INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

POTENTIOMETRIC SELECTIVITY COEFFICIENTS OF ION-SELECTIVE ELECTRODES

PART I. INORGANIC CATIONS

(Technical Report)

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Abstract: Potentiometric selectivity coefficients, $K_{A,B}^{pot}$, have been collected for ionophore-based ion-selective electrodes (ISEs) for inorganic cations reported from 1988–1997. In addition to numerical values of $K_{A,B}^{pot}$, together with the methods and conditions for their determination, response slopes, linear concentration ranges, chemical compositions, and ionophore structures for the ISE membranes are tabulated.

INTRODUCTION

An earlier IUPAC data compilation of potentiometric selectivity coefficients, $K_{A,B}^{pot}$, for ion-selective electrodes (ISEs) was published in 1979 in *Pure and Applied Chemistry* [1]. It covered $K_{A,B}^{pot}$ data reported during 1966–1977 and was later followed by another extensive compilation of such data in a handbook from CRC Press [2]. The latter covered most of the $K_{A,B}^{pot}$ data reported during the years 1966–1988. An updated compilation reported in 1998 was limited to a number of particularly selective ionophores [3], which are lipophilic complexing agents that are incorporated into ISE membranes to selectively and reversibly bind analyte ions.

This paper presents the latest compilation of $K_{A,B}^{pot}$ data for liquid-membrane, inorganic-cation ISEs based on neutral and charged ionophores, reported between 1989 and the end of 1997. Moreover, this new compilation also contains some older data that had not been included in the CRC handbook. The presented $K_{A,B}^{pot}$ data are listed together with the methods and conditions for their determinations; also tabulated are response slopes, linear ranges, chemical compositions, and ionophore structures for the corresponding ISE membranes. This report constitutes the first part in a series. The second and third part, which will be published separately in forthcoming issues of *Pure and Applied Chemistry*, will cover ISEs for inorganic anions and organic ions, respectively.

METHODS FOR THE DETERMINATION OF POTENTIOMETRIC SELECTIVITY COEFFICIENTS [4–7]

Potentiometric selectivity coefficients can be measured with different methods that fall into two main groups, namely (1) mixed solution methods, and (2) separate solution methods. The most commonly used approach is the fixed interference method, which is a mixed solution method. This method was recommended by IUPAC in 1975 [4], but other approaches have also been frequently employed. The details of the definition of each method are given below.

The potentiometric selectivity coefficients are expressed according to the Nicolsky–Eisenman equation as

$$E = E_0 + R\,T\,/\,(z_A\,F)\,\ln\,[a_A + \sum_B K_{A,B}^{pot}\,(a_B)^{\,z_A/z_B}] \tag{1}$$

where E is the measured potential; E_0 is a constant that includes the standard potential of the electrode, the reference electrode potential, and the junction potential; z_A and z_B are charge numbers of the primary ion, A, and of the interfering ion, B; a_A and a_B are the activities of the primary ion, A, and the

interfering ion, B; and $K_{A,B}^{pot}$ is the potentiometric selectivity coefficient for the primary ion A against the interfering ion, B. R, T, and F have the usual meanings. If $K_{A,B}^{pot}$ is larger than 1, the ISE responds to the interfering ions more selectively than to the primary ions. In most cases, $K_{A,B}^{pot}$ is smaller than 1, which means that such ISEs respond to the primary ions more selectively than to interfering ions.

The Nicolsky–Eisenman equation assumes a Nernstian response not only for the primary ion but also for the interfering ion. Obviously, $K_{A,B}^{pot}$ is assumed to be constant. Several experimental methods for the determination of potentiometric selectivity coefficients are based on this equation. These methods will be explained in some detail in the following section. Notably, the Nicolsky–Eisenman equation does not correctly describe responses in the activity range in which primary and interfering ions of a different charge significantly contribute to the potential. More complex equations must be applied to describe correctly such mixed ion responses [8]. Among the four mixed solution methods, the matched potential method is unique in that it depends neither on the Nicolsky–Eisenman equation nor on any of its modifications; this method was recommended in 1995 by IUPAC as a method that gives analytically relevant practical $K_{A,B}^{pot}$ values [6].

Mixed solution methods

Fixed interference method (FIM)
The electromotive force (emf) of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) is measured for solutions of constant activity of the interfering ion, a_B, and varying activity of the primary ion, a_A. The emf values obtained are plotted vs. the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of this plot indicates the value of a_A that is to be used to calculate $K_{A,B}^{pot}$ from the following equation:

$$K_{A,B}^{pot} = a_A / (a_B)^{z_A/z_B} \tag{2}$$

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

Fixed primary ion method (FPM)
The emf of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) is measured for solutions of constant activity of the primary ion, a_A, and varying activity of the interfering ion, a_B. The emf values obtained are plotted vs. the logarithm of the activity of the interfering ion. The intersection of the extrapolated linear portions of this plot indicates the value of a_B that is to be used to calculate $K_{A,B}^{pot}$ from the following equation:

$$K_{A,B}^{pot} = a_A / (a_B)^{z_A/z_B} \tag{3}$$

Two solution method (TSM)
This method involves measuring potentials of a pure solution of the primary ion, E_A, and a mixed solution containing the primary and interfering ions, E_{A+B}. The potentiometric selectivity coefficient is calculated by inserting the value of the potential difference, $\Delta E = E_{A+B} - E_A$, into the following equation:

$$K_{A,B}^{pot} = a_A(e^{\Delta E\, z_A\, F\, /\, (R\, T)} - 1) / (a_B)^{z_A/z_B} \tag{4}$$

Matched potential method (MPM)
This method does not depend on the Nicolsky–Eisenman equation at all. In this method, the potentiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. At first, a known activity (a_A') of the primary ion solution is added into a reference solution that contains a fixed activity (a_A) of primary ions, and the corresponding potential change (ΔE) is recorded. Next, a solution of an interfering ion is added to the

reference solution until the same potential change (ΔE) is recorded. The change in potential produced at the constant background of the primary ion must be the same in both cases.

$$K_{A,B}^{pot} = (a_A{}' - a_A) / a_B \tag{5}$$

Separate solution methods

Separate solution method ($a_A = a_B$) (SSM)

The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with two separate solutions, one containing the ion A at the activity a_A (but no B), the other one containing the ion B at the same activity $a_A = a_B$ (but no A). If the measured values are E_A and E_B, respectively, the value of is calculated from the equation:

$$\lg K_{A,B}^{pot} = \frac{(E_B - E_A)\, z_A\, F}{R\,T \ln 10} + (1 - z_A/z_B)\, \lg a_A \tag{6}$$

which is equivalent to

$$K_{A,B}^{pot} = a_A{}^{(1 - z_A/z_B)}\, e^{(E_B - E_A)\, z_A\, F\, /\, (R\,T)} \tag{7}$$

Separate solution method ($E_A = E_B$) [SSM ($E_A = E_B$)]

The $\log a$ vs E relations of an ISE for the primary and interfering ions are obtained independently. Then, the activities that correspond to the same electrode potential value are used to determine the $K_{A,B}^{pot}$ value.

$$K_{A,B}^{pot} = a_A / (a_B)^{z_A/z_B} \tag{8}$$

ABBREVIATIONS

A complete list of abbreviations that are used in the following tables is given below.

AcCh$^+$	acetylcholine
BBPA	bis(1-butylpentyl) adipate
BEHS	bis(2-ethylhexyl) sebacate
c_{dl}	detection limit
CHEMFET	chemically modified field effect transistor
CP	chloroparaffin
CWE	coated wire electrode
DBE	dibenzyl ether
DBS	dibutyl sebacate
DBP	dibutyl phthalate
2,3-DMNB	2,3-dimethylnitrobenzene
DOA	bis(2-ethylhexyl) adipate
DOP	bis(2-ethylhexyl) phthalate {'dioctyl phthalate'}
DOPP	dioctyl phenylphosphonate
DOS	bis(n-octyl) sebacate
DPE	diphenyl ether
emf	electromotive force
ETH 500	tetradodecylammonium tetrakis(4-chlorophenyl)borate
ETH 5373	*o*-nitrophenyl dihydrophythyl ether

FIA	flow-injection analysis
FIM	fixed interference method
FNDPE	2-fluorophenyl 2-nitrophenyl ether
FPM	fixed primary ion method
ISE	ion-selective electrode
ISFET	ion-sensitive field effect transistor
KTFPB	potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
KTmClPB	potassium tetrakis(2-chlorophenyl)borate
KTPB	potassium tetraphenylborate
KTpClPB	potassium tetrakis(4-chlorophenyl)borate
M	mol dm^{-3}
MPM	matched potential method
MSM	mixed solution method
N	Nernstian
NaTFPB	sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
NaTpClPB	sodium tetrakis(4-chlorophenyl)borate
nN	near-Nernstian
pNP	4-nonylphenol
oNPOE	2-nitrophenyl octyl ether
oNPPE	2-nitrophenyl phenyl ether
$P_{o/w}$	partition coefficient, P, of the ionophore between 1-octanol and water
P_{TLC}	$P_{o/w}$ as estimated experimentally by use of thin-layer chromatography
PVC	poly(vinyl chloride)
PVC-COOH	poly(vinyl chloride) carboxylated
PVC-NH$_2$	poly(vinyl chloride) aminated
r.o.o.g.	read-out of graph (where data in original paper were in graphical rather than numerical form)
SSM	separate solution method (to be used for $a_A = a_B$ method)
SSM ($E_A = E_B$)	separate solution method (to be used for $E_A = E_B$ method)
τ	life time
t_{resp}	response time
t_{90}, t_{95}	time that elapses between the instant at which an ISE and a reference electrode are brought into contact with a new sample solution and the instant at which the potential has changed to a value corresponding to 90% or 95%, respectively, of the activity change
TDDMA$^+$	tridodecylmethylammonium
TDDMACl	tridodecylmethylammonium chloride
TEHP	tris(2-ethylhexyl) phosphate
TOPO	trioctylphosphine oxide
TSM	two solution method

ACKNOWLEDGMENTS

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