The Synthesis of Styrene/4′-vinyl-benzo-24-crown-8 Copolymer and Its Use in Potassium-Ion Selective Electrodes

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Abstract. A synthetic procedure has been developed for the preparation of styrene/4′-vinyl-benzo-24-crown-8 copolymer (SPV-B24C8). The resulting copolymer was used as a membrane carrier to construct a K^+ ion-selective electrode. The electrode exhibits a Nernstian response for K^+ ions over a wide concentration range. The nature of the plasticizer, the additive, the concentration of internal solutions in the electrodes and the composition of the membrane were investigated. The performance of the electrode in terms of electrode reproducibility, response stability and regeneration was also studied. The selectivity coefficients of the electrode for potential interferents including alkali, alkaline earth, some transition and heavy metal ions were found to be in the order of 10^{-3} or less. The electrode was successfully used for the determination of potassium ion in blood serum.

Key words: SPV-B24C8 copolymer, synthesis, ion-selective electrodes, potassium.

1. Introduction

Due to the special metal ion complexing properties of crown ethers [1–3], their extensive use in the construction of ion-selective electrodes has been reported [4–14]. The main drawback of the electrodes based on these monomeric ligands is that they have lower selectivity coefficients than those obtained with electrodes based on some naturally occurring antibiotics such as valinomycin [15]. In recent years it has been shown that the use of bis(crown ether)s as ion carrier in the ion-selective membrane electrodes may greatly enhance their selectivity coefficients over interfering cations [16–22]. The use of polymer based crown ethers in the construction of ion-selective electrodes results in even better performance characteristics than

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those based on crown monomers and bis (crown ether)s [23–26]; they are especially suitable for use in nonaqueous media.

Among crown ethers, the larger molecules such as dibenzo-24-crown-8 and dibenzo-30-crown-10 possess some interesting properties. These molecules, due to their high degree of flexibility and increased number of donating oxygen atoms in the macrocyclic ring, can wrap themselves around metal ions of suitable size to form stable three-dimensional 'wrap around' complexes in which all oxygen atoms of the ring are coordinated to the central cation. Evidence for the existence of such structures both in the solid state [27, 28] and in solution [29–31] have been reported. Despite this unique feature of large crown ethers, there have been few examples of their application in the construction of ion-selective electrodes, as compared with the widespread use of the smaller sized crown ethers. There are only few reports on the use of dibenzo-24-crown-8 [32, 33] and dibenzo-30-crown-10 derivatives [34] in the construction of K^+ ion-selective electrodes.

Crown ethers can be incorporated into linear polymers as components of the backbone structure or as pendant moieties anchored to a macromolecule chain. The latter can be synthesized from a vinyl-containing macrocycle or by reacting a polymer with a functionalized macrocycle. The first polymers with pendant crown ethers were reported by Smid and coworkers [35, 36], who prepared homopolymers and styrene copolymers of vinyl-benzo-15-crown-5 and vinyl-benzo-18-crown-6. These polymeric crown ethers have shown advantages over ordinary crowns when they are used as chromatographic stationary phases [37] and as heterogeneous phase transfer catalysts [38]. In this paper we report the first synthesis of styrene/$4'$-vinyl-benzo-24-crown-8 copolymer (SPV-B24C8, I) and its use in the construction of a potassium-PVC membrane electrode.

2. Experimental

2.1. REAGENTS

3,4-Dihydroxybenzaldehyde, diethyl glycol, 1,2-bis(2-chloroethoxy) ether, *p*-toluenesulfonyl chloride and triphenyl phosphate were purchased from Aldrich and used as received. Heptaethylene glycol, 1,2-dichloro-3,6,9,12,15,18-hexaoxado-decane and $4'$-formylbenzo-24-crown-8 were synthesized as described elsewhere [39].

Reagent grade dibutyl phthalate (DBP), dioctyl phthalate (DOP), tetrahydro-furan (THF), oleic acid, nitrobenzene, nitric acid and high relative molecular weight PVC (all from Merck) were used as received. Reagent grade nitrate salts of the cations used (all from Merck) were of the highest purity available and used with-out any further purification except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout.

2.2. APPARATUS

The ^{13}C-NMR spectra with ^{1}H noise decoupling were recorded on a Varian Gemini XL-200 spectrometer at 50.3 MHz. The ^{1}H-NMR spectra were recorded on a Bruker AMX-400 spectrometer. All chemical shifts are reported in ppm downfield from TMS. The mass spectra were recorded on a VG 7070E mass spectrometer. The high resolution mass spectra were obtained from a Kratos Concept II H instrument with a resolution of 8000 and ionization of 70 eV which was scanned at 10 s/dec and an ac voltage of 8 kV using perfluorokerozine (PFK) as reference. The molecular weights of the copolymers synthesized were measured on a Waters GPC using 0.4% (g wt.) solution of copolymers in THF. Both UV (269 nm) and differential refractometers were used as detectors. Emf measurements were made with a Corning Ion Analyzer 250 pH/mV meter.

2.3. SYNTHESIS

2.3.1. *Heptaethylene glycol ditosylate (*2b*)*

A 250 mL round bottom two-necked flask equipped with a dropping funnel and a magnetic stirrer was charged with anhydrous pyridine (25 mL) and heptaethylene glycol (16.32 g, 0.05 mole) and was stirred under nitrogen in an ice–water salt bath for 15 min. To this, tosyl chloride (20.97 g, 0.11 mole) dissolved in anhydrous pyridine (100 mL) was added dropwise through a dropping funnel over a period of 45 min. The mixture was stirred for a further 2 h, poured into a beaker containing ice (200 g), acidified by HCl (6M) to a pH of 2, then extracted with dichloromethane (3 × 150 mL). The combined extracts were washed with saturated NaHCO$_3$ (2 × 30 mL), saturated NaCl (20 mL) and water (30 mL), and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation at reduced pressure. The resulting oil (22 g) was then purified by flash chromatography on silica gel (grade 60, mesh 230–400) using dichloromethane/ethyl acetate (2 : 1) as eluent to obtain 20 g (63%) oily heptaethylene glycol ditosylate.

^{13}C-NMR (CDCl$_3$), δ_c: 144.76, 132.87, 129.80, 127.82, 70.50, 70.43, 70.38, 70.33, 69.30, 68.46, 21.45 (methyl).

^{1}H-NMR (CDCl$_3$), δ_H: 7.69 (d, 4H, ^3J = 8.4 Hz), 7.24 (d, 4H, ^3J = 8.4 Hz), 4.06–4.03 (m, 4H) (—CH$_2$—OTs), 3.56–3.46 (m, 24H) (O—CH$_2$—CH$_2$—O), 2.33 (s, 6H) (methyl).

CIMS: M + 1 at 635 (14%), other peaks at 547 (4%) and 149 (100%).

2.3.2. *4′-Vinylbenzo-21-crown-8 ether (monomer* **4***)*

To obtain monomer **4**, a mixture of anhydrous 1,2-dimethoxyethane (250 mL), triphenylmethyl phosphonium bromide (5.71 g, 0.016 mole), and sodium hydride (57% suspension) (0.67 g, 0.016 mole) was heated for 1 h at 65 °C in a dry 500-mL three-necked round bottom flask, equipped with a magnetic stirrer, a

condenser, and a dropping funnel. The yellowish mixture was subsequently cooled to 40 °C. Then 4′-formylbenzo-24-crown-8 (**3**) (4.71 g, 0.011 mole) dissolved in anhydrous 1,2-dimethoxyethane (950 mL) was added dropwise over a period of 10 min. The mixture was refluxed for 2 h, then cooled, filtered, and the solvent was removed by rotary evaporation. The yellow-reddish residue oil was dissolved in dichloromethane (100 m L), washed, with water (2×30 mL) followed by saturated sodium chloride (30 mL), then dried over magnesium sulfate and the solvent was removed by evaporation at reduced pressure. The resulting oil was subsequently dissolved in hot n-hexane and left at room temperature overnight. The precipitated triphenylphosphine oxide (2 g) was filtered, the solvent was removed by rotary evaporation, and the remaining oil was purified by flash chromatography on silica gel (grade 60, 230–400 mesh) using ethyl acetate/dichloromethane (1 : 1) as eluent to yield 3.1 g (66%) oily **4**.

^{13}C-NMR (CDCl$_3$), δ_c: 148.90, 136.32 (vinyl methine), 131.26, 120.03, 114.04, 111.99 (vinyl methylene), 111.86; 71.14, 70.91, 70.84, 70.73, 69.83, 69.38, 69.31 (O—CH$_2$—CH$_2$—).

^{1}H-NMR (CDCl$_3$), δ_H: 6.99 (d, 1H, ^4J = 1.9 Hz (H$_d$)), 6.94 (dd, 1H, ^3J = 8.2 Hz, ^4J = 1.9 Hz (H$_e$)), 6.83 (d, 1H, ^3J = 8.2 Hz (H$_f$)), 6.62 (dd, 1H, ^3J = 17.5 Hz, ^3J = 10.8 Hz (H$_a$)), 5.59 (d. 1H, ^3J = 17.5 Hz (H$_b$)), 5.14 (d, 1H, ^3J = 10.8 Hz (H$_c$)), 4.18 (m, 4H), 3.91 (m, 4H), 3.79 (m, 4H), 3.72 (m, 4H), 3.68 (broad s, 8H), 3.66 (s, 4H).

High resolution MS: m/z for C$_{22}$H$_{34}$O$_8$ (M$^+$), *Calc.:* 426.2254; *Found:* 426.2192 (5.3%), other peaks at 162 (100%), 100 (100%), 100 (100%) and 143 (30%). Also, molecular ion with *m/z* 427 was observed by CI method.

2.3.3. *SPV-B24C8 (copolymer* **I***)*

A one-necked flask, equipped with O-ring stopcocks, was charged with benzene (60 mL), monomer **4** (1.28 g, 0.003 mole), styrene (2.31 g, 0.022 mole), and azobis(isobutyronitrile) (AIBN) (0.01 g) and degassed using four freeze–pump–thaw cycles under high vacuum. The flask was sealed under vacuum and heated to 70 °C for 3 days, then cooled to room temperature and the clear benzene solution was poured slowly into the n-hexane (500 mL) with vigorous stirring. Some sticky semisolid was precipitated. The semisolid was then filtered and reprecipitated by dissolving it in dichloromethane (4 mL) and pouring dropwise into the n-hexane (500 mL) to obtain 1.0 g of a white precipitate of SPV-B24C8.

^{13}C-NMR (CDCl$_3$), δ_c: 145.6, 138–140, 128.0–128.9, 126.0, 120–121, 114.0–114.1 (aromatic), 71.0, 70.7, 70.0, 69.7, 69.6 (O—CH$_2$—CH$_2$—), 42–46, 40.6 (CH, CH$_2$ benzylic) ppm.

^{1}H-NMR (CDCl$_3$), δ_H: 6.1–7.1 (aromatic, 20 H), 3.0–4.2 (O—CH$_2$—CH$_2$), 0.9–2.1 (CH, CH$_2$ benzylic, 14 H) ppm.
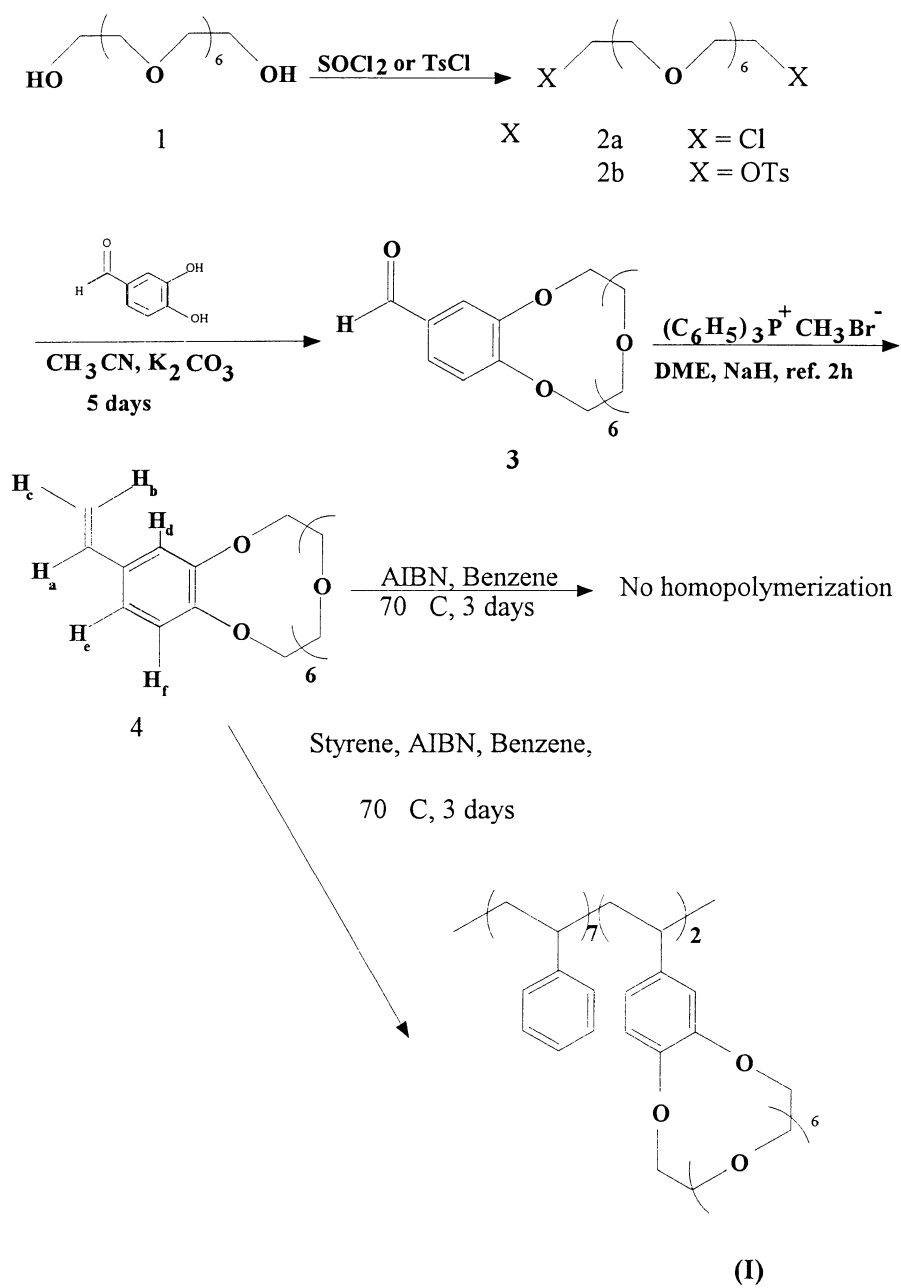
Scheme 1.

2.4. ELECTRODE PREPARATION

The general procedure for preparing the PVC membrane was to thoroughly mix 46 mg of powdered PVC and 114 mg DOP plasticizer in 10 mL THF. 20 mg oleic acid

Table I. Yield of the cyclization step under different experimental conditions for synthesis of compound **3**.

X	Base	Solvent	Reflux time (h)	% Yield
—Cl	NaOH	n-Butanol	33	17
—Cl	t-BuONa	t-Butanol	72	30
—Cl	K_2CO_3	Acetonitrile	120	50
—OTs	K_2CO_3	Acetonitrile	100	51
—OTs	t-BuONa	Tetrahydrofuran	144	49

(as additive) and 20 mg of SPV-B24C8 were added to this solution until thoroughly dissolved. The resulting mixture was transferred into a glass dish of 2 cm diameter. The THF was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (8–10 mm OD) was dipped into the mixture for about 10 s to allow a nontransparent membrane of about 0.3 mm thickness to form. The tube was then pulled out of the solution and kept at room temperature for 1 h. The tube was filled with internal filling solution (1.0×10^{-3} M of KCl). The electrode was finally conditioned for 12 h by soaking in a 1.0×10^{-2} M solution of potassium nitrate. A silver/silver chloride coated wire was used as an internal reference electrode.

2.5. EMF MEASUREMENTS

All emf measurements were carried out with the following cell assembly:

Ag–AgCl / 1.0×10^{-3} M KCl / PVC membrane /

test solution / Hg–Hg_2Cl_2, KCl (satd.)
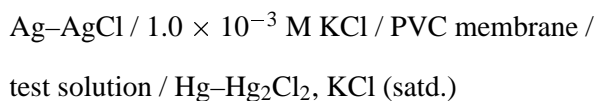
The emf observations were made relative to a double junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. Activities were calculated according to the Debye–Hückel procedure [40].

3. Results and Discussion

3.1. SYNTHESIS AND CHARACTERIZATION OF SPV-B24C8

The experimental route for the synthesis of copolymer SPV-B24C8 is shown in Scheme 1. As seen, 4′-vinylbenzo-24-crown-8 (monomer **4**) is necessary for the synthesis of the target copolymer. The monomer **4** was synthesized in three steps from heptaethyleneglycol (**1**). In order to optimize,the reaction conditions for the cyclization step, three important factors were examined: (a) the base; (b) the concentration; and (c) the template effect. The results are summarized in Table I. The mild base K_2CO_3, a dilute condition (i.e. 0.03 M) using acetonitrile as solvent, and K^+ as central cation were found to be the best. The yields were calculated based on the pure product obtained after purification by flash chromatography.
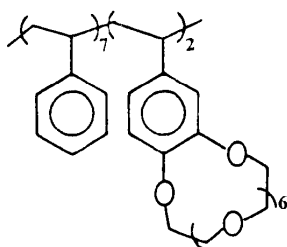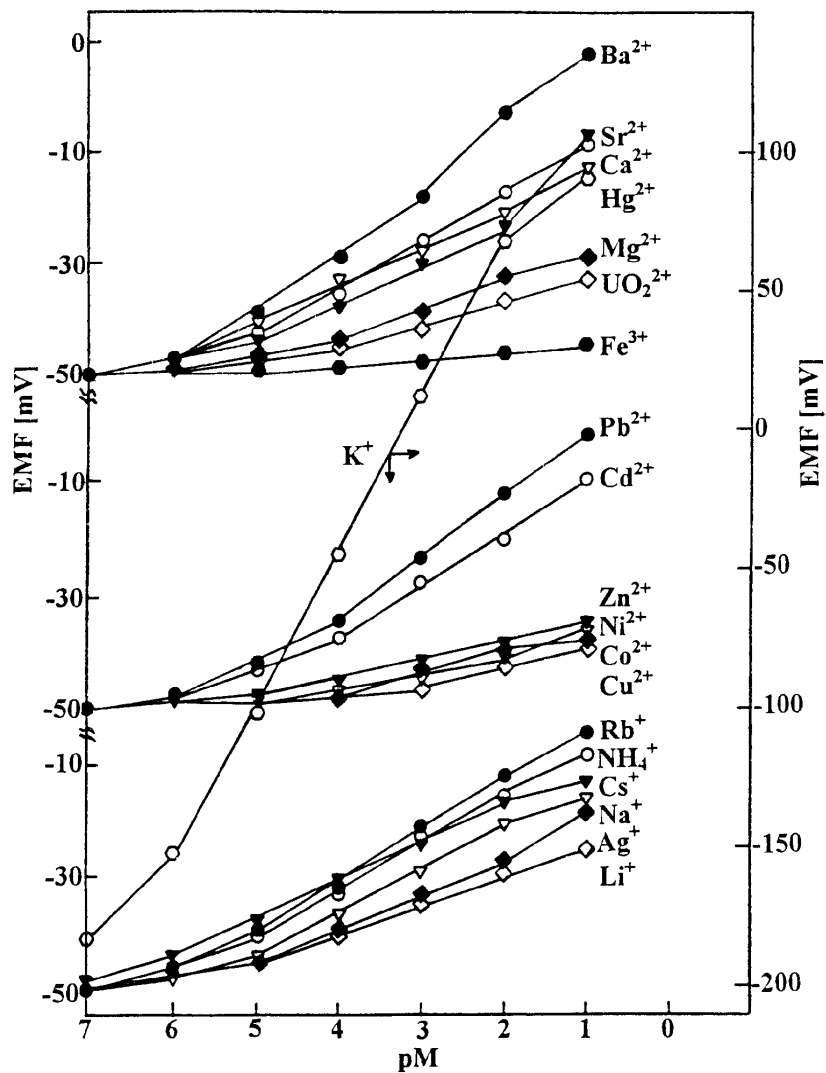
Figure 1. Potential response of various metal ion-selective electrodes based on the SPV-B24C8 copolymer.

Table II. Optimization of membrane ingredients.

Membrane number	Composition				Slope (mV decade^{-1})
	%PVC	%Plasticizer	%SPV-B24C8	%Oleic acid	
1	33	DBP, 67	1	0	10
2	30	DBP, 67	3	0	12
3	28	DBP, 67	5	0	15
4	23	DBP, 67	10	0	25
5	18	DBP, 67	15	0	17
6	23	DOP, 67	10	0	28
7	23	NB, 67	10	0	14
8	23	DOP, 62	10	5	45
9	23	DOP, 57	10	10	58
10	23	DOP, 52	10	15	51
11	33	DOP, 57	0	10	3

The Wittig reaction was carried out in dimethyl ether (DME) using sodium hydride to obtain monomer **4** in 66% yield. As seen from Scheme 1, the radical homopolymerization of **4** failed, although the homopolymerization of a few similar vinyl compounds has been reported previously [35, 41]. Anionic homopolymerization [42] at $-70\,^{\circ}$C using n-BuLi as a base was also tried but no polymer was formed.

The copolymerization of monomer **4** with styrene was carried out at styrene/4$'$-vinyl-benzo-24-crown-8 molar ratios of 1 and 7. No copolymerization occurred at the molar ratio of 1, while at the molar ratio of 7 a copolymer (i.e. SPV-B24C8) was obtained with average molecular weight of 16 000, as determined by GPC. The value of m/m' (see Scheme 1) in the resulting copolymer was determined to be 7/2 from the integration of the corresponding NMR spectrum.

3.2. POTASSIUM-SELECTIVE ELECTRODE

In the preliminary experiments, SPV-B24C8 copolymer was used to prepare PVC membrane ion-selective electrodes for a wide variety of metal ions including alkali, alkaline earth and some transition and heavy metal ions. The potential responses of these electrodes are illustrated in Figure 1. As seen, except with the K^+ ion-selective electrode, in all other cases the slope of the corresponding potential vs. pM plots is much lower than the expected Nernstian slope of 59 and 28.5 mV per decade for the univalent and bivalent cations, respectively. It should be noted that the sensitivities of the potential responses for cations such as Ba^{2+}, Pb^{2+} and Rb^+ are larger than the other cations used, most probably due to the higher stability of their 1 : 1 complexes with the B24C8 ring [2, 3]. However, the K^+ ion-selective electrode exhibits a linear response to the activity of potassium ions within the
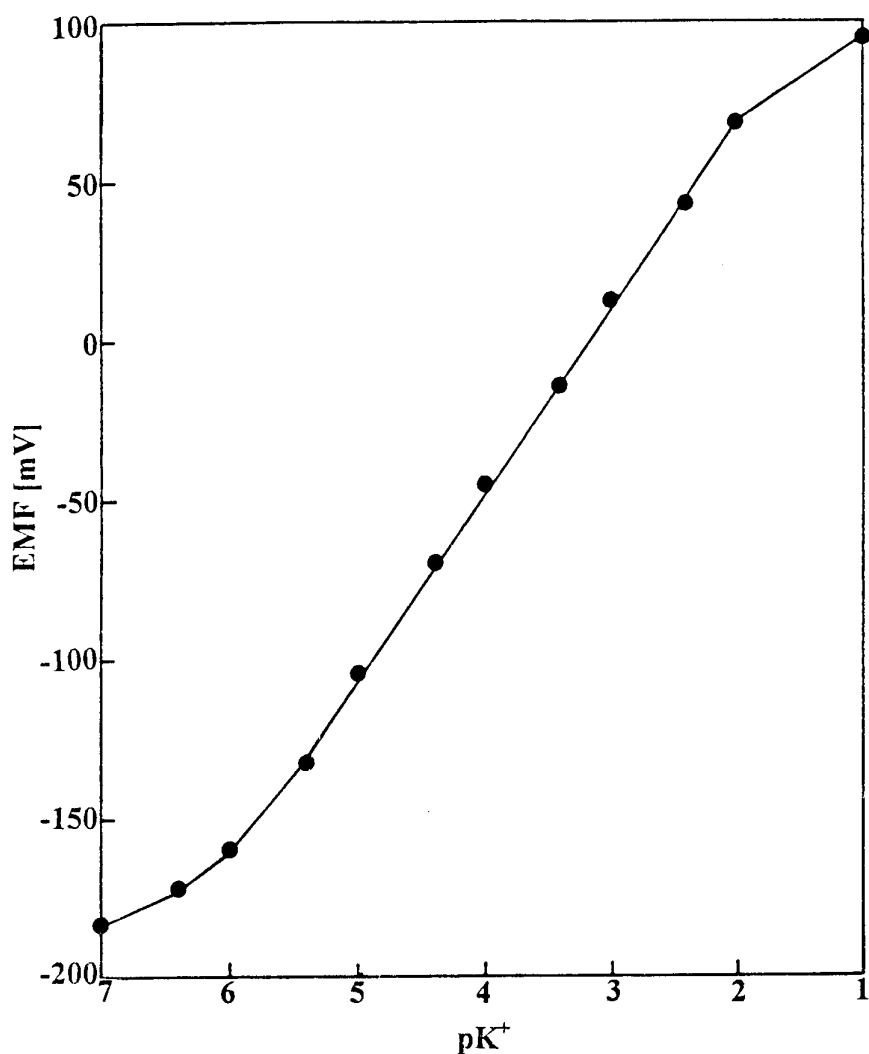
Figure 2. Calibration graph for the potassium ion-selective electrode.

concentration range of about 1×10^{-2} to 4×10^{-6} M with a Nernstian slope of 57 ± 2 mV per decade.

It is well known that the selectivities obtained for a given ionophore depend significantly on the membrane composition and the nature of solvent mediators and additives used [43–45]. Thus, we investigated the influence of the membrane composition and amount of oleic acid as a lipophilic additive on the potential response of the K^+ ion-selective electrode. The results are summarized in Table II. It is immediately obvious that, among three different plasticizers used, the use of 67% DOP in the presence of 10% ionophore results in the best sensitivity, although
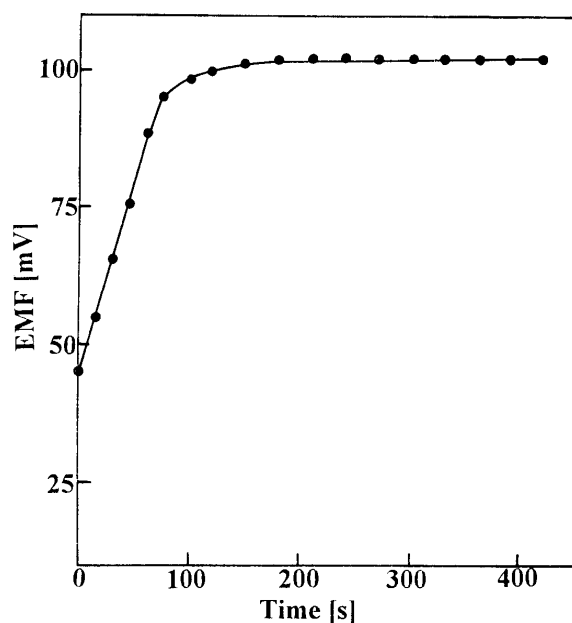
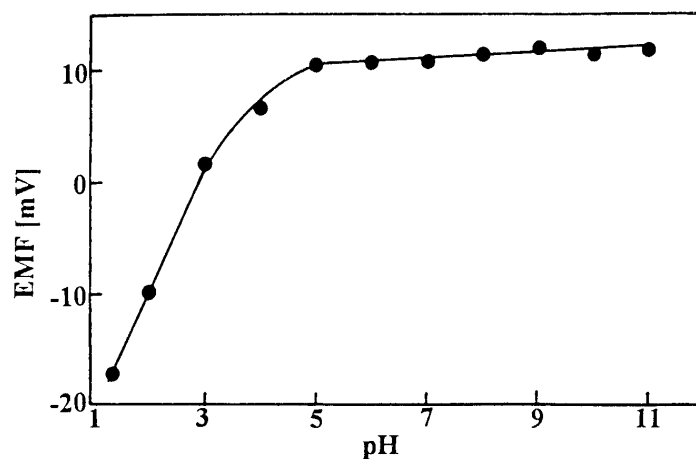*Figure 3.* Response-time profile of the K^+ ion-selective electrode.

Figure 4. Effect of pH of test solution on the potential response of the potassium ion-selective electrode; $[K^+] = 1.0 \times 10^{-3}$ M.

the slope of emf vs. log (concentration) plot in this case is about half the expected Nernstian value. However, addition of 10% oleic acid will increase the sensitivity of the electrode response considerably, so that the selective electrode demonstrates a Nernstian behavior. It is well known that the presence of lipophilic anionic sites in cation-selective membrane electrodes not only diminishes the ohmic resistance [46] and increases the response behavior and selectivity [47], but also, in cases

Table III. Selectivity coefficients of various interfering ions.

Interfering ion	k_K^{pot}	Interfering ion	k_K^{pot}
Li^+	1.2×10^{-3}	Co^{2+}	5.6×10^{-4}
Na^+	1.9×10^{-3}	Ni^{2+}	4.8×10^{-4}
Rb^+	5.3×10^{-3}	Cu^{2+}	5.7×10^{-4}
Cs^+	1.3×10^{-3}	Zn^{2+}	5.8×10^{-4}
NH_4^+	1.9×10^{-3}	Cd^{2+}	1.9×10^{-3}
Ag^+	1.4×10^{-3}	Pb^{2+}	2.2×10^{-3}
Mg^{2+}	5.9×10^{-4}	Hg^{2+}	1.6×10^{-3}
Ca^{2+}	7.5×10^{-4}	UO_2^{2+}	9.4×10^{-4}
Sr^{2+}	1.2×10^{-3}	Fe^{3+}	1.6×10^{-4}
Ba^{2+}	2.5×10^{-3}		

where the extraction capability of the ionophore is poor, enhances the sensitivity of the membrane electrode [48]. It should be noted that the only problem with the use of oleic acid as an additive is its relatively high proton affinity, which may facilitate the interference from protons, especially in acidic solutions with pH values below the pK_a of the carboxylic acid.

The concentration of the internal KCl solution in the electrode was changed from 1×10^{-3} M to 1×10^{-5} M and the potential response of the K^+ ion-selective electrode was obtained. It was found that the variation of the concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. Thus, a 1×10^{-3} M KCl solution was used as internal solution for further studies.

The critical response characteristics of the K^+ ion-selective electrode were assessed according to IUPAC recommendations [49]. The electrodes show a linear response to the activity of K^+ ion in the range of 4×10^{-6} to 1×10^{-2} M (see for example Figure 2). The slopes of the calibration plots were 57 ± 2 mV decade^{-1} of activity change at 25 °C and neutral pH. The limit of detection was 1.0×10^{-6} M, as determined from the intersection of the two extrapolated segments of the calibration graph (see Figure 2).

We measured the average time required for the K^+ ion-selective electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion in a series of potassium ion solutions, each having a 10-fold difference in concentration. Stable responses were achieved after 75 s for concentrations $\leq 1 \times 10^{-3}$ M (see Figure 3). It should be noted that the equilibrium potentials remained constant for more than 5 min, after which only a very slow change was recorded. In addition, the membrane electrodes prepared can be used for at least three months after preparation without any deterioration.

The influence of the pH of the test solution on the potential response of the electrode was studied and the results are shown in Figure 4. In the pH range 4–11 the potential response shows only a negligible drift, but at pH < 3 it does diminish

Table IV. Comparison of selectivity coefficients of different K$^+$ ion-selective electrodes.

Carrier	k_K^{pot}					
	Li$^+$	Na$^+$	Rb$^+$	Cs$^+$	NH$_4^+$	Ref.
Valinomycin	2.0×10^{-2}	2.6×10^{-4}	2	5.0×10^{-1}	2.0×10^{-2}	15, 51
Bis(crown ether) B15C5—CH$_2$—O—CH$_2$—B15C5	1.0×10^{-4}	2.6×10^{-4}	1.6×10^{-2}	3.2×10^{-3}	8.7×10^{-3}	52
Poly(crown ether) —(CH$_2$—CH—)$_m$ | CO | NH | B15C5	–	3×10^{-4}	2×10^{-1}	2×10^{-3}	2×10^{-3}	23
Copolymer SPV-B24C8	1.2×10^{-3}	1.9×10^{-3}	5.3×10^{-3}	1.3×10^{-3}	1.9×10^{-3}	This work

STYRENE/4′-VINYL-BENZO-24-CROWN-8 COPOLYMER

Table V. Determination of potassium ion in blood serum by the K^+ ion-selective electrode.

Sample number	Concentration (μg/mL)		
	Na^+ (AAS)	K^+ (AAS)	K^+ (ISE)
1	3110	121	118 ± 2
2	3252	128	123 ± 2
3	3085	120	116 ± 2
4	3128	127	124 ± 3

considerably. This could be due to high proton affinity of the oleic acid used as additive, as well as the protonation of the crown ether in the membrane, to some extent, which results in improper functioning of the membrane electrode to the K^+ ion concentration.

The selectivity coefficients (k_K^{pot}) were evaluated graphically by the matched potential method [50] from potential measurements on solutions containing a fixed amount of K^+ ion (1×10^{-4} M) and varying amounts of the interfering ions (M^{n+}) according to the equation.

$$k_K^{pot} a_M^{1/n} = a_K \{\exp[(E_2 - E_1)F/RT]\} - a_K \qquad (1)$$

where E_1 and E_2 are the electrode potentials for the solution of K^+ ions alone and for the solution containing interfering ions (M^{n+}) and K^+ ions. According to Equation (1), the k_K^{pot} values for diverse ions can be evaluated from the slope of the graph of $a_K\{\exp[(E_2 - E_1)F/RT]\} - a_K$ vs $a_M^{1/n}$. The resulting values are summarized in Table III. As can be seen, for all diverse ions used, the selectivity coefficients are in the order of 10^{-3} or smaller, indicating they would not significantly disturb the functioning of the K^+ ion-selective membrane. In Table IV, the selectivity coefficients of the potassium electrode based on SPV-B24C8 for Li^+, Na^+, Rb^+, Cs^+ and NH_4^+ ions are compared with the corresponding values previously reported for the K^+-ion selective electrodes based on valinomycin [15, 51], a bis-benzo-15-crown-5 derivative [52] and a poly(crown ether) of benzo-15-crown-5 [23]. As seen, with the exception of Na^+ ion, the k_K^{pot} values obtained with SPV-B24C8 for other cations is either superior or comparable to those reported previously. However, the K^+ selectivity over Na^+ of the SPV-B24C8 based electrode is about one-tenth of that obtained with other K^+ ion-selective electrodes.

The K^+ ion-selective electrode investigated was applied to the determination of potassium in four different blood serum samples. The results obtained by the ion-selective electrode and atomic absorption spectroscopy (AAS) are summarized in Table V. The amounts of Na^+ ion present in the blood serum samples, as determined by AAS, are also included for comparison. There is a satisfactory agreement between the results obtained by the two different methods.

References

1. C.J. Pedersen: *J. Am. Chem. Soc.* **89**, 7017 (1967).
2. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
3. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
4. J. Petranek and O. Ryba: *Anal. Chim. Acta* **72**, 375 (1974).
5. M. Yoshio and H. Noguchi: *Anal. Lett.* **15**, 1197 (1982).
6. M. Takagi and H. Nakamura: *J. Coord. Chem.* **15**, 53 (1986).
7. A.S. Attiyat, G.D. Christian, R.Y. Yie, X. Wen, and R.A. Bartsch: *Anal. Chem.* **60**, 2561 (1988).
8. R.W. Cattrall, L.W. Deady, S. S. Tan, and I.C. Hamilton: *Anal. Chim. Acta* **208**, 283 (1988).
9. A. Cygan, E. Luboch, and J. Biernat: *J. Incl. Phenom.* **6**, 215 (1988).
10. S.R. Sheen and J.S. Shih: *Analyst* **117**, 1691 (1992).
11. K. Suzuki, H. Yamada, K. Sato, K. Watanabe, H. Hisamoto, Y. Tobe, and K. Kobrio: *Anal. Chem.* **65**, 3404 (1993).
12. A. Ohki, J.P. Lu, X. Huang, and R.A. Bartsch: *Anal. Chem.* **66**, 4322 (1994).
13. N. Tavakkoli and M. Shamsipur: *Anal. Lett.* **29**, 2269 (1996).
14. K. Kimura and T. Shono: in Y. Inoue and G.W. Gokel (eds), *Cation Binding by Macrocycles*, Marcel Dekker Inc., New York (1990), pp. 429–463.
15. N. Mascini and F. Pallozzi: *Anal. Chim. Acta* **73**, 375 (1974).
16. T. Chono, M. Okahara, I. Ikeda, K. Kimura, and H. Tamurq: *J. Electroanal. Chem.* **132**, 99 (1982).
17. T.M. Handyside, J.C. Lockhart, M.B. McDonnell, and P.V. Subb Rao: *J. Chem. Soc., Dalton Trans.* 2331 (1982).
18. K. Kimura, A. Ishikawa, H. Tamura, and T. Shono: *Bull. Chem. Soc. Jpn.* **56**, 359 (1983).
19. K. Toth, E. Lindner, M. Horvath, J. Jeney, I. Bitter, B. Agai, T. Meisel, and L. Toke: *Anal. Lett.* **22**, 1185 (1989).
20. H.Y. An, Y.J. Wu, Z.J. Zhang, R.M. Izatt, and J.S. Bradshaw: *J. Incl. Phenom.* **11**, 303 (1991).
21. M.M. Khalil: *Anal. Lett.* **26**, 2071 (1993).
22. A. Li, Z. Zhang, Y. Wu, H. An, R.M. Izatt, and J.S. Bradshaw: *J. Incl. Phenom.* **15**, 317 (1993).
23. K. Kimura, T. Maeda, H. Tamura, and T. Shone: *J. Electroanal. Chem.* **95**, 91 (1979).
24. Nakamura, M. Komai, S. Hosono, and K. Izutsu: *Anal. Chim. Acta* **238**, 351 (1990).
25. N. Akmal, H. Zimmer, and H.B. Mark: *Anal. Lett.* **24**, 1431 (1991).
26. T. Nakamura, C. Hayashi, and K. Izutsu: *Anal. Chim. Acta* **292**, 305 (1994).
27. M.A. Bush and M.R. Truter: *J. Chem. Soc., Perkin Trans. 2,* **345** (1975).
28. J. Hasek, K. Huml, and D. Hlavata: *Acta Crystallogr.* **35B**, 330 (1975).
29. M. Shamsipur and A.I. Popov: *J. Am. Chem. Soc.* **101**, 4051 (1979).
30. M. Shamsipur, G. Rounaghi, and A.I. Popov: *J. Solution Chem.* **7**, 701 (1980).
31. M.K. Amini and M. Shamsipur,: *Inorg. Chim. Acta* **183**, 65 (1991).
32. S.K. Norov, A.K. Tashmukhamedova, O.G. Vartanova, and N.Z. Saifulina: *Elektrokhim.* **14**, 1615 (1978).
33. S.K. Norov, E.S. Gureev, A.K. Tashmukhamedova, O.G. Vartanova, and N.Z. Saifullina: *Elektrokhim.* **15**, 943 (1979).
34. O. Ryba and J. Petrank: *J. Electroanal. Chem.* **67**, 321 (1976).
35. S. Kopolow, T.E. Hogen Esch, and J. Smid, *J. Macromolecules* **4**, 359 (1971).
36. S. Kopolow, T.E. Hogen Esch, and J. Smid: *J. Macromolecules* **6**, 133 (1973).
37. G. Dotsevi, D.J. Cram, and Y. Sogah: *J. Am. Chem. Soc.* **97**, 1259 (1975).
38. J.A. Moor and E.M. Partain: in L.J. Mathias and C.E. Carraher (eds), *Crown Ether and Phase Transfer Catalysis in Polymer Science*, Plenum, New York (1984), p. 291.
39. M.R. Ganjali, A. Rouhollahi, A. Moghimi, and M. Shamsipur: *Polish J. Chem.* **70**, 1172 (1996).
40. S. Kamata, A. Bhale, Y. Fukunaga, and A. Murata: *Anal. Chem.* **60**, 12464 (1988).
41. W. Smid, G.M. Gold, D.M. Teegarden, K.M. Mc Grane, D.J. Luca, P.A. Falsigno, and C.C. Chen: *J. Am. Chem. Soc.* **108**, 5827 (1986).
42. M. Vendo, M. Mano, and H. Ito: *J. Polym. Sci., Part A* **29**, 1979 (1991).
43. J. Koryta: *Anal. Chim. Acta* **233**, 1 (1990).
44. O.S. Wolfbeis: *Anal. Chim. Acta* **250**, 181 (1991).

45. T. Rosatzin, E. Bakker, K. Suzuki, and W. Simon: *Anal. Chim. Acta* **280**, 197 (1993).

46. D. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, and E. Pungor: *Anal. Chim. Acta* **171**, 119 (1985).

47. M. Huser, P.M. Gehrig, W.E. Morf, W. Simon, E. Lindler, J. Jeney, K. Toth, and E. Pungor: *Anal. Chem.* **63**, 1380 (1991).

48. D. Ammann, W.E. Morf, P. Anken, P.C. Meier, E. Pretsch, and W. Simon: *Ion-Sel. Electrode Rev.* **5**, 3 (1983).

49. IUPAC Analytical Chemistry Divison, Commission on Analytical Nomenclature 'Recommendations for Nomenclature of Ion Selective Electrodes', *Pure Appl. Chem.* **48**, 127 (1976).

50. Y. Umezawa, K. Umezawa, and H. Sato: *Pure Appl. Chem.* **67**, 507 (1995).

51. S. Lal and G.D. Christian: *Anal. Lett.* **3**, 11 (1970); J. Pick, K. Toth, E. Pungor, M. Vasak, and W. Simon: *Anal. Chim. Acta* **64**, 477 (1973).

52. K.W. Fung and K.H. Wong: *J. Electroanal. Chem.* **111**, 359 (1980).