the transport numbers of counterions are measured either by Hittorf electrolysis or potentiometrically:

$$\bar{t}_{1, \text{Hitt}} = \left[\frac{\Delta c_a}{\Delta c_a + \Delta c_k} \right] \Delta c \rightarrow 0 \quad (5)$$

Here Δc_a and Δc_k denote the concentration changes in the anode and cathode compartments, respectively.

$$\bar{t}_{1, \text{app}} = - \left[\frac{E}{\Delta\mu_s} \right]_{I=0} \quad (\text{for 1:1 electrolyte}). \quad (6)$$

In Equation (6) E is the electromotive force of the membrane concentration cell, $\Delta\mu_s$ denotes the chemical potential difference of the solute across the membrane.

$$\bar{t}_{1, \text{Hit}} = \bar{t}_{1, \text{app}} = \left[\frac{z_1 F J_1^w}{I} \right]_{\Delta c = 0} \quad (7)$$

$$J_1^w = J_1 - 0.018mJ_w. \quad (8)$$

From both methods one gets the *solvent-fixed* transport numbers, called also *apparent* numbers. The membrane fixed transport number can be calculated if the water transport number, determined in a separate experiment, is known [18].

For the problem discussed here it is essential, however, that from both methods one gets the transport numbers at nearly zero concentration gradient (Eq. (5)) or zero current density (Eq. (6)), i.e., under static conditions *never met in a working unit*.

Therefore the problem of assessing the transport numbers of the counterions, or the membrane permselectivity, in dynamic systems is now clearly shown.

4. PERMSELECTIVITY OF A MEMBRANE IN WORKING SYSTEMS

By the permselectivity of a membrane some authors understand the transport number of counterions itself, $S = \bar{t}_1$, while others mean the ratio:

$$S = (\bar{t}_1 - t_1) / (1 - t_1). \quad (9)$$

In this formula \bar{t}_1 is the transport number of the same ion 1 in an aqueous solution of concentration close to that within the membrane. Since for computing the permselectivity defined in such a way the corresponding data for aqueous electrolytes should be known, it is a somewhat more complicated and a relative value. In this paper we use the term *permselectivity* in the simplest meaning, i.e., as the transport number of counterions in the membrane.

By definition, the transport number \bar{t}_1 represents the ratio of the current transported by counterions to the total current passing through the membrane:

$$S = \bar{t}_1 = \left[\frac{z_1 F J_1}{I} \right]_{\Delta c = 0} \quad (10)$$

When defining the *permselectivity of the membrane in working systems*, it is enough to account for the phenomena produced by the concentration and electric potential difference, leaving the main formula unchanged, i.e.,

$$S_d = \left[\frac{z_1 F J_1}{I} \right]_{\Delta c, I, J_p \neq 0} \quad (11)$$

Since so defined permselectivity accounts for all the fluxes in the membrane at Δc , $I \neq 0$, we call it *dynamic* as opposed to the static one. For 1:1 electrolyte, Eq. (11) is simplified to:

$$S_d = \left[\frac{J_1}{J_1 - J_2} \right]_{\Delta c, I, J_p \neq 0} \quad (12)$$

To solve Eq. (11) the phenomenological transport equation (1) should be applied first. Rearranging this equation (at zero pressure difference), we can derive the equation for permselectivity composed of two terms (see Appendix):

$$S_d = \left[\frac{J_1}{J_1 - J_2} \right]_{\Delta c = 0} + \left[\frac{J_s}{J_1 - J_2} \right]_{\Delta c \neq 0} \quad (13)$$

The first term relates the permeation of counterions to diffusion, and the second one, to the electric transport phenomena. The final rearrangement of Eq. (13) gives the following formula for the dynamic permselectivity:

$$S_d = \bar{t}_1 + \left[\bar{t}_1 \bar{t}_2 \frac{\kappa}{F^2} + L_{12} - 0.018 \bar{m} \left(\bar{t}_w \bar{t}_2 \frac{\kappa}{F^2} + L_{2w} \right) \right] \frac{F \Delta\mu_s}{I} \quad (14)$$

For convenience Eq. (14) can be abbreviated to the form:

$$S_d = \bar{t}_1 + \alpha(\bar{m}) F \Delta\mu_s / I \quad (15)$$

where $\alpha(m)$ is the total bracket.

As intended, we have come to the equation relating S_d to the difference in the molarities of the electrolytes bathing the membrane (through $\Delta\mu_s$) and the current density I , which is even more useful than the equation with the electric potential difference.

The comparison of Eqs. (14), (15) to the one defining selectivity as $S = \bar{t}_1$ makes the difference between the static and dynamic permselectivities distinct.

At $\Delta\mu_s \rightarrow 0$ and $I \rightarrow 0$, $S_d \rightarrow \bar{t}_1$, i.e., at zero condition the dynamic permselectivity approaches the static one. At non-zero parameters $S_d < S$.

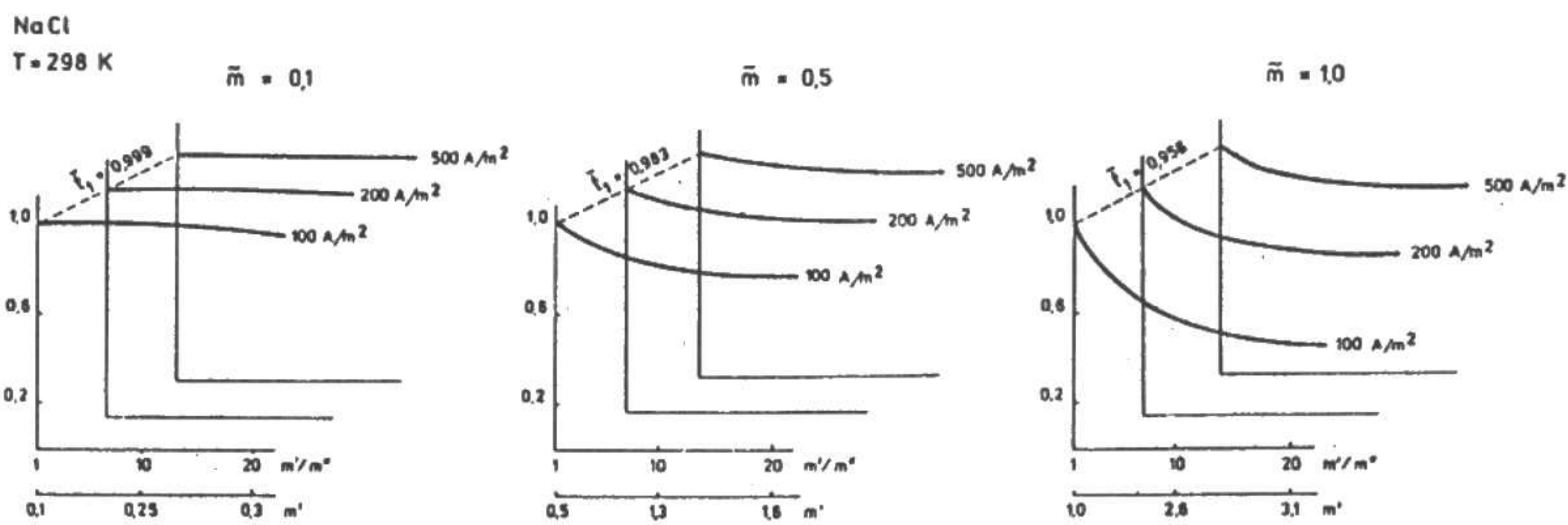


Fig. 2. Dynamic selectivity of Nafion 120 membrane in a contact with aqueous sodium chloride solutions. At logarithmic mean concentrations $\bar{m} = 0.1, 0.5,$ and 1 ; $T = 298$ K

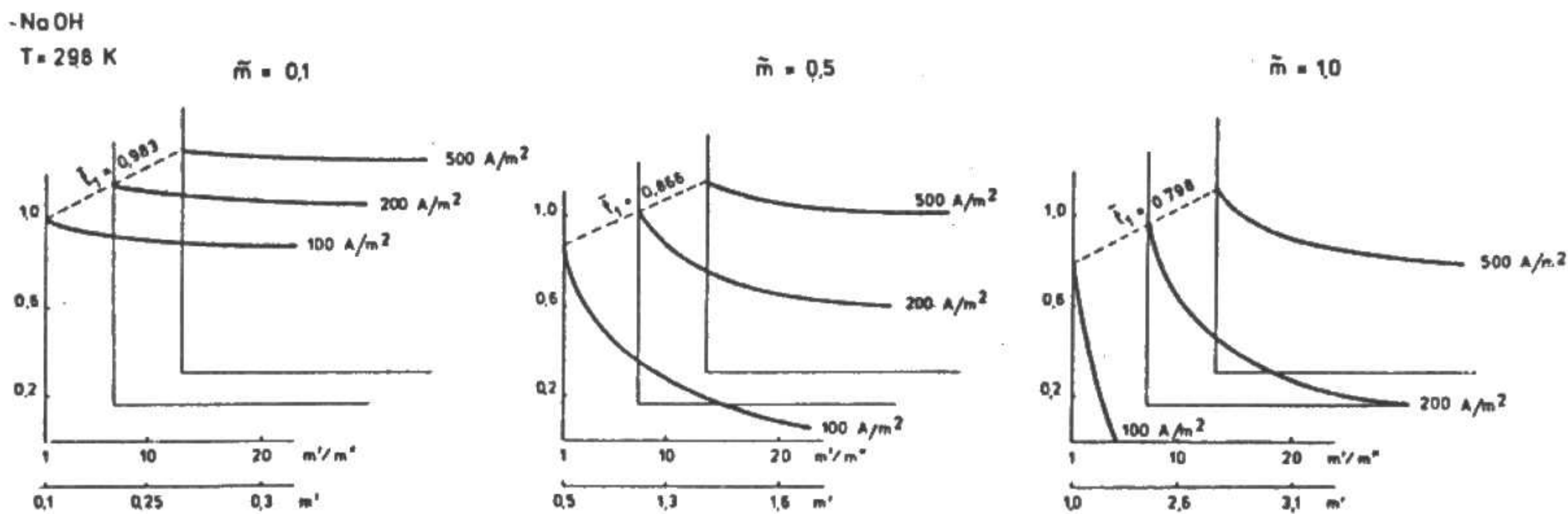


Fig. 3. Dynamic selectivity of Nafion 120 membrane in a contact with aqueous sodium hydroxide solutions; $\bar{m} = 0.1, 0.5,$ and 1 M; $T = 298$ K

The dynamic permselectivity is a complex function of the transport numbers of ions and water, and also of the membrane conductivity K_M and the two conductance coefficients, L_{12} and L_{2w} .

When applying irreversible thermodynamics, some authors assume the interactions between the co- and counterions to be close to zero and neglect the L_{12} coefficient. It has been proved here that by neglecting L_{12} and L_{2w} the results obtained differ by up to 10% from S_D computed while applying the full equation. The results for the Nafion 120 membrane separating sodium chloride solutions or sodium hydroxide of the molarity ratio $m'/m'' = 10$ and at $I = 500$ A/m² are presented in Tab. 2.

Table 2
Permselectivity of Nafion 120 membrane: static (S), dynamic (S_D), and the dynamic one while computed with the simplified equation (S_D^*)

\bar{m}	$S = \bar{r}_1$	S_D^*	S_D^{***}
NaCl (298 K)			
0.1	0.999	0.995	0.998
0.5	0.98	0.95	0.96
1.0	0.96	0.88	0.91
NaOH (298 K)			
0.1	0.983	0.968	0.965
0.5	0.87	0.75	0.73
1.0	0.80	0.56	0.60

* at $m'/m'' = 10, I = 500$ A/m².

** $S_D^* = S_D - (L_{12} - 0.018 \bar{m} L_{2w}) \frac{F \Delta \mu_s}{I}$ at m'/m'' and I as above.

The dynamic permselectivity computed either using the Eq. (14) (column 3) or basing on the same equation, but neglecting the L_{12} and L_{2w} coefficients (column 4), shows the effect of simplification. It should be admitted, however, that at still higher concentration, neglecting the coefficients will result in increasing deviations between the simplified and real values.

The computed results of the dynamic permselectivity obtained when applying Eq. (13) and the experimental data for the Nafion 120 membrane can be seen in Figs. 2 and 3. Here the permselectivity is shown as a function of the molarity of solute in one compartment and the ratio of this molarity to the molarity on the opposite side of the membrane (X -axis). The graphs present the results obtained for the regions characterized by low, mean, and high molarities i.e., 0.1, 0.5, and 1.0.

The curves in the $Z-X$ plane reflect the separation ability of the membrane as desalination proceeds. In every diagram the starting point on the Z -axis corresponds to $m'/m'' = 1$ referred

to the static permselectivity \bar{t}_1 . Because the static permselectivity does not depend on the current density, it has the same value for the family curves, irrespective of I . Every other curve (in the $Z-Y$ plane) shows how much increasing the current improves the membrane permselectivity.

The conclusions summarizing the results presented in Figs. 2 and 3 are as follows:

1. The permselectivity of ion-exchange membranes in working systems with Δc , $I = 0$, called *dynamic*, is below that found in the zero condition (static). With Δc approaching zero the dynamic permselectivity S_d reaches a limiting value, which is the static permselectivity.
2. The increasing molarity ratio of the separated solutions (with progressing desalination) strongly depresses the membrane permselectivity. For sodium hydroxide solutions at high molarity, it is almost impossible to get uphill transport of sodium ions.
3. A high current density limits the effects of diffusion and osmotic flows favouring the effective transport of counterions.

5. DYNAMIC PERMSELECTIVITY AND ENERGY CONVERSION PROBLEMS

As it was stated before, the current efficiency is obfuscated by the imperfect membrane permselectivity and the phenomena which cause the transport of ions in the membrane. These phenomena result in the dissipation of the energy supplied to the system and prevent the conversion of electric energy IE into the free energy of mixing (due to the difference in the molarities of the desalinated water and the brine) from reaching 100%.

In the framework of irreversible thermodynamics the definition of the efficiency of energy conversion starts from the dissipation function which, for electro dialysis, can be written in the form of the so-called *two flow equation*:

$$\Phi = J_1 \Delta\mu_s + IE \quad (16)$$

or, more precisely, the *three flow equation*:

$$\Phi = J_1 \Delta\mu_s + J_w \Delta\mu_w + IE \quad (17)$$

The difference is such that Eq. (17) accounts for the participation of transport of water in the entropy production.

In terms of Eq. (16) and using the Kedem-Caplan definition, the efficiency of energy conversion can be defined as:

$$\eta_{IE} = - \frac{J_1 \Delta\mu_s}{IE} \quad (18)$$

whereas in terms of Eq. (17) it is seen to be [22]:

$$\eta_E = \left[- \frac{J_1 \Delta\mu_s}{IE} \right] + \left[- \frac{J_w \Delta\mu_w}{IE} \right] = \eta_{IE} + \eta_{wE} \quad (19)$$

SOLUTION I

Introducing Eq. (11) into Eq. (18) results in the simple equation:

$$\eta_{IE} = -S_d \frac{\Delta\mu_s}{FE} \quad (20)$$

relating the conversion of energy to the dynamic membrane permselectivity and the two forces acting on the system, i.e., the chemical potential difference of the solute and the voltage of the constant electric field. Aiming again at taking the current density as the variable instead of the electric field potential, further recalculating is possible according to the relation [22]:

$$\frac{\Delta\mu_s}{FE} = \frac{\kappa}{F^2} \left[\frac{I}{F\Delta\mu_s} - \frac{\kappa}{F^2} (\bar{t}_1 - 0.018\tilde{m}\bar{t}_w) \right]^{-1} \quad (21)$$

It follows then that for computing the efficiency of energy conversion, it is enough to know the same experimental membrane characteristics (\bar{t}_1 app, \bar{t}_w , and κ) as in the simplified solution of Eq. (14), and the L_{12} and L_{2w} coefficients – for precise results.

SOLUTION II

In Equation (17), which accounts for the transport of water, the first term is the same as in solution I. The second term is composed of the phenomena induced by the difference in the chemical potential of water:

$$\eta_{wE} = - \bar{t}_w \frac{\Delta\mu_w}{FE} \quad (22)$$

where

$$\bar{t}_w^d = \bar{t}_w + \beta(\tilde{m}) \frac{F\Delta\mu_s}{I} \quad (23)$$

$$\beta(\tilde{m}) = L_{1w} - \bar{t}_1 \bar{t}_w \frac{\kappa}{F^2} - 0.018\tilde{m} \left[L_{ww} - \bar{t}_w \frac{\kappa}{F^2} \right] \quad (24)$$

To assess the effect of water transport on energy conversion, the two conductance coefficients L_{ww} and L_{1w} , in addition to \bar{t}_1 , \bar{t}_w , and κ , should be known. Since in magnitude these coefficients are comparable to other components in the formula of $\beta(\tilde{m})$, they cannot be neglected. Taking into account the problem discussed here, i.e., assessing the membrane characteristics in relatively simple experiments, the results in Tab. 3 need some comments. The data in Tab. 3 correspond to the efficiencies at $I = 500 \text{ A/m}^2$ and molarity ratio 10. In column 2 the total efficiency and in columns 3,4 the component efficiencies η_{IE} and η_{wE} for both electrolytes

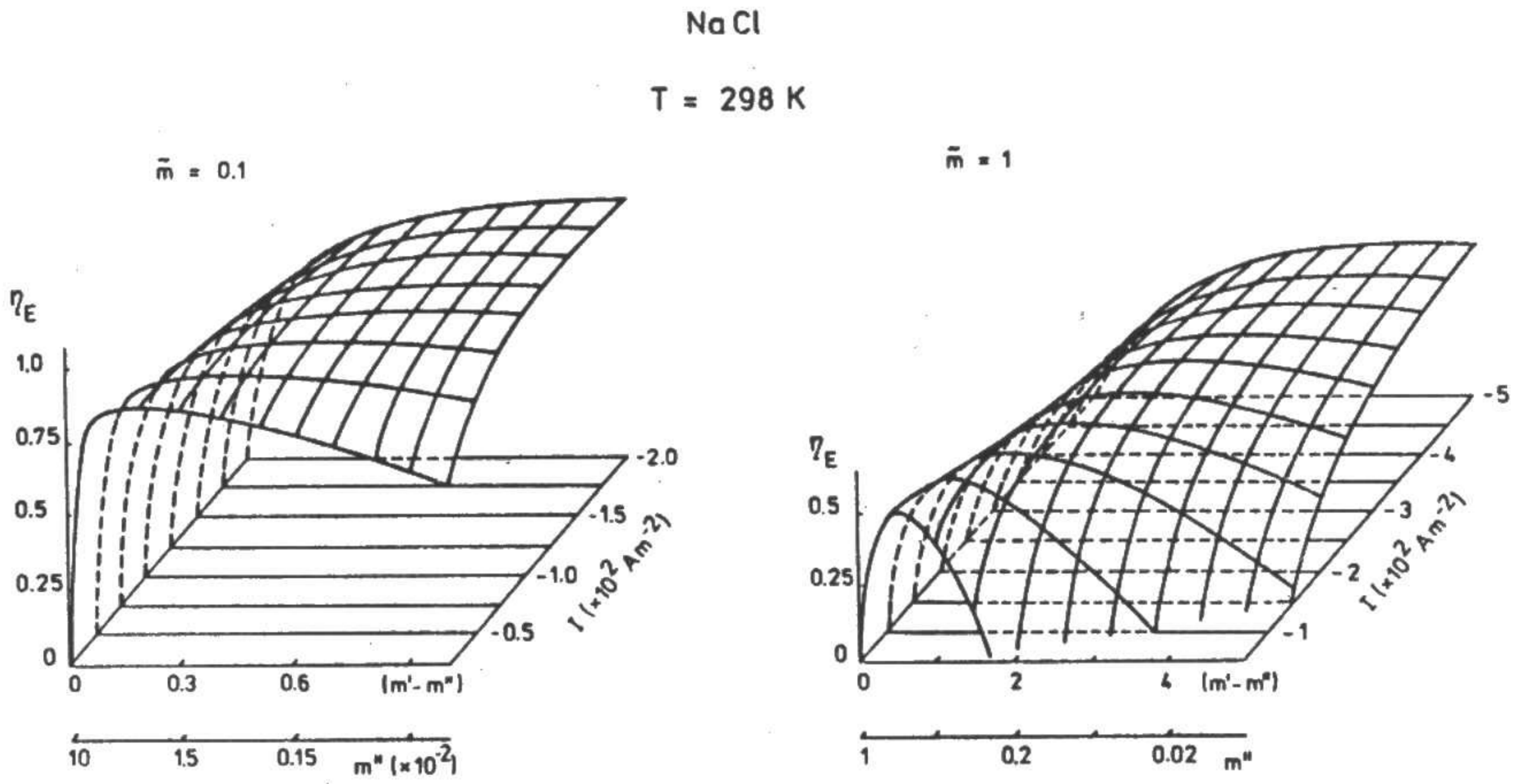


Fig. 4. Energy conversion efficiency during desalination (Nafion 120 membrane—sodium chloride solutions) for two logarithmic mean concentrations: 0.1 and 1 M; $T = 298$ K

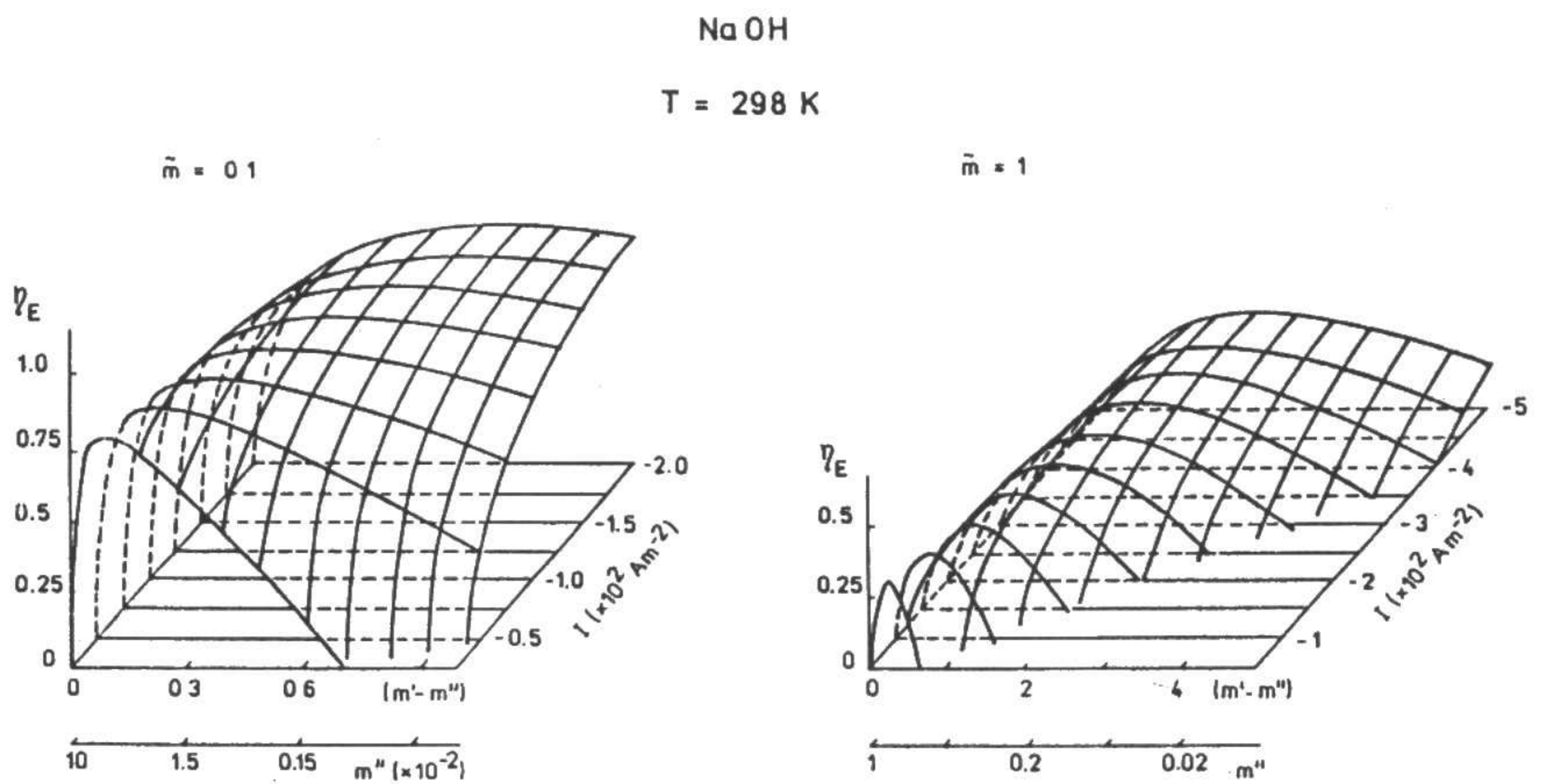


Fig. 5. Energy conversion efficiency during desalination (Nafion 120 membrane—sodium hydroxide solutions) for two logarithmic mean concentrations: 0.1 and 1 M; $T = 298$ K

are inserted. Thus one can conclude that at low salt content, the effect of η_{wE} is rather negligible, however, at increasing salinity the loss of energy due to the transport of water is up to 20% of the total efficiency of energy conversion.

Table 3
Efficiency of energy conversion during desalination
in neutral (NaCl) and alkali (NaOH) media

\tilde{m}	η_E	η_{IE}	η_{wE}
NaCl			
0.1	0.518	0.527	-0.010
0.5	0.504	0.553	-0.049
1.0	0.462	0.558	-0.096
NaOH			
0.1	0.507	0.517	-0.010
0.5	0.422	0.466	-0.045
1.0	0.318	0.401	-0.083

Figures 4 and 5 demonstrate the results for the efficiency of energy conversion computed with sets of all the data necessary. The systems are the same and the coordinates are similar to those on the graphs presenting the permselectivity. It can be easily seen that to achieve the maximum efficiency the parameters of the membrane performance should be selected carefully.

6. CONCLUSIONS

(i) The main idea of this paper, i.e., that irreversible thermodynamics can be useful in evaluating the performance of a working membrane and that it is possible to apply thermodynamics without a deep insight into the theory, has been proved.

(ii) The membrane permselectivity in a working unit, which is fundamental for efficient separation, is below the permselectivity established in the standardization procedure, usually applied in a laboratory. The formula derived by starting from IT (Eq. (14)) makes it possible to assess the dynamic membrane permselectivity. The deviation brought about by simplified calculation (i.e., by neglecting the phenomenological transport coefficients) is within 10% or less compared with the values computed by applying a full data of IT.

(iii) Having found the dynamic permselectivity it is also possible to compute the loss of energy brought about by the nonideal membrane permselectivity and the related transport phenomena, and to search for the most economical range of concentrations of the separated solutions (degree of desalination) and the current density (Eq. (20)).

At that stage the deviations of the computations caused by simplification of equations (i.e., neglecting L_{ww} , L_{1w} coefficients) depend strongly on the molarities of the separated solutions and can easily reach 10–20% of the theoretical value.

At rather high molarity more careful examination of the membrane systems and the total set of empirical results is necessary.

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APPENDIX

S_d, \bar{r}_w^d from the transport equations (1)

Assuming zero pressure difference and taking the usual meaning of the differences of chemical potentials of salt and water:

$$\Delta\mu_s = \nu_1 \Delta\tilde{\mu}_1 + \nu_2 \Delta\tilde{\mu}_2, \quad \Delta\mu_w = -0.018\tilde{m} \Delta\mu_s, \quad (A1, A2)$$

the phenomenological transport equations (1) can be divided into the electric and concentration (diffusional/osmotic) components:

$$J_i = J_i(U \neq 0, \Delta c = 0) + J_i(U = 0, \Delta c \neq 0), \quad i = 1, 2, w, \quad (A3)$$

The meaning of the components is as follows:
a) electric component

$$J_i(U \neq 0, \Delta c = 0) = (z_1 L_{i1} + z_2 L_{i2}) F \Delta\psi^I = \frac{\bar{r}_i}{z_i} \frac{\kappa}{F} \Delta\psi^I, \quad i = 1, 2, w, \quad (A4)$$

where

$$\Delta\psi^I = I/\kappa, \quad (A5)$$

κ is the surface conductivity of a membrane related to the conductance coefficients:

$$\kappa = F^2 (z_1 L_{11} + 2z_1 z_2 L_{12} + z_2 L_{22}), \quad (A6)$$

\bar{r}_i is the transport number of species i :

$$\bar{r}_i = z_i (z_1 L_{1i} + z_2 L_{2i}) \frac{F^2}{\kappa}, \quad i = 1, 2, \quad \bar{r}_w = (z_1 L_{1w} + z_2 L_{2w}) \frac{F^2}{\kappa}; \quad (A7, A8)$$

b) diffusional component (for ions, $i = 1, 2$)

$$J_i(U = 0, \Delta c \neq 0) = J_s = L_{12} (\Delta\mu_1 + z_1 F \Delta\psi^C) + L_{22} (\Delta\mu_2 + z_2 F \Delta\psi^C) + L_{2w} \Delta\mu_w \\ = \left[-\frac{\bar{r}_2}{z_2} \left(\frac{\bar{r}_1}{z_1 \nu_1} - 0.018 \tilde{m} \bar{r}_w \right) \frac{\kappa}{F^2} + L_{12} - 0.018 \tilde{m} L_{2w} \right] \Delta\mu_s, \quad (A9)$$

where $\Delta\psi^C$ denotes the electric potential difference produced by the concentration difference (concentration membrane potential):

$$\Delta\psi^c = -\frac{1}{F} \left[\sum_{i=1}^2 \frac{\bar{r}_i}{z_i} \Delta\mu_i + \bar{r}_w \Delta\mu_w \right]; \quad (A10)$$

c) osmotic component (for water, $i = w$)

$$J_w (I = 0, \Delta c \neq 0) = J_w^{\text{osm}} = L_{w1} (\Delta\mu_1 + z_1 F \Delta\psi^c) + L_{w2} (\Delta\mu_2 + z_2 F \Delta\psi^c) + L_{ww} \Delta\mu_w$$

$$= \left[\frac{1}{p_1} L_{w1} - \bar{r}_w \frac{\bar{r}_1 k}{z_1 F^2} - 0.018 \bar{m} \left(L_{ww} - \bar{r}_w \frac{k}{F^2} \right) \right] \Delta\mu_s. \quad (A11)$$

Substituting Eq. (A3) into Eq. (11) we get Eq. (12). Introducing Eqs. (A4, A9), simplified for the 1:1 electrolyte, into Eq. (12), we obtained the final equation (13). Similarly, using Eqs. (A4, A11), we get the formula for \bar{r}_w^d (Eqs. (22, 23)).

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