ION SELECTIVE PICRATE ELECTRODE WITH LIQUID MEMBRANE

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

An ion selective picrate electrode with a liquid membrane supported by a poly(vinyl chloride) matrix was proposed. Cetyltrimethylammonium cations in n-hexyl-*o*-nitrophenyl ether serve as an ion exchanger. The electrode is suitable for analytical purposes.

The analytical determination of picrate ions is of a relatively wide importance. For example, in the indirect determination of organic bases, picrates are titrated in the medium of acetic acid with perchloric acid[1]. A similar method is used in determining tertiary alcohols according to Schotte and Veibel[2]. The formation of complexes with picrates can be made use of in the determination of some physiologically important compounds, such as acetone, pyruvic acid[3], and amines[4]. The reaction of picrates with creatinine (Jaffé's reaction) is used in the determination of creatine and creatinine in urine and blood plasma[5,6].

The picrate ion selective electrode (ISE) was already described by Bäck[7,8]. A liquid membrane supported by an Orion membrane (type 92–20) contained n-tetrahexylammonium, n-tetrabutylammonium, and n-tetrapropylammonium cations dissolved in methylene chloride as ion exchangers. Other authors[9] described a picrate ISE with a liquid membrane supported by a poly(vinyl chloride) (PVC) matrix, where the ion exchanger was a solution of tetrapentylammonium cations in 2-nitrotoluene. This electrode was used in potentiometric titration of silver with picrate ions in the presence of thiourea[10]. Diamandis and coworkers[11] described a kinetic potentiometric method for determination of creatinine in urine using a picrate ISE developed by them. Their results compared well with those obtained by common spectroscopic methods.

EXPERIMENTAL

The liquid membrane fixed in a PVC matrix was prepared according to Moody, Oke, and Thomas[12]. A 3 percent solution of high molecular weight PVC in cyclohexanone was used to prepare the PVC support. This polymer was prepared by polymerization of vinyl chloride with tert-butyllithium[13], commerical cyclohexanone (Lachema, Brno) was purified by fractionated distillation and dried with sodium sulphate. To the PVC solution, 1/10 of its volume of a 1 percent solution of cetyltrimethylammonium bromide (Lachema, Brno) in n-hexyl-*o*-nitrophenyl ether was added. The resulting solution was poured into a glass plate, where after 2—3 days of drying it formed a PVC film with a liquid membrane.

Prior to the measurement, the membrane was dipped for 2—3 days in a solution of 10^{-2}M sodium picrate, whereby it was brought into the picrate regime. During the measurement, the film was placed into a double cell where it separated two solutions. One of them (0·05M sodium picrate (NaPi)) served as a reference. Both solutions separated with the membrane were provided with salt bridges joined with silver chloride electrodes and a measuring apparatus (a type VA-J-51 millivoltmeter (GDR) and a pen recorder BAK 4 T (Aritma, Czechoslovakia)).

RESULTS AND DISCUSSION

Calibration of Ion-Selective Membrane

The ion-selective membrane was first calibrated in a picrate solution. On one side of the membrane there was a 0·05M-NaPi reference solution, on the other side a picrate solution of varying concentration. The membrane potential was measured in dependence on the activity of picrate and the following relation was found to hold in the interval of picrate concentrations $5 \cdot 10^{-2} - 10^{-5}$M:

$$E_M = \text{const.} - 0{\cdot}059 \log a_{\text{Pi}^-}\,, \qquad (1)$$

where E_M denotes membrane potential of the ion selective membrane and a_{Pi^-} activity of picrate. Deviations from this dependence in the whole concentration region did not exceed ±2 mV in the course of several days.

We tried whether the membrane would function as a perchlorate or nitrate ISE. To this purpose, it was brought into the perchlorate or nitrate regime by staying for several days in 0·01M-$NaClO_4$ or $NaNO_3$. The calibration was carried out similarly

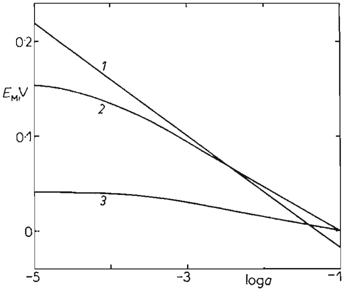

FIG. 1

Dependence of Ion Selective Membrane Potential on Activity of Picrate *1*, Perchlorate *2* and Nitrate *3* as with picrates, $0{\cdot}1\text{M-NaClO}_4$ or NaNO_3 serving as reference solutions, and the concentration range was $0{\cdot}1\text{M}$-10^{-5}M-ClO_4^- or NO_3^-. The dependence of the membrane potential on the activity of ClO_4^- ions corresponds to the equation

$$E_\text{M} = \text{const.} - 0{\cdot}047 \log a_{\text{ClO}_4^-}\,. \tag{2}$$

This dependence holds in the concentration region $0{\cdot}1 - 5\,.\,10^{-4}\text{M-ClO}_4^-$; at lower concentrations the potential decreases.

The dependence of E_M on the activity of NO_3^- ions is given as

$$E_\text{M} = \text{const.} - 0{\cdot}015 \log a_{\text{NO}_3^-}\,. \tag{3}$$

This dependence holds for concentrations down to 10^{-3}M-NO_3^-; at lower concentrations the potential again decreases. The mentioned dependences are shown in Fig. 1. It is seen that the membrane is not suitable as a perchlorate or nitrate ISE.

Selectivity Constants

Some interefering ions were followed and the selectivity constants of the picrate ISE with respect to them were measured. These constants were determined with the aid of the equation of Buck[14]:

$$\ln K^{\text{pot}}_{\text{Pi}^-,\text{K}} = \ln\{\exp[(E_{\text{Pi}^-,\text{K}} - E_{\text{Pi}^-})/S] - 1\} - \ln(a_\text{K}/a_{\text{Pi}^-})\,, \tag{4}$$

where $E_{\text{Pi}^-,\text{K}}$ denotes potential of ISE in the presence of Pi^- and an interfering ion, E_{Pi^-} same without the interfering ion, a_K and a_{Pi^-} are activities of the interfering and Pi^- ions, S is defined by

$$E_\text{M} = \text{const.} + S \log a_{\text{Pi}^-}\,, \tag{5}$$

where E_M is the ion selective membrane potential. These relations can be used in the region of the nernstian dependence of the ISE potential on the picrate activity. In the case of rapid surface processes and a simple diffusion potential in the membrane, the selectivity constant $K^{\text{pot}}_{\text{Pi}^-,\text{K}}$ depends on the ratio of $a_\text{K}/a_{\text{Pi}^-}$.

The dependence of the selectivity constants on the ratio of $a_\text{K}/a_{\text{Pi}^-}$ is shown in Fig. 2. It is seen that a change of this ratio by four orders of magnitude results in a change of the selectivity constants by $1 - 1{\cdot}5$ order of magnitude. Of the studied anions, perchlorate interferes most strongly. The measured selectivity constants for the case that $a_\text{K} = a_{\text{Pi}^-}$ are as follows;

Anion	ClO_4^-	NO_3^-	SO_4^{2-}	I^-	Br^-	Cl^-
$K^{\text{pot}}_{\text{Pi}^-,\text{K}}$	$6{\cdot}5\,.\,10^{-2}$	$3{\cdot}7\,.\,10^{-2}$	$1{\cdot}6\,.\,10^{-2}$	$9{\cdot}8\,.\,10^{-3}$	$9{\cdot}3\,.\,10^{-3}$	$7{\cdot}8\,.\,10^{-3}$

Response Time

Semiempirical equations describing the dependence of the ISE potential on time in the region between the initial E_i and stationary potential E_{st} have an exponential or hyperbolic form:

$$E(t) = E_i + (E_{st} - E_i)\exp(-kt) \tag{6}$$

or

$$E(t) = E_i + (E_{st} - E_i)\,kt/(1 + kt)\,, \tag{7}$$

where k is a constant[15]. The response time is expressed by the parameter t_{95}, *i.e.*, the time after which the ISE potential attains 95 percent of the value of the stationary potential E_{st}. The potential corresponding to t_{95} is denoted as E_{95}.

We measured the time change of the membrane potential during a rapid concentration change of the measured picrate solution. The initial concentration was in the range 10^{-5} – 10^{-3}M-Pi$^-$ and it was increased in turn by an order of magnitude.

It is seen from Fig. 3 that the dependence of the potential of the ion selective membrane on the time is exponential for low concentrations (10^{-5}M) and hyperbolic for higher concentrations (10^{-3}M). The time t_{95} becomes shorter as follows:

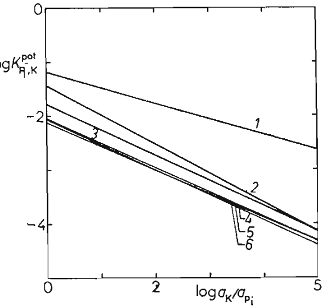

FIG. 2

Dependence of Selectivity Constants of Ion Selective Membrane on a_K/a_{Pi}.
Interfering ions: *1* ClO_4^-; *2* NO_3^-; *3* SO_4^{2-}; *4* I^-; *5* Br^-; *6* Cl^-.

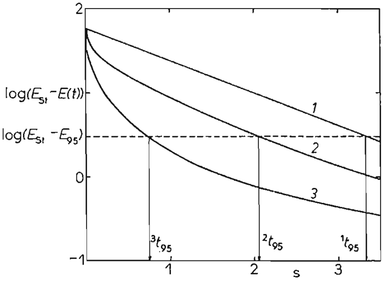

FIG. 3

Time Change of Ion Selective Membrane Potential after Ten-Fold Concentration Increase
Initial concentration: *1* 10^{-5}M-Pi$^-$; *2* 10^{-4}M-Pi$^-$; *3* 10^{-3}M-Pi$^-$. The same numbering refers to the response times t_{95}.

$[Pi^-]$	$1 \,.\, 10^{-5}$	$1 \,.\, 10^{-4}$	$1 \,.\, 10^{-3}$
t_{95}, s	3·30	2·05	0·75

The described ion selective membrane has a sufficiently broad measuring range (down to concentrations under 10^{-5}M-Pi^-) and a short response time. The dependence of its potential on the activity of picrate has a nernstian course. The influence of interfering ions is small except for perchlorates. The proposed picrate ion selective membrane is therefore suitable for analytical purposes.

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