

Membrane potentials for linearly varying fixed charges

Ayten GENÇ

*Department of Environmental Engineering, Zonguldak Karaelmas University,
67100 Zonguldak-TURKEY
e-mail: aytengenc@yahoo.com*

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Abstract

The membrane potentials for asymmetric membranes where fixed charges varied linearly with position were evaluated from the numerical solutions of Nernst-Planck flux and Donnan potential equations. The evaluated membrane potentials were compared with the results obtained from the conventional TMS theory where the fixed charge concentration in the membrane was assumed to be uniform. In the comparison, the number of fixed charges was kept constant by defining an average for the fixed charge concentration. The numerical results showed that the membrane potential increased in magnitude when the distributions of fixed charges at the membrane-solution interfaces were unequal. In addition, the deviation from TMS theory increased more as the charge difference at the interfaces increased.

Key Words: Membrane potential; Donnan potential; Charged membranes; TMS theory; Surface charges; Fixed charge concentration.

Introduction

Charged membranes such as ion exchange, reverse osmosis, and electrodialysis membranes are usually characterized by measuring the membrane potential (Barragan et al., 1995; Bowen and Mukhtar, 1996; Choi et al., 2001; Schaep and Vandecasteele, 2001). By definition, the membrane potential is the potential difference that is generated between 2 solutions of the same electrolyte at different concentrations separated by a charged membrane. According to the studies by Teorell (1935) and Meyer and Sievers (1936), known as TMS theory, the membrane potential can be expressed by the sum of the Donnan potential between the membrane surface and the external solutions and the diffusion potential in the membrane. TMS theory identifies the fixed charges by defining a fictitious fixed charge concentration, i.e. the concentration of fixed charges attached to the matrix of the membrane per unit volume. It also assumes that the fixed charge groups are homogeneously distributed in the membrane. However, it is clear that, as a result of concentration gradient across the membrane, the local concentrations of counterions at the membrane-solution interfaces at both sides show variations during the membrane potential measurements. It has been also reported in the literature that membranes with non-uniformly distributed fixed charges can have different ion selectivity compared to membranes with uniformly distributed charges (Manzanares et al., 1991; Shahi et al., 2003).

The purpose of this study was to investigate the effects of non-uniform distributions of fixed charges on membrane potentials, i.e. having the same number of fixed charges with different distribution profiles. Similar to TMS theory, the membrane potential equation for linearly varying fixed charges was derived based on the Nernst-Planck flux equation and Donnan equilibrium. Then a numerical solution procedure was presented to obtain the membrane potential for uni-univalent electrolyte solutions. According to the simulation results, the effects of non-uniform distribution of fixed charges on membrane potential were discussed and the results were compared with the values obtained from TMS. In addition, the calculations were repeated for different values of the external bulk concentration ratio and the ionic diffusion coefficient ratio and their effects on membrane potential were investigated. Finally, the obtained simulation results were compared with the experimental results presented in the literature.

Modeling of the Membrane Potential

The schematic drawing of the studied membrane system is shown in Figure 1. The membrane, which has a thickness of “d”, separated 2 solutions of uni-univalent electrolyte solutions. C_L and C_R are defined as the concentrations of external bulk solutions in the feed side and permeate side, respectively. It is also assumed that C_L is always greater than C_R . The direction of ion transport is shown by ‘x’ and the membrane-solution interfaces are located at the points $x = 0$ and $x = d$. In addition, the fixed charge concentrations at the interfaces are identified as $\theta(0)$ and $\theta(d)$, respectively.

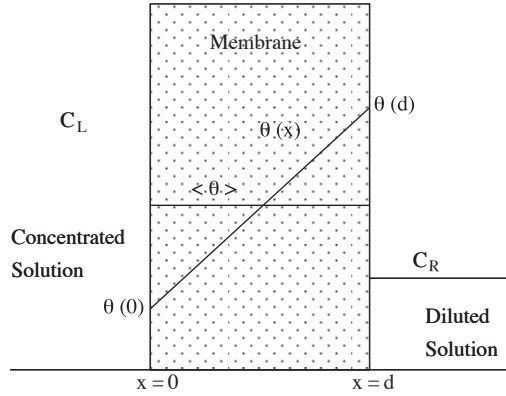


Figure 1. Representation of the studied membrane system.

The flux of ions through a positively charged membrane can be written by using the Nernst-Planck equation (Buck, 1984):

$$J_i = -D_i \left[\frac{dC_i}{dx} + (-1)^{i+1} \frac{F}{RT} C_i \frac{d\psi}{dx} \right] \quad i = 1, 2 \quad (1)$$

where D_i , C_i , and ψ denote the diffusion coefficients, the local molar concentration of the i^{th} ions, and the local electric potential, respectively. In addition, R , T , and F represent ideal gas constant, absolute temperature, and Faraday constant, respectively. According to Eq. (1), the charge of ions is equal to 1 and subscript 1 refers to cations, and subscript 2 to anions.

As a result of the electro-neutrality condition in the membrane, the relation between the concentration of cations and anions is equal to

$$C_1 - C_2 + \theta = 0 \quad (2)$$

where θ is the local fixed charge concentration. According to Figure 1, the variation in θ in the direction of 'x' can be written as

$$\begin{aligned}\theta(x) &= \theta(0) + \frac{\Delta\theta}{d}x \\ \Delta\theta &= \theta(d) - \theta(0)\end{aligned}\quad (3)$$

If the average is defined as the fixed charge concentration divided by the volume of membrane, then the average of fixed charge concentration is equal to

$$\langle\theta\rangle = \frac{\int_0^d \theta dx}{d}\quad (4)$$

It should be pointed out that Eq. (4) is valid when the cross-sectional area of the membrane is constant in the direction of ion transport and when the fixed charge concentration varies only in the x-direction. When the distribution of fixed charges is uniform, the average will be equal to the uniform value ($\langle\theta\rangle = \theta$). In the case of linear variation of fixed charges with position, the average will be equal to the arithmetic averages of the fixed charges at the membrane-solution interfaces.

The concentrations of ions at the membrane-solution interfaces can be written in terms of the external bulk concentrations by using the Donnan equilibrium (Mafe et al., 1997):

$$\begin{aligned}C_1(0) &= \sqrt{C_L^2 + \left(\frac{\theta(0)}{2}\right)^2} - \frac{\theta(0)}{2} \\ C_1(d) &= \sqrt{C_R^2 + \left(\frac{\theta(d)}{2}\right)^2} - \frac{\theta(d)}{2}\end{aligned}\quad (5)$$

Similar equations can also be written for C_2 . The summation of Donnan potentials at the membrane-solution interfaces is equal to (Yamamoto, 2003)

$$[\psi(0) - \psi_L] + [\psi_R - \psi(d)] = \frac{RT}{F} \ln \left(\frac{C_R C_1(0)}{C_L C_1(d)} \right)\quad (6)$$

Diffusion potential through the membrane

When the total current that passes through the membrane is zero, the cation and anion fluxes become equal for uni-univalent electrolyte. If the steady-state ion flux is identified by 'J', it can be easily shown that the potential difference between the membrane-solution interfaces can be obtained from the combination of Eq. (1) and Eq. (2) as

$$\frac{d\psi}{dx} = \frac{RT}{F} \frac{1}{(2C_1 + \theta)} \left(\frac{d\theta}{dx} + J \frac{(D_1 - D_2)}{D_1 D_2} \right)\quad (7)$$

Then the integration of Eq. (7) from $x = 0$ to $x = d$ gives the diffusion potential through the membrane:

$$\psi(d) - \psi(0) = \frac{RT}{F} \left(\frac{\Delta\theta}{d} + J \frac{D_1 - D_2}{D_1 D_2} \right) \int_0^d \frac{dx}{2C_1 + \theta}\quad (8)$$

Numerical solution procedure

A numerical procedure, which was presented by Manzanares et al. (1991), was followed to solve Eq. (1) for uni-univalent electrolytes with the condition presented in Eq. (2). First, the electric potential gradient through the membrane is written by the combination of Eq. (1) and Eq. (2):

$$\frac{d\psi}{dx} = \frac{1}{\theta} \frac{RT}{F} \left(2 \frac{dC_1}{dx} + \frac{d\theta}{dx} + \frac{J_1}{D_1} + \frac{J_2}{D_2} \right) \quad (9)$$

By defining a new variable 'y', the equations can be simplified:

$$y = \frac{C_1}{\theta} \quad (10)$$

If Eq. (9) is substituted into Eq. (1) for $i = 1$, the resulting equation in terms of variable 'y' will be

$$\frac{y + \frac{1}{2}}{y^2 + (1 + g_1 + g_2)y + g_1} dy = -\frac{d\theta}{\theta} \quad (11)$$

where

$$g_i = \frac{J_i}{2D_i \frac{d\theta}{dx}} \quad i = 1, 2 \quad (12)$$

The roots of the 2nd order polynomial that appeared in the denominator of Eq. (11) are

$$\begin{aligned} y_1 &= \frac{1+g_1+g_2+\sqrt{(1+g_1+g_2)^2-4g_1}}{2} \\ y_2 &= \frac{g_1}{y_1} \end{aligned} \quad (13)$$

Accordingly, Eq. (11) can be rewritten in terms of its roots:

$$\frac{y + \frac{1}{2}}{(y - y_1)(y - y_2)} dy = -\frac{d\theta}{\theta} \quad (14)$$

Then the integration of Eq. (14) over the membrane results in

$$(y - y_1\theta)^A (y - y_2)^{(1-A)} \theta = \alpha \quad (15)$$

where 'α' is a constant and 'A' is equal to

$$A = \frac{y_1 + \frac{1}{2}}{y_1 - y_2} \quad (16)$$

Or Eq. (15) can be rewritten in terms of C_1 and θ by using Eq. (10):

$$(C_1 - y_1\theta)^B (C_1 - y_2\theta) = \alpha \quad (17)$$

where

$$B = -\frac{1 + 2y_1}{1 + 2y_2} \quad (18)$$

In order to obtain the constant ‘ α ’, Eq. (17) is written at the membrane-solution interfaces (Figure 1):

$$(C_1(0) - y_1\theta(0))^B (C_1(0) - y_2\theta(0)) = (C_1(d) - y_1\theta(d))^B (C_1(d) - y_2\theta(d)) \quad (19)$$

The steady-state ion fluxes ($J_1 = J$) through the membrane at the condition of zero electric current ($J_1 - J_2 = 0$) can be obtained by solving Eq. (19). In the solution, the method of bisection was applied. Once the value of ‘ J ’ is evaluated, the constant ‘ α ’ is known and Eq. (15) can be used to predict the variation of cation concentrations (C_1) with respect to ‘ x ’ (Figure 1). C_1 profile in the membrane was evaluated by using the method of Newton-Raphson and the error tolerance was set to 1×10^{-12} .

Results and Discussion

Effects of variable fixed charge concentration on membrane potential

According to TMS theory, the fixed charge concentration in the membrane is uniform and the membrane potential is equal to (Beg and Matin, 2002; Xu et al., 2004)

$$\Delta\psi_{mem} = \frac{RT}{F} \left[\ln \left(\frac{C_L \sqrt{4C_R^2 + \langle \theta \rangle^2} - \langle \theta \rangle}{C_R \sqrt{4C_L^2 + \langle \theta \rangle^2} - \langle \theta \rangle} \right) + u \ln \left(\frac{\sqrt{4C_L^2 + \langle \theta \rangle^2} - \langle \theta \rangle}{\sqrt{4C_R^2 + \langle \theta \rangle^2} - \langle \theta \rangle} \right) \right] \quad (20)$$

where

$$u = \frac{D_1 - D_2}{D_1 + D_2} \quad (21)$$

The magnitude of ‘ u ’ gives information about the difference in transport velocity of anions and cations through the membrane. If the diffusion coefficients of cations and anions are equal ‘ u ’ becomes zero and, therefore, the diffusional potential will be equal to zero as well.

When the fixed charge concentration in the membrane varies linearly with position, the membrane potential can be obtained from the summation of Eq. (6) and Eq. (8). In this study, Simpson’s rule was applied to calculate the integral that appeared in Eq. (8) and the error tolerance was set to 1×10^{-12} . The diffusivity coefficients of cations and anions were taken as 1×10^{-5} cm²/s and 2×10^{-5} cm²/s, respectively, and the partition coefficients were assumed to be unity.

The variations in membrane potential depending on the external bulk concentration ratio (C_L/C_R) are presented in Figure 2. Solid lines in the graphs showed the membrane potentials calculated from Eq. (20), where the fixed charge concentration was assumed to be uniform (TMS). When the fixed charge concentration varied linearly with position, the membrane potentials were shown by dashed lines and identified as LINEAR. It was seen that the predictions of membrane potentials from the numerical solutions were usually higher than the predictions obtained from TMS. In Figure 2(a) and (b), the average of fixed charge concentration ($\langle \theta \rangle$) was equal to 5.5×10^{-4} mol/cm³ and, therefore, TMS lines were exactly the same. On the other hand, when θ varied linearly with position (Eq. (4)) the average was equal to the arithmetic average of the fixed charge concentrations at the membrane-solution interfaces, i.e. $\langle \theta \rangle = (\theta(0) + \theta(d))/2$. The degree of non-uniformity increased from Figure 2(a) to Figure 2(b) since the gradient of the fixed charge concentration ($\Delta\theta/d$) lines increased. The gradients were $5.5 \times 10^{-4}/d$ and $9 \times 10^{-4}/d$ in Figure 2(a) and Figure 2(b), respectively. In other words, the difference between the fixed charge concentrations at the membrane-solution interfaces

increased. The calculations were repeated for higher values of $\langle \theta \rangle$ and the results are presented in Figure 2(c) and (d). It was clear that the distribution of fixed charges at the membrane-solution interfaces affected the membrane potential. In addition, the discrepancy between TMS and LINEAR curves increased more as $\langle \theta \rangle$ increased.

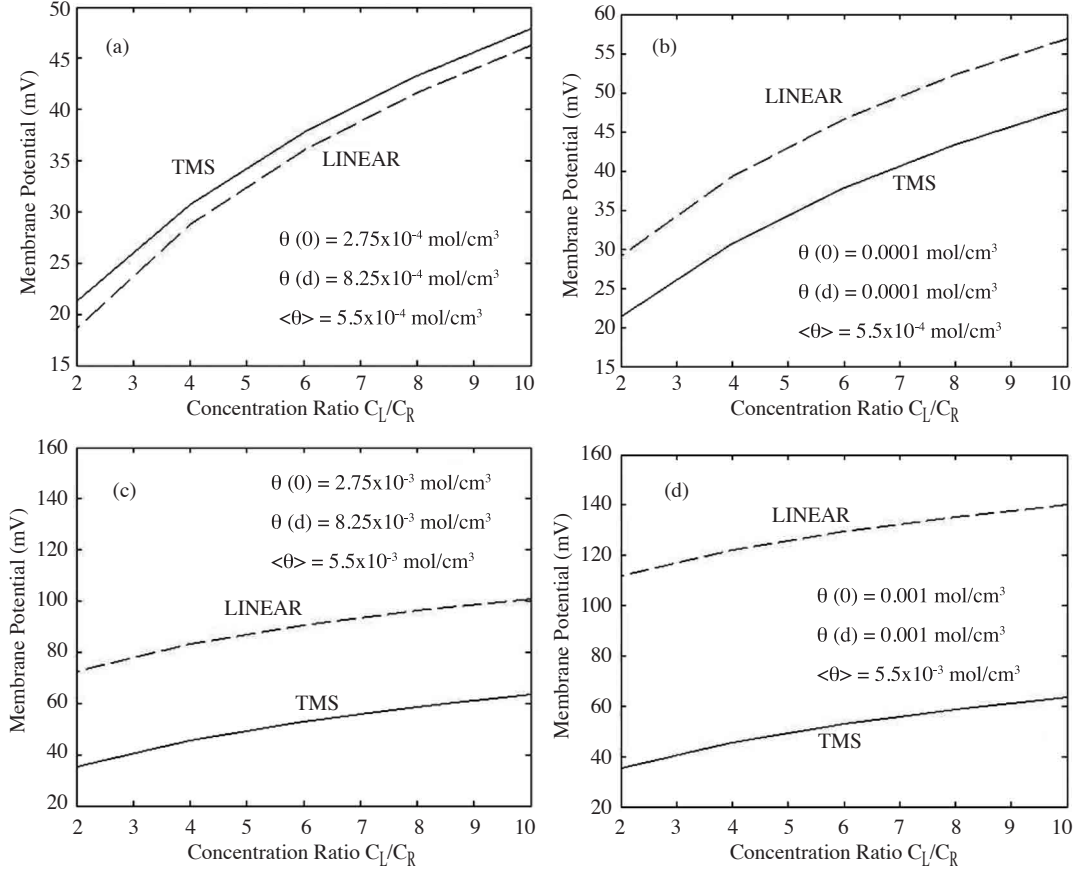


Figure 2. Membrane potentials for uniform and linear variations in fixed charges.

According to the results presented in Figure 2, the membrane potential increased in magnitude as the external bulk concentration ratio increased. This is a common observation in different studies presented in the literature (Bowen and Mukhtar, 1996; Schaep and Vandecastee, 2001; Shaei et al., 2003). For example, Tiwari and Ahmad (2006) prepared some membranes by mixing cellulose acetate and Zeocarb-225 in different ratios and then measured the membrane potential using sodium chloride solutions. They measured the membrane potential by keeping the mean sodium chloride concentration $((C_L + C_R)/2)$ constant and changing the concentration difference in the 2 cells ($C = C_L - C_R$). The data given by Tiwari and Ahmad (2006) on the measured membrane potentials were redrawn with respect to C_L/C_R and are shown in Figure 3. It is observed that the increases in membrane potential were becoming less as C_L/C_R became higher than 6. A similar conclusion could be obtained from all curves presented in Figure 2. Especially for the low values of $\langle \theta \rangle$ (Figure 2(a) and (b)), the curves were much steeper until C_L/C_R was equal to 6. Then the increase in the magnitude of membrane potential with C_L/C_R continued but the change in the increases became smaller. Therefore, it could

be suggested to perform membrane potential measurements at higher bulk concentration ratios in order to have consistent results from the experiments.

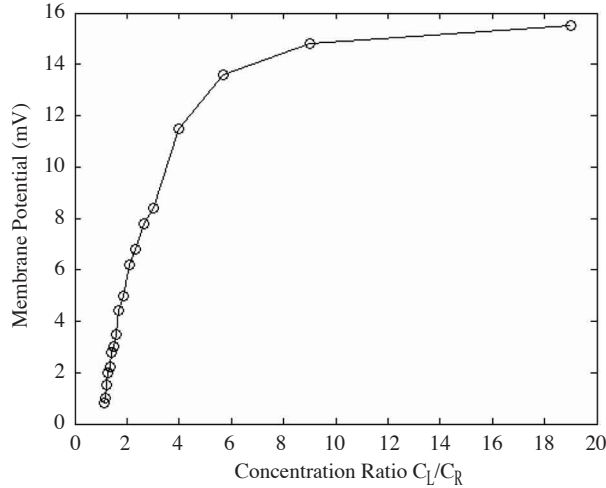


Figure 3. Variation in membrane potential as a function of concentration ratio (data taken from Tiwari and Ahmad (2006)).

Effects of diffusion coefficient ratios of ions on membrane potential

For different values of ionic diffusion coefficient ratio (D_1/D_2), the evaluated membrane potentials are presented in Figure 4. The results obtained from TMS (Eq. (20)) and numerical solutions of Nernst Planck flux (Eq. (8)) and Donnan equilibrium equations (Eq. (6)) for different values of D_1/D_2 are presented as solid and dash lines and named TMS and LINEAR, respectively.

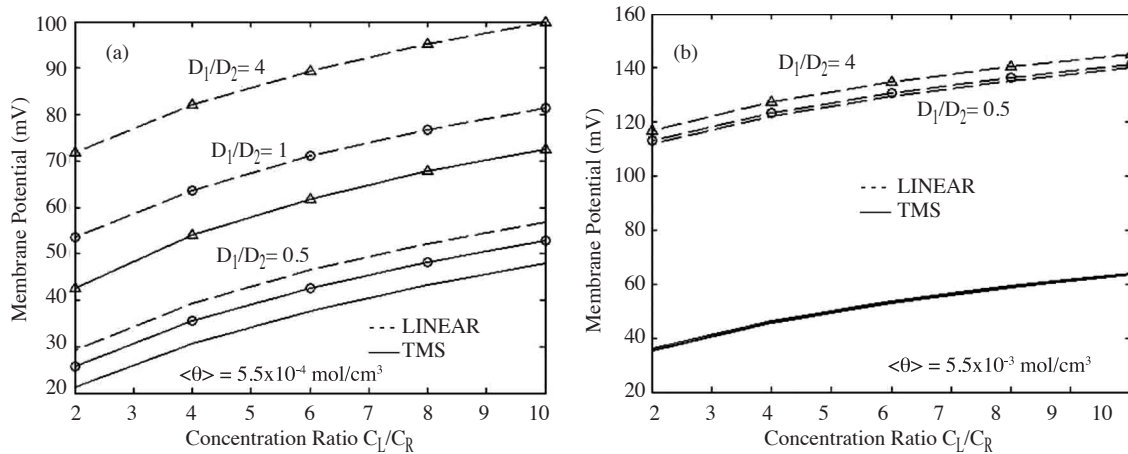


Figure 4. Effects of ionic diffusion coefficients ratio on membrane potential.

The membrane potential showed increases with D_1/D_2 for the uniform and linear variations of fixed charge concentrations since both TMS and LINEAR curves increase with D_1/D_2 . The increases in the membrane potentials could be explained by analyzing the transport of cation through the membrane by diffusion (Shang

et al., 2006). As the D_1/D_2 ratio increases, the diffusivity coefficient of cations increases. As a result, the diffusional force to drive the cations through the membrane towards the lower concentration side increases. On the other hand, cations will also be opposed because of the electroneutrality condition and, therefore, this force needs to be a higher force as the diffusional force increases. In the case of high $\langle \theta \rangle$ values, the effect of diffusion potential is lower than the Donnan potential and, therefore, the increases in membrane potential with D_1/D_2 were low in Figure 4(b).

Conclusions

Based on the numerical solutions of Nernst-Planck flux and Donnan equilibrium equations, the following conclusions are drawn:

- Non-uniform distribution of fixed charges through the membrane causes predictions of lower potentials in magnitude than the ones evaluated from TMS theory.
- As the difference between the fixed charges at the interfaces (i.e. the degree of non-uniformity) increases, much higher potentials than TMS theory are predicted.
- Membrane potential increases with the external bulk concentration ratio and its increase slows down after the external bulk concentration ratio reaches 6.
- For the low fixed charge concentrations, the membrane potential increases with the ionic diffusion coefficient ratio.

Nomenclature

A	cross-sectional area of the membrane (m^2)
C	concentration (mol/m^3)
$C_1(0)$	cation concentration at the left interface (mol/m^3)
$C_1(d)$	cation concentration at the right interface (mol/m^3)
C_L	bulk electrolyte concentration in the left-side cell (mol/m^3)
C_R	bulk electrolyte concentration in the right-side cell (mol/m^3)
d	membrane thickness (m)
D	diffusion coefficient (m^2/s)
F	Faraday constant (C/mol)
J	ion flux ($\text{mol}/(\text{m}^2\text{-s})$)
R	gas constant ($\text{J}/(\text{K}\text{-mol})$)
T	temperature (K)
x	axial coordinate (m)

Greek letters

ψ	electrical potential (V)
$\psi(0)$	electrical potential at the left interface (V)
$\psi(d)$	electrical potential at the right interface (V)
$\theta(0)$	fixed charge concentration at the left interface (mol/m^3)
$\theta(d)$	fixed charge concentration at the right interface (mol/m^3)
$\langle \theta \rangle$	average of fixed charge concentration (mol/m^3)

Subscripts

1	cations	L	left
2	anions	R	right

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