

L version of the transformed Kedem–Katchalsky equations for membrane transport of electrolyte solutions and internal energy conversion

Wersja L przekształconych równań Kedem-Katchalskiego dla membranowego transportu roztworów elektrolitów oraz transformacji energii wewnętrznej

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Abstract

Background. One of the important formalisms of non-equilibrium thermodynamics is Peusner network thermodynamics. The description of the energy conversion in membrane processes, i.e., the conversion of the internal energy of the system into the dissipated energy and the free energy used for the work associated with the transport of solution components, allows us to describe the relationship between these energies and the thermodynamic forces acting in the membrane system.

Objectives. The aim of this study was to develop a procedure to transform the Kedem–Katchalsky equations for the transport of binary electrolytic solutions across a membrane into the Kedem–Katchalsky–Peusner equations based on Peusner network thermodynamics. The conversion of electrochemical energy to free energy in the membrane system was also determined.

Materials and methods. The nanobiocellulose biomembranes (Biofill) were the subject of the study with experimentally determined transport parameters for aqueous NaCl solutions. The research method is the Kedem–Katchalsky–Peusner formalism for binary electrolyte solutions with introduced Peusner coefficients.

Results. The coefficients of the L version of the membrane transport equations and the Peusner coupling coefficients were derived as functions of NaCl concentration in the membrane. Based on these coefficients, the fluxes of internal energy of the system, energy dissipated to the surroundings and free energy related to the transport of electrolyte across the membrane were calculated and presented as functions of the osmotic and electric forces on the membrane.

Conclusions. The Peusner coefficients obtained from the transformations of the coefficients of the Kedem–Katchalsky formalism for the transport of electrolyte solutions through the Biofill membrane were used to calculate the coupling coefficients of the membrane processes and the dissipative energy flux. The dissipative energy flux takes the form of a quadratic form due to the thermodynamic forces on the membrane – second degree curves are obtained. Moreover, the dissipative energy flux as a function of thermodynamic forces allowed us to examine the energy conversion in transport processes in the membrane system.

Key words: membrane transport, Kedem–Katchalsky–Peusner equations, bacterial cellulose membrane, Peusner transport coefficients, internal energy conversion

Streszczenie

Wprowadzenie. Jednym z ważnych formalizmów termodynamiki nierównowagowej jest termodynamika sieciowa Peusnera. Opis transformacji energii w procesach membranowych t.j. energii wewnętrznej układu na energię dyssypowaną w otoczeniu i swobodną wykorzystywaną na pracę związaną z transportem składników roztworu pozwala uchwycić związek tych energii z siłami termodynamicznymi działającymi w układzie membranowym.

Cel pracy. Celem pracy było opracowanie procedury transformacji równań Kedem–Katchalsky’ego dla transportu binarnych roztworów elektrolitycznych przez membranę do równań Kedem–Katchalsky’ego–Peusnera w oparciu o formalizm termodynamiki sieciowej Peusnera. Ponadto, określono konwersję energii elektrochemicznej do energii swobodnej w układzie membranowym.

Materiał i metody. Przedmiotem badań były biomembrany nanobiocelulozowe (Biofill) o eksperymentalnie wyznaczonych parametrach transportu dla wodnych roztworów NaCl. Metodą badawczą jest formalizm Kedem–Katchalsky’ego–Peusnera dla binarnych roztworów elektrolitów, z wprowadzonymi współczynnikami Peusnera.

Wyniki. Współczynniki wersji L równań transportu oraz współczynniki sprzężenia Peusnera zostały wyprowadzone jako zależne od stężenia NaCl w membranie. W oparciu o te współczynniki wyliczone zostały strumienie energii wewnętrznej układu, energii dyssypowanej w otoczeniu i energii swobodnej związanej z transportem elektrolitu przez membranę i przedstawione jako funkcje termodynamicznych bodźców na membranie: stężeniowego i elektrycznego.

Wnioski. Otrzymane współczynniki Peusnera z przekształceń współczynników formalizmu Kedem–Katchalsky’ego dla transportu roztworów elektrolitowych przez membranę Biofill posłużyły do obliczenia współczynników sprzężenia procesów membranowych oraz obliczenia strumienia energii dyssypatywnej. Strumień energii dyssypatywnej przyjmuje postać formy kwadratowej od bodźców termodynamicznych na membranie – krzywe drugiego stopnia. Ponadto, strumień energii dyssypatywnej jako funkcja bodźców termodynamicznych pozwolił zbadać konwersję energii w procesach transportowych w układzie membranowym.

Słowa kluczowe: transport membranowy, równania Kedem–Katchalsky’ego–Peusnera, membrana z celulozy bakteryjnej, współczynniki transportu Peusnera, konwersja energii wewnętrznej

Background

Membrane transport is one of the fundamental non-equilibrium processes that occur at all levels of organization of all physicochemical systems, including biological systems.¹ Many of these processes can be carried out on a different scale in physicochemical systems containing artificial polymeric membranes.² The study of membrane transport processes in such systems is important in many areas of human activity of a cognitive and utilitarian nature, e.g., in science, technology and biomedicine.^{3,4} The controlled drug release systems, membrane dressings to support the healing of chronic wounds, bioreactors for testing strategies to combat bacterial infections using lytic phage application in combination with established and novel antibacterial agents, etc.,^{4,5} are the main examples of biomedical applications. In these systems, the membrane is a selective barrier that ensures the separation of the phases it separates. This role is played by polymeric membranes of various structure and composition, made of polyvinyl chloride, bacterial cellulose, graphene cellulose acetate, etc.^{3–9}

The physical quantity that characterizes non-equilibrium systems is thermodynamic entropy (S-entropy).^{10,11} It plays a fundamental role in the study of non-equilibrium processes, since it numerically characterizes the degree of irreversibility of physico-chemical processes, including biological processes. It is well-known that these processes are subject to the law of entropy growth. Accordingly,

the production of S-entropy is a consequence of irreversible processes of mass, charge, energy, and momentum transport in various types of systems, including membrane systems.^{1,11}

Formalisms and research tools developed in the context of non-equilibrium thermodynamics and/or network thermodynamics have been used to describe membrane transport.^{12,13} These methods include the Kedem–Katchalsky (K–K)¹² and Kedem–Katchalsky–Peusner (K–K–P)¹³ formalisms, along with modifications and extensions.^{14–19} The starting point for deriving the equations for membrane transport and also energy conversion is the determination of the energy dispersion function, which is the product of entropy production and absolute temperature.^{12,13} The temporal change in entropy production is reflected in disease processes and in the aging processes of biological organisms.^{10,20}

Previous studies have presented procedures for transforming the classical equations into L , R , H and P versions using Peusner network thermodynamics methods for membrane transport of homogeneous or heterogeneous non-electrolyte solutions.^{16–19,21} Chemical energy conversion procedures using L , R , H and P versions of the transformed K–K equations are presented. These procedures use thermodynamic forces (hydrostatic pressure and osmotic pressure gradients) and volume and solute fluxes. In this study, in addition to the above forces and fluxes, the electrical potential difference and the ionic flux were used.

Accordingly, the purpose of this paper is to develop a procedure for transforming the K–K equations for

binary electrolyte solutions into the K–K–P equations using the formalism developed in the context of Peusner's network thermodynamics. Using the obtained L -version of the K–K–P equations, a method was developed to evaluate the conversion of electrochemical energy into free energy in a membrane system containing aqueous electrolyte solutions with a concentration field and an electric field superimposed on them. The 1st part of this paper is an introduction. The 2nd part presents the procedure for deriving L -versions of the K–K–P equations describing the membrane transport of homogeneous electrolyte solutions and the equations representing L -versions of the transport parameters L_{ij} of the coupling coefficients l_{ij} and $(Q_L)_{ij}$ and the energy conversion efficiency coefficient $[(e_{ij})_L]_{max}$, where $(i, j \in \{1, 2, 3\})$. In this section, we also present mathematical equations for the S -energy dissipation function $(\Phi_S)_L$ derived from the K–K–P formalism describing the energy dissipation function as a function of thermodynamic forces. The equations obtained were used to calculate the characteristics: $(\Phi_S)_L = f[(\Delta P - \Delta\pi_s), (\Delta\pi_s/C_s), E]$, $[(\Phi_F)_L]_{ij} = f[(\Delta P - \Delta\pi_s), (\Delta\pi_s/C_s), E]$, and $[(\Phi_U)_L]_{ij} = f[(\Delta P - \Delta\pi_s), (\Delta\pi_s/C_s), E]$, based on the characteristics $L_{ij} = f(C_s)$ and $l_{ij} = f(C_s)$, for the bacterial cellulose membrane Biofill. The values of the coupling parameter and the coefficient of energy conversion efficiency $[(e_{ij})_L]_{max}$ were used to evaluate electrochemical energy conversion.

Materials and methods

Membrane system

The membrane transport measurement system is illustrated schematically in Fig. 1. This system consists of a membrane (M), located in the vertical plane and separating 2 aqueous NaCl solutions with concentrations at the initial moment C_h and $C_l = \text{const.}$ ($C_h \geq C_l$). The density of solutions with concentrations of C_h and C_l fulfilled the condition $P_h \leq P_l = \text{constant}$. In this system there are 3 driving forces ($\Delta P = P_h - P_l$, $\Delta\pi = RT(C_h - C_l)$, $E = E_h - E_l$), which generate 3 fluxes (J_v, J_s, I).

According to the K–K formalism, the transport parameters of a membrane are determined by 6 coefficients: hydraulic permeability (L_p), reflection (σ_s), diffusion permeability (ω_s), electroosmotic permeability (β), transference number (τ_c), and conductance (κ).

L -version of the Kedem–Katchalsky–Peusner equations for electrolyte solutions

The L -versions of the K–K–P equations for homogeneous electrolyte solutions are obtained by appropriate transformation of the classical K–K equations.¹² Two alternative sets of these equations can be used for this purpose. In this study, the following form of these equations is used:

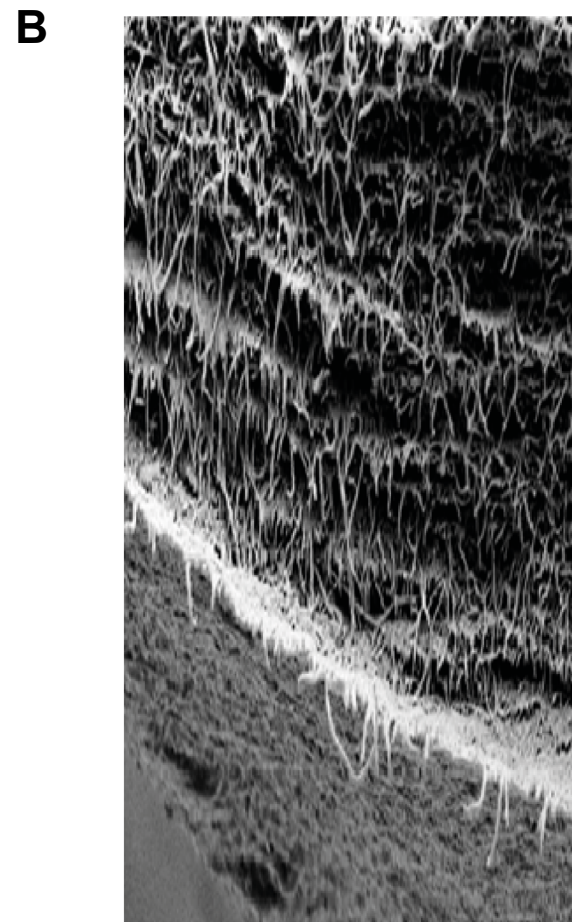
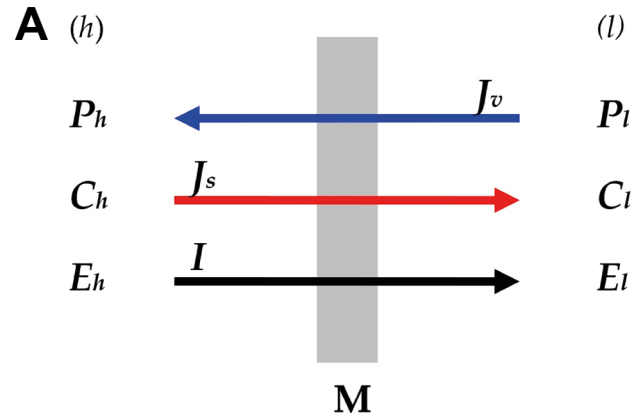


Fig. 1. A. Model of a single-membrane system; M – membrane; P_h and P_l – mechanical pressures; C_h and C_l – total solution concentrations ($C_h > C_l$); C_l^* , J_v – volume flux; J_s – solute flux; I – ionic electric current; E_h and E_l – electrode potentials; B. Cross-sectional image of the Biofill membrane obtained with a scanning microscope at $\times 10,000$ magnification

$$J_v = L_p [(\Delta P - \Delta\pi_i) - \sigma_s \Delta\pi_s + \beta I] \quad (1)$$

$$J_s = C_s (1 - \sigma_s) J_v + \omega_s \Delta\pi_s + \frac{\tau_c}{z_c F} I \quad (2)$$

$$I = \kappa \left(\frac{\tau_c}{z_c F} \frac{\Delta\pi_s}{C_s} - \beta J_v + E \right) \quad (3)$$

where: L_p – hydraulic permeability coefficient, σ_s – reflection coefficient, ω_s – coefficient of diffusion permeability,

J_v – volume flux, J_s – solute flux, I – ionic electric current, $\Delta\pi = RT\Delta C$ – osmotic pressure difference, RT – the product of the gas constant and the absolute temperature, $\Delta C = C_h - C_l$ ($C_h > C_l$) – concentration difference on the membrane, $C_s = (C_h - C_l)(\ln C_h C_l^{-1})^{-1} = \Delta\pi(RT \ln C_h C_l^{-1})^{-1}$ – average concentration of the solution in the membrane, $\Delta\pi_i$ – osmotic pressure difference generated by solute molecules that do not penetrate the membrane, E – the potential difference across the membrane, β – electroosmotic permeability coefficient, τ_c – transference number, F – Faraday constant, and κ – the conductance coefficient.

The phenomenological coefficients appearing in equations (1)–(3) are defined by the following expressions:

$$L_p = \left(\frac{\tau_c}{\Delta P - \Delta\pi_i} \right)_{\Delta P - \Delta\pi_i = 0, I = 0} \quad (4)$$

$$\sigma_s = \left(\frac{\Delta P - \Delta\pi_i}{\Delta\pi_s} \right)_{J_v = 0, I = 0} \quad (5)$$

$$\omega_s = \left(\frac{J_v}{\Delta\pi_s} \right)_{J_v = 0, I = 0} \quad (6)$$

$$\beta = \frac{1}{L_p} \left(\frac{J_v}{I} \right)_{\Delta P - \Delta\pi_i = 0, \Delta\pi_s = 0} \quad (7)$$

$$\kappa = \left(\frac{I}{E} \right)_{J_v = 0, \Delta\pi_s = 0} \quad (8)$$

$$\kappa = z_c F \left(\frac{J_s}{I} \right)_{J_v = 0, \Delta\pi_s = 0} \quad (9)$$

To obtain the L -version of the K–K–P equations for electrolyte solutions, we will transform Equations (1)–(3) using Peusner's network thermodynamics methods. Considering Equations (2) and (3) in Equation (1), we get the L -version of Equation (1):

$$J_v = L_{11}(\Delta P - \Delta\pi_s) + L_{12} \frac{\Delta\pi_s}{C_s} + L_{13} E \quad (10)$$

$$\text{where } L_{11} = \frac{L_p}{1 + L_p \beta^2 \kappa}, \quad L_{12} = \frac{L_p [\beta \tau_c \kappa + C_s (1 - \sigma_s) z_c F]}{z_c F (1 + L_p \beta^2 \kappa)},$$

$$L_{13} = \frac{\kappa \beta L_p}{1 + L_p \beta^2 \kappa}.$$

In turn, considering Equations (10) and (3) in Equation (2), we get the L -version of Equation (2):

$$J_s = L_{21}(\Delta P - \Delta\pi_s) + L_{22} \frac{\Delta\pi_s}{C_s} + L_{23} E \quad (11)$$

$$\text{where } L_{21} = \frac{L_p [C_s (1 - \sigma_s) z_c F + \beta \tau_c \kappa]}{z_c F (1 + L_p \beta^2 \kappa)},$$

$$L_{22} = \frac{C_s z_s^2 F^2 [\omega_s (1 + L_p \beta^2 \kappa) + L_p C_s (1 - \sigma_s)^2] + \tau_c^2 \kappa}{z_c^2 F^2 (1 + L_p \beta^2 \kappa)},$$

$$L_{23} = \frac{\kappa [\tau_c + C_s (1 - \sigma_s) z_c F L_p \beta]}{z_c^2 F^2 (1 + L_p \beta^2 \kappa)}$$

To get the L version of Equation (3), one must transform Equation (3) with Equation (10). As a result of these operations, we get:

$$I = L_{31}(\Delta P - \Delta\pi_s) + L_{32} \frac{\Delta\pi_s}{C_s} + L_{33} E \quad (12)$$

$$\text{where } L_{31} = \frac{L_p \beta \kappa}{1 + L_p \beta^2 \kappa}, \quad L_{32} = \frac{\kappa [\tau_c - L_p \beta C_s (1 - \sigma_s) z_c F]}{z_c F (1 + L_p \beta^2 \kappa)},$$

$$L_{33} = \frac{\kappa}{1 + L_p \beta^2 \kappa}.$$

Equations (10)–(12) can also be written in a matrix form:

$$\begin{bmatrix} J_v \\ J_s \\ I \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} & L_{13} \\ L_{21} & L_{22} & L_{23} \\ L_{31} & L_{32} & L_{33} \end{bmatrix} \begin{bmatrix} \Delta P - \Delta\pi_s \\ \frac{\Delta\pi_s}{C_s} \\ E \end{bmatrix} = [L] \begin{bmatrix} \Delta P - \Delta\pi_s \\ \frac{\Delta\pi_s}{C_s} \\ E \end{bmatrix} \quad (13)$$

where: $[L]$ is a matrix of Peusner coefficients L_{ij} ($i, j \in \{1, 2, 3\}$) for binary homogeneous electrolyte solutions. Equations (11)–(13) are one of the forms of the K–K equations obtained by means of the symmetrical transformation of Peusner network thermodynamics. The comparison of Equations (10)–(13) shows that for nondiagonal coefficients $L_{12} \neq L_{21}$, $L_{13} \neq L_{31}$ and $L_{23} \neq L_{32}$. In turn, the determinant of the matrix $[L]$ $\det[L] \equiv L_{det}$ can be written as:

$$L_{det} = C_s L_p \kappa \quad (14)$$

Cross coefficients $L_{ij(i \neq j)}$ describe the relationship between different irreversible processes. The expression

$$l_{ij} = \frac{L_{ij}}{\sqrt{L_{ii} L_{jj}}}, \quad i, j \in \{1, 2, 3\}, \quad (15)$$

formed from these coefficients determines the degree of coupling. This means that the coefficient l_{ij} is a measure of the degree of coupling. If $L_{ij} = 0$, the irreversible processes are independent, while when $l_{ij} = \pm 1$, the irreversible processes are maximally coupled.

Using Peusner's definition,¹³ the energy coupling parameter Q can be written in the following form:

$$(Q_L)_{ij} = \frac{2|L_{ij} L_{ji}|}{4L_{ii} L_{jj} - 2L_{ij} L_{ji}} = \frac{l_{ij} l_{ji}}{2 - l_{ij} l_{ji}} = (Q_L)_{ij}, \quad i, j \in \{1, 2, 3\} \quad (16)$$

This parameter can be used to study the efficiency and stability of physico-chemical and biological energy conversion systems.

The concept of the degree of coupling was used to determine the energy conversion efficiency $(e_{ij})_L$, $0 \leq (e_{ij})_L \leq 1$. The maximum value of this coefficient is determined by the expression:

$$\begin{aligned} [(e_{ij})_L]_{\max} &= \frac{L_{ij} L_{ji}}{L_{ij} L_{ji} \left(1 + \sqrt{1 - \frac{L_{ij} L_{ji}}{L_{ii} L_{jj}}} \right)^2} \\ &= \frac{2(Q_L)_{ij}}{(1 + Q_{ji}) \left(1 + \sqrt{1 - \frac{2(Q_L)_{ij}}{1 - (Q_L)_{ij}}} \right)^2}, \quad j \in \{1, 2, 3\} \end{aligned} \quad (17)$$

Equation (17) illustrates the relationship between the degree of coupling and the maximum efficiency of energy conversion. It is worth mentioning that full coupling ($l_{ij} = 1$) occurs at $(e_{ij})_l = 1$. This means that the stationary states of flows characterized by minimum entropy production are identical to the state with maximum efficiency.

Mathematical model of energy conversion in the membrane system

The measure of S -energy dissipation is the so-called dissipation function Φ_s , which is equal to the product of absolute temperature (T) and S -entropy production ($d_i S/dt$). To obtain mathematical expressions for S -energy dissipation in a system in which a membrane separates 2 homogeneous electrolytic solutions of different concentrations, we will use the procedure described in previous papers.^{21,22} In stationary state, the membrane transport of homogeneous electrolytic solutions containing 1 solute (s) and solvent (w) is caused by thermodynamic forces, $\Delta\pi$ (osmotic pressure difference), ΔP (hydrostatic pressure difference) and E (electromotive force); then

$$(\Phi_s)_L = J_w \bar{V}_w (\Delta P - \Delta\pi_s) + J_s \left(\bar{V}_s \Delta P + \frac{\Delta\pi_s}{C_s} \right) + IE \quad (18)$$

where: \bar{V}_s and \bar{V}_w denote the partial molar volumes of the s -th and w -th component of the solution, J_s and J_w – fluxes of solute and solvent respectively, I – ionic electric current $C_s = (C_h - C_l)[\ln(C_h C_l^{-1})]^{-1}$, C_h and C_l ($C_h > C_l$) – solute concentrations, $\Delta\pi_s = RT(C_h - C_l)$ – osmotic pressure difference, RT – the product of the gas constant and the absolute temperature, and $E = E_h - E_l$ – the potential difference across the membrane.

Taking into consideration the expressions: $J_s \bar{V}_s + J_w \bar{V}_w \equiv J_v$ and $J_s C_s^{-1} - J_w \bar{V}_w \equiv J_D$ (J_v – volume flux, J_D – diffusive flux) we can write Equation (18) in the form:

$$(\Phi_s)_L = J_v (\Delta P - \Delta\pi_s) + J_s \left(\frac{1}{C_s} + \bar{V}_s \right) \Delta\pi_s + IE \quad (19)$$

Assuming for NaCl $C_h = 100 \text{ mol m}^{-3}$ and $C_l = 0.01 \text{ mol m}^{-3}$, we get $C_s = 10.86 \text{ mol m}^{-3}$ and $1/C_s = 0.092 \text{ m}^3 \text{ mol}^{-1}$. On the other hand, $\bar{V}_s = 2.3 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. This means that $(1/C_s) \gg \bar{V}_s$, so Equation (19) can be written as follows:

$$(\Phi_s)_L = J_v (\Delta P - \Delta\pi_s) + J_s \frac{\Delta\pi_s}{C_s} + IE \quad (20)$$

We will now calculate the $(\Phi_s)_L$ of Equation (20), using the L -versions of the K–K–P equations.

In thermodynamic systems, including membrane systems, the internal energy (U -energy) can be converted into free energy (F -energy) and the dissipated energy (S -energy).^{21,22} The fluxes of these energies satisfy the following equation:

$$[(\Phi_U)_L]_{ij} = [(\Phi_F)_L]_{ij} + (\Phi_s)_L \quad (21)$$

where: $(\Phi_U)_L = A^{-1} dU/dt$ is the flux of U -energy, $(\Phi_F)_L = A^{-1} dF/dt$ is the flux of F -energy, $(\Phi_s)_L = TA^{-1} d_i S/dt$ – the flux of dissipated energy (S -energy), $d_i S/dt$ – the rate of entropy creation in the membrane system by irreversible processes (flux of cumulative entropy creation), T – absolute temperature, and A – the membrane surface area.

If the solutions contain a solvent and 1 dissolved substance, then the L -version of the dissipated energy for the homogeneous solution conditions denoted by $(\Phi_s)_L$ is described by the following equation:

$$(\Phi_s)_L = (\Phi_s)_{J_v} + (\Phi_s)_{J_s} = J_s (\Delta P - \Delta\pi_s) + J_s \frac{\Delta\pi_s}{C_s} + IE \quad (22)$$

where: $(\Phi_s)_L$ is the L -version of the dissipated energy, $(\Phi_s)_{J_v}$ – the dissipated energy produced by J_v , $(\Phi_s)_{J_s}$ – the dissipated energy produced by J_s , $(\Phi_s)_l$ – the dissipated energy produced by I , J_v and J_s – the volume and solute fluxes, respectively; I is the ionic current.

Taking into consideration Equations (10)–(12) into Equation (22), we get:

$$\begin{aligned} (\Phi_s)_L = & L_{11} (\Delta P - \Delta\pi_s)^2 + (L_{12} + L_{21}) \frac{\Delta\pi_s}{C_s} (\Delta P - \Delta\pi_s) \\ & + (L_{13} + L_{31}) E (\Delta P - \Delta\pi_s) + \\ & + (L_{23} + L_{32}) \frac{\Delta\pi_s}{C_s} E + L_{22} \left(\frac{\Delta\pi_s}{C_s} \right)^2 + L_{33} E^2 \end{aligned} \quad (23)$$

The Equation (23) shows the L -version of the S -energy dissipation. The $(\Phi_s)_L$ is the dissipated energy flux, i.e., the time change of energy per unit area of the membrane expressed in W/m^2 . We can calculate the $(\Phi_F)_L$ and $(\Phi_U)_L$ for the concentration polarization conditions using the following equation^{21,22}:

$$[(e_L^r)_{ij}]_{\max} = \frac{[(\Phi_F)_L]_{ij}}{(\Phi_U)_L} = \frac{[(\Phi_F)_L]_{ij}}{[(\Phi_F)_L]_{ij} + (\Phi_s)_L} \quad (24)$$

Transforming Equation (24), we get:

$$[(\Phi_F)_L]_{ij} = \frac{[(e_L^r)_{ij}]_{\max}}{1 - [(e_L^r)_{ij}]_{\max}} (\Phi_s)_L \quad (25)$$

where: $[(e_L^r)_{ij}]_{\max}$ is the energy conversion efficiency defined by means of Kedem–Caplan–Peusner coefficients and can be presented in the following form:

$$[(e_L^r)_{ij}]_{\max} = \frac{l_{ij} l_{ji}}{(1 + \sqrt{1 - l_{ij} l_{ji}})^2} = [(e_L^r)_{ji}]_{\max} \quad (26)$$

From a formal point of view, the cases of $\phi(F)_L = 0$ and $\phi(U)_L = 0$ are excluded, because in order for the denominator of Equations (25) and (26) to be different from 0, the condition $[(e_L^r)_{ij}]_{\max} \neq 1$ must be satisfied.

The values of $[(e_L^r)_{ij}]_{\max}$ coefficients are limited by the relations $0 \leq [(e_L^r)_{ij}]_{\max} \leq 1$; $[(e_L^r)_{ij}]_{\max} = 0$ when $L_{12}L_{21} = 0$ or $l_{12}l_{21} = 0$ and $[(e_L^r)_{ij}]_{\max} = 1$, when $L_{12}L_{21} = L_{11}L_{22}$, and, $L_{12}L_{21} = 1$. Taking into account the Equation (26) in (25), we get:

$$[(\Phi_F)_L]_{ij} = \frac{L_{ij}L_{ji}}{L_{ii}L_{jj} \left(1 + \sqrt{1 - \frac{L_{ij}L_{ji}}{L_{ii}L_{jj}}} \right)^2 - L_{ij}L_{ji}} (\Phi_S)_L$$

$$= \frac{[(e_L)_{ij}]_{\max}}{1 - [(e_L)_{ij}]_{\max}} (\Phi_S)_L \quad (27)$$

To obtain the equation for $[(\Phi_U)_L]_{ij}$, it is necessary to take into consideration Equation (26) in Equation (24). After performing the necessary transformations, we get:

$$[(\Phi_U)_L]_{ij} = \frac{L_{ij}L_{ji}\mathcal{L}^2}{L_{ii}L_{jj}\mathcal{L}^2 - L_{ij}L_{ji}} (\Phi_S)_L = \frac{1}{1 - [(e_L)_{ij}]_{\max}} (\Phi_S)_L \quad (28)$$

where $\mathcal{L} = 1 + \sqrt{1 - \frac{L_{ij}L_{ji}}{L_{ii}L_{jj}}}$.

From the above procedure, based on the Equations (24)–(28), we can calculate the amount of available F -energy that can be converted into useful work and the total internal U -energy.

Biomembrane characteristics

The nanobiocellulose as a main component of the Biofill membrane (Biofill Produtos Biotecnológicos S.A., Curitiba, Brazil) is produced by *Acetobacter xylinum*.^{23–26} Studies using a scanning microscope (Zeiss Supra 35; Carl Zeiss AG, Jena, Germany) have shown that the structure of the Biofill membrane is made up of fibers interwoven into a network that is no more than 130-nm thick, consisting of micro-fibers with a cross section of 0.1–0.2 μm arranged in layers.²⁶ The thickness of the membrane in its hydrated state is about 20 μm . The Bioprocess membrane is symmetric, isotropic and electrically neutral.

The values of transport coefficients (L_p , σ_s , ω_s , β , κ , t_c) of the Biofill membrane, appearing in Equations (1)–(3) and defined by Equations (4)–(9), were taken from the previous work.²⁶ This paper describes the methodology for determining these coefficients in a series of independent experiments. The values of transport coefficients L_p , σ_s and

ω_s in the studied range of NaCl concentrations are constant and amount to $L_p = 6.5 \times 10^{-11} [\text{m}^3/\text{Ns}]$, $\sigma_s = 0.36 \times 10^{-3}$ and $\omega_s = 17.1 \times 10^{-10} [\text{mol}/\text{Ns}]$. In turn, the values of transport coefficients β , κ and t_c in the studied range of NaCl concentrations are concentration-dependent. The dependencies $\beta = f(C_s)$, $\kappa = f(C_s)$ and $t_c = f(C_s)$ are summarized in Table 1.

Bacterial cellulose membranes are used for both biomedical and non-medical purposes. For biomedical purposes, they are used as dressings in the healing process of burns and venous leg ulcers, and in the manufacture of prosthetic blood vessels and as a selective barrier in the controlled release of drugs.^{9,23–25}

Results

Characteristics of $L_{ij} = f(C_s)$ ($i, j \in \{1, 2, 3\}$) and $L_{det} = f(C_s)$

Calculations of the coefficients $L_{ij} = f(C_s)$ ($i, j \in \{1, 2, 3\}$) and $L_{det} = f(C_s)$ were performed for the following data: $R = 8.31 \text{ J/mol K}$, $T = 295 \text{ K}$ and $F = 9.65 \times 10^4 \text{ C/mol}$, and $C_s = 0.06 \div 15 \text{ mol/m}^3$, $C_l = 0.01 \text{ mol/m}^3$ and $C_h = 0.2 \div 144 \text{ mol/m}^3$. To calculate the dependencies $L_{ij} = f(C_s)$, ($i, j \in \{1, 2, 3\}$) and $L_{det} = f(C_s)$, the Equations (13)–(17) were used. The results of the calculations are presented in Fig. 2A–F. They show that the coefficient L_{11} is independent on C_s . Therefore, its value is constant and amounts to $L_{11} = 6.49 \times 10^{-11} \text{ m}^3/\text{Ns}$.

The values of coefficients $L_{ij} = f(C_s)$ ($i, j \in \{1, 2, 3\}$) and $L_{det} = f(C_s)$ are dependent on C_s as is illustrated in Fig. 2A–F. Most of the calculated flux-force coupling coefficients (L_{ij}) in general depend non-linearly on the concentration of the substance in the membrane, except the coefficients $L_{12} = L_{21}$ (showing linear dependence on concentration) and the almost linear dependence of the coefficient L_{22} on the NaCl concentration in the membrane. The values of these coefficients are positive except for the L_{31} coefficient, which is negative in the entire range of considered concentrations. Figure 2A shows that the values of coefficients $L_{12} \approx L_{21}$ are positive and increase with increasing value of C_s . Figure 2B demonstrates that the characteristics $L_{13} \neq L_{31} = f(C_s)$ are nonlinear. The values of coefficient L_{13} are positive and decrease with increasing value of C_s . In contrast, the absolute values of coefficient L_{31} decrease with increase of C_s . A positive coefficient L_{ij} means that an increase in the corresponding thermodynamic force j causes an increase in the corresponding flux i . The absolute values of coefficients L_{13} and L_{31} decrease as the concentration of the substance in the membrane increases. In turn, the remaining coefficients (except L_{23} and L_{32} , which show extreme values) increase with increasing concentration in the membrane. The linear increase of the L_{ij} coefficient with the concentration in the membrane means that a change in the corresponding thermodynamic force

Table 1. Dependencies $\beta = f(C_s)$, $\kappa = f(C_s)$, and $t_c = f(C_s)$ for Biofill bacterial cellulose membrane and aqueous NaCl solutions

$C_s [\text{mol/m}^3]$	$\beta \times 10^{-3} [\text{N/A}]$	$\kappa [1/\Omega \text{ m}^2]$	t_c
0.06	8.5	0.45	0.4
0.1	6.0	0.5	0.5
0.6	2.0	0.9	0.4
1	1.2	1.3	0.3
3	0.5	1.5	0.22
5	0.4	1.7	0.18
7	0.2	2.0	0.15
10	0.02	2.4	0.12
15	0.01	7.0	0.1

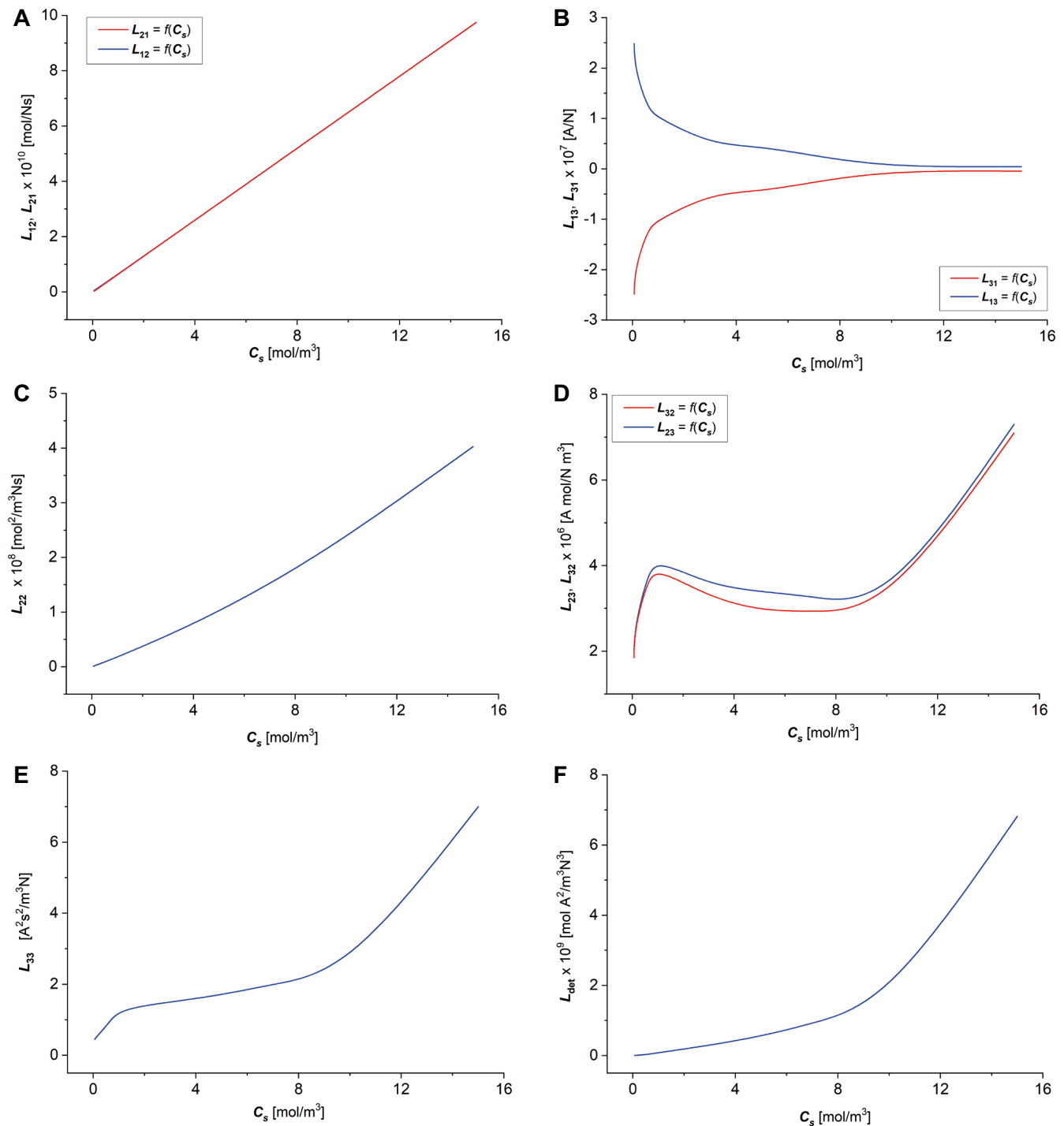


Fig. 2. Graphical representation of the dependencies $L_{ij} = f(C_s)$ ($i, j \in \{1, 2, 3\}$) and $L_{det} = f(C_s)$ for aqueous NaCl solutions. A. $L_{12} = L_{21} = f(C_s)$; B. $L_{13} \neq L_{31} = f(C_s)$; C. $L_{22} = f(C_s)$; D. $L_{23} \neq L_{32} = f(C_s)$; E. $L_{33} = f(C_s)$; F. $L_{det} = f(C_s)$

on the membrane (j) causes a proportional increase in the corresponding flux (i). Non-linear changes of the L_{ij} coefficient make the force-flux relationship more complicated. The greater the slope of the L_{ij} – concentration dependence (i.e. the greater the derivative of L_{ij} with respect to concentration), the greater an influence of given thermodynamic force on the relevant flux. The most interesting dependence on concentration is observed for the coefficients L_{23} and L_{32} , which, after a large increase in the narrow range of low concentrations (up to a concentration

of about 1 mol/m³), show a slight reduction or even stabilization of the coefficient in the concentration range from 1 mol/m³ to about 10 mol/m³. Above the concentration of 10 mol/m³, increase of the concentration in the membrane causes a further non-linear increase in the L_{23} and L_{32} coefficients, but smaller than that observed in the low concentration range (up to 1 mol/m³). These nonlinear dependencies of the coefficients on concentration are related to the structure of the membrane itself and its impact on individual transported substances, and thus

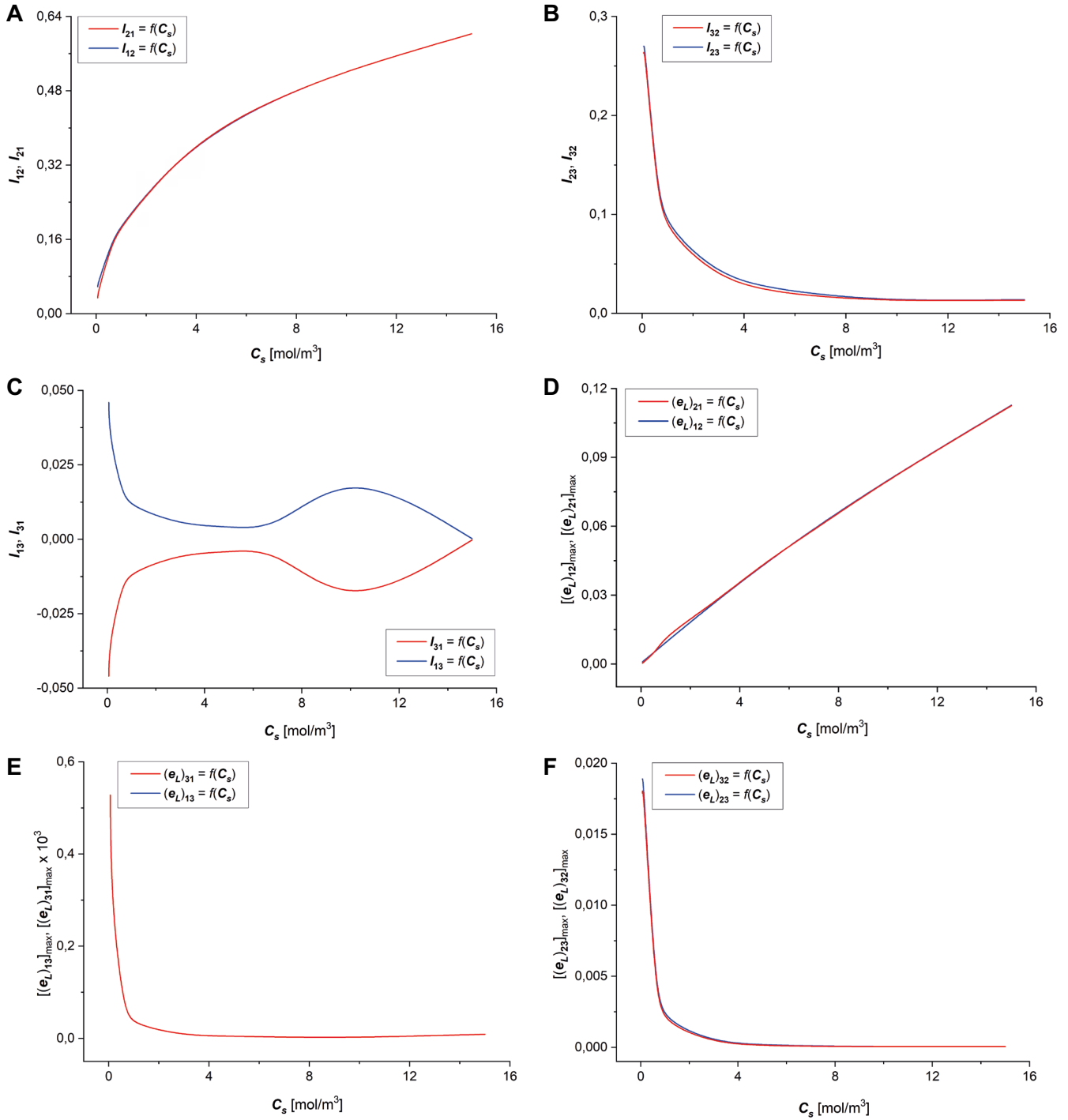


Fig. 3. Graphical representation of the dependencies $l_{ij} = f(C_s)$ ($i, j \in \{1, 2, 3\}$) and $(e_L)_{ij,max} = f(C_s)$, for aqueous NaCl solutions. A. $l_{12} = l_{21} = f(C_s)$; B. $L_{23} = L_{32} = f(C_s)$; C. $L_{13} = L_{31} = f(C_s)$; D. $(e_L)_{12,max} = (e_L)_{21,max} = f(C_s)$; E. $(e_L)_{23,max} = (e_L)_{32,max} = f(C_s)$ and $(e_L)_{13,max} = (e_L)_{31,max} = f(C_s)$

indirectly on the interaction of substances transported through the membrane.

Figure 2C shows that the characteristic $L_{22} = f(C_s)$ is non-linear and values of L_{22} are positive. Figure 2D demonstrates that the characteristics $L_{23} \neq L_{32} = f(C_s)$ are non-linear and values both L_{23} and L_{32} are positive. The curve shown in Fig. 2E shows that the $L_{33} = f(C_s)$ characteristics are nonlinear and the L_{33} values are positive. $L_{det} = f(C_s)$ characteristics are also nonlinear and L_{det} values are positive.

Characteristics $l_{ij} = f(C_s)$ and $[(e_L)_{ij}]_{max} = f(C_s)$ ($i, j \in \{1, 2, 3\}$)

Taking into account the results of calculations obtained for dependencies $L_{ij} = f(C_s)$, ($i, j \in \{1, 2, 3\}$) shown in Fig. 3A–C in the Equation (15), the dependencies $l_{ij} = f(C_s)$ were calculated and presented in Fig. 3A–E.

The curves presented in Fig. 3A show that the characteristics $l_{12} = f(C_s)$ and $l_{21} = f(C_s)$ are nonlinearly dependent on concentration, besides $l_{12} = l_{21}$, and these curves are

of saturation type. Figure 3B shows the characteristics of the $l_{13} = f(C_s)$ and $l_{31} = f(C_s)$. Figure 3B illustrates also that the values of l_{13} are positive and l_{31} are negative. Moreover, these characteristics are symmetrical about the axis passing through the point of zero concentration. The $l_{23} = f(C_s)$ and $l_{32} = f(C_s)$ characteristics shown in Fig. 3C are also nonlinear. These characteristics are of hyperbolic type. In addition, $l_{23} = l_{32}$ in whole range of studied concentrations. A comparison of Fig. 3A, 3B and 3C shows that $l_{12} = l_{21} > l_{23} = l_{32} > l_{13} > l_{31}$. The coupling coefficients l_{ij} between processes occurring in the membrane have values ranging from 0 (no coupling) to 1 (complete coupling). Coupling coefficients with the same indexes (the same process) l_{ij} are equal to 1. The coefficients l_{12} (characterizing coupling of processes $\ll J_v \mid \Delta p - \Delta \pi_i \gg \Leftrightarrow \ll J_s \mid \Delta \pi_s / C_s \gg$ suitably) and l_{21} increase with increasing concentration in the membrane, which indicates greater coupling of these processes with increasing concentration. This may indicate an increasing role of the membrane in the interaction between these processes as the concentration of substances in the membrane increases. In turn, the coefficients l_{23} and l_{32} (coupling of processes $\ll J_s \mid \Delta \pi_s / C_s \gg \Leftrightarrow \ll I \mid E \gg$ respectively) reach higher values at low concentrations (high coupling) and gradually decrease with increasing concentration in the membrane to a value close to 0 (no coupling) for concentrations higher than 8 mol/m³.

Considering the $l_{ij} = f(C_s)$ dependencies shown in Fig. 3A–C, and Equation (17), the dependencies $[(e_L)_{ij}]_{\max} = f(C_s)$ were calculated. The coefficients $(e_L)_{ij}$, characterize the efficiency of energy conversion in the membrane. The curves presented in Fig. 3D show that the characteristics $[(e_L)_{12}]_{\max} = f(C_s)$ and $[(e_L)_{21}]_{\max} = f(C_s)$ are linear and $[(e_L)_{12}]_{\max} = [(e_L)_{21}]_{\max}$. These coefficients increase linearly from 0 (inefficient energy conversion) for low concentrations to values of approx. 0.12 for a concentration in the membrane of 15 mol/m³. Figure 3E shows the characteristics $[(e_L)_{23}]_{\max} = f(C_s)$ and $[(e_L)_{32}]_{\max} = f(C_s)$. These characteristics are nonlinear and are of hyperbolic type. In addition, Fig. 3E shows that $[(e_L)_{23}]_{\max} = [(e_L)_{32}]_{\max}$. Similarly,

the characteristics $[(e_L)_{13}]_{\max} = f(C_s)$ and $[(e_L)_{31}]_{\max} = f(C_s)$, illustrated in Fig. 3F are of hyperbolic type. In addition, Fig. 3F shows that $[(e_L)_{13}]_{\max} = [(e_L)_{31}]_{\max}$. A comparison of Fig. 3D, Fig. 3E and Fig. 3F shows that $[(e_L)_{12}]_{\max} = [(e_L)_{21}]_{\max} > [(e_L)_{23}]_{\max} = [(e_L)_{32}]_{\max} > [(e_L)_{13}]_{\max} = [(e_L)_{31}]_{\max}$. The coefficients presented in Fig. 3E,F, characterize energy conversion in the membrane decrease with increasing concentration, with the highest rate of coefficient reduction being observed in the concentration range from 0 to approx. 1 mol/m³. For concentrations greater than 2 mol/m³, the values of these coefficients are almost equal to 0 (inefficient energy conversion processes in the membrane).

Characteristics $(\Phi_S)_L = f[(\Delta P - \Delta \pi_s), (\Delta \pi_s / C_s), E]$, $[(\Phi_F)_L]_{ij} = f[(\Delta P - \Delta \pi_s), (\Delta \pi_s / C_s), E]$ and $[(\Phi_U)_L]_{ij} = f[(\Delta P - \Delta \pi_s), (\Delta \pi_s / C_s), E]$

Taking into account the results of the calculations obtained for $L_{ij} = f(\Delta \pi)$, ($i, j \in \{1, 2\}$) (Fig. 2A–E) in Equation (23), the dependencies $(\Phi_S)_L = f(\Delta \pi_s / C_s)_{E=\text{const.}}$ and $(\Phi_S)_L = f(E)_{\Delta \pi_s / C_s=\text{const.}}$ were calculated. The results of calculations are presented in Fig. 4A,B. The graphs shown in Fig. 2A–E are 2nd degree curves.

From Fig. 4A,B, it can be seen that $(\Phi_S)_L$ increases both with the increase of $\Delta \pi_s / C_s$ at a fixed value of E and with the increase of E at a fixed value of $\Delta \pi_s / C_s$. It should be noted that $\Delta P - \Delta \pi_s$ had no effect on $(\Phi_S)_L$, as the values of $\Delta P - \Delta \pi_s$ were chosen so that $\Delta P - \Delta \pi_s = 0$. The function $(\Phi_S)_L$ as the flux of energy dissipated in membrane processes allows to estimate the part of the energy required for membrane transport that is dissipated in the environment as heat. In the analysed cases, this function is nonlinearly dependent on both thermodynamic forces on the membrane and symmetrical with respect to zero value of thermodynamic force. In the case of small concentrations (or small electric fields), the energy dissipated is small and increases as the thermodynamic force increases. The increase of this function is larger for the greater thermodynamic force. The shape of the curves resembles parabolas. For

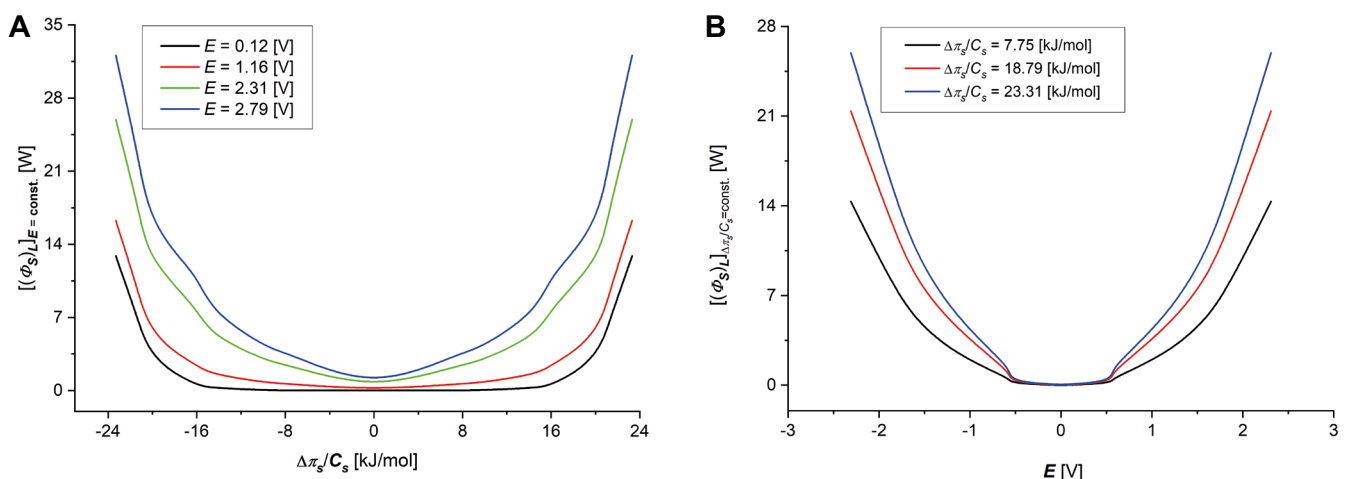


Fig. 4. Graphical representation of the dependencies $[(\Phi_S)_L]_{E=\text{const.}} = f(\Delta \pi_s / C_s)$ ($i, j \in \{1, 2, 3\}$) and $[(\Phi_S)_L]_{\Delta \pi_s / C_s=\text{const.}} = f(E)$, for aqueous NaCl solutions

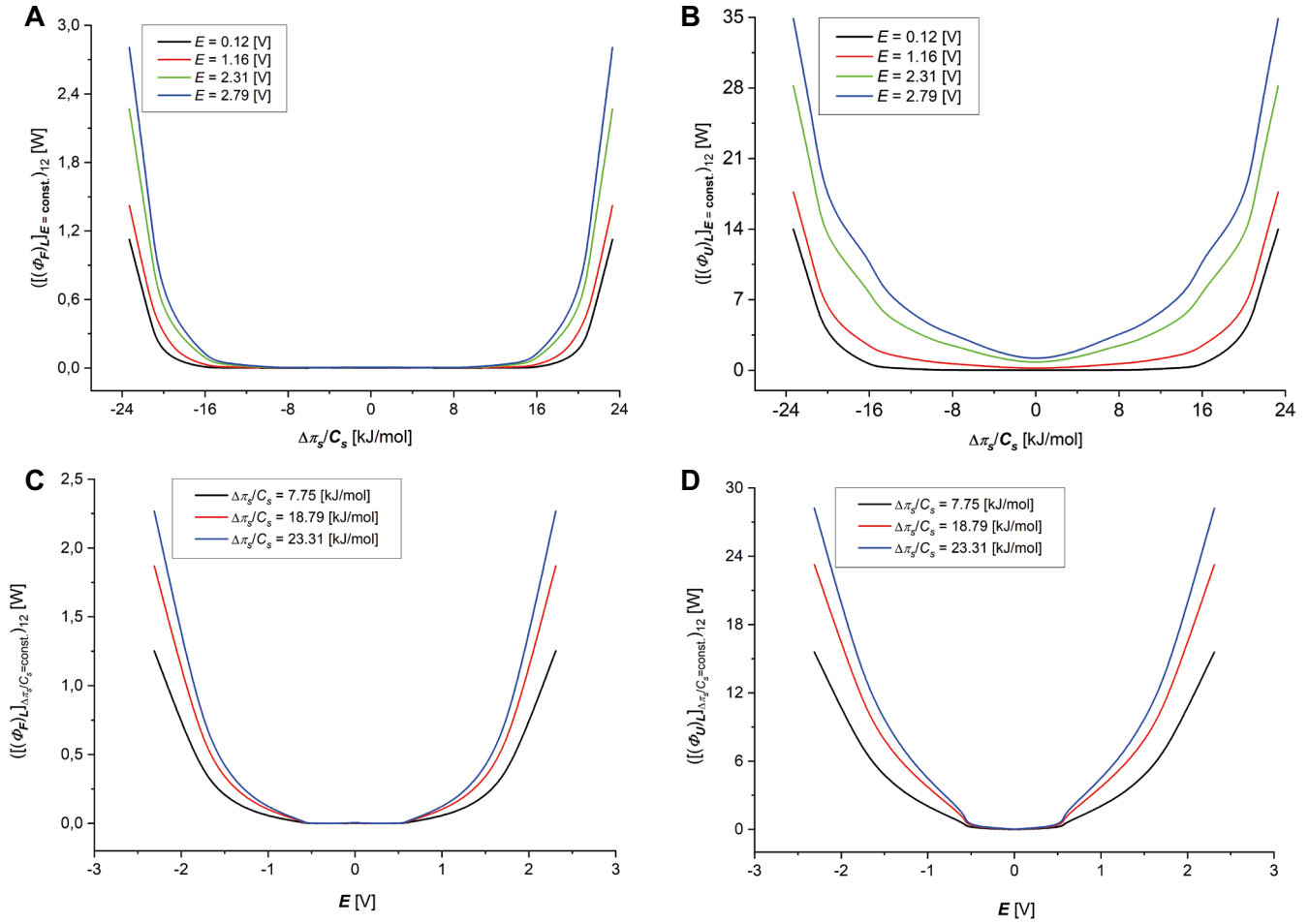


Fig. 5. Graphical representation of the dependencies $[(\Phi_F)_L]_{E=const.} = f(\Delta\pi_s/C_s)$ (A), $[(\Phi_U)_L]_{E=const.} = f(\Delta\pi_s/C_s)$ (B), $[(\Phi_F)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ (C) and $[(\Phi_U)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ (D), for aqueous NaCl solutions

the thermodynamic force $\Delta\pi_s/C_s$ (Fig. 4A), large changes in the dissipated energy flux are observed above 16 kJ/mol, while for greater established 2nd thermodynamic force E , significant changes in $\Phi(S)_L$ are observed for greater values of $\Delta\pi_s/C_s$. The dependence $\Phi(S)_L = f(E)$ is analogous when $\Delta\pi_s/C_s$ is constant, but for E values lower than 0.5 V, $\Phi(S)_L$ increases slightly and only above this value changes of $\Phi(S)_L$ are significant, is larger for greater osmotic pressure difference ($\Delta\pi_s/C_s$). This indicates that the amount of energy dissipated in membrane processes increases with increasing thermodynamic force on the membrane, due to the fact that at small forces, the influence of the membrane on the transported substances and at the same time on the energy dissipated in this transport is small. Increasing thermodynamic forces, especially osmotic force, cause a higher concentration of substances in the membrane and a greater influence of the membrane on transport of substances and cause greater dissipation of energy in membrane.

Taking into account the results of calculations obtained for dependencies $[(e_L)_{12}]_{max}$ (shown in Fig. 3D) in Equations (27) and (28), and dependencies $[\Phi(S)_L]_{E=const.} = f(\Delta\pi_s/C_s)$, $[(\Phi_S)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ presented in Fig. 4A,B, the dependencies $[(\Phi_F)_L]_{E=const.} = f(\Delta\pi_s/C_s)$, $[(\Phi_U)_L]_{E=const.} = f(\Delta\pi_s/C_s)$, $[(\Phi_F)_L]_{\Delta\pi_s/C_s=const.} = f(E)$, $[(\Phi_U)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ were calculated.

The results of calculations are presented in Fig. 5A–D. Comparing the data for $[(\Phi_F)_L]_{E=const.} = f(\Delta\pi_s/C_s)$ and $[(\Phi_U)_L]_{E=const.} = f(\Delta\pi_s/C_s)$ shown in Fig. 5A,B and the data for $[(\Phi_F)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ and $[(\Phi_U)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ shown in Fig. 5C,D, it can be seen that $[(\Phi_F)_L]_{12} \approx 0.1 \cdot [(\Phi_U)_L]_{12}$.

As shown in Fig. 5A–D, both the internal energy flow $(\Phi_U)_L$ and the free energy flow $(\Phi_F)_L$ are symmetrical with respect to the 0 values of both thermodynamic forces $\Delta\pi_s/C_s$ with a fixed $E = const.$, and E with a fixed thermodynamic force $\Delta\pi_s/C_s = const.$ As one of the thermodynamic forces increases, regardless of its direction, the values of both energy fluxes increase nonlinearly. The larger the value of the thermodynamic force, the larger the energy fluxes are observed. This may result, as in the previous cases, from the increased influence of the membrane on the transport processes for larger thermodynamic forces. As could be expected, the values of the internal energy flux are much higher than the values of free energy flux converted into mechanical work related to the transported substances. Taking into account Equation (21), which combines the considered energies, and the corresponding Fig. 4,5, it can be concluded that the flux of released internal energy $(\Phi_U)_L$ in membrane

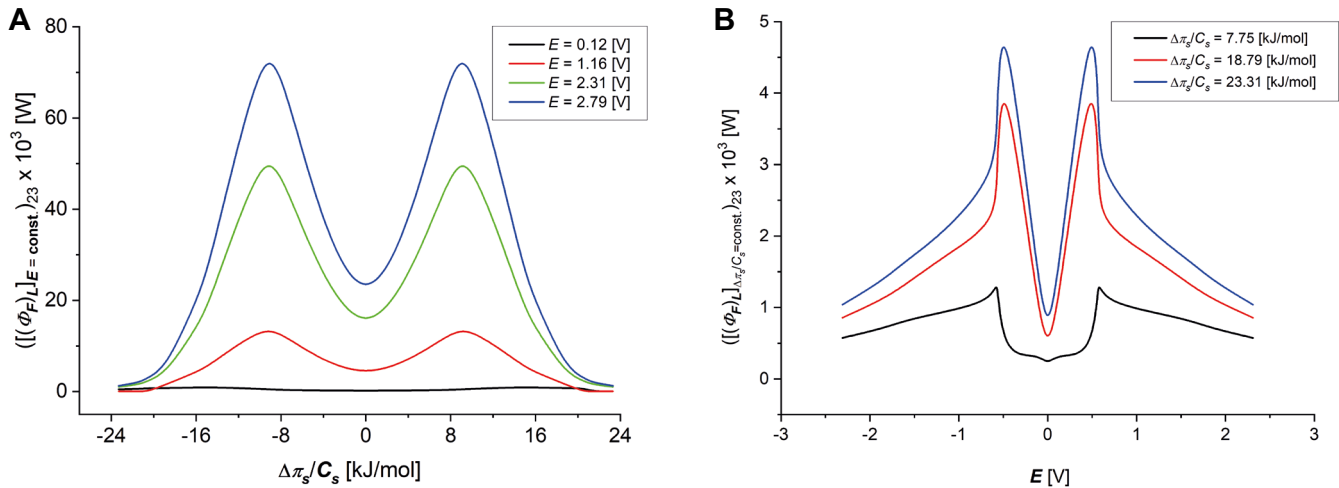


Fig. 6. Graphical representation of the dependencies $((\Phi_F)_{L23})_{E=const.} = f(\Delta\pi_s/C_s)$ and $((\Phi_F)_{L12})_{\Delta\pi_s/C_s=const.} = f(E)$, for aqueous NaCl solutions

processes is converted into 2 fluxes: of free energy $(\Phi_F)_L$ and dissipated as heat $\Phi(S)_L$. For the membrane processes considered, the energy flux dissipated in the form of heat $\Phi(S)_L$ is about 10 times larger than the free energy flux $(\Phi_F)_L$. By comparing $(\Phi_F)_L$ to $(\Phi_U)_L$, the average efficiency of the observed processes can be estimated and is approx. $1/11 = 9.1\%$.

Taking into account the results of calculations obtained for dependencies $[(e_L)_{23}]_{max}$ (shown in Fig. 3E) in Equations (27) and (28), and dependencies $[(\Phi_S)_L]_{E=const.} = f(\Delta\pi_s/C_s)$ and $[(\Phi_S)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ presented in Fig. 3A,B, the dependencies $((\Phi_F)_{L23})_{E=const.} = f(\Delta\pi_s/C_s)$ and $((\Phi_F)_{L23})_{\Delta\pi_s/C_s=const.} = f(E)$, were calculated. The results of calculations are presented in Fig. 6A,B.

The comparison of the data presented in Fig. 5A, Fig. 6A, Fig. 5C, and Fig. 6B shows that $((\Phi_F)_{L12})_{E=const.}$ is 3 orders of magnitude larger than $((\Phi_F)_{L23})_{E=const.}$, while $((\Phi_F)_{L12})_{\Delta\pi_s/C_s=const.}$ is 2 orders of magnitude larger than $((\Phi_F)_{L23})_{\Delta\pi_s/C_s=const.}$. Therefore, $((\Phi_U)_{L12})_{E=const.} \approx ((\Phi_S)_{L23})_{E=const.}$ and $((\Phi_U)_{L12})_{\Delta\pi_s/C_s=const.} \approx ((\Phi_S)_L)_{\Delta\pi_s/C_s=const.}$.

Similar reasoning can be done for $((\Phi_F)_{L12})_{E=const.}$, $((\Phi_F)_{L13})_{E=const.}$, $((\Phi_U)_{L12})_{E=const.}$ and $((\Phi_U)_{L13})_{\Delta\pi_s/C_s=const.}$. Due to the fact that $[(e_L)_{12}]_{max} \gg [(e_L)_{13}]_{max}$ so $((\Phi_F)_{L13})_{E=const.} \ll ((\Phi_F)_{L12})_{E=const.}$. This means that $((\Phi_U)_{L12})_{E=const.} \approx ((\Phi_S)_L)_{E=const.}$ and $((\Phi_U)_{L12})_{\Delta\pi_s/C_s=const.} \approx ((\Phi_S)_L)_{\Delta\pi_s/C_s=const.}$.

Discussion

According to the Peusner network formalism, appropriate transformations of the classical K–K equations for electrolyte solutions lead to L versions of the K–K–P equations for electrolyte solutions for 3 thermodynamic forces (ΔP , $\Delta\pi_s$ and E) and 3 fluxes (J_v , J_s and I). The resulting equations include the Peusner coefficients L_{ij} ($i, j \in \{1, 2, 3\}$) and L_{det} , which characterize the transport properties of any membrane. There are 9 coefficients in these equations – that is, the 3rd thermodynamic

force (E) introduces 5 additional coefficients: L_{13} , L_{31} , L_{23} , L_{32} , and L_{33} . The Peusner coefficients are useful for calculating the degree of coupling, which is determined by the coefficients l_{12} , l_{21} , l_{13} , l_{31} , l_{23} , and l_{32} . It is well known that when $l_{ij} = 0$, the irreversible processes are independent, whereas when $l_{ij} = \pm 1$, the irreversible processes are maximally coupled.

The data presented in Fig. 3A show that, in the concentration range $0 < C_s \leq 15 \text{ mol/m}^3$, the coupling coefficients l_{12} and l_{21} take values in the range $0 < l_{12} = l_{21} \leq 0.64$. This means that the irreversible processes in membrane, measured using the fluxes J_v and J_s , are strongly coupled to each other and that the coupling increases with increasing C_s . In contrast, the data presented in Fig. 3B show that, in the same C_s concentration range, the coupling coefficients l_{13} and l_{31} take the values in the ranges: $0.046 \geq l_{13} \geq 2.1 \times 10^{-4}$ and $-0.046 \leq l_{13} \leq 2.1 \times 10^{-4}$. This means that the irreversible processes, whose measures are the fluxes J_v and I , are weakly coupled to each other. The data presented in Fig. 3C show that in the concentration range $0 < C_s \leq 15 \text{ mol/m}^3$, the coupling coefficients l_{13} and l_{32} take values in the range $0.27 \geq l_{23} = l_{32} \geq 0.014$. This means that the irreversible processes, whose measures are the fluxes J_s and I , are coupled to each other, but this coupling decreases nonlinearly with increasing solute concentration.

According to the procedure proposed by Peusner,^{13,27,28} the coefficients l_{12} , l_{21} , l_{13} , l_{31} , l_{23} , and l_{32} can be grouped into the coefficient $(Q_L)_{ij}$ expressed by Equation (16). From this equation, $0 \leq (Q_L)_{ij} \leq 1$. The concentration dependence of $(Q_L)_{ij}$ coefficients are presented in Fig. 7.

From Fig. 7A, it can be seen that in the concentration range $0 < C_s \leq 15 \text{ mol/m}^3$, $(Q_L)_{12}$ takes the values in the range $0 < (Q_L)_{12} \leq 0.22$. This means that the irreversible processes associated with the fluxes J_v and J_s are coupled. Figure 7B shows that in the same concentration range $(Q_L)_{13}$ satisfies condition $0.106 \times 10^{-2} \geq (Q_L)_{13} \geq 2 \times 10^{-4}$ and $(Q_L)_{23}$ satisfies condition $3.68 \times 10^{-2} \geq (Q_L)_{13} \geq 0.92 \times 10^{-4}$. This means that

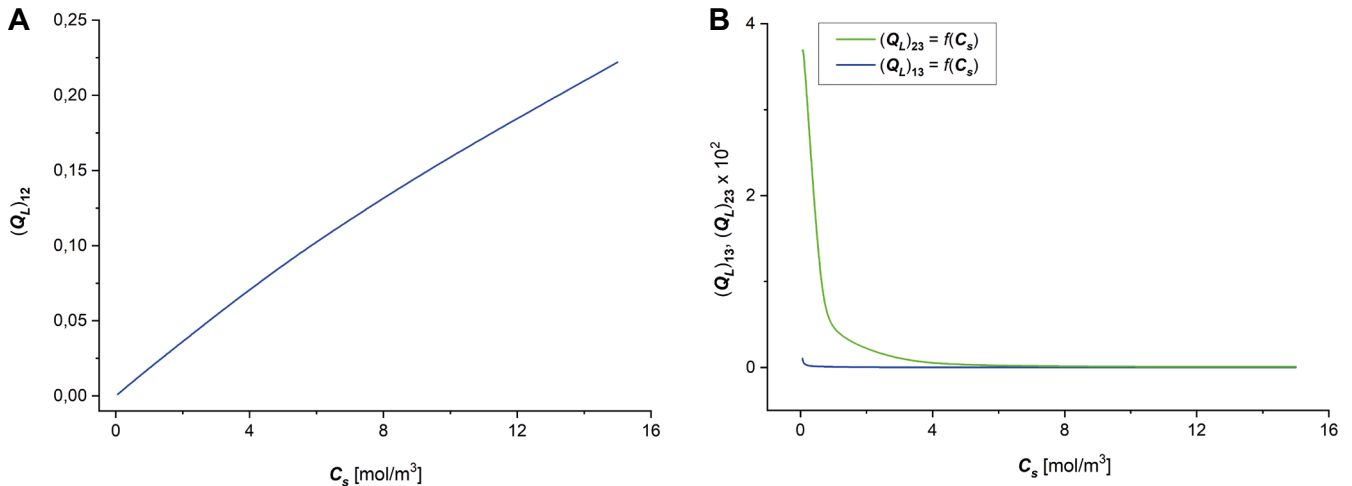


Fig. 7. Graphical representation of the dependencies $(Q_L)_{ij} = f(C_s)$ for aqueous NaCl solutions: $(Q_L)_{12} = f(C_s)$ (A), $(Q_L)_{13} = f(C_s)$ and $(Q_L)_{23} = f(C_s)$ (B)

the irreversible processes associated with J_v and I fluxes and J_s and I fluxes are decoupled.

The conversion of electrochemical energy is a significant natural process. Internal energy, also known as U -energy, is not a usable form of energy.^{27–30} Instead, free energy or F -energy is the useful form.

The electrochemical energy conversion evaluation method presented in this study uses dissipative energy (S -energy), the measure of which is the dispersion function $(\Phi_S)_L$ and the energy conversion efficiency factor $[(e_L)_{ij}]_{max}$. The measure of F -energy is $[(\Phi_F)_L]_{ij}$ and of U -energy is $[(\Phi_U)_L]_{ij}$. The pioneering work of Kedem, Caplan and Peusner is one of the premises for the development of Peusner's network thermodynamics.^{13,27–30}

Conclusions

The L version of the K–K–P equations presented in this study, which contains 3 fluxes (J_v , J_s , I) and 3 thermodynamic forces ($\Delta\pi$, $\Delta\pi_s$, E), introduces 10 Peusner coefficients L_{ij} ($i, j \in \{1, 2, 3\}$) and L_{det} . These coefficients can be calculated using the transport parameters L_p , σ_s and ω_s , which determine the fluxes J_v and J_s , and the transport parameters β , τ_c and κ determining the flux I . Five of them (L_{13} , L_{31} , L_{23} , L_{32} , and L_{33}) are a consequence of considering the additional thermodynamic force E and flux I . The coefficients L_{12} , L_{13} , L_{31} , L_{33} , and L_{32} are necessary to define the 3 groups of coefficients: l_{12} , l_{21} , l_{13} , l_{31} , l_{23} , and l_{32} ; $(Q_L)_{12}$, $(Q_L)_{13}$ and $(Q_L)_{23}$; $[(e_L)_{12}]_{max}$, $[(e_L)_{21}]_{max}$, $[(e_L)_{23}]_{max}$, $[(e_L)_{32}]_{max}$, $[(e_L)_{13}]_{max}$, and $[(e_L)_{31}]_{max}$. The coefficients L_{ij} ($i, j \in \{1, 2, 3\}$) are needed to calculate the energy dissipation $(\Phi_S)_L$.

The equations describing the energy dissipation $(\Phi_S)_L$ take the form of equations that are the sum of quadratic equations of 3 variables: ΔP , $\Delta\pi$ and E . The characteristics $[\Phi(S)_L]_{E=const.} = f(\Delta\pi_s/C_s)$ ($i, j \in \{1, 2, 3\}$) and $[\Phi(S)_L]_{\Delta\pi_s/C_s=const.} = f(E)$ are 2nd degree curves located in the 1st and 2nd quadrants of the coordinate system. Equations for $(\Phi_S)_L$ and for $[(e_L)_{12}]_{max}$, $[(e_L)_{21}]_{max}$, $[(e_L)_{23}]_{max}$, $[(e_L)_{32}]_{max}$, $[(e_L)_{13}]_{max}$,

or $[(e_L)_{31}]_{max}$ are required to examine the energy conversion, and calculate the characteristics $[(\Phi_F)_L]_{12} = f(\Delta\pi_s/C_s)$, $[(\Phi_F)_L]_{12} = f(E)$, $[(\Phi_U)_L]_{12} = f(\Delta\pi_s/C_s)$, and $[(\Phi_U)_L]_{12} = f(E)$.

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