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Membrane Based on Decyl-18-crown-6 for a Potassium Selective Sensor

by Elena Hopârtean[1], Elena Maria Pică[2*], Coroian Ana[1], Viorica Cosma[1] and Ioana Hopârtean[1]

[1]*Institute of Chemistry, Fântânele 30, 3400 Cluj-Napoca, România*
[2]*Technical University of Cluj-Napoca, Muncii 105, 3400 Cluj-Napoca, România*

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Four kinds of 18-crown-6 derivatives were studied as ionophores in plasticized poly(vinyl chloride) (PVC) in order to obtain potassium selective membrane. The properties of the sensor were studied in detail. For the optimization of the selectivity toward K^+ over Na^+ the influence of the following factors was studied: nature and concentration of the ionophore; nature and concentration of the plasticizer and lipophilic salt addition. The potassium ion-selective membrane electrode was designed. The electrode has a fast and Nernstian response in the 1×10^{-1}–2×10^{-5} mol l^{-1} K^+, after six months of continuous measurements. The change of pH in the range 2–10.5 does not affect the response of the electrode. The internal resistance of the electrode was measured. The electrode shows a good stability and can be used in the potentiometric determination.

Badano cztery rodzaje pochodnych związku: 18-korona-6 jako jonofory w plastyfikowanym polichlorku winylu (PVC), w celu uzyskania membrany selektywnej względem jonów potasowych. Szczegółowo badano własności czujnika pomiarowego. W celu optymalizacji selektywności względem jonów K^+ w porównaniu do jonów Na^+ zbadano wpływ następujących parametrów: rodzaj i stężenie jonoforu, rodzaj i stężenie plastyfikatora, oraz dodatek soli lipofilowej. Zaprojektowano jonoselektywną elektrodę membranową, selektywną względem jonów potasowych. Elektroda ma krótki czas odpowiedzi i nernstowską odpowiedź w granicach stężeń: $10^{-1} \times 10^{-5}$ mol l^{-1} K^+ po sześciu miesiącach ciągłych pomiarów. Zmiana pH w granicach 2–10.5 nie wpływa na odpowiedź elektrody. Zmierzono wewnętrzną rezystancję elektrody. Elektrodę cechuje dobra trwałość i można ją używać do oznaczeń potencjometrycznych.

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[*] Corresponding author, E-mail: pica@tempus.east.utcluj.ro

Nature and characteristics of various types of potassium sensitive membrane and potassium selective sensors have been reviewed [1]. Although valinomycin is, by far, the most successful ionophore for potassiun ion, but it is a very expensive reagent [2–6]. Crown ethers based membranes respond to the alkali metals in the order: $Rb^+ > K^+ > Cs^+ > Na^+$ [7–12].

In the work reported here, attempts were made to use four crown ethers (benzo-18-crown-6, dibenzo-18-crown-6, dibenzo-pyridino-18-crown-6 (1,4,7,14,23-pentaoxo[7,2] *ortho*-cyclo [2] (2,6) pyridinophan) and decyl-18-crown-6 as neutral carriers for K^+ ion-selective membranes with PVC matrix.

Performance characteristics of potassium sensors made on membrane based on decyl-18-crown-6 in PVC-matrix have been investigated.

EXPERIMENTAL

Reagents

For membrane preparation, crown ethers (CWE) [decyl-18-crown-6 (D), dibenzo-pyridino-18-crown-6 (P), benzo-18-crown-6 (B), dibenzo-18-crown-6 (DB)], poly(vinyl chloride) (PVC) (H.M.W-powder), potassium-tetrakis-*p*-chlorophenyl borate (KTpClPB), tetrahydrofuran (THF), potassium tetraphenylborate (KTPB) were purchased from Merck.

The plasticizers as: tricresylphosphate (TCP), dibutylphthalate (DBP) and dioctyl sebacate (DOS), were purchased from Fluka.

Alkali, alkaline earth and transition metal salts in the form of chloride or nitrate were purchased from "Reactivul" România. All these chemicals were of analytical reagent grade. Double distilled water was used for the preparation of the solutions.

Standard solutions (1×10^{-1}–10^{-5} mol l^{-1}) with constant ionic strength, $j = 0.1$ (strength adjustor $CaCl_2$ 0.033 mol l^{-1}) were freshly prepared by successive dilution.

Apparatus

The EMF measurements were made at room temperature and constantly stirred solution using the following electrode system (measurement cells):

Cu (rod)/K^+–selective membrane/ K^+–sample solution/SCE (double junction)

Membrane resistance was determined using the method of the potential reduction by known shunt.

A digital pH-meter (0.1 mV precision) was used.

The preparation of membranes and electrode system

The composition (m/m%) of the potassium-selective membranes was: 0.3–20% ionophore, 37–80% plasticizer, 1/2 of ionophore % lipophilic salts, 23–33 % PVC in 2 ml THF. As lipophilic salts, KTPB and KTpClPB was incorporated. The ionophore (D, DB, B and P) was added to a mixture (A) formed by lipophilic salt and solvent THF (mixture B). The PVC and plasticizer was then added to a mixture (B). An adequate quantity from the composition (approximately 3 drops) was immobilized on a Cu rod (99.5% purity) of 6 mm diameter fixed in an appropriate PVC electrode body. The surface of the Cu rod was cleaned and covered with Hg. After solvent evaporation, at room temperature, the K^+ selective membrane (approximately 2–3 μm thickness) is formed on the surface of Cu rod. Schematic diagram of the electrode is presented in the Figure 1.

The resulting system electrode were conditioned for 24 h in 10^{-2} mol l^{-1} KCl solution, before use.

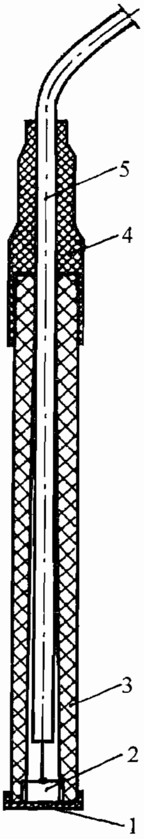

Figure 1. Schematic diagram of the electrode: 1) K^+-selective membrane; 2) copper rod; 3) electrode body; 4) cover of the electrode; 5) connection cable

RESULTS AND DISCUSSIONS

Membrane composition

The composition of the membrane was varied (Tabs 1–3) so as reach the optimum composition which exhibits the best performance characteristics (slope of calibration graph, selectivity and large linear concentration range, reproducibility of results).

By the each ionophore (D, DB, P and B), three membranes were prepared. Membranes were prepared with three plasticiszers: TCP, DBP and DOS, as well as with and without additional salts: KTPB and KTpClPB. For the optimization of selectivity coefficient towards K^+ over Na^+, the influence of the following factors was studied: nature and concentration of the ionophore and plasticizer; the presence of lipophilic salts.

Table 1. The functional characteristics of K-selective electrode

Functional characteristics*	Without lipophilic salts	KTPB	KT_pClPB
Linear response range, mol l^{-1}	1×10^{-4}–5×10^{-2}	5×10^{-5}–5×10^{-2}	2×10^{-5}–10^{-1}
Slope, mV/decade	53.10	54.40	57.50
$K_{K,Na}$	6.3×10^{-2}	7.2×10^{-2}	9.2×10^{-2}

* Membrane composition (0.5% D, 24.95% PVC, 74.3% TCP, 0.25% lipophilic salts).

Table 2. Functional characteristics of the potassium electrode towards membrane composition (natute and concentration of CWE)

Membrane	Composition*, m/m			Slope mV/decade	Linear range mol l	$K_{K,Na}$		s** %
	CWE %	TCP %	KT_p ClPB %			SSM	MSM	
DB	0.3	66.55	0.15	51.57	5×10^{-5}–10^{-1}	6.5×10^{-2}	6.5×10^{-2}	0.42
	0.5	66.25	0.25	53.70	2×10^{-5}–5×10^{-2}	7.1×10^{-2}	6.0×10^{-2}	0.45
	1.0	65.50	0.50	52.00	2×10^{-5}–5×10^{-2}	7.0×10^{-2}	6.2×10^{-2}	0.52
	5.0	59.50	2.50	53.20	5×10^{-5}–5×10^{-2}	6.1×10^{-2}	7.5×10^{-2}	0.50
	10.0	52.00	5.00	53.20	5×10^{-5}–5×10^{-2}	7.3×10^{-2}	9.2×10^{-2}	0.55
	20.0	37.00	10.00	53.40	5×10^{-5}–5×10^{-2}	8.5×10^{-2}	9.5×10^{-2}	0.62
D	0.3	66.55	0.15	54.10	2×10^{-5}–10^{-1}	8.5×10^{-2}	9.0×10^{-2}	0.36
	0.5	66.25	0.25	57.50	2×10^{-5}–10^{-1}	9.1×10^{-2}	9.2×10^{-2}	0.30
	1.0	65.50	0.50	55.30	2×10^{-5}–10^{-1}	8.7×10^{-2}	9.0×10^{-2}	0.40
	10.0	52.50	5.00	52.70	5×10^{-5}–10^{-1}	7.0×10^{-2}	6.8×10^{-2}	0.50
P	0.3	66.55	0.15	51.50	5×10^{-5}–5×10^{-2}	1.5×10^{-1}	1.2×10^{-1}	0.40
	0.5	66.25	0.25	52.00	5×10^{-5}–5×10^{-2}	1.9×10^{-1}	1.8×10^{-1}	0.50
	1.0	65.50	0.50	50.50	5×10^{-5}–5×10^{-2}	2.0×10^{-1}	1.5×10^{-1}	0.54
B	0.3	66.55	0.15	48.50	5×10^{-5}–5×10^{-2}	1.1×10^{-1}	0.97×10^{-1}	0.52
	0.5	66.25	0.25	51.57	5×10^{-5}–5×10^{-2}	1.5×10^{-1}	1.3×10^{-1}	0.50
	1.0	65.50	0.50	50.70	5×10^{-5}–5×10^{-2}	1.7×10^{-1}	1.6×10^{-1}	0.69

* All membranes contain 33% PVC.
** Relative standard deviation of slope (4 determinations).

The selectivity coefficients, $K_{K,Na}$ were determined by the separate solutions method (SSM) [13] and mixed solutions method (MSM) [14] respectively.

Results of these studies are shown in Tables 1, 2, 3 and Figure 2.

As it is seen the following conclusions can be formulated: lipophilic salt addition improves functional characteristics (Table 1), especially the selectivity towards K^+ over Na^+ and slope. The best lipophilic salt was KTpClPB.

The membranes which contain ionophore D, have the best functional characteristics and good selectivity (comparable to valinomycin).

Table 3. Functional characteristics of the potassium electrode towards membrane composition (concentration of the plasticiser)

Membrane	Composition*, wt/wt		Slope mV/decade	Linear range mol l^{-1}	$K_{K, Na}$	
	PVC %	TCP %			SSM	MSM
DB	32.75	66.5	51.70	5×10^{-5}–10^{-1}	7.1×10^{-2}	6.5×10^{-2}
	24.95	74.3	53.80	2×10^{-5}–10^{-1}	7.5×10^{-2}	6.2×10^{-2}
	19.65	79.6	54.50	2×10^{-5}–10^{-1}	7.4×10^{-2}	8.9×10^{-2}
	15.25	84.9	53.70	5×10^{-5}–10^{-1}	8.4×10^{-2}	9.2×10^{-2}
D	32.75	66.5	54.10	2×10^{-5}–10^{-1}	8.2×10^{-2}	9.2×10^{-2}
	24.95	74.3	57.50	2×10^{-5}–10^{-1}	8.7×10^{-2}	9.5×10^{-2}
	19.65	79.6	56.90	2×10^{-5}–10^{-1}	9.1×10^{-2}	9.4×10^{-2}
	15.25	84.9	57.20	2×10^{-5}–10^{-1}	9.5×10^{-2}	6.4×10^{-2}

* All membranes contain 0.5% CWE and 0.25% KTp ClTB.

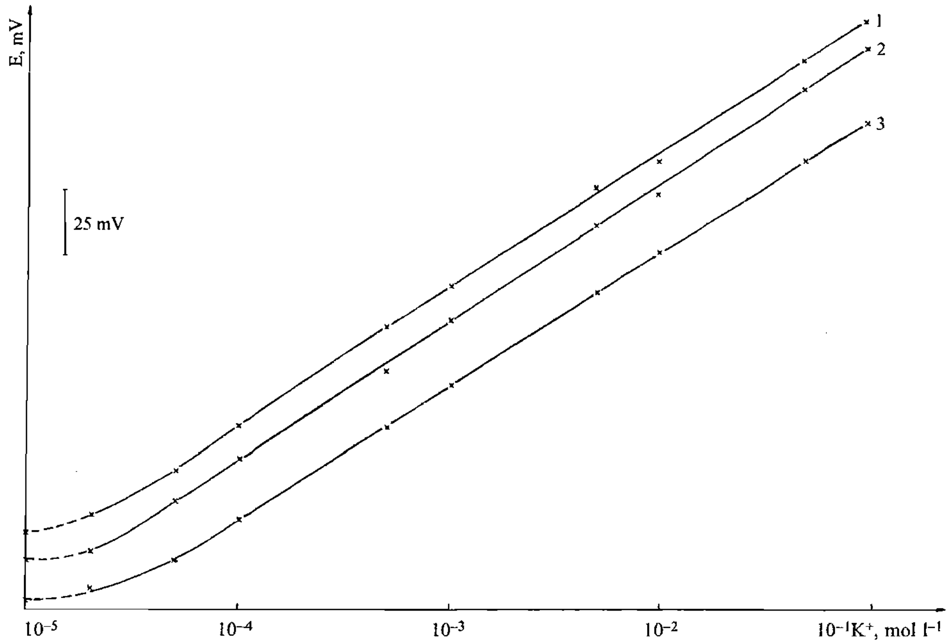

Figure 2. Calibration graphs of K^+– selective membrane based on decyl-18-crown-6 (D) and different plasticizers: 1) DBP; 2) TCP; 3) DOS

Large ionophore concentrations decrease the linear response range and do not improve the selectivity; the optimum ionophore concentration 0.5% m of ionophore, was established (Table 2).

The increase of plasticizer concentration (Table 3), extends slightly the linear response range and improves the selectivity. The optimum concentration of the plasticizer was ~75% m; larger concentrations of the plasticizer modified the physical properties of the membranes (become fragile).

The nature of the plasticizer influences the E_0 value of the calibration graph (Figure 2), the selectivity and other physical properties (*e.g.* appropriate elasticity). The best quality of the membranes was obtained with TCP as plasticizer.

The preparation process of the membrane is fairly reproducible, since the relative standard deviation (4 determinations) calculated for the slope values was small in all cases (Table 2).

Comparing the slope values of the calibration graphs as well as the linear concentration ranges and selectivity of the electrode obtained using the different composition (Tables 1, 2, 3), it is evident that the optimum composition was 0.5% D, 24.95% PVC, 74.3% TCP and 0.25% KTpClPB.

The other functional characteristics such as: internal electrical resistance and its variation with temperature and conditioning time respectively, influence of the temperature and the pH, on the response function, were established for the potassium-selective electrode with optimum composition membrane.

The internal resistance of the potentiometric cell was determined by method using known shunts [15,16] in 1 × 10^{-2} mol l^{-1} KCl. The internal resistance (R_c) of the potentiometric cell was calculated from the initial voltage, the voltage drop and the shunt resistance:

$$R_c = R_s \cdot [\Delta E/(E \cdot \Delta E)]$$

where: R_s – shunt resistance; E – initial potential; ΔE – potential drop.

The variation of the internal resistance with temperature is given in Figure 3.

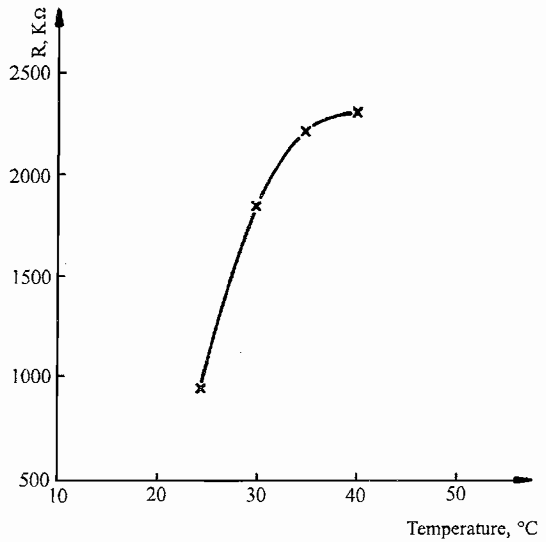

Figure 3. Variation of K^+-selective membrane (D) resistance with temperature in the 1 × 10^{-2} mol l^{-1} K^+ solution

It can be seen that while an increase of temperature takes place, the increase of the internal resistance occurs as far as 35°C. Over this temperature the increase of the internal resistance is small.

The variation of the internal resistance during conditioning time is shown in Figure 4. These data prove that in the first 6 h of conditioning the values of the internal resistance are decreasing and then they become practically constant. The decrease of internal resistance of the membrane during the conditioning (12 h) to a practically constant value has practical consequences for utilization of this membrane in the realization of the K^+-membrane sensor (the reproducibility of functional parameters and life time).

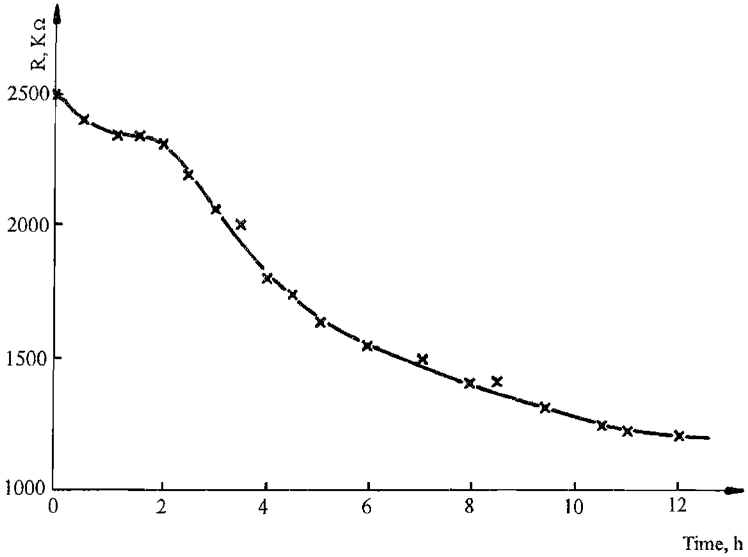

Figure 4. Variation of the membrane (D) resistance during 12 h soaking in the 1×10^{-2} mol l^{-1} K^+ solution

The influence of the pH on the response of the electrode, was studied by adjusting the pH of the potassium solution with the 0.1 mol l^{-1} HCl or 0.1 mol l^{-1} NaOH. The results (Fig. 5) show that the potential of the electrode remains constant in the pH range 2–10.5.

To study the influence of the temperature on the electrode potential 1, calibration graphs have been constructed at different temperatures 20, 25, 30, 40°C (Fig. 6). Variation ΔE/°C are ~ –2.7 mV/ °C. No change occurs in the slope of the calibration curves of the electrode within the temperature 20–40°C. As the temperature is raised beyond 40°C, sharp deviation from Nernstian behaviour was observed. This is attributed to collapse of the membrane, because of the fast leaching phenomenon.

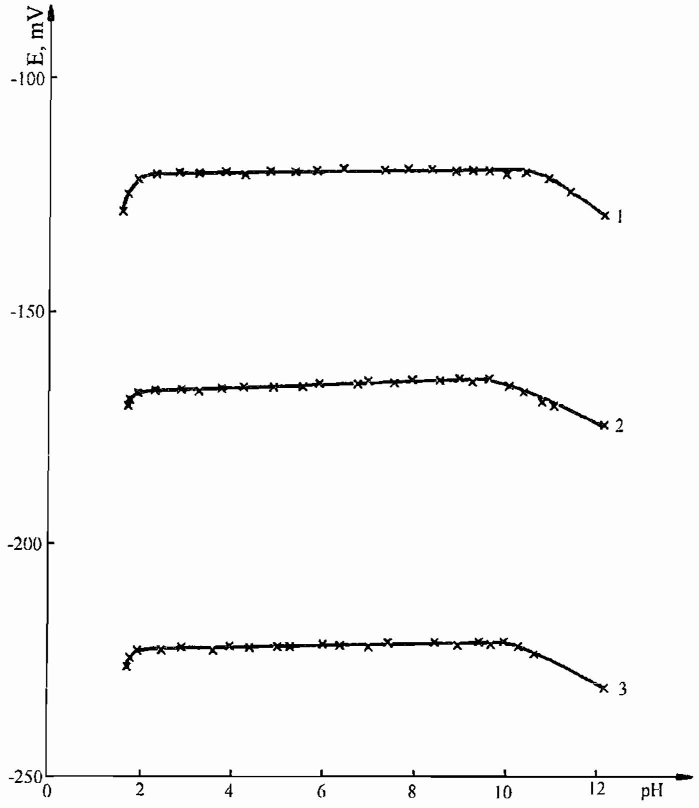

Figure 5. Effect of pH on the potential of K^+-selective membrane (D): 1) 1×10^{-2} mol l^{-1} K^+; 2) 1×10^{-3} mol l^{-1} K^+; 3) 1×10^{-4} mol l^{-1} K^+

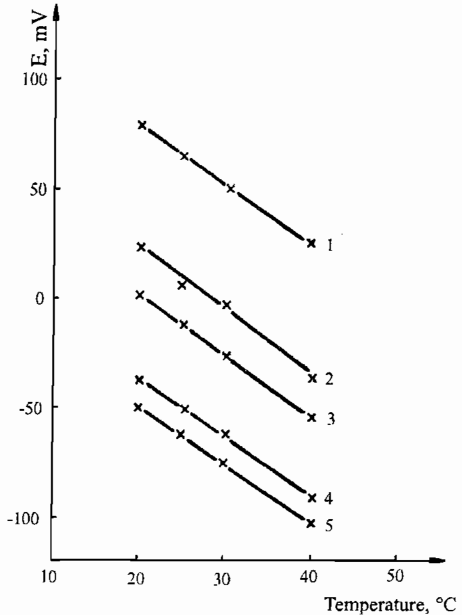

Figure 6. Variation of the K^+-selective membrane (D) potential with temperature: 1) 10^{-2} mol l^1 K^+; 2) 1×10^{-3} mol l^{-1} K^+; 3) 5×10^{-4} mol l^{-1} K^+; 4) 1×10^{-4} mol l^{-1} K^+; 5) 5×10^{-5} mol l^{-1} K^+

CONCLUSIONS

The decyl-18-crown-6, is slightly better to a number of other synthetic crown ethers examined as ionophore for potassium sensor. We have demonstrated the feasibility of using decyl-18-crown-6 immobilized in PVC matrix for the development of potassium sensor. We have found that the decyl-18-crown-6 based membrane, has an excellent electrochemical response, for potassium ion (as well as valinomycin membrane) and the sensor based on it displays a potentiometric selectivity in the order $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. The electrode membrane processes have been optimized. The important features of the proposed sensor are: good analytical properties (large concentration range, Nernstian response, good selectivity for K^+ over Na^+, good reproducibility and short response time); easy construction and simple operation mode; commercial availability.

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