Theoretical calculation on the membrane potential of charged porous membranes in 1-1, 1-2, 2-1 and 2-2 electrolyte solutions

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Abstract

The space-charge (SC) model and the Teorell–Meyer–Sievers (TMS) model are widely employed to calculate the membrane potential of charged porous membranes in 1-1 electrolyte solutions, but few works with the other kinds of electrolyte solutions have been reported. In this article, membrane potentials for 1-1, 1-2, 2-1 and 2-2 electrolyte solutions have been calculated numerically based on the two models using parameters of concentration, pore radius and surface charge density. The results suggest that equivalent electrolyte concentration is more suitable to characterize the membrane potential in different kinds of electrolyte solutions than electrolyte concentration. Membrane potential approaches to the Nernst potential in the low concentration region, which indicates membrane potential in monovalent cation electrolyte solution is twice as large as that in divalent cation electrolyte solution. In the high concentration region, membrane potential as a function of electrolyte concentration is almost linear. In the comparison of the SC and TMS models, theoretical predictions by the two models for 1-2, 2-1 and 2-2 electrolyte solutions appear to be similar to those for 1-1 electrolyte solutions reported earlier by Westermann-Clark and Christoforou [3]. The two models coincide with each other when the radius, \( r_p \), is less than 5.0 nm and the dimensionless charge density in the pore wall, \( q_0 \), is less than 1.0. Otherwise, the TMS model would overestimate the membrane potential. Furthermore, the membrane potential shows dependence on the ratio of the volume charge density to equivalent electrolyte concentration, \( \xi_f \), \( q_0 \) and \( r_p \) by the SC model, but only varies with \( \xi_f \) irrespective of \( q_0 \) and \( r_p \) by the TMS model. These findings have a significant influence on the establishment of an appropriate theory to evaluate membrane potentials in different electrolyte solutions.

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1. Introduction

In our previous paper [1], the nanofiltration membrane was selected as a representative charged porous membrane, which may consist of a bundle of cylindrical charged capillaries with the structural parameters (pore radius, \( r_p \), and the ratio of membrane porosity to membrane thickness, \( A_l/\Delta l \)) and the electrical properties such as the surface charge density, \( q_w \). Salt rejection and membrane parameters (the reflection coefficient, \( \sigma \), and the solute permeability coefficient, \( \omega \)) for 1-1 electrolyte solutions were numerically calculated by the space-charge (SC) model and the Teorell–Meyer–Sievers (TMS) model as a function of two-dimensionless parameters: the electrokinetic radius, \( r_p/\lambda_D \), and the dimensionless potential gradient in the pore surfaces, \( q_0 \). The research reveals that the TMS model shows good agreement with the SC model in the calculation of salt rejection and membrane parameters if \( q_0 \) is less than 1.0 [1].

In the present study, we will focus on membrane potential that is defined as a potential difference arising between the solutions of an electrolyte with different concentrations at the constant temperature and pressure when they are separated by a uniform membrane with fixed ionizable groups [2]. At the interface between membrane and electrolyte solutions, the Donnan potential occurs due to the transfer of ions. Inside the membrane, the diffusion potential arises since ions would diffuse from the high concentration side to the low concentration side under a certain concentration gradient. Membrane potential is the summation of the Donnan potential and the diffusion potential, and it can be also named as the exclusion–diffusion potential [3]. Membrane
potential can be measured directly by determining the electrical properties of a membrane or the activities of ions inside the membrane. Also, it can be calculated by the TMS model and the SC model, respectively [2–7].

The earlier theoretical studies on membrane potential were almost based on the TMS model and developed by Kobatake and co-workers [2,4,5] and Lakshminarayanaiiah and co-workers [6,7]. Kobatake and co-workers [2,4,5] derived an equation of membrane potential for uni-univalent electrolyte solutions and first proved that the derived equation agreed well with typical corresponding experimental data. Nikonenko et al. [8] investigated the influence of the 1-1 salt concentration, and the ratio of the diffusion boundary layers length and the counter-ions diffusion coefficient on the membrane potential of an ion-exchange membrane. The research work concluded that the membrane potential carried out numerically by the TMS model were similar to those obtained experimentally by Dammak if the salt concentration is less than 100 mol m⁻³. Lefebvre et al. [9] derived the general equations of the membrane potential, and the filtration potential of a charged membrane in an arbitrary electrolyte solution using an analytical approach. The group has only limited their studies to the related aspects of the comparison of normalized filtration potential calculated numerically and analytically with no discussion on membrane potential [9]. The above analysis demonstrates that most studies of membrane potential evaluated by the TMS model have been emphasized with attention being given to the uni-univalent electrolytes. Nevertheless, there is not enough convincing theoretical investigation concerning the other kinds of electrolytes. It is worthwhile clarifying the fact whether the TMS model can be employed to evaluate membrane potential in multivalent electrolyte solutions.

The SC model, originally proposed by Osterle and co-workers [10–12], is a more realistic model to evaluate the membrane potential, since the SC model take into account the radical variation of ionic concentrations and electrical potential within cylindrical membrane capillaries. Over the past several decades, much work has been done with the algorithm and applications of the SC model in charactering membrane potential of the charged porous membrane. Osterle and co-workers [10–12] first adopted the series transformed methods to calculate the Poisson–Boltzmann equation. The membrane potential for 1-1 electrolyte solutions was studied, and the pioneer investigations revealed that the membrane potential approached to the Nernst potential when the Debye length was great enough. Ruckenstein and co-workers [13] employed a fourth-order Runge-Kutta numerical method to investigate the membrane potentials for 1-1, 1-2, 2-1, and 2-2 electrolyte solutions as a function of the salt concentration in the permeate side. The typical experiments verified the validity of the SC model were carried out by Westermann-Clark and Christoforou once compared the results obtained by the two model for 1-1 electrolytes [3]. The authors showed that the two models gave similar results for low surface charge densities of pore wall, but for large surface charge densities, the results from the TMS model differed strongly from those of the SC model. The research work has contributed to understand the sources and implications of the agreements and the discrepancies in evaluating the membrane potential by the two models. However, the effect of electrovalence of different electrolytes on the membrane potential of charged membrane must be taken into account, so that a general appropriate theory to evaluate membrane potentials in different electrolytes could be established.

The purpose of this article is to extend the application of TMS model in estimating membrane potential for 1-1 electrolyte solutions to multivalent electrolyte solutions, and establish an applicable scope of the straightforward analytical TMS model through the comparison with the complex numerical SC model. The membrane potential suitable for an arbitrary electrolyte solution by the TMS model can be obtained according to the derivation of Lefebvre et al. [9]. During the calculation, we firstly introduce the Cardano formula to compute the Donnan equation analytically, which is more convenient and precise than the deduction method reported in the literature [9]. Concerning the SC model, we adopt the Runge–Kutta–Gill method to calculate Poisson–Boltzmann equation. Membrane potentials for 1-1, 1-2, 2-1, and 2-2 electrolyte solutions have been numerically calculated by the TMS model and SC model as a function of concentration and two-dimensionless parameters: the ratio of the volume charge density to salt concentration, ξ(V), and the electrokinetic radius, r_p/λ_f. The results estimated by the two models will be compared strictly. Finally, based on the comparison, the range where the two models coincide with each other will be provided.

2. Theory and calculation

2.1. Space-charge (SC) model

The space-charge model was originally proposed by Osterle and co-workers [10–12], and has been mainly applied to describe electrokinetic phenomena and transport characteristics of charged capillaries [13–23]. The basic equations of the SC model are the Poisson–Boltzmann equation for the radial
distribution of electric potential and ion concentration, the Nernst–Planck equation for ion transport, and the Navier–Stokes equation for volumetric flow.

Wang et al. [1] followed the basic derivations used by Ruckensteın [13,24,25] and Smit [22,23], and presented the relationship of three flows and three relevant driving forces with the following phenomenological equations:

\[ J_V = \frac{r_p^2}{8\mu} \left( -\frac{dP_0}{dx} \right) + \frac{r_p^2 \nu_{1} K_{12}}{2\mu} \left( -RT \frac{d\ln c}{dx} \right) + \frac{RT \varepsilon_0 K_{13}}{z_1 F \mu} \left( -\frac{d\phi}{dx} \right) \]

\[ J_1 + J_2 = \frac{v_1 r_p^2 c K_{21}}{8\mu} \left( -\frac{dP_0}{dx} \right) + \frac{D_1 v_1 c K_{22}^*}{RT} + \frac{v_1^2 r_p^2 c^2 K_{22}''}{2\mu} \left( -RT \frac{d\ln c}{dx} \right) + \left[ \frac{z_1 v_1 D_1 F c K_{31}'}{RT} + \frac{v_1 RT \varepsilon_0 c K_{33}''}{z_1 F \mu} \right] \left( -\frac{d\phi}{dx} \right) \]

\[ I = \frac{r_p^2 z_1 v_1 F c K_{31}}{8\mu} \left( -\frac{dP_0}{dx} \right) + \frac{D_1 z_1 v_1 F c K_{32}^*}{RT} + \frac{z_1 v_1^2 r_p^2 c F K_{33}''}{2\mu} \left( -RT \frac{d\ln c}{dx} \right) + \left[ \frac{z_1^2 v_1 D_1 F c^2 K_{33}'}{RT} + \frac{v_1 RT \varepsilon_0 c K_{33}'}{z_1 F \mu} \right] \left( -\frac{d\phi}{dx} \right) \]

\[ J_V, J_1 + J_2 \text{ and } I \text{ are the total volume flux, solute flux through a capillary and electric current, respectively. } P_0 \text{ corresponds to eff}

Introducing the dimensionless form and using the no electrical current condition, we can obtain the dimensionless expressions of three driving forces as follows [1]:

\[ \frac{d\bar{P}_0}{\bar{x}} = \frac{(v_1 + v_2/v_1) J_s^* L_3 - Pe \bar{c} L_1}{(L_2 L_3 - L_1 L_4) \bar{c}} \]

\[ \frac{d\bar{c}}{\bar{x}} = \frac{(v_1 + v_2/v_1) J_s^* L_4 - Pe \bar{c} L_2}{(L_2 L_3 - L_1 L_4) \bar{c}} \]

\[ \frac{d\bar{\phi}}{\bar{x}} = \frac{(v_1 + v_2/v_1) J_s^* L_5 - Pe \bar{c} L_5}{(L_2 L_3 - L_1 L_4) \bar{c}} \]

\[ J_s^* \text{ and } Pe \text{ are the dimensionless expressions of solute flux and the total volume flux through a capillary, } \bar{c} \text{ is the dimensionless concentration, } v_i \text{ are the stoichiometric coefficients of electrolyte, } 1 \text{ represents counterion and } 2 \text{ denotes co-ion. } L_i \text{ are the coefficients listed in Appendix B of our previous paper [1].} \]

Integrating the Eqs. of (4)–(6) from the high concentration side (c_i) to the low concentration side (c_f) through the membrane, one can obtain the following equations:

\[ \Delta \bar{\phi}|_{SC} = \int_{0}^{c_f/c_i} \frac{(v_1 + v_2/v_1) (J_s^* / Pe) L_5 - \bar{c} L_5 \Delta \bar{c}}{(v_1 + v_2/v_1) (J_s^* / Pe) L_4 - \bar{c} L_2 \Delta \bar{c}} \]

\[ \Delta \bar{P}_0 = Pe_p - Pe_\pi = \int_{0}^{c_f/c_i} \frac{(v_1 + v_2/v_1) (J_s^* / Pe) L_3 - \bar{c} L_1 \Delta \bar{c}}{(v_1 + v_2/v_1) (J_s^* / Pe) L_4 - \bar{c} L_2 \Delta \bar{c}} \]

2.2. Teorell–Meyer–Sievers (TMS) model

The Teorell–Meyer–Sievers model was originally proposed by Teorell, Meyer and Sievers [26,27], and has been applied to describe transport characteristics and electrokinetic phenomena of charged capillaries [2–9,28–33]. The basic equations of the TMS model are the Donnan equation for the partition coefficients of ion concentrations at the surface between the membrane and the external solution, the Nernst–Planck equation, and the different electroneutrality conditions for the inside membrane and the external solutions.

According to the derivation of Lefevbre and co-workers [9,33], the dimensionless membrane potential can be expressed

\[ \Delta \bar{\phi}|_{TMS} = \frac{1}{z_2} \ln \frac{k_2^p}{k_1^p} + \frac{D_1 - D_2}{z_2 D_2 - z_1 D_1} \ln \left( \frac{T_0 k_2^p + t_1 \xi_1}{k_1^p + t_1 \xi_1} \right) \]
where

\[ \Delta \phi = \frac{F \Delta \phi}{R_g T}, \quad \xi_i = \frac{|X_m|}{\vert z_i \vert v_i c_i}, \quad T_r = \frac{c_p}{c_i}, \]

\[ z_i, D_i \text{ and } k_i \] are the electrochemical valence, diffusion coefficient and partition coefficient of ion \( i \). \( T_r \) is the transmission, which denotes the ability of solute to pass through the membrane. \( \xi_{i(p)} \) is the ratio of the volume charge density to equivalent salt concentration in the feed side or in the permeate side of membrane. \( F \) is the Faraday constant, \( R_g \) is the gas constant and \( T \) is the temperature. \( \Delta \phi \) represents the dimensionless form of the membrane potential, \( \Delta \phi \). \( X_m \) is the constant volume charge density of charged membrane (mole/l of pore volume).

The membrane is assumed to be a positively charged membrane. Concerning the 1-1 electrolyte, the partition coefficient of co-ion is expressed as follows:

\[ k_2^{p(f)} = -\xi_{p(f)} + \frac{\xi_{p(f)}^2 + 4}{2}, \quad \xi_{p(f)} = \frac{-X_m}{z_1 v_1 c_{p(f)}} \quad (12) \]

By combining the Eqs. of (11) and (12), membrane potential can be obtained in another version

\[ \Delta \phi_{\text{TMS,1:1}} = -\ln \frac{1 + \sqrt{1 + 4/\xi_{p(f)}^2}}{\xi_{p(f)} + 1 + \sqrt{1 + 4/\xi_{p(f)}^2}} - W \ln \left( \frac{\sqrt{1 + 4/\xi_{p(f)}^2 + W}}{\sqrt{1 + 4/\xi_{p(f)}^2 + W}} \right), \quad W = \frac{D_1 - D_2}{D_1 + D_2} \quad (13) \]

The Eq. of (13) is a well-known expression predicting the dimensionless membrane potential for 1-1 electrolyte by the TMS model [2–5,34–36]. It is noted that the dimensionless membrane potential is caused only by the concentration differences with no volumetric flux condition. That is, the contribution of the osmotic pressure to the volumetric flux is negligible. Therefore, it may be applicable for very narrow pore or very low concentrations.

Regarding other symmetric electrolytes (\([z:z]\)), the expressions of the ionic partition coefficient and dimensionless membrane potentials are the same as 1-1 electrolyte [9,33].

As to 1-2 asymmetric salt, the partition coefficient of co-ion can be expressed as follows [9,33]

\[ k_2^{p(f)} = \left[ \Gamma_{1:2,p(f)}^{-1} \right]^{-1}, \quad k_2^{p(f)} = \left[ \frac{\Lambda(1,1,-\xi_{p(f)})^{1/3}}{6} - \frac{2\xi_{p(f)}}{\Lambda(1,1,-\xi_{p(f)})^{1/3}} \right]^{-1} \quad (14) \]

where

\[ \Lambda(1,1,-\xi_{p(f)}) = 108 + 12\sqrt{3}(27 + 4\xi_{p(f)}^3) \]

As far as a 2-1 asymmetric salt is concerned, the expression of the partition coefficient of co-ion is more complicated. When \( 27 - 4\xi_{p(f)}^3 \) is larger than zero, the expression of the ionic partition coefficient of a 2-1 asymmetric salt is similar to that of a 1-2 asymmetric salt [9,33]

\[ k_2^{p(0)} = \left[ \Gamma_{1:1,p(f)}^{-1} \right]^{-1}, \quad \Gamma_{1:1,p(f)}^{-1} = \frac{\Lambda(1,1,-\xi_{p(f)})^{1/3}}{6} + \frac{2\xi_{p(f)}}{\Lambda(1,1,-\xi_{p(f)})^{1/3}} \quad (15) \]

where

\[ \xi_{p(f)} = \frac{-X_m}{z_1 v_1 c_{p(f)}} \]

When \( 27 - 4\xi_{p(f)}^3 \) is less than zero, the Eq. of (15) is inapplicable. Fortunately, Cardano formula is powerful enough to deal with the situation. According to the Cardano formula, there are three roots for normal cubic equation with one argument unknown as \( x^3 + px + q = 0 \) [37]

\[ x_1 = \sqrt[3]{-\frac{q}{2} + \sqrt{\Delta}} + \sqrt[3]{\frac{-q}{2} - \sqrt{\Delta}}; \quad x_2 = \omega \sqrt[3]{-\frac{q}{2} + \sqrt{\Delta}} + \omega^2 \sqrt[3]{\frac{-q}{2} - \sqrt{\Delta}}; \quad x_3 = \omega^2 \sqrt[3]{-\frac{q}{2} + \sqrt{\Delta}} + \omega \sqrt[3]{\frac{-q}{2} - \sqrt{\Delta}} \quad (16) \]

where

\[ \Delta = \left( \frac{q}{2} \right)^3 + \left( \frac{p}{3} \right)^3, \quad \omega = \frac{-1 + \sqrt{3}i}{2} = \cos \frac{2\pi}{3} + i \sin \frac{2\pi}{3}, \quad \omega^2 = \frac{-1 - \sqrt{3}i}{2} = \cos \frac{4\pi}{3} + i \sin \frac{4\pi}{3} \]

If \( \Delta > 0 \), the normal cubic equation has only one real root, \( x_1 \), and two imaginary roots, \( x_2, x_3 \). If \( \Delta > 0 \), the normal cubic equation have three real roots, \( x_1, x_2, x_3 \), represented as follows:

\[ x_1 = 2 \sqrt[3]{\frac{-q}{2}}; \quad x_2 = x_3 = -\sqrt[3]{\frac{-q}{2}} \quad (17) \]

If \( \Delta < 0 \), \( x_1, x_2, x_3 \) are all real roots to normal cubic equation

\[ x_1 = \sqrt[3]{\rho e^{\theta/3}} + \sqrt[3]{\rho e^{-\theta/3}} = 2\sqrt[3]{\rho} \cos \frac{\theta}{3} = 2\sqrt[3]{\rho} \cos \frac{\theta}{3}; \quad x_2 = 2\sqrt[3]{\rho} \cos \frac{\theta + 2\pi}{3} = 2\sqrt[3]{\rho} \cos \frac{\theta + 2\pi}{3}; \quad x_3 = 2\sqrt[3]{\rho} \cos \frac{\theta + 4\pi}{3} = 2\sqrt[3]{\rho} \cos \frac{\theta + 4\pi}{3} \quad (18) \]

where

\[ \rho = \sqrt{\left( \frac{-q}{2} \right)^2 + \left( \sqrt{-\Delta} \right)^2} = \sqrt{\left( \frac{p}{3} \right)^2}, \quad \cos \theta = -\frac{q/2}{\rho} , \quad \left( 0 < \theta < \frac{\pi}{2} \right) \quad (19) \]

From the Eqs. of (17) and (19), it is easy to verify \( x_1 > 0, x_2 < 0, x_3 < 0 \). In practice, \( x_1 \) is the right root.
Utilizing the above-mentioned Cardano formula, one can easily obtain the ion partition coefficients of 1-2 and 2-1 asymmetric electrolyte solutions and solve the problem existed in the Eq. of (15). When \( 27 - 4e_3^3p_0(\ell) \) is less than zero, the partition coefficient of co-ion in a 2-1 asymmetric salt is expressed as follows:

\[
k_2^p = \left[ \Gamma_{\pm 1,p}(\ell) \right]^{-1}, \quad \Gamma_{\pm 1,p}(\ell) = 2 \sqrt{\frac{e_3 p_0(\ell)}{3}} \cos \frac{\theta}{3},
\]

\[
\theta = \arccos \left( \frac{1}{2} \left( \frac{e_3 p_0(\ell)}{3} \right)^{-1.5} \right)
\]

The scheme is as follows. The partition coefficient of co-ion is first solved for different values of \( c_I \) and with the concentration ratio \( c_I/c_p \) constant through the Cardano formula introduced in this article. Then, \( \Delta \phi_{TMS} \) can be obtained according to the Eq. of (11) for various values of \( c_I \).

### 3. Results and discussion

#### 3.1. The effect of the electrovalence, concentration ratio, \( c_I/c_p \), and diffusion coefficients ratio, \( D_2/D_1 \), of an electrolyte solution on the membrane potential

**3.1.1. The influence of the ion valence on the membrane potential**

The dimensionless membrane potential, \( \Delta \phi \), of the eight salt solutions was obtained by the SC model and TMS model under the conditions that negatively charged porous membranes with the pore radius \( r_p \) of 5.0 nm and the surface charge density \( q_w \) of \(-6.672 \times 10^{-3}\) C m\(^{-2}\). The pore radius employed here is according to the interesting features on molecular weight cut-off (MWCO) of charged porous membrane [1]. In accordance with the Stokes–Einstein relationship, the pore diameters suitable for electrolyte solutions range from 1 to several nm. In our study, we choose 5.0 nm as a representative pore radius to study the influence of different electrolyte solutions since the impact of pore radius on membrane potential are discussed in the following aspect. In terms of the surface charge density, many studies suggest that the magnitude is about \( 10^1 \) esu cm\(^{-2}\) [13,14]. Moreover, the value of \( 10^3 \) esu cm\(^{-2}\) is equal to \( 3.336 \times 10^{-3}\) C m\(^{-2}\) in the standard unit. To survey the effect of different electrolyte solutions, we choose 2.0 times of the magnitude of \( 10^3 \) esu cm\(^{-2}\) as a typical surface charge density since the impact of surface charge density on membrane potential are discussed as another separate aspect. The eight salts are KCl, NaCl, K\(_2\)SO\(_4\), Na\(_2\)SO\(_4\), MgCl\(_2\), CaCl\(_2\), MgSO\(_4\), and CaSO\(_4\) with the concentration from 1.0 to 1000.0 mol m\(^{-3}\). The relationship of the surface charge density, \( q_w \) and the volume charge density, \( X_m \) is \( X_m = 2q_w/\zeta r_p \), where \( F \) is the Faraday constant.

As shown in Fig. 1, \( \Delta \phi \) calculated by the two models tend to coincide with each other. It is indicated that \( \Delta \phi \) approaches to some certain values in the low- and high-concentration regime. In the low-concentration range, the co-ions are almost completely excluded from the pores due to the high double-layer repulsion, and the distribution of ions arising by the diffusion of counterion is the main reason to the membrane potential [13].

Under such circumstances, the diffusion effect can be ignored, and the membrane potential is mainly dominated by the Donnan effect. Assuming the ideal circumstances, \( \mu_1^L = \mu_1(0^+) \), and \( \mu_1^L = \mu_1(l^m_m) \). According to the expressions of \( \mu_1^{L(p)} \) [9], one can get

\[
RT \ln c_I^L - z_1 F \Delta \phi_i = RT \ln c_I^{\Delta p} - z_1 F \phi_i
\]

\[
\Delta \phi_i \approx -\Delta \phi_i^{\Delta p} + \Delta \phi_i^p = \frac{1}{z_1} \ln \left( \frac{c_I^{\Delta p}}{c_I^p} \right)
\]

\( c_I^{\Delta p} \) represent the counter-ion concentrations in the feed side and the permeate side. The Eq. of (21) states that membrane potentials approaches to the Nernst potential at very low concentrations. That is, the membrane potential corresponds to the diffusion potential at high concentrations. That is, the membrane potential closes to the Nernst potential at very low concentrations. The Eq. of (22) implies that the membrane potential is nothing but the free diffusion potential given by [9]

\[
\Delta \phi_i \approx \Delta \phi_i^{d} = \frac{D_2 - D_1}{z_2 D_2 - z_1 D_1} \ln \left( \frac{c_I}{c_p} \right)
\]

The Eq. of (22) implies that the membrane potential closes to the diffusion potential at high concentrations. That is, the membrane potential is a function of ionic diffusion coefficients, ionic electrovalences and the ratio of solute concentrations in both sides of charged porous membranes.

In the intermediate-concentration regime, neither the Donnan effect nor the diffusion effect can be negligible. As a result, the
values of membrane potentials, between the above two limits, increase as the concentrations of the electrolytes becomes lower. As to two different kinds of electrolytes with the membrane potentials between the same Donnan potential and different diffusion potentials, such as KCl and K₂SO₄, NaCl and Na₂SO₄, their dimensionless membrane potentials have a crossover in intermediate-concentration regime. The crossover phenomena can be explained by the electrovalence of ions.

As shown in Fig. 2, the crossover phenomena disappears when the argument of the salt concentration is multiplied with \( z_i \nu_i \). That is, the membrane potential as a function of electrolyte concentration is redesigned by the membrane potential as a function of equivalent electrolyte concentration. The crossover phenomenon may be also disappears when the other parameters (ion rejection rate, the partition coefficient of ions and so on) calculated by the two models is represented as a function of equivalent electrolyte concentration. Concerning the other two different kinds of electrolytes, MgCl₂ and MgSO₄, CaCl₂ and CaSO₄, there are no crossover phenomena whether the variable is the concentration or the equivalent concentration. The reason is that the products of \( z_i \nu_i \) for 2-1 and 2-2 electrolyte are equal. The relationship between the membrane potential and the concentration is only a valid compressed

![Fig. 2](image)

\[ \Delta \phi \] as a function of \( z_i \nu_i c_i \) for eight electrolyte solutions (NaCl; KCl; Na₂SO₄; K₂SO₄; MgCl₂; CaCl₂; MgSO₄; CaSO₄) under the condition that \( c_i/c_p \) is 2.0, \( r_p \) is 5.0 nm, and \( q_w \) is \(-6.672 \times 10^{-3} \text{ C m}^{-2}\).

![Fig. 3](image)

\[ \Delta \phi \] as a function of \( c_i \) for four electrolyte (NaCl (1); Na₂SO₄ (2); MgCl₂ (3); MgSO₄ (4)) solutions under the condition that \( r_p \) is 5.0 nm, and \( q_w \) is \(-6.672 \times 10^{-3} \text{ C m}^{-2}\), and \( c_i/c_p \) is from 1.25 to 5.0.

![Fig. 1](image)

\[ \Delta \phi \] as a function of \( c_f \) for eight electrolyte solutions (NaCl; KCl; Na₂SO₄; K₂SO₄; MgCl₂; CaCl₂; MgSO₄; CaSO₄) under the condition that \( c_i/c_p \) is 2.0, \( r_p \) is 5.0 nm, and \( q_w \) is \(-6.672 \times 10^{-3} \text{ C m}^{-2}\).
approximation to the exact connection between the membrane potential and the equivalent concentration. Therefore, the employment of equivalent electrolyte concentration is favorable to investigate the membrane potential of different kinds of electrolytes.

Besides, the correlative interesting thing indicated by Fig. 2 is that ionic strength is also beneficial to study membrane potential. Ionic strength is a common quantity as half of the summary of ionic concentration multiplied by ionic electrovalence squared. If $I$ is employed to describe ionic strength, it can be expressed, $I = \frac{1}{2} \sum_i z_i^2 c_i$. $c_i$ here is the concentration of ion $i$ in mole/kg, which is approximate to the concentration of ion $i$ in mole/l. According to the electroneutrality condition, $z_1 c_1 + z_2 c_2 = 0$, one can get another version of ionic strength, $I = \frac{1}{2}(z_1 - z_2)c_1 = \frac{1}{2}(z_1 - z_2)c_1 c_s$. Where $c_s$ is the concentration of salt solution. The difference between ionic strength, $I$, and equivalent electrolyte concentration, $z_1 c_1 c_s$, is the expression of $\frac{1}{2}(z_1 - z_2)$. When the argument of equivalent electrolyte concentration is multiplied by $\frac{1}{2}(z_1 - z_2)$, the horizontal axis will reduce to 1.0, 1.5, 1.5, and 2.0 times for 1-1, 1-2, 2-1 and 2-2 electrolyte solutions, respectively. Moreover, the variation is beneficial to eliminate the crossover phenomena. In other words, ionic strength is favorable for membrane potential as well as equivalent electrolyte concentration.

3.1.2. The influence of the concentration ratio ($c_f/c_p$) on the membrane potential

Fig. 3 presents $\Delta \phi$ as a function of $c_f$ for four electrolyte (NaCl(1); Na$_2$SO$_4$(2); MgCl$_2$(3); MgSO$_4$(4)) solutions at the radius $r_p$ of 5.0 nm, the surface charge density $q_w$ of $-6.672 \times 10^{-3}$ C m$^{-2}$ and the concentration ratio $c_f/c_p$ from 1.25 to 5.0. It should be noted that the selection of $c_f/c_p$ as 5:1, 5:2, 2:1 and 5:4 is due to the widely application of binary logarithm and decimal logarithm.

As shown in the figure, $\Delta \phi$ for different electrolyte systems vary differently with the concentration ratio. As far as Na$_2$SO$_4$ is concerned, $\Delta \phi$ decreases with the decrease of the concentration ratio monotonely. While for the other three electrolyte, $\Delta \phi$ firstly decreases as the concentration ratio decreases in the low-concentration region, but then increases as the concentration ratio decreases in the high-concentration region. The differences can be explained from Eq. of (21), valid at low feed concentration, and (22), valid at high feed concentration. The Eq. of (21) can predict the same order of $\Delta \phi$
as a function of the concentration ratio as the figure provided. The Eq. of (22) can be written as

\[ \Delta \bar{\phi} \approx \Delta \bar{\phi}^d = \frac{D_2}{D_1} - 1.0 = \frac{\ln \left( \frac{c_f}{c_p} \right)}{z_2 D_2 / D_1 - z_1} \]  

(23)

The relation reflected by the Eq. of (23) clearly shows that the order of membrane potentials as a function of the concentration ratio is inverted depending on whether the diffusion coefficients ratio, \( D_2/D_1 \) is less or more than 1.0. Consequently, the diffusion coefficients ratio is only source of the differences.

In the intermediate-concentration regime, Figs. 3 and 4 indicate that the membrane potential as a function of electrolyte concentration is almost linearity. This relationship can also be found in some experiment work [2–5,38,39].

3.1.3. The influence of the diffusion coefficients ratio (\( D_2/D_1 \)) on the membrane potential

To clarify the effect of the diffusion behaviors to the membrane potential farther, fictitious electrolytes are introduced, which are composed of suppositional ions with different valence and diffusion coefficient. Fig. 4 describe \( \Delta \bar{\phi} \) as a function of \( c_f \) for four fictitious electrolyte (1-1(1); 1-2(2); 2-1(3); 2-2(4)) solutions at the radius \( r_p \) of 5.0 nm, the surface charge density \( q_0 \) of \(-6.672 \times 10^{-3} \text{ C m}^{-2}\) and the concentration ratio \( c_f/c_p \) of 2.0. The diffusion coefficients ratio, \( D_2/D_1 \), is chose in the range of 0.5–5.0. The selection is based on the commonly known ionic diffusion coefficients. Generally, counter-ionic diffusion coefficient varies between 0.5 and 2.0 except H\(^+\), while co-ionic diffusion coefficients change from 1.0 to 2.5 except OH\(^-\). Thus, membrane potential is calculated under the condition that the values of \( D_2/D_1 \) vary between 0.5 and 5.0.

From the figure, \( \Delta \bar{\phi} \) decreases with the increase of \( D_2/D_1 \) for the same electrolyte. When \( D_2/D_1 \) more than 1.0, the membrane potential would be reversed, in the high concentration region compared with those in the low concentration region without reference to the electrovalence of an electrolyte. Furthermore, the concentration resulted in the reversed membrane potential decrease with the increase of \( D_2/D_1 \). Take the ratios of diffusion coefficients up to 5.0 for an instance, the concentration is less than 25.0 mol m\(^{-3}\) for four fictitious electrolyte (1-1(1); 1-2(2); 2-1(3); 2-2(4)) solutions. The reversed behaviors can be interpreted form the Eq. of (23) effortlessly. However, the more interesting thing implied by the figure is that ionic mobilities or even the rejection change greatly. Since the diffusion coefficients

Fig. 5. \( \Delta \bar{\phi} \) as a function of \( r_p/\lambda_f \) and \( q_0 \) for four electrolyte (NaCl (1); Na\(_2\)SO\(_4\) (2); MgCl\(_2\) (3); MgSO\(_4\) (4)) solutions under the condition that \( c_f/c_p \) is 2.0, \( r_p \) is 5.0 nm, and \( q_0 \) is from 0.047 to 2.34.
are independent of the Donnan potential, the reversed membrane potential is determined by the diffusion potential. According to the dimensionless diffusion potential in the membrane reported earlier [7], it can be expressed

\[ \Delta \bar{\phi} = \left( \frac{t_{S1}}{z_1} - \frac{t_{S2}}{z_2} \right) \ln \left( \frac{c_f}{c_p} \right) \]

(24)

\( t_s \) represents ionic transport rate. The Eq. (24) reveals that the mobilities of counter-ion and co-ion will intersect before the membrane potential is equal to zero if \( D_2/D_1 \) is greater than 1.0. That is, when compared a positive membrane potential with a negative membrane potential at the same concentration of different electrolytes, such as curve a and curve f for 1-1 fictitious electrolyte, the mobilities of counter-ion and co-ion have a crossover for the electrolyte with the negative membrane potential, but have no crossover for the electrolyte with the positive membrane potential. The transformation of ionic mobilities may again influence electrolyte transport properties, and the rejection of membrane to ions may also changed from great to small, or even become minus at certain concentration region. Thus, the diffusion coefficients ratio is an important parameter on the prediction and interpretation of electrolyte electrical and transport properties.

Besides, when the counter-ion and the ratio of the diffusion coefficients ratio, \( D_2/D_1 \), is the same, the membrane potential decreases with the increasing of co-ion valence. It can also be interpreted form the Eq. of (23) without needing much effort.

From the above study of the impact of the electrovalence, concentration ratio, \( c_f/c_p \), and diffusion coefficients ratio, \( D_2/D_1 \), of an electrolyte solution on the membrane potential, one can reach another conclusion that simple analytical TMS model can predict membrane potential for 1-1, 1-2, 2-1, and 2-2 electrolyte solutions perfectly as well as the complex numerical SC model. Moreover, various anomalous phenomena can be explained expediently by the TMS model when compared with the SC model. The possible reason is that the linearized transport equations (Eqs. of (1)–(3)) are difficult to analyze due to the concentration gradient and the concentration dependence of the coupling coefficients \( K_{ij} \) [3].

3.2. Membrane potential as a function of two-dimensionless parameters: \( \xi_f, \lambda_r/\lambda_f \) under various \( r_p \) and \( q_0 \) of charged porous membranes

In this part, the dimensionless membrane potential, \( \Delta \bar{\phi} \), was calculated by the SC model and TMS model as a function of

![Fig. 6. \( \Delta \bar{\phi} \) as a function of \( \xi_f \) and \( q_0 \) for four electrolyte (NaCl (1); Na₂SO₄ (2); MgCl₂ (3); MgSO₄ (4)) solutions under the condition that \( c_f/c_p \) is 2.0, \( r_p \) is 5.0 nm, and \( q_0 \) is from 0.468 to 4.68.](image-url)
three-dimensionless parameters: the ratio of the volume charge density to the salt concentration on the feed side, \( \xi_f \), the electrophoretic radius, \( r_p/\lambda_D \), and the dimensionless charge density in the pore wall, \( q_0 \). As mentioned in our previous paper [1], the effect of equivalent concentration at the feed side can be expressed by the Debye length, \( \lambda_D = \left[ 2y_1 |z_1| F^2 c_f / R_g T \varepsilon_0 \right]^{-0.5} \). Since \( 1/\lambda_D \) is proportional to \( [y_1 |z_1| c_f]^{0.5} \), \( F \) is the Faraday constant, \( R_g \) is the ideal gas constant, and \( T \) is the temperature (K). The dimensionless parameter \( q_0 \) is comprised of the surface charge density, \( q_w \), and the pore radius, \( r_p \), in the form of their products, \( q_0 = Fr_p q_w / (4 \varepsilon_r \varepsilon_0 RT) \). While the dimensionless parameter \( \xi_f \) is the ratio of the constant membrane charge density (mole/l of pore volume) and ion concentration, \( \xi_f = |X_m| / |z_1| y_1 \varepsilon_1 = 16q_0 / (r_p/\lambda_D)^2 \). The calculation was carried out under the conditions that negatively charged porous membranes for four salt solutions (NaCl, Na$_2$SO$_4$, MgCl$_2$ and MgSO$_4$) with the concentration from 1.0 to 1000.0 mol m$^{-3}$. As shown before, the pore diameters suitable for electrolyte solutions range from 1 to several nm and the magnitude is about $10^3$ esu cm$^{-2}$, that is, $3.336 \times 10^{-3}$ Cm$^{-2}$ in the international unit. In this section, we choose \( r_p \) in the range of 1.0–20.0 nm and \( q_w \) from $-6.672 \times 10^{-4}$ to $-6.672 \times 10^{-2}$ Cm$^{-2}$ to investigate membrane potential.

3.2.1. Membrane potential as a function of \( r_p/\lambda_D \), and \( \xi_f \) under different \( q_0 \)

As indicated in Fig. 5, the SC model and the TMS model coincide with each other when \( q_0 \) is lower enough irrespective of the ionic valance and the value of \( r_p/\lambda_D \). If \( q_0 \) is less than 1.0, the membrane potential can be obtained by the TMS model with simple analytical calculation instead of the SC model with cumbersome numerical calculation of the PB equation. The result can also be understood in our previous paper [1] for the explanation of the coincidence of the salt rejection and the membrane parameters by the SC model and TMS model. Moreover, Fig. 5 indicates that TMS model agrees better with SC model in the calculation of membrane potential for univalent counter-ionic salt solution than those for bivalent counter-ionic salt solution. The possible reason is that the electrostatic force between bivalent ion and membrane surface is more remarkable than that between

![Fig. 7. \( \Delta \phi \) as a function of \( r_p/\lambda_D \), and \( r_p \) for four electrolyte (NaCl (1); Na$_2$SO$_4$ (2); MgCl$_2$ (3); MgSO$_4$ (4)) solutions under the condition that \( c_f c_p \) is 2.0, \( q_w \) of \( -6.672 \times 10^{-3} \) Cm$^{-2}$, and \( r_p \) is from 1.0 to 20.0 nm.](image-url)
univalent ion and membrane surface. Another possible reason may due to the dispersal difference between bivalent ions and equivalent monovalent ions.

Basing on the relationship among $\xi_t$, $r_p/\lambda_D$ and $q_0$, the membrane potential as a function of $r_p/\lambda_D$ with different $q_0$ can be also represented as a function of $\xi_t$ with different $q_0$. As illustrated in Fig. 6, $\Delta \phi$ by the SC model shows dependence on both $\xi_t$ and $q_0$. With $\xi_t$ increasing, $\Delta \phi$ grows monotonously and approaches In 2.0 (the dimensionless value of Nernst potential for the concentration ratio of 2.0), while for the constant value of $\xi_t$, the larger $q_0$ is, the smaller $\Delta \phi$ is. However, $\Delta \phi$ by the TMS model only varies with $\xi_t$ irrespective of $q_0$. The TMS model overestimates $\Delta \phi$ as compared with the SC model. It can be explained that the partition coefficients obtain from the TMS is only related to $\xi_t$ [9]. Basing on the expression of membrane potential (Eq. of (11)) by the TMS, one can find that $\Delta \phi_{TMS}$ is connected with $\xi_t$ uniquely, which is the result of neglecting the effects of the radial non-uniform ionic distribution inside pores [3]. Regarding the SC model, it assumes that the radial electrical potential and radial ion concentration obeys the Poission–Boltzmann distribution. When $q_0$ changes, the electrical potential, ion concentration and the coupling coefficients all change accordingly. For the case of low $q_0$ ($q_0$ less than about 1.0), $\Delta \phi$ by the two models tend to coincide and show almost the same values irrespective of $\xi_t$. That is to say, if $q_0$ is less than 1.0, one can predict $\Delta \phi$ by the TMS model with analytical expression instead of the SC model with cumbersome calculation of the Poission–Boltzmann equation. The same conclusion was obtained for the calculation of the salt rejection and the membrane parameters by the SC model and the TMS models [1,3].

3.2.2. Membrane potential as a function of $\xi_t$ and $r_p/\lambda_D$ under different membrane radius

Fig. 7 delineate $\Delta \phi$ as a function of $r_p/\lambda_D$ under different $r_p$ for four electrolyte (NaCl(1); Na$_2$SO$_4$(2); MgCl$_2$(3); MgSO$_4$(4)) solutions at the concentration ratio $c_f/c_p$ of 2.0, and the surface charge density $q_w$ of $-6.672 \times 10^{-3}$ C m$^{-2}$. From the figure, the membrane potential predicted by the TMS model show good agreement with those estimated by the SC model in a low radius range irrespective of the value of $r_p/\lambda_D$. When $r_p$ is less than 5.0 nm, the TMS model can completely replace the SC model in evaluating the membrane potential. The causes may be that the TMS model does not depend on the geometry [3]. The TMS model disagrees with the SC model whether the pore radius become larger.

Fig. 8. $\Delta \phi$ as a function of $\xi_t$ and $r_p$ for four electrolyte (NaCl (1); Na$_2$SO$_4$ (2); MgCl$_2$ (3); MgSO$_4$ (4)) solutions under the condition that $c_f/c_p$ is 2.0, $q_w$ of $-6.672 \times 10^{-3}$ C m$^{-2}$, and $r_p$ is from 1.0 to 40.0 nm.
Fig. 8 shows similar to the membrane potential as a function of two-dimensionless parameters, $r_p/\xi_0^p$ and $q_0$. That is, the membrane potential shows dependence on $\xi_0$ and $r_p$ by the SC model, but only varies with $\xi_0$ irrespective of $r_p$ by the TMS model. If $r_p$ is less than 5.0 nm, the membrane potential predicted by the TMS model is consistent with those obtained by the SC model. Otherwise, the TMS model would overestimate the membrane potential. The reason is probably due to the fact that the SC model is based on the assumption of the electrical potential and ion concentration with a radial distribution in space, while the TMS model ignores the effects of the radial non-uniform ionic distribution inside pores [3]. On the other hand, it illuminates that the TMS model is independent of pore geometry, while the SC model is related with pore geometry. The similar result was obtained by examining membrane potential for a cylindrical pore and for an infinite slit pore [3].

4. Conclusions

In this present study, the TMS model, generally adopted in estimating membrane potential for 1-1 electrolyte solutions, is extended to evaluate multivalent electrolyte solutions. Through the calculation of the TMS model, the Cardano formula, introduced in the article, is favorable to calculate the Donnan equation analytically for asymmetry electrolyte (1-2, and 2-1).

On the basis of the study of different electrolyte solutions (electrovalence, concentration ratio, $c_1/c_2$, and diffusion coefficients ratio, $D_2/D_1$), the following conclusion can be made. Firstly, equivalent electrolyte concentration is more suitable to characterize the membrane potential in different kinds of electrolyte solutions than electrolyte concentration. Membrane potential approaches to the Nernst potential in the low concentration region, which indicates membrane potential in monovalent cation electrolyte solution is twice as large as that in divalent cation electrolyte solution. In the high concentration region, membrane potential closes to the diffusion potential. It implies membrane potential would be reversed if the diffusion coefficient, $D_2/D_1$, is larger than 1.0. The reversed behavior means that the mobilities of counter-ion and co-ion have a crossover correspondingly, and the rejection of membrane to ions may changed from great to small, or even become minus at certain concentration region. While in the intermediate concentration region, membrane potential as a function of electrolyte concentration is almost linearity and the relationship can also be found in experiment work. The various above-mentioned anomalous phenomena can be explained expediently by the TMS model when compared with the SC model. The possible reason is that the linearized transport equations (Eqs. of (1)–(3)) are difficult to analyze due to the concentration gradient and the concentration dependence of the coupling coefficients ($K_{ij}$) [3] by the SC model.

From the investigation of membrane structural and electrical parameters, membrane potentials by the two models for 1-2, 2-1 and 2-2 electrolyte solutions appear to be similar to those for 1-1 electrolyte solutions reported earlier by Westermann-Clark and Christoforou [3]. The TMS model shows good agreement with the SC model in the calculation of the membrane potential when dimensionless surface charge density, $q_0$, is less than 1.0, and the radius, $r_p$, is less than 5.0 nm. Otherwise, the TMS model would overestimate the membrane potential. Furthermore, the membrane potential shows dependence on the ratio of the volume charge density to equivalent electrolyte concentration, $\xi_0$ and $q_0/r_p$ by the SC model, but only varies with $\xi_0$ irrespective of $q_0/r_p$ by the TMS model. The reason is probably due to the fact that the SC model considers the radial of the electrical potential and ion concentration in space, while the TMS model ignores the effects of the radial non-uniform ionic distribution inside pores [3].

In view of the theoretical results presented above, it seems the TMS model is favorable to calculate the membrane potential of charged porous membrane and explain the various correlative phenomena in many physical situations.

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</table>
\[ q_w \] the surface charge density of capillary (\( \text{C m}^{-2} \))

\[ q_0 \] dimensionless potential gradient on the capillary wall

\[ r \] radial variable of capillary (m)

\[ r_p \] radius of capillary (m)

\[ R \] rejection

\[ R_g \] or gas constant (\( 8.314 \text{J mol}^{-1} \text{K}^{-1} \))

\[ \mathrm{ts} \] ionic mobility

\[ \psi \] electrostatic potential divided in radial direction

\[ \omega \] solute permeability coefficient (\( \text{mol m}^2 \text{J}^{-1} \text{s}^{-1} \))

\[ \phi \] electrostatic potential divided in axial direction

\[ \pi \] osmotic pressure in capillary defined as \( RT(\nu_1 + \nu_2)c \) (Pa)

\[ \rho_c \] excess charge density of electrolyte in capillary (\( \text{C m}^{-3} \))

\[ \sigma \] reflection coefficient

\[ \Phi \] total electrostatic potential inside capillary (V)

\[ \Phi_p \] electrostatic potential divided in axial direction (V)

\[ \psi_p \] electrostatic potential divided in radial direction (V)

\[ \omega \] solute permeability coefficient (\( \text{mol m}^2 \text{J}^{-1} \text{s}^{-1} \))

Greek letters

\[ \epsilon_r \] relative dielectric constants of aqueous electrolyte solution (78.303)

\[ \epsilon_0 \] dielectric constants of vacuum (\( 8.8542 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1} \))

\[ \lambda \] ratio of Debye length of electrolyte to pore radius

\[ \lambda_D \] Debye length of electrolyte solution (m)

\[ \mu \] viscosity of electrolyte solution (Pa s)

\[ \nu_1 \] stoichiometric coefficient of electrolyte

\[ \xi \] ratio of volume charge density in membrane to electrolyte concentration

\[ \pi \] osmotic pressure in capillary defined as \( RT(\nu_1 + \nu_2)c \) (Pa)

\[ \rho_c \] excess charge density of electrolyte in capillary (\( \text{C m}^{-3} \))

\[ \sigma \] reflection coefficient

\[ \Phi \] total electrostatic potential inside capillary (V)

\[ \Phi_p \] electrostatic potential divided in axial direction (V)

\[ \psi_p \] electrostatic potential divided in radial direction (V)

\[ \omega \] solute permeability coefficient (\( \text{mol m}^2 \text{J}^{-1} \text{s}^{-1} \))

Subscripts

b bulk solution

i \( i = 1: \) counterion; \( i = 2: \) co-ion

p permeate

s solute

Superscripts

D Donnan equilibrium

m membrane phase

- dimensionless factor

References


