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The influence of CO_2 on ISFETs with polymer membranes and characterization of a carbonate ion sensor

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ABSTRACT

The influence of CO_2 and acetic acid on the response of ISFET sensors with PVC and photocured polyurethane polymer membranes with valinomycin as an ionophore was assessed. Experimental results show that the presence of these compounds has no effect on sensors parameters even after prolonged soaking in a water solution. Using a photocured polyurethane polymer as an ion-selective membrane matrix for an ISFET, a carbonate ion sensor was developed with hexyl-p-trifluoroacetylbenzoate (HE) as an ionophore. Effect of cationic and anionic lipophilic additives on the sensors response was studied. Sensors with the optimized membrane composition based on HE (7.9%, w/w) and tridodecylmethylammonium chloride (5.7%, w/w) show sensitivity of 27–30 mV per decade of carbonate ion concentration, sufficient selectivity in front of chloride ions, and a lifetime of 3–5 months.

1. Introduction

There exists a necessity of a durable carbonate sensor for biomedical applications and in clinical analysis. Moreover, carbonates play an important role in a food industry [1] and their determination is important in environmental analysis [2,3] as they are forming part of carbon dioxide cycle in nature.

Published results on a carbonate sensor development may be divided in two groups. In the first group there are different Severinghaus-type electrodes used to measure the dissolved CO_2 gas concentration with pH sensitive ion-selective electrodes [4,5] or pH-ISFET as a sensitive element [6,7]. In the second group are situated carbonate selective sensors with trifluoreacetophenone derivatives as neutral ionophores [8–11]. Both groups have their advantages and disadvantages. In the first case very long response time that depends on the diffusion of the CO_2 molecules through the gas permeable membrane and some technological difficulties of production and miniaturisation of this type of sensors can be mentioned [5,12,13]. Direct carbonate ion determination with ion selective sensors is preferable. New ionophores based on trifluoreacetophenone derivatives with improved selectivity for carbonate have been reported [10,11,14], but in many cases their selectivity, especially in front of lipophilic anions like acetate or salicylate, is not very high. To enhance the selectivity putting some additional membrane is recommended to eliminate interfering ions [8,15] or to shift the pH of the analyzed solution to more basic values in order to increase the concentration of carbonate ions [16,17]. Another drawback of carbonate sensors is that practically all of them have very limited lifetime, between 2 and 5 days [12,15] and 1 month [18].

Using ISFET-based sensors [19] with ion-selective membranes, it is possible to achieve miniaturization and apply different sensors in a line in an analyzer to determine concentrations of various physiologically important ions in the same small sample of blood [20] or to use them as a base of sensor arrays in a multi-component liquid analyzers, the so-called Electronic Tongues [21,22]. However, response of a carbonate sensitive ISFET with a polymer membrane may be affected by alternative processes. Starting from the paper of Fogt et al. [23] published in 1985, it is universally [24] assumed that ISFETs with a polymer membrane deposited directly over a silicon oxide or silicon nitride gate inevitably suffer from the interference caused by penetration of the carbon dioxide and organic acids from a water solution to the membrane organic phase. Though results on the CO_2 and organic acids response of ISFETs with plasticized PVC and silicon rubber membranes presented in the article [23] are claimed to be preliminary, no further publication by the same authors appeared to confirm the invulnerability of the published data. The postulated mechanism of this response involves diffusion of the CO_2 or protonated organic acids through the polymer membrane into the gate region of an ISFET with posterior dissociation within an "ill-defined" hydrated layer. Subsequent changes of the pH in this layer affect the gate potential of an ISFET due to the intrinsic pH-sensitivity of an oxide or nitride gate material. After this first publication several other authors tried to confirm

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Table 1
Different membrane compositions used to prepare CO_3^{2-}-ISFET and the response of corresponding sensors.

Composition	M1	M2	M3	M4	M5
Ionophore, (HE), % (w/w)	5.8	2.6	7.7	2.1	7.9
Additives, mol%	TDA_2CO_3 5.6, KTClPhB 10.8	ETH500 25	ETH500 10, TDMACl 20	ETH500, 10, TDMACl 40	TDMACl 40
Slope (mV/pa) in pure $NaHCO_3$	26–28 cationic influence	23–25 cationic influence	27–29	28–30	29–30
Slope (mV/pa) in 0.05 M TRIS–SO_4–$NaHCO_3$, pH 7.4	No response	No response	28–29	28–30	29–30
Slope (mV/pa) in 0.1M TRIS–SO_4–$NaHCO_3$, pH 8.7	No response	No response	No response	28–30	27–29

this observation and to find a suitable remedy to prevent the mentioned above effect in polymer gate ISFETs, but published data are contradictory. Reported in ref. [25] potassium ISFETs with PVC membrane deposited directly over an ISFET's Si_3N_4 gate showed no CO_2 interference in the Ringer solution saturated with air containing 10% of the CO_2. Harrison and co-workers [26,27] studied potassium sensitive PVC membranes with dioctyl adipate and valinomycin deposited onto Si/SiO_2 and $Si/SiO_2/Si_3N_4$ structures and, measuring the open circuit potential of such structures, confirmed the effect of benzoic, carbonic and ascorbic acids at pH 4.5 on the device potential at a constant potassium concentration level. The PVC membrane spectroscopic data, impedance analysis and capacitance–voltage characterization of semiconductor structures with the membrane [26] confirmed the penetration of benzoic acid into the membrane phase and its influence on the bulk membrane properties. It was suggested to prevent this type of interferences using an Ag/AgCl layer separating the membrane and an ISFET gate [26,27]. Unfortunately this introduces another ill-defined interface between the membrane and the silver/silver chloride layer. Moreover, this device is equal to a polymer membrane ion-selective electrode with a solid inner contact and in this configuration does not require a field-effect transistor at all.

Reinhoudt and co-workers in 1986 patented [28] and in 1990 published [29] their approach to the solution of the CO_2 interference in polymer membrane ISFETs consisting of the deposition over an ISFET gate of an intermediate covalently anchored polyHEMA hydrogel layer equilibrated with a 0.1 M potassium chloride solution buffered at pH 4. They have shown that saturation of a 0.1 KCl solution with the gaseous CO_2 has no effect on an ISFET with the intermediate layer and a PVC-based potassium sensitive membrane. The effect of organic acids was not studied. This approach was used by the same research group in designing other ISFETs with PVC membranes [30] and was equally transferred to modified polysiloxane membranes [31–33], though, to our knowledge, no experimental data on the effect of the CO_2 on ISFETs with such membranes was presented.

Similar strategy was used in the work [34] where a 20% dextran gel with a fixed ion concentration and buffered at pH 4 or 8 was applied as an intermediate layer between an ISFET gate and a potassium sensitive PVC membrane. It is shown that at pH 8 the intermediate layer does not prevent the interference from the CO_2. At pH 4 the effect of the CO_2 disappears while the presence of benzoic, ascorbic and acetic acids in a test solution at pH close to 4 still affects the sensor response.

However, as it was noted by Janata [35] this strategy will work only in the case when the osmolality of the internal layer is equal to that of the sample solution. If not, even a relatively small deviation from the osmotic equilibrium will cause water molecules transport across the polymer membrane which will result in drift and mechanical failure of this structure.Another proposed method for eliminating the CO_2 sensitivity of polymer membrane coated ISFETs [36] implies the usage of an alumosilicate glass intermediate layer separating the membrane and the gate pH sensitive insulator. The reported CO_2 sensitivity of such device [36] seems to be a little bit strange, because the major response to the CO_2 presence of a potassium sensitive ISFET occurs not in acidic solutions but at neutral pH, where bicarbonate mainly exists in HCO_3^- form.

Presented published results show that the CO_2 and organic acids easily penetrate through plasticized PVC and, in case of ISFETs with this kind of membranes, affect the stability at the membrane/ISFET gate interface. As demonstrated by Li and Harrison [37] a water profile exists in these hydrophobic polymeric membranes, which is time-dependent and under extreme circumstances this may lead to phase separation. In case of ISFETs this may provoke formation of water droplets at the membrane/insulator interface causing the loss of adhesion to the solid support and/or encapsulation. In cases when instead of PVC other polymer materials, like silicone resins [7,38], Urushi polymer [39], polyacrylates [40] and others [41] are used as membrane matrices, the information about this type of interference is limited or does not exist.

The aim of this work is to test the effect of the CO_2 and organic acids on ISFET with photocured polyurethane membranes that we have reported previously [21,22] and with the help of obtained results investigate a carbonate selective ISFET with membrane containing hexyl-p-trifluoroacetylbenzoate as an ionophore [42].

2. Experimental

2.1. Reagents

Commercial potassium ionophore valinomycin, plasticizer bis(2-ethylhexil)sebacate (DOS), potassium tetrakis(p-chlorophenyl)borate (K-TpClPB), tridodecylmethylammonium chloride (TDMACl), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) and PVC were purchased from Fluka. Aliphatic urethane diacrylate (oligomer Ebecryl 270) and cross-linker hexanediol diacrylate (HDDA) were from UCB Chemicals. Photoinitiator 2,2′-dimethoxyphenylacetophenone (IRG 651) was from Ciba-Geigy. Hexyl-p-trifluoroacetylbenzoate (HE) and tetradecylammonium carbonate salt (TDA_2CO_3) was synthesized in the laboratory as presented elsewhere [43].

All other chemicals were of analytical reagent grade. Standard solutions were prepared with deionized water.

2.2. Preparation of ion-selective membranes

Photocurable membrane composition was prepared as presented earlier [21]. First the main polymer composition was mixed putting together the aliphatic urethane diacrylate oligomer, reactive diluent HDDA and photoinitiator Irgacure 651 in a 81:17:2 (w/w/w) ratio. Then 0.3 g of the main polymer composition was dissolved in 0.2 ml of tetrahydrofuran and to this solution plasticizer, ionophore and lipophilic salt were added. The final membrane composition for potassium sensor is formed by the main polymer composition (59%), the plasticizer (38.5%), valinomycin (2%) and K-TpClPB (0.5%). The studied compositions of carbonate ion selective membranes are given in Table 1. The mixture was thoroughly stirred in an ultrasonic bath until homogeneous and then left for several hours to evaporate the solvent.

PVC-based membranes were prepared in a conventional manner [44] by dissolving 165 mg of PVC powder in 1.5 ml of THF. To this solution valinomycin, plasticizer and K-TpClPB were added to obtain final concentrations of 2%, 64.5% and 0.5% respectively.

2.3. *Sensor fabrication*

Sensors were made using n-channel ISFETs with SiO_2 gate insulator. After scribing and wire bonding, ISFETs were encapsulated with photocurable polymer composition, as presented elsewhere [45]. To enhance the adhesion of the acrylated urethane polymer ISFET devices were preliminarily silylated by exposure to a 10% (v/v) (methacryloxy)propyltrimetoxysilane solution in methanol with a subsequent heat treatment during 1 h under 100 °C in an oven. The membrane composition was then applied by a microsyringe into the well formed by encapsulated layer over the gate region of an ISFET and was exposed to UV using standard mask aligner equipment with irradiance of $22\,\text{mW} \times \text{cm}^{-2}$ at the wavelength of 365 nm. Typical exposure time was 15 s for the K-membrane and 15–30 s for carbonate (see Table 1). This resulted in the membrane formation with the thickness of 150–200 μm.

A mixture for PVC-based membranes was applied by a syringe into the well of an encapsulated chip in one single step and devices were left for a night in a closed vessel to evaporate the solvent slowly. The estimated thickness of formed membranes was 200–300 μm.

2.4. *Evaluation of chemical response*

ISFET devices were measured in a conventional manner in a constant drain current mode ($I_D = 100\,\mu\text{A}$, $V_D = 0.5\,\text{V}$) using a computer controlled experimental set-up. A double-junction Ag/AgCl reference electrode (Orion 90-02) was used as an external electrode. To prevent interference due to leaching of the solution the salt bridge of the reference electrode was filled with a 0.1 M solution of lithium acetate in case of the K-sensor and saturated KCl solution in case of the carbonate sensor. Solution pH values were controlled by a standard pH-meter with a glass electrode.

Compositions of test solutions are presented further in the text. The single-ion activity of potassium ion in solutions with different ion strength was calculated according to the Debye–Hückel theory with equations and coefficients given elsewhere [46]. To calculate the activity of the carbonate ion from the known concentration of sodium bicarbonate, solution pH value and its ionic strength we used coefficients of the polynomials given in [47].

3. Results and discussion

3.1. *Response of silylated SiO_2 gate ISFET to pH*

Taking into consideration that surface modification of silicon dioxide with silanes may affect their pH sensitivity [48], bare SiO_2—gate ISFETs and ISFETs subjected to treatment with (methacryloxy)propyltrimetoxysilane were tested for their pH-response. Experimental results obtained in 0.05 M TRIS buffer titrated with HCl are presented in Fig. 1. Both ISFETs show nearly identical response with 30 mV/pH slope in neutral and basic pH regions, typical for SiO_2—gate sensors [49].

3.2. *K-ISFET response to pH*

First of all, potassium ion response has been tested for both types of sensors with photocurable and PVC membranes in pure solutions of KCl. The slope and the limit of detection determined were 57–59 mV per decade and 3×10^{-6} M for ISFETs with PVC membranes and 56–58 mV per decade and 1×10^{-5} M for ISFETs with polyurethane membranes, respectively.

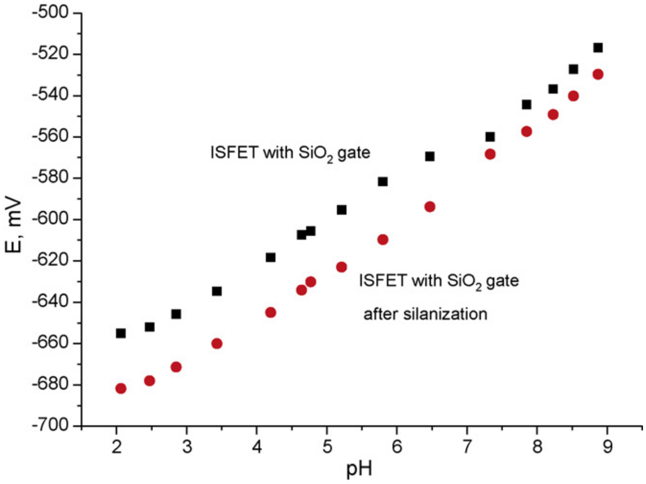

Fig. 1. pH response of SiO_2 gate ISFETs before (squares) and after silanisation (circles).

The influence of the solution pH changes on ISFETs response was tested in a 5×10^{-2} M TRIS buffer containing 5×10^{-3} M KCl. The solution pH was changed by adding drops of a solution containing 1 M HCl and 5×10^{-3} M KCl. Results presented in Fig. 2 show that PVC as well as polyurethane membrane ISFETs do not have any pH response in the tested pH range.

3.3. *K-ISFET response to CO_2 and acetate ion*

The influence of CO_2 on ISFETs response was measured in a citrate pH buffer prepared from a 0.1 M sodium citrate solution to which a 1 M HCl was added until pH 4.35. This stock solution also contained 5×10^{-3} M KCl as a constant potassium ion background. To test the effect of CO_2 fixed volumes of a 0.2 M $NaHCO_3$ solution containing 5×10^{-3} M KCl were added to a 50 ml of the stock solution under stirring, while sensors output signal was measured in time. The CO_2 concentration was calculated at each point. First measurements performed on ISFETs with both types of polymer membranes showed that CO_2 has no effect on sensor response. To check whether possible penetration of water into the membrane

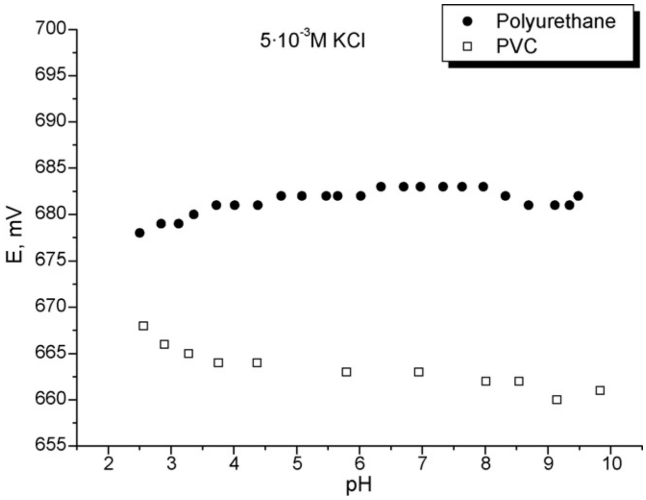

Fig. 2. pH response of PVC (square) and polyurethane (circle) gate ISFETs measured in a 5×10^{-3} M KCl background solution.

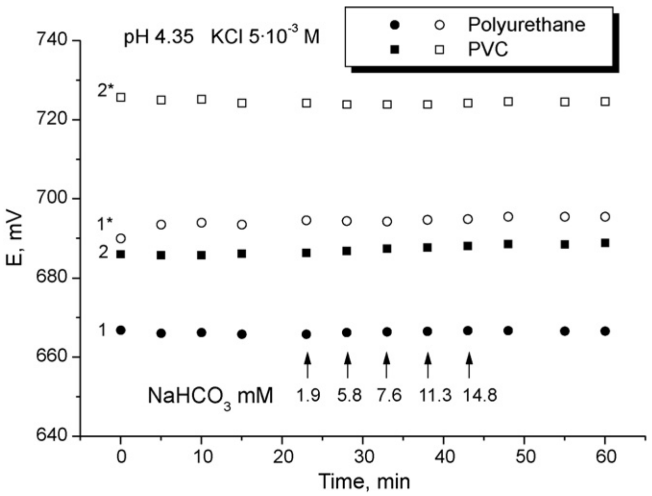

Fig. 3. The influence of CO_2 on the potential of ISFETs with photocured polyurethane (1) and PVC (2) membranes. 1* and 2*: Response of the same ISFETs in the presence of CO_2 after keeping them in 10^{-3} M KCl solution during 72 h.

phase, which may occur with time, affects sensors characteristics, sensors have been left in a 10^{-3} M KCl solution for 72 h. The experiment was repeated in the same manner. Fig. 3 presents results of both experiments from which it follows that ISFETs with PVC and polyurethane membranes show no response to a CO_2 presence in the solution.

The same stock citrate buffer solution was used as a background to test ISFETs response to acetate ion. In this case a 1 M sodium acetate solution containing 5×10^{-3} M KCl was added in small fixed volumes to cover the acetate ion concentration range from 4.0 to 131.9 mM as in experiments of Fogt et al. [23]. No response was registered in case of ISFETs with PVC, as well as with photocured polyurethane membranes.

Performed experiments showed that the presence of CO_2 and acetate ions in test solutions has no effect on studied ISFET sensors. It means that no water layer is formed at the membrane/dielectric interface where acidification, affecting an ISFET signal, may occur due to penetration of CO_2 or acetic acid. This may be attributed to technological peculiarities of the sensor design, when the membrane composition is deposited into a well formed by a polymer encapsulating layer which prevents possible lateral attack of water at the membrane/insulator interface. It also should be mentioned that adhesion of photocured polyurethane membranes to the silylated surface of silicon dioxide is very good.

The absence of the above mentioned effect permitted us to use the polyurethane-based polymer matrix for preparation of carbonate-selective ISFET sensors.

3.4. *Carbonate-selective ISFET*

Continuing the study begun earlier [42], along with an equimolar mixture of cationic (K-TpClPB) and anionic (TDMACl or TDA_2CO_3) lipophilic additives (membrane composition M1, Table 1) we also used a lipophilic salt of tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) (membrane composition M2). As it follows from data presented in Table 1, sensors with both membrane compositions showed no response for carbonate ions in solutions with TRIS–SO_4 buffer background. In pure bicarbonate solutions with concentrations higher than 10^{-3} M ($10^{-4.5}$ M of ${CO_3}^{2-}$) the cationic influence of sodium ions on the sensor response occurs. This can be explained as follows [50]. When the concentration of the anionic additive is low relative to the ionophore such membranes exhibit little or no response to carbonate in TRIS–SO_4 buffer and usually show sub-Nernstian response in water background solutions. Taking into consideration the high association constant of interaction between the carbonate ion and the ionophore, we may say that cationic response indicates overloading of these membranes with negatively charged species even at low carbonate levels in the sample. Thus, a high constant concentration of $TRIS^+$ in the background buffer in our experiments apparently negates the anionic response of these membranes. However, the use of a pH buffer is a requirement in this case because all carbonate selective membranes with trifluoreacetophenone derivatives as neutral ionophores have low selectivity in front of hydroxide ions [51] and to exclude this interference pH of calibration and test solutions must be fixed.

Increasing the ratio of lipophilic additives (TDMACl) to ionophore concentration from 10 molar percent (membrane M2) to 20 molar percent (membrane M3) results in appearance of carbonate response in 0.05 M TRIS–SO_4 buffer solutions (pH 7.4). For membrane composition M4 with 40 molar percent of TDMACl it was possible to calibrate carbonate selective ISFETs in 0.1 M TRIS–SO_4 solutions (pH 8.7).

Comparing chemical response of sensors with membrane compositions M1–M4 we can see that introduction of equimolar mixture of cationic and anionic additives (or some compounds like ETH 500) is senseless as it does not permit to enhance the selectivity. Moreover, sensors M1–M3 show no response in TRIS buffer solutions with sufficient buffer capacity. Only introduction of a large amount of TDMACl (composition M4) improves the situation.

The idea of introduction of equimolar mixture of cationic and anionic additives was originally advanced by Smirnova [52] who showed that incorporation of small amounts of anionic sites inside the anion-selective membrane, e.g., carbonate-selective, leads to an increase of carbonate selectivity in the presence of lipophilic anions. However, in the cited work selectivity coefficients for anion-selective membranes were determined by separate solutions method without any buffer and these results may be not quite correct. Later Grekovich and Mikhelson [53] showed that for carbonate and phosphate ion-selective membranes with low concentration of quaternary ammonium sites none of these ions may be regarded as potential-determining and the sensors actually respond to OH^- ion.

Typically ionophore content in ion-selective membranes is within 1–2% (w/w). However, in the initially proposed carbonate ion-selective membrane electrodes [51,54] trifluoroacetyl-p-butylbenzene was used as a plasticizer and some of the reported membrane compositions [8,50] are loaded with up to 25–30% of trifluoroacetophenone derivatives. Taking this into account we studied membrane composition with 8% of the ionophore and 40 molar percent of the lipophilic salt (M5, Table 1). Carbonate-selective ISFETs with this membrane maintained their response during 3 months of constant contact with solution of sodium bicarbonate in a 0.1 M TRIS–SO_4 (pH 8.7) buffer (Fig. 4). After this time the slope of the calibration curves goes down from 27 to 29 mV/pa to 17–20 mV/pa. This may be explained by the fact that most of trifluoroacetophenones tend to become slowly hydrated. However, partial reactivation of the sensors response is possible to achieve by storing them in hydrochloric acid for several hours [18]. In our experiments to restore the sensors response we kept carbonate selective ISFETs in 0.1 M HCl during 4 h with following reconditioning in 0.1 M sodium bicarbonate solutions. After that the sensors response to carbonate ions was completely restored with the sensitivity back to their original value (27–29 mV/pa) and sensors maintained their parameters during next 2 months. Thus, the total lifetime of sensors with this membrane composition may be considered as 5 months, which is much higher than reported for other carbonate-selective sensors.

The selectivity of these membranes permits to measure carbonate concentration in the presence of chloride ions in maximal

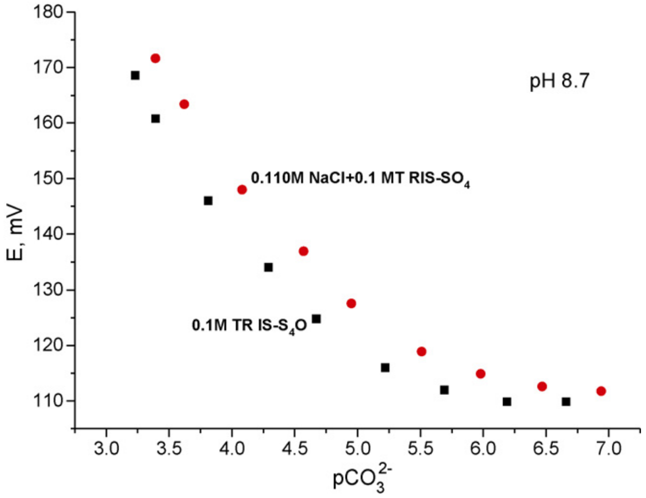

Fig. 4. Calibration curves for carbonate selective ISFET in 0.1 M TRIS–SO_4 solution (squares) and in the presence of 0.11 M of chloride ion (circles).

physiological concentration (110 mM, Fig. 4), but unfortunately under therapeutic concentration of salicylate ions (0.15–2 mM) the slope of the calibration curve decreases till 14 mV/pa.

4. Conclusions

Presented results show that presence of CO_2 or acetic acid in test solutions has no effect on the sensors' response and stability in case of studied ISFET sensors with polymeric membranes based on traditional PVC and photocured polyurethane. This effect was not present even after prolonged contact with solutions that might cause penetration of water into the membrane phase. We interpret these results as indicating that studied membranes have good adhesion to the surface of the ISFET gate dielectric, so that no water layer is formed at the membrane/dielectric interface where acidification may occur due to penetration of CO_2 or acetic acid.

This permitted us to study the possibility of developing an ISFET-based carbonate ion selective sensor with polyurethane membrane and traditional carbonate-selective neutral carrier ionophore hexyl-p-trifluoroacetylbenzoate. Different membrane compositions varying in the amount of cationic and anionic lipophilic additives were studied. It was found that it is not reasonable to introduce an equimolar mixture of cationic and anionic lipophilic additives as sensors with these membranes have no carbonate ion response in solutions with TRIS pH buffer as a background. The optimal membrane composition requires only two components: 7.9% (w/w) of the ionophore and 40 mol% of the lipophilic salt TDMACl, to be added to the polymer matrix. ISFET sensors with this membrane composition show stable and reproducible response to carbonate ions with sufficient selectivity in front of chloride ions with the lifetime of 3–5 months.

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