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Research Article

Potentiometric Polymeric Film Sensors Based on 5,10,15-tris(4-aminophenyl) Porphyrinates of Co(II) and Cu(II) for Analysis of Biological Liquids

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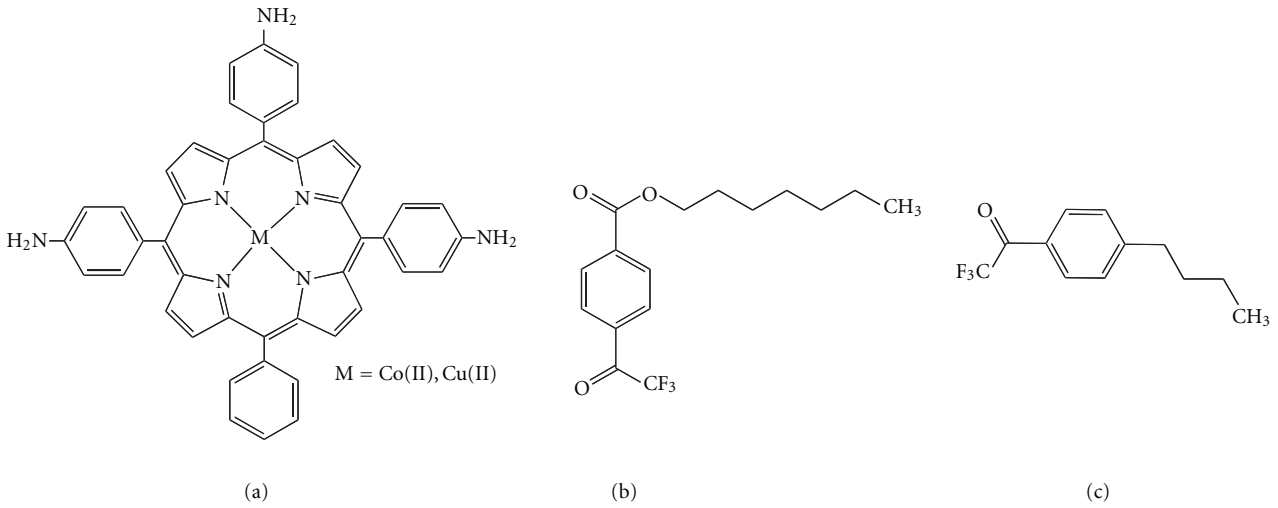
Novel carbonate-selective potentiometric sensors based on 5,10,15-tris(4-aminophenyl)-20-phenyl porphyrinates of Cu(II) and Co(II) have been developed. Ionophore functioning mechanism and possible source of carbonate sensitivity have been evolved. Potentiometric properties of Co(II)- and Cu(II)TATPP-based sensors were compared with common carbonate-ISEs containing trifluoroacetophenone derivatives. The analytical utility of newly developed sensors has been demonstrated by measuring the bicarbonate content in human blood plasma.

1. Introduction

An accurate detection of hydrophilic anions, carbonate in particular, in physiological fluids, seawater, industrial, and environmental samples is still a big challenge. Ion-selective potentiometric sensors represent a useful approach to this task [1]. After pioneering work of Herman and Rechnitz in 1974 [2], several studies on trifluoroacetophenone (TFAP) derivatives as ionophores for carbonate-selective solvent polymeric membrane sensors development have been reported [3–6]. The effect of acceptor substituents incorporation in para- [7, 8] and meta- [9, 10] positions of phenyl ring of TFAP, as far as the influence of lipophilic cationic sites addition [3, 11, 12] on selectivity properties of such sensors have been studied. Various constructive and strategic modifications such as incorporation of TFAP ionophore in photocurable polyurethane [13] and cellulose acetate membranes [14] have been applied in order to diminish the influence of lipophilic anions on carbonate ion response. The other types of ionophores are such as tweezer-type derivatives of cholic acid [15], urea-functionalized calix[4], arenes [11], and hydrogen bonding diamide receptors [16] and metallocorroles [17]. Unfortunately, many of reported membranes were still exhibiting much higher selectivity for several lipophilic anions, like salicylate, over carbonate, which is a serious drawback for their application, for example, in clinical analysis (e.g., human serum) [8, 12].

In this contribution we report a development of novel carbonate-selective potentiometric sensors based on 5,10,15-tris(4-aminophenyl)-20-phenyl porphyrinates of Co(II) and Cu(II) (Co(II)TATPP and Cu(II)TATPP correspondingly). PVC solvent polymeric membranes doped with Co(II)TATPP alone and containing lipophilic cationic additive (TDACl), and films of poly-Co(II)TATPP and poly-Cu(II)TATPP electropolymerized on Pt working electrodes (WE) from various organic solvents (acetonitrile, dimethylformamide, pyridine) have been studied with the aim to evolve the origin of sensitivity towards carbonate ion. Potentiometric properties of Co(II)- and Cu(II)TATPP-containing sensors were compared with those based on TFAP (carbonate ionophore I, ETH-6010, and carbonate ionophore IV), Scheme 1. The analytical utility of



Scheme 1: Molecular structures of studied ionophores: (a) 5,10,15-tris(4-aminophenyl)-20-phenyl porphyrinate of Cu(II) and Co(II), (b) heptyl-4-trifluoroacetylbenzoate (carbonate ionophore I), and (c) 4-butyl-α,α,α-trifluroacetophenone (carbonate ionophore IV).

newly developed electrodes has been demonstrated by measuring the bicarbonate content in human blood plasma.

2. Experimental

2.1. Reagents. Poly(vinyl chloride) (PVC) high molecular weight; plasticizer bis(2-ethylhexyl) sebacate (DOS), heptyl-4-trifluoroacetylbenzoate (Carbonate Ionophore I), 4-butyl-α,α,α-trifluroacetophenone (Carbonate Ionophore IV), tetradodecyl ammonium chloride (TDACL), potassium tetra-*p*-chlorophenylborate (TpClPBK), tetrabutylammonium perchlorate ($TBAClO_4$), 2-amino-2-(hydroxymethyl)-1,3-propanediol (TRIS), tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF), pyridine, and aniline were purchased from Sigma-Aldrich. 5,10,15-tris(4-aminophenyl)-20-phenyl porphyrinates of Cu(II) and Co(II) were synthesized according to the literature methods [6–19] and fully characterized by NMR and UV-visible spectroscopy. All other chemicals were of analytical grade and were used without further purification. All solutions were prepared by using distilled water.

2.2. Sensors' Preparation and Evaluation. PVC membranes were prepared according to a common procedure. Membrane of 100 mg weight contained 1.5–3.5 wt% of ionophore and/or 1–6 wt% of lipophilic additive distributed in PVC/DOS (1 : 2) polymeric matrix, Table 1. Membrane components were dissolved in 1 mL of THF with addition of 7 wt% of pyridine to membranes III, IV in order to improve an ionophore solubility. Membrane cocktails were then cast out on flat GC electrode surface (3 mm in diameter) previously buffed with alumina slurries, cleaned in ultrasonic bath, rinsed with methanol, and dried on air. THF was allowed to evaporate overnight. Porphyrin electropolymers (EP) were deposited by means of cyclic voltammetry on Pt WE (3 mm surface diameter) from 1.0 mM/L Co(II)TATPP or Cu(II)TATPP and 0.1 M/L $TBAClO_4$ solutions in (a) acetonitrile, (b) DMF, (c) pyridine, and (d) DMF: 0.5 M aniline in 1 M/L H_2SO_4 = 1 : 1. Solutions were deoxygenated by bubbling N_2 for 10 min before the experiment. The potential of WE was cycled in the range from −0.2 to 0.8–1.4 V versus SCE with a scan rate of 50 mV/sec by AMEL 7050 potentiostat (AMEL, Italy). Pt 0.5 mm wire was used as counterelectrode.

Table 1: Membrane compositions and deposition details.

	Ionophore, wt%	Additive, wt%	Film/solvent
I.a-d	Co(II)TATPP	—	EP/(a-d)[a]
II	Cu(II)TATPP	—	EP/(d)
III	Co(II)TATPP, 1.5%	TDACl, 1%	PVC/DOS
IV	Co(II)TATPP, 1.5%	—	PVC/DOS
V	Carb.Ion I, 2.7%	TDACl, 2%	PVC/DOS
VI	Carb.Ion IV, 3.5%	TDACl, 2%	PVC/DOS
VII	—	TDACl, 6%	PVC/DOS
VII	PANI	—	EP[b]

[a] See experimental section for details.
[b] Deposition from 0.5 M/L aniline solution in 1 M/L H_2SO_4.

Freshly prepared EP and solvent polymeric membrane sensors were soaked in 0.1 M/L $NaHCO_3$ at least for 24 hours before first measurement. The potentiometric responses of sensors have been studied in solutions of several salts in a range 10^{-7}–10^{-1} M/L. The known volumes of standard salts solutions were added to 0.1 M Tris-H_2SO_4 buffer pH 8.6 or distilled water (with simultaneous pH control). Three replica electrodes were studied with each membrane formulation. Sensor potentials were measured versus double-junction SCE reference electrode (AMEL, Italy) and recorded using high-impedance 8-channel potentiometer LiquiLab (Ecosens, Italy). Selectivity coefficients were calculated by the separate solution method (SSM) using EMF values measured in 0.01 M salt solutions and theoretical slope values [1].

2.3. Optical Measurements. UV-visible spectroscopic data were acquired with a Cary-50 Scan spectrophotometer.

The quartz and methacrylate cells 45 × 10 × 10 mm with a path length of 10 mm were used. 15 μL of the same membrane cocktails as used in the potentiometric measurements were deposited on glass slides (20 × 6 × 1 mm). After THF evaporation, a thin polymer film was left adhered to the glass slide. Absorption spectra of dry polymer films and those exposures for 10 min period in aqueous solutions of several salts of varied concentration were registered. In order to evaluate the absorption spectra of Co(II)- and Cu(II)TATPP electropolymers, they were electrochemically deposited over transparent the 15 × 7 × 1 mm indium tin oxide-modified glass slides (ITO, Aldrich) with a nominal resistance of 30–60 Ω/cm^2.

2.4. Plasma Measurements. Arterial blood samples were taken from 5 male subjects (3 healthy persons and 2 with respiratory acidosis, samples A, C). Blood plasma was isolated by centrifugation of fresh samples and following removal of suspended blood cells. Samples were analyzed few hours after collection. At least tree replicas were performed for each plasma sample during the same day. If not analyzed immediately, samples were stored at −20°C. Standard addition method was applied to detect bicarbonate ion content in samples [20]. For this 50 μL of plasma, sample has been dissolved in 50 mL of 1 mM/L NaCl ($E1$), and two consecutive 150 μL injections ($E2$, $E3$) of 0.01 M $NaHCO^3$ were performed. The concentrations of CO_3^{2-} and HCO_3^- ions were then evaluated on the base of $R = \Delta E3/\Delta E2$ ratio, solution pH, and dissociation constants of carbonic acid ($pK_1 = 6.4$, $pK_2 = 10.3$). For comparison, the amount bicarbonate in plasma samples was analyzed with GEM Premier 3000 blood analyzer (Instrumentation Laboratory, USA).

Sensor array was composed of 5 carbonate-selective electrodes and pH glass electrode. Prior to measurements in real plasma samples, array was calibrated in 25 model solutions mimicking human plasma composition. Each solution contained 4 salts; the salt concentration was similar to those in plasma and varied in the following range: 70–100 mM/L NaCl, 20–60 mM/L $NaHCO_3$, 1–8 mM/L Na_3PO_4, 1 mM/L NaSal; solutions pH was fixed in a range 7.2–7.4 by addition of 0.1 M/L HCl.

2.5. Data Analysis. Partial Least Square regression (PLS) method was applied to train multisensory array in artificial solutions mimicking human blood plasma samples and to correlate bicarbonate content determined commercial blood analyzer with multisensory array response. The autoscaling procedure was applied to the data. Since the number of measurements composing the dataset was not big enough to divide the dataset in a training and test set, a leave-one-out validation was applied. The Unscrambler v.9.1 (2004, CAMO PROSESS AS, Norway) was used for data treatment.

3. Results and Discussion

3.1. Electropolymerized Films of Co(II)- and Cu(II)TATPP. Porphyrin electropolymers based on polyaniline (PANI) are well studied. The electropolymerisation of mono-, bis-, tris- and tetra-2- or 4-aminophenyl substituted porphyrinates of various metals on Pt or GC WE has been previously reported by several authors [21–24]. Bettelheim et al. have found that the electropolymerisation of aminophenyl-substituted porphyrins occurs oxidatively via the *meso*-aniline rings in a head-to-tail fashion, the same way as aniline itself. The resulting material is in practice a polyaniline chain with bridged porphyrin units. Anion-selective electrodes, based on such a films, were reported to possess selectivity different from the Hofmeister selectivity series [25, 26]. Moreover, an inherent advantage of these electrodes is their stability and a prolonged lifetime due to the retention of the ionophore in the polymer film.

In the present study we have focused on the development and investigation of the potentiometric behavior of sensors based on Co(II)- and Cu(II)-tris-4-aminophenyl porphyrinates due to their known sensitivity towards hydrophilic anions [27]. First, an optimization of electropolymerisation conditions for deposition of poly-Co(II)TATPP films from four various solvents (see Section 2 for details) has been performed. No film formation on the Pt WE surface has occurred from acetonitrile, insulating yellow-colored poly-Co(II)TATPP films have formed from DMF and pyridine, while a conductive film growth has been detected from DMF/aniline solution (membrane I.d), Figure 1. In the latter case, a dominating PANI film formation process was accompanied by a partial Co(II)TATPP embedding in PANI film during the first 5 cycles. The cyclic voltammograms after first, fifth, and tenth potential scan during the electrodeposition of membrane I.d in the range from −0.2 to 1.5 V are shown in Figure 2. The oxidative wave at about 0.2 V may be attributed to the PANI emeraldine form formation; with growth of scan number this wave shifts to the more positive potential and covers the reversible peak at about 0.4 V corresponding to the reversible Co(II)/Co(III) one-electron redox process. The sharp anodic peaks at 0.65, 0.85, and 1.35 V evident during the first five scans are typical for oxidation of both aryl-substituted porphyrins and aniline [23]. A high capacitive background anodic current which appears in the range 0.3–1.1 V is probably caused by an incorporation to the PANI film either free SO_4^{2-} ions or negatively charged Co(II)TATPP/SO_4^{2-} complexes [28].

The incorporation of Co-TATPP in PANI backbone formed on the ITO glass electrodes was confirmed by the presence of Soret's band ($\lambda = 454$ nm), a typical signature of porphyrin aromatic ring, on UV-visible absorption spectra of membrane I.d, Figure 3. The broadening of Soret's band indicates a multilayer film formation, while the bathochromic shift of the peak maximum in polymeric film in the comparison to the fresh monomer solution in CH_2Cl_2 may be attributed to the axial coordination of porphyrin aminophenyl fragments (which in part remain nonoxidized during the electropolymerisation) on the central Co ions of the neighboring porphyrin units.

Potentiometric responses of poly-Co(II)TATPP electropolymerized membranes I.b–I.d deposited from DMF, pyridine, and DMF/aniline towards several anions have been studied. Membranes I.b and I.c did not show any

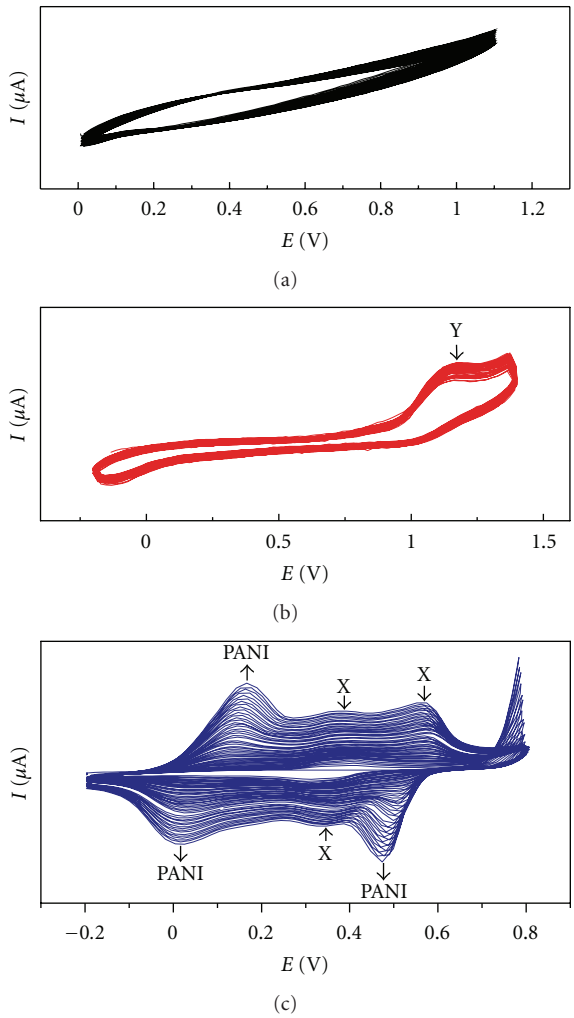


Figure 1: Cyclic voltammograms of PANI-Co(II)TATPP film electrodeposition on Pt WE from (a) acetonitrile; (b) DMF; (c) DMF: 0.5/L M aniline in 1 M/L H_2SO_4 = 1 : 1. The working and counterelectrodes were platinum, and the scan rate was 0.1 V/s. On figure X corresponds to incorporation of Co(II)TATPP in film; Y indicates the decrease of current and insulating film formation.

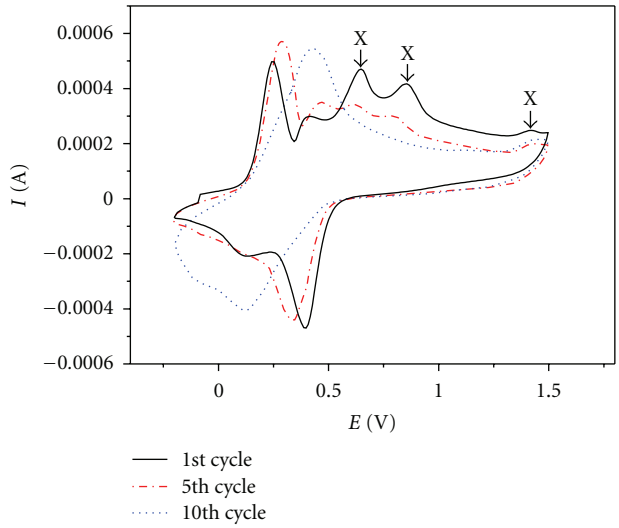


Figure 2: The details of PANI-Co(II)TATPP membrane I.d electropolymerisation from DMF/aniline solution. Peaks indicated as X show an incorporation of Co(II)TATPP in PANI film during first 5 cycles.

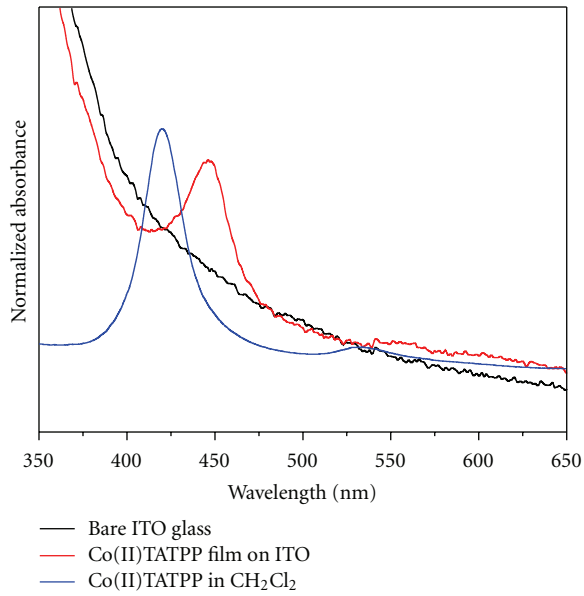


Figure 3: UV-visible absorption spectra of PANI-Co(II)TATPP electropolymer (membrane I.d) deposited on ITO glass slide. The spectra of Co(II)TATPP in CH_2Cl_2 and bare ITO glass are given for comparison.

significant response to all the tested anions probably due to the prevalence of insulating EP formation. Selectivity patterns significantly different from the Hofmeister series were detected for membrane I.d, as far for membrane II based on Cu(II)TATPP-doped PANI film, Figure 4. For both membranes, the highest response with a slope close to theoretical Nernstian was found towards CO_3^{2-} ions (27 and 28 mV/dec correspondingly). Strong interference influence of I^- and SCN^- ions (slopes of 56 and 59 mV/dec correspondingly) was also detected. Membrane VII (PANI) did not show any specific response to all studied anions and was strongly influenced by solution pH. In fact, the pH sensitivity of PANI films is well known, and several sensors for pH detection based on polyaniline have been previously reported [30, 31].

A high sensitivity of membranes I.d and II towards $NaHCO_3$ concentration change could be explained either by PH influence on Co(II)TATPP- and Cu(II)TATPP-doped PANI films or by selective complexation of bicarbonate/carbonate ions by metalloporphyrins. In fact, the growth of $NaHCO_3$ concentration increase the solution pH, and; hence, the correct determination of various forms of CO_2 (i.e., CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}) existing in analyzed sample requires either simultaneous pH control or the application of an appropriate buffer background [14].

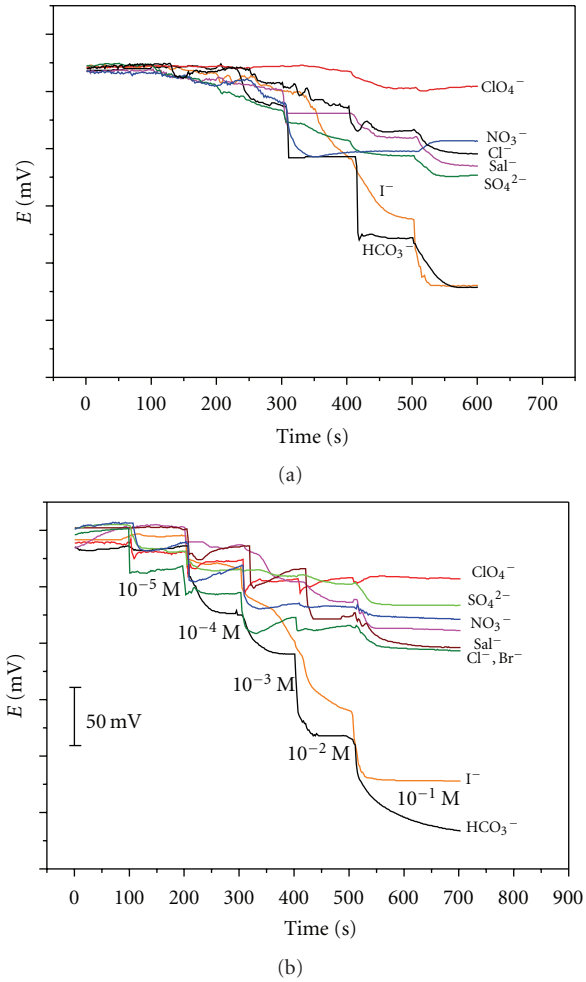


Figure 4: Potentiometric dynamic response of EP films towards several anions: (a) membrane I .d based on Co(II)TATPP and (b) membrane II based on Co(II)TATPP.

The pH response of membranes I.b–I.d, II, and VIII has been, hence, studied by stepwise addition of 1 M/L NaOH to the universal buffer (11.4 mM/L boric acid, 6.17 mM/L citric acid, 10 mM/L NaH_2PO_4, pH 2.75) and achieving the final solution pH 10. A relatively little effect of pH on electrodes with membranes I.b–I.d and II have been detected in a pH range from 6 to 10 (−9.1, −2.9, and −14.0 mV/pH correspondingly), while PANI membrane VIII has shown a significant pH response in the all examined range with a slope −41.2 mV/decade (data not shown). It can hence be assumed that Co(II)- and Cu(II)-5,10,15-tris(4-aminophenyl)-20-phenyl porphyrinates may selectively coordinate carbonate ions and are promising candidates as ionophores for carbonate-selective sensor development.

3.2. Potentiometric and Optical Study of Co(II)TATPP Ionophore Functioning Mechanism. In order to evolve the source of high sensitivity towards carbonate as far as elucidating the ionophore functioning mechanism, potentiometric and optical properties of solvent polymeric PVC/DOS membranes III and IV doped with Co(II)TATPP (see Table 1) have been studied and compared with membranes V and VI based on commercially available TFAP derivatives (carbonate ionophores I and IV) and membrane VII based on anion exchanger TDACl. During the sensors' preparation, we have faced the problem of a low Co(II)TATPP solubility in THF-dissolved PVC membrane cocktails. Such a low solubility can be attributed to the partial monomer self-aggregation occurring via axial coordination of porphyrin phenylamine substituents on the metallic centers of neighboring molecules. An addition of 7 wt% of pyridine to the membrane cocktail resulted in aggregate breakage and improved the ionophore solubility due to the prevalent axial coordination of pyridine. Membrane IV doped with 1.5 wt% of Co(II)TATPP ionophore without any lipophilic additive showed a partial anionic response towards several anions, while an addition of 1 wt% of anionic $TpClPB^-$ sites (data not shown) resulted in a cationic response with slopes 40–45 mV/decade towards all studied aqueous salt solutions. Such a behavior indicates the neutral carrier functioning mechanism of Co(II)TATPP ionophore. As well known, to stabilize potentiometric properties of neutral carrier-based membrane, an addition of cationic lipophilic sites is often required [1]. Moreover, basing on the amount of incorporated cationic sites, an assumption on possible stoichiometry of forming ionophore/primary ion complexes can be made [4]. It has been found that the ratio Co(II)TATPP/TDACl = 1.5 in membrane III gives the best performance and selectivity towards carbonate ions close to selectivity of TFAP-derivative-based membranes, Figure 5. A potentiometric response towards CO_3^{2-}-ions with a slope of 30.3 mV/decade close to a theoretical Nernstian has been found for membrane III in a range 3×10^{-6}–10^{-3} M/L at the distilled water background and 28.7 mV/decade in a range 3×10^{-5}–10^{-1} M for 0.1 M/L Tris-H_2SO_4 buffer pH 8.6. The fact of higher carbonate selectivity of EP membrane I.d should be noticed and will be discussed later.

The formation both of 1 : 1 and 2 : 1 adducts between metalloporphyrin and CO_3^{2-} ions in membrane phase may be supposed. UV-visible spectroscopy of thin films of membrane III deposited on glass slides and measured dry and in solutions of $NaHCO_3$ in 10^{-6}–10^{-2} M/L concentration range showed that three concurrent processes occur in a membrane phase, Figure 6. First, the decrease of absorbance intensity at 444 nm and the growth of 420 nm absorbance peak indicate a partial substitution of pyridine initially coordinated on metal center [32] by primary anion (red shifted 444 nm peak) followed then by the liberation of Co(II)TATPP monomers in membrane phase (formation of 420 nm peak) and finally by formation of hydroxide-/or carbonate ion-bridged dimers (appearance and growth of blue shifted 367 nm peak) [33]. The comparison of selectivity patterns observed by the optical transduction in solutions of $NaHCO_3$, NaCl, $NaNO_3$, and NaSCN and those obtained potentiometrically showed the high ability of carbonate ions to shift the dimer-monomeric equilibrium within the membrane phase. Thus, it has been found that carbonate ions in higher degree than

Table 2: Results of developed sensors application for bicarbonate detection in plasma*.

	HCO_3^- content, mM/L			
	Co(II)TATPP		Carbonate ionophore I, membrane VI	Blood analyzer
	Membrane I.d	Membrane III		
A	48.4 ± 3.7	52.4 ± 4.2	48.3 ± 2.2	51.4
B	31.9 ± 2.3	—	29.7 ± 1.7	31.8
C	—	—	42.1 ± 1.5	42.8
D	—	20.8 ± 2.2	—	21.2
E	30.7 ± 4.6	25.2 ± 4.4	30.3 ± 2.2	28.9

* Data reprinted from [29] with the author's permission.

other studied anions are responsible for a fast breakage of Co(II)TATPP-pyridine complexes and following partial formation of ionophore dimers in membrane phase.

On the contrary to PVC/DOS solvent polymeric membranes, no ionophore dimerization occurs in electropolymerized membrane I.d due to the rigid fixation of Co(II)TATPP inside PANI matrix. The only process that takes place in EP film is an axial coordination of target primary ion on metal center of porphyrin ionophore. This fact may explain the higher carbonate selectivity of EP membranes I.d and II over the solvent polymeric PVC membrane III.

3.3. An Application of Developed Co(II)- and Cu(II)TATPP-Based Sensors for Human Plasma Analysis. Due to the fact of elevated CO_3^{2-} selectivity, an attempt to apply Co(II)TATPP-based sensors with membranes I.d and III for detection of carbonate ions and following evaluation of HCO_3^- content in human blood plasma have been performed. The results of the bicarbonate content determination in 5 human plasma samples are given in Table 2. A good correlation between bicarbonate content evaluated with Co(II)TATPP-based membranes I.d and III, TFAP derivative-based membrane VI, and commercial blood analyzer has been achieved.

The effectiveness of single sensor application for bicarbonate content analysis in human plasma has been compared to the multisensory approach. For this purpose sensor array composed of 5 carbonate-selective sensors with membranes I.d, II, III, VI, and VIII, and pH electrode has been utilized. Before application in plasma, array was calibrated in artificial solutions mimicking human plasma composition (see Section 2 for details). The potential of each sensor was measured in every calibration solution at least in 3 replicates, so the final dataset was composed of $6*25*3 = 450$ readings. A good PLS correlation between the array response and real amount of HCO_3^- ions detected with blood analyzer (slopes of $S_{cal} = 0.949$ and $S_{val} = 0.941$ and correlation coefficients $R_{cal} = 0.974$ and $R_{val} = 0.969$ for calibration and full cross-validation correspondingly) was received, while no influence of salicylate and phosphates presence on sensors response was detected, Figure 7.

From PLS1 model the concentration of HCO_3^- was then evaluated as 50.2 ± 1.5 mM/L and 30.2 ± 1.1 mM/L for plasma samples A and E correspondingly. Hence, the application of

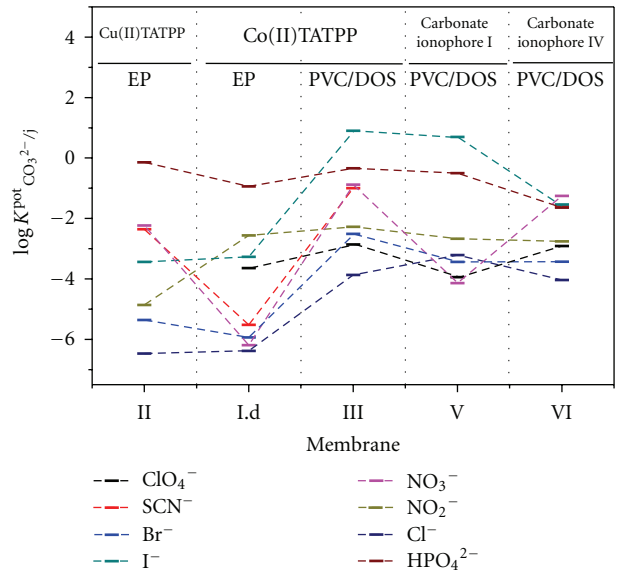


Figure 5: The comparison of the selectivity coefficients of electropolymerized (EP) and solvent polymeric membranes (PVC/DOS) containing Co(II)- and Cu(II)TATPP and TFAP derivatives (commercially available carbonate ionophore I and IV). Selectivity coefficients were evaluated by SSM method, the theoretical Nernstian slope of 29 mV/pCO_3 was used in calculations.

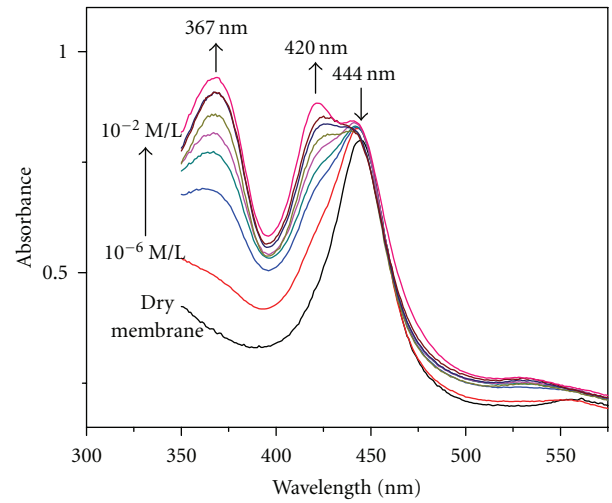


Figure 6: UV-visible spectra of dry membrane III and soaked in 10^{-6}–10^{-2} M/L solutions of $NaHCO_3$.

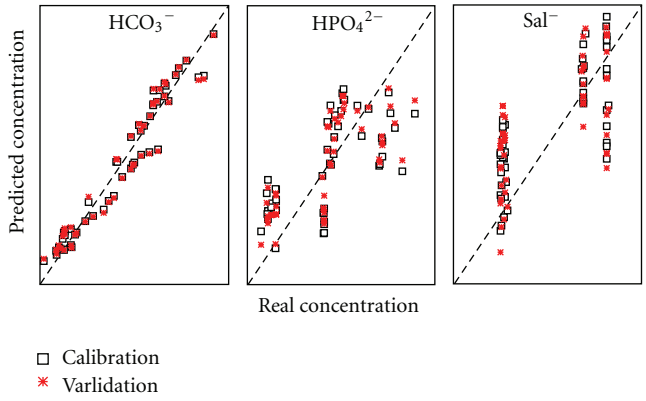


Figure 7: The results of PLS model calibration and validation in multicomponent solutions mimicking plasma for bicarbonate, hydrophosphate, and salicylate ion content detection.

sensor array has permitted to decrease the relative error of HCO_3^- content evaluation in human plasma in comparison to the single ISEs.

4. Conclusions

Newly developed sensors prepared by formation of electropolymerized PANI film doped with 5,10,15-tris(4-aminophenyl)-20-phenyl porphyrinates of Co(II) and Cu(II) have showed a high capability to detect CO_3^{2-} and HCO_3^- ion content and were effective for physiological sample analysis. An inherent advantage of these electrodes is a prolonged lifetime due to the retention of ionophore in the polymeric film and a possibility of an easy miniaturization, which is fundamental when the small sample volume is available or *in vivo* measurements are required.

Acknowledgments

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