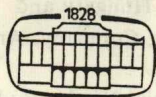


ION-SELECTIVE ELECTRODES, 3

Third Symposium
held at Mátrafüred, Hungary,
13—15 October, 1980

Edited by
Prof. E. PUNGOR, Ph. D., D. Sc.
Member of the Hungarian Academy of Sciences

Associate editor
I. BUZÁS, Ph. D., C. Sc.



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PREFACE

For the third time, a Symposium on Ion-Selective Electrodes was organized at Mátrafüred by the Analytical Chemical Committee of the Hungarian Academy of Sciences.

The form of the Symposium, adopted ever since the first of these meetings, again proved to be very effective. The method employed implies that the lectures only serve as starting points for the discussion rather than being a simple statement of final results, as is common at many conferences. The time spent on presentation and on discussion was roughly equally divided between the two.

As with the previous symposia, a special topic was selected with which to end. This was then discussed by the participants with the intention of making it a principal object of further research. One of the most exciting current problems is that of the standardizing of ion-selective electrodes, and this topic was introduced by an internationally recognized expert, Professor Bates, whose presentation elicited a lively response.

As before, the material presented at the Symposium is here published by the Publishing House of the Hungarian Academy of Sciences jointly with Elsevier Scientific Publishing Company. It is our fervent hope that this publication of the lectures and discussions will be found valuable by all those engaged in research activity in the field, and those interested in the analytical applications of ion-selective electrodes.

We hope that it will help to stimulate even greater interest in ion-selective electrode development and application.

E. Pungor

LIST OF PARTICIPANTS

Ammann, D. (Switzerland)	Mezei, P. (Hungary)
Bálint, T. (Hungary)	Morf, W. E. (Switzerland)
Bartalits, L. (Mrs) (Hungary)	Müller, H. (GDR)
Bates, R. G. (USA)	Nagy, G. (Hungary)
Bertényi, I. (Hungary)	Nagy, K. (Norway)
Boksay, Z. (Hungary)	Pál, F. (Hungary)
Boran, R. B. (GDR)	Pethő, G. (Hungary)
Bouquet, G. (Hungary)	Petr, J. (Czechoslovakia)
Buck, R. P. (USA)	Petrukhin, O. M. (USSR)
Burger, K. (Hungary)	Porjesz, E. (Mrs) (Hungary)
Deák, É. (Mrs) (Hungary)	Pretsch, E. (Switzerland)
Domokos, L. (Hungary)	Pólos, L. (Hungary)
Ebel, M. F. (Mrs) (Austria)	Pungor, E. (Hungary)
Fehér, Zs. (Mrs) (Hungary)	Radovanovicz, M. (Mrs) (Yugoslavia)
Fjeldly, T. A. (Norway)	Rakiás, F. (Hungary)
Gábor, T. (Mrs) (Hungary)	Scherr, Z. (Mrs) (Hungary)
Garai, T. (Hungary)	Senkyr, J. (Czechoslovakia)
Gracza, M. (Mrs) (Hungary)	Siemroth, J. (GDR)
Gráf, Z. (Mrs) (Hungary)	Simon, W. (Switzerland)
Gratzl, M. (Hungary)	Szepesváry, P. (Mrs) (Hungary)
Gyenge, R. (Mrs) (Hungary)	Szűcs, Z. (Mrs) (Hungary)
Hankó, K. (Mrs) (Hungary)	Tenno, T. (USSR)
Hopkala, H. (Mrs) (Poland)	Thomas, J. D. R. (Wales)
Hulanicki, A. (Poland)	Tomcsányi, L. (Hungary)
Jänchen, M. (GDR)	Tóth, K. (Mrs) (Hungary)
Johansson, G. (Sweden)	Trojanowicz, M. (Poland)
Johansson, K. (Finland)	Umezawa, Y. (Japan)
Jovanovic, M. S. (Yugoslavia)	Varga, M. (Hungary)
Józan, M. (Hungary)	Vasilikiotis, G. (Greece)
Juhász, E. (Hungary)	Vesely, I. (Czechoslovakia)
Koryta, J. (Czechoslovakia)	Virtanen, R. (Finland)
Lewenstam, A. (Poland)	Vlasov, Yu. G. (USSR)
Lindner, E. (Hungary)	Werner, G. (GDR)

CONTENTS

Preface	ix
List of Participants	xi

Plenary Lectures

R. G. BATES	
Thermodynamic Behavior of Ion-Selective Electrodes	3
R. P. BUCK	
The Impedance Method Applied to the Investigation of Ion-Selective Electrodes	27
J. KORYTA	
Electrolysis at the Interface of Two Immiscible Electrolyte Solutions and its Analytical Aspects	53
P. OGGENFUSS, W. E. MORF, R. J. FUNCK, H. V. PHAM, R. E. ZÜND, E. PRETSCH and W. SIMON	
Transport of Ions through Neutral Carrier Membranes	73

Keynote Lectures

M. F. EBEL	
X-Ray Photoelectron Spectroscopy – Applied to Investigations of Copper(II) Ion-Selective Electrodes	89
A. HULANICKI	
Selectivity Problems of Ion-Selective Electrodes	103
J. D. R. THOMAS	
Some Recent Improvements in Ion-Selective Electrodes	123

K. TÓTH, E. LINDNER and E. PUNGOR	
Problems Related to the Interpretation of Response Time Curves of Ion-Selective Electrodes	135

YU. G. VLASOV	
Electrochemical Studies of Some Solid-State Ion-Selective Electrodes	147

Discussion Lectures

D. AMMANN, P. ANKER, H.-B. JENNY and W. SIMON	
Valinomycin Based Silicone Rubber Membrane Electrodes for Continuous Monitoring of Potassium in Urine	179

I. BERTÉNYI and L. TOMCSÁNYI	
The Sodium Ion-Selective Glass Electrode as a New Monitor in the BAYER-Process	185

Z. BOKSAY, G. BOUQUET and M. VARGA	
On the Variation of Electrical Potential between the Bulk of Glass Electrode and the Solution	191

É. DEÁK	
Metrological Basis of Calibration of Ion-Selective Electrodes at Elevated Temperature	203

T. A. FJELDLY and K. NAGY	
All-Solid State Ion-Selective Electrodes with Integral Amplifier Electronics . .	215

T. GARAI, T. BÁLINT and M. SZÜCS	
Simultaneous Determination of Tetrahydro-thiophene, Volatile Thiols and Hydrogen Sulphide Using Ion-Selective Electrodes	225

E. GHALI and A. LEWENSTAM	
Anodic Behaviour of Synthetic Copper(II) Sulphide	235

J. HAVAS, E. PORJESZ, G. NAGY and E. PUNGOR	
A Glucose-Selective Sensor for the Determination of Glucose in Blood and Urine	241

A. HULANICKI, M. TROJANOWICZ and Z. AUGUSTOWSKA	
Anion Interferences of Calcium Selective Electrode	251

M. S. JOVANOVIĆ, M. DJIKANOVIC, B. D. VUCUROVIC and Z. ABRAMOVIC About the Determinations of Tetraethyl-Lead Content of Gasolines Using Ion-Selective Electrodes	257
W. E. MORF Diffusion Phenomena: Their Effect on the Characteristics of Ion-Selective Electrodes	267
H. MÜLLER Chloride and Cyanide Determination by Use of the Flow-Injection Method Using Ion-Selective Flow-Type Electrodes	279
K. NAGY and T. A. FJELDLY Response Time Studies on Solid-State Ion-Selective Electrodes with Integral Electronics	287
G. PETHŐ and K. BURGER Equilibrium Reactions in Potentiometric Analysis	297
O. M. PETRUKHIN, YU. V. SHAVNJA, A. S. BOBROVA and YU. M. CHIKIN Ion-Selective Electrodes for Determination of Gold(I) and Silver in Thiourea Solutions	305
E. PRETSCH, M. GRATZL, E. PUNGOR and W. SIMON Model Calculations on the Structure/Selectivity Relationship of Ionophores , .	315
J. SENKYR and J. PETR Method for Calculation of the Concentration Dependence of k^{Pot} Value for Liquid Membranes with Charged Carrier	327
J. SIEMROTH and I. HENNIG Comparative Study of the Structure and the Function of Some Commercial Copper-Selective Electrodes	339
Y. UMEZAWA, K. SHIBA, T. WATANABE, S. OGAWA and S. FUJIWARA A Micro-Immuno-electrode	349
Y. UMEZAWA, T. TASAKI and S. FUJIWARA Dynamic Calibration and Memory Effect for Various Kinds of Ion-Selective Electrodes	359
R. VIRTANEN A Flow Injection Analyzer with Multiple ISE-Detector	375

YU. G. VLASOV, A. V. BRATOV and V. P. LETAVIN	
Investigation of the Ion Selectivity Mechanism of Hydrogen Ion-Sensitive Field Effect Transistors (ISFET)	387
V. A. ZARINSKII, L. K. SPIGUN, G. E. VLASOVA, I. V. VOLOBUEVA, E. V. RYBAKOVA and YU. A. ZOLOTOV	
Investigations of Liquid Membranes Based on Chelates of Copper(II) with Dialkyldithiophosphoric Acids in Different Organic Solvents	399

Panel Discussion

Panel Discussion on Selected Topics	413
Subject Index	423

PLENARY LECTURES

THERMODYNAMIC BEHAVIOR OF ION-SELECTIVE ELECTRODES

ROGER G. BATES

Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA

ABSTRACT

Although ion-selective electrodes (ISE) have provided a valuable tool for the determination of ion concentrations, these sensors respond most directly to some function of ion activities. As such, they have great possibilities, as yet largely unexplored, in the determination of precise thermodynamic quantities for ionic systems. As a first step, one must evaluate the quality of the electrode response; this is often difficult to accomplish, for scales of single ion activity are not uniquely defined by thermodynamics. If the electrode is combined with a second electrode of demonstrated reliability, however, thermodynamic data for neutral ion combinations can be obtained. When these data agree with accepted values resulting from other precise thermodynamic measurements, one has evidence that the ISE is functioning in a reversible manner.

This procedure for characterizing the thermodynamic behavior of ion-selective electrodes will be illustrated and examples given of data for systems difficult to study by conventional techniques. An attempt is also made to evaluate the extent to which certain electrodes function thermodynamically over ranges of temperature and in nonaqueous and partially aqueous solvents. A novel and convenient relative method, making use of the Na-ISE, for determining the dissociation constants of weak bases in water, water/methanol mixtures, and deuterium oxide over the range 15 to 40°C, is described.

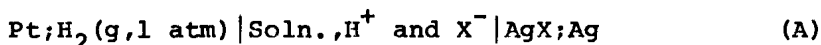
INTRODUCTION

The development of electrochemical sensors selective for one species of ion or even for a variety of specific compounds of critical importance in biomedicine and industrial processes has proved one of the exciting events of the past 15 years. Analytical chemists in particular have been able to profit from the availability of ion-selective electrodes which offer a convenient and rapid means of estimating the concentrations of certain elements which formerly were difficult to determine. The practical results have been enormously beneficial to the laboratory scientist. In addition, the development of the theory of operation of these sensors has led to an increased understanding of membrane behavior in general and of the mechanisms of transfer through membranes important to human physiology (1,2). Extensive and detailed studies of the selectivity of these electrodes (3) add much to this understanding and aid materially in increasing the accuracy of analytical determinations of ion concentrations.

When the transfer process is viewed from the macroscopic vantage point, it becomes clear that the electrochemical response of a membrane electrode is a function of the activities of the selected ion on the two sides of the membrane and of the rates of mass transfer through the membrane (4). In other words, the electrode is a device permitting the transport of a single species of ion between two states of differing Gibbs energy. This restriction has both advantages and disadvantages. If the analytical chemist wishes to determine ion concentrations in one of the separated phases most directly, some provision for equalizing activity coefficients must be made. However, these sensors also provide the possibility of determining very conveniently the activity function and other properties of systems related to the free energy.

In the application of ion-selective electrodes to determine the thermodynamic properties of solutions, no new techniques are usually involved. Ion-selective electrodes may, however, be extremely useful as replacements for more conventional electrodes that have found extensive use for many years.

For example, Harned and his co-workers (5) led the way in applying the cell with hydrogen electrodes and silver-silver halide electrodes



to the determination of activity coefficients for the halogen acids (HX) in water and water/organic solvents alone and in mixtures with other electrolytes, as well as for the study of weak acid equilibria and associated thermodynamic properties in a variety of solvent media.

In spite of its versatility, this cell has its limitations. The hydrogen electrode is subject to poisoning by heavy metals and certain other materials, while some organic acids are reduced at the platinum surface. The proper functioning of silver halide electrodes requires the establishment of a simple solubility equilibrium governed by the solubility product constant. This equilibrium is disturbed by ammonia and amines and by anions (such as sulfide) which form silver compounds of lower solubility than the halide. In some aprotic media, chloro complexes of high stability may be formed (6). These difficulties make it impossible to determine accurate thermodynamic data with the hydrogen-silver halide cell in every instance, and then ISE's may offer a successful substitute.

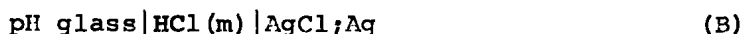
Inasmuch as the mechanism of operation of a membrane electrode is one of ion transfer, these electrodes may be useful in oxidizing and reducing media which would affect adversely those electrodes whose potentials depend on electron transfer. Nevertheless, the standard potential of a given type of membrane electrode is not usually fixed and may fluctuate to some extent with time. Furthermore, the change of electrode potential with changes in the logarithm of the activity of the selected ion may not conform to theoretical expectations and thus may require calibration. In this regard, the extensive program of Pungor and his associates in the Budapest laboratory for determining and collecting selectivity coefficients (7) is of the highest usefulness. For these reasons, the use of ISE's to determine reliable thermodynamic data should be preceded by an examination of the behavior of the cell system involved.

It is the purpose of this paper to review some of the most important thermodynamic applications of ion-selective electrodes and to outline studies that enable one to establish the suitability of these sensors for thermodynamic measurements, together with the limits of their applicability. The status of this subject was capably summarized by Butler in 1969 (8). Many more recent studies provide valuable guidance bearing on this problem, and it is not possible here to give an exhaustive review of all that has been done. Instead, these procedures will be illustrated by selected examples.

FREE ENERGY OF AQUEOUS SYSTEMS

1. Activity Coefficients

A comparison of activity coefficients determined with the aid of ion-selective electrodes and those based on emf data of proved reliability or on static or isopiestic vapor pressure methods provides one of the most direct ways of assessing the performance of the ISE. To avoid the uncertainties of liquid junctions, cells without transference should be chosen. The response of the pH glass electrode, the earliest of the current group of ISE's, can, for example, be readily examined by measurement of the emf of the cell



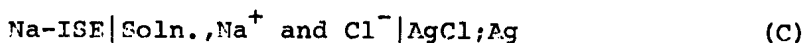
over wide ranges of the molality m . The AgCl/Ag electrode is known to display a Nernstian response up to $m=3$ or higher. The mean ionic activity coefficient (γ_{\pm}) of HCl is given by

$$-\log \gamma_{\pm} = (E - E^{\circ})/2k + \log m \quad (1)$$

where k is written for the Nernst slope $(RT \ln 10)/F$. Inasmuch as E° (the standard potential) for the ISE is unknown, it must be determined by a suitable extrapolation to $m=0$ or calculated from measurements of E at a low molality where γ_{\pm} is precisely known (9). Since these values of the activity coefficient were derived from measurements of cell A, it is sufficient to show that $E_A - E_B$ is constant, independent of m . Oddly, neither type of measurement is commonly used to check the response of pH glass electrodes, for which purpose pH

buffers are usually chosen, in cells with liquid junction.

On the other hand, the sodium glass electrode has been employed rather extensively to determine activity coefficients of sodium salts in aqueous solutions (10-13). By use of the cell



the Na-ISE was shown to yield activity coefficients for NaCl in agreement with accepted values derived by other thermodynamic methods. This agreement is apparent in Table 1, where the results of Schindler and Wälti (13) are compared with the activity coefficients of NaCl determined by isopiestic vapor pressure methods (14). The Na-ISE was standardized in a relatively concentrated solution (molality $0.1007 \text{ mol kg}^{-1}$), for which the activity coefficients from vapor pressure measurements were adopted.

Data for the activity coefficient of calcium chloride in its aqueous solutions (triangles) derived from a cell with the Orion 92-20 calcium electrode combined with the AgCl;Ag electrode (15) are shown in Figure 1. The solid line is drawn through the accepted values over the experimental range, and the reference point is the solution of $I=0.01$. Similar measurements can be used to confirm simultaneously the thermodynamic behavior of two ion-selective electrodes, as also shown in Figure 1 (15), based on the cell



Cell D was standardized in a 0.01 m solution of NaF. Again, the reasonable agreement between the experimental points (circles) and accepted data (solid line) shows that these electrodes are functioning thermodynamically in the range $0.001 < I < 1 \text{ mol kg}^{-1}$.

Figure 2 shows a comparison of the activity coefficients of choline chloride (trimethyl- β -hydroxyethylammonium chloride) derived from emf measurements of the cell



with those determined by the isopiestic method over a wide range of molality (16). It appears that this electrode also

functions reversibly in choline chloride solutions.

Inasmuch as activity coefficients at 25°C of dozens of electrolytes in aqueous solutions of concentration exceeding 0.1m have been determined precisely (14), this procedure may have wide application in testing the behavior of other electrodes. For acceptable results, it is necessary that no side reaction with the second (reference) electrode occur. Unfortunately, a lack of extensive data for activity coefficients precludes the application of this procedure to many nonaqueous and mixed solvents and at temperatures other than 25°C.

2. Mixtures of Electrolytes

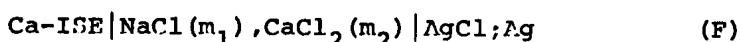
Many electrodes are remarkably selective for one species of ion, yet for accurate measurements the need for selectivity coefficients is general. Furthermore, interest in the specific interactions of ions in salt mixtures has been increasing steadily in recent years, and notable progress has been made in accounting for activity-coefficient behavior in electrolyte mixtures (17-19). Ion-selective electrodes offer a means of providing the data needed to enlarge the scope of these studies. At the same time, data already available can be used to confirm the response of an ISE in the presence of a possible interferent. This procedure is, however, of limited applicability at the present time, but an example will illustrate its nature.

Activity coefficients of acids HX in the presence of a number of other electrolytes, especially salts MX_n , have been determined by emf methods. In general, cell A was used. Substitution of the pH glass electrode for the hydrogen electrode, as in cell B, would evidently enable one to compare the behavior of the glass electrode with the hydrogen electrode in a mixture of electrolytes. A more interesting application would utilize the activity coefficients of NaCl and $CaCl_2$ in their mixtures, determined by isopiestic vapor pressure measurements (20) or with sodium amalgam electrodes (21). Figure 3 shows the variation of $\log \gamma_{NaCl}$ and $\log \gamma_{CaCl_2}$ at 25°C with the composition of the mixture at a total fixed ionic strength (I) of 3.0 mol kg⁻¹. The linear Harned rule is obeyed for both components at this value of I:

$$\log \gamma_{\text{NaCl}} = -0.1463 + 0.0018 I_{\text{CaCl}_2} \quad (2)$$

$$\log \gamma_{\text{CaCl}_2} = -0.3010 + 0.0165 I_{\text{NaCl}} \quad (3)$$

where I_{NaCl} and I_{CaCl_2} are the contributions of the two salts to the total ionic strength (3.0) and the first terms on the right are the values of $\log \gamma_{\text{NaCl}}$ and $\log \gamma_{\text{CaCl}_2}$ in pure solutions of these salts at $I=3.0$. To check the performance of the Ca-ISE in the presence of NaCl, one prepares the following cell



containing a series of solutions of constant total ionic strength, $I=3.0=m_1+3m_2$. The mean activity coefficient of CaCl_2 is given by

$$-\log \gamma_{\text{CaCl}_2} = \frac{2}{3} \frac{E-E^\circ}{k} + \frac{1}{3} \log [m_2 (m_1+2m_2)^2] \quad (4)$$

and E° is readily obtained by measuring E in a pure CaCl_2 solution ($m_2=1.0$, $m_1=0$, $I=3.0$) for which γ_{CaCl_2} is known from Equation 3.

Although it is often not possible to make a thorough-going confirmation of thermodynamic behavior in advance, ion-selective electrodes have proved useful in the study of salt mixtures. One may mention the use of the Na-ISE to study the properties of mixtures of NaCl and tris(hydroxymethyl)aminomethane hydrochloride ($\text{Tris} \cdot \text{HCl}$) (13) and the study of mixtures of NaCl with eight different salts of the 1:1, 1:2, and 2:1 valence types by Lanier (22). In these instances, the adherence to Harned's rule offers some confirmation of the proper functioning of the electrode.