

A Simplified Theory on Response of an Ion Exchange Membrane Electrode to a Foreign Ion in Flow Analysis

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A theory describing response patterns of an ion exchange membrane electrode to foreign ions in a flow system is proposed on the basis of some simplifying approximations. The theory can semi-quantitatively simulate the response patterns to the foreign ions in flow analyses. In particular, the theory clarifies physicochemical meanings of negative peaks, which have been observed in the use of the electrode as detectors in FIA as well as in HPLC.

In the use of an ion exchange membrane electrode as a detector in flow injection analysis (FIA) as well as in high performance liquid chromatography (HPLC), it is important to understand a general aspect of response patterns to foreign ions in flow systems, in which the electrode frequently exhibits characteristic responses that can not be easily explained by the steady state theories on the potentials of the ion exchange membrane electrode. In pioneer works on the use of the electrode as a detector in HPLC and FIA, for instance, negative peaks have been reported in the detection of foreign ions¹⁾ or in the determination of the primary ion in the presence of interfering ions.²⁾ These negative peaks can not be easily explained by the steady state theories. Thus, theories describing the response patterns to foreign ions in the flow systems are strongly desired. However, few theoretical works in this filed have been reported because of

mathematical difficulties in treatments of the membrane system under non-steady state conditions.

In this work, we have proposed a theory on the response of the ion exchange membrane electrode to foreign ions in the flow analyses under some simplifying approximations.

Theoretical

Figure 1 shows the schematic diagram of the solution-membrane system. The origin is placed at the interface between sample and membrane phases. In both the sample and membrane phases, existence of the diffusion layers is assumed. Since diffusion coefficients of species in the membrane phase are usually much less than those in the sample, the steady state assumption on fluxes of

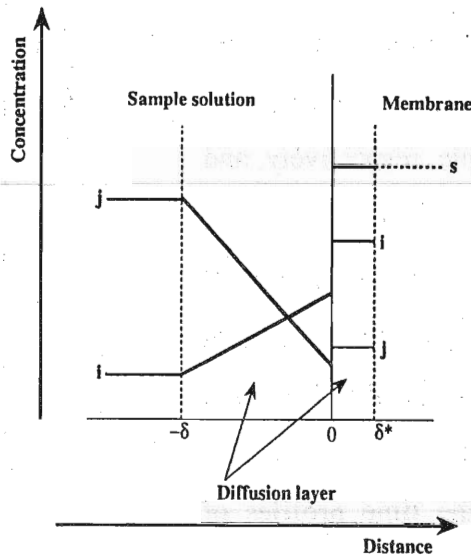


Figure 1. Schematic diagram of the sample-membrane system. The symbols i , j and s represent the primary ion, the foreign ion, and the ion exchange site, respectively. In this treatment, the lumped parameter model is adopted in the ionic distribution in the diffusion layer of the membrane side.

chemical species across the membrane is not valid in usual flow analyses, especially in the case of FIA. In the membrane, thus, we assume that only the diffusion layer is active to the ion exchange between the two phases but not the remaining part of the membrane. For mathematical simplicities, in addition, we assume that the ionic distribution within the diffusion layer of the membrane side is flat and all chemical species in given phases have equal mobilities. As the concentrations of

species at the detecting part in FIA as well as in HPLC can be approximated by a Gaussian distribution, we analyze the case that the ionic composition in the bulk of the sample is expressed by the following Equations:

$$C_i = \text{Constant} \quad (1)$$

$$C_j = C_j^{\text{max}} \exp\{-(t-t_1)^2/\sigma^2\} \quad (2)$$

where C_i and C_j are concentrations of the primary ion i and the foreign ion j in the bulk of the sample, respectively, and where C_j^{max} represents the maximum concentration of the j ion and σ is a standard deviation of the Gaussian distribution. Figure 2 shows the time profiles of the concentrations of the i and j ions in the bulk of the sample depicted by using Equations (1) and (2).

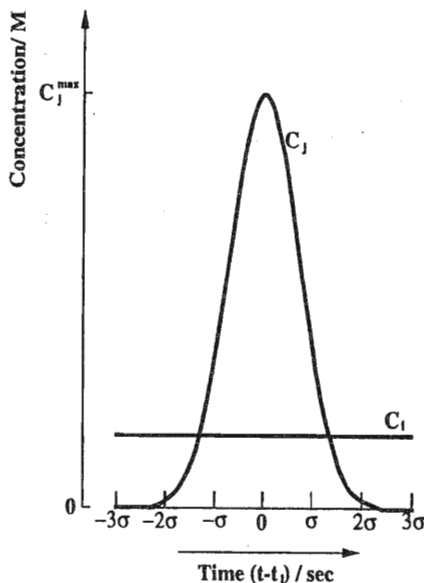


Figure 2. Time profiles of concentrations of the i and j ions in the bulk of the sample. C_j is represented by a Gaussian distribution and can be essentially regarded as 0 when $|t-t_1| > 3\sigma$. C_i is time-independent.

The local chemical equilibrium at the interface allows us to write the relation:

$$\frac{N_j^*(0,t) C_i(0,t)}{N_i^*(0,t) C_j(0,t)} = K_{i,j} \quad (3)$$

Here, $N_i^*(0,t)$ and $N_j^*(0,t)$ are mole fractions of the respective ions i and j at the boundary of the the membrane side at a given time t , $C_i(0,t)$ and $C_j(0,t)$ are

concentrations of the ions i and j in the sample on the membrane surface at $t=t$, respectively, and $K_{i,j}$ is the ion exchange constant. From the continuity of a flux of each chemical species across the interface, mass balances in the respective phases, and from Equation (3), the following differential Equation can be obtained:

$$-\frac{dN_i^*(0,t)}{dt} = k \frac{K_{i,j} N_i^*(0,t) C_j - (1-N_i^*(0,t)) C_i}{K_{i,j} N_i^*(0,t) + (1-N_i^*(0,t))} \quad (4)$$

where $k=D/(\delta\delta^*C_s^*)$ and D is the diffusion coefficient of species in the sample. Solving Equation (3) under pertinent boundary conditions, $N_i^*(0,t)$ can be determined. Substituting $N_i^*(0,t)$ into Equations (5) and (6), concentrations of the ions i and j in the sample on the membrane surface at given time t ($C_i(0,t)$ and $C_j(0,t)$) can be calculated.

$$C_i(0,t) = \frac{K_{i,j}(C_i + C_j) N_i^*(0,t)}{(K_{i,j}-1) N_i^*(0,t) + 1} \quad (5)$$

$$C_j(0,t) = C_i + C_j - C_i(0,t) \quad (6)$$

Under the forgoing assumptions, the electrode potential can be expressed by Equation (7) :

$$E_M = \text{Const.} + (RT/ziF) \ln(C_i(0,t) + K_{i,j}C_j(0,t)) \quad (7)$$

Because of the equal mobility assumption, mobilities of the ions are not appeared in Equation (7). Substituting Equations (5) and (6) into Equation (7), the electrode potential can be calculated as a function of time.

Discussion

Since we have selected the Gaussian distribution as C_j , the solution of the differential Equation (4) can not be expressed by elementary functions. Then, it was numerically solved by the Runge-Kutta-Gill method.³⁾ By changing parameters C_i , C_j^{\max} , t_1 , σ , k and $K_{i,j}$, responses of the electrode were simulated. Since the parameter k is closely related to the rate of the mass transfer between the sample and membrane, the conversion of the membrane from the initial i ion form to the j ion form becomes larger with an increase in the k value. The simulation study have revealed that the time profiles of the simulated potentials are in semi-quantitatively agreement with so far reported ones^{1,2)} when k lies between 1 and $50 \text{ sec}^{-1}\text{M}^{-1}$. To illustrate the simulated responses, the responses to two kinds of the j ions with the $K_{i,j}$ value of $10^{2.55}$ or $10^{-2.55}$ are shown in Fig. 3. Here, the k value of $25 \text{ sec}^{-1}\text{M}^{-1}$ and the following C_i and C_j are employed:

$$C_i = 10^{-4} \quad (8)$$

$$C_j = 10^{-3} \exp[-\{(t-30)/10\}^2] \quad (9)$$

In the case of the $K_{i,j}$ value of $10^{2.55}$, namely in the detection of a strongly interfering j ion, the present theory predicts that (i) the potential after the detection is hardly recovered to the initial baseline potential when k is greater than 10, and that (ii) the peak height is always less than one estimated from the steady state theories, *i.e.*,

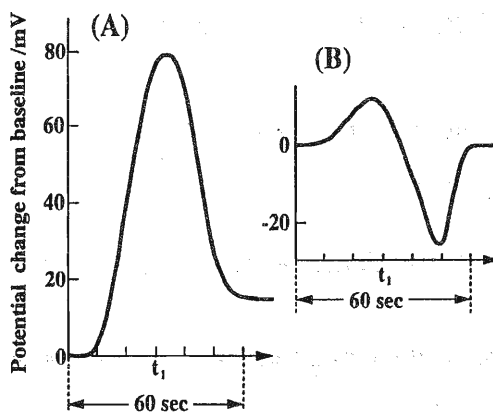


Figure 3. The simulated responses of the electrode to the j ions with $K_{i,j}$ value of $10^{2.55}$ or $10^{-2.55}$.

(A) $K_{i,j} = 10^{2.55}$. (B) $K_{i,j} = 10^{-2.55}$. Other parameters: $C_i = 10^{-4} \text{ M}$; $C_j^{\max} = 10^{-3} \text{ M}$; $t_1 = 30 \text{ sec}$; $\sigma = 10 \text{ sec}$; $k = 25 \text{ sec}^{-1}\text{M}^{-1}$.

$(RT/z_j F) \ln \{ (C_i + K_{i,j} C_j^{\max}) / C_i \}$. When the membrane contacts with the j ion, the membrane in the vicinity of the interface is rapidly converted into the j ion form from its initial i ion form. The larger the value of k the greater the conversion. The j ion entered into the membrane can not be rapidly and easily eluted by the i ion since the membrane prefers the j ion to the i ion. Consequently, the potential after the detection of the j ion can not rapidly recovered to the initial baseline potential. It was also clarified that the baseline shift after the detection can be essentially ignored when k is less than unity. In addition, detailed analyses of the ionic concentrations on the membrane surface clarified that the potential determining factor $(C_i(0,t) + K_{i,j} C_j(0,t))$ on the membrane surface is always less than that in the bulk of the sample $(C_i + K_{i,j} C_j)$ because of the concentration polarization between the membrane surface and the bulk of the sample. Then, the peak height is less than that expected from the steady state theories.

In the detection of the weakly interfering j ion with the $K_{i,j}$ value of $10^{-2.55}$, the present theory predicts the appearance of the negative peak followed by the small positive peak and the potential rapidly returns to the initial baseline potential followed by the negative peak. Clearly the steady state theories, *i. g.*, the Nikolsky-Eisenman equation never predicts the appearance of negative peak.. On the other hand, the present theory clearly predicts the negative peak in the detection of weak interfering j ions. By means of detailed analyses of the ionic concentrations in the sample on the membrane surface, the mechanism of the negative peak appearance was clarified. Even if the $K_{i,j}$ is much smaller than unity, the j ion can invade into the membrane to some extents when the membrane contact with the j ion. In this case, the membrane prefers the i ion to the j ion, then the invaded j ion is easily and rapidly eluted with the i ion. During this elution process, the potential determining factor on the membrane surface $(C_i(0,t) + K_{i,j} C_j(0,t))$ becomes temporally less than C_i . Thus, the negative peak appears followed by the positive peak.

As shown in this work, steady state theories can not explain the behavior of the electrode in flow analyses. This is natural that the steady state assumption across the membrane is not satisfied in the time scale of FIA and HPLC. Although the real situations may be far from our idealizations, the present theory gives the semi-quantitative explanations on the response of the ion exchange membrane electrode to foreign ions in flow systems suggesting the validity of our approach as the first approximation.

References

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Symbols

- i: primary ion
- j: foreign ion
- s: ion exchange site
- δ : thickness of diffusion layer in the sample [cm]
- δ^* : thickness of diffusion layer in the membrane [cm]
- D: diffusion coefficient of species in the sample [cm^2/sec]
- C_j : concentration of the j ion in the bulk of the sample [$M = \text{mol}/\text{dm}^3$]
- C_i : concentration of the i ion in the bulk of the sample [M]
- C_s^* : concentration of the ion exchange site in the membrane [M]
- $k = D/(\delta \delta^* C_s^*)$ [$\text{sec}^{-1}M^{-1}$]
- K_{ij} : ion exchange constant between the sample and membrane phases [-]
- $C_i(0,t)$: concentration of the i ion in the sample on the the membrane surface [M]

$C_j(0,t)$: concentration of the j ion in the the sample on the membrane surface [M]

$N_i^*(0,t)$: mole fraction of the i ion in the diffusion layer of the membrane [-]

$N_j^*(0,t)$: mole fraction of the j ion in the diffusion layer of the membrane [-]

(和文要旨)

イオン交換膜型電極のフロー分析系における異種イオンに対する応答挙動を記述する理論を、幾つかの単純化のための近似を導入して、構築した。この理論は、フロー分析系における電極の異種イオンに対する応答挙動を半量的に再現する。特にFIAやHPLCの検出器として電極を用いたときに観測されてきた負の検出信号の物理化学的意味を、本理論により初めて明かにできた。

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