Reexamination of electrodiffusion time scales

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The characteristic time scales in ac ionic conduction near equilibrium are reassessed via consideration of a selection of one-dimensional model problems. It is observed that, in addition to the two basic electrodiffusion time scales, those of diffusion relaxation in the macroscopic- and Debye-scale domains, T and t_D (the latter identical with the bulk charge relaxation time), some intermediate time scales are present in each system. It is concluded that, due to insensitivity of the electric double layers to harmonic voltage disturbances, the short-time response on the t_D scale is determined by the quasielectroneutral bulk.

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Electrodiffusion of ions is a basic transport mechanism in aqueous ionic systems such as electrolyte solutions and ion exchangers. A clear understanding of the characteristic time scales involved in electrodiffusion is important for the rational design of microfluidic devices, such as microfluidic pumps [1], and for study of the related electrochemical systems by the methods of chronopotentiometry and electric impedance spectroscopy [2]. A detailed review of the time-dependent aspects of electrodiffusion was given in recent papers by Bazant and Adjari with co-workers [3].

In a macroscopic system, the characteristic electrodiffusion time scales include the macroscopic diffusion time $T=L^2/D$ [or $t_0=O(1)$ scale in dimensionless terms], with L the macroscopic length scale and D typical ionic diffusivity; and the microscopic time scale $T_D=l_D^2/D$ [or $t_D=O(\varepsilon^2)$], with l_D the Debye length and $\varepsilon=l_D/L$ the crucial small parameter in the system. This short-time scale universally originates in any binary system of charges from a rapid diffusional relaxation of the large $[O(1)]$ space charge of an $O(\varepsilon)$ thin electric double layer (EDL) along with relaxation to the small residual values $[O(\varepsilon^2)]$ of the space charge of a macroscopic quasielectroneutral bulk.

In addition to these two fundamental time scales, various additional ones may appear in particular electrodiffusional systems. Thus, as pointed out and analyzed in [3], charging of an EDL at a perfectly blocking electrode (such that no dc electric current flows through it upon application of a voltage) occurs at an intermediate time scale $t_i=O(\varepsilon)$—a geometric average of t_0 and t_D. The appearance of this intermediate time scale was traced analytically and interpreted in terms of an equivalent electric circuit consisting of a capacitor with $O(\varepsilon)$ capacitance, standing for the EDL at a blocking electrode, in series with a resistor with $O(1)$ resistance, standing for the adjacent electrolyte diffusion layer.

As transparent as this interpretation is, a question arises as to how general the t_i time scale is when the assumption of a perfect blocking of the conduction current is relaxed. In particular, what are the typical time scales for an ac current passage through a charge-selective solid, such as an ion exchange membrane? Are there any additional time scales besides t_0, t_D, and t_i? In this paper we will attempt to answer these question by analyzing a selection of simple one-dimensional (1D) models for an ion exchange membrane in a binary electrolyte solution near complete ionic equilibrium (zero dc bias). In a subsequent study we shall address the same questions away from equilibrium, under a finite dc current bias. In particular, in that study we shall assess the feasibility of probing the extended nonequilibrium space charge, developing in such systems near the limiting current [4], by applying an ac signal superimposed on a constant dc bias.

We precede the formulation of the model problems with the following straightforward remark. For a binary electrolyte, assuming equal ionic diffusivities D, the expression for the dimensionless total electric current I reads

$$I=-\varepsilon^2\varphi_{xt}+j_+-j_-. \tag{1}$$

Here φ is the dimensionless electric potential (normalized by the thermal potential kT/e), x is the dimensionless spatial coordinate (normalized by the macroscopic length scale L), t is the "slow" dimensionless time (normalized by T), and j_+,j_- are the dimensionless ionic fluxes defined as

$$j_\pm=-(c_{\pm x}\pm c_\pm\varphi_x). \tag{2}$$

The first term in the right-hand side of Eq. (1) is the displacement current, whereas the difference of j_+ and j_- forms the conduction current. Thus, e.g., through a finite difference approximation of Eq. (1), the entire system may be represented in terms of an equivalent circuit, as a series connection of elementary circuits, each consisting of a capacitor connected in parallel with a resistor. Assuming an order-ε capacitance and resistance for each, typical values for an EDL, every such elementary circuit is characterized by the t_D time scale.

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In this picture, the perfect blocking, modeled as an $O(\varepsilon)$ capacitance in series with $O(1)$ resistance, may be recovered by assuming that the resistance of one of the series elements becomes infinite.

Below we shall analyze three model problems: two for a solution layer flanked by either two perfectly blocking electrodes, or two ideal permselective membranes (ideal nonblocking electrodes), and a three-layer setup resulting from inserting a nonideal cation exchange membrane between the two ideal cation-selective membranes of the second model. The first case is identical with that analyzed in Ref. [3], albeit there the analysis was carried out for a stepwise rather than harmonically applied voltage. The second model concerns the analysis of a time-dependent version of a formulation used on several previous occasions to study the nonequilibrium space charge [4]. The third model with a nonideal middle membrane is meant to bridge the two.

The first model reads

$$c_{\pm t} = -j_{\pm x}, \tag{3}$$

$$\varepsilon^2 \varphi_{xx} = c_- - c_+, \tag{4}$$

$$\varphi(0,t) = -\varphi(1,t) = \frac{V}{2} + \frac{\alpha}{2} e^{i\omega t}, \tag{5}$$

$$j_\pm(0,t) = j_\pm(1,t) = 0, \tag{6}$$

$$\int_0^1 c_\pm dx = 1. \tag{7}$$

Here V is a constant voltage bias applied between the blocking electrodes, inducing an equilibrium EDL at them, and α is a small perturbation parameter. Equation (3) is the ionic mass conservation (Nernst-Planck) equation, Eq. (4) is the Poisson equation with space charge in the right-hand side due to the local ionic concentration disbalance. The boundary conditions (6) stand for impermeability for ions of the blocking electrodes, whereas the normalization condition (7) specifies at unity the average ionic concentration in the layer. For small harmonic perturbations we seek a solution to the problem (3)–(7) in the form

$$c_\pm = e^{\mp \varphi_0} + \alpha C_\pm(x) e^{i\omega t}, \quad \varphi = \varphi_0 + \alpha \Phi(x) e^{i\omega t}. \tag{8}$$

Here φ_0 is the electrical potential for the unperturbed state,

$$\varphi_0 = 2 \ln \frac{1 - \tanh \frac{V}{8} \exp \frac{-x}{\sqrt{2\varepsilon}}}{1 + \tanh \frac{V}{8} \exp \frac{-x}{\sqrt{2\varepsilon}}} \frac{1 + \tanh \frac{V}{8} \exp \frac{x-1}{\sqrt{2\varepsilon}}}{1 - \tanh \frac{V}{8} \exp \frac{x-1}{\sqrt{2\varepsilon}}}. \tag{9}$$

For the electric current we have

$$I = \alpha \sigma e^{i\omega t}, \tag{10}$$

where σ is the complex electrical conductivity or admittance, defined as the reciprocal of the electrical impedance $Z(V)$,

$$Z(V,\varepsilon) \overset{\text{def}}{=} \frac{1}{\sigma} = Z_r(V,\varepsilon) + iZ_i(V,\varepsilon). \tag{11}$$

Here the real part $Z_r = \mathrm{Re}\, Z$ is the resistance and $Z_i = \mathrm{Im}\, Z$ is the reactance. For a zero voltage, there is no EDL in the unperturbed initial state, and an analytical solution of the linearized problem for the perturbations yields

$$Z(0,\varepsilon) = \frac{1}{2 + \omega^2 \varepsilon i} - \frac{\sqrt{2}}{\omega\varepsilon} i. \tag{12}$$

The first term in Eq. (12) is the electrical impedance of the quasielectroneutral bulk, whereas the second term stands for a blocking EDL charging impedance. Their corresponding characteristic frequencies are

$$\omega_1 = O(\varepsilon^{-1}) = \frac{1}{t_i}, \quad \omega_2 = O(\varepsilon^{-2}) = \frac{1}{t_D} \tag{13}$$

with

$$\omega_3 = O(\varepsilon^{-3/2}), \tag{14}$$

their geometric average, appearing as the locus of the maximum ($\omega \approx 2\varepsilon^{-3/2}$) on the reactance-frequency plot. For the general case ($V \neq 0$), numerical integration of the linearized problem for perturbations yields

$$Z(V,\varepsilon) = Z(0,\varepsilon) + [Z_r^0(\omega) + Z_i^0(\omega) i]V - \frac{F(V)}{\omega\varepsilon} i. \tag{15}$$

To determine the correction $F(V)$, we calculate numerically the deviation $Z_d \overset{\text{def}}{=} Z(V,\varepsilon) - Z(0,\varepsilon)$ for various ε to infer that the expression $[Z_d(V,\varepsilon_1) - Z_d(V,\varepsilon_2)]\omega/(1/\varepsilon_1 - 1/\varepsilon_2)$ depends only on the applied voltage V:

$$F(V) \overset{\text{def}}{=} \omega \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_2 - \varepsilon_1} [Z_d(V,\varepsilon_1) - Z_d(V,\varepsilon_2)]. \tag{16}$$

Similarly, considering the expression $Z(V,\varepsilon) - Z(0,\varepsilon) + F(V)i/(\varepsilon\omega)$ for various ε, we conclude that it is independent of ε and proportional to V,

$$[Z_r^0(\omega) + iZ_i^0(\omega)]V \overset{\text{def}}{=} Z(V,\varepsilon) - Z(0,\varepsilon) + \frac{F(V)}{\varepsilon\omega} i. \tag{17}$$

In Fig. 1 we present plots of the corrections $Z_r^0(\omega)$, $Z_i^0(\omega)$, and $F(V)$. We note the exponential vanishing of the expression $F(V) + \sqrt{2}$ [see inset to Fig. 1(b)], standing in good agreement with the classical Gouy-Chapman theory [5] predicting an exponential dependence of the EDL capacitance C_{DL} on high ζ potentials (potential drop across the EDL, $V/2$ in our case):

$$C_{\mathrm{DL}} = \frac{\varepsilon}{\sqrt{2}} \cosh \frac{V}{4}. \tag{18}$$

The second model for ideal cation-exchange membranes reads

$$c_{\pm t} = -j_{\pm x}, \quad \varepsilon^2 \varphi_{xx} = c_- - c_+, \tag{19}$$

$$j_-(0,t) = j_-(1,t) = 0, \tag{20}$$

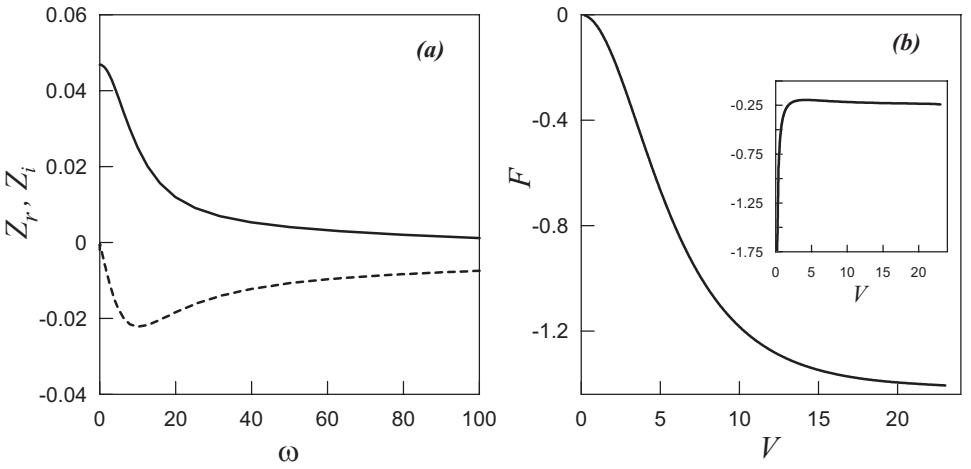

FIG. 1. Reactance and resistance corrections for nonzero voltage: (a) Z_r^0 (continuous line) and Z_i^0 (dashed line) frequency dependencies; (b) $F(V)$ plot. Inset: $\{\ln[F(V)+\sqrt{2}]\}/V$ versus voltage plot.

$$c_+(0,t) = c_+(1,t) = N, \tag{21}$$

$$\varphi(0,t) = -\varphi(1,t) = \frac{\alpha}{2} e^{i\omega t}, \tag{22}$$

$$\int_0^1 c_- dx = 1. \tag{23}$$

Here $N \gg 1$ is the fixed charge density in the membranes. Equation (20) asserts impermeability of the membranes for coions, Eq. (21) fixes the counterion concentration in the membranes equal to the concentration of the fixed charges, whereas the normalization condition (23) specifies at unity the average coion concentration in the system. We seek a solution to the problem (19)–(23), in the form (8). Linearization followed by integration across the EDL, using the continuity of the electrochemical potential of counterions across the EDLs and antisymmetry with respect to the middle point $x=\frac{1}{2}$, yields the following equations for the harmonic perturbations in the quasielectroneutral bulk:

$$C_+(x) = C_-(x) = C(x), \tag{24}$$

$$i\omega C = C_{xx}, \quad (i\omega\varepsilon^2 + 2)\Phi_x = -\sigma, \tag{25}$$

$$C(1/2) = \Phi(1/2) = 0, \tag{26}$$

$$C(0) + \Phi(0) = 1/2, \quad C_x(0) - \Phi_x(0) = 0. \tag{27}$$

Solution of Eqs. (25)–(27) yields

$$Z = \frac{1}{2 + i\omega\varepsilon^2} + \frac{\tanh(\lambda/2)}{\lambda}, \quad \lambda = (1+i)\sqrt{\frac{\omega}{2}}. \tag{28}$$

The first term in Eq. (28) is the electrical impedance of the quasielectroneutral bulk, whereas the second term is EDL related in the sense that the equilibrium across the EDL transforms a diffusional concentration delay of the bulk into an electric potential delay. In the absence of an EDL, the same effect would be induced by differing ionic diffusivities. At the high-frequency edge this term yields a square root frequency dependence in accordance with the classical Warburg picture [6]. This is illustrated by a Nyquist plot in Fig. 2. We note that the loci of the maxima on the Nyquist plot [see Eq. (28) and Fig. 2] correspond to the time scales t_0 and t_D:

$$\omega_4 \approx 5.082, \quad \omega_5 \approx 2\varepsilon^{-2}. \tag{29}$$

We also note the appearance of the time scale $t_P = O(\varepsilon^{4/3})$ as the locus of the minimum on that plot, where the "Bulk" and "Warburg" branches meet. [The corresponding frequency

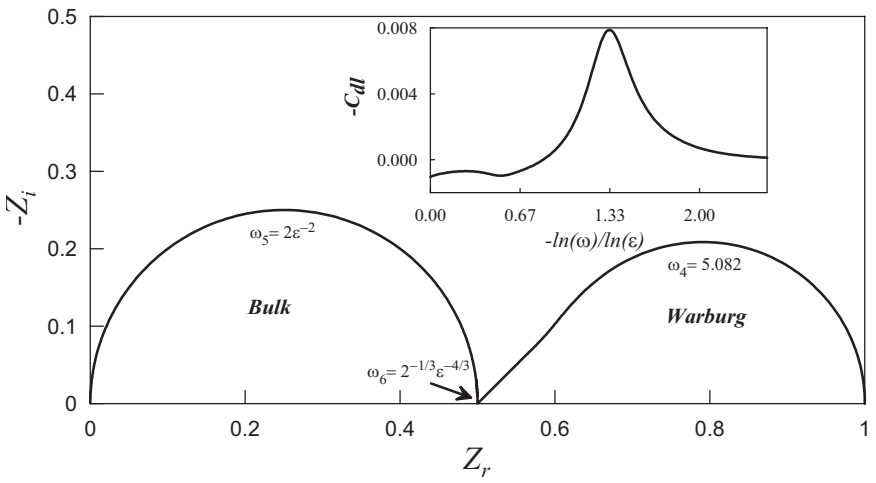

FIG. 2. Nyquist plot for a solution layer between two ideal cation-selective membranes: two characteristic branches, Warburg impedance $[\omega \leqslant O(\varepsilon^{-4/3})]$ and quasielectroneutral bulk impedance $[\omega \geqslant O(\varepsilon^{-4/3})]$. Inset: the EDL capacitance C_{DL} versus frequency plot, $N=10$, $\varepsilon=0.001$.

$$\omega_6 \approx 2^{-1/3}\varepsilon^{-4/3} \tag{30}$$

appears as the geometric average of the parameters $\omega\varepsilon^2$ and $\sqrt{\omega}$ controlling Z in Eq. (28)]. For this same frequency the contributions of the two terms to the expression (28) for Z_i balance. Thus, for $\omega \gg \varepsilon^{-4/3}$ the bulk dominates, yielding

$$Z \approx \frac{1}{2 + i\omega\varepsilon^2}. \tag{31}$$

We note that heretofore the time scale t_P and its corresponding length scale $\varepsilon^{2/3}$ were related to the limiting current regime characterized by transition of the EDL from a quasiequilibrium to a nonequilibrium state accompanied by the appearance of an extended space charge, added to the usual one of a quasiequilibrium EDL [4]. To make this emergence of the $\varepsilon^{2/3}$ length scale in both contexts more intuitive, let us trace it twice through suitable heuristic dc and ac arguments.

Consider first an order-unity conduction current I carried by a single positive charge carrier with concentration p. The expression for the conduction current

$$p\varphi_x = -I, \tag{32}$$

combined with the Poisson equation

$$\varepsilon^2\varphi_{xx} = -p, \tag{33}$$

yields the equation

$$\varepsilon^2\varphi_x\varphi_{xx} = I. \tag{34}$$

By estimating φ_x, φ_{xx} in Eq. (34) as

$$\varphi_x \sim \delta^{-1}, \quad \varphi_{xx} \sim \delta^{-2}, \tag{35}$$

where δ is the length scale to be evaluated, we arrive at the estimate

$$\delta \sim \varepsilon^{2/3}. \tag{36}$$

Next, let this time I be an order-unity displacement current

$$-\varepsilon^2\varphi_{xt} = I, \tag{37}$$

yielding the estimate

$$\frac{\varepsilon^2}{\delta T} = I, \tag{38}$$

where T is the relevant time scale. Assuming the diffusion relation

$$T = \delta^2 \tag{39}$$

between the length and time scales, we obtain upon substitution into Eq. (38) the estimate (36) for the length scale.

We stress that the quasielectroneutral bulk dominates the harmonic time response for all high frequencies, $\omega \gg 1$. This stands in contrast with the perfect blocking case, for which the entire time response is determined by the charging dynamics of the EDL. In the current example lack of contribution from the EDL to the time response scales is caused by the insensitivity of the EDL at a nonblocking interface to current or voltage disturbances (vanishing to leading order perturbations of the ionic concentrations and electric potential in the EDL). This latter follows from the boundedness of the displacement current in the EDL, implying

$$|\omega\varepsilon^2\Phi_x| = O(1) \Rightarrow C(0) = O\left(\frac{1}{\sqrt{\omega}}\right). \tag{40}$$

This vanishing disturbance in the EDL is a general feature of any nonblocking interface. To illustrate this, let us modify Eq. (28) by introducing in the second term the EDL capacitance in parallel with the Warburg element in accordance with the Randles equivalent circuit:

$$Z = \frac{1}{2 + i\omega\varepsilon^2} + \frac{1}{\dfrac{\lambda}{\tanh(\lambda/2)} + iC_{\mathrm{DL}}\omega}. \tag{41}$$

The impedance Z in Eq. (41) corresponds to a series connection of the following two circuits. The first circuit is formed by the bulk resistance $(\frac{1}{2})$ in parallel with the bulk capacitance (ε^2). The second circuit is formed by the Warburg element in parallel with the EDL capacitance $[O(\varepsilon)]$. We evaluate the EDL capacitance $C_{\mathrm{DL}}=O(\varepsilon)$ from a numerical solution of the problem (19)–(23) (see inset to Fig. 2). We note the domination of the Warburg impedance over the EDL capacitance in the Randles circuit up to extremely high frequencies $\omega < O(\varepsilon^{-2})$. For $\omega = O(\varepsilon^{-2})$, both contributions to the impedance balance, whereas, as mentioned previously, the overall reactance in this frequency range is dominated by the quasielectroneutral bulk.

The analysis of a mixed setup for an electrolyte layer flanked by a blocking electrode and an ideal cation-exchange membrane shows that the impedance in this case is a superposition of the respective terms for blocking electrodes (15) and ideal ion-exchange membranes (28). In this expression all four time scales (13), (14), (29), and (30) are present. In terms of equivalent circuits, this corresponds to a series connection of the following three elements: (1) the blocking electrode capacitance, (2) bulk resistance in parallel with the bulk capacitance, and (3) a Warburg element.

Finally, to connect the perfectly blocking electrode model (3)–(7) with that for ideal membranes (19)–(23), we consider a three-layer setup resulting from inserting a nonideal cation-exchange membrane between the two ideal cation-selective membranes of the second model. The effect of the EDL on the characteristic time scales (frequencies) will be illustrated by considering different fixed charge densities in the middle membrane (the infinite fixed charge density limit corresponds to an ideal cation-exchange membrane) and different membrane resistances (the infinite resistance limit corresponds to a perfect blocking). Thus, the three-layer problem to be analyzed reads [left electrolyte layer $(0<x<1)$–middle ion-exchange membrane $(1<x<2)$–right electrolyte layer $(2<x<3)$]

$$c_{\pm t} = -j_{\pm x}, \quad \varepsilon^2\varphi_{xx} = Q(x) + c_- - c_+, \tag{42}$$

$$Q(x) = Q[H(x-1) - H(x-2)], \tag{43}$$

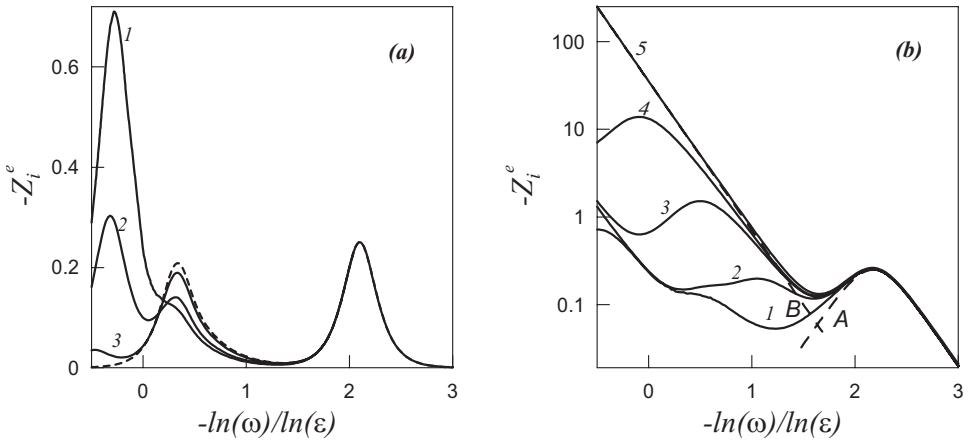

FIG. 3. Reactance frequency dependencies for a three-layer system with different fixed charge densities (a) and diffusivities (b) of the middle membrane. (a) $D_0=0.1$, $N=10$, $\varepsilon=0.001$; $Q=(1)$ 1, (2) 2.5, and (3) 10; dashed line ($Q=\infty$) model (19)–(23). (b) $Q=1$, $N=10$, $\varepsilon=0.02$; D_0 (1) 0.1, (2) 0.01, (3) 0.001, (4) 0.0001, and (5) 0 limit, Eq. (50); dashed line *A*, perfect blocking asymptotics $Z_i=-\sqrt{2}/\omega\varepsilon$, dashed line *B*, quasielectroneutral bulk reactance $Z_i=-\omega\varepsilon^2/(4+\omega^2\varepsilon^4)$.

$$\varphi(0,t)=-\varphi(3,t)=\alpha e^{i\omega t}, \tag{44}$$

$$j_-(0,t)=j_-(3,t)=0, \tag{45}$$

$$c_+(0,t)=c_+(3,t)=N, \tag{46}$$

$$\int_0^3 c_- dx=2+\frac{-Q+\sqrt{Q^2+4}}{2}. \tag{47}$$

The dimensionless ionic fluxes are specified by Eq. (2) in the electrolyte layers ($0<x<1$ and $2<x<3$) and equal

$$j_\pm=-D_0(c_{\pm x}\pm c_\pm\varphi_x) \tag{48}$$

inside the membrane ($1<x<2$). Here $D_0=D_m/D$ is the relative ionic diffusivity inside the membrane, D_m being the dimensional ionic diffusivity equal for both ions. In Eq. (43) $Q>0$ is the fixed charge density (negative) in the membrane and $H(x)$ is the Heaviside function, whereas the boundary conditions (45) and (46) and the normalization condition (47) are analogous to conditions (20), (21), and (23) in the previous model. Similarly to the one-layer models (3)–(7) and (19)–(23), the solution to the problem (42)–(48) is sought in the form (8). The suitable linearized problem for the space-dependent amplitudes $C_\pm(x)$ and $\Phi(x)$ is solved numerically. We distinguish between the electrical impedance of the entire three-layer system defined by Eq. (11) and that of a single electrolyte layer ($2<x<3$, for definiteness) given by

$$Z^e=Z_r^e+iZ_i^e=\frac{\Phi(2)-\Phi(3)}{\sigma}. \tag{49}$$

In Fig. 3(a) we present the reactance-frequency plots for different values of fixed charge density in the middle membrane. We note the validity of the approximation Eq. (31) for all fixed charge densities, and the good agreement in the high-frequency range of the numerical solution in the three-layer model with the analytic one for two ideal cation-selective membranes. We recall that in this latter the analysis of EDL dynamics was skipped through the use of continuity of the electrochemical potential of counterions across the EDLs. In Fig. 3(b) we present similar plots for different middle membrane diffusivities along with that for the zero-voltage case in a mixed setup for which the analysis yields

$$Z=\frac{1}{2+\omega\varepsilon^2 i}+\frac{1}{2}\left(\frac{\tanh\lambda/2}{\lambda}-\frac{\sqrt{2}}{\omega\varepsilon}i\right). \tag{50}$$

We note in the limit of infinitely high membrane resistance, $D_0\ll 1$, the appearance of the time scales (13), (14), (29), and (30), characteristic of a perfect blocking.

Summarizing, upon the transition from perfect blocking to unimpeded ionic conductance the sets of characteristic time scales transform from $O(\varepsilon)$, $O(\varepsilon^{3/2})$, $O(\varepsilon^2)$ to $O(1)$, $O(\varepsilon^{4/3})$, $O(\varepsilon^2)$. In any system the short-time response on the t_D scale is entirely determined by the quasielectroneutral bulk, as opposed to the electric double layers. This is due to the almost complete insensitivity of a quasiequilibrium EDL to harmonic voltage (current) disturbances in the $O(\varepsilon^{-2})$ frequency range. In equivalent circuit terms, this suggests that the classical Randles circuit should be complemented by an order-ε^2 bulk capacitance in parallel with the bulk resistance.

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