

## POTASSIUM POLYMERIC MEMBRANE ELECTRODES BASED ON NEUTRAL CARRIERS

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Potassium ion selective electrodes based on valinomycin and macrocyclic polyethers in homogeneous poly(vinyl chloride) membranes have been described. The effect of the polyether structure on the properties of the electrodes has been studied.

Not long ago Simon and other authors revealed the specificity of a number of antibiotics during the formation of complexes with cations<sup>1</sup>. This fact was made use of in the preparation of ion selective electrodes. In the case of the potassium electrode, of all the antibiotics investigated the highest selectivity for potassium ion over sodium ion was attained with valinomycin as the active component of the membrane<sup>2-3</sup>. Neutral carriers of natural origin have been supplemented by a group of synthetic carriers — cyclic polyethers, the so-called crown compounds<sup>4</sup>. The potassium ion selective electrodes described in the literature, in which valinomycin or crown compounds are used as the membrane components<sup>5-6</sup>, are as to their arrangement typical liquid membrane electrodes. In these electrodes, the inert porous supporting membrane consisting of a glass frit or a millipore-type filter disc is wetted by a neutral carrier dissolved in a hydrophobic solvent. Such an arrangement brings about certain complications involved in the construction of the electrode body; moreover, in some cases it has an unfavourable effect on the electrode response time.

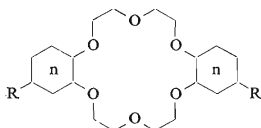
The present paper is dealing with potassium electrodes in which the neutral carrier is contained directly in the homogeneous plastified polymeric membrane. For such homogeneous membranes, the effect of some structural changes of the macrocyclic polyethers used on the electrode properties has also been investigated.

### EXPERIMENTAL

**Chemicals.** The cyclic polyethers were obtained from catechol, 4-methyl catechol and 4-n-propyl catechol by a procedure described by Pedersen<sup>4</sup>. All products were purified chromatographically on aluminium oxide (Woelm) by an elution with the mixture benzene: diethyl ether (1 : 1). The compounds thus obtained had the following properties: Dibenzo-18-crown-6 (*Ia*, trivial nomenclature after ref.<sup>4</sup>), m.p. 161–162°C (ref.<sup>4</sup>, 162–164°C). Dimethyldibenzo-18-crown-6 (*Ib*, m.p. 126 to 127°C; for C<sub>22</sub>H<sub>28</sub>O<sub>6</sub> (388.4), calculated: 68.02% C, 7.26% H; found: 68.10% C, 7.51% H; M<sup>+</sup> 388. Dipropyldibenzo-18-crown-6 (*Ic*), m.p. 109–112°C; for C<sub>26</sub>H<sub>36</sub>O<sub>6</sub> (444.5), calculated: 70.24% C, 8.16% H; found: 70.76% C, 8.25% H; M<sup>+</sup> 444. Dimethyldibenzo-24-crown-8 (*II*), m.p. 68–70°C; for C<sub>26</sub>H<sub>36</sub>O<sub>8</sub> (476.5), calculated: 65.52% C, 7.61% H; found: 65.84% C, 7.87% H;

$M^+$  476. For the alkyl derivatives prepared in this work it was not possible to decide whether the mutual position of the alkyl groups was 4,4' or 4,5'. Dicyclohexyl derivatives *Id*–*If* were prepared by hydrogenation of the respective dibenzo derivatives in butanol with 10% water at 110°C and 100 at hydrogen while using ruthenium dioxide as catalyst. The crude hydrogenation products were purified chromatographically on aluminium oxide by elution with the mixture heptane-diethyl ether (1 : 1). Mixtures of *cis* and *trans* isomers were used for the measurements; their purity was checked by mass spectrometry and UV spectra (zero absorption at 278 nm). The properties of the individual derivatives were as follows: Dicyclohexyl-18-crown-6 (*Id*), m.p. 36–56°C,  $M^+$  372; dimethyldicyclohexyl-18-crown-6 (*Ie*), m.p. 35–60°C,  $M^+$  400; dipropyl-dicyclohexyl-18-crown-6 (*If*), m.p. 45–60°C,  $M^+$  456.

Dipentyl phthalate (DPP) was prepared from phthalic anhydride and n-pentanol: b.p. 175 to 178°C/0.1 Torr. Cyclohexanone, reagent grade (Lachema). High-molecular weight poly(vinyl chloride) was prepared by polymerization of vinyl chloride with tert-butyllithium<sup>7</sup>.



*Ia*;  $n = \text{benzo}$ ,  $R = \text{H}$

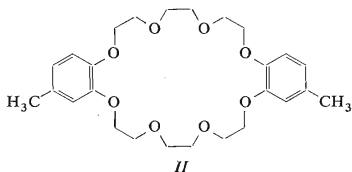
*Ib*;  $n = \text{benzo}$ ,  $R = \text{CH}_3$

*Ic*;  $n = \text{benzo}$ ,  $R = \text{C}_3\text{H}_7$

*Id*;  $n = \text{cyclohexyl}$ ,  $R = \text{H}$

*Ie*;  $n = \text{cyclohexyl}$ ,  $R = \text{CH}_3$

*If*;  $n = \text{cyclohexyl}$ ,  $R = \text{C}_3\text{H}_7$



*II*

**Membrane preparation and method of measurement.** 1 ml of 0.01M valinomycin or of 0.025 to 0.07M cyclic polyether in dipentyl phthalate was added to 10 ml of 5% poly(vinyl chloride) in cyclohexanone. Membranes were prepared from these solutions by casting on a horizontal glass plate, 7 × 15 cm in size. After evaporation of cyclohexanone at room temperature, a film c. 0.15 mm thick was obtained. The membranes were then preconditioned in  $10^{-3}\text{M-KSCN}$  for at least 24 h. A ring was cut out from the membranes and fixed between rubber packing O rings in a simple teflon electrode body by means of a teflon nut. The diameter of the exposed membrane area was 8 mm; the resistance of the membrane electrode in  $10^{-3}\text{M-KCl}$  varied around 1MΩ. To measure the EMF of the cell  $\text{Ag}/\text{AgCl}(\text{s}), 0.001\text{M-KCl}/\text{membrane}/\text{measured solution}/0.1\text{M-NH}_4.\text{NO}_3/\text{KCl}(\text{sat.}), \text{Hg}_2\text{Cl}_2(\text{s})/\text{Hg}$ , an E336 (Metrohm A. G., Herisau) potentiograph was used. Alternatively, the measurement was performed with a membrane prepared from the above components in cyclohexanone by evaporation directly on the platinum wire (0.2 mm dia.) using the cell  $\text{Pt}/\text{membrane}/\text{measured solution}/0.1\text{M-NH}_4.\text{NO}_3/\text{KCl}(\text{sat.}), \text{Hg}_2\text{Cl}_2(\text{s})/\text{Hg}, 0.1\text{M-KCl}$  was prepared from dried potassium chloride, reagent grade (Lachema). Gradual dilution yielded  $10^{-2}$ – $10^{-6}\text{M-KCl}$ . Solutions of potassium chloride containing simultaneously  $10^{-2}$  or  $10^{-1}\text{M}$ -

NaCl were prepared in a similar way. The activity of the potassium ions was determined by using of the individual ionic activity coefficients calculated according to Debye-Hückel's theory<sup>8</sup> on the basis of the data published for effective ionic radii<sup>9</sup>.

## RESULTS AND DISCUSSION

Quantitative evaluation of the selective properties of membranes with neutral carriers in a homogeneous polymeric matrix was made assuming that their behaviour was adequately expressed by Nikolski's equation<sup>10</sup>:

$$E = E_0 + \frac{RT}{F} \ln (a_{K^+} + K_{K^+,Na^+}^{Pot} \cdot a_{Na^+}),$$

here,  $E$  is the electrode potential,  $E_0$  is a constant,  $a_{K^+}$ ,  $a_{Na^+}$  are activities,  $K_{K^+,Na^+}^{Pot}$  is the selectivity constant of the electrode.

The values of the selectivity constant in this equation obtained for the individual cases from the ratio of the activities of the potassium and sodium ions by using the equipotential method are listed in Table I. The highest selectivity for potassium was attained with the valinomycin based electrode; the order of magnitude of the selectivity constant is in agreement with the results obtained with this natural antibiotic for liquid membranes<sup>2,3</sup> where they vary within  $10^{-3} - 10^{-4}$ . The electrode function is linear within the range from  $10^{-1}$  to  $10^{-5}$  M-KCl and has a slope corresponding to the theoretical one according to the given equation (theor. 59.2 mV/log  $a_{K^+}$  at 25°C). Also the response of the electrode is instantaneous, so that the use of the membrane with a carrier in a homogeneous polymeric matrix fulfils all requirements of ion selective electrodes. Identical results were obtained with a valinomycin membrane formed directly on the platinum wire. However, the slope of the potential dependence of these coated wire electrodes on the activity of the potassium ions is a function of the thickness of the wire coating. Theoretical values were obtained with electrodes, the coating of which corresponded to a membrane thickness of about 0.15 mm.

TABLE I

Electrode Properties of Homogeneous Polymeric Membranes with Neutral Carriers

Concentration of valinomycin (VM) in DPP is 0.01M, of carrier Ia 0.025M, of the other carriers 0.05M.

Carrier	VM	Ia	Ib	Ic	Id	Ie	If	II
$\Delta E / \log a_{K^+}$ , mV	60	51	60	59	58	58	60	59
$K_{K^+,Na^+}^{Pot} \cdot 10^2$	0.03	7.7	7.0	6.3	1.1	1.0	1.8	7.7

As follows from Table I, the selectivity of the membrane electrodes with synthetic carriers of the cyclic polyether type is lower compared with the valinomycin based electrode. The dependence of the EMF on the activity of the potassium ions for a membrane with the simplest dibenzo-18-crown-6 (*Ia*) under investigation is shown in Fig. 1. The electrode function of this membrane is linear only within  $10^{-2.5}$  to  $10^{-5}$ M-KCl and the slope of the straight part is smaller ( $51 \text{ mV}/\log a_{\text{K}^+}$ ) than required by theory. The region of linear response disappears in the presence of  $10^{-2}$ M-NaCl; at a higher concentration of sodium the electrode potential is independent of the concentration of potassium ions over the whole range under investigation. Moreover, even at a low concentration of this crown-compound it crystallizes in the membrane after some time. To prevent this phenomenon, derivatives have been prepared which were substituted with methyl and propyl groups on the benzene rings. These derivatives allowed the preparation of membranes with a relatively higher concentration of the active component. The results of measurements for a membrane with dimethyldibenzo-18-crown-6 are shown in Fig. 2. Similar results were obtained with the propyl derivative. The presence of an alkyl in a molecule of cyclic polyether was reflected in an improvement of the electrode function of these membranes which has a linear course with a theoretical slope within the concentration range from  $10^{-1.5}$ – $10^{-5}$ M-KCl. Alkylation also led to a faster electrode response and the potential attained its final value almost immediately. Changing the concentration of the active component in dipentyl phthalate during the preparation of membranes within the range 0.025–0.07M did not result in any significant changes of their electrode properties. The reason leading to an improvement in the electrochemical properties of membranes with alkylated crown-compounds is not evident; it is probable, however, that the effect of the alkyl group results in favourable changes in the conformation of the molecule.

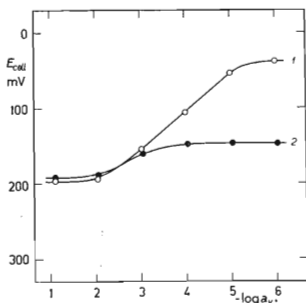


FIG. 1

Dependence of the EMF of the Cell for an Electrode with Dibenzo-18-crown-6 (*Ia*) on the Potassium Ions Activity in a Solution of Pure KCl (1) and in the Presence of  $10^{-2}$ M-NaCl (2).

It can be seen from the selectivity constants in Table I that hydrogenation of benzene rings in the crown-compounds with an eighteen-membered polyether ring leads to a substantial increase in selectivity for potassium over sodium. On the other hand, the response is somewhat slower. In the case of the unsubstituted derivative *Id* the potential attains its final value after c. 15 min. Here too the effect of alkylation is a favourable one; the potential drift is smaller for dimethyldicyclohexyl-18-crown-6 (*Ie*), and the response of the membrane with the propyl derivative *If* is practically instantaneous. However, the selectivity of this compound is lower. Fig. 3 shows the electrode response for a membrane with dimethyldicyclohexyl-18-crown-6 (*Ie*) which within the range  $10^{-1.5} - 10^{-5}$  M-KCl is linear and has the theoretical slope. Similar results were obtained with a wire platinum electrode coated with this membrane. It is interesting that no pronounced improvement in selectivity was observed with the Orion electrode body<sup>5-6</sup> in the case of liquid membrane electrodes with dicyclohexyl-18-crown-6 (*Id*).

An important factor of the formation of complexes of cations with the crown-compounds is the diameter of the macrocycle cavity. An increase of the ring to form a twenty-four membered one in the case of dimethyldibenzo-24-crown-8 (*II*) did not lead to a rise in selectivity for potassium compared to the eighteen-membered ring. The effect of a further increase of the macrocycle, as well as the problem of the influence of hydrogenation on the selectivity of larger rings and of the possibility

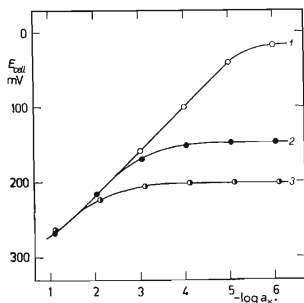


FIG. 2

Dependence of the EMF of the Cell for an Electrode with Dimethyldibenzo-18-crown-6 (*Ib*) on the Potassium Ions Activity in a Solution of Pure KCl (1) and in the Presence of  $10^{-2}$  M-NaCl (2) or  $10^{-1}$  M-NaCl (3).

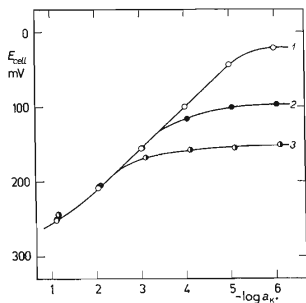


FIG. 3

Dependence of the EMF of the Cell for an Electrode with Dimethyldicyclohexyl-18-crown-6 (*Ie*) on the Potassium Ions Activity in a Solution of Pure KCl (1) and in the Presence of  $10^{-2}$  M-NaCl (2) or  $10^{-1}$  M-NaCl (3).

of affecting the conformation of the polyether ring by its structural changes are being further investigated.

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