

Capacitive and conductive dynamic response of ion-selective electrodes

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Abstract — Dynamic response of ion selective electrode, ISE, which is so widely used in analytical chemistry as the monitor or the detector should be studied in detail with respect to the varieties of external triggering to ISE, because the work of ISE actually relies on the response towards the external force which brings ISE into the out-of-equilibrium condition. Investigation has been made with respect to three cases, 1) to see the effect of strong pulse electric field, 2) to see effect of the environmental electromagnetic fields, 3) to see the contact with the aqueous solution of the ISE specific ions. All three cases resulted in a same result showing that the response is formed of a superposition of two relaxation mechanisms, one with a short relaxation time (τ), and the other with a longer τ . It is assumed that the mechanism with a shorter τ refers to the relaxation of the electronic energy transfer and that of the longer τ to the relaxation due to the ionic energy transfer. The ISE's examined can be classified into two types, one for which the dynamic response is dominantly made by the capacitive, or electronic mechanism and the other by the ionic conductivity. The Ag^+ , Cu^{2+} and Pb^{2+} ISE's belong to the former category and those of F^- , Cl^- , Br^- and I^- to the latter. All the ISE's present the dynamic response which is formed of two τ 's, short and long, regardless of the difference with respect to the classification cited above. This fact may suggest that even the capacity dominant ISE responds to the external perturbation with the conductant relaxation, and vice versa.

INTRODUCTION

The memory effect or the response time (ref. 1) of the ion selective electrode, ISE, is related with its dynamical character and still needs to be elucidated. Although the ISE is usually taken as referring to the equilibrium potential between the electrode and the solution, this is actually not so; the ISE depends greatly on the dynamical characters of the surface of the electrode. This problem is particularly important in the practical use of ISE's. For example, when the ISE is used as the sensor as in the case of FIA or the flow injection analysis, the function of ISE is dynamical and not the one of equilibrium. Accordingly, it is necessary and useful to investigate the time dependence of the response of ISE's towards the external triggering of electric field or of chemical solution. The dynamic response of ISE has been measured, first, with respect to two extreme external electric fields, one very weak: the environmental electromagnetic waves in space and the other strong: a rectangular pulse electric field. Secondly, measurement has been made with respect to the contact with the solutions of ISE specific ions. Dynamic response of the ISE refers, as a matter of fact, to the result of perturbation which is applied to the ISE causing it to go out of equilibrium. The space field refers to the case of a weak perturbation and the pulse electric field to a strong one. The contact with the solution will be referred to as the chemical perturbation. The characteristic behavior of the ISE may be taken as an equivalent circuit, as shown in Fig. 1, where C and R refer to the capacity and the resistance of the surface of the electrode (ref. 2). The reaction of the electrode with the solution is actually dynamical

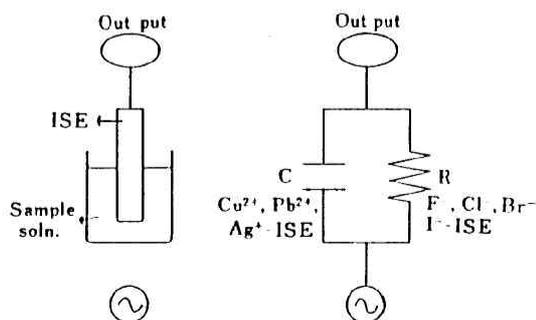


Fig. 1. Equivalent circuit of the electrical characters of the surface of ISE.

in nature. Accordingly, the output of the electrode must depend on the magnitudes of C and R , and refers to a kind of relaxation phenomenon at the surface of the electrode. Thus, efforts have been made to measure the magnitude of the latter relaxation time.

EXPERIMENTAL

Weak perturbation

The outputs of the ISE's were compared to each other for the cases where the ISE is or is not insulated from the external electromagnetic waves in space (ref. 3). For the insulation, not only the ISE but all other components of measurement such as the amplifier and ion meter were kept inside a large box of aluminum metal.

The ISE's of Ag^+ , Cu^{2+} , Pb^{2+} , F^- , Br^- , Cl^- and I^- and the double junction type reference electrode of Tokyo Denki-kagaku Keiki Co. were used in the experiment.

Figure 2 shows some examples of the time dependence of the outputs of the ISE's after they are immersed in the solutions as listed in the figure. The solution was stirred by a glass stirrer connected to a small power dc motor fed by a battery. The ionic strength was controlled at 0.1 by potassium nitrate for the solutions of the concentration lower than 0.1 mol/l. The outputs of all ISE's show positive (jumping) or negative (dropping) drift just after the contact with the solution. They then reach the equilibrium values. A fairly long time of a few hundred seconds is necessary before the equilibrium is achieved. The ISE's can be classified into two types by the effect of insulation: one shows sizable difference in the outputs between the cases with and without insulation, and the other shows no difference. The ISE's of Ag^+ , Cu^{2+} and Pb^{2+} belong to the former category and those of F^- , Cl^- and I^- electrodes to the latter. After consideration of the meaning of the capacitance and the resistance, we assume that the characteristics of the ISE's of the former category are determined by the capacity of the surfaces of the electrodes, whereas those of the latter are determined by their conductivity.

Because the power of the spatial electromagnetic waves is assumed to be very small, the perturbation to the surface of ISE's is also assumed to be weak. For practical use of the ISE's of the former kinds of electrodes, insulation may be necessary to make precise measurements. This is assumed important for the use of ISE for trace element analysis, particularly when the computer-aided on-line based accumulation of the ISE output is performed (ref. 4).

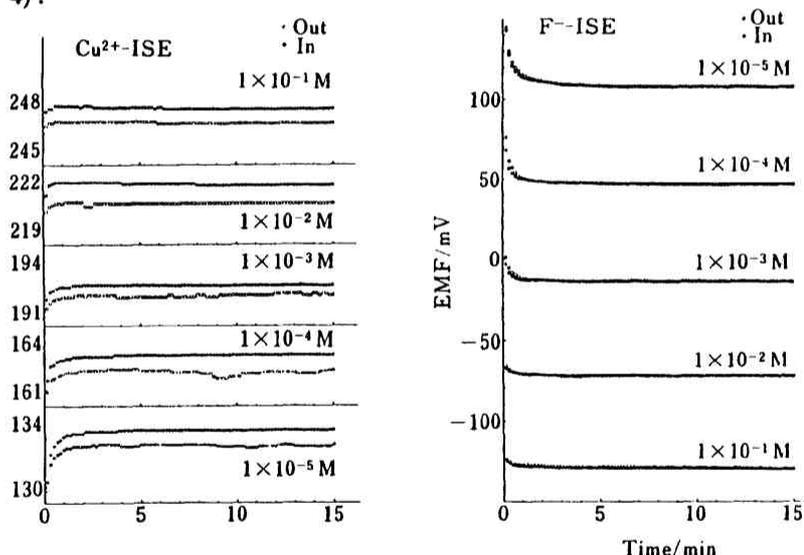


Fig. 2. Time dependence of the output of ISE's with and without insulation from the electromagnetic waves in space.

Strong perturbation

A rectangular pulse electric voltage was applied to the ISE (ref. 3). The response of the ISE was measured by a fast digital memoryscope (DMS), DMS 6430 of Iwatsu Elect. Inc. The pulse field was produced by a function generator (FG) of Yokokawa-Hewlett-Packard, 3310B, and fed to a platinum square plate of 10 mm \times 10 mm with a range from a few millivolts to 3 volts. This plate was placed in parallel to the surface of the ISE ca. 10 mm apart from the latter. The platinum plate worked as the source of the triggering voltage.

The interval (frequency) of the pulse ranged from 0 to 10 kHz. The pulse height was set in various ways, $-V$ mV to zero, zero to V mV, or $-V$ to $+V$ mV, where V was chosen in the range from 100 to 3000. A drastic change of the output is observed at the time of the straight rise or the drop of the voltage, and then a decay follows. Exactly speaking, a short delay of a few tenths of μs exists between the vertical change of the pulse field and the start of the response. The initial step of the vertical change can not be caught by the memoryscope used in the present investigation for F^- , Cl^- , Br^- and I^- ISE's. However, it is caught for the cases of Cu^{2+} and Pb^{2+} ISE's. The classification of the ISE's which has been achieved by the present experiment agrees with that of weak perturbation except F^- ISE. The

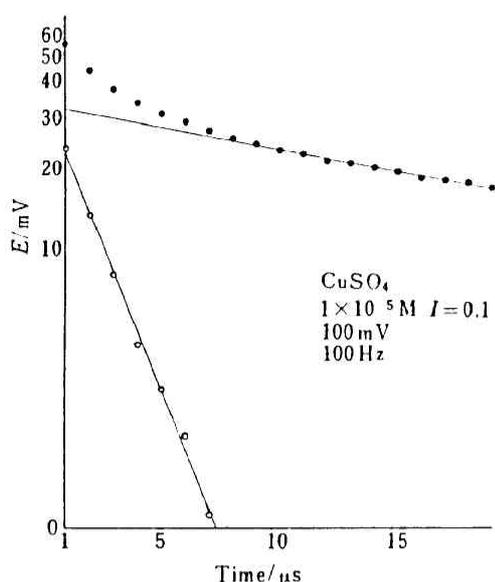


Fig. 3. Time dependence of the response of Cu^{2+} ISE towards the triggering voltage of 100 mV, 100 Hz pulse.

decay curves obey the logarithmic formula, $E = E_0 \exp(-t/\tau)$, as shown in Fig. 3 where E , E_0 , t and τ refer to the observed height, the response constant, the time of the measurement and the relaxation time, respectively. Values of τ were obtained for the cases of various conditions of the voltage of the pulse height, the species of the electrodes, the ionic species and their concentrations. The response curve has been analysed as the additives of two logarithmic function with different relaxation times, one very short, X , and the other longer, Y . No sizable change of τ was noticed when the distance between the ISE and the working platinum plate was changed from ca. 10 mm to ca. 2 or 3 mm.

The τ values for X and Y of Cu^{2+} ISE are about 2 and $20 \pm 5 \mu\text{s}$, respectively. The values for X of Pb^{2+} ISE is about $1 \mu\text{s}$ and Y is about $5 \mu\text{s}$. The case of the Cl^- or Br^- electrode may be one where the relaxation time is too short for the measurement and has been missed. With the F^- electrode, the X component is missed because it is too short, and only Y is observed whose value is around $80 \mu\text{s}$. This classification of the τ values holds for all species of ISE's.

Chemical perturbation

Measurement of the τ values is also useful for the quantitative evaluation of memory effects of ISE's, such as the effects of the "conditioning solutions (ref. 5)". The term "conditioning" here refers to the procedure of placing an ISE in a specific solution in order to stabilize the surface of the electrode, and the experiment following will refer to the investigation of the chemical perturbation. In the experiment, the ISE's of F^- , Cl^- and Cu^{2+} conditioned by three different solutions and the τ 's of Eq. (1) have been measured:

$$\Delta V = \Delta V_0 e^{-t/\tau} \quad (1)$$

where $\Delta V t$ is the output difference between the values at the time t and zero of an ISE and the time $t=0$ is taken as the start of the contact of the ISE with the sample solution. Actually $\tau_{1/2}$'s, to be defined by analogy to the half life time of the radioactive nucleus, had been calculated from the observed values of $\Delta V t$.

The experimental conditions are as follows. The ISE's are the ones produced by the Denki Kagaku Keiki (DKK) Co. and by the Toa Dempa Co. For conditioning, the ISE's have been held in three different solutions: a) pure water of pH 6.8, which is twice distilled, b) 10^{-6} mol/l of KF, NaCl and CuSO_4 aqueous solutions for F^- , Cl^- and Cu^{2+} ISE's, respectively, and c) the buffer solutions of pH 5.0 for F^- and Cl^- ISE's and pH 6.0 for Cu^{2+} ISE. The latter two buffer solutions have been prepared by adding few drops of acetic acid to a solution which contains ca. 0.010 mol/l KNO_3 and ca. 0.015 mol/l CH_3COONa . The ionic strengths of the sample solutions have been set at 0.001 with KNO_3 . The latter condition has been adopted because it is assumed effective for the comparison of the effects of different conditioning solutions.

After the ISE is held in the conditioning solution for 15 min and is found to exhibit a stabilized output, the ISE is placed in the sample solution of 10^{-6} mol/l ions of F^- , Cl^- or Cu^{2+} whose ionic strength is 0.001 and the output is measured at intervals of 2 s. An example of the measurement for a F^- ISE is as shown in Fig. 4. The results of the measurement are analyzed in terms of a superposition of two logarithmic curves as shown in Fig. 5, for all ISE's examined. The black circles in Fig. 5 refer to the logarithmic presentation of the observed data. They are decomposed into two parts as shown in the figure, one which refers to a straight line with respect to the later time measurement data and the other, being presented by the white circles, which refers to the remainder after reducing the former part contribution from the observed data. Thus, the $\tau_{1/2}$ values of two

Table I $\tau_{1/2}$ values for F^- , Cl^- and Cu^{2+} electrodes conditioned with different solutions

Electrode	Conditioning solution	X'/s	Y'/s
F-ISE (DKK)	Water	3.5 ± 1.0	24.1 ± 3.2
	10^{-6} mol/l KF	2.3 ± 0.4	19.2 ± 1.9
	buffer soln.	3.1 ± 0.6	16.8 ± 1.6
Cl-ISE (Toa)	water	3.0 ± 0.7	15.1 ± 2.8
	10^{-6} mol/l NaCl	2.2 ± 0.5	13.4 ± 3.1
	buffer soln.	2.3 ± 0.3	12.7 ± 0.5
Cu^{2+} ISE (Toa)	water	1.9 ± 0.6	13.3 ± 3.4
	10^{-6} mol/l CuSO_4	2.7 ± 0.5	17.9 ± 4.8
	buffer soln.	2.5 ± 0.7	19.2 ± 3.8

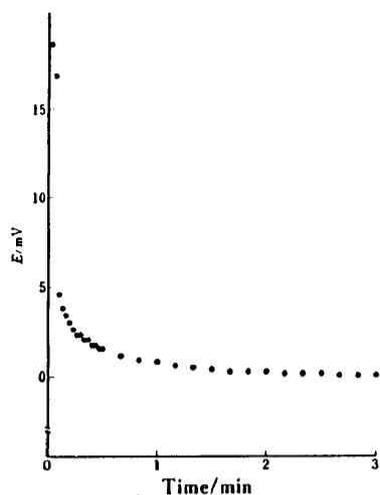


Fig. 4. Time dependence of the output of F⁻ ISE for the interface with 10⁻⁴ mol/l KF solution after the conditioning with 1 × 10⁻⁶ mol/l KF solution.

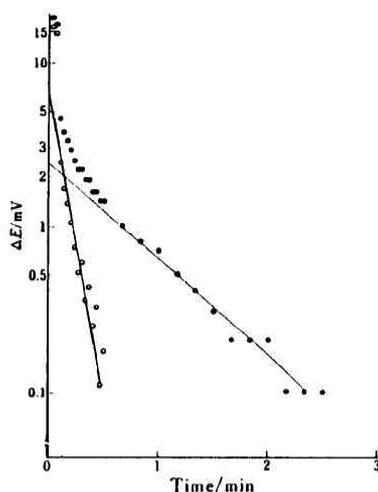


Fig. 5. Logarithmic presentation of the data of Fig. 4. F⁻ ISE-(B); KF, 1 × 10⁻⁴ M.

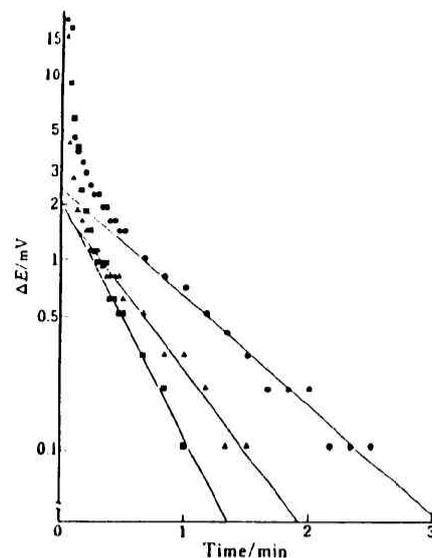


Fig. 6. Y' part outputs of F⁻ ISE's with different conditionings. ●, Distilled water, ▲, KF 1 × 10⁻⁶ mol/l soln, ■, acetate buffer.

categories are obtained, one short, X' and the other long, Y'. The X' values for a new F⁻ ISE are in the range around 3(±0.5) s and the Y's around 20(±3) s. Figure 6 and Table 1 present the effect of different conditionings for three ISE's examined. The results of Table 1 suggest that the $\tau_{1/2}$ values for ISE's are varied depending on the kinds of the ISE. The $\tau_{1/2}$ values shown here are assumed to refer to the times which are necessary for the establishment of the equilibrium conditions of ions at the surface of the electrode. The $\tau_{1/2}$ values show a trend to be elongated after the repetition of measurement of several hundred times, and also with the application of electric voltage triggering or UV light even when the surface of the ISE is polished by calcium carbonate powder.

DISCUSSION

Essential remark on the results of the present investigation is that the dynamical response of ISE's is formed of two relaxation times regardless of the kinds of perturbation, either the application of the external triggering electric voltage or the contact with the chemical solution. This fact may suggest that the response of the ISE's follows a mechanism which is formed of two characteristic relaxation times. It is assumed that those relaxation times refer to the fact that ISE works as the resonant tuning circuit towards the external perturbation. Depending on the kinds of ISE's, the features of the relaxation circuit, i.e., the dominant components of the resonant circuit are varied as either capacitive or conductive. The Ag⁺, Cu²⁺ and Pb²⁺ ISE's belong to the capacity dominant case and those of F⁻, Cl⁻, Br⁻ and I⁻ to the conductance determining. As to the magnitudes of the relaxation time, two different ranges have been measured, one in the range of μ s and the other of several seconds or longer. The short value of μ second order is obtained in the case of the strong perturbation of the pulse electric field and the long one of several second or longer with the chemical perturbation.

Those results cited may suggest that ISE's can be classified into two kinds with respect to the mechanism of relaxation, one where the capacitive mechanism is dominant and the other ionic. The ISE's which can be assigned as those of the capacity response dominant may refer to the ones of the electronic response and those of the conductance to the ionic conductivity. It must be noted, however, that both of course carry the contribution of the counter side component, either conductive or capacitive. Biological concerns of the results of the present investigation may also be referred to here. The ISE membrane is often taken as the model for the biological membrane in the sense that both systems of membrane carry the capacitive and the conductive characters and also that both works interfaced with the aqueous solution. The biological significance of the results of the present investigation may lie in the fact that 1μ s order response to the external triggering has been evidenced, which will be significant for the functioning of a biological system like the nervous system.

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