ION-SELECTIVE ELECTRODES BASED ON POLARIZABLE ELECTROLYTE/ELECTROLYTE SOLUTIONS INTERFACE

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Abstract The interface between two immiscible electrolyte solutions can function as the electrode surface which responds selectively to specified ion(s), that is, as the ion-selective electrode (ISE). Both amperometry (or voltammetry) and potentiometry can be used. The amperometric ISE gives the current response which is proportional to the concentration of ion(s); whereas the potentiometric ISE gives the potential response which changes linearly with the logarithm of the activity of ion. Ion sensors based on the amperometric ISE are described.

Key words ion-selective electrode, ion sensor

Recent electrochemical studies on the transfer of ions across the interface between two immiscible electrolyte solutions (review[1,2]), such as the interface between nitrobenzene and water solutions, or in short, the electrolyte/electrolyte solutions interface or oil/water (O/W) interface have shown that the O/W interface can electrically be polarized under certain conditions and that this polarizable O/W interface can function as the ion-selective electrode interface, that is, the electrode interface which responds selectively to specified ion(s) that are transferable across the interface in the polarizable potential range (review[3,4]). Theory and some methodological aspects of the electroanalytical chemistry with the polarizable O/W interfaces, that is, the ion-selective electrodes based on this interface are discussed and some analytical applications of the amperometric ion-selective electrodes are described in this paper.

VOLTAMMETRY AT ELECTROLYTE/ELECTROLYTE SOLUTIONS INTERFACES

Ideal-polarized interface

We consider first the interface between an organic or oil (O) phase which contains an extremely hydrophobic electrolyte B_1A_1 or B_1^+ and A_1^- (e.g., tetrabutylammonium tetraphenylborate (TBATPB) in nitrobenzene) and an aqueous or water (W) phase which contains an extremely hydrophilic electrolyte B_2A_2 or B_2^+ and A_2^- (e.g., LiCl in water). Such interface can be studied using the following cell;

where B_i^+ and A_i^- ($i=1, 2$) represent the cation and anion (here assumed to be mono-valent, unless otherwise stated) and R_i ($i=1, 2$) the reference electrode (usually reversible to either B_i^+ or A_i^-). An electric field is applied across the organic/aqueous or oil/water (O/W) interface (indicated by the mark * in cell I) by an external source. As long as the potential difference across the interface, $\Delta\phi (= \Delta_0^W\phi = \phi^W - \phi^O, \phi^\alpha$ being the Galvani potential of α phase) does not exceed a certain range of positive and negative magnitude, the transfer of B_1^+ and A_1^- ions from O to W and that of A_2^- and B_2^+ ions in the opposite direction should be negligible, since B_1^+ and A_1^- ions are extremely hydrophobic and A_2^- and B_2^+ ions extremely hydrophilic (Fig.1A). In Fig.1, we define that the positive (or anodic) current stands for the transfer of cation from W to O and anion from O to W

and the negative (or cathodic) current for those in the opposite direction. Thereby the O/W interface behaves as an ideal-polarized interface in this range of the applied potential difference across the interface, which we shall call the polarizable potential range or the potential window, likewise as the ideal-polarized metal/electrolyte solution interface.

Amperometry (or voltammetry) at polarized O/W interface

We consider the second case when a moderately or "semi-" hydrophilic (or -hydrophobic) ion j is present in one of the two phases, e.g. a semi-hydrophilic cation B_3^+ such as tetramethylammonium (TMA^+) ion, in the W phase;

Then the transfer of the j -ion across the O/W interface will take place at the intermediate potential within the polarizable potential range in cell I. Consequently we shall observe the current due to the transfer of j -ion across the O/W interface, I , as a function of the potential difference applied to the interface (Fig. 1B). In most cases the transfer of ions across such polarizable O/W interface is rapid and reversible, hence the ratio of the surface concentration of transferable ion j (here B_3^+ ion) between O and W phases can be expressed by Nernst equation (see eq. 4 below). The ions B_1^+ , A_1^- , B_2^+ , A_2^- etc. function as the supporting electrolyte. Thus we shall observe, e.g. for the transfer of B_3^+ ion from W to O phase, the (positive) current vs. potential curve (or wave) of the same form as the ordinary polarographic current vs. potential curve, as schematically shown in Fig. 1B. The (reversible) half-wave potential should be given by

$$\Delta\phi_{1/2,j} = \Delta\phi_j^\ominus (RT/z_jF) \ln[(D_j^O/D_j^W)^{1/2}] \quad (1)$$

where $\Delta\phi_j^\ominus$ is the standard potential of transfer of j -ion (here B_3^+ ion) at the O/W interface, z_j the number of charge including the sign of j -ion, D_j^α the diffusion coefficient of j -ion in α phase ($\alpha = O, W$) and F, R , and T are used in their usual meanings. $\Delta\phi_j^\ominus$ is related to the standard Gibbs energy of transfer of j -ion from O to W phase, $\Delta G_{tr,j}^0$ by

$$\Delta\phi_j^\ominus = -\Delta G_{tr,j}^0 / z_j F \quad (2)$$

The limiting current, $I_{l,j}$ (in Fig. 1B, or the peak current in the case of linear potential sweep voltammetry, etc.) is proportional to the bulk

Fig. 1. (A) Ideal-polarized O/W interface. (B) Polarographic current-potential curve of ion transfer at the O/W interface. (C) Composite positive-negative current-potential curve and (zero-current) potentiometry.

concentration of j-ion in α phase, $*C_j^\alpha$ (here $j=B_3^+$ and $\alpha=W$);

$$I_{1,j} = k_j * C_j^\alpha \quad (3)$$

where k_j is the constant which is determined by D_j^α as well as the scheme of voltammetric techniques. These equations describing the basic character of the voltammetric current-potential curve of the transfer of ion(s) across the polarizable O/W interface clearly indicate that this interface can function as an electrode interface for voltammetric (here, amperometric) determination of j-ion in W phase. In other words, the left-hand half-cell of cell II works as an ion sensor for amperometric determination of j-ion in test solution (here the W phase).

Potentiometry at polarizable O/W interface

We consider the third case where a "semi"-hydrophobic ion j, which is transferable across the interface within the polarizable potential range (here B_3^+ ion) is present in both O and W phases;

Then we shall observe the composite positive-negative current-potential curve (or wave) of the transfer of j-ion (here B_3^+ ion, Fig.1C) from W to O (positive) and from O to W (negative) and thereby the zero-current potential or the equilibrium potential should be given by Nernst equation;

$$\Delta\phi_e(I=0) = \Delta\phi_j^\ominus + (RT/z_jF) \ln[a_j^O/a_j^W] \quad (4)$$

where a_j^α is the activity of j-ion in α phase ($\alpha = O, W$). Thus for varying activity (or concentration) of j-ion, e.g. in the W phase while the activity of j-ion in the O phase is kept constant, we should have the potential response (that is, the electromotive force) of cell III which changes linearly to the logarithm of varying j-ion activity in the W phase. It can be seen that here the left-hand half-cell of cell III works as an ion sensor for potentiometric determination of j-ion activity in test solution (here the W phase).

Facilitated transfer of ions across O/W interface

When a hydrophobic ligand (or ionophore), L, which selectively associates with a specified ion, M, to form a hydrophobic complex, ML, is present in the O phase, the transfer potential of M ion from W to O phase is facilitated by $\Delta\Delta\phi$ as given by

$$\Delta\Delta\phi = \Delta\phi_M^\ominus - \Delta\phi_{ML}^\ominus = (RT/z_MF) \ln[K_{ML}^O C_L^O] \quad (5)$$

where z_M is the number of charge including the sign of M-ion, K_{ML}^O the formation constant of ML in O phase ($ML(O) = M(O) + L(O)$) and C_L^O the concentration (activity) of L in O phase. (Here it is also assumed that $K_{ML}^O C_L^O \gg 1$. Generalization of the present argument and general theoretical equations are presented [5-7]. Now we suppose the case that the M-ion, being assumed here to be a cation, is so hydrophilic that its transfer across the O/W interface can take place only at very positive potential (that is, around $\Delta\phi_M^\ominus$) beyond the polarizable potential range (Fig.2). The presence of the ionophore L will selectively shift the transfer potential of M-ion to less positive potential (that is, around $\Delta\phi_{ML}^\ominus$), if $\Delta\Delta\phi$ is sufficiently large, within the polarizable potential range of the O/W interface, making

Fig. 2. Facilitated transfer of M-ion from the aqueous(W) to the organic(O) phase by the presence of an ionophore L in the O phase.

the polarizable O/W interface respond selectively to the M-ion. Equations 1 and 4 can be used for amperometry (or voltammetry) and potentiometry with this M ion-selective electrode by replacing $\Delta\phi_j^{\ominus}$ by $\Delta\phi_{ML}^{\ominus}$ in these equations.

ION-SELECTIVE ELECTRODES (ISE)

The above discussion shows that the polarizable O/W interface can function as the ion-selective electrode interface for potentiometry as well as amperometry of ion(s), both based on the same electrochemical principle of the transfer of ions across the interface. In other words there are two types of ion-selective electrodes (ISE); one is the potentiometric ISE which gives the potential response linear to the logarithm of the activity (concentration) of the specified ion and the other is the amperometric ISE which gives the current response linear to the concentration of the specified ion(s). The above examples of ISE, that is the left-hand half-cells in cells II and III are organic or oil (e.g. nitrobenzene) ISEs for assay of ion(s) in aqueous test solution. Likewise aqueous or water ISEs for amperometry and potentiometry of ion(s) in organic or oil test solution have been studied[8]. Gelation of the liquid electrodes appear to have advantages in practical applications[8]. Membrane-stabilized or -covered O/W interface electrodes also appear very useful for practical applications[9-11]. Organic solvents of low vapor pressure[12] like o-nitrophenyl-octylether, o-nitrophenylphenylether and 2-fluoro-2'-nitrodiphenylether as the O phase may be preferred for construction of practical ion sensors.

Potentiometric ISEs

Potentiometric ISEs based on polarizable O/W interface, such as poly(vinyl-chloride)-nitrobenzene gel/water interface[13] have been studied. Theory of the ion selectivity coefficient of these ISEs has been presented and experimentally verified (review[2]). Further discussion on the potentiometric ISEs has been given elsewhere[3].

Amperometric ISEs

Every amperometric or voltammetric techniques can be applied for determination of ion(s) using the amperometric ISEs (review[1-4]). Likewise, kinetics and thermodynamics of the ion transfer across the electrolyte/electrolyte solutions interface using various voltammetric techniques has also extensively been studied[1,2,14,15].

At the amperometric ISE two or more ions can be determined simultaneously if their half-wave potentials are reasonably separated[11]. Also, voltammetric behavior of a micro-ISE, fabricated at the tip of a micropipette, has been studied and stripping ion-transfer voltammetry for trace analysis is suggested[16].

Application of the pulse amperometry technique to amperometric ISEs is promising[17], where the initial potential is kept at the potential range where no ion transfer takes place and a voltage pulse of short duration (e.g., 100 ms) and constant amplitude, large enough to give the limiting current of a polarographic curve, is applied at a certain interval (e.g., 5s). The current is sampled, e.g., at the end of each pulse. Since the ion transfer process is generally reversible, after application of each pulse the electrode interface is recovered to the initial state before the next pulse is applied. Hence high reproducibility can be obtained. Double pulse amperometric technique has been developed for simultaneous determination of two ions with a single ISE[11].

ION SENSORS BASED ON AMPEROMETRIC ISE

Potassium and sodium ion sensors

The interface between nitrobenzene (NB) solution containing an ionophore, BB15C5 (bis((benzo-15-crown-5)-4'-ylmethyl)-pimerate) and water (NB(BB15C5)-/W) works satisfactorily as an ISE for amperometric determination of K^+ and Na^+ ions:

In this cell, TPenACl and TPenATPB are tetrapentylammonium chloride and tetrapentylammonium tetrphenylborate, respectively, and $M \text{ mol dm}^{-3}$. The NB(BB15C5)/W interface was stabilized by placing a thin, hydrophilic semipermeable membrane (HSM, e.g. a dialysis membrane of $20 \mu\text{m}$ thickness) at the interface. Thus the left-hand half cell constitutes a membrane-covered ISE sensor which is easy to be fabricated, convenient for handling and stable more than a month. K^+ and Na^+ ions in the test solution ($0.01 \text{ M MgCl}_2(\text{W})$) give the voltammetric current response at $E_{1/2} = 0.198 \text{ V}$ and 0.381 V (with cell IIa), respectively. Figure 3 shows the representative, pulse amperometric responses of a membrane-covered ISE sensor. The response time was 20 s to reach 95% of the steady state. The half-wave potentials of the two ions are separated enough for simultaneous determination of the two ions with a single electrode. The dual pulse amperometric technique was developed for the simultaneous determination of potassium and sodium ions and was applied to the analysis of drinks and foods[11].

Fig. 3. Pulse amperometric response of a membrane-covered K/Na ion sensor for successive addition of 0.1 mM K^+ ion at the time marked by arrows. The current(A) was measured at $E=0.29 \text{ V}$ and corrected(B) for the base current(C) measured at $E=0.12 \text{ V}$.

Volatile amines sensors

The membrane(HSM)-covered NB/W interface gives the current response proportional to the concentration of ammonium ions of volatile amines like NMe_3H^+ ion (but no response to NH_4^+ ion); whereas the membrane(HSM)-covered NB(containing an ionophore like DB18C6, dibenzo-18-crown-6)/W interface to the sum of the concentrations of NMe_3H^+ and NH_4^+ ions, eventually giving the concentration of NH_4^+ ion by subtracting the former response from the latter. The HSM-covered NB/W and NB(DB18C6)/W ISE surfaces were further covered by a thin, gas permeable membrane(GPM, e.g., a Teflon membrane of $50 \mu\text{m}$ thickness) with a thin, inner solution (e.g., L-lysine solution, pH 9.8, with a space of nylon mesh of $100 \mu\text{m}$ thickness) between HSM and GPM:

where TBACl and TBATClPB are tetrabutylammonium chloride and tetrabutylammonium tetra-p-chloro-phenylborate. The counter (right-hand) reference Ag/AgCl electrode is connected to the cell through the inner L-lysine solution and the whole cell is separated from test solution by the gas permeable membrane(GPM). Sample was syringed into the test solution (carbonate-borate-KCl buffer of pH 10.5). This membrane-covered volatile amines sensor gave the linear current response to the concentration of ammonium ions of volatile amines in the test solution (Fig. 4), with response time of typically ca. 100 s , and was applied to determine NH_4^+ and NMe_3H^+ ions separately (for volatile base nitrogen analysis) in fish meats[12].

Urea biosensor based on amperometric ammonium ISE

On the surface of a membrane(GPM)-covered ammonia sensor based on NB(DB18C6)/W ISE (cell IIb), urease was immobilized by coating the sensor surface with a thin, semipermeable membrane (HSM, e.g., a dialysis membrane of 20 μm thickness) to fabricate an amperometric urea biosensor. This urea biosensor gave the (pulse amperometric) response proportional to the concentration of urea in the range of μM to a few mM with response time of typically 300 s [18,19].

Fig. 4. Pulse current response of a membrane-covered volatile amines sensor for successive addition of NMe_3H^+ ion into the test solution at the time marked by arrows. Initial potential: 0.30 V; pulse height: 0.2V.

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