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Central role of the observable electric potential in transport equations

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Nonequilibrium systems are usually studied in the framework of transport equations that involve the true electric potential (TEP), a nonobservable variable. Nevertheless another electric potential, the observable electric potential (OEP), may be defined to construct a useful set of transport equations. In this paper several basic characteristics of the OEP are deduced and emphasized: (i) the OEP distribution depends on thermodynamic state of the solution, (ii) the observable equations have a reference value for all other transport equations, (iii) the bridge that connects the OEP with a certain TEP is usually defined by the ion activity coefficient, (iv) the electric charge density is a nonobservable variable, and (v) the OEP formulation constitutes a natural model for studying the fluxes in membrane systems.

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I. INTRODUCTION

Since Volta's time thousands of papers on electrochemical systems have been published using the true electric potential (TEP) in their transport equations. It is assumed that the TEP is that of the Maxwell's laws of electrodynamics and for that reason is also named electrostatic potential (EP). In these systems the flux of each dissolved species is described by an equation with three kinds of terms, successively named, migration, diffusion, and convection.

Unfortunately, this quantity has a very restrictive condition: the TEP can only be measured between themodynamically identical pieces, those at the same pressure p, temperature T, and chemical components $i=1,2,3,\ldots,\ k$ of concentrations c_i, as it has been repeatedly shown [1,2]. Therefore it is easy to understand the difficulties of dealing with nonequilibrium systems, where gradients of these quantities are nonzero. In fact, many of the concepts that use TEP quantities are nonobservable variables, e.g., diffusion potential, membrane potential, Donnan potential, etc.

This heavy limitation extraordinarily reduces the possibility of observing the TEP, but at the same time, is the key to approaching the electrochemical systems in a new way. The solution proposed is to interpose electrochemical probes between the system and the meter. In each case two identical probes are built, reversible to one solution ion. Thus, when they are placed inside the system, one in a reference site and the other in whatever point, an electric potential difference may be measured between the terminals of the two probes. The measurement is carried out by a potentiometer or a high impedance voltmeter. The electric potential measured has been called observable electric potential (OEP). Here the OEP is denoted by ψ_i, where the subindex $i=+,-$ points out that the electrodes are reversible to either the cation or the anion of the electrolyte solution [3]. Obviously the OEP at the reference site is zero. The OEP is a well-defined experimental quantity. In a theoretical sense the OEP is not a new concept. However, it is new in the sense of an alternative to other concepts used in irreversible thermodynamics.

With the OEP, the thermodynamics of irreversible processes has generated a formalism that can be applied with success to very different electrochemical phenomena [3–7]. In the transport equations derived within this frame the OEP plays a central role. In this paper the observable transport equations of binary solutions are applied to describe the OEP profile at different values of the electric current density. Then several possibilities of building bridges between the OEP and TEP will be discussed. From these transformations and applying the Poisson's equation of electrodynamics, the profile of the electric charge density in a nonequilibrium KCl solution will be obtained. Finally, following the OEP formalism, the changes in the transport equations caused by a membrane will be analized. Thus three basic properties about the OEP will be deduced and emphasized: (i) the OEP depends on the thermodynamic state of the solution, (ii) the electric charge density is a nonobservable variable, and (iii) the membranes act over the solution by modifying the values of transport coefficients. For the sake of simplicity, only the systems at constant temperature and pressure are considered.

II. TRANSPORT EQUATIONS

A. Transport coefficients in observable electrical potential equations

Consider a solution constituted by a binary electrolyte and an unionized solvent in a nonequilibrium state. Two identical probes reversible to the electrolyte anion X^{z-} are used. The experimental gradients of the OEP are related to the gradients of the anion electrochemical potential $\tilde{\mu}_-$ by [3]

$$\vec{\nabla}\psi_- = \frac{1}{z_-F}\vec{\nabla}\tilde{\mu}_-, \tag{1}$$

where z_- is the charge number and F is Faraday's constant.

Within the framework of thermodynamics of irreversible processes, the transport equations are deduced from the dissipation function [8]

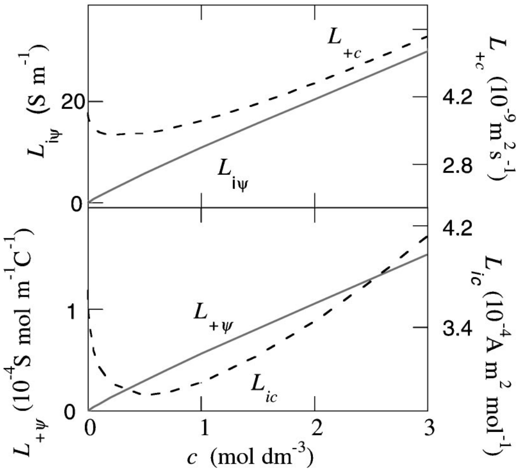

FIG. 1. Observable transport coefficients versus concentration c for a KCl solution at 25 C and 1 atm. Experimental data of D, t_+, κ, and γ have been used [9].

$$-\Psi = \vec{j}_+ \cdot \vec{\nabla}\tilde{\mu}_+ + \vec{j}_- \cdot \vec{\nabla}\tilde{\mu}_-, \tag{2}$$

where the electrochemical potential gradients $\vec{\nabla}\tilde{\mu}_i (i=+,-)$ are the driving forces and $\vec{j}_i$ are the flux densities of the ion constituents in the solvent-fixed reference frame. When Eq. (1) is introduced in the dissipation function, the following transport equations may be deduced [7]:

$$-\vec{j}_+ = L_{+c}\vec{\nabla}c + L_{+\psi}\vec{\nabla}\psi_-, \tag{3a}$$

$$-\vec{i} = L_{ic}\vec{\nabla}c + L_{i\psi}\vec{\nabla}\psi_-, \tag{3b}$$

where $L_{+c}, L_{+\psi}, L_{ic}$, and $L_{i\psi}$ are transport coefficients, c is the electrolyte concentration; and $\vec{i}$ is the electric current density. These coefficients have the properties of intensive thermodynamic variables and depend on the local values of the variables T, p, and c. They are related with the usual transport coefficients, i.e., with the electrolyte diffusion coefficient in the solvent-fixed reference frame D, with the electrical conductivity κ, and with the Hittorf's transport number t_+ by [7]

$$L_{+c} = \nu_+ D + \frac{\nu R T t_+^2 \kappa}{z_+^2 \nu_+ F^2 c}\left(1 + \frac{d\ln\gamma}{d\ln c}\right), \tag{4a}$$

$$L_{+\psi} = \frac{t_+ \kappa}{z_+ F}, \tag{4b}$$

$$L_{ic} = \frac{\nu R T t_+ \kappa}{z_+ \nu_+ F c}\left(1 + \frac{d\ln\gamma}{d\ln c}\right), \tag{4c}$$

$$L_{i\psi} = \kappa, \tag{4d}$$

where ν_+ and ν_- represent the stoichiometric coefficients of the electrolyte, $\nu = \nu_+ + \nu_-$, R is the gas constant, and γ is the mean activity coefficient of the electrolyte. Figure 1 shows the values of these coefficients at 25 °C and 1 atm in the range 0–3 M for a KCl solution; experimental data of D, t_+ and κ have been used [9]. Only three of the coefficients $L_{+c}, L_{+\psi}, L_{ic}$, and $L_{i\psi}$ form a set of independent coefficients, according to the Onsager reciprocal relation [8].

B. The bridge

The observable character of the OEP attributes a privileged value to this variable. Nevertheless, almost all the electrochemical studies have used the nonobservable TEP. This variable is built in electrochemistry by using complementary criteria. The experiments will have to validate if the auxiliary criteria are significant.

The more common bridge between the TEP ϕ and the OEP ψ_- is based in the splitting of the electrochemical potential in two terms:

$$\tilde{\mu}_- = \mu_- + z_- F\phi, \tag{5}$$

where the chemical potential of the ionic constituent μ_- is also a nonobservable variable usually expressed by

$$\mu_- = \mu_-^* + RT\ln\nu_- c\gamma_-. \tag{6}$$

Here μ_-^* is the standard chemical potential of the anion, and γ_- is the anion activity coefficient. These two quantities are nonobservable variables. Within the frame of statistical mechanics, Debye and Hückel deduced $\gamma_- = \gamma_-(c)$, in the case of diluted solutions only [10,11]. Since that time, a lot of improvements have been made allowing us to extend the statistical theory to higher concentrations. But this result cannot be rigorously validated with experimental values of the mean activity coefficient of the electrolyte $\gamma = \gamma(c)$, because an observable variable can never be related with only one nonobservable variable. In the relationship $\gamma_-\gamma_+ = \gamma^2$, the uncertainty in γ_- is exactly compensated with the uncertainty in γ_+.

The TEP-OEP bridge can be crossed in the two directions. Usually works have been developed in the TEP formalisms and then the results have been checked with OEP data. In the following, the systems will be studied in the OEP formalism and the bridge will be passed over in the reverse direction.

C. Charge-density profiles

The electrical potential observed in an electrochemical system has traditionally been considered as a consequence of a distribution of electrical charges; this is the scope of Maxwell's laws of electrodynamics. Nevertheless the observable transport equations relate the electric potential to the thermodynamic state of the system. An example better explains this question.

Consider a KCl solution with a linear concentration profile from 0.1000 M at $x=0$ to 0.0001 M, with $x=1$ m, at 25 °C, and standard pressure [12]. Two working electrodes fix successively the electric current density at the values $i = +0.1$, 0 and -0.1 A m^{-2}. Therefore, three OEP profiles $\psi_- = \psi_-(x)$ across the system, each one for a given value of electric current density, can be measured between the terminals of the Ag/AgCl electrodes; the reference electrode is placed at $x=0$. These profiles can be calculated by applying

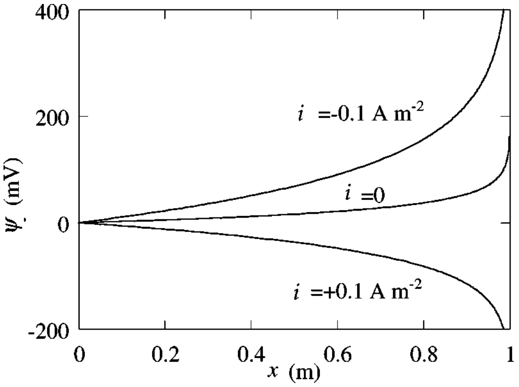

FIG. 2. Observable electric potential along a KCl solution, with a linear concentration gradient between 0.1000 M and 0.1 mM, for three different values of the electric current density i.

Eq. (3b); the values of transport coefficients given in Fig. 1 are used, and the results are shown in Fig. 2.

Two very interesting conclusions may be obtained from the above example: (i) the OEP profile in the solution depends on both the concentration distribution and the electric current density, i.e., on the two quantities that define the local nonequilibrium thermodynamic state, and (ii) the usual relation between electric potential and electric charge does not appear in the OEP formalism.

For relating the electric potential with the electric charges, the bridge has first to be crossed from the OEP formalism to the TEP formalism, that is, the OEP profile has to be transformed in a TEP profile. Later Poisson's equation of electrodynamics $\rho = -\varepsilon(d^2\phi/dx^2)$ can be applied; here ρ is the electric charge density and ε is the dielectric permittivity.

From Eqs. (1) and (5)–(6) the following bridges are obtained

$$d\phi = d\psi_- + \frac{RT}{F} d\ln \nu_- c\gamma_- . \tag{7}$$

Each one of these transformations $\psi_- \rightarrow \phi$ is characterized by the function $\gamma_- = \gamma_-(c)$. The three usual ways to postulate the anion activity coefficient may be considered: (i) $\gamma_- = 1$, (ii) $\gamma_- = \gamma$, and (iii) $\gamma_- = \gamma^2$. Figure 3 shows the three ρ profiles that can be deduced from the ψ_- profile shown in Fig. 2 when $i=0$. A surprising result is reached: the same OEP profile produces three very different ρ profiles. This uncertainty could explain the very often paradoxical results for electric charge density profiles deduced in the frame of TEP formulations [13–15].

D. In the pores of a membrane

The experiments show a different behavior when the solution is inside a membrane. In the scope of the OEP formalism, a good first approach to study membrane systems is to consider that the thermodynamics remain the same. That is to say, the same transport equations apply with new values for the transport coefficients. This will be the way used to analyze the pore solution of a membrane in this section.

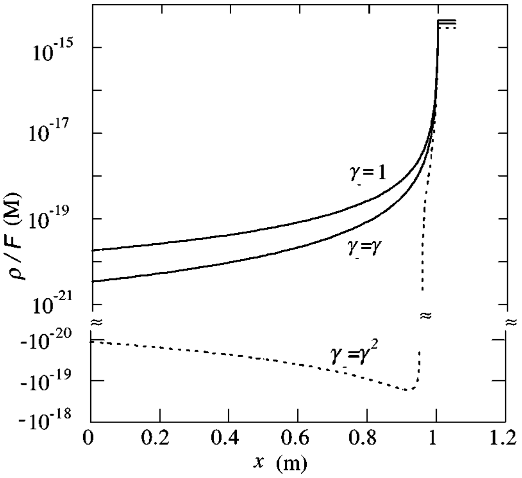

FIG. 3. Electric charge density along a KCl solution, with a linear concentration gradient between 0.1000 M and 0.1 mM, when $i=0$, according to three different proposals of anion activity coefficient.

Consider a binary solution from a binary electrolyte. The membrane is placed between two subsystems of concentrations $(c)_L$ and $(c)_R$; the subindexes denote left (L) and right (R) solutions. Temperature and pressure are considered uniform. We assume that the pore solution is of the same kind as in the bulk solutions, with a concentration $\bar{c}$ that varies along the x direction between the values $(c)_L$ and $(c)_R$; the overbar denotes a variable inside the pore. The transport equations inside the pore solution will be

$$-\bar{j}_+ = \bar{L}_{+c}\frac{d\bar{c}}{dx} + \bar{L}_{+\psi}\frac{d\bar{\psi}_-}{dx}, \tag{8a}$$

$$-\bar{i} = \bar{L}_{ic}\frac{d\bar{c}}{dx} + \bar{L}_{i\psi}\frac{d\bar{\psi}_-}{dx}. \tag{8b}$$

We assume also that Eqs. (4) establish the relations between the coefficients $(\bar{L}_{+c}, \bar{L}_{+\psi}, \bar{L}_{ic}, \bar{L}_{i\psi})$ and $(\bar{D}, \bar{t}_+, \bar{\kappa})$. All these coefficients are functions of concentration. The action of a membrane on the solution generates changes in the value of the transport coefficients with respect to those of the bulk

$$\bar{L}_{kl} \neq L_{kl} \quad k = +, i; \quad l = c, \psi, \tag{9a}$$

$$\bar{D} \neq D, \tag{9b}$$

$$\bar{\kappa} \neq \kappa, \tag{9c}$$

$$\bar{t}_+ \neq t_+ . \tag{9d}$$

Until now nothing has been said about the mean activity coefficient $\bar{\gamma}$ of the electrolyte in the pore. Only the case of permeable membranes will be considered here. These membrane systems evolve following a relaxation process, from a nonequilibrium state with concentration gradients towards the equilibrium, i.e.,

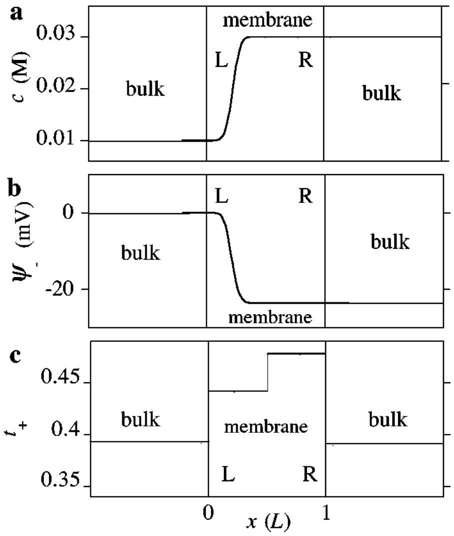

FIG. 4. Profiles in a polysulfone membrane soaked in NaCl solutions: (a) electrolyte concentration at the initial time; the whole concentration variation lays in the left-half of the membrane, (b) profile of the observable electric potential ψ_-, and (c) profile of the cation transport number t_+.

$$(c)_L = \overline{c} = (c)_R, \tag{10a}$$

$$(\mu)_L = \overline{\mu} = (\mu)_R, \tag{10b}$$

where μ is the chemical potential of the electrolyte. From the two equations, it is deduced that

$$(\gamma)_L = \overline{\gamma} = (\gamma)_R. \tag{11}$$

On this basis the transport coefficients can be measured and therefore the membrane system is characterized. In the following, the case of the transport number $\overline{t_+}$ will be analyzed. Consider a polysulfone membrane placed between two subsystems, which contains a NaCl solution; in each subsystem a Ag/AgCl electrode is submerged [16]. The concentration profile shown in Fig. 4 is built working in this way: (i) First the two subsystems are filled with the same solution $(c)_L = (c)_R = 0.03$ M. After several hours the concentration in the pore has also reached the same value, i.e., $\overline{c} = 0.03$ M. (ii) The solution of the container L is interchanged with another of concentration $(c)_L = 0.01$ M. A relaxation process is initiated. From Eqs. (4), (8), and (9) it is deduced that

$$\mathrm{d}\,\overline{\psi_-} = -\frac{2RT\overline{t_+}}{F\overline{c}}\left(1 + \frac{d\ln\overline{\gamma}}{d\ln\overline{c}}\right)\mathrm{d}\,\overline{c}, \tag{12}$$

which is integrated assuming $\overline{t_+}$ constant along the whole pore

$$\overline{t_+} = \frac{F\Delta\overline{\psi_-}}{2RT(\ln c_L\gamma_L - \ln c_R\gamma_R)}. \tag{13}$$

The quantity $\Delta\overline{\psi_-}$ is the membrane OEP, i.e., $\Delta\psi_- = (\psi_-)_R - (\psi_-)_L$. In nonhomogeneous membranes, two values of the transport number can be measured, one for the left part of the pore $(\overline{t_+})_L$ and other for the right part $(\overline{t_+})_R$.

The values for the transport number in the two bulk solutions have been taken from literature [9]. Figure 4 shows the profile of the transport number in the bulk and in the pore of the polysulfone membrane.

This way of studying the membrane system is different from others developed in the formalism of the TEP [17]. This formulation assumes (i) a charge fixed to the pore walls, and (ii) discontinuities of the ionic concentrations at the two membrane bulk solution interfaces. This last assumption may cause a jump in the TEP at these interfaces

$$(\Delta\phi)_k = (\overline{\phi})_k - (\phi)_k = \frac{(\overline{\mu})_k - (\mu)_k}{F}, \quad k = L,R \tag{14}$$

named the Donnan potential. On the contrary, as the observable formulation assumes continuity for the electrolyte concentration at the membrane bulk solution interfaces, i.e., $(\overline{c})_k = (c)_k$, $k = L,R$, the same will occur in the OEP profile (see Fig. 4).

III. CONCLUSIONS

The experimental measurements give to the OEP a privileged value with respect to other electrical potentials. Nevertheless this assertion does not disqualify the TEP, because thousands of papers have found in the TEP a very useful variable, which can easily be applied to most systems. On the other hand, very few papers that use OEP transport equations are found in the literature. Time needs to pass until these transport equations attain a real validation.

The observable transport equations provide a complementary way to study the electrochemical systems. In this paper the following conclusions have been deduced: (i) the electric potential in electrochemical systems is a thermodynamic variable, (ii) it does not seem that there is an unambiguous way to relate electric charge density with the electric potential, (iii) the transport coefficients change their values when the solution is inside the pores of a membrane, (iv) different bridges can be built between the OEP and the nonobservable electric potential, and (v) it seems that the way in which the Maxwell's laws of electrodynamics are applied to electrochemical systems has to be reconsidered.

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