

A Method of Determining Selectivity Coefficients Based on the Practical Slope of Ion Selective Electrodes

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Abstract: It is a problem to be solved that the experimental selectivity coefficients of ion selective electrodes (ISEs) depend on the activity. This paper studied the new method of determining selectivity coefficients. A mixed ion response equation, which was similar to Nicolsky-Eisenman (N-E) equation recommended by IUPAC, was proposed. The equation includes the practical response slope of ISEs to the primary ion and the interfering ion. The selectivity coefficient was defined by the equation instead of the N-E equation. The experimental part of the method is similar to that based on the N-E equation. The values of selectivity coefficients obtained with this method do not depend on the activity whether the electrodes exhibit the Nernst response or non-Nernst response. The feasibility of the new method is illustrated experimentally.

Keywords: Ion selective electrodes, potentiometric selectivity coefficients, Nicolsky-Eisenman equation.

Ion selective electrodes (ISEs) have been widely applied in a variety of fields, especially in the area of life science, clinical diagnostics and pharmacological analysis. A selectivity coefficient ($K_{A,B}^{pot}$) is an important parameter of ISEs. The method of determining $K_{A,B}^{pot}$ is still unsatisfactory. In 1976, IUPAC reported a recommendation on the method of determining $K_{A,B}^{pot}$ based on the Nicolsky-Eisenman (N-E) equation¹. The "separate solution method (SSM)" and "mixed solution method (MSM)" were recommended in the report. These recommended methods were available only if the electrode exhibits a Nernst behavior not only for the primary ion but also for interfering ions. Most reports on $K_{A,B}^{pot}$ have violated this prerequisite, because only few electrodes exhibit the Nernst behavior for the primary ion and interfering ions at the same time. When the electrode exhibits non-Nernst response, the values of $K_{A,B}^{pot}$ obtained by the SSM or MSM method depend on the activity. Therefore, when reporting the values of $K_{A,B}^{pot}$, it is necessary to report the activity under which the $K_{A,B}^{pot}$ are determined. Obviously, it is inconvenient for comparing the selectivity of different ISEs. In the recommendation report of IUPAC in 1995 on the determination of $K_{A,B}^{pot}$, the prerequisite of the SSM and MSM method was emphasized and another method named the "matched potential method (MPM)" was recommended². In the MPM method, neither the N-E equation nor the other response equations were considered, and it did not take account of ion charge. When the primary ion and/or the interfering ion dissatisfies with the Nernst response or the involved ions are unequal in charge, the

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MPM method is recommended. In fact, under the non-Nernst condition, the $K_{A,B}^{pot}$, which was determined by the MPM method, still depends on the activity². The limitations of the MPM method have been pointed out in the literatures^{3,4,5}. Some improvements have also been made on the bases of N-E equation or Nernst response^{4,5,6,7}. However, the method of determining $K_{A,B}^{pot}$ of ISEs with the non-Nernst response is still unsatisfactory and worthy to be researched. This work proposed the method for determination of $K_{A,B}^{pot}$, which was based on the practical slope of ISEs.

According to IUPAC's recommendation, the conventional writing of cell in potentiometry with ISEs is



The experimental relations of $\lg a$ vs E of the primary ion and the interfering ion are as follows:

$$E = E_A^{\circ} + S_A \lg a_A \quad (1)$$

$$E = E_B^{\circ} + S_B \lg a_B. \quad (2)$$

Where, a_A and a_B are the activities of the primary ion A and the interfering ion B respectively. E is the measured electromotive force (EMF) of cell. S_A and S_B are the practical slopes of the studied ISEs for ion A and B respectively. E_A° is the EMF at $a_A=1$ and $a_B=0$, and E_B° is the EMF at $a_B=1$ and $a_A=0$. Equation (2) can be expressed alternatively as

$$\begin{aligned} E &= E_A^{\circ} + E_B^{\circ} - E_A^{\circ} + \frac{S_B}{S_A} \cdot S_A \lg a_B \\ &= E_A^{\circ} + S_A \lg 10^{(E_B^{\circ} - E_A^{\circ})/S_A} + S_A \lg a_B^{S_B/S_A} \\ &= E_A^{\circ} + S_A \lg \left(10^{(E_B^{\circ} - E_A^{\circ})/S_A} \cdot a_B^{S_B/S_A} \right). \end{aligned} \quad (3)$$

In equation (3), we assign

$$10^{(E_B^{\circ} - E_A^{\circ})/S_A} = K_{A,B}^{pot} (PSM) \quad (4)$$

Then, by analogy to N-E equation, in the test solution which contain the primary ion A and interference ion B, the mixed ion response equation can be write as

$$E = E_A^{\circ} + S_A \lg \left(a_A + K_{A,B}^{pot} (PSM) \cdot a_B^{S_B/S_A} \right). \quad (5)$$

The $K_{A,B}^{pot}(PSM)$ in equation (5) is defined as the selectivity coefficient based on the practical slope including Nernst response and non-Nernst response. The difference

between equation (5) and the N-E equation is that the former introduces the practical slope of the ion A and the ion B. When the slope of electrode is Nernst value, Equation (5) restores to the N-E equation.

The $K_{A,B}^{pot}(PSM)$ can be determined by the SSM method and MSM method. The experimental procedures of methods are as the same as IUPAC's recommendation. The calculation formula of $K_{A,B}^{pot}(PSM)$ is different from IUPAC's recommendation although the same measured data of EMF are acquired.

If using the MSM, whether by the fix interference method (FIM) or by the fixed primary ion method (FPM), the calculation formula of $K_{A,B}^{pot}(PSM)$ is

$$K_{A,B}^{pot}(PSM) = \frac{a_A}{a_B^{S_B/S_A}} \quad (6)$$

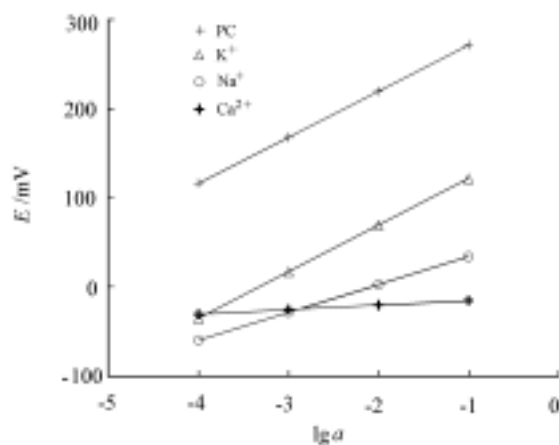
If using SSM and assuming $a_A = a_B$, the calculation formula of $K_{A,B}^{pot}(PSM)$ is

$$\lg K_{A,B}^{pot}(PSM) = \frac{E_B - E_A}{S_A} + (1 - S_B / S_A) \cdot \lg a_A \quad (7)$$

It will be shown below experimentally that the $K_{A,B}^{pot}(PSM)$ is independent on the activity. A procaine hydrochloride (PC) ISE⁸ is used as the studied electrode. Outer salt bridge solution of SCE is 0.1 mol·L⁻¹ LiAc. The EMF is measured with PHS-3C pH/mV meter. The Interfering ion is K⁺, Na⁺ and Ca²⁺. The SSM method is used. The experimental temperature is at 25°C.

The EMF for studied ions at several activities is measured. **Figure 1** showed linear relationship of $E/\lg a$ curve for the each studied ion. It can be seen from **Figure 1** that the electrode slope for PC, K⁺, Na⁺, and Ca²⁺ is 51.7, 52.3, 31.2 and 5.1 mV/decade respectively. The electrode exhibits non-Nernst responses for the all ions.

Figure 1 $E / \lg a$ curve of the primary ion and interference ions



The values of selectivity coefficients calculated by the recommended method^{1,2} are denoted as $K_{A,B}^{pot}(N-E)$ and shown in **Table 1**. Those calculated from equation (7) (that is $K_{A,B}^{pot}(PSM)$) are shown in **Table 2**.

The **Table 1** and **Table 2** showed that, 1) when the electrode exhibit non-Nernst response, the $K_{A,B}^{pot}(N-E)$ depend on the activity, but the $K_{A,B}^{pot}(PSM)$ does not. 2) As the ratio of the practical slope of ISE, S_B/S_A , is nearer to the ratio of the Nernst slope, z_A/z_B , the change of $K_{A,B}^{pot}$ with activity is smaller.

In conclusion, $K_{A,B}^{pot}$ based on practical slope does not depend on the activity. The new determining method of $K_{A,B}^{pot}$ can be used whether the electrode exhibits the Nernst response or not.

Table 1 $K_{A,B}^{pot}(N-E)$ determined by IUPAC method under several activities

ion	lga = -4	lga = -3	lga = -2	lga = -1
K ⁺	2.7×10 ⁻³	2.8×10 ⁻³	2.9×10 ⁻³	2.9×10 ⁻³
Na ⁺	1.1×10 ⁻³	4.8×10 ⁻⁴	2.2×10 ⁻⁴	9.7×10 ⁻⁵
Ca ²⁺	3.3×10 ⁻⁵	1.7×10 ⁻⁵	8.8×10 ⁻⁶	4.5×10 ⁻⁶

Table 2 $K_{A,B}^{pot}(PSM)$ determined according to equation (4) under several activities

ion	lga = -4	lga = -3	lga = -2	lga = -1
K ⁺	1.6×10 ⁻³	1.3×10 ⁻³	1.3×10 ⁻³	1.3×10 ⁻³
Na ⁺	1.0×10 ⁻⁵	1.0×10 ⁻⁵	1.0×10 ⁻⁵	1.0×10 ⁻⁵
Ca ²⁺	3.6×10 ⁻⁷	3.6×10 ⁻⁷	3.6×10 ⁻⁷	3.5×10 ⁻⁷

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