Phosphoryl Containing Podands as Carriers in Plasticized Membrane Electrodes Selective to Quaternary Ammonium Surfactants

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Abstract. Open chain polyethers with phosphoryl-containing terminal groups have been studied as carriers in plasticized membrane electrodes that are selective towards cationic surfactants. Host–guest complexation has also been studied by means of batch extraction and bulk membrane transport experiments. For the various guests, the bulk membrane (chloroform) transport rate decreases in the series tetraalkyl ammonium > alkyl pyridinium > alkyl ammonium, while the series of solvent extraction efficiency is exactly opposite; an explanation for this behaviour is proposed. The performance of electrode membranes follows the series for bulk membrane transport. Among the ISE membranes of various composition, one containing the longest (seven oxygen atoms) podand, *o*-nitrophenyl octyl ether (plasticizer), and sodium tetraphenyl borate (anionic additive) performs the best. The slope of the electrode function equals 58.5 mV/decade, the detection limit for dodecyltrimethylammonium is 3.2×10^{-6} M. ISE response time is 5–10 s, the working pH range is 2–11 and lifetime is at least 6 months. The electrode selectivity is significantly better than that of conventional ion-association and crown ether based electrodes.

1. Introduction

Neutral carriers are widely used in plasticized membrane ion-selective electrodes (ISE) for the determination of organic compounds. Some recent examples are ISEs for primary amines [1–3], amino acid esters [1, 4–6], and guanidine [7]. The chemical mechanisms which are utilized in these electrodes are based on host–guest complexation, i.e., non-covalent association of carrier with analyte. The association is typically driven by hydrogen bonding and charge–dipole interactions and, in principle, may provide high binding efficiency and selectivity towards the substrate of proper size, shape, and functionality [8–10]. This justifies the growing interest of analytical chemists in host–guest complexation.

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Quaternary ammonium compounds represent a particularly important though challenging target for the development of 'host–guest based' electrodes. Due to the widespread use of these compounds (as cationic surfactants, phase-transfer catalysts, food and cosmetics additives, etc.), there exists a growing need for fast and reliable methods to analyze them. Selective electrodes provide a unique combination of selectivity, simplicity, cheapness, and ability to determine the target compounds in the required concentration range. However, only a few reports have been published on such ISEs based on host–guest complexation [11, 12]. The main reason is in the difficulty in choosing appropriate carriers (hosts).

As is well known in host–guest complex chemistry, the more protons on the nitrogen of an ammonium guest, the better it will be complexed by classic crown ether hosts. Unfortunately, quaternary ammonium and related *N*-alkyl pyridinium guests lack protons and are not capable of any hydrogen bonding. Not surprisingly, it was reported that the introduction of dibenzo-18-crown-6, DB18C6, into the plasticized membrane of an ISE for detecting dodecylpyridinium cation does not lead to improved electrode performance [12].

We suggest that the use of long and flexible open-chain polyethers, podands, will lead to better results. One may expect that many oxygen atoms, which are combined into a very flexible framework, should 'encircle' the guest and provide multiple ion–dipole interactions. Though a single interaction of that type is much weaker than a hydrogen bond, the complexation may still be efficient if the number of interactions is high. This leads to a choice of 'polydentate' hosts with minimal steric constraints, podands. We also propose the use of podands with electron-enriched terminal atoms for further strengthening of the binding. Our previous experience has revealed that podands containing electron-rich phosphoryl groups are eminently effective carriers in various ISEs [13, 14].

Here we report on the successful use of such podands as carriers in cationic surfactant selective electrodes. We also present the data for extraction and bulk membrane transport, which explains the details of host–guest complexation, which underlie analytical applications.

2. Experimental

2.1. Chemicals

The structures of the hosts and guests used in the present study are shown in Chart 1.

2.1.1. *Podands*

All the structures of the synthesized compounds were verified by elemental analysis and ^{1}H and ^{31}P NMR spectra (recorded on a Bruker CXP-200 spectrometer in CDCl$_3$ with tetramethylsilane as internal and 85% H$_3$PO$_4$ as external references). Melting points (uncorrected) were measured on a Boetius PHMK-05 instrument.

	n	m
MO$_3$	1	1
M$_2$O$_3$	1	2
MO$_5$	3	1
MO$_7$	5	1

TG

DB18C6

TPPO

n-H$_{25}$C$_{12}$—N$^+$⟨⟩   Br$^-$ (Cl$^-$)   DDP

n-H$_{25}$C$_{12}$—N$^+$—Me   Br   DDTMA

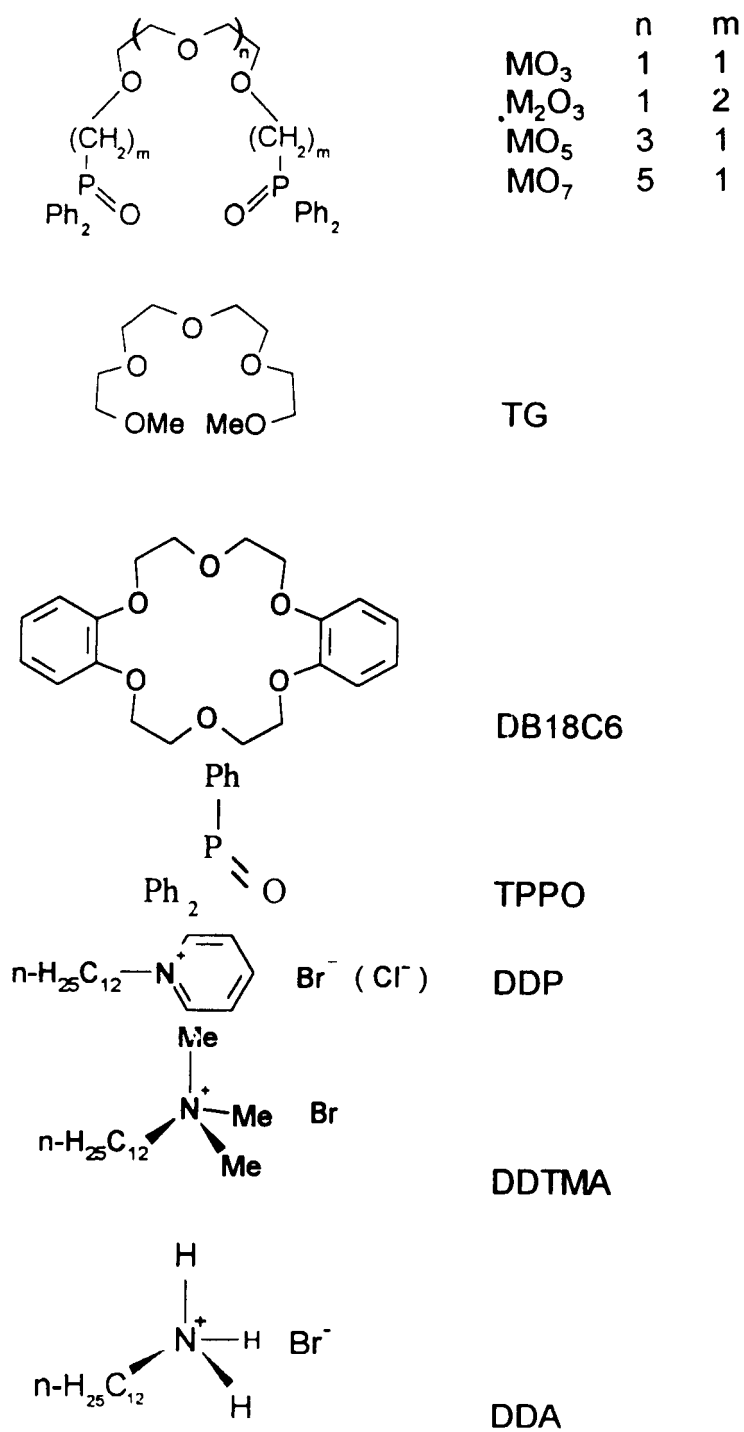n-H$_{25}$C$_{12}$—N$^+$—H   Br$^-$ DDA

Chart 1. The hosts and guests studied in this work.

1,11-Bis(diphenylphosphinyl)-3,6,9-trioxaundecane (M₂O₃) was synthesized as described previously [15].

1,9-Bis(diphenylphosphinyl)-2,5,8-trioxanonane(MO₃). A mixture containing 15.0 g (64.0 mmol) of diphenylphosphinylmethanol [16], 10.52 g (32.0 mmol) anhydrous caesium carbonate, 12.8 g (32.0 mmol) ethylene glycol di-*p*-tosylate and 80 mL anhydrous dioxane was heated and stirred at 100 °C for 12 h under dry argon. After the reaction the mixture was diluted with 350 mL of water and extracted into $CHCl_3$ (4 × 50 ml). The organic layer was separated, washed with dilute (1 : 1) hydrochloric acid (3 × 30 mL), water (3 × 40 mL) and evaporated under reduced pressure; after addition of diethyl ether a crude solid was obtained. Column chromatographic purification ($CHCl_3$—EtOH (20 : 1) on SiO_2 yields 12.8 g (75%) as white crystals, m.p. 102–104 °C (acetone–ether) [17]. *Found:* C 67.40, 67.45; H 5.20, 5.25; P 11.70, 11.85. $C_{30}H_{32}O_5P_2$ *Calculated:* C 67.40, H 5.10, P 11.60. ^{1}H NMR ($CDCl_3$ (δ, ppm): 3.50 (m, 4H, $2OCH_2$); 3.69 (m, 4H, $2OCH_2$); 4.30 (d, 4H, 3JHP3D6 Hz, $CH_2P(O)$); 7.44 (m, 12H, Ar—H); 7.86 (m, 8H, Ar—H). ^{31}P NMR ($CDCl_3$ (δ, ppm): 27.76.

1,15-Bis(diphenylphosphinyl)-2,5,8,11,14-pentaoxapentadecane(MO₅).   1,15-Bis(diphenylphosphinyl)-2,5,8,11,14-pentaoxapentadecane(MO₅) was obtained analogously to MO_3 from 15.00 g (64.0 mmol) of diphenylphosphinylmethanol, 10.52 g (32.0 mmol) anhydrous caesium carbonate, and 8.49 g (26.63 mmol) 1,17-dichloro-3,6,9,11,14-pentaoxaheptadecane in 40 mL anhydrous dioxane. After the reaction, the mixture was diluted with 250 mL of water and extracted into $CHCl_3$ (4 × 50 mL). The organic layer was separated, washed with dilute (1 : 1) hydrochloric acid (3 × 30 mL), water (3 × 40 mL) and evaporated under reduced pressure. Column chromatographic purification ($CHCl_3$–EtOH (20 : 1) on SiO_2 yields 13.93 g (70%) as an oil. *Found:* C 65.60, 65.55; H 6.50, 5.45; P 10.10, 10.15. $C_{34}H_{40}O_7P_2$ *Calculated:* C 65.60, H 6.47, P 9.95. ^{1}H NMR ($CDCl_3$ (δ, ppm): 3.40–3.74 (m, 16H, $8OCH_2$); 4.34 (d, 4H 3JHP=3D6 Hz, $CH_2P(O)$); 7.41 (m, 12H, Ar—H); 7.80 (m, 8H, Ar—H). ^{31}P NMR ($CDCl_3$ (δ, ppm): 27.97.

1,21-Bis(diphenylphosphinyl)-2,5,8,11,14,17,20-heptaoxaheneicosane(MO₇).
1,21-Bis(diphenylphosphinyl)2,5,8,11,14,17,20-heptaoxaheneicosane(MO₇) was obtained analogously to MO_5 from 12.36 g (53.27 mmol) of diphenylphosphinylmethanol, 10.52 g (32.0 mmol) anhydrous caesium carbonate, 7.39 g (32.0 mmol) 1,11-dichloro-3,6,9-trioxaundecane in 40 mL anhydrous dioxane. After the reaction, the mixture was diluted with 250 mL of water and extracted into $CHCl_3$ (4 × 50 mL). The organic layer was separated, washed with dilute (1 : 1) hydrochloric acid (3 × 30 mL), water (3 × 40 mL) and evaporated under reduced pressure. Column chromatographic purification ($CHCl_3$—EtOH (20 : 1) on SiO_2 yields 13.13 g (77%) as oil. *Found:* C 64.10, 64.25; H 6.60, 5.75; P 8.70, 8.75. $C_{38}H_{48}O_9P_2$ *Calculated:* C 64.21, H 6.80, P 8.72. ^{1}H NMR ($CDCl_3$ (δ, ppm):

3.47–3.75 (m, 24H, 12OCH$_2$); 4.35 (d, 4H, 3JHP=3D6 Hz, CH$_2$P(O)); 7.48 (m, 12H, Ar—H); 7.85 (m, 8H, Ar—H). ^{31}P NMR (CDCl$_3$ (δ, ppm): 27.93.

2.1.2. *Other reagents*

Commercially available DB18C6 (Cherkassy, Ukraine) was used without further purification; tetraglym (TG) was from Merck. We also used alkyltrimethylammonium and alkyl pyridinium bromides (chlorides); dioctyl phthalate (DOP) from Aldrich; *o*-nitrophenyl octyl ether (*o*-NPOE) from Sigma; triphenylphosphineoxide (TPPO), sodium tetraphenyl borate (NaTPB) and poly(vinyl chloride) (PVC) C-70 (Russia). Tetrahydrofuran (THF) was distilled before use. The other chemicals were 'chemically pure' grade. The water solutions were prepared with bidistillate.

2.2. MEMBRANE TRANSPORT

A U-shaped vessel containing 5 mL of both aqueous source (1.0×10^{-2} M guest) and receiving phases, separated with 10 mL of liquid membrane (10 mL of CHCl$_3$, 5.0×10^{-3} M host or blank) was used for measuring cation transport rates. The organic phase was vigorously stirred with a magnetic stirrer and an air stream was passed through the water phase. A custom-made film membrane electrode and an Ag/AgBr electrode were used for monitoring the guest content in the receiving phase. Transport rate was calculated as the slope of linear part of the graph of guest content, M, in receiving phase vs. time (through a linear least-squares approximation).

2.3. ELECTROCHEMICAL MEASUREMENTS

Electrode membranes were fabricated as described previously [14]. They contained poly(vinyl chloride), PVC (66.7–95 mg), plasticising solvent mediator (93–133.3 mg) and a carrier (10 mg) either alone or in a mixture with a lipophilic additive (NaTPB, 4 mg). Some control membranes were of PVC and plasticising solvent mediator alone or with lipophilic additive (10 mg). Membrane discs were assembled into electrodes using DDTMA (2.5×10^{-4} M) as the inner filling solution.

All potentiometric measurements were made with the following electrochemical cell (at 22 ± 1 °C):

Ag	AgCl	internal solution	membrane	sample solution	saturated KCl solution	AgCl	Ag
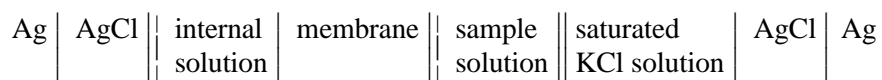
The reference electrode was silver chloride electrode EVL-1M3 (Russia). Responses were recorded with an I-130 ionomer (Russia); pH was monitored using a glass electrode ESL-63-07 (Russia). Electrodes were calibrated by spiking test

solutions at 22 ± 1 °C with a standard solution of DDTMA after conditioning in DDTMA solution (2.5×10^{-5} M) for 24 h before use.

Selectivity coefficients $K_{i,j}^{\text{pot}}$ (i = primary ion, j = interfering ion) were determined by the separate solution method using the following relationship [18]:

$$-\log K_{i/j}^{\text{pot}} = \frac{(E_1 - E_2)}{S}$$

where E_1 and E_2 are the response potentials of the alkyltrimethylammonium electrode for $[i]$ and $[j]$ at 1×10^{-3} M, respectively, and S is the slope of the electrode function (mV/decade).

2.4. SOLVENT EXTRACTION

The aqueous solution of the guest ($V = 5$ mL, $C = 5 \times 10^{-4}$ M) was contacted in a separating funnel with a chloroform solution of the host ($V = 5$ mL, $C = 1 \times 10^{-3}$ M) for the time required to establish equilibrium. After separating, the aqueous layer was analyzed for surfactant with either a custom-made film membrane electrode or the Ag/AgBr electrode.

After calculating guest distribution coefficients, D, equilibrium constants were derived from their concentration dependencies. The following system was considered:
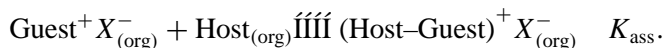
(1) Extraction facilitated by host–guest complexation

$$\text{Guest}_{(aq)}^+ + X_{(aq)}^- + \text{Host}_{org} \rightleftharpoons (\text{Host–Guest})^+ X_{(org)}^- \quad K_{ex};$$
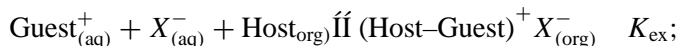
(2) 'Blank' extraction with pure solvent (measured in a separate run)

$$\text{Guest}_{(aq)}^+ + X_{(aq)}^- = \text{Guest}^+ X_{(org)}^- \quad K_{ex}^{\text{Guest}X};$$

(3) Host–guest association in organic phase

$$\text{Guest}^+ X_{(org)}^- + \text{Host}_{(org)} \rightleftharpoons (\text{Host–Guest})^+ X_{(org)}^- \quad K_{ass}.$$

(We neglected the distribution of the host into water.)

Evidently,

$$\log K_{ex} = \log D - \log[X^-]_{(aq)} - \log[\text{Host}]_{(org)}$$

$$\log K_{ass} = \log K_{ex} - \log K_{ex}^{\text{Guest}X}.$$

Table I. Bulk membrane transport of dodecyltrimethylammonium. Chloroform; $C_{\text{host}} = 5 \times 10^{-3}$ M, $C_{\text{guest}} = 1 \times 10^{-2}$ M.

Host	Transport rate (μmol/h)
Pure solvent	0.8 ± 0.1
MO$_3$	2.6 ± 0.1
M$_2$O$_3$	6.7 ± 0.8
MO$_5$	12.0 ± 1.0
MO$_7$	13.0 ± 1.0
DB18C6	5.4 ± 0.2
TG	3.5 ± 0.4
TPPO	2.9 ± 0.1

3. Results and Discussion

3.1. BULK MEMBRANE TRANSPORT

Without the host, DTMA is transported across a bulk chloroform membrane at a low rate. All the hosts studied significantly increase the rate of transport, as illustrated in Table I.

Phosphoryl podands, which do have many more potential binding centres (oxygen atoms of two terminal phosphoryl groups and oxyethylene units), are more effective ionophores than 'unidentate' TPPO, which is an analogue of the podand's terminal functionality. Performance of the conventional 'non-phosphoryl' podand tetraglym, TG, is comparable to that of TPPO. Macrocyclic 'non-phosphoryl' polyether DB18C6 is a better carrier than TG. However, a combination of high 'denticity' and electron-enriched phosphoryl groups leads to the best performance.

The ionophoric activity of phosphoryl containing podands depends crucially on the flexibility of the molecule and the number of oxygen atoms. The rate of transport of DDTMA with small and rigid MO$_3$ is lower than that with simple polyether TG having the same number of oxygens; it is also slightly lower than the rate of transport with TPPO. However, replacing a single methylene by the more flexible ethylene at the bridge 'polyether chain-phosphoryl ends' dramatically increases transport efficiency. Podand M$_2$O$_3$ is at least twice as effective an ionophore as MO$_3$, TG or TPPO. Actually, it is even a better carrier than the macrocycle DB18C6. We may conclude that the expected increase of a host's performance through adding phosphoryl ends to a polyether chain is a fact. As expected, too, the increase depends crucially on the placement of phosphoryl groups and the flexibility of the whole molecule. Increasing the number of oxyethylene units (length of the polyether chain) leads to a significant increase of ionophoric activity (MO$_5$
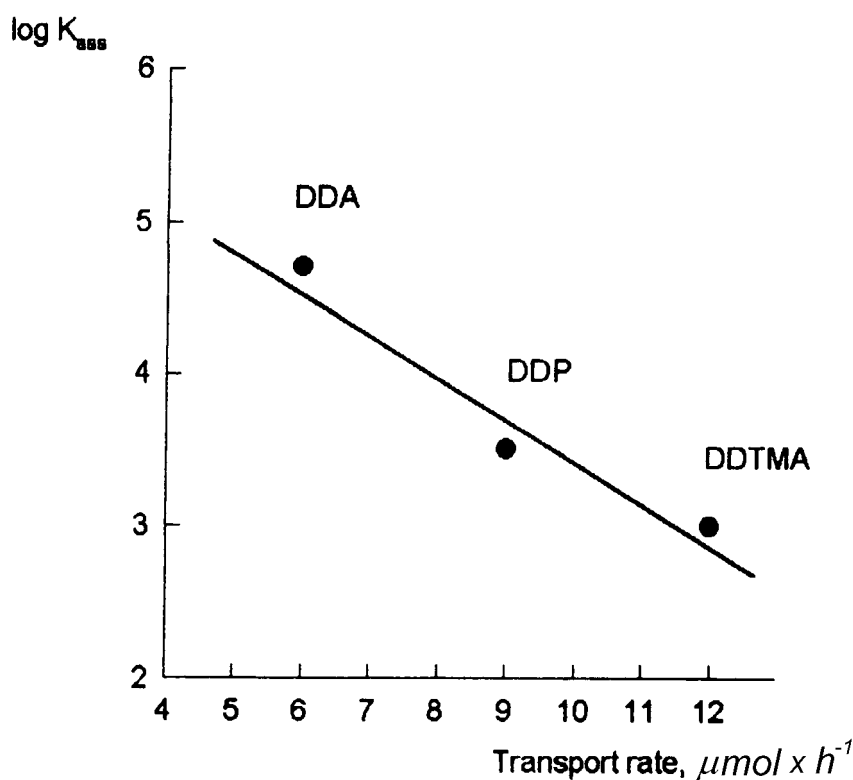
Figure 1. The correlation between transport rate and log K_{ass}.

vs. MO_3, M_2O_3) followed by saturation. The longest podand MO_7 performs only slightly better than MO_5 (Table I).

We assumed that the force underlying host–guest complexation is an ion–dipole interaction between the podand's oxygens and the guest's cationic centre. The more oxygens present, the stronger is the interaction. The 'saturation' pattern may be related to increased steric clashing in the complexes. The practical conclusion is that the best carriers for tetraalkyl ammonium are podands comprising a long polyether chain with phosphoryl terminal groups.

Another point of practical interest is the host's selectivity with respect to various guests. For the podands, we observed an exact inverse of the common series, which is typical of crown ethers [12]: tetraalkyl ammonium is transported better than alkyl pyridinium, and alkyl pyridinium better than monoalkyl ammonium (with the same number of carbons at the guest's N-alkyls; data for host MO_5 are presented as an example, Figure 1). This is very interesting behaviour, since monoalkyl ammonium usually interacts with polyethers more strongly due to its ability to form hydrogen bonds. In order to reveal the nature of this unusual selectivity, we studied the solvent extraction of various guests.

Table II. Extraction with various hosts. Chloroform; $C_{host} = 1 \times 10^{-3}$ M, $C_{guest} = 5 \times 10^{-4}$ M; pH 2–9.

	DB18C6 DDTMA	TG DDTMA	MO$_5$ DDTMA	MO$_7$ DDP	DDA	DDTMA
Equilibrium attainment time, min	10	5	5	15	30	5
Recovery, %	40	30	50	76	90	72
log K_{ex}	6.3 ± 0.1	5.9 ± 0.1	6.6 ± 0.1	6.5 ± 0.1	7.3 ± 0.1	7.2 ± 0.1
log K_{ass}	2.7 ± 0.1	2.3 ± 0.1	3.0 ± 0.1	3.4 ± 0.1	4.7 ± 0.1	3.6 ± 0.1

3.2. SOLVENT EXTRACTION

Our extraction study immediately indicated that the unusual selectivity series is of purely 'transport origin' and is not related to the selectivity of host–guest complexation *per se*. Both extraction and association constants (1 : 1 host–guest complexation confirmed with bilogarithmic plots) for MO$_5$ shows that the podand does favour monoalkyl ammonium and alkyl pyridinium (Table II), as is usual. We must conclude that the affinity of RNH_3^+ and R—Py$^+$ guests towards the host is too strong, which results in slow release at membrane phase interface (back extraction) thus depressing membrane transport (some examples of similar behaviour have been reported earlier [19, 20]).

As seen from Tables I and II, the other extraction and membrane transport data are in direct correlation.

3.3. PLASTICIZED MEMBRANE ELECTRODES

Podands MO$_5$ and MO$_7$, as well as reference macrocycle DB18C6, were used as carriers in *o*-NPOE plasticized membrane electrodes. For the sake of comparison, a conventional ion-association tetraphenyl borate membrane was also studied.

The main features of the electrodes are presented in Table III. As can be seen, they are reversible with respect to DDTMA$^+$ cation over a wide pH range, 2–11. The upper limit of analyte concentration is determined by the critical micellar concentration of the surfactant.

In general, the performance of all electrodes is comparable. However, podand-based ISEs gain advantages in terms of limit of detection, response time and, in particular, in reproducibility (Table III). The improvement of electrode selectivity is more drastic (Figure 2). It is worth noting that the conventional ion-association membrane has worse selectivity than all neutral-carrier membranes.

Interestingly, even the DB18C6-based membrane provides better selectivity in the presence of alkali metal ions. This may seem strange, since DB18C6 is well

Table III. Electrochemical properties of membranes plasticized by *o*-NPOE and based on neutral carriers in the solutions of dodecyltrimethylammonium.

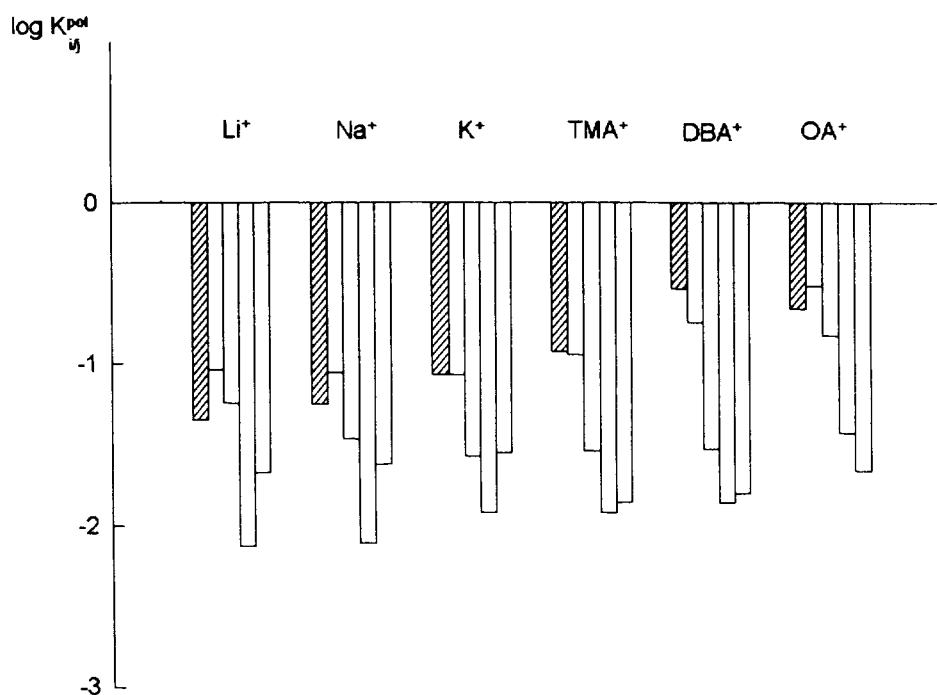| Carrier	Slope (mV/decade)	Response time (s)	Linear range (M)	Limit of detection (M)
NaTPB	58.8 ± 2.2	10	$5.0 \times 10^{-5} - 1.4 \times 10^{-5}$	1.4×10^{-5}
DB18C6	55.7 ± 6.6	20	$5.0 \times 10^{-5} - 1.4 \times 10^{-2}$	1.3×10^{-5}
MO_5	54.3 ± 0.7	20	$2.5 \times 10^{-5} - 1.4 \times 10^{-2}$	6.3×10^{-6}
MO_7	53.0 ± 1.0	15	$1.0 \times 10^{-5} - 1.4 \times 10^{-2}$	5.0×10^{-6}
MO_7*	58.5 ± 0.3	5	$5.0 \times 10^{-6} - 1.4 \times 10^{-2}$	3.2×10^{-6}
MO_7**	55.2 ± 6.9	20	$5.0 \times 10^{-5} - 1.4 \times 10^{-2}$	2.5×10^{-5}

 * Lipophilic additive.
** DOP.

Figure 2. The influence of the host structure on potentiometric selectivity of ISEs reversible to dodecyltrimethylammonium (the bars on chart correspond to hosts: no-carrier, NaTPB, DB18C6, MO5, MO7, left to right; TMA$^+$-trimethylammonium, DBA$^+$-dibutylammonium, OA$^+$-octylammonium).

Table IV. The influence of homologous surfactants ($C_nH_{2n+1}N(CH_3)_3Br$) to response of MO_7-based ISE.

	$n = 10$	$n = 12$	$n = 14$	$n = 16$
Slope (mV/decade)	49.9 ± 0.3	53 ± 1	57 ± 1	59.2 ± 0.8
Linear range (M)	5.0×10^{-5}– 6.0×10^{-2}	1.0×10^{-5}– 1.4×10^{-2}	1.0×10^{-5}– 3.6×10^{-3}	5.0×10^{-6}– 9.0×10^{-4}
Limit of detection (M)	1.0×10^{-5}	5.0×10^{-6}	3.5×10^{-6}	2.5×10^{-6}
Response time (s)	30	15	10	5–10

known for its ability to bind these cations, particularly potassium; it is actually used as the membrane-active component in K^+-selective electrodes [21]. Interestingly too, the series of alkali metal interfering influence for our $DDTMA^+$-selective crown ether electrode is an exact inverse: $Li^+ > Na^+ > K^+$. We suggest that this may be attributed to different ligand preorganization. Indeed, since the $DDTMA^+$-selective membrane was conditioned in DDTMA solutions for at least 4 days prior to our experiments, one may expect that the carrier in the membrane phase (or, at least, near the interface) should exist as a complex with this cation. Obviously, the crown ether in such a complex should have a conformation which is different from both those of free DB18C6 and DB18C6 complexed with potassium (encapsulating mode of complexation). This may lead to an anomalously low affinity for alkali metals, in general, and to unusual selectivity in particular.

The podand-based membranes demonstrate the best potentiometric selectivity. The interfering influence of both metal and primary ammonium cations is lower than those for ion-association and DB18C6-membranes. One should note that literature data (alkali metals [22]) and our previous reports (primary ammonium selective electrodes [13, 14]) indicate that podands can be used in electrodes for both these kinds of analytes. However, this is true for shorter podands, while the use of longer MO_5 and MO_7 leads to weaker interaction with these ions and a low interfering influence.

A particularly important question is the influence of interfering surfactants. As expected, podand-based membranes do respond to other ammonium surfactants (Table IV). Moreover, they may be used for the determination of DDTMA homologues. The longer the alkyl chain, the better is the performance of the corresponding electrode. Naturally, this is related to the higher hydrophobicity of the host–guest complex. The interfering influence increases in the series:

$$RNMe_3^+ < RPy^+ < RNH_3^+,$$

which reflects both the guest's ability to form hydrogen bonds and the steric accessibility of its cationic charge.
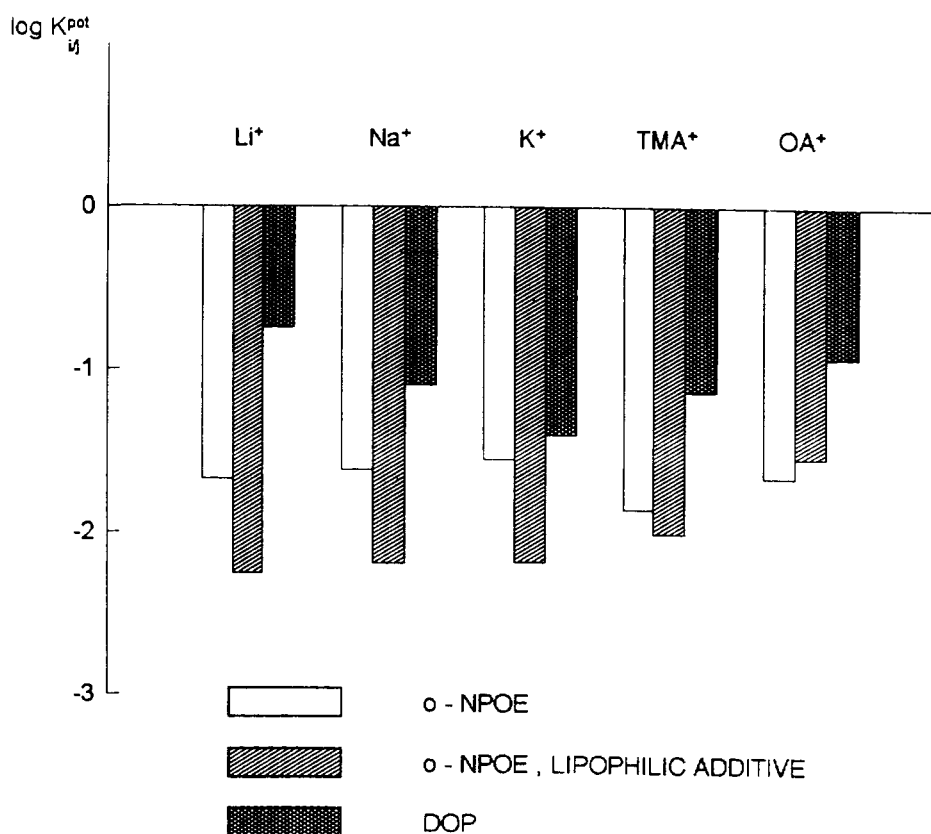
Figure 3. The potentiometric selectivity of MO7-based membranes in solution of dodecyltrimethylammonium vs. nature of plasticizer and liphophilic additive.

The nature of the plasticizer used strongly influences electrode performance. Use of DOP rather than o-NPOE results in a narrower linear range and reduced selectivity (Table III, Figure 3). Conversely, use of a lipophilic anionic additive leads to a broadening of the electrode's working range and an improvement of selectivity (Table III, Figure 3). In summary, the best electrodes for $DDTMA^+$ determination are those based on phosphoryl podands, o-NPOE plasticizer and, preferably, a specially introduced lipophilic additive.

The electrodes developed were successfully used for the determination of alkyl ammonium surfactants in environmental samples and in cosmetics ($S_r \leq 0.04$), as well as for the evaluation of surfactant critical concentration of micelle formation. The application to the detection in FIA/HPLC and to the study of the interaction of water-soluble polymers with cationic surfactants is reported elsewhere [23, 24].

Acknowledgements

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