

Working mechanism of ion-selective electrodes

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Abstract

A theory for the interpretation of the operation mechanism of ion-selective membrane electrodes is briefly outlined. The statements are based on the accumulated results concerning the electrochemical and spectrochemical behaviour of ion-selective membranes.

INTRODUCTION

The first ion-selective electrode, the glass electrode (refs. 1, 2) was invented in the first decade of the century. The potential response of the glass electrode was elaborated by Donnan (ref. 3) in terms of a semipermeable membrane separating the contacting solution phases. This approach served as basis for defining the thermodynamic function valid for the linear part of the calibration curve (E vs. $\log a_{\text{H}^+}$) glass electrodes. In the 1930s it was observed that pH glass electrodes are sensitive also to sodium ions under certain conditions (ref. 4). Nikolsky (ref. 5) attempted to explain this phenomenon. Based on the assumption that the two ions (primary and interfering) compete for the ion-exchanger sites located in the glass and by considering the selectivity of the ion-exchange reaction the phenomena was interpreted. By incorporating the potentiometric selectivity factor into the Nernst equation, a generally accepted function, the so called Nikolsky equation was developed. This theoretical work initiated a systematic search for new materials with ion-exchanger properties and certain selectivity towards different ions. First of all clay materials and a number of organic ion-exchangers were studied in this respect. At the same time the use of ion-exchangers for deionization of water brought up a number of theoretical problems concerning the ion transport across ion-exchanger membranes. The results accumulated in this field initiated scientists dealing with the glass electrode to find out the nature and the role of the ion transport within the glass membrane. It has been stated that protons cannot take part in the ion transport, while sodium ions that are present in the silicated lattice have been accepted as components transporting charge.

MECHANISTIC STUDIES OF NON-GLASS BASED ION-SELECTIVE ELECTRODES

Based on experiences gained during my surface and colloid chemical studies on silver halides over ten years (ref. 6) I started research on the application of silver iodide precipitate as a sensing material for an ion-selective electrode in the late 1950s. At that time the results of thorough theoretical studies on the photochemical reactions of this precipitate were already available. From the very beginning I could not accept the assumption that the operation of ion-selective electrodes is based either an ion-exchange reaction or an ion-exchange coupled transport across the membrane bulk.

Starting in the early 1960s I have studied the behaviour of silver iodide precipitate embedded in silicone rubber (ref. 7). A silver or a platinum sheet was sandwiched between two silicone rubber based silver iodide membranes. The electrodes thus prepared showed no difference in their potential response to silver or iodide ions as compared to that obtained with the very same membranes without metal sheet (ref. 8).

In the 1980s our research group has extended studies to valinomycin based softnated PVC membrane electrodes, and to bis-crown ethers based ones (ref. 9). Detailed response time studies on valinomycin and bis-crown ether based potassium sensitive electrodes and various silver-halide based electrodes have shown (Figs 1-2) that response time values measured for different membrane based electrodes at the same activity perturbation (e.g. one order of magnitude) fall in all cases into the ms range.

This suggests that response time of the electrodes is determined in all cases by phase boundary reaction.

Assuming a 1 μm thick adhering solution layer at the electrode surface and considering the rate of diffusion of ions across this layer the response time was calculated and found to be in fair agreement with the experimental values. Hence, in this case the response time is determined by the rate of diffusion across the adhering solution layer. The fast rate of response experienced does not seem to allow the assumption that ion transport across the electrode membrane may play a major role in the potential establishment, its effect may only cause a reduction in the slope value.

A similar approach was presented for the interpretation of the membrane potentials by Theorell, Meyers and Sievers (refs. 10, 11) as early as in the late 1930s. According to this due to the electrochemical potential difference at the two solution sides of the membrane a constant, ionic activity dependent phase boundary potentials are established, which go over into the electrochemical potential within the membrane bulk (which is difficult to define) with a sharp break at the membrane-solution interface.

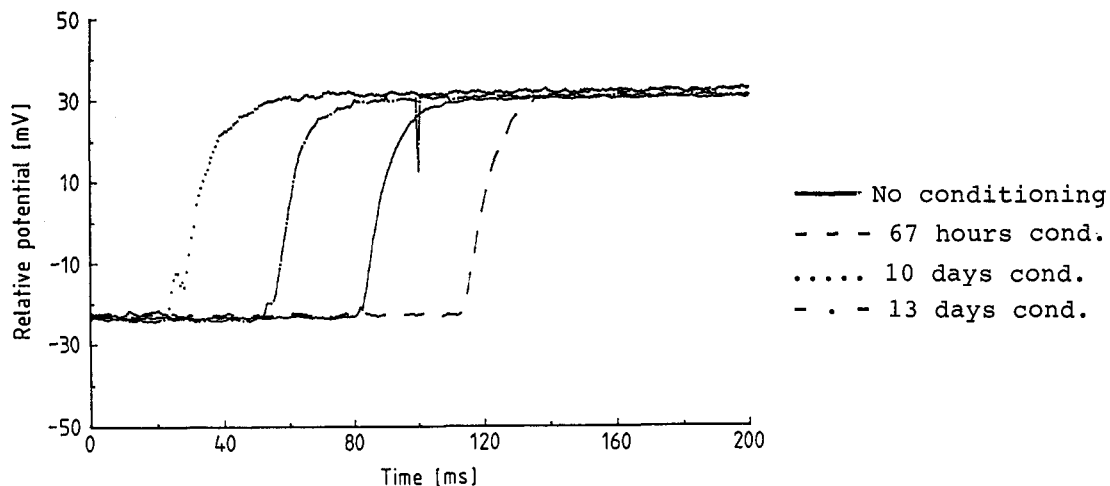


Fig. 1. Effect of conditioning in 10^{-3} M KCl solutions on the response time curves of bis-crown ether |DOS|PVC based potassium selective electrodes (ref. 13)

Activity step: 10^{-3} M KCl \rightarrow 10^{-2} M KCl

Ionic strength: 10^{-1} M NaCl,

Flow rate: 115 ml/min.

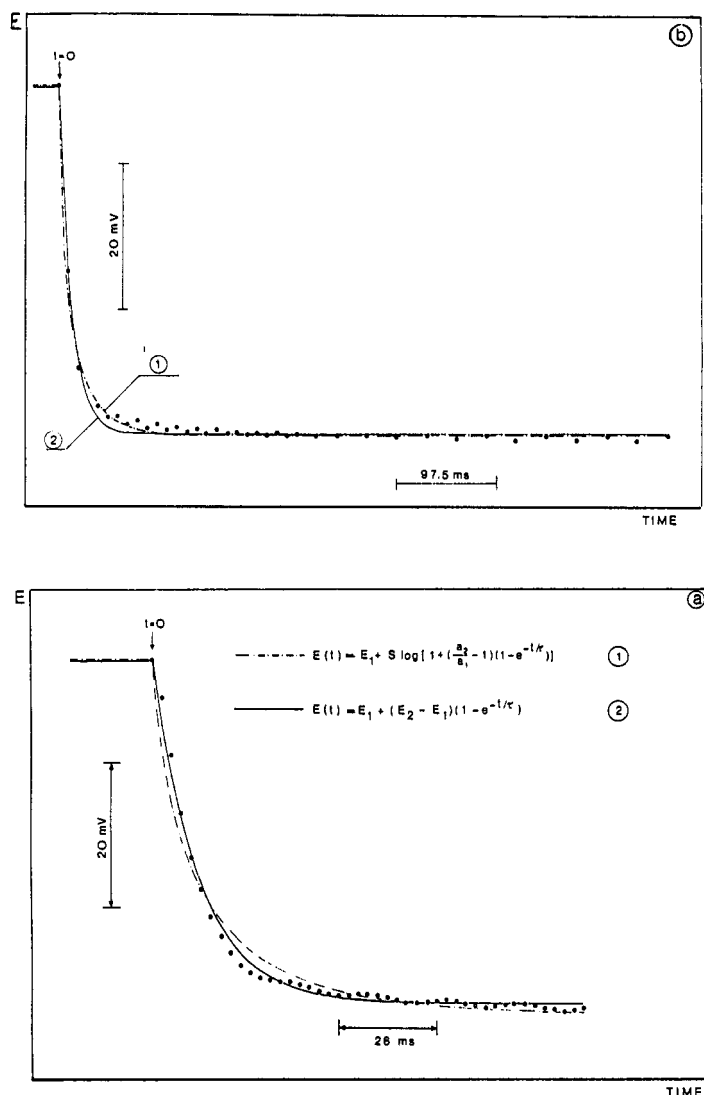


Fig. 2. Comparison of the dynamic response curves recorded experimentally and fitted in two different time domains (ref. 15)

electrode: AgI-based iodide ISE, RADELKIS OP-7112-I;

Activity step: $10^{-3} \longrightarrow 10^{-4} \text{ M KI}$;

Supporting electrolyte: 10^{-1} M KNO_3 .

The experimental results obtained with the sandwich membrane, discussed earlier, is only an indirect proof to justify the assumption, that the formation of the electrode potential is a surface chemisorption, and seemed to be insufficient to convince those who interpret the membrane potential in terms of carrier mechanism (ref. 12).

In addition to response time studies, the molecule specific attenuated total reflectance Fourier transformed infrared spectroscopy (FTIR-ATR) were employed for studying bis-crown ether based potassium selective membrane electrodes (ref. 13).

The absorbance of the potassium complex measured by this technique was found to be several hundred times higher than that of the free ligand. In the course of the experiments plasticized PVC membranes containing 2 % bis-crown ether as complexing ligand and dioctyl sebacate as plasticizer were used.

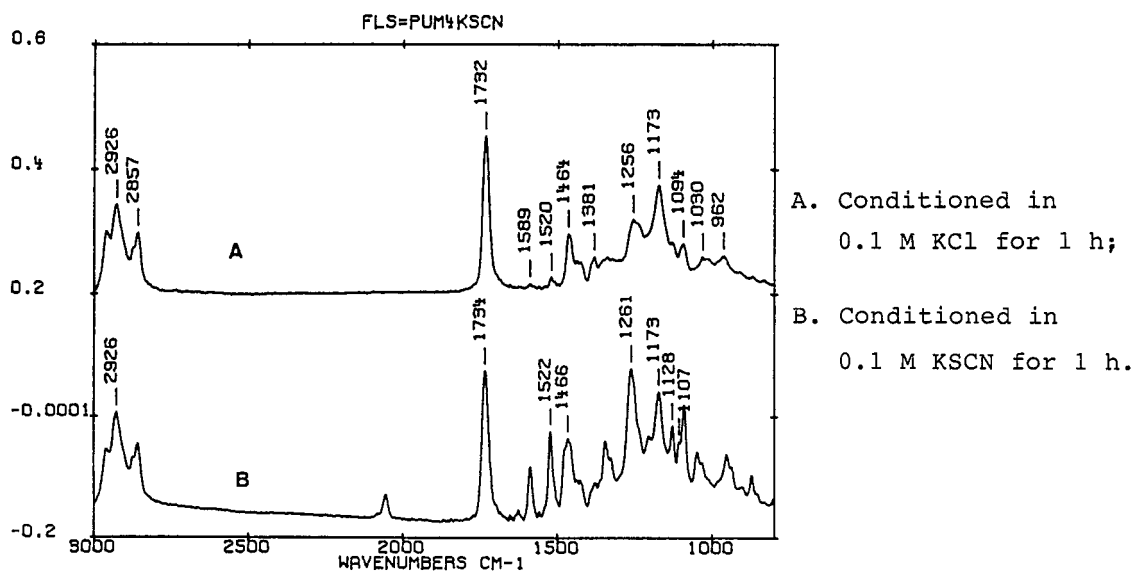


Fig. 3. FTIR-ATR spectrum of a typical K-sensitive membrane (ref. 16)
Membrane composition: 4 mg bis crown ether (BME-44);
120 mg dioctyl sebacate (DOS); 65 mg PVC.

In these studies we made use of the fact that thiocyanate ions are much more lipophilic than chloride ions. During the experiments the membrane was conditioned either in 1 M KSCN or in 1 M KCl solution for one hour. The conditioning time allowed was at least twice as long as the time necessary to reach a penetration depth of the potassium complex equal to the depth available for reflectance infrared technique. The comparison of the relevant FTIR-ATR spectra in Figs 3 and 4 showed that the intensity of the two absorption bands (ν_{1520} ; ν_{1580}) characteristic of the potassium complex normalized with respect to a selected band of the plasticizer (ν_{1730}), was much higher for the

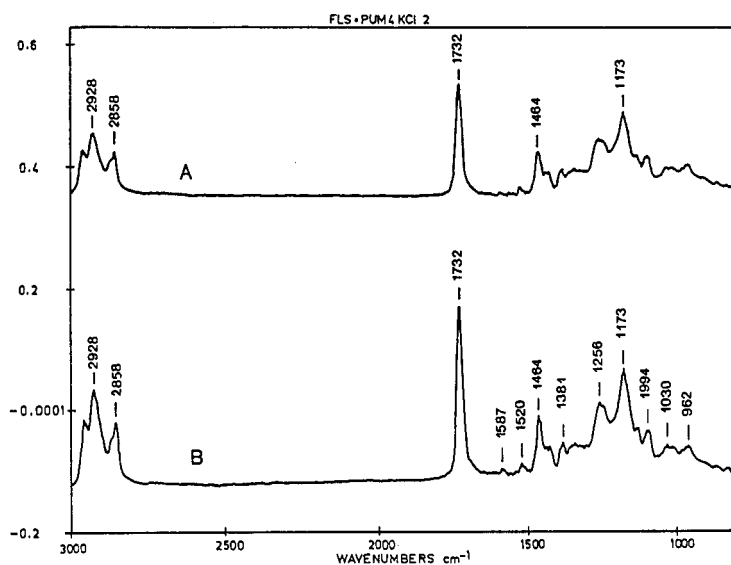


Fig. 4. FTIR-ATR spectrum of a typical K-sensitive membrane (ref. 16)
A.) as in Fig. 3A., but rinsed with H₂O for 10 s;
B.) same as Fig. 3B., but not rinsed with water.

membrane soaked in KSCN solution. Based on the intensities the average penetration depth of the complex was calculated to be penetration depth of the complex was calculated to be maximum 15 nm.

CONCLUSIONS

The operation of ion-selective electrodes has been proved to be due to phase-boundary processes. This is in contrast with the approach based on a carrier mechanism across the electrode membrane.

It seems to be important to state that it is a physical nonsense to assume a simple ion-exchange reaction between the solution and the electrode surface or the bulk of the electrode membrane as the basis of the electrode potential formation as it is found in many textbooks. An electromotive force may only be the result of accumulation of free charges which cannot be the consequence of a simple ion-exchange.

In order to find out how free charges may be formed the ion-exchange capacity of the valinomycin based PVC membranes were determined. It was found that only 5-10 % of the total ligand concentration is complexed and compensating the anionic sites in the membrane bulk and about 90-95 % of the free ligand is available to react with potassium in a complexation reaction to result excess charge at the membrane surface (ref. 14). For ensuring electroneutrality in the surface region the cations are excluded and located in the nearest adhering solution phase, i.e. the chemisorption of the primary ion is responsible for the charge separation.

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