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Theoretical study of the permselectivity of an anion exchange membrane in electrodialysis

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ABSTRACT

Electrodialysis (ED) is one of the useful membrane processes to produce a drinking water from underground water, brine water and other water sources. In ED, the monovalent anion selectivity is a very important property of anion exchange membranes (AEMs) to remove harmful ions like NO_3^- and F^- ions from feed solutions and to protect the precipitation of scale. In this paper, we theoretically discussed the effect of parameters on permselectivity and suggested ways to improve the monovalent anion selectivity of ED system using the equivalent circuit model. The results showed that a decrease in the thickness of diluted compartment was very important to properly reflect the membrane properties on the permselectivity. It was also shown that the multivalent anion selectivity of an AEM was increased by increasing the positive charge density of the AEM. On the other hand, the monovalent anion selectivity was improved by modifying the AEM with a negatively charged layer. Finally, we discussed a method for estimating the monovalent anion selectivity of ED system.

1. Introduction

Recently, water shortage has been a serious problem, globally. Many membrane processes are used to produce drinking water from seawater, underground water and other water sources. Electrodialysis (ED) is one of the useful membrane processes as well as reverse osmosis (RO) and nanofiltration (NF) processes. ED is an electrochemical separation process that uses an ion permselectivity of cation and anion exchange membranes [1]. In ED processes, ions are selectively transported from one compartment (the diluted compartment) to another compartment (the concentrated compartment) through ion exchange membranes (IEMs) under the driving force of an electrochemical potential gradient. One advantage of ED compared with other processes, such as RO, is that a higher brine concentration can be achieved because there are no osmotic pressure limitations. Notably, ED is used to remove harmful ions such as F^- and NO_3^- [2–7]. It can also be used to soften water [8] and to remove heavy metals [9].

One of the most important properties of IEMs is the permselectivity towards specific ions. In particular, the monovalent anion selectivity of anion exchange membrane (AEM) is very important, because most of the harmful anions we have to remove from feed water are monovalent, such as F^- and NO_3^-. Infants younger than 6 months old are susceptible to nitrate poisoning because, within an infant's body, nitrate is changed to toxic nitrite by bacteria. Once formed, nitrite enters the blood-stream and forms methemoglobin, which interferes the blood's ability to carry oxygen [10]. High concentration of fluoride in drinking water results in fluorosis (dental/skeletal abnormalities) and several types of neurological damage [11]. In addition, AEMs must be impermeable to sulfate ions to prevent the precipitation of calcium sulfate during the ED process [12]. Calcium sulfate precipitates as a scale in the concentrated compartment, causing serious problems in the ED process. Moreover, by selectively removing target ions from feed solutions, we can readily produce high quality water to satisfy specific water standards. Thus, the high monovalent anion selectivity is demanded for AEMs. A monovalent ion permselective membrane has the capability to separate monovalent ions from a solution containing both mono- and multi-valent ions [13]. It has been reported that the selectivity for sulfate ions (relative to chloride ions) depends on the method used to prepare an AEM in the ED process [14]. It is also known that the permselectivity of specific anions through the AEM depends on the hydration energy of the anions and the hydrophilicity of the membrane, apart from the membranes having a negatively charged layer on the membrane surface [12,15].

A number of researchers have investigated the fabrication of AEMs with high monovalent anion selectivity [12–14,16,17]. However, as far as we know, there have been few theoretical

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investigations on the monovalent anion selectivity of ED system. Identifying and understanding the parameters that affect monovalent anion selectivity will allow us to theoretically estimate the monovalent anion selectivity from physicochemical properties of system. This would also provide us a good understanding of fundamental nature of ED and a guideline to fabricate AEMs with high monovalent selectivity. In addition, it would be very useful in the design of ED process.

We previously proposed the equivalent circuit model [6] to explain the performance of ED process and showed this model fit very well with experimental results. In this paper, we theoretically discuss the effect of several parameters of system (including AEM) on the monovalent selectivity using the equivalent circuit model. We then discuss the way to estimate the monovalent selectivity from physicochemical properties of system.

2. Theoretical

2.1. Equivalent circuit model

Fig. 1 shows the fundamental system of ED. In ED system, the feed solution is divided by the pair of anion exchange membrane (AEM) and cation exchange membrane (CEM). When a DC voltage is applied to the system, anions migrate towards the anode through the AEM while cations migrate to the cathode through CEM. However, anions cannot permeate the CEM and cations cannot permeate the AEM because of the electric repulsion between ions and membrane charge. Consequently, the ion concentration in the central compartment between AEM and CEM decreases. The central compartment is thus called the “diluted compartment”. At the same time, the ion concentration increases in the compartment next to the diluted compartment and therefore this compartment is called the “concentrated compartment”.

Considering k indicates all ionic species including cations and anions, the ion flux of ion k through the membrane, J_k (eq/s m^2) is obtained from the electrochemical potential gradient and is given by Eq. (1) [18,19].

$$J_k = -\frac{\alpha_k RT}{N_A} B_k \left(\frac{\partial [k]_M}{\partial x}\right) - z_k \frac{\alpha_k F}{N_A} B_k [k]_M \left(\frac{\partial E_M}{\partial x}\right) \tag{1}$$

Here, B_k denotes the diffusion coefficient (m^2/s J) of ion k within the membrane, $[k]_M$ the concentration (eq/m^3) of ion k within the membrane and $\partial E_M/\partial x$ the electric potential gradient (V/m) across the membrane. α_k is the parameter that shows the sieving effect of membrane for ion k [20]. z_k Denotes the sign of ionic charge of ion k (1 or -1). R denotes the gas constant (J/K eq), T the temperature (K), F the Faraday constant (C/eq) and N_A the Avogadro constant (1/eq). The first term of right hand side of Eq. (1) shows the ion flux due to the diffusion along the concentration gradient and the second term the ion flux induced by the electric potential. The electric potential includes the externally applied potential and the diffusion potential within the membrane. When a membrane divides two electrolyte solutions with different concentrations and/or different electrolytes, the potential difference, so called a membrane potential, is generated between tow electrolyte solutions. This potential consists of diffusion potential within the membrane and Donnan potentials at membrane/solution interfaces. However, the Donnan potential is a potential resulted from the partition of ions into the membrane and the potential which affects the ion flux is only the diffusion potential [19].

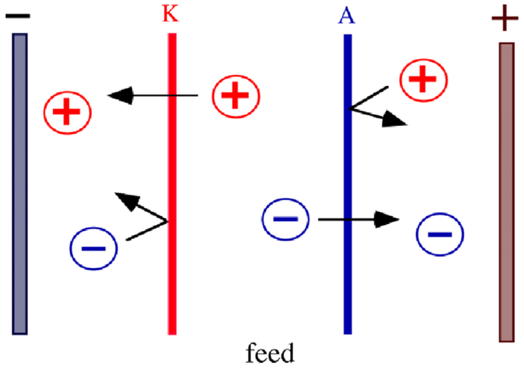

Fig. 1. Fundamental system of ED. K: cation exchange membrane (CEM); A: anion exchange membrane (AEM).

Considering the system which contains n kinds of electrolytes, the concentration of ion partitioned into the membrane is obtained from the electroneutrality condition, Eq. (2) and the Donnan equilibrium condition, Eq. (3) [21,22]. In Eq. (3), the concentration dependency of activity coefficient is neglected and the standard chemical potential within the membrane is assumed to be the same as that in bulk solution.

$$[i1]_M + \cdots + [in]_M - [a1]_M - \cdots - [an]_M + \theta_M = 0 \tag{2}$$

$$\left(\frac{[i1]_M}{[i1]_B}\right)^{1/z_{i1}^{v}} = \cdots = \left(\frac{[in]_M}{[in]_B}\right)^{1/z_{in}^{v}} = \left(\frac{[a1]_M}{[a1]_B}\right)^{1/z_{a1}^{v}} = \cdots = \left(\frac{[an]_M}{[an]_B}\right)^{1/z_{an}^{v}} \tag{3}$$

where $[in]$ and $[an]$ indicate the concentrations (eq/m^3) of cation and anion of nth electrolyte, respectively. z_k^v Denotes the ionic valence of ion k. Subscripts M and B indicate the membrane and the bulk solution, respectively. θ_M denotes the membrane charge density (eq/m^3) and is assumed to be homogeneous in this paper. It is clear from Eqs. (2) and (3) that it is impossible to obtain an analytical equation for concentration of each ion partitioned into membrane in general case. Only in some cases, we can obtain the analytical equation.

Here, in this paragraph, we treat the simple system which contains one kind of uni-univalent electrolyte, i^+a^- like NaCl to discuss the fundamental concept. In this case, the concentration of ions partitioned into the membrane are given by Eq. (4) from Eqs. (2) and (3) [19,21].

$$[i]_M = \left\{\left(\vartheta_M^2 + 1\right)^{1/2} - \vartheta_M\right\} C_{B,} \quad [a]_M = \left\{\left(\vartheta_M^2 + 1\right)^{1/2} + \vartheta_M\right\} C_B \tag{4}$$

where ϑ_M denotes $\theta_M/2C_B$ and C_B the bulk concentration (eq/m^3). In ED system, the membrane charge density of IEM is required to be higher than the bulk concentration, $\vartheta_M \gg 1$, to show a high permselectivity of counterion for membrane charge. The high counterion permselectivity is resulted from the high Donnan exclusion for coion. It is clear from Eq. (4) that only counterion is partitioned into IEM and the concentration of coion within the membrane is negligibly small under the condition of $\vartheta_M \gg 1$. In addition, the concentration of counterion within the membrane is equal to the membrane charge density. It means that there is no concentration gradient within the membrane and the diffusion potential is zero under the condition of $\vartheta_M \gg 1$. Thus, it is found from Eq. (1) that the ion flux in ED system is determined by the ion flux induced by the externally applied electric potential gradient across the membrane. This discussion will be supported by the report stating that the diffusion contribution is negligible in most of the ED condition [23]. This condition will be satisfied under the condition of $\theta_M > 20C_B$. The membrane charge density is determined from the membrane potential [21,24] or will be estimated from the ion exchange capacity (meq/dry g) of IEM using a specific gravity and a water content.

In ED system, it is well known that the counterion concentration at IEM/bulk solution in diluted compartment interface decreases depending on the electric current density that flows through IEM. This phenomenon is called as a concentration