Observable Electric Potential and Electrostatic Potential in Electrochemical Systems

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The role of the electric potential in the description of transport processes in electrochemical systems is critically analyzed. Since the electrostatic potential drop between two parts of a system which differ in temperature, pressure, or concentration cannot be measured, an observable electric potential (OEP) is defined from the potential difference measured between the electrodes reversible to one of the ion constituents in equilibrium with the system. The OEP formalism is compared to the Nernst−Planck equations (NPE) formalism. The comparative study is applied to the mass transport process that occurs in a liquid junction of a binary electrolyte solution when the electric current density is zero. The potential profiles are shown for the OEP and the electrostatic potential, the latter being calculated for different definitions of the activity coefficient γ_-. It is concluded that the OEP formalism presents clear benefits with respect to the NPE formalism.

Introduction

Systems such as a mass spectrometer or a cathode ray tube can be described by using only the laws of Electrodynamics, in terms of an electrostatic potential which is related to the electric charge distribution by Poisson's equation. Electrochemical systems, however, require a thermodynamic description because it is not possible to measure the electric potential difference between two parts of a system which are thermodynamically different, i.e., which differ in temperature, pressure, or concentration.[1−3] Such a restriction constitutes the basis, from a positive point of view, for the present study. To observe an electric potential difference in nonequilibrium systems two reference electrodes must be interposed between the electric meter and the system. The observable electric potential (OEP) difference is then measured between the electrode terminals, and placing the electrodes at different locations it is even possible to define (and measure) the profile of the OEP.[4−7]

The conditions of thermal and mechanical equilibrium are expressed as uniform temperature and pressure. Similarly, the equilibrium condition for electric charge is sometimes expressed as uniform electric potential.[8] This wrong conclusion is deduced when the electric charge is considered independently of the nature of the matter where it is supported. The derivation of an equilibrium condition for the electric charge should take into account the ion constituents, and therefore refer to the electrochemical potentials of these constituents. In fact, the electric potential is a variable that does not appear in the purely thermodynamic description of most nonequilibrium states. Thus, a critical review of how the electric potential is involved in the description of transport processes in electrochemical systems is very convenient and constitutes the subject of the next sections.

In this work, the OEP formalism[9,10] is compared to the traditional Nernst−Planck equations (NPE) formalism.[11,12] The first aspect of such a comparison involves the transport coefficients and the Nernst−Einstein assumption introduced in the NPE formalism which limits its applicability to moderately dilute solutions. The second and main aspect of the comparison involves the electric potential and aims at clarifying that the electrostatic potential in the NPE formalism requires the definition of the activity coefficient of the ionic species, which in turn affects the values of the electrostatic potential, while the OEP formalism overcomes this problem. It is worth mentioning that other aspects of the comparison are not worked out. In particular, the two formulations use different kinds of components, ionic constituents in the case of OEP versus ionic species in the case of NPE, but the present study is restricted to dilute solutions of strong electrolytes, where the dissociation degree is unity, and there is no difference between the two kinds of components.

As an application example, the transport process in a liquid junction of KCl + H_2O under thermal and mechanical equilibrium and open-circuit conditions is described. Since the time evolution of the liquid junction potential is not relevant for the purpose of this study, a linear concentration profile is assumed. The description is carried out both in terms of the OEP and NPE formalisms and potential profiles are presented for the OEP and the electrostatic potential, the latter being calculated for different definitions of the activity coefficient γ_-.

Phenomenological Transport Equations

The system under study is a moderately dilute solution of a binary electrolyte and an un-ionized solvent in a nonequilibrium state where temperature T and pressure p are uniform and the electrolyte molar concentration c varies along the x direction. The two ion constituents are denoted by subscripts + and −.

Within the framework of thermodynamics of irreversible processes (TIP),[3] the phenomenological transport equations are deduced from the dissipation function

$$\Psi = -j_+\frac{d\tilde{\mu}_+}{dx} - j_-\frac{d\tilde{\mu}_-}{dx} \qquad (1)$$

where the electrochemical potential gradients $d\tilde{\mu}_i/dx$ (i = +, −) are the driving forces and j_i are the flux densities of the

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ion constituents in the solvent-fixed reference frame. The corresponding phenomenological transport equations

$$-j_+ = L_{++}\frac{d\tilde{\mu}_+}{dx} + L_{+-}\frac{d\tilde{\mu}_-}{dx} \tag{2a}$$

$$-j_- = L_{-+}\frac{d\tilde{\mu}_+}{dx} + L_{--}\frac{d\tilde{\mu}_-}{dx} \tag{2b}$$

introduce three transport coefficients (L_{++}, $L_{-+} = L_{+-}$, and L_{--}) which are local magnitudes, i.e., position dependent.

Although this description of the transport process in terms of the ion constituents is considered to be the most fundamental, practical approaches often consider the electric current density and the flux density of matter. The phenomenological transport coefficients L_{ij} are then related to the electrolyte diffusion coefficient in the solvent-fixed reference frame D, the electrical conductivity κ, and the Hittorf's transport number t_+, which are measurable and only depend on T, p, and c.

One such approach uses the gradient of the chemical potential of the electrolyte

$$\mu = \nu_+\tilde{\mu}_+ + \nu_-\tilde{\mu}_- \tag{3}$$

and

$$\frac{d\varphi_{\text{ext}}}{dx} = \frac{1}{F}\left(\frac{t_+}{z_+}\frac{d\tilde{\mu}_+}{dx} + \frac{t_-}{z_-}\frac{d\tilde{\mu}_-}{dx}\right) \tag{4}$$

as driving forces, where F is Faraday's constant, and z_i is the charge number of the ion constituent i. In eq 3, ν_+ and ν_- represent the stoichiometric coefficients, which satisfy the relation $z_+\nu_+ + z_-\nu_- = 0$. The dissipation function takes then the form

$$\Psi = -j_{\text{m}}\frac{d\mu}{dx} - i\frac{d\varphi_{\text{ext}}}{dx} \tag{5}$$

where

$$j_{\text{m}} = \frac{t_-j_+}{\nu+} + \frac{t_+j_-}{\nu_-} \tag{6}$$

$$i = F(z_+j_+ + z_-j_-) \tag{7}$$

are the flux density of matter and the electric current density, respectively. The corresponding transport equations

$$-j_{\text{m}} = L_{\text{mm}}\frac{d\mu}{dx} + L_{\text{mq}}\frac{d\varphi_{\text{ext}}}{dx} \tag{8a}$$

$$-i = L_{\text{qm}}\frac{d\mu}{dx} + L_{\text{qq}}\frac{d\varphi_{\text{ext}}}{dx} \tag{8b}$$

introduce the coefficients L_{mm} and L_{qq}, which can be related to the electrolyte diffusion coefficient D and the conductivity κ, respectively. Note that φ_{ext} cannot be identified with the electric potential of electrostatics.

OEP Formalism

It is widely known that it is not possible to measure an electric potential difference between two parts of a system which differ in temperature, pressure, or concentration.[2,3] But there is no need to try such an impossible measurement. A more positive point of view is to accept that the only observable magnitude is the difference in the electrochemical potential of the ion constituent i, which can be measured with two electrochemical probes reversible to this ion constituent in local equilibrium with the system. The gradient of this observable electric potential (OEP) holds

$$\frac{d\psi_i}{dx} = \frac{1}{z_iF}\frac{d\tilde{\mu}_i}{dx} \tag{9}$$

and may be considered as a driving force in the description of the transport process.[4-7]

If electrochemical probes reversible to the anion ($i = -$ in eq 9) are used, the dissipation function takes the form

$$\Psi = -\frac{j_+}{\nu_+}\frac{d\mu}{dx} - i\frac{d\psi_-}{dx} \tag{10}$$

and the transport equations are[10]

$$-\frac{j_+}{\nu_+} = l_{++}\frac{d\mu}{dx} + l_{+\psi}\frac{d\psi_-}{dx} \tag{11a}$$

$$-i = l_{\psi+}\frac{d\mu}{dx} + l_{\psi\psi}\frac{d\psi_-}{dx} \tag{11b}$$

These transport equations can be transformed to[9]

$$-j_+ = \left[\nu_+D + \frac{\nu RTt_+^{\,2}\kappa}{z_+^{\,2}\nu_+F^2c}\left(1 + \frac{d\ln\gamma}{d\ln c}\right)\right]\frac{dc}{dx} + \frac{t_+\kappa}{z_+F}\frac{d\psi_-}{dx} \tag{12a}$$

$$-i = \frac{\nu RTt_+\kappa}{z_+\nu_+Fc}\left(1 + \frac{d\ln\gamma}{d\ln c}\right)\frac{dc}{dx} + \kappa\frac{d\psi_-}{dx} \tag{12b}$$

by expressing the phenomenological coefficients l_{++}, $l_{+\psi} = l_{\psi+}$, and $l_{\psi\psi}$ in terms of the measurable transport coefficients D, κ, and t_+ and making use of[13]

$$\mu = \mu^* + \nu RT\ln(\gamma Qc) \tag{13}$$

where $\nu = \nu_+ + \nu_-$, $Q = (\nu_+^{\nu_+}\nu_-^{\nu_-})\,)^{1/\nu}$, R is the gas constant, γ is the mean activity coefficient, and μ^* the standard chemical potential of the electrolyte.

The comparison of the OEP transport eqs 11a and 11b with eqs 8a and 8b yields the relation

$$L_{\text{mq}} = l_{+\psi} - \frac{t_+l_{\psi\psi}}{z_+\nu_+F} \tag{14}$$

which leads to the interesting conclusion $L_{\text{mq}} = L_{\text{qm}} = 0$, when the expressions $l_{+\psi} = t_+\kappa/z_+\nu_+F$ and $l_{\psi\psi} = \kappa$ are introduced. Thus, the mass and charge transport are uncoupled and the equilibrium condition for charge transport reduces to uniform φ_{ext}. Note, however, that three transport coefficients are still needed, since the transport number t_+ has been introduced in the definition of φ_{ext} (see eq 4).

NPE Formalism

Transport processes in electrochemical systems can be described by a wide variety of transport equations, whose complexity depends on whether the solutions are infinitely dilute, moderately dilute, or concentrated.[14] In the case of moderately dilute solutions, the most widely used are the Nernst−Planck equations[15−17]

$$-j_i^{\mathrm{NPE}} = D_i\left(\frac{\mathrm{d}c_i}{\mathrm{d}x} + c_i\frac{\mathrm{d}\ln\gamma_i}{\mathrm{d}x} + \frac{z_ic_iF}{RT}\frac{\mathrm{d}\phi}{\mathrm{d}x}\right) \tag{15}$$

where j_i^{NPE}, D_i, c_i, and γ_i are the flux density in the laboratory reference frame, the diffusion coefficient, the molar concentration, and the activity coefficient of the ionic species i ($i = +, -$), respectively, and ϕ denotes the electrostatic potential.

The NPE can be obtained from eqs 2a and 2b by introducing the approximation

$$L_{+-}^{\mathrm{NPE}} = L_{-+}^{\mathrm{NPE}} \approx 0 \tag{16}$$

and the usual decomposition[2,18]

$$\tilde{\mu}_i = \mu_i^* + RT\ln(\gamma_ic_i) + z_iF\phi \tag{17}$$

where μ_i^* is the standard chemical potential of the ionic species i. Note that eq 16 does not mean that the flux densities j_+ and j_- are uncoupled, because the migrational term in eq 15 accounts for such a coupling. The other phenomenological coefficients in eqs 2a and 2b are given the values

$$L_{ii}^{\mathrm{NPE}} = \frac{D_ic_i}{RT} = \frac{t_i\kappa}{z_i^2F^2} \tag{18}$$

where

$$t_i = \frac{z_i^2D_ic_i}{z_+^2D_+c_+ + z_-^2D_-c_-} \tag{19}$$

is the local migrational transport number of ionic species i and

$$\kappa = \frac{F^2}{RT}(z_+^2D_+c_+ + z_-^2D_-c_-) \tag{20}$$

is the local conductivity.

The transport formalisms presented in the two previous sections (eqs 1 and 10) incorporate three phenomenological transport coefficients which can be related to the three measurable coefficients D, κ, and t_+. The NPE formalism eliminates one transport coefficient because of eq 16, which can be written as $l_{+\psi}^{\mathrm{NPE}} = z_+\nu_+Fl_{++}^{\mathrm{NPE}}$ in the OEP formalism and assumes the following relation between the measurable coefficients D, κ, and t_+

$$\frac{Dc}{RT} = \frac{\nu t_+t_-\kappa}{z_+^2\,\nu_+^2F^2}\left(1 + \frac{\mathrm{d}\ln\gamma}{\mathrm{d}\ln c}\right) \tag{21}$$

It can be shown that eq 16 is equivalent to assuming the Nernst−Einstein relation, $D_i = RTu_i$, where u_i is the mobility of ionic species i, and therefore the NPE formalism should be used in the range of dilute solutions only, where the Nernst−Einstein relation holds. Note, finally, that the transport of matter and the transport of charge are also decoupled in the NPE formalism, $L_{\mathrm{mq}}^{\mathrm{NPE}} = L_{\mathrm{qm}}^{\mathrm{NPE}} = 0$.

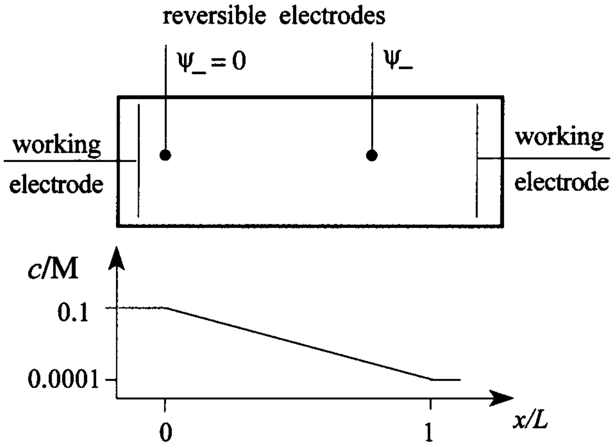

Figure 1. Scheme of the device for studying a liquid junction KCl + H_2O of thickness L. The probes of the reversible electrodes are in local equilibrium with solution; their terminals measure the OEP ψ_- with respect to position $x = 0$, where $\psi'_- = 0$. The working electrodes control the value of the electric current density i.

OEP vs Electrostatic Potential

The electrostatic potential drop across the liquid junction, $\Delta\phi = \phi'' - \phi'$, and the observable electric potential drop measured with two reversible electrodes, $\Delta\psi_- = \psi''_- - \psi'_-$, are related by

$$\Delta\psi_- = \Delta\phi + \Delta\phi_{\mathrm{E}} \tag{22}$$

where

$$\Delta\phi_{\mathrm{E}} = \frac{RT}{z_-F}\ln\frac{\gamma''_-c''_-}{\gamma'_-c'_-} \tag{23}$$

is the electrodes contribution, i.e., the sum of the two Nernst potentials, which represent the difference in electrostatic potential between the solution and the electrode. Note that the condition of local equilibrium between each reversible electrode and the system implies that there is no difference in OEP between these phases.

The relation between the local values of ϕ and ψ_- can be easily obtained from eqs 9 and 17. If local electroneutrality is assumed (see Appendix),

$$\nu_-c_+ = \nu_+c_- \tag{24}$$

the ion concentrations are proportional to the electrolyte concentration c, and the relation between ϕ and ψ_- can be written as

$$\phi(x) = \psi_-(x) - \frac{RT}{z_-F}\ln\frac{\gamma_-c(x)}{\gamma'_-c'} \tag{25}$$

where γ_- is a function of the local concentration $c(x)$, and γ'_- denotes its value at $x = 0$ where concentration is c' and potential is set equal to zero, $\psi'_- = \phi' = 0$.

Since the electric current density i is zero, eqs 11b and 12b reduce to

$$\frac{\mathrm{d}\psi_-}{\mathrm{d}x} = -\frac{t_+}{z_+\nu_+F}\frac{\mathrm{d}\mu}{\mathrm{d}x} = -\frac{\nu RTt_+}{z_+\nu_+Fc}\left(1 + \frac{\mathrm{d}\ln\gamma}{\mathrm{d}\ln c}\right)\frac{\mathrm{d}c}{\mathrm{d}x} \tag{26}$$

which can be integrated to obtain the OEP profile $\psi_-(x)$. This integration is carried out for a given concentration profile $c(x)$ (e.g., the linear profile in Figure 1) and making use of the data $t_+(c)$, $\gamma(c)$ available in ref 19.

Equations 23 and 25 clearly show that $\Delta\phi$ and $\Delta\phi_{\mathrm{E}}$ are two nonobservable magnitudes which are affected by the definition of the activity coefficient γ_-. This definition is somehow

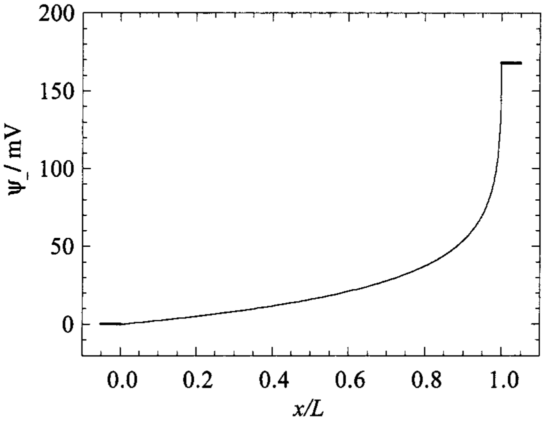

Figure 2. OEP profile $\psi_-(x)$ calculated from eq 26. The values of the thermodynamic coefficients t_+ and γ have been taken from ref 19.

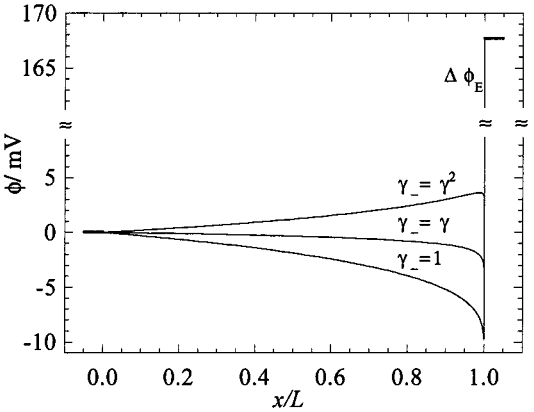

Figure 3. Electrostatic potential profile $\phi(x)$ calculated from eq 25 for different definitions of the activity coefficient γ_-. The electrodes contribution has been added to $\phi(L)$, thus yielding the observable potential drop $\Delta\psi_- = \Delta\phi + \Delta\phi_E$.

arbitrary because the description of an electrolyte solution in terms of ionic species involves two (nonobservable) activity coefficients, γ_+ and γ_- and the description in terms of the mean concentration c involves only the mean activity coefficient

$$\gamma = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/\nu} \tag{27}$$

The use of the OEP, however, allows evaluation of a profile $\psi_-(x)$ and a total (observable) potential drop $\Delta\psi_-$ which do not require any definition of the activity coefficient γ_-.

The KCl + H_2O Liquid Junction

As an example, the electric potential profiles $\phi(x)$ and $\psi_-(x)$ are evaluated in this section for the state of the liquid junction shown in Figure 1. The concentration profile considered is linear, varying from $c' = 0.1$ M at $x = 0$ to $c'' = 0.1$ mM at $x = L$. The system is KCl + H_2O so that $\nu = 2$ and $z_+\nu_+ = 1$. The pressure is 1 atm and the temperature 25 °C. The OEP is measured with reversible Ag|AgCl electrodes in local equilibrium with the solution. The system in under open-circuit conditions so that the electric current density is zero.

The transport process that occurs in this liquid junction is characterized by the flux density of matter (electrolyte), $j_m = -D(dc/dx)$, and the observable liquid junction potential, $\Delta\psi_- = \psi''_- - \psi'_-$. Since the concentration profile has been assumed, results are presented for the electric potential only. Figure 2 shows the profile $\psi_-(x)$ obtained from the integration of eq 26. Figure 3 shows the profiles $\phi(x)$ obtained from eq 25 and the following options for the γ_- definition: (i) $\gamma_- = 1$ (i.e., $\gamma_+ = \gamma^2$); (ii) $\gamma_- = \gamma_+ = \gamma$; (iii) $\gamma_- = \gamma^2$ (i.e., $\gamma_+ = 1$). Note that γ_- can be arbitrarily defined (being eq 27 and $\lim_{c\to 0} \gamma_- = 1$ the only requirements) and that different definitions lead to significant changes in the profile $\phi(x)$. It is true, however, that most authors use option (ii), while some others assume ideal behavior, $\gamma_- = \gamma_+ = \gamma = 1$. Since the liquid junction considered involves dilute solutions, the ideal behavior assumption leads to a potential profile $\phi(x)$ which can hardly be differentiated from option (ii) in Figure 3; the former yields $\Delta\phi = -3.46$ mV and $\Delta\psi_- = 167.52$ mV and the latter yields $\Delta\phi = -3.30$ mV and $\Delta\psi_- = 167.68$ mV. This small difference is partly responsible for the common belief that the electrostatic potential in the NPE formalism is not related to the ionic activity coefficients.

Conclusions

Different formulations of the transport equations in electrochemical systems have been compared in order to show the benefits of the OEP formalism. The comparative study has been applied to the mass transport process that occurs in a liquid junction of a binary electrolyte solution when the electric current density is zero.

The most important difference is that the OEP formalism is based on the potential ψ_-, which can be measured with electrodes reversible to the anion, while the NPE formalism is based on the nonobservable electrostatic potential ϕ. Furthermore, the OEP formalism does not require definition of γ_-, while the NPE formalism does and yields a potential profile $\phi(x)$ which depends on such a definition. Most limitations of the NPE formalism are well-known from the excellent review by Buck,[20] but the implications of the definition of the ionic activity coefficients are not usually commented upon. From this point of view, both the OEP and the electrostatic potential are phenomenological magnitudes which are defined within a phenomenological description of the transport process.

The NPE formalism introduces only two transport coefficients (which are also nonobservable) and assumes a relation between the electrical conductivity and the electrolyte diffusion coefficient, eq 21, which limits its validity to the range of moderately dilute solutions. On the contrary, the OEP formalism introduces three observable transport coefficient and can be applied to concentrated solutions.

The recently developed OEP formalism[10] presents clear benefits (at least for the cases considered so far) with respect to the NPE formalism and therefore it is worth considering it for the description of other transport processes. Nevertheless, the present study should not be regarded as a work against the NPE formalism. The NPE formalism has proved for over 1 century[11,12] its usefulness in the description of a huge variety of transport processes. Furthermore, the introduction of the electrostatic potential makes it convenient for those problems where there is a nonnegligible space charge density.

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Appendix

The complete formulation of the transport problem must combine the flux equations with the continuity equations for mass, $\partial j_m/\partial x + \partial c/\partial t = 0$, and electric charge, $\partial i/\partial x + \partial \rho/\partial t = 0$, where ρ is the electric charge density. Because of its macroscopic character, the TIP does not provide any equation that relates ρ to any other transport variable, and this is a serious limitation of the TIP formalisms, including the OEP formalism.

TABLE 1: Residual Charge Density ρ at the Boundaries of the Liquid Junction for the Electrostatic Potential Profiles $\phi(x)$ Corresponding to the Three Choices of $\gamma_-(c)$

		ρ/F (M)		
x/L	c (M)	$\gamma_- = 1$	$\gamma_- = \gamma$	$\gamma_- = \gamma^2$
0	10^{-1}	1.8×10^{-20}	3.4×10^{-21}	-1.1×10^{-20}
1	10^{-4}	4.2×10^{-15}	3.5×10^{-15}	2.8×10^{-15}

The NPE formalism is based on the electrostatic potential and therefore includes Poisson's equation

$$\rho = -\epsilon \frac{d^2\phi}{dx^2} \tag{28}$$

as one transport equation to be solved in combination with eq 15 (and the continuity equation, in the case of non-steady-state problems). In eq 28, ϵ is the dielectric permittivity, which can be considered constant along the liquid junction.

Most transport problems, including the binary electrolyte liquid junction considered here, can be solved using eq 24 instead of eq 28 (i.e., the so-called local electroneutrality assumption). The validity of this approximation is often checked by evaluating the residual charge,[21] defined as the space charge density ρ obtained from eq 28 when the electrostatic potential profile is the approximate profile obtained from eqs 15 and 24. Table 1 shows the values of the residual charge density ρ at the boundaries of the liquid junction for the three electrostatic potential profiles $\phi(x)$ and two different electrolyte concentrations c. Since ρ/F and c differ in many orders of magnitude, it is concluded that, although a charge separation must certainly exist, eq 19 is a very good approximation in the solution of the transport equations.

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