Recent Advances in Analytical Potentiometry with Ion-Selective Electrodes [and Discussion]

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Recent advances in analytical potentiometry with ion-selective electrodes

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Historical developments in analytical potentiometry are briefly introduced and compared with those in polarography and coulometry: in the discussion special emphasis is given to the selectivities of these methods.

Next, recent advances are described in ion-selective electrodes of both the solid membrane and the liquid membrane types; an extremely small ion-selective reference electrode assembly made with a field effect transistor is described and the use of solid solvent as membrane material is discussed. The enhancement of the selectivity of anion electrodes by *p-tert*-octylphenol is introduced and the effect of the enhancement is explained after a discussion from a voltammetric standpoint of the mechanisms of potential generation at the electrode–solution interface.

As an example of the applications of the ion-selective electrode, the use of the cation-sensitive glass electrode for the measurement of the activities of metal ions in non-aqueous solvents is introduced.

1. ADVANCES IN ANALYTICAL POTENTIOMETRY

In 1875, Sir William Thomson presented a paper entitled ‘Electrolytic conduction in solids’ in which he suggested that glass was an electrolytic conductor. Thirty years later, this suggestion led to the development of the most typical ion-selective electrode, the glass electrode (Cremer 1906). It is more surprising that more than half a century elapsed before the introduction of other ion-selective electrodes. Today, analytical potentiometry can be said to have entered a new era, a *renaissance*, with the development of ion-selective electrodes.

Potentiometric methods of analysis with the ion ‘non-selective’ electrode is one of the oldest methods of electrometric analysis, but was mostly used for the detection of the equivalence point in titrimetric analyses; titration using a reagent was an inevitable process in attaining selectivity. In 1922, Heyrovsky, in collaboration with Shikata, initiated polarography, in which a polarizing diffusion current gave rise to a method with enough selectivity. Together with its higher sensitivity, polarography thus overtook potentiometry in many fields of applied analysis. Coulometry is also an old electrometric method of analysis which, thanks to the introduction of the electronic potentiostat and of the column electrode in the flow system, has played an important role in contemporary trace analysis.

It is well known that electronics were introduced into most physical methods of analysis in the 1920s, but their main contribution to practical analysis was not realized until the 1940s with the introduction of an electronic potentiometer in potentiometry, an electronic galvanometer in polarography and an electronic potentiostat in coulometry. It would be interesting to consider the degree to which future contributions of electronics, especially of computerization, could benefit each of these instrumental electrometric methods of analysis with respect to sensitivity and selectivity.

2. RECENT ADVANCES IN ION SELECTIVE ELECTRODES

Solid electrodes

The glass electrode has long been thought of as usable only for the hydrogen ion. Eisenman and his colleagues (1957) developed a specialized glass electrode selective to monovalent cations such as Na^+, K^+, Ag^+, NH_4^+, Tl^+, Li^+ and Cs^+. Membranes of single crystals that are conductive and hardly soluble in water, such as silver halides (Kolthoff & Sanders 1937) and lanthanum fluoride (Frant & Ross 1966) were used for the determination of various inorganic cations and anions.

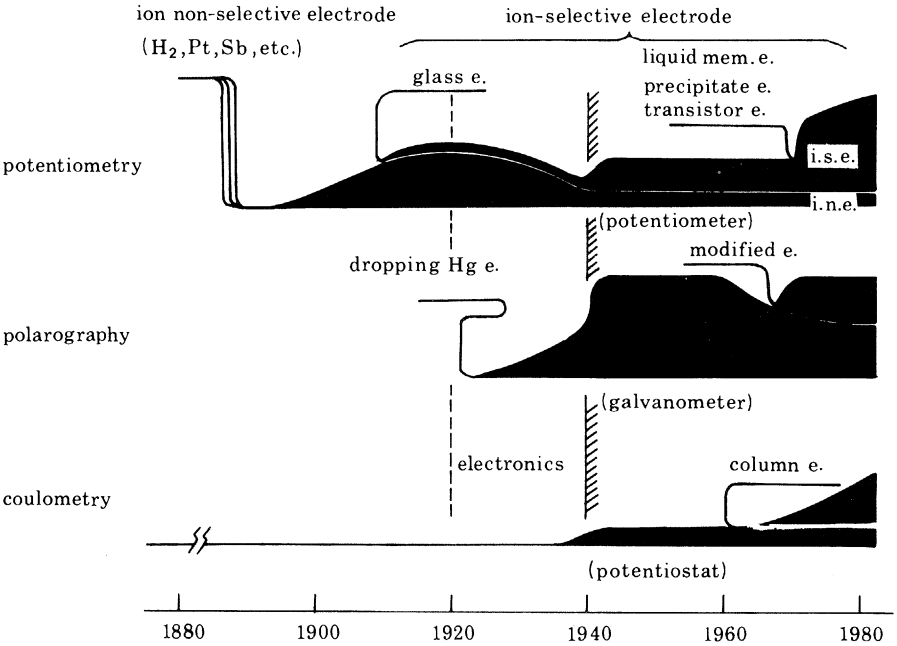


FIGURE 1. Advances in analytical potentiometry, polarography and coulometry.

In order to maintain an electroconductive precipitate in a membrane, silicone rubber (Pungor *et al.* 1964) has been used as a supporting material. Such heterogeneous membranes have been used especially for the determination of various anions. Hirata *et al.* (1970) developed an ion-selective electrode (i.s.e.) with a ceramic membrane of lanthanum fluoride doped with europium fluoride. The ceramic membrane prepared under high pressure and temperature showed stable potentials and was selective to the objective ions.

Bergveld (1972) initiated the idea of using a field-effect transitor (f.e.t.) as an i.s.e. The gate potential of the f.e.t. in contact with the sample solution gives rise to a change in current flowing from the drain to the source of the f.e.t., which is logarithmically proportional to its concentration.

The f.e.t.–i.s.e. has various advantages over other solid i.s.es: for instance it can be very small, and the input impedance can be kept extremely high.

Recently, Oka (1981) developed a combined electrode pair of ion-sensing f.e.t. and reference f.e.t., 6.5 mm long, 0.6 mm wide and 0.2 mm thick (figure 2). For the measurement of pH, the ion-sensing f.e.t. was prepared by plating Ta_2O_5 onto the gate. The reference f.e.t. attached on the back was prepared by plating on styrene polymer; this reference cell kept a constant potential independent of pH from 3 to 11.

This type of electrode pair is expected to be especially useful for clinical measurements.

Liquid membrane electrodes

A water-immiscible solvent that contains an appreciable amount of objective ions in the membrane phase can function as a liquid ion exchanger. When proper electronic or ionic connection is made with the exchanger, it forms a liquid membrane electrode. Ross (1967) constructed a calcium i.s.e. with calcium organophosphate dissolved in di-*n*-octyl phenyl phosphate as the membrane medium.

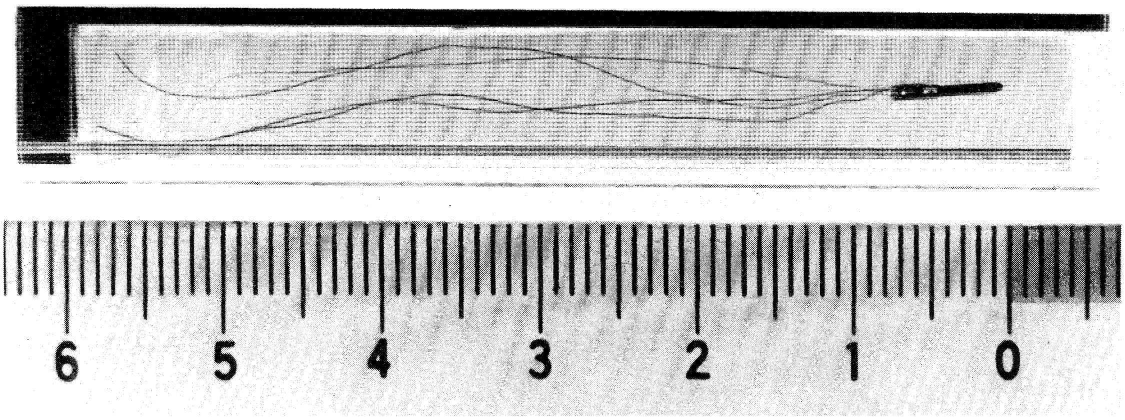


Figure 2. Ion-sensing f.e.t. electrode for pH measurement. One division: 1 mm.

In 1967, Stefanac & Simon used an antibiotic macrocyclic compound, valinomycin, as the additive in a liquid membrane of a potassium i.s.e., which showed extremely high selectivity to potassium ions. Recent progress in the synthesis of macrocyclic compounds has made it possible to prepare cation-selective membrane electrodes comparable in selectivity with those containing antibiotics.

Fujinaga *et al.* (1978) and Hara *et al.* (1980) have found a similar effect with an anion i.s.e.; a *para*-substituted multi-branched alkylphenol used as the additive in the membrane of an anion i.s.e. enhanced the selectivity greatly. This effect was attributed to hydrogen bonding between the phenol and the anion (§4).

3. The use of solid solvent as membrane medium

Liquid membrane electrodes (l.m.es) should have more advantages than solid membrane electrodes, owing to the variety of ion-exchangers. However, their potentiometric response is liable to be disturbed by hydrostatic pressure or by stirring of the sample solution, or the membrane liquid may leak into the sample solution. In order to overcome these difficulties various studies have been made, resulting in the development of an l.m.e. based on plastic matrices (Moody *et al.* 1970; James *et al.* 1972), carbon paste (Qureshi & Lindquist 1973) and the solidification of nitrobenzene in the membrane by the addition of naphthalene (Kataoka & Kambara 1974).

In our laboratory, organic sulphonate-selective electrodes had been investigated by the use of a coated wire type of electrode (Fujinaga *et al.* 1974) and also a method based on a solid solvent extraction had been initiated by Fujinaga *et al.* (1969).

In connection with these investigations, we have developed a new type of i.s.e., one that uses organic compounds with a high melting point, i.e. that solidify at room temperature, as a membrane solvent (Hara *et al.* 1981). This type of electrode is hereafter called a solid-solvent membrane electrode (s.s.m.e.). After various experiments, it was concluded that the effects of the solvent on the selectivity pattern were rather small with the s.s.m.e. in contrast to the l.m.e. The potentials of s.s.m.e. seem to be governed mainly by direct ion-exchange reactions at the membrane–solution interface and are affected little by phenomena at the inner membrane.

TABLE 1. RESPONSE BEHAVIOUR OF *p*-TOLUENESULPHONATE ION-SENSITIVE ELECTRODES WITH (A) LIQUID MEMBRANE AND (B) SOLID-SOLVENT MEMBRANE

solvent	m.p. / °C	type of membrane	slope / mV/pA	limit of linear response/pA	response time/min at 10^{-2} M	at 10^{-4} M
1-decanol	7	A	64.2	3.8	1.2	4.6
1-octadecanol	59	B	64.7	3.7	2.0	3.7
nitrobenzene	6	A	66.1	3.4	1.0	4.1
m-dinitrobenzene	90	B	62.9	3.6	0.5	3.4
o-dichlorobenzene	−17	A	63.4	3.4	1.6	2.7
1,2,4,5-tetrachlorobenzene	140	B	67.1	3.6	0.1	2.5
tributyl phosphate	−80	A	62.1	3.4	1.6	2.3
triphenyl phosphate	49	B	67.9	3.7	0.1	2.4

Ion pair, *ca.* 0.1 M trioctylmethylammonium-*p*TS; temperature, 25 °C.

In conclusion, s.s.m.es with 1-octadecanol membranes have several advantages over l.m.es with common aromatic compounds: (1) the membrane is insoluble in water, (2) it does not sublime, and (3) it can be used as a matrix of a coated wire-type electrode instead of a conventional PVC matrix.

For the preparation of a coated wire-type s.s.m.e., a platinum or copper tip was dipped into the extract of the ion-pair in molten 1-octadecanol. An s.s.m.e. with an inner reference electrode type was also prepared. A pressed membrane should be thick enough, *ca.* 0.5 mm, to minimize damage. The reproducibility of the electrode potential was better than ± 2 mV.

Therefore, the s.s.m.es examined so far have the advantages of both solid and liquid membranes; they show a fast response and are applicable as sensors in a flowing system; contamination of the sample solution with the eluted solvent from the membrane can be minimized; a wide choice of objective ions is possible, as with l.m.es.

Highly selective organic sulphonate and sulphate ion electrodes, with alkylphenol in 1-octadecanol as the membrane, have been developed (§ 4).

4. Enhancement of selectivity in anion-selective electrodes by use of alkyl phenols as anion carriers

In our laboratory, the enhancing effect of alkyl phenols on the selectivity of l.m.es responsive to organic sulphonate, benzoate and nitrite ions has been investigated. Recently, in l.m.es, more interest has been shown in the membrane solvent than in the ion-exchange site as the

Table 2. Solvent effects on selectivity coefficients, lg K_{XY}, in the presence and absence of *pt*OP

(Ion exchanger: 0.5 M TOMA-*p*TS without (or with 0.5 M) *pt*OP in each solvent.)

		lg K_{XY}											
solvent	δ_h	ClO_4^-	BF_4^-	SCN^-	RSO_3^-†	I^-	ClO_3^-	ϕSO_3^-	NO_3^-	Br^-	NO_2^-	BrO_3^-	Cl^-
o-dichlorobenzene	3.3	2.3	1.6	1.2	1.1	0.6	−0.2	−0.3	−0.4	−1.0	−1.3	−1.5	−1.9
with 0.5 M *pt*OP		−0.6	−1.2	−0.3	0.8	−1.1	−1.5	−0.5	−1.3	−1.5	−1.2	−2.0	−1.8
nitrobenzene	4.1	2.0	1.4	1.1	0.8	0.7	−0.1	−0.3	−0.2	−0.8	−1.0	−1.1	−1.6
with 0.5 M *pt*OP		0.0	−0.6	0.1	0.7	−1.0	−1.3	−0.5	−1.0	−1.4	−1.1	−1.8	−1.7
chloroform	5.7	1.8	1.1	1.1	1.0	1.1	−0.1	−0.3	−0.3	−0.6	−1.2	−1.2	−1.5
with 0.5 M *pt*OP		−0.7	−1.2	−0.3	0.7	−0.9	−1.3	−0.5	−1.1	−1.4	−1.1	−1.6	−1.6
1-octanol	11.9	0.1	−0.5	0.3	0.7	−0.2	−0.8	−0.5	−0.9	−1.0	−1.2	−1.7	−1.5
with 0.5 M *pt*OP		−0.3	−0.9	0.1	0.7	−0.5	−1.0	−0.5	−1.0	−1.1	−1.1	−1.7	−1.5

† 1-Naphthalene sulphonate.

dominant factor for selectivity. Solvents such as nitrobenzene and 1,2-dichloroethane have been recommended because of their wide selectivity ranges, but the selectivity of the liquid membrane with these solvents is generally insufficient.

In the course of our study on the selectivity characteristics of the *p*-toluenesulphonate (*p*TS) ion-selective electrode, we have found that the selectivity coefficient (lg K_{xy}) of perchlorate decreased from +2.3 to −0.6 in the presence of 0.5 M *p*-*tert*-octylphenol (*p*-1,1,3,3-tetramethylbutylphenol) (*pt*OP). This effect of the phenol occurs not only with the *p*TS ion electrode but also with various oxyacid electrodes, such as benzoate, dodecyl sulphate and nitrite i.s.es. The effect was attributed to hydrogen bonding between the phenol and the anion (figure 3).

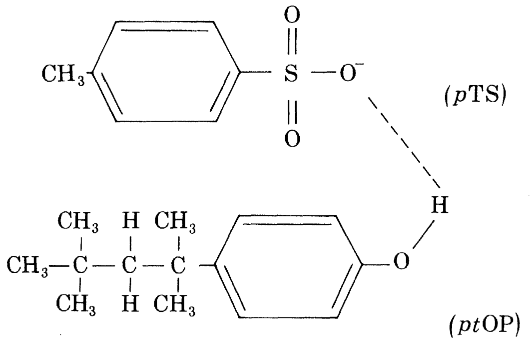


FIGURE 3. Association of *p*-toluenesulphonate with *p*-*tert*-octylphenol through hydrogen bonding.

TABLE 3. SELECTIVITY COEFFICIENTS, lg K_{XY}, OF BENZOATE ELECTRODE

(Ion exchangers: A, 0.05 M trioctylmethylammonium benzoate in *o*-dichlorobenzene; B, A+0.5 M *p*-*tert*-octylphenol.)

anion tested	lg K_{XY} A	lg K_{XY} B	Δ lg K_{XY}	anion tested	lg K_{XY} A	lg K_{XY} B	Δ lg K_{XY}
ClO_4^-	3.5	−0.5	−4.0	$C_6H_5SO_3^-$	0.7	−0.4	−1.1
$CF_3SO_3^-$	2.9	−0.4	−3.3	NO_3^-	0.6	−1.2	−1.8
SCN^-	2.2	−0.2	−2.4	Cl_2CHCOO^-	0.3	−0.6	−0.9
$C_6H_4(OH)COO^-$†	1.8	0.6	−1.2	Br^-	−0.1	−1.5	−1.4
$C_6H_4(COOH)COO^-$‡	1.8	0.1	−1.7	NO_2^-	−0.5	−1.2	−0.7
I^-	1.8	−1.0	−2.8	BrO_3^-	−0.5	−1.9	−1.4
Cl_3CCOO^-	1.6	0.1	−1.5	Cl^-	−1.0	−1.8	−0.8
$CH_3C_6H_4SO_3^-$§	1.1	0.2	−0.9	$ClCH_2COO^-$	−1.0	−1.2	−0.2
$C_2H_2(COOH)COO^-$¶	0.9	−0.6	−1.5	$CH_3SO_3^-$	−1.3	−1.9	−0.6
ClO_3^-	0.9	−1.4	−2.3	$HCOO^-$	−1.6	−1.4	+0.2
CF_3COO^-	0.7	−0.8	−1.5	CH_3COO^-	−1.8	−1.1	+0.7

†, Salicylate; ‡, hydrogen phthalate; §, *p*-toluenesulphonate; ¶, hydrogen maleate.

Table 2 summarizes the effect of phenol and some solvents on the selectivities of the sulphonate electrode; the hydrogen bonding component, δ_h, of the solubility parameters is also listed. The interference of inorganic anions, such as perchlorate, tetrafluoroborate and others, decreased with a solvent of increasing δ_h. In the presence of *pt*OP, however, no remarkable effect of solvent was observed. This shows that the selectivity is primarily determined by *pt*OP. Little effect of solvents on the selectivity of 1-naphthalenesulphonate, benzenesulphonate and nitrite was observed. These anions seem to interact with solvent or *pt*OP in the same way as the objective ion of *p*TS.

In conclusion, it was found that the best ion-exchanger for *p*-toluenesulphonate was 0.05 M tri-octyl-methyl-ammonium *p*-toluenesulphonate with 0.5 M *p-tert*-octylphenol in *o*-dichlorobenzene. The potentiometric response characteristics of this ion exchanger were: (1) the usable response range is 10^{-1} to 10^{-5} M, (2) the slope is 61 mV per decade, and (3) the response time at 10^{-2} M is within 3 min.

Similar enhancement of selectivity was observed with a benzoate i.s.e., as shown in table 3.

This anion sequestering effect of *pt*OP was applied to the dodecyl sulphate i.s.e., which was used as an indicator electrode in the potentiometric titration of anionic surfactants. A differential titration of a binary mixture of sodium dodecyl sulphate and sodium octyl sulphate was feasible.

The simultaneous determination of a binary mixture of nitrate and nitrite by means of i.s.es was also investigated. The selectivity coefficient of the nitrate i.s.e. to nitrite was 0.3–0.4, while that of the nitrite i.s.e. to nitrate became 0.8–1.0 by the addition of *p-tert*-octylphenol to the membrane. By using two modified Nernst equations for nitrate and nitrite mixtures of 1:1–1:5, concentrations between 10^{-2} M and 10^{-4} M were determined with a relative standard deviation of 15 %.

5. VOLTAMMETRIC INTERPRETATION OF THE BEHAVIOUR OF L.M.E. ION-SELECTIVE ELECTRODES

I (Fujinaga 1982) have studied the basic interpretation of electrode potentials of the i.s.e. from a voltammetric standpoint, as described below.

A reliable and stable potential at an electrode can only be maintained if it is depolarized. If an i.s.e. of the liquid membrane type shows a stable potential responsive to the concentration of an objective ion in the solution in the Nernstian way, the electrode would be depolarized by the ions.

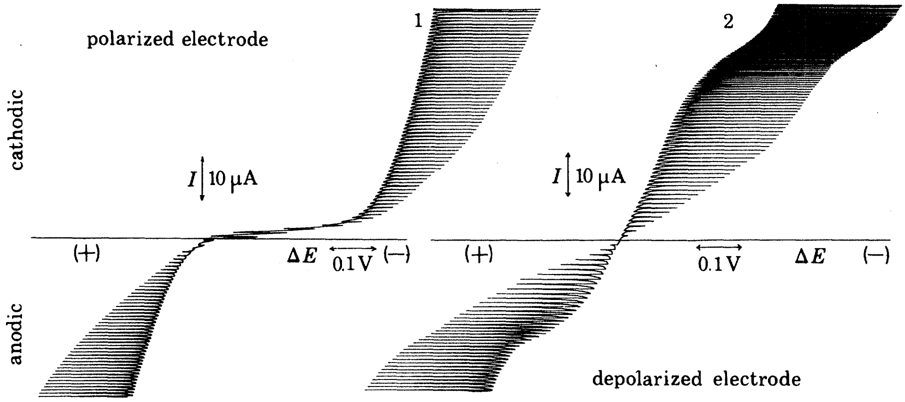


FIGURE 4. Current-scan polarograms of the base electrolytes 0.05 M LiCl + 1 M $MgSO_4$ in water and 0.05 M TBA-TPB in nitrobenzene in the absence (curve 1) and presence (curve 2) of 0.5 mM TMA cations in both phases. (According to Fujinaga *et al.*)

Recently, Samec *et al.* (1979) and Koryta *et al.* (1980) at the Heyrovsky Institute, Prague, showed polarograms at the electrolyte dropping electrode of an aqueous lithium chloride solution in a nitrobenzene solution containing tetrabutyl ammonium tetraphenyl borate (TBA-TPB) as the supporting electrolyte, and later Fujinaga *et al.* (1982) showed current-scan polarograms (Ishibashi & Fujinaga 1957) with the same electrolyte system.

$$\text{s.s.e.} \mid M^{+}{}_{w} \quad Z^{-}{}_{w} \,\vdots\, P^{-}{}_{o} \quad R^{+}{}_{o} \mid \text{s.s.e.}$$

Under this experimental condition, lithium chloride ($\mathrm{M^+{}_wZ^-{}_w}$) is hardly soluble in nitrobenzene, and TBA-TPB ($\mathrm{R^+{}_oP^-{}_o}$) is also slightly soluble in the aqueous solution, respectively. The interface is therefore polarized and does not show a definite potential, as shown in curve 1 in figure 4, and also as shown in curve I in figure 5.

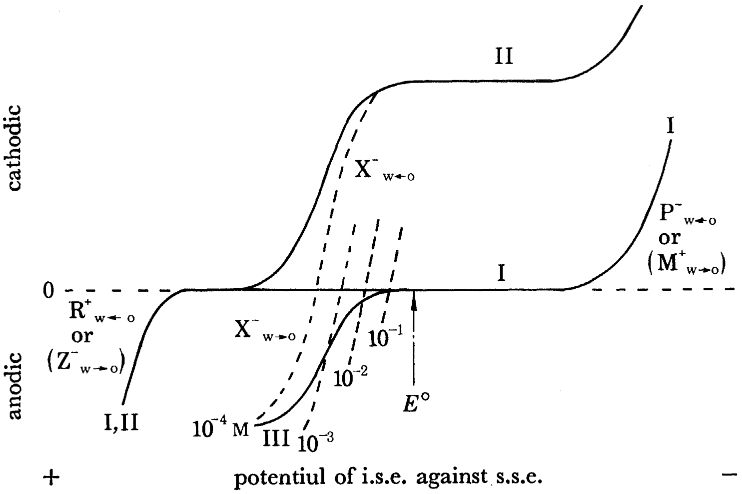
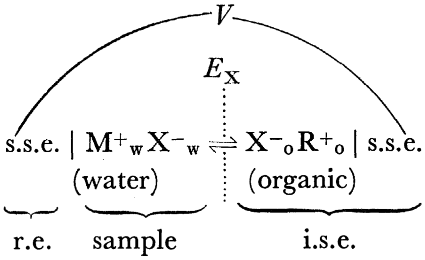


FIGURE 5. Schematic representation of voltammetric curves at the liquid membrane electrode. Curve I, polarized interface with $\mathrm{R^+{}_oP^-{}_o/M^+{}_wZ^-{}_w}$; curve II, depolarized interface with $\mathrm{R^+{}_oX^-{}_o/M^+{}_wX^-{}_w}$.

In figure 5, the current–voltage curve is similar to that for polarography, and the cathodic current at the i.s.e. is taken as positive. If the applied potential of the i.s.e. is shifted enough to a negative potential, a cathodic current begins to flow and to show its final rise, owing to the electrode reactions of the TPB anions in the nitrobenzene which move to the aqueous phase ($\mathrm{P^-{}_{w\leftarrow o}}$). Otherwise, lithium ions in the aqueous phase may move to the nitrobenzene phase ($\mathrm{M^+{}_{w\rightarrow o}}$). On the other hand, if the potential of the i.s.e. is shifted to a positive enough potential, the final descent of the anodic current begins because of the electrode reactions of TBA cations in the nitrobenzene, which move to the aqueous phase ($\mathrm{R^+{}_{w\leftarrow o}}$) or the chloride ions to the organic phase ($\mathrm{M^+{}_{w\rightarrow o}}$).

Current–voltage curve of the composite wave of X^- *at the i.s.e.*

Let us now consider the i.s.e. for a monovalent anion X^-. Unlike the conditions mentioned above, a definite amount of ion pair $\mathrm{R^+{}_oX^-{}_o}$ is dissolved in the organic phase, and ions $\mathrm{M^+{}_w}$ and $\mathrm{X^-{}_w}$ are present in the aqueous phase. Under ideal conditions, X^- in both phases is freely permeable across the organic–water (or membrane–solution) interface. However, the organic



cation $R^+{}_o$ is trapped within the organic (membrane) phase and the inorganic cation $M^+{}_w$ within the water (solution) phase. The membrane–solution interface is then depolarized by the mutual transport reaction $X^-{}_w \rightleftharpoons X^-{}_o$.

The electrode potential of the i.s.e. against the silver–silver-chloride electrode (s.s.e.) is therefore represented by

$$E = (RT/F) \ln ([X^-]_o/[X^-]_w), \tag{1}$$

where $[X^-]_o$ and $[X^-]_w$ denote the concentrations of the monovalent anion X^- in the organic and aqueous phases, respectively. Therefore, in the presence of a constant concentration of ion pairs in the organic phase, equation (1) can be written as

$$E_X = E_X^\circ - (RT/F) \ln [X^-]_w. \tag{2}$$

Here, if an interfering anion $Y^-{}_w$ is also present, the potential of the i.s.e. may shift to a more negative potential causing a positive error in the determination of $[X^-]_w$. Nicolsky (1937) formulated the degree of interference in the following equation:

$$E_{XY} = E_X^\circ - (RT/F) \ln ([X^-]_w + K_{XY}[Y^-]_w), \tag{3}$$

where K_{XY} is defined as the selectivity coefficient. As can be seen from curve II in figure 5, anion $X^-{}_o$ in the membrane (organic phase) moves to the aqueous phase, showing a diffusion current. On the other hand, anion $X^-{}_w$ in the sample solution (aqueous phase) moves to the organic phase in a way similar to that shown in curve III in figure 5, when the concentration $[X^-]_w$ is 10^{-4} M.

Thus the actual current–voltage curve appears as a composite wave of both curves II and III. The electrode potential of the i.s.e. is therefore located at the point where the composite wave intersects the zero current line and where the transports of $X^-{}_{w\leftarrow o}$ and $X^-{}_{w\rightarrow o}$ are taking place at an equal rate. Hence, the two exchange currents cancel each other out. The i.s.e. potential, E_X, shifts, becoming more negative by 59.1 mV per decade increase in $[X^-]$ at 25 °C, as shown by the dotted lines in the figure in accordance with equation (2).

Interference of other anions present together

Under the same experimental conditions, if the interfering anions $Y^-{}_w$ are present together with $X^-{}_w$, and the equilibrium constant K_{XY}^{ex} of the exchange reaction is large enough, the anodic wave Y appears at a more negative potential than that of X:

$$R^+{}_oX^-{}_o + Y^-{}_w \rightleftharpoons R^+{}_oY^-{}_o + X^-{}_w;$$

$$K_{XY}^{ex} = \frac{[R^+Y^-]_o[X^-]_w}{[R^+X^-]_o[Y^-]_w}. \tag{4}$$

Consequently, the composite wave XY due to $X^-{}_w$ and $Y^-{}_w$ is shifted by ΔE to a more negative potential than that due to $X^-{}_w$ alone. The magnitude of the shift gives the degree of interference of $Y^-{}_w$,

$$\Delta E = E_{XY} - E_X = -(RT/F) \ln (1 + K_{XY}[Y^-]_w/[X^-]_w). \tag{5}$$

However, if the interfering anion $Z^-{}_w$, whose equilibrium constant K_{XZ}^{ex} of exchange reaction is very small, is present, the anodic wave Z appears at a more positive potential than that of the wave X, and hence the potential of the i.s.e. does not shift practically from E_X.

Enhancement of selectivity by alkyl phenol

Under the same conditions, if the alkyl phenol (*pt*OP = Ph) is added to the membrane medium, the phenol combines with the objective anion X^- to form the associated ion PhX^-, but only slightly with anion Y^- to form PhY^-, then

$$Ph + X^- = PhX^-. \tag{6}$$

The formation constant K is given as

$$K = \frac{[PhX^-]}{[Ph]\,[X^-]}. \tag{7}$$

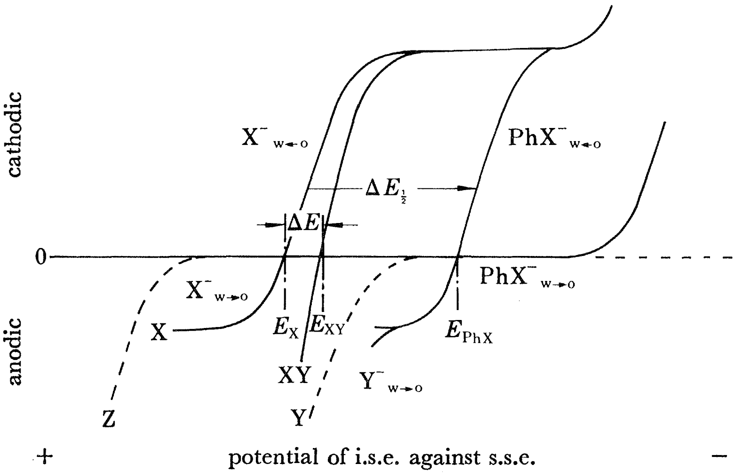


FIGURE 6. Schematic representation of voltammetric curves at the liquid membrane electrode. Curves show voltammetric relations of depolarizers $X^-{}_o$ and $X^-{}_w$ in the presence of interfering anions $Y^-{}_w$ and $Z^-{}_w$ in the presence and absence of phenol (Ph).

Therefore the potential of the i.s.e. with Ph is given by

$$E = E^{\circ}_{X} - \frac{RT}{F}\ln\frac{K[Ph]_o}{K_w[Ph]_w} + \frac{RT}{F}\ln\frac{[PhX^-]_o}{[PhX^-]_w} = E^{\circ}_{PhX} - \frac{RT}{F}\ln\frac{[PhX^-]_o}{[PhX^-]_w}. \tag{8}$$

Under the experimental conditions, where $[PhX^-]_o/[PhX^-]_w$ is nearly equal to $[X^-]_o/[X^-]_w$, the wave of X^- with the phenol shifts as follows:

$$\Delta E = E^{\circ}_{PhX} - E^{\circ}_{X} \approx \frac{RT}{F}\ln\frac{K_o[Ph]_o}{K_w[Ph]_w}. \tag{9}$$

Since both the formation constant and the solubility of the phenol are larger in the organic phase, the wave shifts to a more negative potential than without phenol. Additionally, since the perchlorate ion (Y^-) scarcely exhibits hydrogen bonding with the phenol, the wave Y remains unaltered.

Consequently, in the presence of enough phenol, the interference of $Y^-{}_w$ can be neglected. This feature is demonstrated in figure 6.

A similar voltammetric interpretation can also be made with an enhancement of selectivity in cation i.s.es with a neutral carrier as the additive.

These remarkable changes in selectivity brought about by the addition of *pt*OP were examined in detail on the basis of Sandblom–Eisenman–Walker theory (1967). As a result, it was concluded that the enhancement of selectivity of the *p*TS electrode against the perchlorate ion by the addition of *pt*OP can be attributed to the decrease of the equilibrium constant K^{ex} of the exchange reaction

$$(\text{TOMA-}p\text{TS})_o + (\text{ClO}_4^-)_w \rightleftharpoons (\text{TOMA-ClO}_4)_o + (p\text{TS}^-)_w. \tag{10}$$

It was calculated that the value K^{ex} decreased from 53 to 0.091 in *o*-dichlorobenzene by the addition of 0.5 M *pt*OP in accordance with the decrease of the selectivity coefficient lg K_{XY} from 2.3 to -0.6 (see table 2). This result agrees well with the voltammetric interpretations described above.

6. APPLICATIONS OF ION-SELECTIVE ELECTRODES IN NON-AQUEOUS SOLUTIONS

The domains of i.s.es are extremely broad and are still expanding rapidly, and so the general views of applications in the fields of analytical potentiometry with the i.s.e. cannot be delineated in full in a short article such as this. However, some examples of investigations on i.s.es applied to characterization in non-aqueous solutions are given below.

The ion-selective electrodes that have hitherto been available were prepared for use in aqueous solutions; they are difficult to use in non-aqueous media mainly because the materials making up the electrodes tend to become damaged in those solutions. Glass electrodes and some solid membrane electrodes, however, can work in such media, and examples of their successful application have been increasing recently.

Glass electrodes

Glass electrodes (as the H^+ i.s.e.) have been used widely as indicator electrodes in acid–base titrations in non-aqueous solutions. Recently, they have been confirmed to respond in a Nernstian way to pH and have often been applied to the determination of acid–base equilibrium constants in such solvents.

Univalent cation-sensitive glass electrodes also respond in a way similar to their behaviour in aqueous solutions. Alkali metal ions in a non-aqueous solution, for example, can be titrated with various macrocyclic polyethers by using glass electrodes, and the titration curves can give formation constants of the complexes of these metal ions with such ligands.

Glass electrodes have been used conveniently to study interactions between univalent cations and solvents. Izutsu *et al.* (1980) studied potentiometrically the complex formation of lithium, sodium, potassium, rubidium, ammonium and thallium ions in acetonitrile (AN) with various co-solvents, such as water, methanol (MeOH), dimethylformamide (DMF), dimethylacetamide (DMA), dimethylsulphoxide (DMSO) and hexamethylphosphoric triamide (HMPA). They obtained successive formation constants for each ion. Though other methods, i.e. n.m.r. and i.r. spectrometry and conductometry, have been used in such studies, the potentiometric method with a glass electrode seems to be the only one that can give reliable constants. A similar method has been applied by Cox *et al.* (1979) to obtain the successive complex formation constants of sodium and lithium ions in propylene carbonate (PC) with DMA and DMSO. They found complex species bearing four co-solvent molecules per ion.

Glass electrodes can also be used to compare the activities of univalent cations in different solvents, though there are some limitations. Eisenman (1965) measured the potentials of a cation-sensitive glass electrode (NAS 11–18) against a Ag/AgCl electrode in saturated solutions of sodium chloride in pure water, pure methanol, and mixtures of water and methanol. In all solutions, the potentials were the same within a fraction of a millivolt. This result shows that there was no specific solvent effect on the surface of the glass electrode and that the electrode can be used to compare the ionic activities in solvents of different compositions. Covington & Thain (1975) applied these results to determine free energies of the transfer of alkali metal fluorides and chlorides from water to aqueous methanol.

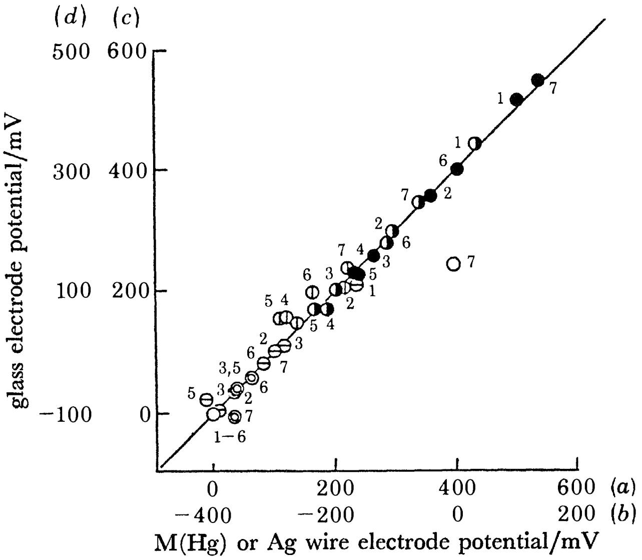


FIGURE 7. Comparison of e.m.f.s of cells (I) and (II): (*a*) and (*b*) for cell (I); (*c*) and (*d*) for cell (II). (*a*, *c*) [e.m.f.(D) − e.m.f.(D = AN)] for M other than Ag; (*b*) [e.m.f.(D) − e.m.f.(D = AN)] for M = Ag; and (*d*) e.m.f.(D) for M = Ag. M: 1, Li^+; 2, Na^+; 3, K^+; 4, Rb^+; 5, Cs^+; 6, Tl^+; 7, Ag^+. D: ○, AN; ⊙, PC; ⦶, H_2O; ⊖, MeOH; ◑, DMF; ●, DMSO.

To study the behaviour of the glass electrode in more detail, Izutsu *et al.* (1980) and Nakamura (1975) measured the e.m.f.s of cells (I) and (II), where D is AN, PC, MeOH, H_2O, DMF

$$\mathrm{Ag} \mid 5\times10^{-3}\,\mathrm{M}\,\mathrm{AgNO_3(AN)} \mid 0.1\,\mathrm{M}\,\mathrm{Et_4NClO_4(AN)} \mid \mathrm{M^+ClO_4^-},\ 0.10\,\mathrm{M}\,\mathrm{Et_4NClO_4(D)} \mid \mathrm{M(Hg)}\dagger \qquad \text{(I)}$$

$$\mathrm{Ag} \mid 5\times10^{-3}\,\mathrm{M}\,\mathrm{AgNO_3(AN)} \mid 0.1\,\mathrm{M}\,\mathrm{Et_4NClO_4(AN)} \mid \mathrm{M^+ClO_4^-},\ 0.01\,\mathrm{M}\,\mathrm{Et_4NClO_4(D)} \mid \text{glass electrode} \qquad \text{(II)}$$

or DMSO, and M^+ is Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+ or Ag^+. The only difference between cells (I) and (II) is that the amalgam electrode in (I) was replaced by a univalent cation-sensitive glass electrode (Beckman, 39047) in (II). The results are shown in figure 7, in which AN is chosen as the reference solvent. In many cases, both the amalgam electrode and the glass electrode responded in a Nernstian way to the solvent effect. There are some exceptions, however: as can be seen in the figure, a large deviation from linearity is observed for Ag^+ in AN, and smaller deviations are seen for some cations in water.

Cox *et al.* (1979) used the above properties of the glass electrode to estimate the free energies of the transfer of Li^+ and Na^+ ions from PC to DMA. They calculated the free energies by using successive formation constants of complexing of the ions in the above solvents, by assuming that the interaction energies outside the first coordination sphere were independent

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† Ag wire was used instead of Ag amalgam for $M^+ = Ag^+$.

of the solvent species. It is interesting that the value obtained by the calculations agreed well with the experimental values, supporting their assumptions about the relations between solvation and the complexation of solvent molecules.

Other solid membrane electrodes

Dissolution and swelling of the active materials, the electrode matrix and the electrode body limit the use of many non-glass ion-selective electrodes in non-aqueous solvents. Some solid electrodes selective to halides, including fluoride, and to some heavy metal ions have, however, been used in non-aqueous solvents. Some of them were found to respond in a Nernstian or near-Nernstian way to the ionic activity changes caused by the solvent effect as well as those by the concentration effect. They can therefore be used to investigate complex formation constants, solubility products and free energies of the transfer of ions from one solvent to another. Recently, very interesting studies of such applications were reported by Coetzee & Istone (1980) for fluoride and copper ion selective electrodes. These electrodes seem to be extremely promising for use in non-aqueous solutions.

Conclusion

Ion selective electrodes of various categories have been used as ion sensors in various fields such as chemistry, physics and biology, as well as in applied sciences such as pharmaceutical, clinical, agricultural and industrial chemistry.

General views of recent developments have been published in many textbooks, which are readily available. Because of limitations of space, I have discussed chiefly a few topics being studied in my laboratory at the University of Kyoto.

I wish to express my heartfelt thanks to the Royal Society and to Professor J. M. Thomas, F.R.S., Professor R. Belcher and Dr T. S. West for giving me this opportunity to present a paper at this Discussion Meeting.

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Discussion

J. D. R. Thomas (*Chemistry Department, U.W.I.S.T., Cardiff, U.K.*). What are the constructional details of the 'solid-solvent' electrode and what proportion of the sensor would be used in the membrane matrix?

T. Fujinaga. For the preparation of the *p*-toluenesulphonate (*p*TS) electrode membrane, an ion-pair of methyltrioctylammonium *p*-toluenesulphonate (TOMA-*p*TS) prepared by solvent extraction was recrystallized from ethyl acetate. Then the ion pair TOMA-*p*TS and the *p*-*tert*-octylphenol (*pt*OP) as the carrier of *p*TS ions were dissolved in the solid-solvent (e.g. *o*-dichlorobenzene) molten at an elevated temperature. After cooling to room temperature, the solidified ion-exchanger was ground into powder and pressed onto a polished silver disc 1 cm in diameter at *ca.* 300 MPa. The thickness of the membranes was in the range 0.2–0.5 mm.

For the preparation of the coated-wire electrode, a platinum wire rounded at the top was dipped into the melt. It was then taken out and used as the electrode after cooling to room temperature.

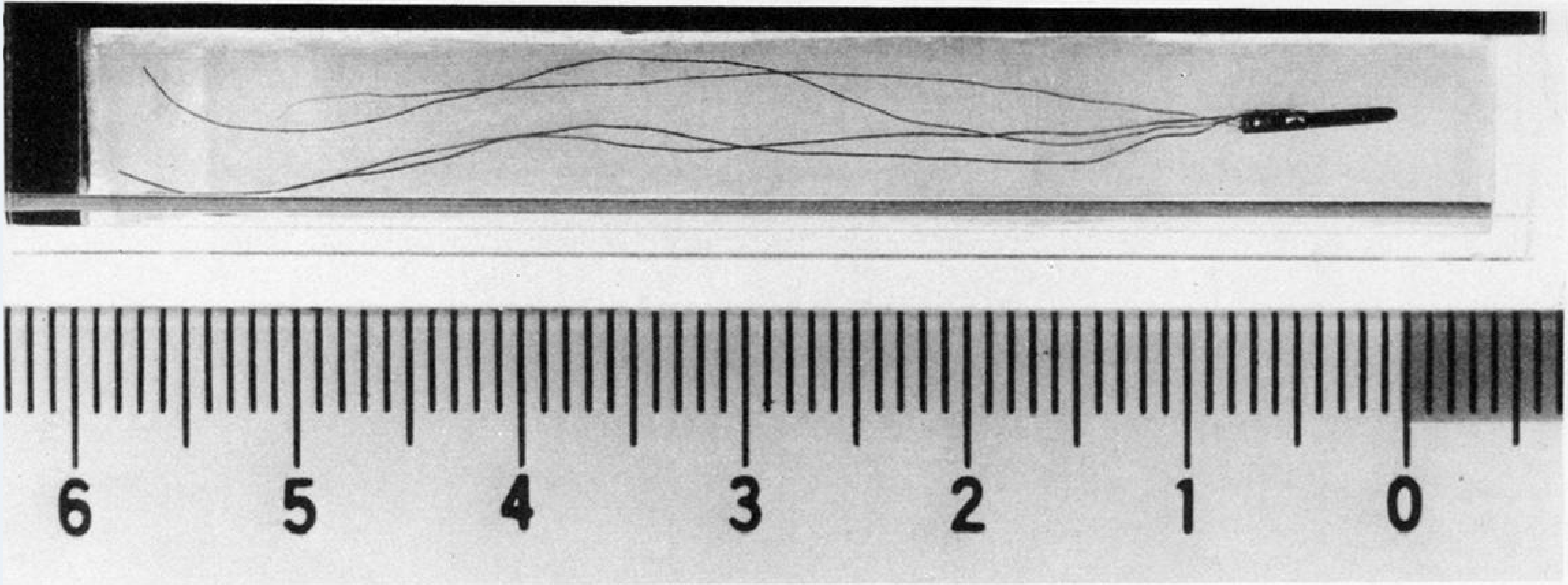

Figure 2. Ion-sensing f.e.t. electrode for pH measurement. One division: 1 mm.