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# SELECTIVITY COEFFICIENTS FOR ION-SELECTIVE ELECTRODES: RECOMMENDED METHODS FOR REPORTING $K^{pot}_{A,B}$ VALUES

(Technical Report)

*Prepared for publication by*

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# Selectivity coefficients for ion-selective electrodes: Recommended methods for reporting $K_{A,B}^{pot}$ values (Technical Report)

**Synopsis:** The limitations of the Nicolsky-Eisenman (N-E) equation for the determination of potentiometric selectivity coefficients, $K_{A,B}^{pot}$, were critically evaluated in terms of $K_{A,B}^{pot}$ values for ions of unequal charge, non-Nernstian behavior of interfering ions, and activity dependence of $K_{A,B}^{pot}$. The reasons for the activity dependence of $K_{A,B}^{pot}$ and for non-equalities of values depending on the method employed were thus elucidated. Also, when ions of different charge were involved, $K_{A,B}^{pot}$ values obtained were found to be either unrealistically large or small depending on whether the ion of higher charge was considered as a primary or an interfering ion. On the basis of these considerations, new approaches including the matched potential method, a method independent of the N-E equation, were recommended for the determination of $K_{A,B}^{pot}$.

## INTRODUCTION

The first IUPAC recommendation on potentiometric selectivity coefficients ($K_{A,B}^{pot}$) for ion-selective electrodes (ISEs) was published in 1976 as part of "Recommendations for nomenclature of ion-selective electrodes" (ref. 1). Since then, no further IUPAC recommendation on potentiometric selectivity coefficients has been reported.

The following is an excerpt of the above IUPAC recommendation.

*Methods for determining $K_{A,B}^{pot}$*

*1. Fixed interference method. The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of interference, $a_B$, and varying activity of the primary ion, $a_A$. The potential values obtained are plotted vs. the activity of the primary ion. The intersection of the extrapolation of the linear portions of this curve will indicate the value of $a_A$ which is to be used to calculate $K_{A,B}^{pot}$ from the equation:*

$$K_{A,B}^{pot} = a_A/(a_B)^{z_A/z_B} \qquad (1)$$

*where both $z_A$ and $z_B$ have the same signs, positive or negative.*

*2. Separate solution method. The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with each of two separate solutions, one containing the ion A at the activity $a_A$ (but no B), the other containing the ion B at the same activity $a_B = a_A$ (but no A). If the measured values are $E_1$ and $E_2$, respectively, the value of $K_{A,B}^{pot}$ may be calculated from the equation:*

$$log\ K_{A,B}^{pot} = \frac{E_2 - E_1}{2.303\ RT/z_A F} + (1 - z_A/z_B)log\ a_A \qquad (2)$$

*This method is recommended only if the electrode exhibits a Nernstian response. It is less desirable because it does not represent as well the actual conditions under which the electrodes are used.*

The popularity of this IUPAC recommendation has been fairly high. Among over 1600 electrodes cited in papers published from 1966 through summer 1988, more than 60 % followed the IUPAC recommendation (ref. 2).

However, it has been reported by many researchers that some discrepancies were found among selectivity coefficients determined under different conditions, e.g., with different activities of the primary and/or interfering ions and/or by different methods (refs. 2, 3). This suggests that a selectivity coefficient is not a physical constant but a value which changes according to experimental conditions. There are several reasons for the inconsistency of the selectivity coefficients presented by various authors:

(1) Non-validity of theoretical assumptions that were used in calculations of selectivity coefficients, (2) Differences in the membrane composition for nominally the same ion-selective electrodes, especially variations of functional groups of plasticizers and dielectric constants, (3) Differences in analyte activities, (4) Response mechanisms that are not based on the assumption of the Nicolsky-Eisenman equation (N-E equation), e.g., ion-exchange (ref. 4).

In view of the above consideration, systematic studies were conducted as follows: Theoretical (calculated) values, literature values and additional measured values of selectivity coefficients were critically evaluated with respect to the (a) method employed, (b) dependence on $a_A$, $a_B$ and $a_A/a_B$ and (c) cases where $z_A$ is not equal to $z_B$, where $a_A$ and $a_B$ are the activities of the primary ion A and the interfering ion B, respectively, and $z_A$ and $z_B$ are the corresponding charges. We thus critically evaluated the present problems and made the most rational recommendations for the method of determining selectivity coefficients for ISEs.

## LIMITATION OF THE NICOLSKY-EISENMAN (N-E) EQUATION

### $K_{A,B}^{pot}$ with Ions of Unequal Charge

A precise description of the glass electrode potential in mixtures of any two monovalent cations was given as an empirical equation by Eisenman et al. as follows (ref. 5):

$$E = const. + (RT/F) \ln \{(a_A)^{1/n} + (K_{A,B}^{pot})^{1/n} (a_B)^{1/n}\}^n \qquad (3)$$

where $R$, $T$, and $F$ have their usual meanings, and $n$ is an empirical constant for a given glass composition

and cation pair (A, B). Equation (3), when $n$ equals to 1, is identical with the equation theoretically predicted by Nicolsky for a monovalent cation selective glass electrode (ref. 6). Indeed, $n$ was found experimentally, in many cases, to be nearly 1. Eisenman et al. regarded $K_{A,B}^{pot}$ as a measure of the sensitivity to the interfering ion B, as compared to that of the primary ion A, for the glass electrode under study. Eisenman and co-workers extensively studied the electrode response behavior of glass electrodes to binary or ternary mixtures of monovalent cations and established experimentally and theoretically that equation (3) can describe potential behavior of the glass electrode (ref. 7). Later, they showed theoretically that the potential of a monovalent ion-selective ion-exchange liquid membrane as well as a neutral carrier liquid membrane in a binary mixture of monovalent cations can also be fitted to equation (3), where $n = 1$ (refs. 8, 9).

Garrels et al. obtained also similar empirical equations for the potentials not only of monovalent but also divalent cation selective glass electrodes with different compositions in mixtures of two divalent cations and of a divalent and a monovalent cations (ref. 10).

$$E = \text{const.} + (RT/z_A F) \ln \{(a_A)^{1/n} + (K_{A,B}^{pot})^{1/n} (a_B)^{z_A/n\, z_B}\} \tag{4}$$

where $z_A$ and $z_B$ are the charges of the primary and interfering ions and are 1 or 2.

Ross claimed that the electrode potential of a calcium ion-selective liquid ion-exchange membrane electrode immersed in mixed solutions containing $Ca^{2+}$ and $M^{r+}$ (r = 1 or 2) can be fitted by equation (4), where $n = 1$ (ref. 11).

On the basis of these studies, the following N-E equation (5) was eventually established.

$$E = \text{const.} + (RT/z_A F) \ln \{a_A + \sum_{B \neq A}^{B} K_{A,B}^{pot} (a_B)^{z_A/z_B}\} \tag{5}$$

This equation has a symmetrical form with respect to the primary and interfering ions and assumes the Nernstian electrode response not only to the primary but also to interfering ions.

In the late 1960s, several different workers started using the N-E equation to determine the selectivity coefficients for multivalent cation selective electrodes, such as $Ca^{2+}$ and $La^{3+}$ selective liquid membrane electrodes. The N-E equation thus became popular as an equation to be chosen to describe the potential of an ISE in mixtures of not only monovalent cations but also of multivalent ions (ref. 12).

However, the situation was not so simple. Although Garrels et al. were able to describe by equation (4) the potentials of glass electrodes immersed in a mixture of univalent and divalent cations, they did not show as to whether the selectivity coefficient values obtained could be used as an appropriate measure of sensitivity to the interfering ion B as compared to that of the primary ion A (ref. 10). The calibration curve for $Ca^{2+}$ is drawn here from Garrels and co-workers' numerical data, obtained with measurements carried out under a constant background of $10^{-3.016}$ M $K^+$ as an interfering ion (ref. 10) (Figure not shown). The calibration curve becomes linear with a nearly Nernstian slope for $Ca^{2+}$ activities above $10^{-4}$ M, suggesting that the electrode is more selective to $Ca^{2+}$ than $K^+$. If the electrode preference to $K^+$ is nearly the same as to $Ca^{2+}$, i.e., $K_{Ca,K}^{pot} \sim 1$, then the calibration curve should still be governed by $K^+$ at the $Ca^{2+}$ activity of $10^{-4}$ M. Garrels et al. obtained the value of 42.8 for $K_{Ca,K}^{pot}$, using the empirical

equation (4) and the numerical data, i.e., potential and activity values, which seems too large, and therefore it does not seem to be useful for actual analytical purpose. From the above consideration, it is already clear that the N-E equation does not apply even to the $Ca^{2+}/K^+$ system at a glass electrode, to obtain a reasonable selectivity coefficient value in an analytical sense.

When the N-E equation became popular, the similar problems as the above mentioned one in determining selectivity coefficients for systems with ions of unequal charge have been reported simultaneously by several workers (refs. 12b, 13). Harrell et al. pointed out that the values of $K_{A,B}^{pot}$ could be somewhat misleading in the case of $A^{3+}$-$B^{1+}$ combinations for the primary and interfering ions, because the $(a_B)^{z_A/z_B}$ term became quite small for low activities of $B^{1+}$. The $B^{1+}$ ions interfered little for $K_{A,B}^{pot}$ =100 and even for $K_{A,B}^{pot}$ =1,000, determined by the two solution method (see Appendix), as the change in EMF was only 2 - 3 % (ref. 12b). The same effect was able to be seen even more clearly in the case of an adenosine 5'-triphosphate ($ATP^{4-}$) ISE against $Cl^-$ (ref. 13d). The smaller charge of the interfering ion, $Cl^-$, compared to that of the primary ion, $ATP^{4-}$ ($z_A$=-4), made the measured value of $K_{ATP,Cl}^{pot}$ determined with the N-E equation (5) unrealistically large. Cattrall et al. found that the obtained value of 1.15 for $K_{Ca,Na}^{pot}$ that was calculated by the two solution method, with a 10 mV potential change by the addition of a 100-fold excess of $Na^+$ over $Ca^{2+}$, was too large (ref. 14). Thus, they omitted the index $z_A/z_B$ from the base $a_B$ in the N-E equation.

$$E = \text{const.} + (RT/z_A F) \ln[a_A + K_{A,B}^{pot} a_B] \qquad (6)$$

The resulting value for $K_{Ca,Na}^{pot}$ using equation (6) was found to be 0.012, which was thought to be a far more meaningful value for practical situations.

In order to scrutinize this problem concerning the power term, numerical calculations were also performed by the two solution-, fixed interference- and separate solution methods based on the N-E equation for various model experimental conditions (ref. 15). Some of the results from these calculations are presented in Figure 1, where appropriate values of activities for the primary and interfering ions, $a_A$ and $a_B$, and the potential change or potential difference, $\Delta E$, which showed each electrode's preference to the
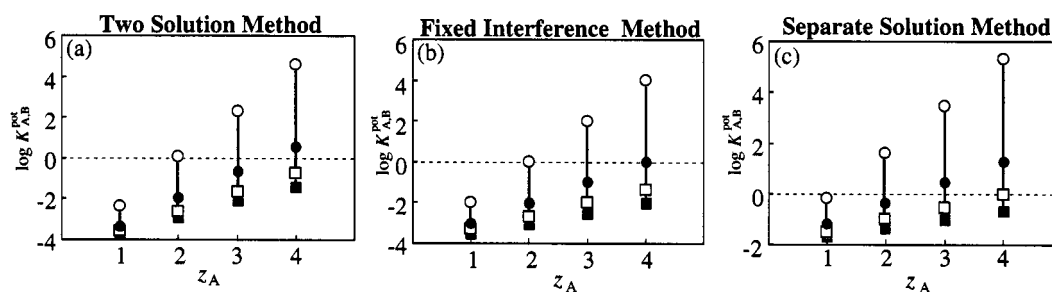


**Figure 1.** Numerical calculations of the power term ($a^{z_A/z_B}$) dependence of selectivity coefficients based on the N-E equation (5). The x-axis indicates the charge of the primary ions ($z_A$), and the y-axis covers ranges of calculated $K_{A,B}^{pot}$ values depending on $z_B$ values, 1(○), 2(●), 3(□) and 4(■), respectively.
(a) Selectivity coefficients calculated from the two solution method with numerical values of $\log a_A$= -4, $\log a_B$= -2 and $\Delta E$ = 10 mV. (b) Selectivity coefficients calculated from the fixed interference method with numerical values of $\log a_A$= -4 and $\log a_B$= -2. (c) Selectivity coefficients calculated from the separate solution method with numerical values of $\log a_A$ = $\log a_B$= -2 and $\Delta E$ = -10 mV.

primary ion over the interfering ion, were given for the model experimental conditions. As can be seen in Figure 1, selectivity coefficients calculated are either unrealistically large or small depending on whether the ion of higher charge was considered as the primary or the interfering ion. These distorted values can again be explained as being due to the power term $(a_B)^{z_A/z_B}$ in the N-E equation, meaning that equation (5), in general, is not valid for cases when $z_A \neq z_B$.

Meanwhile, it was reported by Bagg et al. that the potential of a calcium ion-selective liquid membrane electrode in mixed solutions of $CaCl_2$-$M^+X^-$, i.e., $z_A \neq z_B$, did not obey the N-E equation, but followed equation (7) (ref. 16).

$$E = \text{const.} + RT/F \ln \{(a_{Ca^{2+}})^{1/2} + K_{Ca,M}^{pot}(a_{M^+})\} \tag{7}$$

Buck extended equation (7) and recently proposed the following modified N-E equation (ref. 17), based on the theoretical consideration and digital simulation (ref. 18).

$$E = \text{const.} \pm RT/F \ln [(a_A)^{1/|z_A|} + \sum_{B \neq A}^{B} K_{A,B}^{pot}(a_B)^{1/|z_B|}] \tag{8}$$

where choice of the sign + or - is dependent on the charge of the primary ion. This equation becomes identical to the N-E equation for $|z_A|=|z_B|=1$, but is different in other cases, including $|z_A|=|z_B|=2$, 3, and 4. Buck's modified N-E equation (8) also assumes Nernstian response to interfering ions as well. Selectivity coefficients obtained based on equation (8) exhibit a weaker power-term dependence as compared to those based on the conventional N-E equation where the same values of $a_A$, $a_B$, and $\Delta E$ with those in Figure 1 were given to calculate selectivity coefficients (calculated results not shown). This weaker power-term dependence is due to the power term being $1/|z_B|$ instead of $z_A/z_B$. In the N-E equation, the term $(a_B)^{z_A/z_B}$ varies from $(a_B)^4$ to $(a_B)^{1/4}$, assuming that the value of $\pm 4$ is a maximum charge of $z_A$ and $z_B$, while in Buck's modified equation, $(a_B)^{1/|z_B|}$ varies from $a_B$ to $(a_B)^{1/4}$. The numerical range of variation for the magnitude of the activity term for interfering ions in equation (8) is obviously smaller than that in the N-E equation. However, equation (8) still does not appear to yield values which can be used readily for the interpretation of selectivity values.

From the above experimental and numerical considerations, it is concluded that selectivity coefficients based on the conventional N-E equation, including its modified equations, for cases with ions of unequal charge are inaccurate and unacceptable. The reason for this is that the validity of equation (3) described earlier was tested only for the glass electrode that senses alkali metal cations, and its *a priori* extension to the ions of different charge and to other types of membranes has not been justified yet. Recommendations are, therefore, needed in some cases by a method independent of the N-E equation, concerning selectivity coefficients for systems with ions of *different charge*.

## Non-Nernstian Behavior of Interfering Ions

When a new electrode is constructed, log $a$ vs. $E$ relations are measured first. One is pleased in this case if only a primary ion shows a Nernstian behavior and others do not. However, as far as the validity for the use of the N-E equation is concerned, this involves a fatal paradox, because the N-E equation assumes a Nernstian behavior for interfering ions as well.

We experimentally reexamined calibration curves of some of the most typical representative electrodes, including a F⁻ ISE, a Br⁻ ISE, a $NO_3^-$ ISE, two $Ca^{2+}$ ISEs and a $K^+$ ISE at 25 ± 1 °C (Figures not shown). The results clearly show that the calibration curves for most of the interfering ions exhibit non-Nernstian slopes, although each primary ion leads to a Nernstian slope: A F⁻ ISE based on $LaF_3$ showed a typical Nernstian slope of -59 mV/decade for F⁻; however, only -32 mV/decade for OH⁻. A Br⁻ ISE based on $AgBr/Ag_2S$ also shows a slope of -59 mV/decade for Br⁻, but -53 mV/decade for Cl⁻. Also, a $Ca^{2+}$ ISE based on ETH 1001 exhibits a slope of 29 mV/decade for $Ca^{2+}$, but 24 mV/decade and 8 mV/decade for $Sr^{2+}$ and $Ba^{2+}$, respectively. A $Ca^{2+}$ ISE based on an ion-exchanger, calcium salt of bis(4-octylphenyl)phosphate, gave a slope of 28 mV/decade for $Ca^{2+}$, but 10 mV/decade for $Mg^{2+}$, 19 mV/decade for $Cd^{2+}$, and 24 mV/decade for $Sr^{2+}$. A $NO_3^-$ ISE based on an ion-exchanger gave a slope of -55 mV/decade for $NO_3^-$, but -40 mV/decade for Cl⁻, -50 mV/decade for Br⁻, -59 mV/decade for I⁻ and -162 mV/decade for $ClO_4^-$. A $K^+$ ISE based on valinomycin shows a Nernstian slope of 59 mV/decade for $K^+$, $Rb^+$ and $Cs^+$. Among these popular ISEs, only the valinomycin based $K^+$ ISE was thus found to show a Nernstian behavior for both primary and some of interfering ions. However, these results were naturally just what was desired from the viewpoint of quality ISE developments. If one tries to be faithful to the original assumption of the N-E equation and $K_{A,B}^{pot}$ values are calculated, thereby problems arise. Like the case of the power-term problem with ions of unequal charge (*vide supra*), this is another inherent problem of the N-E equation (*vide infra*). Again the N-E equation was established essentially for the glass electrode for alkali metal ions, and therefore it was initially not expected to be used universally for all kinds of modern ISEs for which each interfering ion is often expected to exhibit non-Nernstian slopes.

## *Activity Dependence of $K_{A,B}^{pot}$ Values*

According to the previous IUPAC recommendation on the determination of selectivity coefficients (ref. 1), the separate solution method alone explicitly specifies that both primary and interfering ions need to exhibit Nernstian responses. However, for obtaining selectivity coefficients based on the N-E equation, Nernstian responses are always required not only for the primary ion but also for the interfering ions (*vide supra*). This results from the power term $(a_B)^{z_A/z_B}$ in the N-E equation. As long as this principle is fulfilled, the evaluation of the selectivity coefficients should give the same result independently of the detailed measurement procedure, including the method employed, and of the activities of the ions A and B at which selectivity coefficients are determined. But the dependence of $K_{A,B}^{pot}$ on $a_A$ and/or $a_B$ values, at which $K_{A,B}^{pot}$ values are determined, occurs when the response of the electrode to the primary and/or the interfering ions is non-Nernstian.

The activity dependence of selectivity coefficients obtained by several methods based on the N-E equation for representative ISEs, which showed non-Nernstian behavior to the interfering ions (*vide supra*), are typically shown in Table 1. The only exceptions are values of $K_{K,Rb}^{pot}$ and $K_{K,Cs}^{pot}$ obtained for a valinomycin based $K^+$ ISE; these values were dependent neither on activities nor methods employed and agreed well with each other. The latter results are simply due to the fact that the responses of the above

Table 1. Experimental Selectivity Coefficients Determined by Several Different Methods

| Electrode | Interfering ion | Selectivity coefficient, $K_{A,B}^{pot}$ | | | |
| --- | --- | --- | --- | --- | --- |
| | | Separate solution method[a] | Two solution method[b] | Fixed primary ion method[c] | Matched potential method[d] |
| F⁻ ISE[e] | OH⁻ | $7.5 \times 10^{-2}$ ($10^{-4.11}$)<br>$2.4 \times 10^{-2}$ ($10^{-3.11}$)<br>$7.5 \times 10^{-3}$ ($10^{-2.11}$) | $4.0 \times 10^{-2}$ ($10^{-5.11}$, $10^{-4.11}$)<br>$5.6 \times 10^{-2}$ ($10^{-4.86}$, $10^{-4.11}$) | $5.0 \times 10^{-2}$ ($10^{-5.11}$)<br>$3.6 \times 10^{-2}$ ($10^{-4.86}$) | $3.1 \times 10^{-2}$ ($10^{-5.11}$)<br>$2.5 \times 10^{-2}$ ($10^{-4.86}$) |
| Br⁻ ISE[f] | Cl⁻ | $1.0 \times 10^{-2}$ ($10^{-4.07}$)<br>$3.2 \times 10^{-3}$ ($10^{-3.07}$)<br>$2.9 \times 10^{-3}$ ($10^{-2.08}$) | $2.6 \times 10^{-3}$ ($10^{-6.07}$, $10^{-4.07}$)<br>$3.4 \times 10^{-3}$ ($10^{-6.07}$, $10^{-3.07}$)<br>$3.2 \times 10^{-3}$ ($10^{-6.07}$, $10^{-2.08}$)<br>$3.5 \times 10^{-3}$ ($10^{-5.07}$, $10^{-3.07}$)<br>$4.0 \times 10^{-3}$ ($10^{-5.07}$, $10^{-2.08}$) | $3.7 \times 10^{-3}$ ($10^{-6.07}$)<br>$7.1 \times 10^{-3}$ ($10^{-5.07}$) | $3.4 \times 10^{-3}$ ($10^{-6.07}$)<br>$2.2 \times 10^{-3}$ ($10^{-5.37}$)<br>$2.6 \times 10^{-3}$ ($10^{-5.07}$) |
| K⁺ ISE[g] | Rb⁺ | $2.7$ ($10^{-5.11}$)<br>$2.9$ ($10^{-4.11}$)<br>$2.9$ ($10^{-3.11}$)<br>$3.0$ ($10^{-2.11}$) | $2.9$ ($10^{-5.11}$, $10^{-4.11}$)<br>$2.8$ ($10^{-4.11}$, $10^{-3.11}$) | $2.9$ ($10^{-5.11}$)<br>$2.7$ ($10^{-4.11}$) | $3.0$ ($10^{-5.11}$)<br>$2.8$ ($10^{-4.11}$) |
| | Cs⁺ | $4.6 \times 10^{-1}$ ($10^{-5.11}$)<br>$4.5 \times 10^{-1}$ ($10^{-4.11}$)<br>$4.5 \times 10^{-1}$ ($10^{-3.11}$) | $4.2 \times 10^{-1}$ ($10^{-5.11}$, $10^{-4.11}$)<br>$4.6 \times 10^{-1}$ ($10^{-4.11}$, $10^{-3.11}$) | $4.5 \times 10^{-1}$ ($10^{-5.11}$)<br>$4.3 \times 10^{-1}$ ($10^{-4.11}$) | $4.7 \times 10^{-1}$ ($10^{-5.11}$)<br>$4.3 \times 10^{-1}$ ($10^{-4.11}$) |
| | Na⁺ | | $6.0 \times 10^{-6}$ ($10^{-8.11}$, $10^{-4.11}$)<br>$1.7 \times 10^{-5}$ ($10^{-7.11}$, $10^{-3.11}$) | | $2.0 \times 10^{-4}$ ($10^{-8.11}$)<br>$8.2 \times 10^{-5}$ ($10^{-7.11}$) |

Figures in parentheses refer to; [a] activities of the primary and interfering ions ($a_A = a_B$); [b] activities of the primary and interfering ions ($a_A$, $a_B$); and [c, d] activities of the primary ion ($a_A$); at which selectivity coefficients were determined. [e] A single crystal $LaF_3$ based F⁻ ISE. [f] An $AgBr/Ag_2S$ based Br⁻ ISE. [g] A valinomycin based K⁺ ISE; (valinomycin 1wt%, dioctyl sebacate 66 wt%, poly(vinyl chloride) 33 wt%). [e, f, g] Slopes for the primary and interfering ions of these ISEs are given in Text. All activity values were calculated using an extended Debye-Hückel equation (ref. 24).

valinomycin based K$^+$ ISE to these two interfering ions, Rb$^+$ and Cs$^+$, were Nernstian, and ideally satisfied the prerequisite for the use of the N-E equation. In contrast, selectivity coefficients against Na$^+$, which did not yield a Nernstian slope to the valinomycin based K$^+$ ISE, showed an activity dependence as expected.

## A METHOD INDEPENDENT OF THE N-E EQUATION

Although Rechnitz et al. described the use of the activity ratio method (separate solution method) for a preliminary definition of selectivity coefficients already in 1966 (ref. 19), the necessity to develop methods, if any, independent of the extended Nernst equations appears to be first discussed by Gadzekpo and Christian only in 1984 (ref. 20). They proposed the "matched potential method", which is totally independent of the N-E equation, to overcome the above-stated difficulty in obtaining accurate selectivity coefficients when ions of unequal charge are involved. In this method, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion which gives the same potential change in a reference solution. To determine the selectivity coefficient, one would measure the change in potential upon changing the primary ion activity (concentration). The interfering ion would then be added to an identical reference solution until the same potential change is obtained. The change in potential must be produced in a constant initial background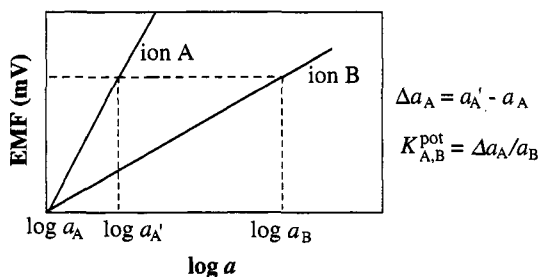 of the primary ion and must be the same in both cases (Figure 2). This method has thereby a sound analytical basis on which we judge obtained values of $K_{A,B}^{pot}$ to be practically realistic. The same or similar approach has been intuitively applied already by users and developers of ISEs. An electrode maker has used probably a similar concept to specify their products (ref. 21): They defined, for convenience, the following two terms: "level of interference for 10 % error" (e.g., at $10^{-3}$ M NO$_3^-$, $10^{-7}$ M ClO$_4^-$ etc. for an Orion 93-07 NO$_3^-$ ISE) and "maximum ratio (interference/sensed ion) for no interference" (e.g., $10^{-1}$ M I$^-$ for an Orion 94-06 CN$^-$ ISE).



$$\Delta a_A = a_A' - a_A$$

$$K_{A,B}^{pot} = \Delta a_A / a_B$$

**Figure 2.** Determination of selectivity coefficients by the matched potential method (ref. 20). ion A, the primary ion; ion B, the interfering ion; $a_A$, initial background activity of ion A.

The characteristics of the matched potential method are: (1) The charge number of the primary and interfering ions does not need to be taken into consideration, and (2) Nernstian responses are assumed neither to the primary nor interfering ions. These characteristics lead to the following advantages: (1) The power-term problem for ions of unequal charge disappears, and (2) This method is widely applicable, even to non-Nernstian interfering ions. However, this method is independent of the N-E equation or its modified forms, and it is therefore difficult to correlate the values of $K_{A,B}^{pot}$ obtained by this method with any particular physical phenomena such as ion-exchange. In other words, the values obtained by this method should be regarded as of practical significance. It should be noted, however, that the $K_{A,B}^{pot}$ values obtained by the matched potential method for cases in which both primary and interfering ions have the same

charge and respond in a Nernstian manner should agree well with those obtained by methods based on the N-E equation. A typical example is illustrated in Table 1 for the case of a valinomycin-based $K^+$ ISE. Table 2 shows the comparison of $K_{A,B}^{pot}$ values for an $ATP^{4-}$ ISE obtained experimentally by the matched potential- and two solution methods. The $K_{A,B}^{pot}$ values obtained by the matched potential method can be regarded as being consistent in magnitude with a real analytical situation in that the influence of the interfering ions is evaluated as the ratio of $ATP^{4-}$ concentration to the interfering ion concentration which gives the same potential change in a reference solution (*vide supra*). The values based on the N-E equation, the two solution method in this case, are misleading and unrealistic when ions of different charge are involved.

When the extent of interference is small, in applying the matched potential method, it sometimes occurs that an equal potential change can not be obtained even by adding a very concentrated interfering ion solution. In such cases, it is necessary to measure a smaller primary ion increment or a potential change in a more dilute reference solution (ref. 20). As the slopes of the primary and interfering ions are often neither Nernstian nor linear, it is natural to expect that $K_{A,B}^{pot}$ values determined by the matched potential method might show the dependence on the activity of the primary ion contained in a reference solution.

**Table 2.** **Comparison of Experimental Selectivity Coefficients for an $ATP^{4-}$ ISE Against Various Possible Interfering Anions Determined by the Matched Potential- and Two Solution Methods**

| | Selectivity coefficient, log $K_{A,B}^{pot}$ | |
|---|---|---|
| Ion B | Matched Potential Method[a] | Two Solution Method[b] |
| $Cl^-$ | -3.24 | 2.03 |
| $Br^-$ | -1.40 | 9.39 |
| $NO_3^-$ | -0.90 | 11.39 |
| $SCN^-$ | -0.36 | 13.55 |
| $ClO_4^-$ | -0.26 | 13.95 |
| $SO_4^{2-}$ | -2.83 | -0.67 |
| $HPO_4^{2-}$ | -2.83 | -0.67 |
| $AMP^{2-, c}$ | -1.52 | 1.95 |
| $ADP^{3-, d}$ | -1.45 | -0.28 |
| $P_3O_{10}^{5-}$ | -0.08 | -1.73 |
| $P_4O_{13}^{6-}$ | -0.06 | -1.06 |

[a] Taken from ref. 13d. [b] Calculated based on the same levels to those used in ref. 13d for the primary and interfering ions at which the selectivity coefficients were determined. [c] $AMP^{2-}$; adenosine 5'-monophosphate. [d] $ADP^{3-}$; adenosine 5'-diphosphate.

It is recommended, therefore, to report several $K_{A,B}^{pot}$ values at some different activities of the primary ion in such cases.

## CONCLUSION

1. The best requisite for quality ISEs, an ideal Nernstian slope for the primary ion and negligible responses for interfering ions, involves in itself a fatal paradox when one faces measurement of selectivity coefficients using the N-E equation. In fact, although the N-E equation requires both the primary and interfering ions to lead to Nernstian responses, few electrodes seem to exhibit a Nernstian behavior for both the primary and interfering ions. As a result of this, most reports have violated the prerequisite for the use of the N-E equation. This is the major reason for the activity dependence of $K_{A,B}^{pot}$ and non-equality of $K_{A,B}^{pot}$ values based on different methods.

2. In addition, the N-E equation and modifications of it were not found to be well suited when ions of different charge were involved. Selectivity coefficients obtained were either unrealistically large or small, depending on whether the ion of higher charge was considered as the primary or interfering ion. This problem resulted from the use of equation (5) for ions of unequal charge without experimental and theoretical justifications.

3. In the above two cases, obtained $K_{A,B}^{pot}$ values do not have an obvious physical significance, even if the N-E equation is formally used.

4. As expected from its measurement procedure, the matched potential method was found to give $K_{A,B}^{pot}$ values quantitatively identical to those obtained with the N-E equation based method when both the primary and interfering ions lead to Nernstian responses and have equal charge.

## RECOMMENDATIONS

1. Under the condition that both the primary and interfering ions lead to Nernstian responses, the N-E equation or its modification is recommended when ions of equal charge are involved.

2. When ions of unequal charge are involved, the matched potential method is recommended, as it gives practical $K_{A,B}^{pot}$ values.

3. When interfering ions and/or the primary ion do not satisfy the Nernstian condition, the matched potential method is recommended also, even if the charges of the primary and interfering ions are equal.

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## APPENDIX

In this paper, the described selectivity coefficients were based on several different methods, but were used without explaining their determination procedures except for those of the separate solution method, the fixed interference method and the matched potential method. A brief explanation for each of the other methods employed is given here.

(1) Fixed primary ion method (refs. 2, 22): The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of the primary ion, $a_A$, and varying activity of the interfering ion. The potential values obtained are plotted vs. the activity of the interfering ion. The intersection of the extrapolation of the linear portions of this curve will indicate the value of $a_B$ which is to be used to calculate $K_{A,B}^{pot}$ from the equation:

$$K_{A,B}^{pot} = a_A/(a_B)^{z_A/z_B}$$

(9)

(2) Two solution method (refs. 2, 23): This method was usually called as the mixed solution method and used widely, i.e., about 30 % of about 500 papers (ref. 2). And the name "two solution method" was newly named by us to make clear the difference from other mixed solution methods, such as the fixed

interference method. This method involves measuring potentials of a pure solution of the primary ion, $E_A$, and of a mixed solution containing the primary and interfering ions, $E_{A+B}$. Activities of the primary ion are the same in both solutions. And the selectivity coefficient is calculated by inserting the values of the potential difference, $\Delta E = E_{A+B} - E_A$, $a_A$ and $a_B$ into the following equation:

$$K_{A,B}^{pot} = a_A(10^{\Delta E z_A F/2.303RT} - 1)/(a_B)^{z_A/z_B} \qquad (10)$$

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