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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

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Online publication date: 23 June 2010

To cite this Article Poduval, R. , Kurzątkowska, K. , Stobiecka, M. , Dehaen, W. F. A. , Dehaen, W. , Radecka, H. and Radecki, J.(2010) 'Systematic study of interaction of the neutral form of anilines with undecylcalix[4]resorcinarene derivatives by means of potentiometry', *Supramolecular Chemistry*, 22: 7, 413 – 419

To link to this Article: DOI: 10.1080/10610278.2010.486437

URL: <http://dx.doi.org/10.1080/10610278.2010.486437>

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Systematic study of interaction of the neutral form of anilines with undecylcalix[4]resorcinarene derivatives by means of potentiometry

R. Poduval^{a1}, K. Kurzątkowska^a, M. Stobiecka^a, W.F.A. Dehaen^b, W. Dehaen^b, H. Radecka^a and J. Radecki^{a*}

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(Received 11 March 2010; final version received 14 April 2010)

The elucidation of the mechanism of potentiometric signals generation by liquid membrane electrodes incorporating undecylcalix[4]resorcinarene derivatives upon stimulation by uncharged aniline derivatives is the main aim of the research presented. A series of molecules which play the role of host and guests in the molecular recognition process occurring at the aqueous–organic membrane interface were explored. It was proved that in the conditions where all aniline derivatives exist as uncharged molecules, cationic potentiometric signals were observed for all undecylcalix[4]resorcinarene liquid membrane electrodes. The main parameters crucial for this phenomenon are the acidity/basicity of the hosts as well as the guests. The lipophilicity of the guests plays a secondary role.

Keywords: undecylcalix[4]resorcinarene; aniline derivatives; molecular recognition; potentiometry; neutral analytes

Introduction

Molecular recognition refers to the specific non-covalent interactions such as hydrogen bonding, hydrophobic forces, van der Waals forces, π – π interactions and electrostatic effects between two or more molecules (1, 2).

A receptor (host) can recognise a substrate (guest) on the base of the structural complementarities of the two molecular species. The design and characterisation of synthetic host–guest pairs is still an open challenge in supramolecular chemistry.

Different techniques such as NMR, mass spectroscopy, X-ray crystallography, laser technologies, isothermal titration calorimetry, cyclovoltammetry and also computational methods have been employed to study supramolecular interactions (3–7). Potentiometry is also of importance in this regard (8). Potentiometric techniques help to provide an insight into the recognition at the liquid–liquid interface where the mechanism of generation of a potentiometric signal depends on the charge separation between the two phases which in turn is the result of a selective transfer of guest molecule from the aqueous to the organic phase.

Vital components of such types of sensors are poly(vinyl chloride) (PVC) membranes modified with specific ionophores, which are responsible for important parameters, from an analytical point of view, such as selectivity and sensitivity as well as the time of response and reproducibility. Different types of molecules such as

calixarenes (9, 10), macrocyclic polyamines (11–13), calixpyrroles (14), corroles (15) and calix[4]phyrins (16) were applied as a host in PVC-supported liquid membranes. The chemical structure complementarities between the host and specific guest are crucial in selective molecular recognition. The structure of the host is usually read out by the guest.

Potentiometric sensors have some outstanding advantages including simple design and operation, wide linear dynamic range, relatively fast response and rational selectivity. Because of this, their construction is particularly interesting from the perspective of the supramolecular chemists. The potentiometric sensors could be applied as useful tools for the observation of the molecular recognition process at the border of two phases.

In classical potentiometry, the analytes are ionic species. So far, there are only a few examples of the potentiometric recognition of neutral molecules. In a pioneering paper by Umezawa and co-workers, the possibilities of potentiometric signal generation by polymeric membranes modified with quaternary ammonium salts (17) and lipophilic polyamines (18, 19), after their stimulation with uncharged phenol derivatives, were described for the first time. This research dealt with permanently charged ligands (tetraalkylammonium salts), or formally neutral amines which gain a plus charge after being in contact with the aqueous phase (e.g. macrocyclic polyamines). Next, new classes of ligands which are able to recognise undissociated

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nitrophenols and generate changes in membrane potential were described by our group. These new ligands belong to the family of calix[4]pyrroles, corroles, calix[4]phyrins and metalloporphyrins (20–26). The first three of them are tetrapyrrolic macrocyclic compounds and are members of a very wide family of porphyrin analogues. They are well known as sensitive and selective receptors for anions (27–32).

In general, the host–guest recognition process in the case of these compounds could be realised mainly by the creation of hydrogen bonds between the ligand and target molecules, and also by electrostatic interactions, Lewis acid–base and π – π electron interactions (33–36).

In our previous paper, concerning the generation of potentiometric signals by neutral analytes, we have shown that PVC-supported liquid membrane electrode incorporated with undecylcalix[4]resorcinarene generates cationic potentiometric signals in the presence of unprotonated diaminobenzene isomers (37). The *para* isomer with the highest basicity generates the highest potentiometric response. We confirmed by spectroscopic methods that the potentiometric signals were generated based on the formation of a supramolecular complex between the undecylcalix[4]resorcinarene host and the diaminobenzene isomer guest at the organic–aqueous interfaces (37).

In the same paper, we have suggested a hypothetical mechanism of cationic potential signal generation as a result of intermolecular recognition process between the undecylcalix[4]resorcinarene in the polymeric membrane and diaminobenzene isomers in solution. The observed recognition process is selective and allows distinguishing between the particular isomers (37).

The main goal of our research was showing the generation of potentiometric signals by uncharged molecules and the possibility of changing the direction of potentiometric signals by changing the nature of host and guest molecules.

The anionic potentiometric signals were observed when macrocycles containing nitrogen atoms were applied as the host molecules, and phenol derivatives playing role of the guests (17–25). When macrocycles containing phenolic groups were applied as the host molecules and aniline derivatives playing role of the guests – the cationic potentiometric responses were observed (37).

Here, we summarise the results of the systematic potentiometric investigation of the intermolecular recognition processes at the water/polymer membrane border between some derivatives of undecylcalix[4]resorcinarenes and neutral (unprotonated) forms of aniline derivatives such as diaminobenzene, chloroaniline, hydroxyaniline, methylaniline, methoxyaniline and nitroaniline. In particular, we focused on the effect of ligand and analyte structure on the generation of the membrane potential changes.

The structures of the host molecules are illustrated in Figure 1.

Experimental

Reagents and materials

The receptor (host) molecules used for this study are tetra-undecyl-tetra-*p*-nitrophenylazocalix[4]resorcinarene (**Ligand 1**), tetra-undecylcalix[4]resorcinarene (**Ligand 2**), tetra-undecyl-tetra-*p*-phenylazocalix[4]resorcinarene (**Ligand 3**), tetra-undecyl-tetra-bromocalix[4]resorcinarene (**Ligand 4**) and tetra-undecyl-tetra-hydroxycalix[4]resorcinarene (**Ligand 5**) (Figure 1). All ligands were synthesised by previously reported procedures (38–39).

2-Nitrophenyl-octylether (NPOE) was purchased from Fluka–Aldrich (Poznań, Poland). High molecular weight PVC ($n_{av} = 1100$), which was used as the polymer matrix was purchased from Wako (Osaka, Japan). Tetrahydrofuran (THF) was obtained from POCh (Gliwice, Poland) and was distilled over solid sodium hydroxide prior to use. Aniline, isomers of anisidine, toluidine and chloroaniline, *ortho*- and *meta*-diaminobenzene, *para*-hydroxyaniline and *para*-nitroaniline were purchased from Sigma–Aldrich (Poznań, Poland). *Para*-aminoaniline and disodium hydrogen phosphate anhydrous were obtained from POCh. All solutions were prepared using deionised water with resistivity of 18.2 M Ω cm just before the potentiometric measurements.

Electrode preparation and potential measurements

The PVC membranes were prepared using the following components: 1% (wt.) of the host, 66% (wt.) of plasticiser and 33% (wt.) of PVC. All components were dissolved in 2 ml of freshly distilled THF and the homogenous mixture was poured into a glass ring of 30 mm diameter and left for 24 h to allow THF to evaporate. The membranes obtained were of 100 μ m (ca.) thickness. Circles of 6 mm diameter were cut from the membrane and directly mounted on to a liquid membrane-type Philips ISE body (Glasbläserie Möller, Zürich, Switzerland). All potentiometric measurements were performed at room temperature ($\sim 20^\circ\text{C}$) on a multi-channel station, EMF-16 (Lawson Labs, Malvern, PA, USA). A double junction Ag|AgCl electrode was used as the reference electrode. The electrode cell assembly is presented below:



The electrodes were conditioned in 1.0×10^{-1} M phosphate buffer (pH 7.0) for 24 h. The calibrating solutions of the guest molecules were prepared in 1.0×10^{-1} M phosphate buffer, pH 7.0.

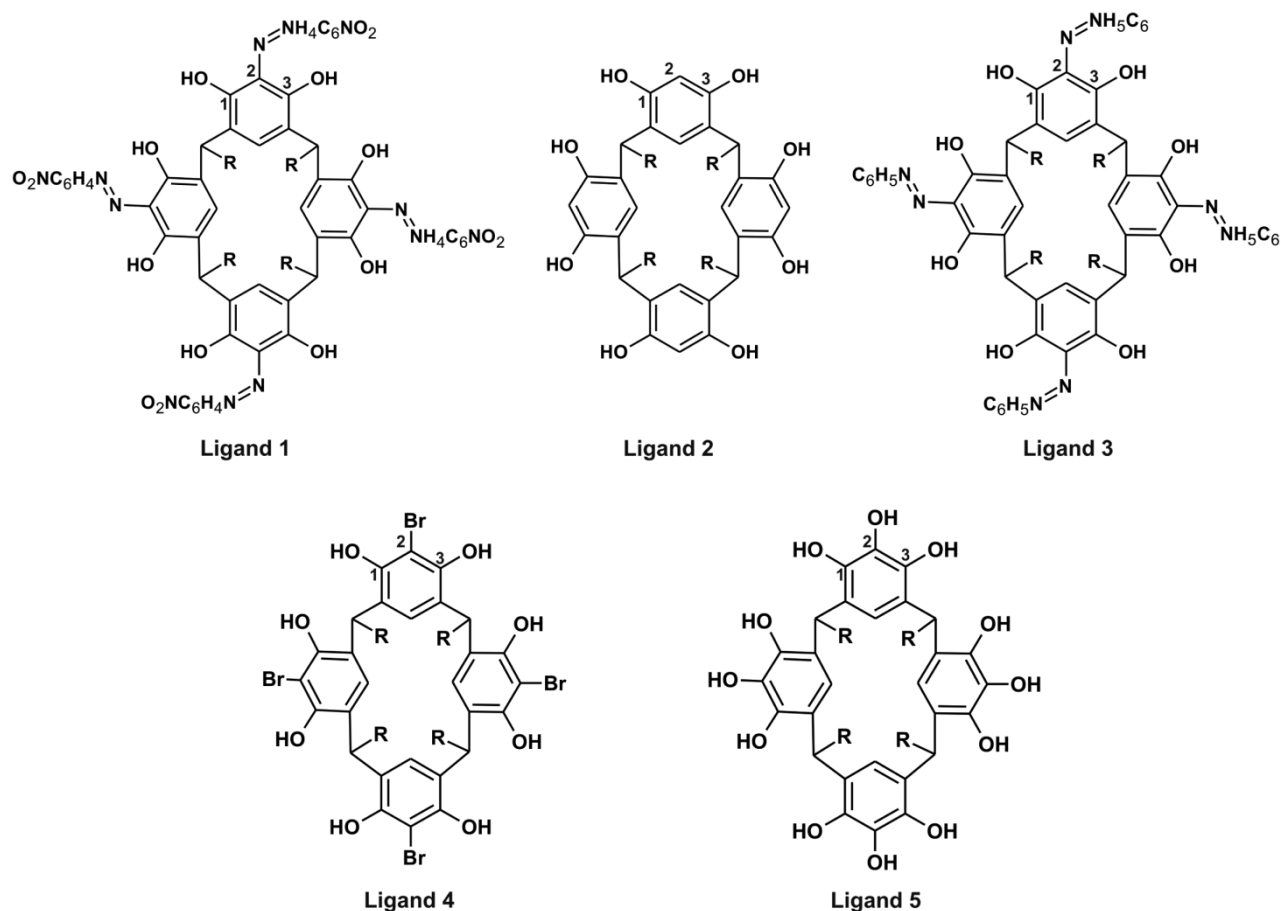


Figure 1. The chemical structure of host molecules under study, where $R: -C_{11}H_{23}$.

Results and discussion

Cationic potentiometric responses of PVC-supported liquid membranes incorporating undecylcalix[4]resorcinarene hosts in the presence of neutral forms of aniline derivatives

Our previous study on the potentiometric responses of liquid membrane electrodes incorporated with undecylcalix[4]-resorcinarene in the presence of diaminobenzene isomers was performed at pH 3.0 and pH 7.0. The potentiometric signals were observed only at pH 7.0, where all guests exist in uncharged form. The potentiometric signals were not observed at pH 3.0, where all isomers exist in the cationic form (37). Therefore, all potentiometric measurements presented here were performed at pH 7.0. Under such conditions, all aniline derivatives investigated exist in water almost entirely as the neutral (unprotonated) compounds (Table 1).

Figure 2 illustrates an example of potentiometric responses of PVC membranes containing **Ligand 1** towards diaminobenzene isomers. The results obtained for all aniline derivatives and all type of membranes studied are collected in Table 2. It has been proved that all

types of membranes generate cationic responses towards uncharged aniline derivatives.

Comparison of the results for all analytes showed the general tendency: with the increase in the analyte basicity, the response increases. In most cases, the *para* isomer generates the highest response. For *ortho* and *meta* isomers, it is difficult to estimate which one generates higher signal (Table 2).

Based on the results obtained, we can show only general qualitative relationship between potentiometric signals and acidity of the guests. This is because the others' parameters such as lipophilicity, steric hindrance also have some influence on the phenomenon studied.

Similar trends we have observed in the case of membranes modified with pyrrole-containing macrocycles stimulated with isomers of dihydroxybenzene (21, 23).

An explanation of the weak response of membranes after stimulation with *ortho* isomers is the possibility to form intramolecular hydrogen bonds. Because of that, the formation of intermolecular (host-guest) hydrogen bonds is relatively more difficult.

Table 1. Percentage of protonated and neutral species at pH 7.0.

S.No.	Analyte	pK_1	pK_2	pH 7.0	
				RNH_2 (%)	RNH_3^+ (%)
1	<i>p</i> -Nitroaniline	1.02		100.0	0.0
2	<i>o</i> -Chloroaniline	2.66		100.0	0.0
3	<i>m</i> -Chloroaniline	3.52		100.0	0.0
4	<i>p</i> -Chloroaniline	3.98		99.9	0.1
5	<i>m</i> -Anisidine	4.20		99.8	0.2
6	<i>o</i> -Toluidine	4.45		99.7	0.3
7	<i>o</i> -Anisidine	4.53		99.7	0.3
8	<i>o</i> -Aminoaniline	4.61	1.81	99.6	0.4
9	<i>m</i> -Toluidine	4.71		99.5	0.5
10	Aniline	4.87		99.3	0.7
11	<i>m</i> -Aminoaniline	5.01	2.56	99.0	1.0
12	<i>p</i> -Toluidine	5.08		98.8	1.2
13	<i>p</i> -Anisidine	5.36		97.8	2.2
14	<i>p</i> -Hydroxyaniline	5.48		97.1	2.9
15	<i>p</i> -Aminoaniline	6.22	2.99	85.8	14.2

We have not observed the relationship between potentiometric responses and partition coefficients of the aniline guests. This is evident that the phenomenon observed is governed by acidity–basicity of the host–guest. The hydrophobicity of the guests plays a secondary role.

The weakest response was observed for nitro- and chloro-derivatives of aniline. These guests are the strongest acids among the investigated compounds. In the case of membranes modified with pyrrole-containing macrocycles stimulated with nitro phenol, the opposite phenomenon was observed. The strongest responses were observed in the case of guests with the strongest acidity (21).

The ligands under study have different structures of the upper rim. In **Ligand 1**, there are dihydroxybenzene substituents in which the OH groups are in positions 1 and 3 in relation to each other. These distances make intramolecular hydrogen bonds very weak. Additionally **Ligand 1** is substituted in position 2 with azonitrobenzene. The presence of this substituent because of its inductive and mezomeric effect causes a substantial increase in the acidity of the phenol groups from the upper rim. **Ligand 2** possesses in its structure dihydroxybenzene in positions 1 and 3. Next, **Ligand 3** consists in its upper rim the dihydroxyazobenzene. The OH groups are in positions 1 and 3. The azobenzene substituent is in position 2. This substituent because of its inductive and mezomeric effect increases the acidity of phenolic groups in relation to **Ligand 2**. **Ligand 5** contains in its structure pyrogallol units (1, 2, 3-trihydroxybenzene). The close vicinity of OH groups leads to the formation of intramolecular hydrogen bonds. **Ligand 4** possesses in the upper rim 2-bromo-1,3-hydroxybenzene. Similarly as in **Ligand 5**, this system allows to create an intramolecular hydrogen bonds network. Additionally, the bromine atom is rather a large

atom and because of this it hinders the approach of guest molecules towards the host.

A comparison of the values of potentiometric response for each ligand showed a general tendency, which is as follows:

Ligand 1 > Ligand 2 > Ligand 3,
Ligand 4 > Ligand 5.

This sequence indicates that an increase in the acidity of the phenol groups causes an increase in the potentiometric response value.

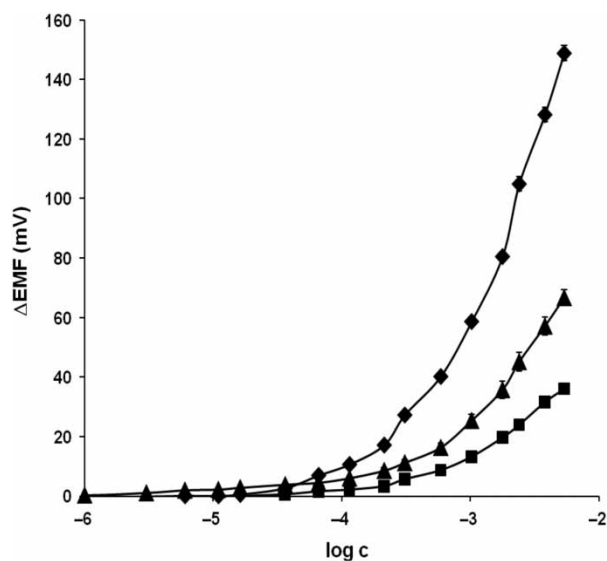


Figure 2. Potential responses of PVC membranes plasticised with NPOE incorporated with **Ligand 1** towards: (▲) *ortho*-aminoaniline, (■) *meta*-aminoaniline, (◆) *para*-aminoaniline in the presence of 1.0×10^{-2} M phosphate buffer pH 7.0 ($n = 3$, $3.11 < SD < 0.13$).

Table 2. The potentiometric response of PVC liquid membranes incorporating calixarene host generated in the presence of aniline derivatives; ΔE [mV].

Guests	pK ₁	Log P _{o/w}	Ligand 1	Ligand 2	Ligand 3	Ligand 4	Ligand 5
<i>p</i> -Diaminobenzene	6.22	-0.26	148.9	138.4	88.4	86.9	41.5
<i>p</i> -Anisidine	5.36	1.15	118.6	68.9	53.9	59.4	37.4
<i>m</i> -Anisidine	4.20	1.32	92.6	62.2	55.1	20.1	28.4
<i>o</i> -Diaminobenzene	4.61	0.37	66.8	57.2	64.2	31.0	31.5
<i>m</i> -Diaminobenzene	5.01	0.03	36.2	42.1	35.8	13.8	7.6
<i>p</i> -Toluidine	5.08	1.43	92.3	36.2	44.1	27.0	30.2
<i>p</i> -Chloroaniline	3.98	1.81	31.5	24.2	22.8	-0.6	6.2
<i>o</i> -Anisidine	4.53	1.65	62.7	20.1	35.7	19.8	7.8
<i>p</i> -Hydroxyaniline	5.48	-0.24	27.6	15.5	25.2	-2.1	2.4
Aniline	4.87	1.24	57.7	12.8	34.5	10.7	13.1
<i>m</i> -Toluidine	4.71	1.59	84.2	9.7	32.9	14.9	22.0
<i>o</i> -Toluidine	4.45	1.61	75.8	9.4	20.8	10.7	7.7
<i>p</i> -Nitroaniline	1.02	1.19	4.7	3.0	-	-	2.4
<i>m</i> -Chloroaniline	3.52	1.88	19.8	0.7	2.0	-	9.2
<i>o</i> -Chloroaniline	2.66	2.02	8.6	-4.5	1.2	-	1.9

Note: ΔE [mV] = $E_i - E_0$; E_0 , potential recorded in buffer solution and E_i , potential recorded in the presence of analyte.

We observed the strongest response for the membrane modified with **Ligand 1** containing in its structure dihydroxybenzene substituted with the electron-withdrawing azonitrobenzene. The acidity of these OH groups is the highest.

Next in this sequence is **Ligand 2** with unsubstituted resorcinol. In this case, the acidity of the OH group is lower than in **Ligand 1**, but the accessibility of **Ligand 2** for analytes is much easier. In consequence, the creation of a hydrogen bond (H—O—H—N) between analyte and ligand is relatively easy. **Ligand 3** contains in its structure a resorcinol substituted with azobenzene. This causes an increase in the phenolic acidity, but at the same time, the presence of a rather large substituent hinders the access of OH group for analyte molecules. The signal value generated by membrane modified with **Ligand 3** is a result of these two opposite effects.

Ligand 4 containing the bromo-derivatives of resorcinol in its structure is next in the sequence of the response value. In this case, similarly as it was in the previous one, two factors compete: from one side the inductive and mesomeric effects, which causes an increase in the acidity of the phenol group and the large bromine atom, which is a significant hindrance for the approach of the analyte.

We have obtained the lowest response for the membrane modified with **Ligand 5**, which possesses pyrogallol (trihydroxybenzene) in its structure. In this ligand, the strong intramolecular hydrogen bonds are present. As the consequence, this lowers overall phenolic acidity. Because of this, the formation of a supramolecular complex with the analyte is relatively the most difficult among the ligands under study.

Analysis of the data obtained shows that there is no direct relation between the lipophilicity of the amine guests and the values of the signal generated by them.

However, the low lipophilicity of *para*-hydroxyaniline may be one of the reasons of its weak potentiometric response in spite of its high basicity (Table 2).

Checking the possibility of transport of *para*-anisidine through the PVC membrane modified with tetra-undecyl-tetra-*p*-nitrophenylazocalix[4]resorcinarene

The possibility of transporting *para*-anisidine across the tetra-undecyl-tetra-*p*-nitrophenylazocalix[4]resorcinarene (**Ligand 1**) membrane was checked by performing a long-term experiment in two solutions (1) 1.0×10^{-1} M KCl and solution (2) 1.0×10^{-4} M of *para*-anisidine in 1.0×10^{-2} M phosphate buffer pH 7.0. The cells were separated by a piece of membrane containing **Ligand 1**. The transport of *para*-anisidine through the modified membrane was monitored by UV-vis measurements. After 24 h, the KCl solution was free of *para*-anisidine. This means that *para*-anisidine is not able to penetrate through a PVC membrane modified with **Ligand 1** during this time interval. Therefore, it might be concluded that the potentiometric signals observed in the present study were not generated as a result of diffusion of the analyte through the polymeric membranes, but there is a consequence of the supramolecular recognition phenomena occurring at the organic-aqueous interface.

The mechanism of the generation of the potentiometric signal of undecylcalix[4]resorcinarene modified membranes after stimulation by unprotonated derivatives of aniline

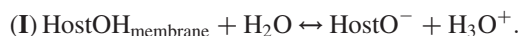
Based on the obtained results and data from the literature, we propose the following mechanism of cationic potentiometric signal generation by membranes modified

with derivatives of undecylcalix[4]resorcinarene, after stimulation with unprotonated aniline derivatives. In the first step, during conditioning, some of the phenolic groups of undecylcalix[4]resorcinarene derivatives, located at the surface of polymeric membranes, dissociate and the membranes gain a minus charge. Such type of dissociation of OH groups at the upper rim of undecylcalix[4]resorcinarene was already reported (40–42). In the next step, a network of hydrogen bonds between the aniline derivatives and the phenolate groups is created. Thus, a supramolecular complex of undecylcalix[4]resorcinarene and aniline derivatives is formed at the water–membrane interface. The amino groups are donors of hydrogen atoms in hydrogen bonds. Their polarity correlates with the acidity of phenol groups.

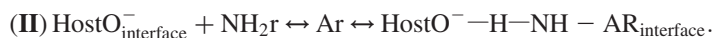
The formation of such a hydrogen bond network in one phase was already reported (43–45). The measurements were carried out at pH 7.0. Under this condition, all of the investigated anilines exist in solution mostly as unprotonated compounds (Table 1). The increase in the electron density at the amine nitrogen atom upon complex formation causes an increase in its basicity and this is the driving force for transferring the proton from the surface of the aqueous phase to the surface of the organic (membrane) phase. Proton transfer leads to an increase in the plus charge on the membrane surface, and we can observe the generation of a potentiometric cationic signal.

Generally, the proposed mechanism is based on three steps.

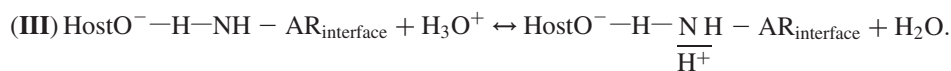
The first one concerns dissociation of some phenolic groups from the upper rim of the investigated resorcinarene ligands



The next step consists of the transfer of the analyte from the bulk solution to the interface and the formation of a supramolecular complex between the ligand and the analyte through hydrogen bonds



A consequence of this is the increase in the basicity of the nitrogen atom of the supramolecular complex, and its protonation



The confirmation of the first step is based on the results we have obtained with the membrane modified with **Ligand 1** in which the acidity of phenolic groups is the highest. The results we observed for bromo- and azobenzene-derivatives of investigated undecylcalix[4]resorcinarene

show that the accessibility of phenols groups is a very important parameter for the intermolecular recognition process, which is taking place between the investigated ligands and the analytes.

The weakest response we have observed in the case of membranes modified with **Ligand 5**, which possesses in its structure trihydroxybenzene could be explained by the low acidity and the possibility to form the intramolecular hydrogen bonds. This is a relatively strong energetic barrier for the described phenomenon.

The second step of the proposed mechanism, which relies on proton transfer from the water to the organic phase, is supported by the fact that regardless of the ligand, the strongest signal was observed for the strongest bases between compounds under study. The results obtained show that the lipophilicity of the analytes is not a crucial parameter.

Conclusions

The systematic work we have carried out (21–25) on the study of the potentiometric signal generated by uncharged molecules was inspired by the first pioneer papers by Umezawa (18–20) on the anionic potentiometric responses of membranes modified with macrocyclic polyamines or quaternary ammonium salts stimulated with undissociated dihydroxybenzenes.

It was proved that PVC-supported membranes incorporating hosts with amino groups upon stimulation with phenolic guests generate anionic potentiometric signals. The base of this phenomenon is a proton transfer from supramolecular complexes located at the interface towards the aqueous phase.

In this paper, we proved that membranes modified with hosts possessing phenolic groups generate cationic potentiometric responses upon stimulation by uncharged guests possessing NH₂ groups. In this case, the base of the potentiometric signal generation relies on the proton transfer from the aqueous phase on the supramolecular complexes located at the interface.

In both cases, the acidity and basicity of the ligands, as well as the analytes, are crucial parameters, which govern these phenomena. The shape of the cavity of the

macrocyclic ligand is also significant. The lipophilicity of the analytes plays a secondary role.

Based on the Umezawa papers, as well as our already published work and the research presented, we can conclude that the generation of potentiometric signals by

uncharged molecules is governed by the transport of protons between the aqueous and membrane–aqueous interface. The acidity–basicity of the hosts decides about the direction of the transfer of protons.

Acknowledgements

The work was supported by European Union Marie-Curie Transfer of Knowledge Research Grant MTKD-CT-2006-042708, the Polish Ministry of Sciences and Higher Education no. 105/6.PR. UE/2007/7 and Institute of Animal Reproduction and Food Research of the Polish Academy of Science, Olsztyn, Poland. W.F.A.D. and W.D. thank the University of Leuven, the Ministerie voor Wetenschapsbeleid and the F.W.O. for continuing support.

Note

1. PhD fellow of EU grant Marie-Curie Transfer of Knowledge, No: MTKD-CT-2006-042708.

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