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Electric-field-driven transport of valence-asymmetric salts within stagnant fluid films

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ABSTRACT

For many decades, the concentration polarization (CP) of uni-univalent salts arising within stagnant fluid films adjacent to charged surfaces in the presence of an electric field has been described by a simplistic model, designated here as classical theory. Barry [1] demonstrated that for a uni-univalent electrolyte the CP equation obtained by the aforementioned theory could also be derived from the Nernst–Planck equations. Here, as an extension of Barry's work, we deduce a CP equation based on the Nernst–Planck equations applicable to steady transport of valence-asymmetric salts (salts containing ions of distinct valences, e.g., Na_2SO_4, $CaCl_2$, $FeCl_3$) within stagnant fluid films in the vicinity of charged surfaces and in the presence of an electric field. It is shown that the expression derived, $C_b - C_m = \frac{i\delta}{FD_S}\left(t_1^m - \frac{z_1D_1}{z_1D_1 - z_2D_2}\right)$, matches the classical CP equation for similar conditions, despite some deceptive hypothesis assumed by the latter.

Keywords: Concentration polarization; Electrodialysis; Nernst–Planck equations; Transport numbers; Valence-asymmetric salts

1. Introduction

It is very well-known that the passage of an electric current from a salt solution into a charge-selective surface, such as a metal electrode or an ion exchange membrane, gives rise to a salt concentration distribution within the stagnant film adjacent to the surface. This phenomenon is the so-called concentration polarization (CP), and for many decades, it has been described based on the diffusion and migration of the charged species, as presented in Section 2.1.

In the late 90s, the deduction of the classical CP equation was questioned somehow and Barry proved that for a uni-univalent electrolyte the aforementioned equation could also be derived from the Nernst–Planck equations [1]. It is worth to remark that this equation is also valid for di-divalent salts (e.g., $CaSO_4$).

Nevertheless, throughout the modelling of multi-ionic transport in stagnant films adjacent to ion exchange membranes [2], we questioned the validity of the classical CP model for valence-asymmetric salts (salts containing a cation and an anion of distinct valences, e.g., Na_2SO_4, $CaCl_2$, $FeCl_3$). Hence, the main goal of this rapid communication was to derive a CP expression based on the Nernst–Planck equations applicable to steady transport of single valence-asymmetric salts within stagnant fluid films adjacent to charged surfaces in the presence of an electric field and compare it with the classical equation derived for analogous conditions.

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2. Theory

2.1. Classical theory [3–5]

In the presence of an electric potential gradient, the total flux of a cation (species 1) through a cation-exchange membrane, $N_1{}^m$, inside which the cation concentration is assumed to be nearly constant (negligible diffusion), consists solely in the migration flux:

$$N_1^m = \frac{t_1^m i}{|z_1|F} \tag{1}$$

whereas the total flux of the cation within the stagnant film adjacent to the membrane surface, $N_1{}^s$, consists in the sum of the diffusion and migration fluxes, i.e.,

$$N_1^s = -D_S \frac{dC_1}{dx} + \frac{t_1^s i}{|z_1|F} \tag{2}$$

where i is the electric current density, F is the Faraday constant (9.64867×10^4 C/eq), D_S is the salt diffusivity, C_1 and $|z_1|$ are the cation concentration (mol/m^3) and valence (eq/mol), respectively, and $t_1{}^m$ and $t_1{}^s$ are the cation transport numbers in the membrane and solution (stagnant film), respectively (Fig. 1).

In the steady-state, $N_1{}^m$ and $N_1{}^s$ are equal, hence:

$$\frac{t_1^m i}{|z_1|F} = -D_S \frac{dC_1}{dx} + \frac{t_1^s i}{|z_1|F} \tag{3}$$

or

$$\frac{\left(t_1^m - t_1^s\right) i}{|z_1|FD_S} = -\frac{dC_1}{dx} \tag{4}$$

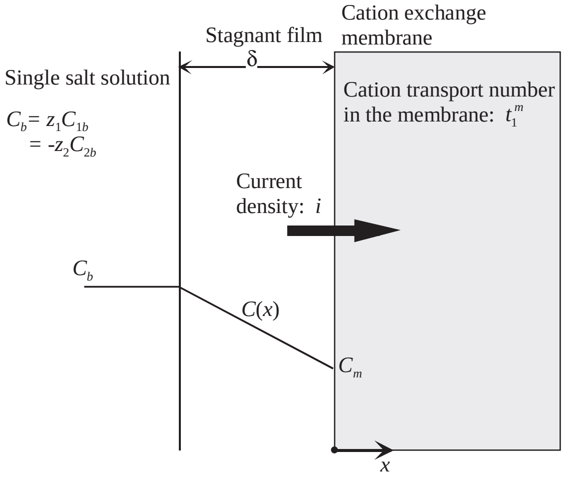

Fig. 1. Ionic transport through a stagnant fluid film adjacent to a negatively charged membrane (cation exchange membrane).

Using the following boundary conditions:
$x = 0 \quad C = C_m$ (solution/membrane interface)
$x = -\delta \quad C = C_b$ (edge of the stagnant film toward the bulk solution),
the integration of Eq. (4) gives:

$$\begin{aligned}\frac{\left(t_1^m - t_1^s\right) i}{|z_1|FD_S} &= -\frac{C_{1b} - C_{1m}}{-\delta} \\ &= \frac{C_{1b} - C_{1m}}{\delta}\end{aligned} \tag{5}$$

so that

$$C_{1b} - C_{1m} = \frac{i\delta}{|z_1|FD_S}\left(t_1^m - t_1^s\right) \tag{6}$$

Since the concentrations of the cation and anion (species 2) fulfil the electroneutrality requirement:

$$|z_1|C_1 = |z_2|C_2 = C\left(\text{eq/m}^3\right) \tag{7}$$

Eq. (6) becomes:

$$C_b - C_m = \frac{i\delta}{FD_S}\left(t_1^m - t_1^s\right) \tag{8}$$

At this point, it is worth to recall that the cation transport number in the solution phase, $t_1{}^s$, is the fraction of the total current density carried by the cation of ionic charge (or charge number) z_1 [6]:

$$\begin{aligned}t_1^s &= \frac{i_1}{i_1 + i_2} \\ &= \frac{z_1C_1F\left(-z_1F\frac{D_1}{RT}\frac{d\psi}{dx}\right)}{z_1C_1F\left(-z_1F\frac{D_1}{RT}\frac{d\psi}{dx}\right) + z_2C_2F\left(-z_2F\frac{D_2}{RT}\frac{d\psi}{dx}\right)}\end{aligned} \tag{9}$$

where R is the molar gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, and ψ is the electric potential difference. Bearing in mind the electroneutrality condition once again, $t_1{}^s$ is given by:

$$t_1^s = \frac{z_1D_1}{z_1D_1 - z_2D_2} \tag{10}$$

Substituting $t_1{}^s$ into Eq. (8), we finally obtain the classical CP equation for valence-asymmetric salts:

$$C_b - C_m = \frac{i\delta}{FD_S}\left(t_1^m - \frac{z_1D_1}{z_1D_1 - z_2D_2}\right) \tag{11}$$

2.2. *Nernst–Planck approach* [7]

Let us derive a CP equation from the first principles established by the Nernst–Planck equations within a stagnant fluid film[1] in the vicinity of a cation exchange membrane placed in between an anode and a cathode and dipped in a dilute single salt solution containing a cation, and an anion of ionic charges z_1, and z_2[2], and diffusivities D_1 and D_2, respectively (Fig. 1).

In the presence of a moderate electric potential difference[3] and under steady-state conditions, the Nernst–Planck equations and the electroneutrality requirement within the stagnant film may be written as follows:

$$N_1 = -D_1\frac{dC_1}{dx} - z_1C_1D_1\frac{F}{RT}\frac{d\psi}{dx} = \frac{t_1^m i}{z_1F} \tag{12}$$

$$\begin{aligned} N_2 &= -D_2\frac{dC_2}{dx} - z_2C_2D_2\frac{F}{RT}\frac{d\psi}{dx} \\ &= \frac{t_2^m i}{z_2F} = \frac{(1 - t_1^m)i}{z_2F} \end{aligned} \tag{13}$$

$$z_1C_1 = -z_2C_2 = C \tag{14}$$

where C is the salt concentration in eq/m^3, which being substituted into Eqs. (12) and (13) yields:

$$\frac{t_1^m i}{z_1F} = -\frac{D_1}{z_1}\frac{dC}{dx} - CD_1\frac{F}{RT}\frac{d\psi}{dx} \tag{15}$$

$$\frac{(1 - t_1^m)i}{z_2F} = \frac{D_2}{z_2}\frac{dC}{dx} + CD_2\frac{F}{RT}\frac{d\psi}{dx} \tag{16}$$

Dividing Eqs. (15) and (16), respectively, by D_1 and D_2, we obtain:

$$\frac{t_1^m i}{z_1D_1F} = -\frac{1}{z_1}\frac{dC}{dx} - C\frac{F}{RT}\frac{d\psi}{dx} \tag{17}$$

$$\frac{(1 - t_1^m)i}{z_2D_2F} = \frac{1}{z_2}\frac{dC}{dx} + C\frac{F}{RT}\frac{d\psi}{dx} \tag{18}$$

Thus, the cation and anion migration terms cancel out by adding Eqs. (17) and (18) and we have:

$$\frac{i}{F}\left[\frac{t_1^m}{z_1D_1} + \frac{(1 - t_1^m)}{z_2D_2}\right] = \left(-\frac{1}{z_1} + \frac{1}{z_2}\right)\frac{dC}{dx} \tag{19}$$

or

$$\frac{i}{F}\left[\frac{t_1^m z_2D_2 + (1 - t_1^m)z_1D_1}{z_1z_2D_1D_2}\right] = \left(\frac{z_1 - z_2}{z_1z_2}\right)\frac{dC}{dx} \tag{20}$$

so that

$$\frac{i}{F}\left[\frac{t_1^m z_2D_2 + (1 - t_1^m)z_1D_1}{(z_1 - z_2)D_1D_2}\right] = \frac{dC}{dx} \tag{21}$$

Making use of the aforementioned boundary conditions, the integration of Eq. (21) yields:

$$\frac{i}{F}\left[\frac{t_1^m z_2D_2 + (1 - t_1^m)z_1D_1}{(z_1 - z_2)D_1D_2}\right] = \frac{C_b - C_m}{-\delta} \tag{22}$$

or

$$C_b - C_m = -\frac{i\delta}{F}\left[\frac{t_1^m z_2D_2 + (1 - t_1^m)z_1D_1}{(z_1 - z_2)D_1D_2}\right] \tag{23}$$

For single salt solutions in the absence of electric current, the cation and anion fluxes are constrained by the electroneutrality requirement. Due to this constraint, the salt diffusivity in water, D_S, and the cation and anion diffusivities, D_1 and D_2, respectively, are related by [8]:

$$D_S = \frac{(z_1 - z_2)D_1D_2}{z_1D_1 - z_2D_2} \tag{24}$$

Now multiplying and dividing the right-hand side of Eq. (23) by the salt diffusivity, D_S, and rearranging it, we finally obtain the CP equation for valence-asymmetric salts:

$$\begin{aligned} C_b - C_m &= -\frac{i\delta}{FD_S}\frac{(z_1 - z_2)D_1D_2}{z_1D_1 - z_2D_2} \\ &\quad \left[\frac{t_1^m z_2D_2 + (1 - t_1^m)z_1D_1}{(z_1 - z_2)D_1D_2}\right] \\ &= -\frac{i\delta}{FD_S}\left[\frac{t_1^m(z_2D_2 - z_1D_1) + z_1D_1}{z_1D_1 - z_2D_2}\right] \\ &= \frac{i\delta}{FD_S}\left(t_1^m - \frac{z_1D_1}{z_1D_1 - z_2D_2}\right) \end{aligned} \tag{25}$$

Inserting in Eq. (25) the definition of the CP index, $\Gamma \equiv (C_b - C_m)/C_b$, and the stagnant film thickness as assumed by the film theory [10–12], $\delta = D_S/k_c$, we finally obtain the expression for the CP index:

$$\Gamma = \frac{i}{FC_bk_c}\left(t_1^m - \frac{z_1D_1}{z_1D_1 - z_2D_2}\right) \tag{26}$$

where k_c is the mass transfer coefficient for the salt diffusion within the stagnant film adjacent to the charged membrane surface.

3. Discussion

Comparing Eqs. (11) and (25), it is clear that the derivations of both the classical theory and the Nernst–Planck approach led to the same expression for the CP of single valence-asymmetric salts within stagnant fluid films adjacent to charged surfaces in the presence of an electric field. This fact is somehow astonishing since the diffusive flux in the classical theory involves the salt diffusivity, D_S, instead of the cation diffusivity, D_1. Furthermore, the electric current across the solution results from the contributions of both diffusion and migration, thus it appears awkward to express the migration flux as $t_1^s i/|z_1|F$ (Eq. (2)). Therefore, we believe that the Nernst–Planck approach illustrated in the current work is more reliable.

An equation for the limiting electric current density in Electrodialysis of single salt solutions of valence-symmetric and asymmetric salts was also derived from the Nernst–Planck equations [9]. The match between the predictions and the experimental data of monovalent (Na^+, K^+, Li^+), divalent (Ca^{2+}, Mg^{2+}) and trivalent (Al^{3+}) cations was striking, except for H^+.

4. Conclusions

In this work, we derived an expression based on the Nernst–Planck equations to describe the CP of single valence-asymmetric salts within stagnant fluid films adjacent to charged surfaces in the presence of an electric field. The equation deduced, $C_b - C_m = \frac{i\delta}{FD_S}\left(t_1^m - \frac{z_1 D_1}{z_1 D_1 - z_2 D_2}\right)$, matches the classical CP equation for identical conditions, despite some misleading assumptions of the latter.

Notes

1. There are two distinct layers adjacent to a charged membrane surface. The electric double layer thickness is just a few nanometres, whilst the stagnant film thickness is tens of microns. ''Solution/membrane interface'' stands for a plane in the vicinity of the membrane surface, that separates the electric diffuse layer from the stagnant film, beyond which the electroneutrality requirement is fulfilled, dispensing with the Poisson equation.
2. z_i is the elementary charge on species i (e.g., -1 for the ion Cl^-).
3. Whether a moderate electric potential difference is applied across a freely suspended fluid film, the electroconvection that leads to a spatially periodic flow pattern comprising counter-rotating vortices is negligible and may be disregarded.

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