Reviews

The Theory of Ion-Selective Electrodes

Ernö PUNGOR

Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary and
Bay Zoltan Foundation for Applied Research, Budapest, Hungary

The paper discusses the anomalies of the former interpretation of the working mechanism of ion-selective electrodes. It was thoroughly discussed why the Donnan experiment could not be applied as the theoretical background of glass electrodes. It was assumed according to the Donnan interpretation that the measurable potential is produced by the transfer of the primary ion through the membrane. Since the 1960s, the author and coworkers have been investigating the problem of what can be the reason for the potential response of the electrodes. Practical measurements in connection with the response time, surface hindered reactions *etc*. were interpreted. Furthermore, the energy problems according to the Gibbs theory using two electrode components were investigated. It was established that the electrodes on which chemical reactions may occur with the primary ion have a surface reaction as the chemical basis of the response. For electrodes that work on the principle of the lyotropic series, surface reactions are also involved, but their response is not always Nernstian. The energy demand is covered by the charge separation at the electrode–solution interface.

Keywords Ion-selective electrode, theory of ion-selective electrode; potential response of ion-selective electrode, electrode potential, super-Nernstian response

1   Introduction

To make declarations it is first necessary to elucidate the details of the basic reactions. Otherwise, the facts may not be enough for the understanding of the behavior of the systems. This kind of interpretation of phenomena and its consequences has resulted in a lot of useless research.

The subject that I deal with now is the interpretation of the phenomena observed for glass electrodes and later for all the ion-selective electrodes. At the beginning of the 1900s, the phenomenon observed by Haber and Clemensiewitz[1] was a great surprise among the electrochemical phenomena, namely that the glass electrode produced an electrochemical signal in response to the acidity of solutions (the definition of the pH was given later). It was also a surprise that this potential signal could only be measured by electrometers of high input resistance (impedance), in contrast to the method worked out earlier by the Nernst school.

For electrodes of the first kind, the transfer of electrons was the potential-determining reaction, but this interpretation did not seem to be applicable for glass electrodes. A few years after the discovery of this phenomenon, a new experiment was made by Donnan.[2] He separated a solution of an alkali halide from a solu-

tion of a protein by a membrane, and found that there was an equilibrium, if the protein, which did not diffuse through the membrane, and the halide, which diffused through the membrane, established an electrochemical equilibrium, as a consequence of which an electrical potential could be measured across the membrane. Such an explanation of this experiment was plausible and clear. But it was not clear why this explanation could be applied to the phenomena of the glass electrode and why it was assumed that the glass electrode worked on the principle that ions diffused into and through the glass electrode membrane, *i.e.* why the transport mechanism was introduced for the interpretation of the operation of the glass electrode.

When other ion-selective electrodes were also developed besides glass electrodes, this transport mechanism was applied for them, too. In Figs. 1 and 2 we illustrate the application of this theory for the interpretation of the working mechanism of electrodes. In Fig. 2 the trajectories are given, but they have never been measured through the membrane profile.

A further question of interpretation was raised by Guggenheim[3], who deduced the electrochemical potential from the chemical potential by applying the new term of the Galvani potential, which changes proportionally to the electrochemical potential. Hereby the only real measurable term in the equation was the
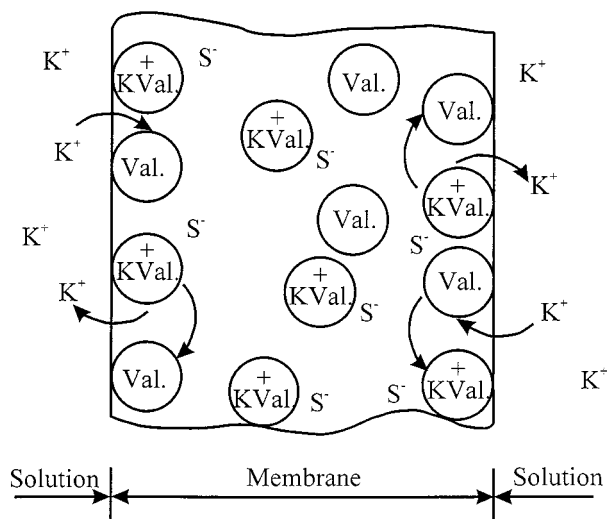
Fig. 1   Negatively-sited membrane (mobile or fixed sites S⁻) containing dissolved neutral carrier, valinomycin, exposed to bathing solutions of counter ion K⁺.
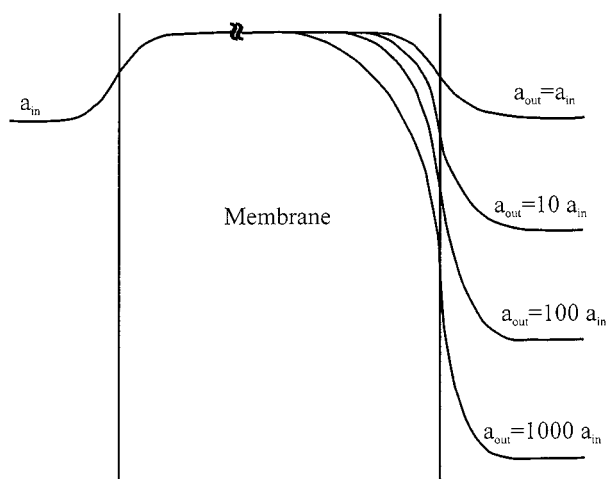

Fig. 2   Potential profile for a membrane containing exchangeable cations, with lower cation concentration in the membrane than in either bathing solution. The membrane is bathed on one side at constant activity a_{in} and at a variety of activities on the sample or "outer" side (theoretical investigation). a_{out} and a_{in} curve labels correspond to +1 ions for negative ions (–1 charge); the lower three labels corresponds to $0.1a_{in}$, $0.01a_{in}$ and $0.001a_{in}$.
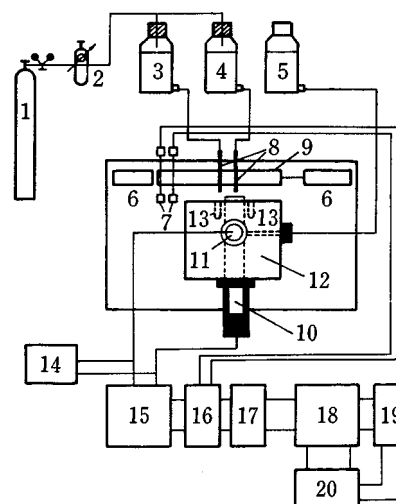

Fig. 3a   Measuring set-up for response time studies. 1, nitrogen tank; 2, high precision reduction valve; 3&4, sample solutions of different concentrations; 5, salt bridge electrolyte; 6, pneumatic pistons; 7, optical detectors; 8, jets; 9, mobile clamping arrangement for the jets; 10, ISE; 11, reference electrode; 12, electrochemical cell; 13, drainage holes for sample solutions; 14, pH-meter; 15, high impedance amplifier (Keithley 604); 16, experimental control interface; 17, HP 82941A BCD interface; 18, HP-85 desk-top computer; 19, HP 7470A digital plotter; 20, HP-226 microcomputer.

chemical potential. He assumed that on both sides of the membrane (inside and on the solution side) the electrochemical potentials have to be defined, and in the case of equilibrium we can obtain a measurable electrical potential.

2   Experimental Investigations

Using the Donnan potential concept, various types of investigations were conducted on glass electrodes, *e.g.*

studies on the transfer of Na⁺, Li⁺, *etc.*, but even so, it was difficult to understand the behavior of glass electrodes. Just therefore, to clear up the phenomena, we decided to investigate the physical and chemical characteristics of membrane electrodes containing different compounds. The aim of one of these fundamental experiments was to examine whether the transport of ions can really be measured. For this purpose we prepared "sandwich electrodes" as follows:[4] we put silicone-rubber based silver iodide electrode membranes[5] on both sides of a metal plate. The sandwich electrode thus prepared was immersed in an electrolyte solution, and the potential of the electrode was measured *versus* a reference. We changed the metal, and applied platinum, silver or aluminum (the surface of the latter was covered by an oxide layer), and in each case, the measured potential values were equal, *i.e.* the quality and thickness of the metal plate did not influence the potential values. We applied the three different metals because, as a first approximation, it was claimed by some researchers that the silver plate covered by the silver iodide membrane could take part in the silver transport. It became clear that this could not be the case with the other metals.

   In the 1960s we developed an instrument for measuring the response times of ion-selective electrodes.[6] With this instrument real electrode response times could be measured (in contrast to systems where the response time was measured in an electrochemical cell assembly in which internal eddy currents influenced the
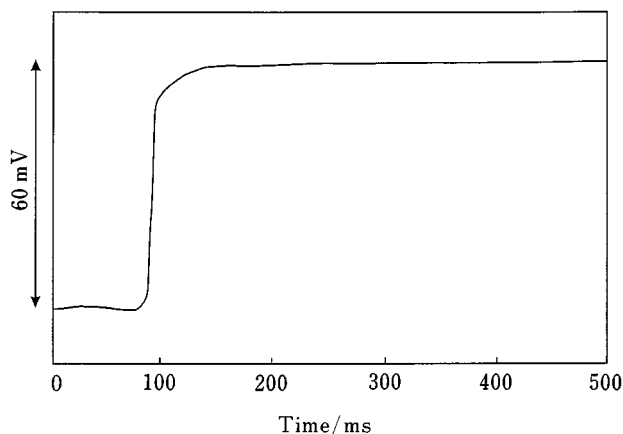
Fig. 3b   Response–time curve of an AgI electrode: change of activity from 10^{-3} to 10^{-2} mol/l I^-.
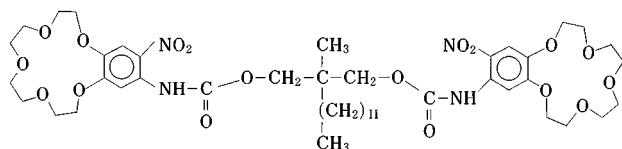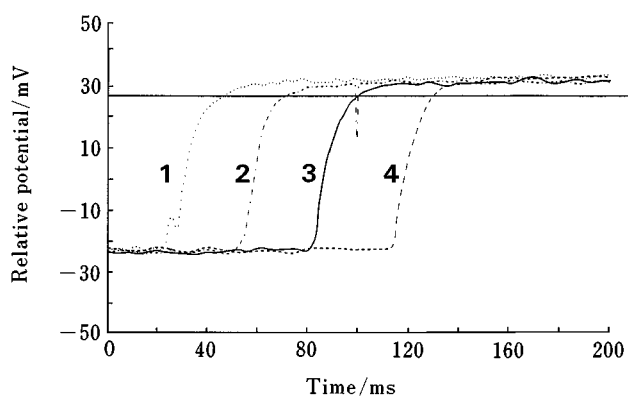

Fig. 3c   Effect of conditioning in 10^{-3} mol/l KCl solution on the response time curves of BME-44/DOS based potassium selective electrode.   Activity step: 10^{-2} mol/l KCl $\rightarrow 10^{-3}$ mol/l KCl.   Ionic strength, 0.1 mol/l (NaCl); flow rate, 115 ml/min.   (1) no conditioning; (2) 67-h cond.; (3) 10-d cond.; (4) 13-d cond.

measured response times).   The solution was jetted onto the surface of the electrode at a high velocity.   For the iodide electrode the concentrations of the solutions used were 10^{-2} and 10^{-3} mol/l.   The change of solution at the electrode surface took a very short time, less than 1 ms.   We measured the response time of a silver plate electrode, of silver halide electrodes, and later on the response times of potassium ion-selective electrodes which contained a potassium-measuring component built into a polymer membrane.[7]   To our surprise, we obtained in each case practically the same response time of 20 ms.   This response time indicated that after changing the concentration of the electrolyte, the components of the new solution need so much time to get

onto the surface of the electrode through the stagnant layer of solution (Fig. 3a, 3b, 3c).   This finding proves that the diffusion of ions into the membrane should be excluded, since diffusion of ions in the membrane is much slower than in the solution, and the establishment of the potential would take a much longer time than the value measured.

The next question was whether the electrode potential could be influenced by changing the electrode surface.   The copper sulfide precipitate based copper ion-selective electrode was an excellent example in this respect.[8]   When we immersed the electrode with a Nernstian response into the solution of an oxidant, the electrode gradually failed to produce a Nernstian response as a function of the time of oxidation (Fig. 4a, 4b, 4c).   Photoelectron spectroscopy revealed that a blocking layer containing sulfate was formed on the electrode surface.   The thickness of the layer was measured as 0.8 nm.   For this purpose the determination of the take-off angle was used, which indicated molecular dimensions.   The Nernstian response of the electrode was restored by treatment with a reducing agent, e.g. ascorbic acid.

The investigation of a lead sulfide-based lead-selective electrode seemed to be another interesting example[9], for which, in contrast to the copper-selective electrode, the response of the electrode did not cease entirely after the oxidation treatment; only the slope of the electrode calibration curve decreased below a certain solution concentration limit.   In order to interpret this finding, we studied the surface by electron microscopy and determined the composition of the layer formed on the surface of the electrode.   We stated
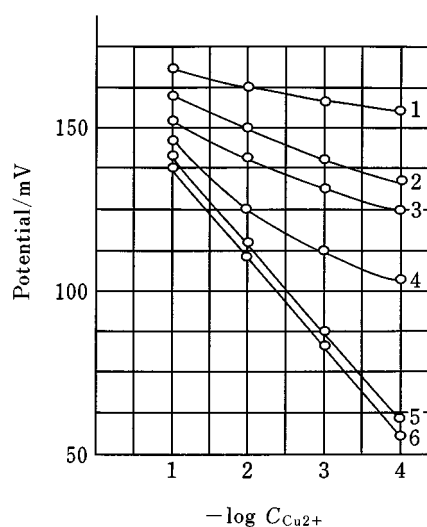

Fig. 4a   Copper(II) response of a pressed pellet electrode after soaking in cerium(IV) solutions and regenerating in ascorbic acid solutions for different times.   (1) soaking for 30 min in Ce(IV); (2) soaking for 10 min in Ce(IV); (3) regenerating in ascorbic acid for 10 min; (4) regenerating in ascorbic acid for 30 min; (5) regenerating in ascorbic acid for 80 min; (6) untreated electrode.
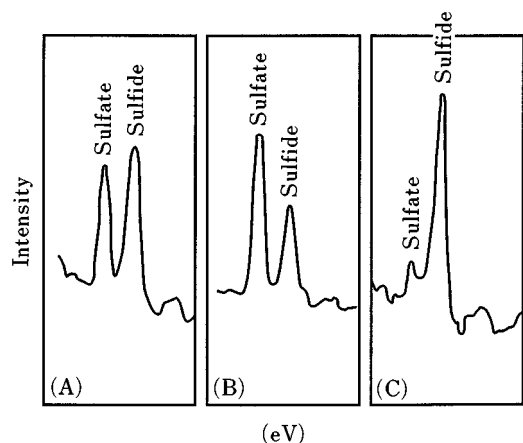
Fig. 4b   Photoelectron spectra. Mg K_α x-ray, 6 keV, 40 mA, 240 W, 1.3×10^{-4} Pa. (A) untreated CuS electrode; (B) electrodes treated in $KMnO_4$; (C) after treatment with $KMnO_4$ and then ascorbic acid.
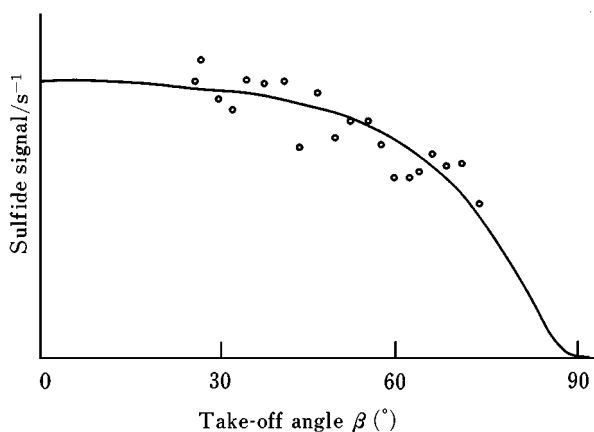

Fig. 5a   Potential of a lead ion-selective electrode *vs*. a saturated calomel electrode plotted against the logarithm of lead ion concentration: (a) new electrode without any pretreatment; (b) electrode treated with 2% hydrogen peroxide for 20 min. The electrode was prepared from Ag_2S/PbS (2:1 molar ratio) pressed pellet membrane (for all Pb electrodes).

Fig. 4c   Determination of the thickness of the sulfate layer by application of the variable take-off angle technique.

Fig. 5b   Micrographs of a lead-selective electrode taken, from graphite replicas, after oxidation in 3% H_2O_2 for 3.5 h. (a) secondary electron image; (b) sulfur S K_α element-specific image; (c) lead Pb M_α element-specific image; (d) oxygen O K_α element-specific image. The same surface was used in each case (magnification 3550×).

that part of the electrode surface was covered by lead sulfate. At low concentrations of lead ions in the solution, dissolution of the lead sulfate assured the lead ion concentration in the solution at the electrode surface, which was higher than that originally present in the solution. We obtained a Nernstian response only at higher lead ion concentrations in the solution (Fig. 5a, 5b).

A further interesting experiment seemed to be to measure the depth of penetration of the primary ion into the electrode membrane.[10] We made our experiments with two types of electrode: one was a solvent-polymeric membrane responding to potassium ions, and the other was a glass electrode.

The experiment was carried out by ATR-IR technique on polymer membrane electrodes containing a selective complexant of potassium. The electrode was soaked for a long period of time in a solution containing either KSCN or KCl. In the presence of the lyophobic SCN⁻
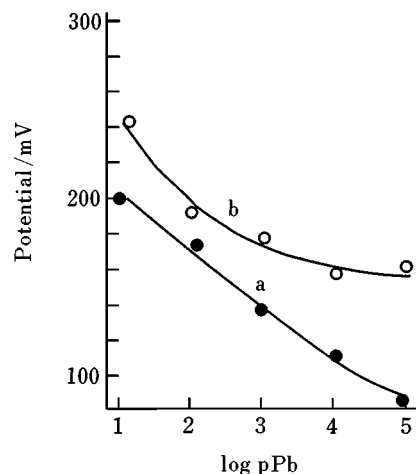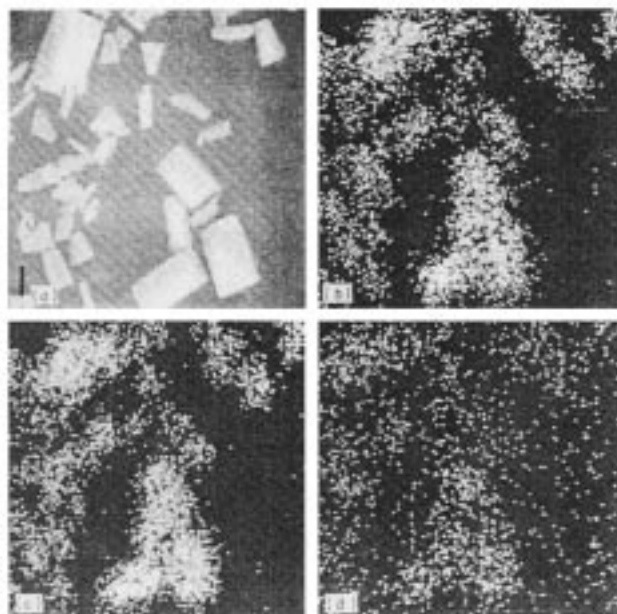
ions, K⁺ ions entered the membrane and during the relatively long time of soaking reached to a depth exceeding that of the penetration depth of the IR rays. In the presence of the lyophilic Cl⁻, K⁺ ions only enter the outermost surface layers, down to a depth of only 5 – 10 nm. Thermal diffusion may also have influenced the determination of the penetration depth (Fig. 6a).

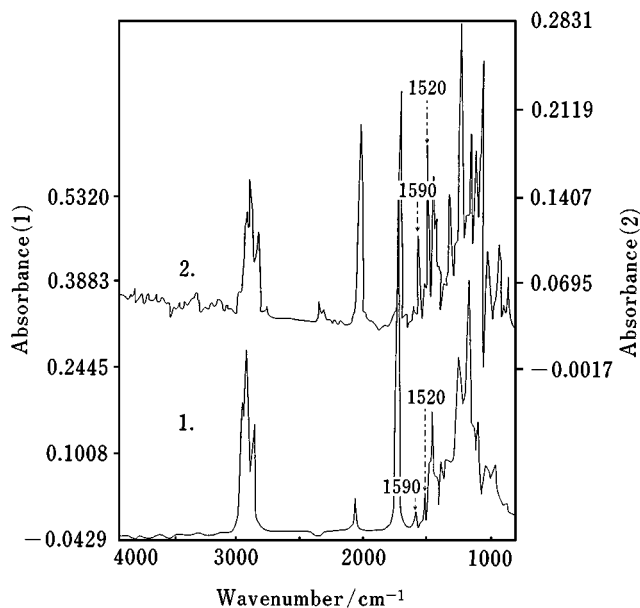For a better indication of the phenomena, in the

Fig. 6a   Spectrum of the K-salt of the bis-crown ether, in the case of 1, KCl; 2, KSCN. Peaks of the complex are at 1590 and 1520 cm^{-1}, the peak of SCN^- at 2300 cm^{-1}. Composition: 60% DOS (dioctylsebacate) in PVC with 3% bis-crown ether.
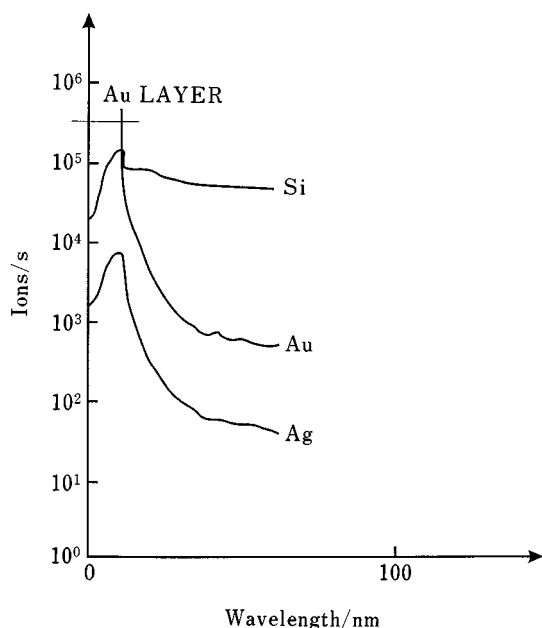

Fig. 6b   Results of experiments with a glass electrode.

experiments with glass electrodes[11], instead of protons, Ag^+ ions were used, to which glass electrodes also respond. An electrode was immersed in a 10^{-3} mol/l solution of Ag^+ for 20 – 30 s, until the potential was stabilized. The electrode was then dried, and covered by a gold layer. The removal of the surface layers was studied by means of SIMS technique. It was found that the depth distribution of silver and gold was the same (Fig. 6b). The comparison of the two phenomena verified that the surface of the electrodes is not uniformly plain.

All the above findings speak against the phenomenon of ion transfer through the electrode, and we have to reject the assumption that an ion transfer mechanism can be applied for ion-selective electrodes on the basis of the Donnan phenomenon.

A further question that can be raised is whether there may occur any transport of ions through electrode membranes. Yes, there may, but only if we apply an external voltage greater that the potential of the membrane electrode. The electrode then operates as a resistance, through which the current flows. In case of transfer, there can also be a selective partner (ionophor) conducting the current through the electrode, as the experiment of Professor Simon[12] excellently proved. If we do not produce a coulometric system, i.e., we do not apply an external voltage, the transfer cannot be established. In an ideal case we cannot measure any current across the electrodes, if the resistance of the electrode can be considered negligible compared to the input impedance of the measuring system. When we apply an electrometer for measuring the potential of electrodes, we achieve a situation where negligible polarization current flows in the system. Practically, the impedance of the measuring system should be about 10000-fold that of the impedance of the electrode.

3   Super-Nernstian Potential Response

Typical examples of unscientific misinterpretation are papers defining super-Nernstian potentials for ion-selective electrodes.[13,14] A number of papers have been published with this strange claims which contradicts the rules of thermodynamics. The phenomenon misinterpreted here can be traced back to the phenomena appearing at the surface of electrodes. We approached the interpretation of this phenomenon as follows:

We applied a microcell (Fig. 7a), in which the electrode surface to volume of solution ratio was great, and the equilibrium was set up at the electrode in a few minutes. We used various sorts of electrodes in these experiments. As such (super-Nernstian) phenomenon was published in the literature for silver halides and silver sulfide, we made our experiments with silver iodide and silver sulfide-based electrodes (Fig 7b, 7c). The results represented by the figures verified that the pretreatment of the electrodes, i.e. whether the electrode had been soaked in the solution of one or the other ion of the components of the membrane material, was reflected by the potential of the electrode, i.e. a sort of memory effect was measured. After the equilibrium was set up, i.e. a stable electrode potential was measured, we analyzed the solution in the microcell by means of an independent method and found that the potential data corresponded to the actual concentrations measured, assuming a Nernstian response.

If this is true, i.e. the measurable potential depends only on the ionic composition of solution at the surface of the electrode after equilibration, then we can influ-
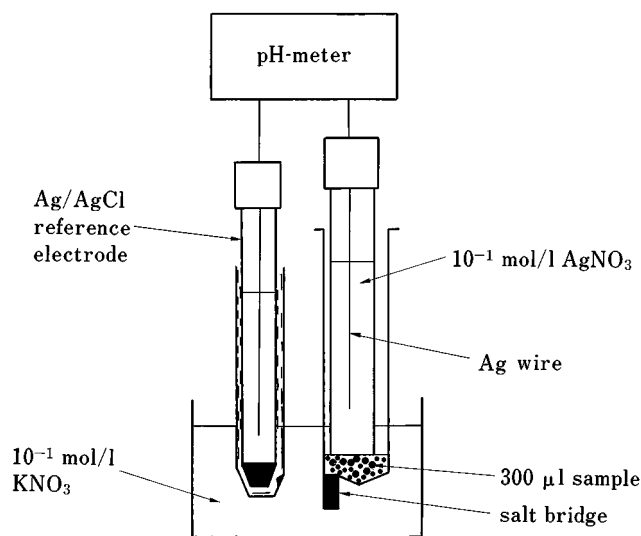
Fig. 7a   Arrangement for the measurement of the electrode potential.

Fig. 7c   Calibration curves for silver and sulfide ions measured.
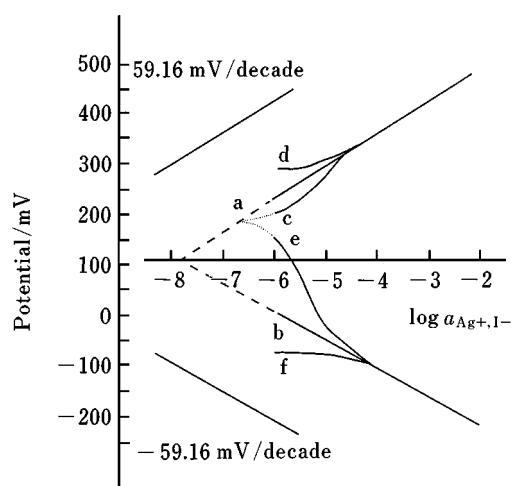

Fig. 7b   Calibration curves taken with the silver iodide ion selective electrode: (a) silver calibration curve in 50 ml solution volume; (b) iodide calibration curve in 50 ml solution volume; (c) silver calibration curve taken in 300 μl solution volume, the electrode conditioned in distilled water; (d) silver calibration curve taken in 300 μl solution volume, the electrode conditioned in 10^{-1} mol/l silver nitrate solution; (e) iodide calibration curve taken in 300 μl solution volume, the electrode conditioned in distilled water; (f) iodide calibration curve taken in 300 μl solution volume, the electrode conditioned in 10^{-1} mol/l potassium iodide solution. Composition: 5% AgI in polysilicone rubber.

ence the concentration at the surface by means of a coulometric method, by applying an external current. It can be seen in the figure that the limit of electrode response is shifted to lower concentrations (Fig. 8).

Accordingly, the super-Nernstian relation is a false interpretation of the measured data. Of course, a sub-Nernstian relation can also be obtained. In the latter case, further parallel reactions can produce this effect.
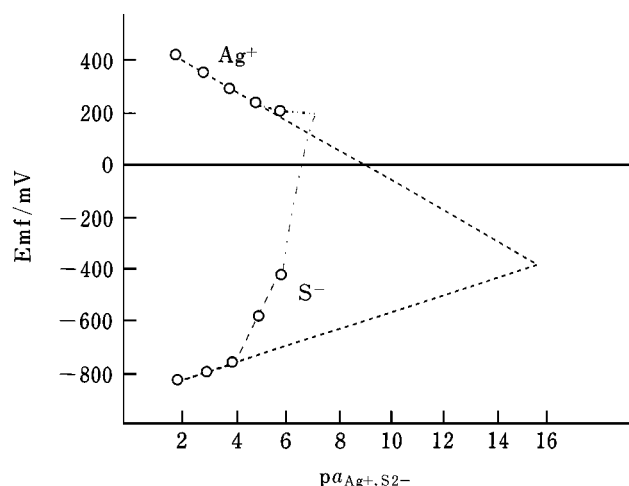
4   How Is the Electrode Potential Produced?

The establishment of an electrode potential is caused by charge separation at the surface of the electrode. The interpretation is connected with the chemisorption of the primary ion from the solution phase onto the surface of the electrode. In this case counter ions accumulate in the solution phase, and this is the charge separation. A further informative finding was that by using potassium electrodes containing different complexing agents (valinomycin or a bis-crown-ether compound) we measured the same potential for the same potassium ion concentration of the solution. This can be understood only if the chemical potential of the solute is responsible for the electrochemical signal. To express the thermodynamics, the Gibbs–Duham relation can be given as:

$$-\Delta G = nFE$$

where ΔG is the change of chemical potential of the solute, n the number of charges, F the Faraday constant and E the electrical potential.

In the field of ion-selective electrodes, the experience and interpretation of Nicholsky[15] brought about an enormous change, i.e. the ion exchange conception was introduced for glass electrodes and later, of course, for all electrodes. The selectivity coefficients of the electrodes were practically calculated for the first time using precipitate-based electrodes, where the solubility equilibrium was known. For other electrodes the selectivity coefficient could not be deduced from such thermodynamic data.[16] In this case, the selectivity coefficients did not contain any other factors; they contain only the thermodynamic data and no other factors which include transfer coefficients.

This really brilliant approach of Nicholsky had a lot of negative effects, too. One of them was that a great

number of researchers set about investigating ion-exchange systems, for which they thought to prepare electrodes. From the end of the 1930s the literature records such investigations by the hundreds. But "selective" electrodes could not be invented in this way. The other negative effect was caused when, besides the Nicholsky equation, textbooks and other books presented a formula standing opposite to the principles of physics. Knowing that if the quantity of charges in the system does not change, one must conclude that no potential change can appear, *i.e.* the following equation cannot be given as the basic equation describing the operation of an electrode:

$$A^+ + \text{polymer } B \rightleftharpoons \text{polymer } A + B^+$$
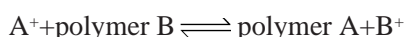
5   Classification of the Electrodes

The electrodes used currently can be divided into two groups:
1) basic electrodes suitable for measurement of ions and
2) electrodes suitable for measurement of molecules. The signal is provided by a so-called basic electrode and the measured component is produced, by some chemical (*e.g.* enzyme reaction) or physical (diffusion *etc.*) reactions, from the molecules.

According to our present knowledge, the basic electrodes can also be divided into two groups:
1) Electrodes giving chemisorption, the three types of which are as follows:
    a) electrodes based on the principle of acid-base reactions
    b) electrodes based on the principle of precipitation reactions
    c) electrodes based on the principle of complexation reactions
2) Electrodes whose operation is based on the lyotropic series, for which the ideal Nernstian relation is not always valid, the potential is shifted in time *etc.*

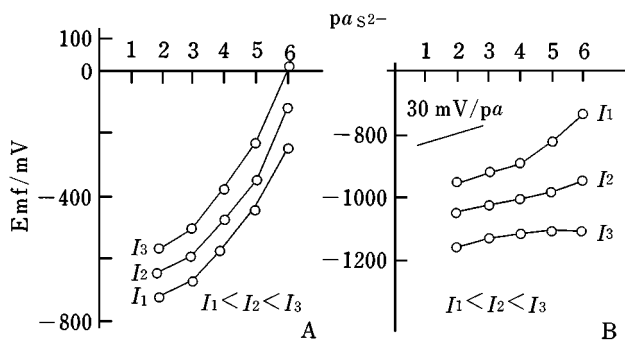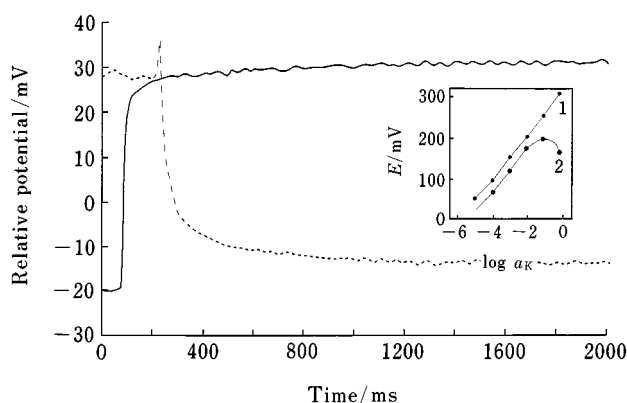The Donnan exclusion effect can be understood if we

Fig. 9   Comparison of the response time curves of BME-44/DOS based potassium selective membranes (composition: 60% DOS in PVC with 3% BME-44 compound (see Fig. 3c)) recorded in concentrated KCl and KSCN solutions. Insert: EMF-log a_k calibration plot of the BME-44/DOS based electrode in (1) KCl and (2) KSCN solutions. The response time curves were recorded in the concentration ranges marked with arrows. Activity step: (A) 0.1 mol/l KCl→1.0 mol/l KCl or (B) 0.1 mol/l KSCN→1.0 mol/l KSCN; flow rate: 115 ml/min.

realize that, if the electrode is in contact with a solution concentrated enough for the cation to saturate the active sites of the surface, then the anion may enter the membrane, and the electrode will respond to the anion (Fig. 9).

According to the above, the electroanalytical definition of ion-selective electrodes by IUPAC must be reworded[17], and in the same way the determination technique of selectivity coefficients could also be touched upon.[18]

This paper has criticized the old theory of transfer reactions as producing the potential signal of ion-selective electrodes. It presented experimental results proving definitely the occurrence of chemisorption reactions. In case of certain electrodes, the operation can be interpreted in terms of the lyotropic series. Thus this paper places not only the interpretation, but also the possibility of invention of new electrodes, on a new basis.

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Fig. 8   Calibration curves for sulfide: (A) with anodic current; (B) with cathodic current; applied current: I_1=5.9 μA; I_2=11.8 μA; I_3=17.7 μA. Composition: Ag_2S dispersed in polysilicone rubber.

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