The effect of heterogeneity in ion-exchange membrane structure on Donnan Exclusion

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Abstract. Ion-exchange membrane (IEM) can be classified into homogeneous and heterogeneous membrane according to the heterogeneity of membrane structure. Results of various studies indicated that the degree of heterogeneity significantly affects the properties and performance of IEMs, such as conductivity, permselectivity, mechanical and chemical stability, energy consumption, and limiting current density. In the case of transport properties, it may be associated with efficacy of Donnan exclusion influenced by the presence of interstitial solution and inert phase in the membrane matrix. Therefore, understanding the effect of heterogeneity on Donnan exclusion is important to provide preliminary information about IEM transport properties. In this paper, the effect of IEC/Wu on Donnan exclusion is discussed. The effect of heterogeneity on Donnan exclusion is expressed as a correlation of IEC/Wu ratio with Donnan equilibrium constant, KD, and transport number of counter-ion, τi.

1. Introduction

Recently, membrane technology has been applied in the various field which is primarily due to its features of relatively low energy consumption, low operating cost, easy to scale-up, lower footprint, and intensive process [1–9]. Ion-exchange membrane (IEM) which has charge groups fixed in the membrane matrix is basically used for ionic separation. IEM-based processes have found many applications in fields such as water treatment, wastewater treatment, chemical synthesis, and energy conversion [10–16].

To which extent the separation efficiency in IEM-based processes depends on membrane properties i.e. electrochemical properties, chemical and thermal stabilities, and mechanical strength [11,17]. Those properties are primarily determined by water uptake and ion-exchange capacity of IEM [18]. Furthermore, the structure of IEM is also an important factor that affects the transport properties [19–22]. According to the microheterogeneous model, there is a heterogeneity in the membrane structure [23–26]. Generally, the heterogeneity is defined as the number of phases in the IEM structure. According to the microheterogeneous model, the heterogeneity of IEM is based on the fraction of gel and inter-gel phase in the membrane. The heterogeneity increases with increasing the fraction of inter-gel phase. The degree of heterogeneity can affect the ionic transport across in IEM such as conductivity and permselectivity. According to Xu et al. [18], parameters of ion-exchange capacity (IEC) and water uptake (Wu) can be used to determine the other IEC properties, qualitatively. In this paper, the effect of heterogeneity on Donnan exclusion phenomenon is discussed. The effect of
heterogeneity on Donnan exclusion is expressed as a correlation of IEC/Wu ratio with Donnan equilibrium constant, KD, and transport number of counter-ion, ti.

2. Donnan Equilibrium Theory and Transport-Structural Parameter

Generally, IEMs can be classified into cation- and anion-exchange membrane (CEM and AEM) according to fixed charge in the membrane structure (Figure 1). CEM has the negative charge which allows permeating cation (counter-ion) while excluding anion (co-ion). Meanwhile, AEM allows the permeation of anion (counter-ion) while excluding cation (co-ion) due to the positive charge in the membrane structure. This phenomenon is well-known as ‘Donnan Exclusion’. This phenomenon has been explained by Donnan equilibrium theory [27]. In this theory, the concentration of ion in the solution will be in an equilibrium state with the concentration of ion in the IEM. This correlation is expressed as follows. The Donnan equilibrium constant, K, is defined by the equation [18]:

\[ K = \left( \frac{C_{i,m}}{C_{i,s}} \right)^{1/z_i} \]  

where \( C_{i,m} \) and \( C_{i,s} \) are the concentration of ions in membrane and solution, respectively, \( i \) is for cation and anion, and \( z_i \) is valence of the ion.

![Figure 1. Schematic illustration of ion separation in an electrodialysis process.](image)

From an electroneutrality condition both in the membrane and in solution, the \( K \) of cation (\( K_K \)) can be calculated from the concentration of solution, \( C_s \), and ion-exchange capacity of the membrane, \( C_{ex} \), [18]:

\[ K_K = \frac{-\omega C_{ex}}{2C_s} + \sqrt{1 + \left( \frac{\omega C_{ex}}{2C_s} \right)^2} \]  

while for anion, \( K_A \):

\[ K_A = \frac{\omega C_{ex}}{2C_s} + \sqrt{1 + \left( \frac{\omega C_{ex}}{2C_s} \right)^2} \]  

Then from equation (1) to (3), the concentration of cation and anion in the membrane (\( C_{K,m} \) and \( C_{A,m} \), respectively) can be calculated. The concentration of cation in IEM, \( C_{K,m} \) can be determined by [18]:

\[ C_{K,m} = \frac{-\omega C_{ex}}{2} + \sqrt{(C_s)^2 + \left( \frac{\omega C_{ex}}{2C_s} \right)^2} \]
and anion, $C_{A,m}$:

$$C_{A,m} = \frac{\omega c_{ex}}{2} + \sqrt{\left(C_s\right)^2 + \left(\frac{\omega c_{ex}}{2c_s}\right)^2} \quad (5)$$

In equation (2) to (5), the value of $\omega$ is $+1$ for AEM and $-1$ for CEM.

There are several models which have been proposed to explain the relationship between membrane structure (especially the heterogeneity) and membrane separation properties, for example, microheterogeneous, three-wire, and extended three-wire models [23,25,26,28]. In the microheterogeneous model proposed by Zabolotsky and Nikonenko [23], effective conductivity of the membrane, $L_{i,m}$, is defined as the conductivity fraction of the gel phase and the inter-gel phase (Figure 2). The relationship between the fraction of those phases is explained as follows. The effective conductivity generalized conductivity of the membrane is described as [23]:

$$L_{i,m} = \left(f_1 L_{i,g} + f_2 L_{i,s}\right)^{1/\alpha} \quad (6)$$

where $L_{i,g}$ and $L_{i,s}$ are generalized conductivities of gel and inter-gel phases, $f_1$ and $f_2$ are volume fractions of gel-phase and inter-gel phases, respectively, and $\alpha$ is a geometrical parameter which illustrates the arrangement of gel and inter-gel phases in the membrane. Furthermore, the generalized conductivities in the gel and inter-gel phases are correlated with diffusion coefficient, $D$ [23]:

$$L_{i,g} = \frac{D_{i,g} c_{i,g}}{RT} \quad (7)$$

$$L_{i,s} = \frac{D_{i,s} c_{i,s}}{RT} \quad (8)$$

where $R$ is gas constant and $T$ is absolute temperature. The value of $D_{i,p}$ can be further defined from $(RT/F^2)(\sigma_{iso}/C_{ex})$ [23,29]. Here, $F$ is Faraday constant and $\sigma_{iso}$ is an isoconductance point.

**Figure 2.** Schematic of homogeneous and heterogeneous IEM.

Selectivity of IEM is generally characterized by determining the transport number of counter ion, $t_{i,m}$. Transport number counter-ion is defined by [23]:

$$t_{i,m} = \frac{z_i^2 L_{i,m}}{z_k^2 L_{K,m} + z_A^2 L_{A,m}} \quad (9)$$
According to equations (4) to (9), transport number of counter-ion in the membrane is determined by solution concentration (ion concentration), ion-exchange capacity of the membrane, and the structural parameters i.e. fraction and geometrical arrangement of gel and inter-gel phases in the membrane matrix.

The conductivity of the membrane, \( \sigma_{\text{m}} \), can also be correlated with the fraction of phases element in the membrane. For alternating current conductivity (AC), \( \sigma_{\text{m,a}} \), it is defined as [23]:

\[
\sigma_{\text{m,a}} = \left( f_1 \sigma_{\text{g},a}^\alpha + f_2 \sigma_{\text{s},a}^\alpha \right)^{1/\alpha}
\]  

(10)

Meanwhile, the direct current conductivity of IEM is expressed and can be simplified to [23]:

\[
\sigma_{\text{m,d}} = (\sigma_{\text{g},t_{i,g}})^{f_1}(\sigma_{\text{s},t_{i,s}})^{f_2}
\]  

(11)

Here, the transport number of counter-ion in the gel phase can be supposed to \( \approx 1 \) considering the ideal selectivity of the gel phase.

### 3. Analysis of Donnan Equilibrium Constant

Properties of several IEMs from two classes of the membrane, i.e. homogeneous and heterogeneous are summarized in Table 1. It can be seen from the table that heterogeneous IEMs have higher inter-gel phase. It will result in the lower membrane permselectivity and counter-ion transport number (t).

It has been explained by Xu et al. [18] that ion-exchange capacity (IEC) and water uptake (Wu) can be used to qualitatively determine the others IEM properties. Wu is the amount of water adsorbed in the membrane matrix at the swelling state. Wu may also be used to indicate the void fraction in the membrane matrix filled by a solution or electrolyte. Therefore, Wu may be used as the indicator of the membrane heterogeneity. On the other hand, IEC represents the number of functional sites in the membrane matrix. Functional site concentration in the membrane is important for providing a higher selectivity. Furthermore, the ratio of functional sites to the solution in the membrane matrix may represent this fixed charge concentration. Therefore, ratio of IEC to Wu (IEC/Wu) will determine the efficacy of Donnan Exclusion as well as the membrane selectivity. This IEC/Wu value is then used in equation (2) and (3) as \( C_{\text{ex}} \), by assuming the equilibrium condition occurs in the membrane matrix.

| Membrane | Type | Properties | \( C_{\text{ex}} \) (meq/cm\(^3\)) | \( f_2 \) | \( \sigma_{\text{m,ao}} \) (mS/cm) | \( t_i \) | Ref. |
|----------|------|------------|--------------------------|--------|-----------------|--------|-----|
| AMV      | AEM; Hm | 2.09 | 0.06 | 3.79 | 0.986 (0.01 M) | [30] |
| AMX      | AEM; Hm | 1.43 | 0.10 | 3.04 | 0.999 (0.01 M) | [30] |
| AR-204-SZRA-412 | AEM; Hm | 0.34 | 0.10 | 8.9 | 0.93 (0.5 M) | [31–33] |
| CMS      | CEM; Hm | 2.55 | 0.13 | 2.72 | 0.97 | [34] |
| CR-67-HMR | CEM; Htr | 0.36 | 0.10 | 5.2 | 0.945 (0.01 M) | [24,31,33] |
| HGA      | AEM; Htr | 0.41 | 0.17 | 0.80 | 0.84 (0.1 M) | [35,36] |
| HGC      | CEM; Htr | 0.673 | 0.27 | 1.05 | 0.859 (0.01 M) | [35] |
| HJA      | AEM; Htr | 1.52 \( b \) | 0.35 | 0.25 | 0.89 (0.5 M) | [32] |
| IPA      | AEM; Hm | 0.784 | 0.32 | 1.13 | 0.92 (0.1 M) | [35,36] |
| IPC      | CEM; Hm | 1.401 | 0.37 | 1.32 | 0.94 (0.1 M) | [35,36] |
| LNA      | AEM; Htr | 1.63 \( b \) | 0.28 | 2.65 | 0.91 (0.5 M) | [32] |
| MA-40    | AEM; Htr | 3.2 | 0.28 | - | - | [26,37,38] |
| MA-41    | AEM; Htr | 1.3 | 0.18 | 5.8 | - | [31,38] |
| MC-40C   | CEM; Htr | 1.8 | 0.2 | 6.4 | - | [23] |
| MK-40    | CEM; Htr | 1.7 | 0.16 | 3.5 | 0.87 (1 M) | [29,31,37] |

\( a \) In NaCl solution; \( b \) meq/g; Hm – homogeneous IEM; Htr – heterogeneous IEM.
It can be observed from Figure 3 (a) that the value of KD is linearly increased with increasing IEC/Wu as indicated by equation (2). The value of KD is also increased by reducing solution concentration. Similar to KD vs IEC/Wu, the value of t also increases with KD and IEC/Wu (Figure 3 (b) and (c)). It is obvious since the increasing IEC/Wu results in improving the efficiency of Donnan exclusion leading to the increased membrane selectivity (shown by transport number).

![Figure 3](image)

Figure 3. (a) Donnan equilibrium constant (KD) at various IEC/Wu (calculated by equation (2) and (3)), (b) transport number vs KD, and (c) transport number vs IEC/Wu. Membranes: AMX, 204SZRA, HJA, LNA, HGA, IPA, IPC, CR67-HMR-402, AR204-SZRA-412, ASM, ASM-F; their properties (IEC, Wu, t) are from ref: [32,33,35,36,39].

4. Conclusion

Results of various studies indicated that the degree of heterogeneity significantly affects the separation properties of IEMs such as conductivity and perme selectivity. It can be associated with efficacy of Donnan exclusion which is influenced by the presence of inter-gel phase filled by an electrolyte and inert phase in the membrane matrix. Therefore, understanding the effect of heterogeneity on Donnan exclusion is important to provide preliminary information about the transport properties. In this paper, the effect of IEC/Wu on Donnan exclusion is discussed. The effect of heterogeneity on Donnan exclusion is expressed as a correlation of IEC/Wu ratio with Donnan equilibrium constant and transport number of counter-ion, t. Results of this study showed that membrane transport number is increased with increasing IEC/Wu ratio. The IEC/Wu may be used for preliminary determination of IEM transport number.

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