

Determination of Selectivity Coefficients of Ion Selective Electrodes by Continuous Variation Method

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A new method for the determination of the selectivity coefficient of an ion selective electrode is proposed. In the proposed method, a series of mixed solutions of the primary ion i and interfering ion j is prepared in which the sum of the logarithm of i concentration and logarithm of j concentration is kept constant. The potential of the electrode, E , is measured for the series of the mixed solutions. The result is plotted with the activity of i , a_i , as abscissa against E on semi-logarithmic graph paper. The activity at the intersection of two extrapolated linear parts of the $\log a_i$ - E curve is determined. From the activity at the intersection of the primary ion, the selectivity coefficient is calculated. The proposed method was applied to the determination of selectivity coefficients of fluoride, chloride, bromide and potassium selective electrodes. The selectivity coefficients determined by the proposed method, named "continuous variation method", agreed with those obtained with the conventional mixed solution method.

Keywords Selectivity coefficient, continuous variation method, ion selective electrode

Various kinds of methods for the determination of selectivity coefficients of ion selective electrodes have been proposed. Okazaki and Freiser reported an improved method of the mixed solution method¹ and Macca and Čakrt proposed a linearized multiple standard addition method.² Recently, a matched-potential method was proposed by Gadzekpo and Christian.³ It is well known that the most popular method for the determination of selectivity coefficient is the mixed solution method.⁴ However, the values of selectivity coefficient determined by the mixed solution method vary according to the activity of the interfering ion mixed in the solution at the fixed level. The experiments for the determination of selectivity coefficient should be repeated twice or three times, if the value is not presumed.

We propose a new method for the determination of selectivity coefficients which could overcome the above mentioned drawbacks in the mixed solution method. In the proposed method, a series of mixed solutions of the primary ion i and interfering ion j is prepared in which the sum of the logarithm of primary ion concentration and the logarithm of interfering ion concentration is kept constant. The potential of the electrode, E , is measured for the series of the mixed solutions. The result is plotted with activity of i , a_i , as abscissa against E on semi-logarithmic graph paper. The activity at the intersection of two extrapolated linear parts of the $\log a_i$ - E curve is determined. From the activity of the primary ion at the intersection, selectivity coefficient,

K_{ij}^{Pot} is calculated.

We propose that the new method for the determination of selectivity coefficient be named the "continuous variation method".

Theory

The electrode potential, E , of a mixed solution of a monovalent ion i and a monovalent ion j is expressed by the Nicolsky-Eisenman equation as follows:

$$E = E^\circ \pm S \log(a_i + K_{ij}^{\text{Pot}} a_j). \quad (1)$$

Where S is the potential difference for a decade change of a_i . When a_i is much higher than $K_{ij}^{\text{Pot}} a_j$, namely $a_i \gg K_{ij}^{\text{Pot}} a_j$, Eq.(1) can be approximated by

$$E = E^\circ \pm S \log a_i. \quad (2)$$

On the other hand, when $K_{ij}^{\text{Pot}} a_j$ is much higher than a_i , Eq.(3) is obtained as the approximation:

$$E = E^\circ \pm S \log K_{ij}^{\text{Pot}} + S \log a_j. \quad (3)$$

Now, let us assume that the sum of $\log a_i$ and $\log a_j$ in a series of the mixed solutions of i and j is constant:

$$\log a_i + \log a_j = \text{constant} = A. \quad (4)$$

Substituting Eq.(4) into Eq.(3),

$$E = E^\circ \pm S \log K_{ij}^{\text{Pot}} + SA - S \log a_i. \quad (5)$$

At the intersection of two extrapolated linear parts of

the $\log a_i$ - E curve, the potential expressed by Eq.(2) is equal to the potential by Eq.(5), where $a_i = a_i'$,

$$E^\circ \pm S \log a_i' = E^\circ \pm S \log K_{ij}^{\text{Pot}} + SA - S \log a_i' \quad (6)$$

that is,

$$K_{ij}^{\text{Pot}} = a_i'^2 \times 10^{-A} \quad (7)$$

When i is a z valent ion and j is a n valent ion, the general form of Eq.(7) is expressed by

$$K_{ij}^{\text{Pot}} = a_i'^z \left(\frac{z}{n}\right) \times 10^{-\left(\frac{zA}{n}\right)} \quad (8)$$

The above mentioned theory show that the selectivity coefficient, K_{ij}^{Pot} , can easily be calculated from a_i' , the activity at the intersection of the two extrapolated linear parts of the $\log a_i$ - E curve, and A , the sum of $\log a_i$ and $\log a_j$ in the series of the mixed solution.

Experimental

Apparatus

All the electrode potential measurements were made with an Orion Model 801A Digital Ionanalyzer with an Orion Model 90-02-00 double junction reference electrode. The electrodes used were commercially available Orion's 94-09 fluoride selective, Matsushita's pCl IE-510103 chloride selective, and pBr IE-510104 bromide selective electrodes. A potassium ion selective electrode was prepared in our laboratory from 4 mg of valinomycin, 400 mg of dioctylphthalate and 0.17 g of polyvinylchloride.

All the chemicals used were of reagent grade quality.

Procedure

Prepare a series of mixed solutions of a primary ion i and an interfering ion j . The sum of the logarithm of activity i and the logarithm of activity of j in the mixed solutions should be kept constant. However, the preparation of such a series of mixed solutions is difficult in the most rigorous sense. Therefore, adjust the sum of the logarithm of concentration of i and the logarithm of concentration of j to a constant value, A' (see Results and Discussion). Measure the electrode potential with the series of mixed solutions. Plot the electrode potential on a semi-logarithmic graph paper with the activity of the primary ion as abscissa. Extrapolate the two linear parts of the logarithm of the activity-potential curve and determine the activity of the primary ion at the intersection of the two lines. Calculate the selectivity coefficient, K_{ij}^{Pot} , using the Eq.(8).

Results and Discussion

For the determination of the selectivity coefficient of the fluoride selective electrode against anions, a series of mixed solutions, such as 10^0 M fluoride and 10^{-6} M anion, 10^{-1} M fluoride and 10^{-5} M anion, 10^{-2} M

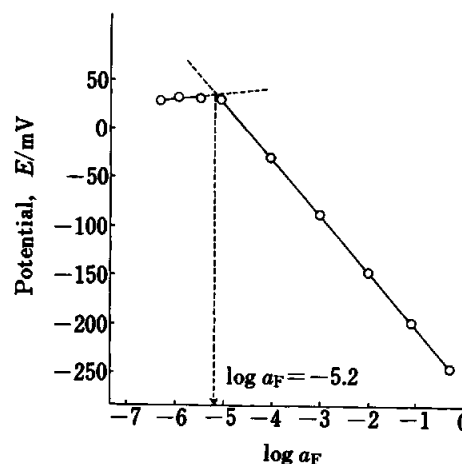


Fig. 1 Activity-potential curve obtained with the proposed method. Electrode, Orion 94-09 fluoride selective electrode; volume of solutions, 50 ml; temperature, 25°C. $A' = -6.0$.

fluoride and 10^{-4} M anion and so on, was prepared. In this series of mixed solutions, the sum of the logarithm of concentration of fluoride and the logarithm of concentration of anion was kept at a constant value, *i.e.*, $A' = -6.0$. Then, the activity of fluoride ion in each mixed solution was calculated, using Eq(9):

$$\log f = -0.511z^2 \sqrt{\mu} / (1 + \sqrt{\mu}) \quad (9)$$

where f is the activity coefficient of fluoride ion, z is its charge and μ is the ionic strength of the solution.

An example of $\log a_i$ - E (i is F^- ion) curve, obtained with the fluoride selective electrode using the series of mixed solutions prepared from fluoride and chloride, is shown in Fig. 1. The logarithm of activity of fluoride ion at the intersection of the two linear parts of the $\log a_F$ - E curve was found to be -5.2 . The sum of the logarithm of fluoride and chloride activities for the series of the mixed solutions was between -6.0 and -6.5 . The mean value of the sum of the logarithms of the activities was calculated to be -6.2 . The selectivity coefficient, K_{ij}^{Pot} , was calculated with Eq.(10):

$$K_{F-Cl}^{\text{Pot}} = 10^{-5.2 \times 2} \times 10^{6.2} = 10^{-4.2} = 6.3 \times 10^{-5} \quad (10)$$

The selectivity coefficient was also determined with the well-known mixed solution method, with 10^0 M concentration of chloride ion as a constant level of the interfering ion. The selectivity coefficient, K_{F-Cl}^{Pot} determined with the mixed solution method was 5.0×10^{-5} and agreed with that determined with the proposed continuous variation method. Following the same procedure, selectivity coefficients for the fluoride selective electrode against other halogenide ions were determined using the proposed continuous variation method and the mixed solution method. The results are summarized in Table 1.

Small differences were found between selectivity coefficients obtained by the two methods. These differences can be attributed to the following reasons. In the proposed method, A , the sum of the logarithms

Table 1 Selectivity coefficients for a fluoride selective electrode determined with the two methods

	Proposed method	Mixed solution method
K_{F-Cl}^{Pot}	6.3×10^{-5}	5.0×10^{-5} (10^0 M)
K_{F-Br}^{Pot}	5.0×10^{-4}	2.0×10^{-4} (10^{-1} M)
K_{F-I}^{Pot}	7.9×10^{-5}	4.0×10^{-5} (10^0 M)

Electrode, Orion 94-09 fluoride selective electrode; volume of solutions, 50 ml; temperature, 25°C. A' was adjusted at -6.0 in the proposed method. The concentration of interfering ions in the mixed solution method is shown in the parentheses.

Table 2 Selectivity coefficients for chloride and bromide selective electrodes determined with the two methods

	Proposed method	Mixed solution method
K_{Cl-F}^{Pot}	1.0×10^{-3}	5.9×10^{-4} (10^{-1} M)
K_{Cl-Br}^{Pot}	16	3.2 (10^{-3} M)
$K_{Cl-SO_4}^{Pot}$	3.0×10^{-4}	5.0×10^{-4} ($10^{-0.5}$ M)
K_{Br-I}^{Pot}	1.6	4.0 (10^{-4} M)
$K_{Br-CO_3}^{Pot}$	1.0×10^{-3}	2.0×10^{-2} (10^{-3} M)

Electrode, Matsushita pCl IE-510103 chloride selective and Matsushita pBr IE-510104 bromide selective electrodes; volume of solutions, 50 ml; temperature, 25°C. A' was adjusted at -6.6 in the proposed method. The concentration of interfering ions in the mixed solution method is shown in the parentheses.

of activities of fluoride and anion in a series of the mixed solutions was not strictly constant, and the mean value of the sum of the logarithms of activities of the two ions was used. The approximation may result in a small error in the determination of the selectivity coefficient. On the other hand, in the mixed solution method, the values of selectivity coefficient varied according to the activity of the anion in the mixed solutions.

In the proposed method, the intersection of the two linear parts of the $\log a_i-E$ curve can be determined easily, because the activity ratio of i and j ion in a series of the mixed solutions changes more widely than the ratio in the mixed solution method. However, it is preferable that at least 3 points of the measurements on each linear part of the $\log a_i-E$ curve should be necessary for the accurate determination of the selectivity coefficient, as shown in Fig. 1.

Selectivity coefficients of a chloride selective electrode, Matsushita pCl IE-510103, and a bromide selective electrode, Matsushita pBr IE-510104, against various anions were determined with the proposed method. Mixed solutions of chloride or bromide (primary ion) and anions (interfering ion) in which A' was adjusted at -6.6 , were prepared. The mixed solution method was also applied to the determination of selectivity coefficients. Table 2 shows the results. The selectivity coefficients determined with the pro-

Table 3 Selectivity coefficients for a potassium ion selective electrode determined with the two methods

	Proposed method	Mixed solution method
$K_{K-NH_4}^{Pot}$	3.6×10^{-2}	2.4×10^{-2} (10^{-1} M)
K_{K-Li}^{Pot}	2.5×10^{-4}	1.2×10^{-4} (10^{-1} M)
K_{K-Na}^{Pot}	7.9×10^{-4}	6.0×10^{-4} (10^{-1} M)
K_{K-Rb}^{Pot}	1.0×10^0	4.8×10^{-1} (10^{-2} M)
K_{K-Cs}^{Pot}	5.6×10^{-1}	7.4×10^{-1} (10^{-2} M)

Electrode, valinomycin-based potassium selective electrode; volume of solutions, 50 ml; temperature, 25°C. A' was adjusted at -6.6 in the proposed method. The concentration of interfering ions in the mixed solution method is shown in the parentheses.

posed continuous variation method and the mixed solution method coincided, except for the selectivity coefficient of a bromide selective electrode against nitrate. Here the value obtained by the proposed method was one-twentieth of that obtained by the mixed solution method.

The proposed method was applied to the determination of selectivity coefficients of a valinomycin-based potassium ion selective electrode prepared in our laboratory. A series of mixed solutions of potassium chloride and alkali chloride, in which A' was adjusted at -6.6 , was prepared. The mixed solution method was applied to the determination of the selectivity coefficients of the potassium ion selective electrode for various alkali ions. The results are summarised in Table 3. Good agreement was observed between the selectivity coefficients determined by the two methods.

In conclusion, the selectivity coefficient determined with the proposed continuous variation method agreed with those obtained with the conventional mixed solution method. The main advantage of the proposed method was that only one series of measurements was necessary with a series of mixed solutions of the primary and the interfering ions, even when the value of the selectivity coefficient could not be presumed.

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