

POTENTIOMETRIC RESPONSE OF LIQUID MEMBRANE ELECTRODES INCORPORATED WITH NEW CALIX[4]PYRROLE AND PYRROLE DERIVATIVES TOWARDS NEUTRAL NITROPHENOL

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Recognition of neutral nitrophenol isomers by calix[4]pyrrole and pyrrole derivatives was investigated using poly(vinyl chloride) (PVC) matrix liquid membrane electrodes. The influence of macrocyclic calix[4]pyrrole cavity and different kind of substituents on the mechanism of phenomenon studied and its possible analytical application was discussed.

INTRODUCTION

A rapid advance in science and technology increases longevity and comfort of human life. It is, however, accompanied by new threats to human health. This hazardous phenomenon is often a result of hasty introduction of new technologies based on insufficient research. So, this obliges scientists to work on completely new, low-cost, rapid analytical methods for marking inorganic and organic chemical residues, radioactive isotopes and pharmaceuticals in food, water and other environmental sources linked to food chain.

To realize this goal, it is necessary to apply new sensing material which might be able to selectively recognize target molecules by intermolecular interaction with the receptor substrate. Such an interaction is commonly known as supramolecular interaction [Lehn, 1978].

In this paper, we have introduced the results on the application of potentiometric sensors based on liquid membrane modified with some pyrrole derivatives for detection of the neutral nitrophenol isomers.

Potentiometric methods are very chip and simple in application. Hence they are widely used in screening analysis [Brzózka, 1997]. Till now, they have been limited only for the determination of electrically charged molecules. In our previous papers, we have shown that it is possible to apply potentiometric method for detection of neutral compounds [Piotrowski *et al.*, 2000; 2001; 2002].

The development of direct potentiometric sensors for neutral molecules has been an interesting task from the analytical point of view, in practical and fundamental meaning. There is still a puzzling problem: how to form a complex between host and neutral guest and subsequently generate a charge separation at the interface between electrode surface and the supporting electrolyte? Some instances in which membrane potentials are affected by uncharged molecules have been already ex-

plored. Such systems include poly(vinyl chloride) (PVC) matrix liquid membranes [Ito *et al.*, 1998 a,b; Sugawara *et al.*, 1984], Langmuir-Blodgett type monolayers [Kurihara *et al.*, 1991], and lipid bilayer vesicles [Kurihara, 1990].

This report introduced the result obtained by the application of this method for detection of electrically neutral nitrophenols using calix[4]pyrrole and pyrrole derivatives as the host molecules in liquid membrane electrodes. Calix[4]pyrrole discovered by Baeyer in 1886 [Baeyer, 1886], has now become a subject of many researches concerning the molecular recognition of anionic and neutral molecules [Floriani, 1996; Gale *et al.*, 1996; 1997; 1998; 1999; 2001].

The structures of pyrrole derivatives studied are illustrated in Figure 1.

MATERIALS AND METHODS

Reagents. Bis(2-ethylhexyl) phthalate ["dioctyl phthalate" (DOP)] used as a membrane solvent and poly(vinyl chloride) (PVC; $n_{av} \cong 1100$) used as a polymer matrix were purchased from Wako Pure Chemical (Japan). Ortho-, meta-, and para-isomers of nitrophenols, citric acid, and lithium acetate were purchased from Sigma-Aldrich Co. (Poznań, Poland). Tetrahydrofuran was purchased from POCH-Gliwice (Poland) and was distilled from solid NaOH just before use. The pyrrole derivatives (Figure 1) were synthesized according to the procedure previously reported [Depretere *et al.*, 1999].

All the samples and buffer solutions were prepared with deionized water with resistance of $18.2 \text{ M}\Omega\text{cm}^{-1}$ and bubbled with nitrogen for 30 min just before potentiometric measurements in order to protect phenolic analytes from oxidation.

Electrode preparation and potential measurements.

Due to solubility problems occurring with hosts **1** and **2** during the preparation of membranes, the experiments were made

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at two values of hosts concentration in DOP: 1.0×10^{-2} M and 0.5×10^{-3} M respectively. Hence, the membrane composition was: 0.4% ligand, 67.7% DOP, 31.9% PVC in the first case and 0.2% ligand, 67.8% DOP, and 32% PVC in the second. All components were dissolved in approximately 3 mL of freshly distilled THF. The solution obtained was placed into a glass ring (30-mm diameter) and left for 24 h to allow THF evaporation. Circles of 6-mm diameter were cut from the "dry" membrane and mounted on a liquid membrane type Philips ISE body (Glasbläserei Möler, Zürich, Switzerland). The membrane free of ligand was prepared the same way, but without host compound. In order to obtain reproducible results and to avoid the solubility problems, the measurements were made only with fresh membranes. The cell assembly for potential measurements was:

Ag/AgCl | 10^{-1} M KCl | membrane | sample solution | 1 M CH_3COOLi | 3 M KCl | Ag/AgCl.

Measurements were performed at room temperature (20°C) by means of multi-channel station pH meter made by DonauLab (Warsaw, Poland). A double junction electrode Ag/AgCl from Philips was used as a reference electrode. Before measurements, electrodes were kept 24 h for conditioning in a buffer solution (citric buffer, pH=4.0 or pH=6.0).

The simultaneous measurements of potential and pH were done with a METTLER TOLEDO 355 Ion Analyser.

The pH influence on the membrane potential was measured starting from acidic pH (2.5) to basic pH (10.0) and

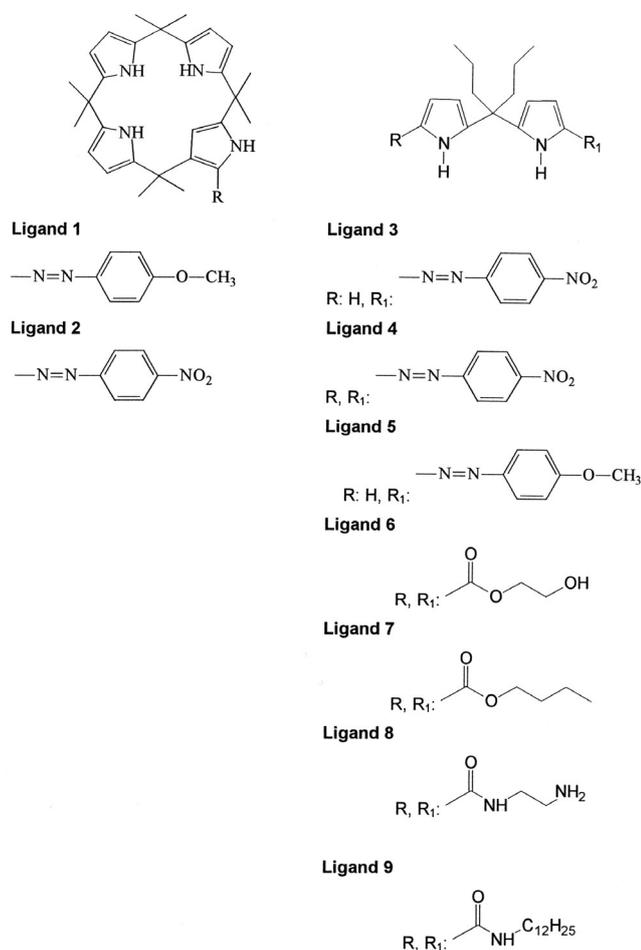


FIGURE 1. Chemical structures of calix[4]pyrrole derivatives.

reverse, by adding NaOH solution (containing 1.0×10^{-2} M Na_3PO_4) to a solution of 1.0×10^{-2} M H_3PO_4 , and respectively by adding H_3PO_4 solution (containing 1.0×10^{-2} M NaOH) to a solution of 1.0×10^{-2} M NaOH. Before these measurements, electrodes were kept 24 h for conditioning in a sodium dihydrogenphosphate solution 1.0×10^{-2} M.

In order to ensure the neutrality condition for the guests, the potentiometric response of the calix[4]pyrrole and pyrrole derivatives incorporated membranes towards nitrophenol isomers were measured in the presence of 1.0×10^{-2} M citric buffer (at pH=4.0 and pH=6.0).

RESULTS AND DISCUSSION

Figure 2 illustrates the response of the investigated membranes to the changes of pH of sample solutions. As it can be seen, the membranes modified with cyclic calix[4]pyrroles (ligand 1 and 2) showed relatively high response to changes of sample solutions pH. These responses were reversible. This means that a shape of curves is independent of the initial pH of the measurements. Responses of other ligands (pyrrole derivatives) to pH changes were negligible.

The relationship between the potential of electrode membranes and value of pH of sample solution illustrates the affinity of the applied membranes towards protons [Piotrowski *et al.*, 2000, 2001, 2002]. As it can be seen, the highest affinity to protons was demonstrated by membranes modified with macrocyclic calix[4]pyrroles. Of unicyclic pyrrole derivatives, only these which possess amine groups in their structures could be protonated. This indicates that protonation of unicyclic and cyclic derivatives of pyrrole proceeds by different mechanism.

Figures 3-11 illustrate the response of the membrane investigated to the changes of the concentration of particular isomers of nitrophenols. As it can be seen, of all membranes studied only seven respond after stimulation with *meta* and *para* nitrophenols. The value of those responses is strongly effected by the changes of pH of a sample solution. But it is difficult to indicate the general tendency in the case of stimulation with *para*-nitrophenol. For membranes with ligands 5 and 7 we have obtained the highest response under pH 4.0

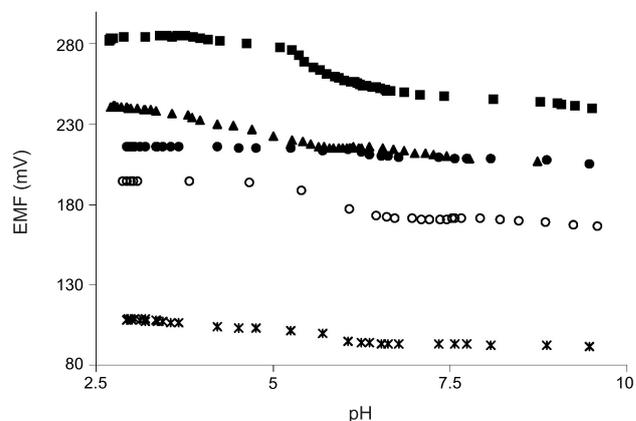


FIGURE 2. Potential vs. pH curves obtained by an electrode containing ligand 1 (■), ligand 2 (▲), ligand 3 (Ж), ligand 4 (●), ligand 5 (○). The initial condition was 0.01 M H_3PO_4 . The pH was adjusted by adding NaOH aqueous solution containing 0.01 M H_3PO_4 .

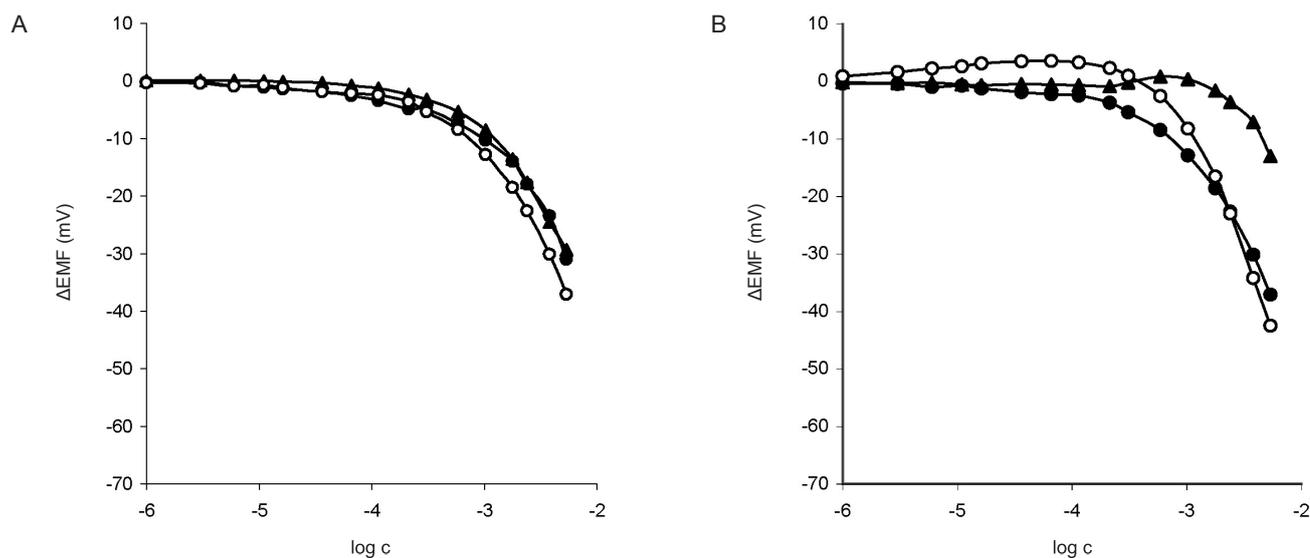


FIGURE 3. Potential vs. concentration curves obtained by electrodes containing ligand 1 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (- \blacktriangle -) *ortho*-nitrophenol, (- \bullet -) *meta*-nitrophenol, (- \circ -) *para*-nitrophenol.

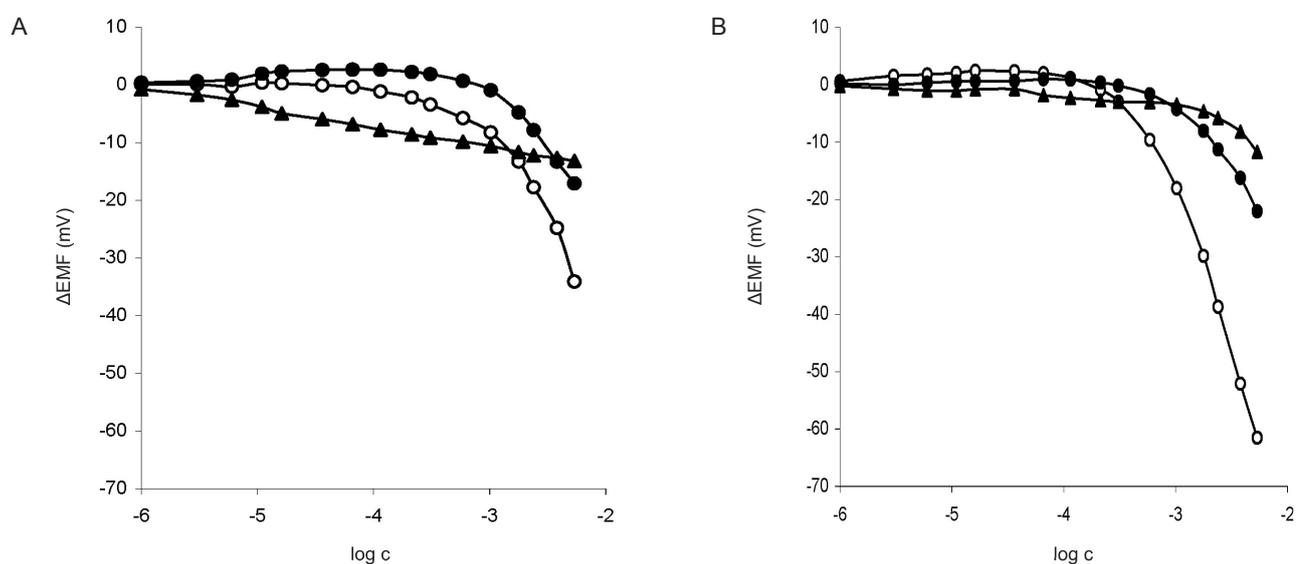


FIGURE 4. Potential vs. concentration curves obtained by electrodes containing ligand 2 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (- \blacktriangle -) *ortho*-nitrophenol, (- \bullet -) *meta*-nitrophenol, (- \circ -) *para*-nitrophenol.

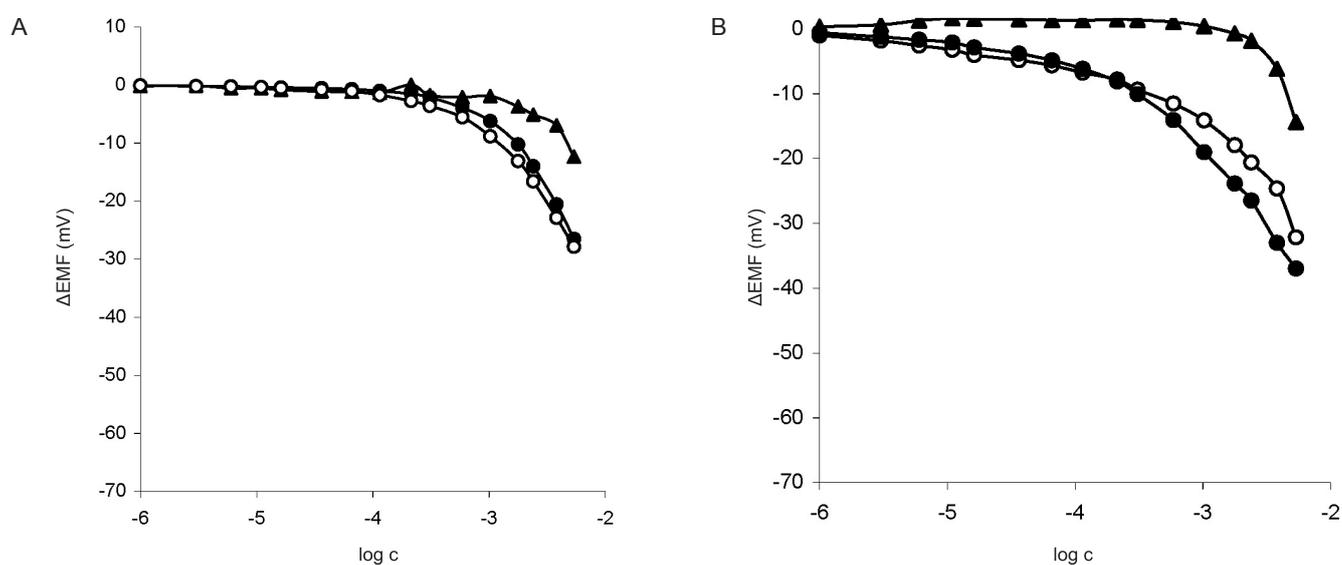


FIGURE 5. Potential vs. concentration curves obtained by electrodes containing ligand 3 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (- \blacktriangle -) *ortho*-nitrophenol, (- \bullet -) *meta*-nitrophenol, (- \circ -) *para*-nitrophenol.

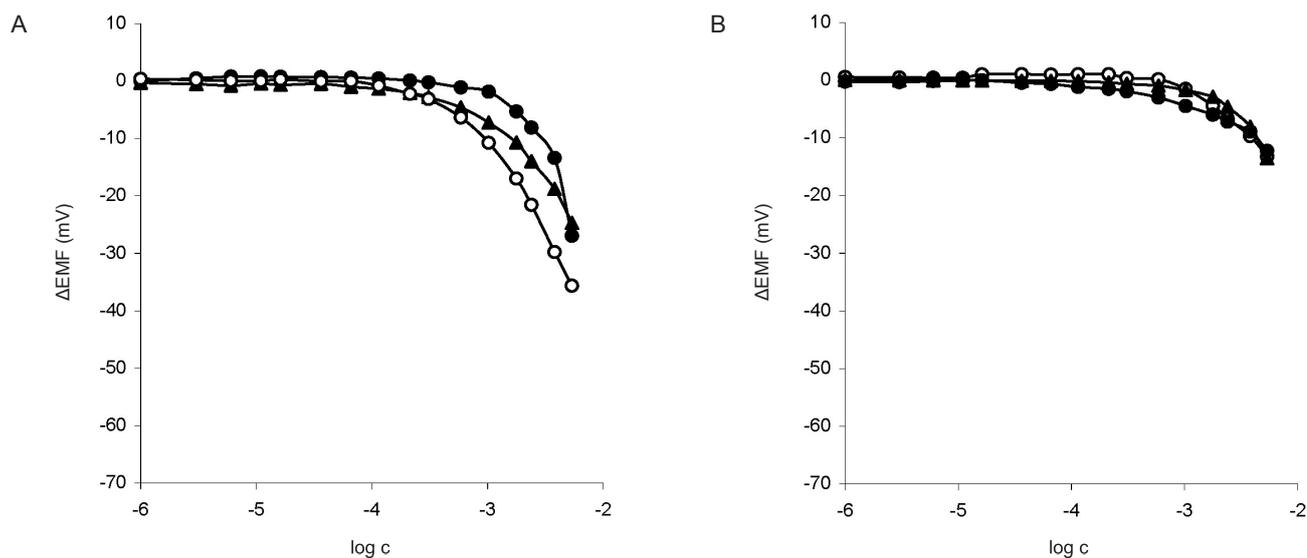


FIGURE 6. Potential vs. concentration curves obtained by electrodes containing ligand 4 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (-▲-) *ortho*-nitrophenol, (-●-) *meta*-nitrophenol, (-○-) *para*-nitrophenol.

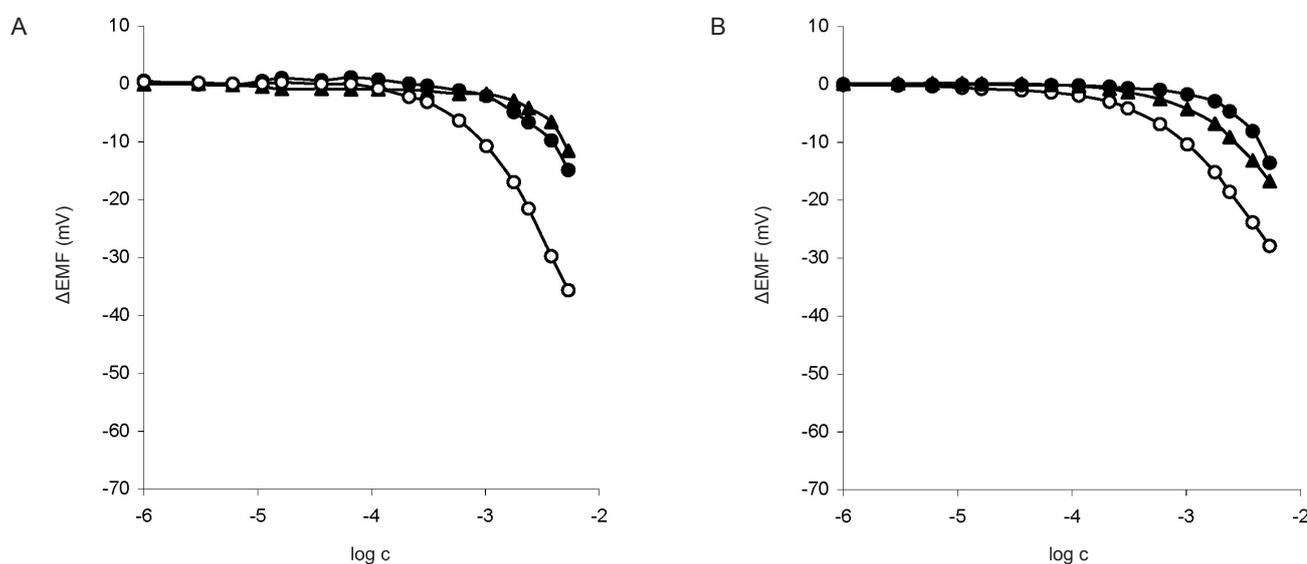


FIGURE 7. Potential vs. concentration curves obtained by electrodes containing ligand 5 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (-▲-) *ortho*-nitrophenol, (-●-) *meta*-nitrophenol, (-○-) *para*-nitrophenol.

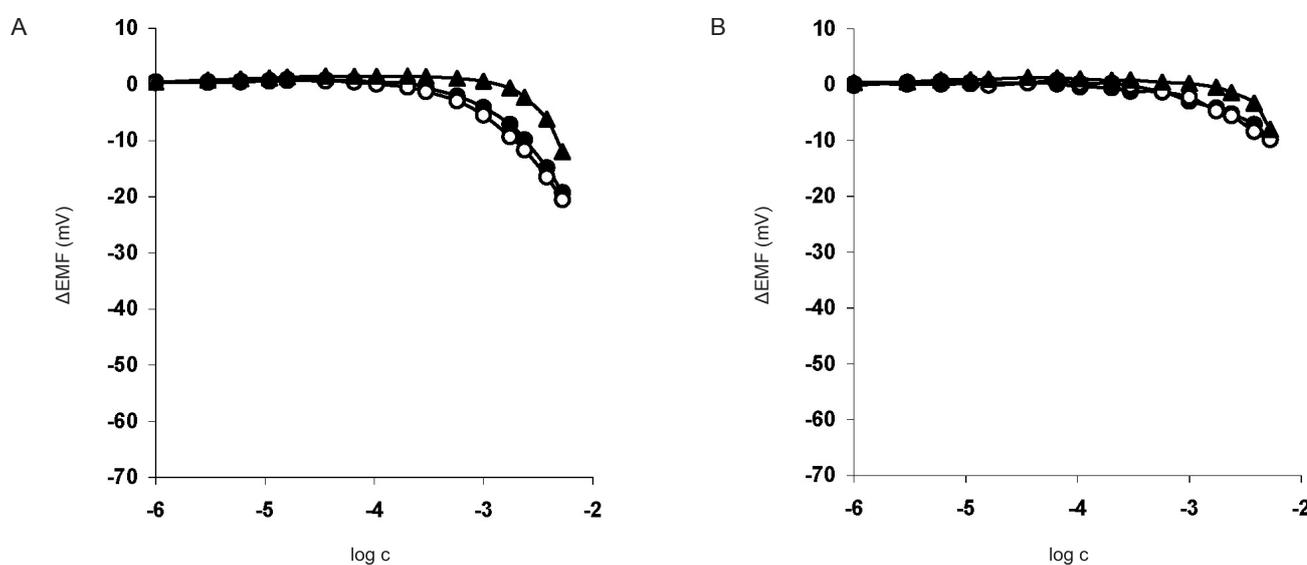


FIGURE 8. Potential vs. concentration curves obtained by electrodes containing ligand 6 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (-▲-) *ortho*-nitrophenol, (-●-) *meta*-nitrophenol, (-○-) *para*-nitrophenol.

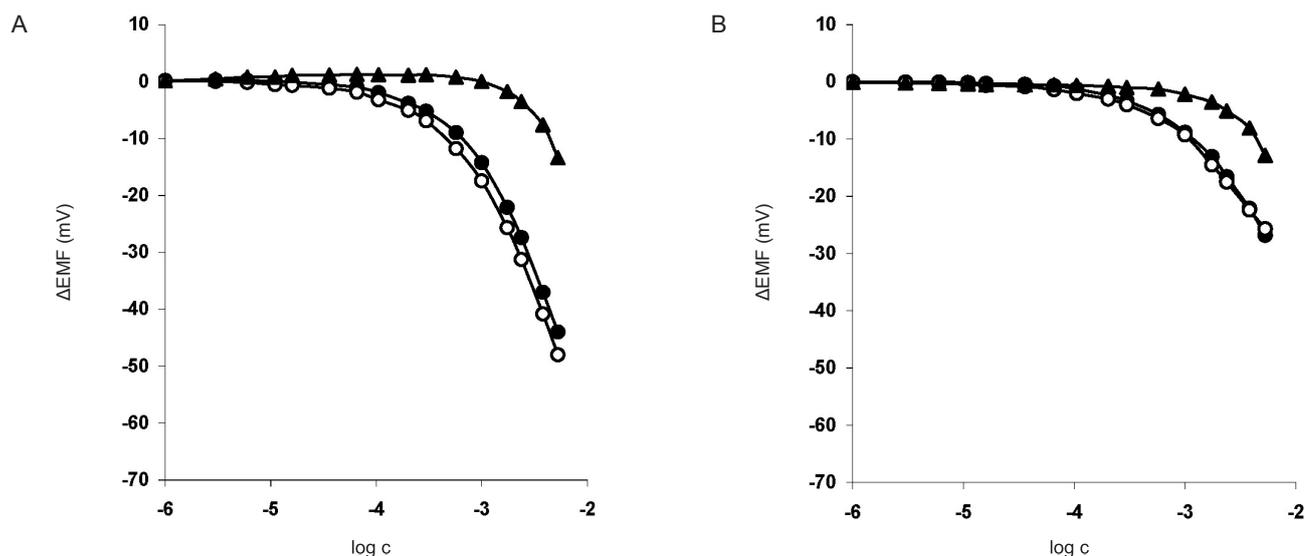


FIGURE 9. Potential vs. concentration curves obtained by electrodes containing ligand 7 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (-▲-) *ortho*-nitrophenol, (-●-) *meta*-nitrophenol, (-○-) *para*-nitrophenol.

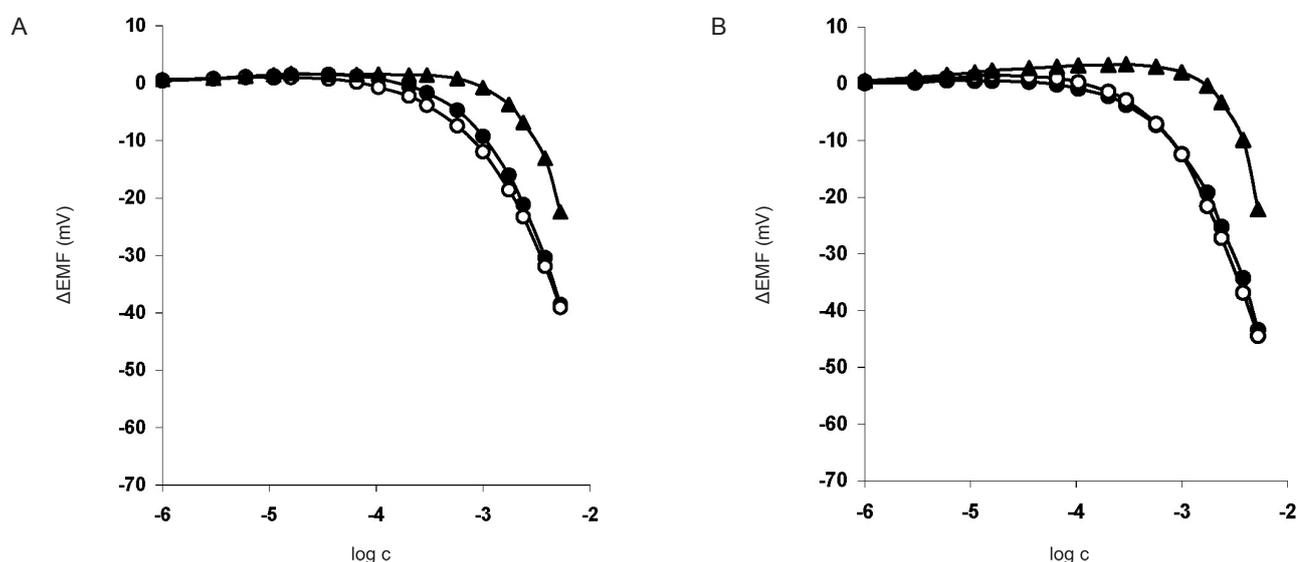


FIGURE 10. Potential vs. concentration curves obtained by electrodes containing ligand 8 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (-▲-) *ortho*-nitrophenol, (-●-) *meta*-nitrophenol, (-○-) *para*-nitrophenol.

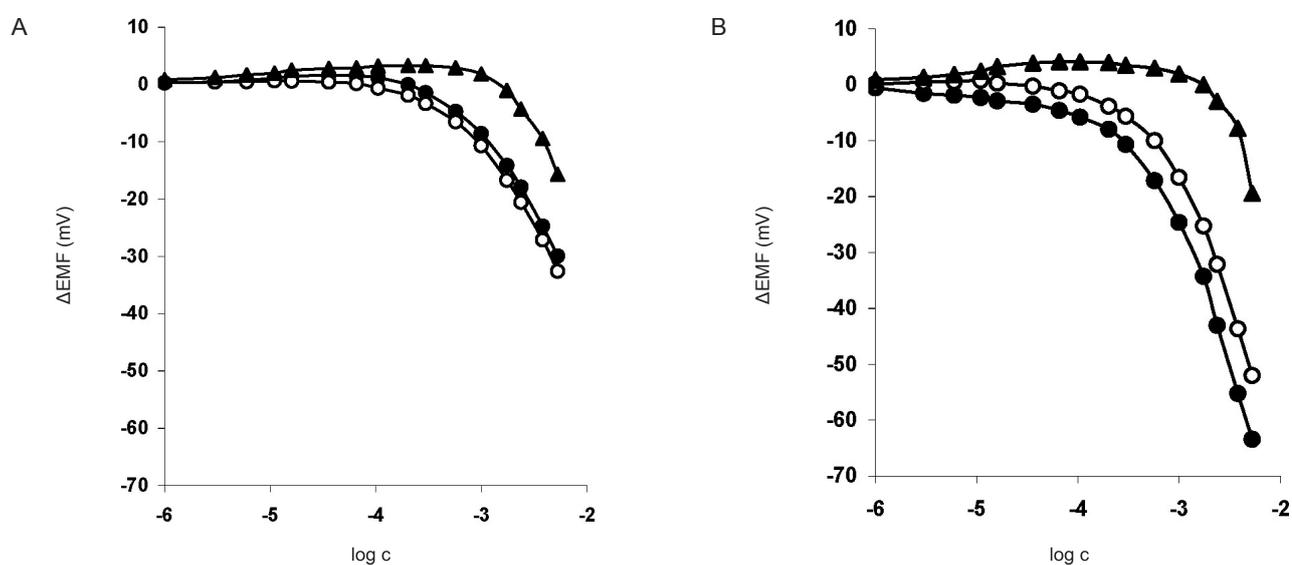


FIGURE 11. Potential vs. concentration curves obtained by electrodes containing ligand 9 towards nitrophenol isomers measured at: (A) pH 4.0; (B) pH 6.0; 0.01 M citric buffer (-▲-) *ortho*-nitrophenol, (-●-) *meta*-nitrophenol, (-○-) *para*-nitrophenol.

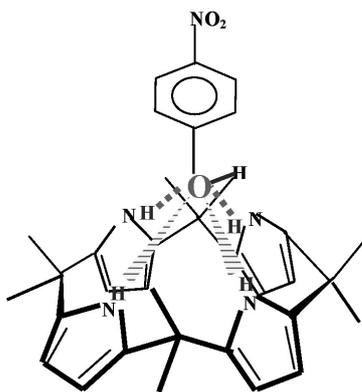


FIGURE 12. The illustration of supramolecular complex calix[4]-pyrrole-*para*-nitrophenol.

of a sample solution. Whereas, for ligands **2**, **3**, **8** and **9**, the highest responses were observed for this isomer at pH 6.0 of a sample solution. In the case of stimulation of membranes by *meta*-nitrophenol, this tendency was very similar.

All of the membranes studied were insensitive to *ortho*-nitrophenol under both pHs investigated. Generally, we can state that the response of the membranes studied depends on the type of isomer of nitrophenols as well as pH of sample solution.

From the ligands studied, we can separate two groups according to the value of the response. To first group contains ligands **1**, **2**, **3**, **5**, **7**, **8** and **9** which are able to generate the potentiometric responses towards nitrophenols. The second group contains ligands **4** and **6**. The membranes they modified were insensitive to neutral nitrophenol molecules.

The possible explanation of this phenomenon might be as follows. According to our previous investigations [Piotrowski *et al.*, 2000; 2001; 2002], the generation of potentiometric response of membranes under study consists in the creation of supramolecular complex between the nitrophenol and pyrrole rings by hydrogen bond (Figure 12). As a consequence of this interaction, the OH phenol group becomes more acidic, and dissociation of nitrophenol is possible at the border between the organic and aqueous phases in spite of high concentration of protons in bulk solution. The dissociation leads to the transfer of protons from organic layer to water, and as a consequence the potential of membranes decreases.

Ligands **4** and **6** contain in their structure rather large substituents, which makes pyrrole rings unavailable for nitrophenols and supramolecular complex cannot be created. Our investigation indicates that the availability of hydrogen from pyrrole ring is crucial for potentiometric response of the membranes studied.

Ligands **1**, **2**, **3**, **5**, **7** and **9** shown in Figure 1 demonstrated the same selectivity. They are able to distinguish isomer *meta* and *para* in the presence of isomer *ortho*. The lack of response of the membranes studied to the *ortho* isomer is the consequence of creation of intramolecular hydrogen bond between OH and NO₂ groups in *ortho*-nitrophenol molecule. This bond makes the creation of supramolecular complex between the ligands studied and *ortho*-nitrophenols difficult.

CONCLUSIONS

The macrocyclic cavity of calix[4]pyrrole, confused or not, plays a crucial role in the mechanism of molecular recognition of neutral compounds. The membranes incorporated with calix[4]pyrrole derivative have shown higher changes of potential in the presence of neutral nitrophenol isomers than pyrrole derivatives, especially in the case of *para*- and *meta*- isomers. The attached substituents have influence on the calix[4]pyrrole derivatives solubility and sensitivity towards nitrophenol isomers. From the results obtained, it might be concluded that macrocyclic cavity plays a crucial role in the phenomenon studied.

The membranes incorporated with macrocyclic calix[4]-pyrrole (**1**, **2**) have displayed the higher potentiometric responses to nitrophenols than the membrane containing the pyrrole derivatives (**3**, **4**, **5**). Thus, the ligands **1** and **2** could be applied as the host molecules in liquid membrane electrodes for direct potentiometric determination of neutral nitrophenol isomers.

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