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Review

Recognition of Anions Using Metalloporphyrin-Based Ion-Selective Membranes: State-of-the-Art

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Abstract

The principles, recent achievements and challenges related to the use of metalloporphyrins as ionophores in the development of polymeric anion-selective membranes are reported. The advantages and disadvantages of dimer-monomer equilibria existing within the membrane phase when using certain metalloporphyrins are discussed with respect to their effect on the response characteristics of the resulting anion sensors. The influence of membrane composition and pH of sample solution on these equilibria is described. The possibility of employing both potentiometric and optical transduction modes for anion recognition with metalloporphyrin doped polymer membranes is shown.

Keywords: Metalloporphyrins, Anion-selective membranes, Dimer-monomer equilibrium, Potentiometric sensors, Optical sensors

1. Introduction

The development of potentiometric membrane-based anion sensors with analytical useful selectivities remains a formidable challenge. Indeed, there are relatively few types of lipophilic ionophores, required for preparation of such sensors, that display significant preference for one anion over others [1, 2]. Metalloporphyrins are one class of anion host structures that have proven useful in the preparation of both potentiometric and optical anion sensors. Herein, we summarize the current state of this field and provide data from recent experimental work in our laboratories.

2. What are the Principles of Metalloporphyrin Functioning as Anion-Selective Ionophores?

The very first articles reporting the applications of metalloporphyrins, namely Mn(III)-porphyrin, as ionophores to prepare anion-selective polymeric membrane based electrodes were published in the middle 1980s [3, 4]. Mn(III)[TPP]Cl (TPP: tetraphenylporphyrin) was described as ionophore selective toward chloride and salicylate; however selectivity coefficients for those anions were only slightly better than for electrodes doped with a classical dissociated anion exchanger. Since then, various metalloporphyrins have been tested as potential ionophores for anions. Response characteristics of chosen metalloporphyrin-based membrane electrodes reported in the literature are summarized in Table 1. It can be seen clearly that the specific nature of the metal cation present in the metalloporphyrin structure governs the selectivity of membranes

doped with these ionophores. Beyond testing various metalloporphyrins, research has also focused on elucidating the working mechanism of the porphyrin-doped polymeric anion-selective membranes. It is now well established that metalloporphyrins exhibit unique anion ionophore selectivities when incorporated into plasticized polymeric membranes due to preferential coordination of given anions as axial ligands to the central metal ion of the porphyrin structure (see Fig. 1). Initially anion selective polymeric membranes were formulated without any lipophilic ionic additives and hence only the presence of intrinsic anionic site impurities within PVC and plasticizer has yielded the degree of selectivity often reported. It has been shown that the operative mechanism is governed by the charge of the central metal ion within the porphyrin structure [5]. Knowledge of the working mechanism (neutral carrier versus charged carrier) is critical since optimization of membrane selectivity is highly dependent on the incorporation of lipophilic membrane additives [6]. Indeed, membranes doped with ionophores that function as charged carriers require lipophilic anionic additives (e.g., tetraphenylborate derivatives), while cationic additives (tetraalkylammonium salts) are needed in the case of ionophores that serve as neutral carriers. As listed in Table 1, except for Co(II)- [7] and Co(III)- [6, 8] porphyrins, the majority of metalloporphyrin examined to date function via a charged carrier mechanism that requires the presence of anionic additives for proper membrane functioning, including optimized selectivity. It should be noted that electrodes with membranes doped with Mn(III)-, In(III)-, Ga(III)-, Sn(IV)- and Zr(IV)-porphyrins tend to exhibit super-Nernstian behavior toward analyte anions [3, 4, 6–13]. Slopes of calibration

Table 1. Characteristics of chosen metalloporphyrin-based membrane electrodes. PVC: poly(vinyl chloride), PU: polyurethane, *o*-NPOE: *o*-nitrophenyloctylether, DOS: bis(2-ethylhexyl) sebacate, BEHP: bis(2-ethylhexyl)phthalate, DBS: dibutyl sebacate.

Metal center [a]	Suggested analyte	Polymeric matrix	Slope	Working mechanism	References
Mn(III)	Cl [−] , Sal [−]	PVC/ <i>o</i> -NPOE	super-Nernstian	–	[3, 4]
Co(II)	SCN [−]	PVC/ <i>o</i> -NPOE	Nernstian	–	[7]
Co(III)	NO ₂ [−] /SCN [−]	PVC/ <i>o</i> -NPOE	Nernstian	neutral carrier	[6, 8]
Ga(III)	F [−]	PVC/ <i>o</i> -NPOE	super-Nernstian	charged carrier	[10, 15]
In(III)	Cl [−]	PVC/ <i>o</i> -NPOE	super-Nernstian	charged carrier	[6, 9, 15]
In(III)	Cl [−]	PU/ <i>o</i> -NPOE	Nernstian	charged carrier	[25]
In(III)	Cl [−]	PVC/DOS	Nernstian	charged carrier	[23]
In(III)	Cl [−]	silicone rubber / DBS	Nernstian	charged carrier	[24]
Cr(III)	Sal [−]	PVC/BEHP	Nernstian	charged carrier	[27]
Tl(III)	Cl [−]	PVC/ <i>o</i> -NPOE	Nernstian	charged carrier	[10]
Mo(V)	SCN [−] /Sal [−]	PVC/ <i>o</i> -NPOE	Nernstian	charged carrier	[16]
Sn(IV)	Sal [−]	PVC/ <i>o</i> -NPOE	super-Nernstian	charged carrier	[6, 12, 13, 16]
Zr(IV)	F [−]	PVC/ <i>o</i> -NPOE	super-Nernstian	charged carrier	[11]

[a] metal center of octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP)

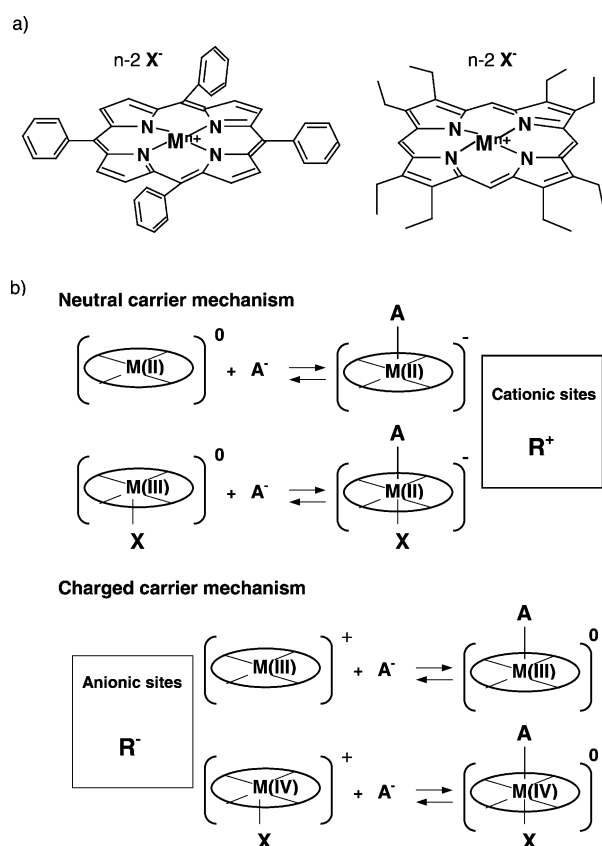


Fig. 1. Metalloporphyrins as ionophores: a) structures of the two most widely used metalloporphyrins for preparing anion selective membrane electrodes; b) anion – metalloporphyrin interactions; X[−]: initially present axial ligand, A[−]: analyte anion. Neutral ligands are not shown.

plots are typically much higher than -59 mV/dec, predicted for monovalent anions by the Nernst equation.

It should be further noted that Table 1 does not list the values of potentiometric selectivity coefficients reported in the cited articles. This is due to the fact that for several metalloporphyrin-based membrane electrodes, significant

differences in slopes have been observed for the calibration plots of the examined anions (super-Nernstian, Nernstian or sub-Nernstian). Thus selectivity coefficient values calculated using the separate solution method are strongly dependent on anion concentration taken for measurement process. Therefore, we strongly support the idea [14] to present, in such instances, the selectivity results as a set of calibration plots for the series of examined anions.

3. What is the Origin of Super-Nernstian Response of Membranes Formulated with Certain Metalloporphyrins?

Recently it has been demonstrated that the origin of super-Nernstian behavior for membranes doped with Ga(III)- and In(III)- octaethylporphyrins can be ascribed to a unique dimer-monomer equilibrium that exists for these porphyrin species within the organic membrane phase of the electrode [15]. It was shown that in the absence of the target anion, the porphyrin species exists as a positively charged, hydroxide ion bridged dimer, with the borate additive as the predominant counter-anion. However, in the presence of anions in the aqueous test solution that exhibit preferred axial ligation with metal center, the dimer is broken into a monomeric species. This results in an equilibrium change in the free ion activities of hydroxide and target anion within the membrane phase as a function of the bathing analyte anion activity in the sample solution. A schematic representation of this equilibrium is shown on Figure 2. This process yields a theoretically predicted super-Nernstian anion response behavior under equilibrium conditions. This phenomenon has also been observed for metalloporphyrins containing tetravalent metal cations, namely Sn(IV)- [16] and Zr(IV)- [11] porphyrins.

A very useful method for monitoring dimer-monomer equilibria (both in organic solvents and thin polymeric films) is UV-vis spectrophotometry [11, 15–18]. It has been shown that in the spectrum of a given metalloporphyrin, a

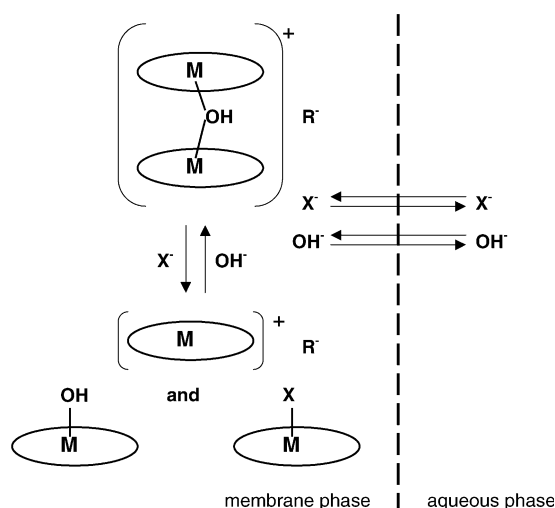


Fig. 2. Equilibrium between dimeric and monomeric forms of M(III)-porphyrin in a polymeric membrane doped with anionic site R^- , conditioned in aqueous solution containing analyte anion X^- .

Soret band (at around 400 nm), related to its monomeric form, can be seen (see Fig. 3 a, b). The formation of a hydroxide bridged metalloporphyrin dimer in the presence of lipophilic anionic additives can be detected by an appearance of a new band shifted by 10–20 nm towards a shorter wavelength, compared to the initial band corresponding to the monomeric species. However, in the presence of anions that can strongly interact with metal center of the metalloporphyrin, the dimeric band of the metalloporphyrin diminishes while an increase in intensity of the band related to monomeric forms of the metalloporphyrin appears. This clearly indicates that analyte anion can break the metalloporphyrin dimer, presumably via favorable axial ligation with the central metal cation of the monomeric species. This process results in changes of the membrane composition during calibration run, in terms of the nature of the porphyrin species, and, finally, in super-Nernstian slopes for the measured calibration plots [15].

The ability of certain metalloporphyrins to form hydroxide bridged dimers, stabilized by lipophilic anions (e.g.,

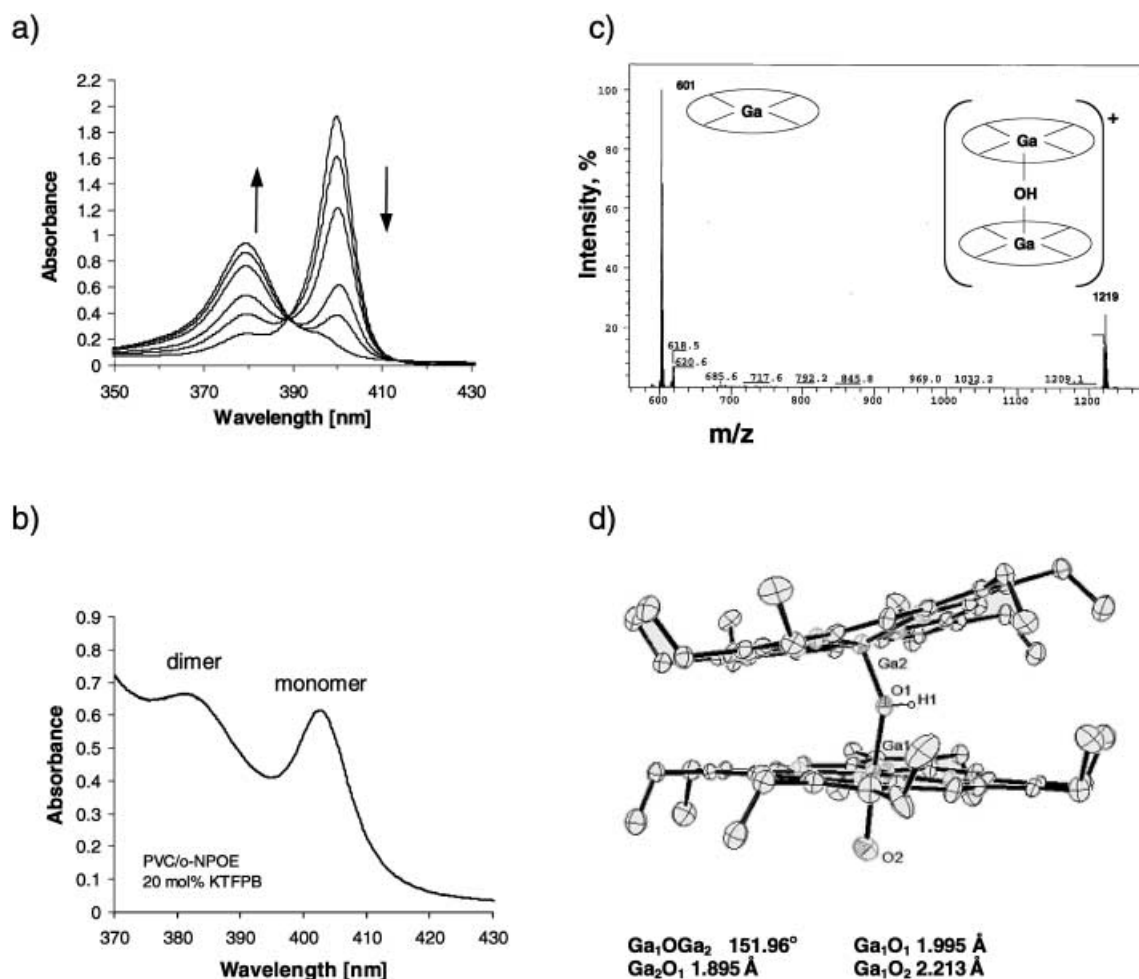


Fig. 3. Evidences for Ga(III)-octaethylporphyrin dimerization: a) the UV-vis spectra of CH_2Cl_2 solution of metalloporphyrin as a function of increasing concentration of the anionic additives (KTFPB); arrows indicate the trends in spectrum changes; b) the UV-vis spectrum of thin PVC/o-NPOE film containing metalloporphyrin and 20 mol% of KTFPB conditioned in buffer solution pH 5.5; c) electrospray ionization mass spectrum of CH_2Cl_2 solution containing metalloporphyrin and 50 mol% KTFPB; d) X-ray crystallography structure of Ga(III)-octaethylporphyrin dimer.

tetraphenyl borate derivatives or perchlorates) was also confirmed by X-ray crystallography [17–19] and mass spectrometry [20] (Fig. 3 c, d).

4. Dimer Formation: an Advantage or a Disadvantage?

An important question can be asked: is the dimerization process and resulting super-Nernstian slopes of the calibration plots beneficial from analytical point of view? Of course, higher than theoretical slopes of the calibration plots mean greater sensitivity of the ISE measurement. However, the diffusion of membrane components, caused by dimer-monomer equilibrium reactions, is very likely responsible for the long response times and slow recovery times observed for electrodes based on polymeric membranes doped with metalloporphyrins that form dimers within the membrane phase. Such behavior can lead to hysteresis (see Fig. 4) of the sensors' response and is viewed as a disadvantage from a practical analytical standpoint. The best way to overcome these problems is to prevent dimer formation. Indeed, for electrodes based on metalloporphyrins that do not dimerize (e.g., Mo(V)O-porphyrins [16]) fast response and Nernstian slopes for calibration plots toward the preferred anion (salicylate, in this case) have been observed.

Thus, for potentiometric measurements, the prevention of dimer formation can be viewed as beneficial. Dimer-monomer equilibrium can be presumably affected by changing the composition of the membrane phase (concentration of anionic sites, type of plasticizer and polymeric matrix) and/or by adjusting of sample solution pH.

Lipophilic anionic additives are used to optimize selectivity of membranes doped with metalloporphyrins that function via a charged carrier mechanism. The amount of such lipophilic salt added to the membrane used for potentiometric measurements is typically in the range of

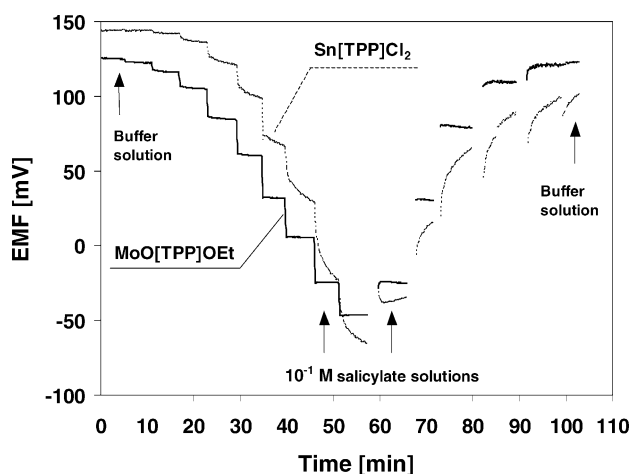


Fig. 4. Dynamic EMF response of the electrodes with PVC/*o*-NPOE (1:2) membranes containing 1 wt% O = Mo(V)[TPP]OEt and 20 mol% NaTFPB (solid line) or 1 wt% Sn(IV)[TPP]Cl₂ and 10 mol% of NaTFPB (dotted line), MES buffer, pH 5.5 [16].

10–20 mol% relative to the ionophore. Spectrophotometric measurements have shown that such anionic additives stabilize metalloporphyrin dimers and that the degree of dimerization can be diminished by lowering the amount of additives (see Fig. 3 a, b). However, dimer formation cannot be totally eliminated by decreasing the anionic site content within the plasticized poly(vinyl chloride) membrane phase due to the presence of intrinsic anionic impurities [21] within this matrix.

It is known that the dimer-monomer equilibrium can be shifted towards dimer formation when organic solvents of higher dielectric constant are used [22]. Thus, it can be expected that by using a less polar plasticizer to formulate the polymer membrane, a decrease in dimer formation can be achieved. However, when DOS ($\epsilon = 4.6$) was employed as plasticizer, instead of *o*-NPOE ($\epsilon = 24$), electrodes with membranes doped with Ga(III)-, Sn(IV)- and Zr(IV)-porphyrins still responded with super-Nernstian response slopes toward fluoride, salicylate and fluoride, respectively (data not shown). Only in the case of In(III)-porphyrins has it been demonstrated that the use of DOS [23] and DBS [24] as plasticizers results in electrodes with near-Nernstian and fast responses toward chloride (primary anion for In(III)-porphyrins). This strongly suggests that dimerization of In(III)-porphyrins was indeed avoided in these membranes (Fig. 5).

Metalloporphyrins have most often been investigated as ionophores within plasticized PVC membranes. There are only a few examples of their incorporation in other polymeric matrices, such as silicone rubber [24] and polyurethanes (PU) [25]. When replacing PVC with Tecoflex PU, electrodes formulated with In(III) porphyrins yielded Nernstian response toward chloride. Spectrophotometric measurements of these PU membranes revealed that a much lower concentration of chloride in sample solution, compared to PVC-based membranes, is needed to break the dimer (see Fig. 6.). Consequently, data for calibration plots are collected when the monomeric form of In(III)-porphyrin is already present in the membrane phase as the predominate species and this is responsible for the Nernstian behavior of such membranes.

At this point it can be summarized that the specific composition of membrane can influence the equilibrium between dimeric and monomeric forms of metalloporphyrins; however, only in some cases can the dimer formation be completely prevented by judicious choice of membrane composition.

Another factor that can have some effect on dimer-monomer equilibria within the membrane phase is the pH of sample solution. The dimer of the metalloporphyrin is bridged by hydroxide, which is in equilibrium between the sample solution and the membrane phase. The concentration of hydroxide anion in the sample solution (i.e., pH of sample solution) determines the concentration of this anion in the membrane phase and influences the degree of metalloporphyrin dimerization. It has been shown for Zr(IV)-porphyrins, via spectrophotometric measurements, that in PVC membranes conditioned in MES buffer

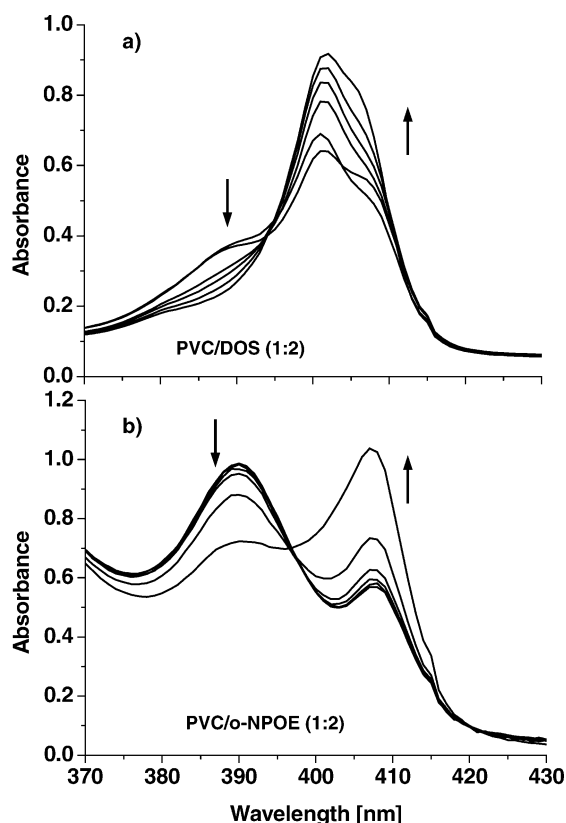


Fig. 5. Changes in spectra of thin PVC films doped with In(III)[OEP]Cl and 40 mol% KTFPB, plasticized with a) *o*-NPOE and b) DOS, under conditioning in aqueous solutions of different Cl^- concentrations; MES buffer, pH 5.5.

solution, pH 5.5, the molar dimer/monomer ratio of Zr(IV)-octaethylporphyrin is considerably higher than when Gly/HCl buffer solution, pH 3, is used [11] as the soaking solution. These results correlate well with potentiometric measurements (Fig. 7). The slopes of calibration plots toward fluoride (primary anion for Zr(IV)-porphyrin-based

electrodes) are slightly lower when pH 3 buffer solution is employed, compared to a pH 5.5 buffer solution, but still remain super-Nernstian.

As described above, adjusting the membrane composition and sample solution pH cannot be a general method for eliminating metalloporphyrin dimer formation. The only way to totally prevent the dimerization process is to modify the metalloporphyrin structure by adding large peripheral groups leading to steric hindrance of metalloporphyrin dimer formation. Such an approach was already employed for gallium(III) and indium(III) porphyrins [15]. For this purpose, a so-called “picket fence” porphyrin was used, possessing four tert-butyl groups attached to the porphyrin core via amide linkages. All four groups are perpendicular to the plane of the porphyrin and this is why the porphyrin molecules cannot get close enough to form a dimeric species via the hydroxide ion bridge. The response of electrodes with polymeric membranes doped with Ga(III)- and In(III)-“picket fence” porphyrins was fast and near-Nernstian. These results suggest that use of picket fence type metalloporphyrin structures with other metal ion centers will yield other anion selective sensors with greatly improved response times.

5. How to Make Use of Dimer Formation?

Preventing dimer formation seems to be a good strategy when constructing potentiometric sensors based on metalloporphyrins. However, dimer formation can be also beneficial. Indeed, it is possible to make use of the dimer-monomer equilibria by changing the transduction mode from potentiometric to spectrophotometric. As mentioned above, the primary target anion is able to break metalloporphyrin dimers, due to the strong interaction of the anion with the metal center cation present within the porphyrin structure. As the concentration of analyte anion in the aqueous phase increases, the degree of dimerization

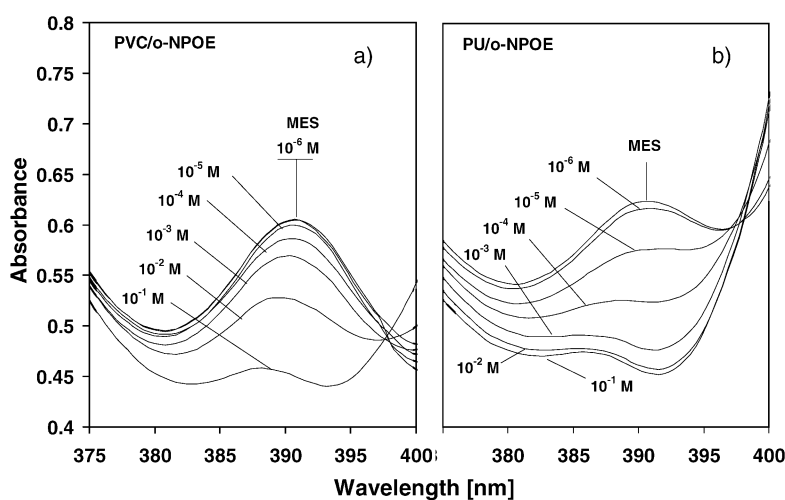


Fig. 6. The influence of polymeric matrix on spectra of thin films doped with In(III)[OEP]Cl and 20 mol% KTFPB, conditioned in aqueous solutions containing different Cl^- concentrations; MES buffer, pH 5.5; a) PVC- and b) PU-based membranes.

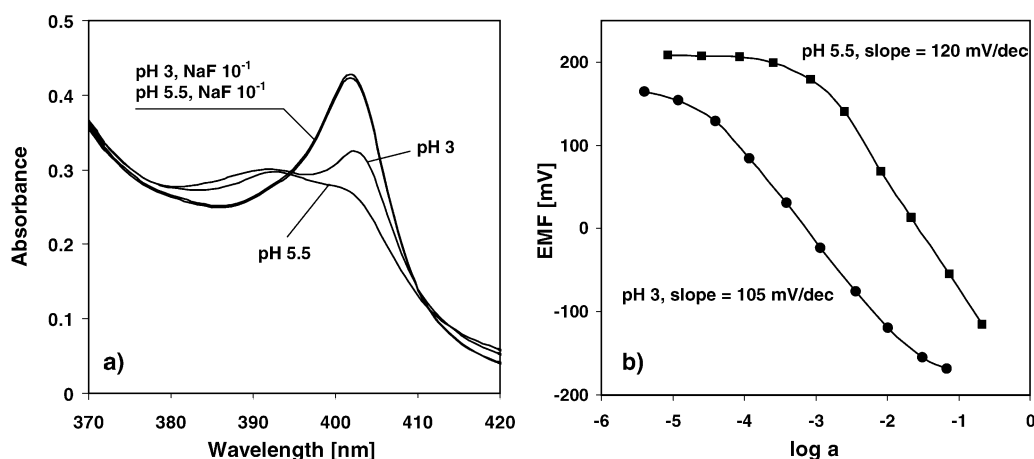


Fig. 7. The influence of sample pH on: a) UV-vis spectra and b) potentiometric response toward F^- for PVC/*o*-NPOE membranes doped with $Zr(IV)[OEP]Cl_2$ and 10 mol% KTFPB.

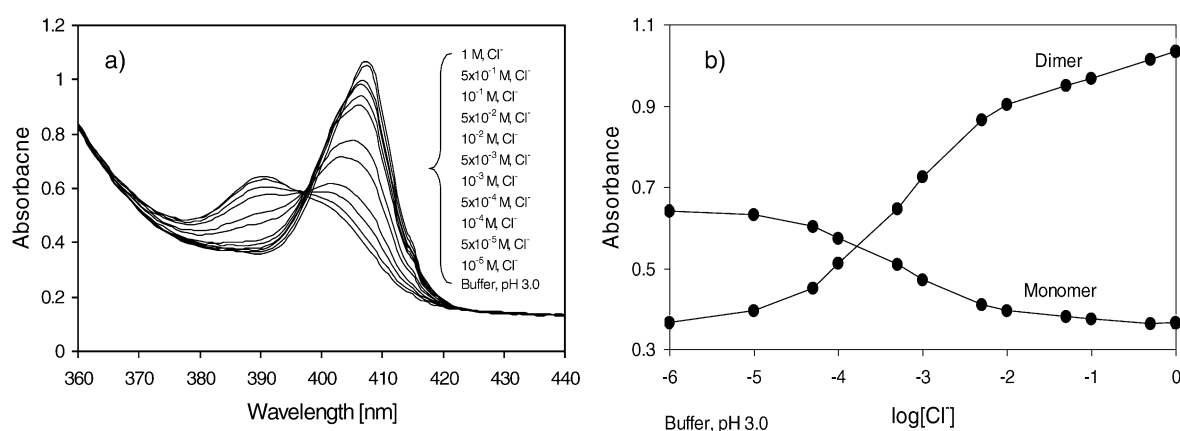


Fig. 8. Spectra of optode film containing $In(III)[OEP]OH$ at 1 wt% and NaTFPB at 45 mol% (relative to $In[OEP]OH$) as a function of bathing chloride ion concentration added to 0.05 M phosphate buffer, pH 3.0 (a) and changes in absorbance of monomer ($\lambda = 408$ nm) and dimer ($\lambda = 390$ nm) as the function of chloride concentration (b).

diminishes, which can be observed spectrophotometrically. Very recently, such a transduction mode was exploited to develop an optical chloride sensor based on the dimer-monomer equilibrium of indium octaethylporphyrin [26]. The changes in intensity of dimeric band rather than monomeric one were used to measure chloride concentration in the sample solution, as the selectivity pattern obtained in this way was more reliable (Fig. 8). The optimized amount of anionic additives that ensures dimer stabilization in thin polymeric films used for optical measurements was found to be 45 mol% (relative to the metalloporphyrin) which is significantly greater than in the case of polymeric membranes used for ISEs. (10–20 mol%). As analogous dimer-monomer equilibria were also observed for other metalloporphyrins (Ga(III)-, Sn(IV)- and Zr(IV)-porphyrins), reports on optical sensors selective toward other anions based on a similar strategy can be envisioned.

6. Conclusions

Use of metalloporphyrins as ionophores to create novel anion selective polymeric membrane electrodes has yielded not only a variety of potentially useful analytical sensors (see Table I), but also the discovery of very interesting reversible chemical reactions (spontaneous formation of hydroxide ion bridged dimers) that can occur within the organic polymeric matrix. While the occurrence of such chemistry can degrade the anion response characteristics of potentiometric sensors based on given metalloporphyrin structures, an understanding of how to prevent such secondary equilibrium reactions can be used to improve the performance of such devices. At the same time, by monitoring the degree of monomer formation under sample conditions that favor the dimer, analytically useful anion selective optical sensors can be devised. It is likely that analogous optical sensors for uncharged neutral species may

also be possible, if such species can serve as strong axial ligands for metalloporphyrin monomers. Indeed, use of In(III) porphyrin dimers within thin PVC films to optically detect gas phase amine species at sub-ppm levels has recently been demonstrated [27].

7. Acknowledgement

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7. References

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