PVC-based Ion-Selective Electrodes with a silicon rubber outer coating with improved analytical performance

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ABSTRACT: An outer layer of silicone rubber (SR) was applied on top of a poly(vinyl chloride) (PVC) based K^+-selective membrane in a solid-contact ion-selective electrode (SC-ISE). The influence of the outer SR coating on the analytical performance of the SC-ISE was studied. The presence of the SR coating did not affect the selectivity of the SC-ISE, indicating that the plasticizer, ionophore and lipophilic anion are distributed into the SR layer during electrode conditioning. Interestingly, the reproducibility of the standard potential of the conditioned SC-ISE was significantly improved from $E^0 \pm 35.3$ mV to $E^0 \pm 3.5$ mV simply by adding the SR coating on top of the plasticized PVC based K^+-selective membrane. Moreover, the adsorption of bovine serum albumin (BSA) was significantly reduced at the SR coated ion-selective membrane. Thus, the addition of a SR coating on a plasticized PVC ion-selective membrane seems to be a feasible method to improve the analytical performance and to reduce the biofouling of potentiometric ion sensors.

Ion-selective membranes (ISMs) based on plasticized poly(vinyl chloride) (PVC) are commonly applied in potentiometric ion-selective electrodes (ISEs) and selective optodes.[1–3] PVC-based ISMs may, however, suffer from leaching of plasticizer,[4,5] ionophore[6] and other additives[7] from the ISM to the solution phase. This in turn influences the overall potential response and lifetime of the sensor. Furthermore, water from the solution phase can enter into the ISM. Thus, in the case of solid-contact ion-selective electrodes (SC-ISEs), a water layer formed beneath the plasticized PVC based ISEs is considered to be one of the reasons of their potential drift.[5,8–10]

Several alternative membrane matrices have been used for the fabrication of ISEs, including silicon rubber (SR).[11,12] One advantage of SR is its excellent adhesion to various substrates.[13] Moreover, slow diffusion of ions in the SR matrix may help to retain the membrane components and to slow down the transport of water in the ion-selective membrane, thereby extending the life time of the ion sensors.[14] Additionally, SR was proven to show anti-biofouling/biofouling-release properties,[15,16] which could benefit the performance of ISEs when measurements are performed in clinical and environmental samples.[17,18] On the other hand, the utilization of SR as the matrix material for ISM fabrication was hampered by poor solubility of ionophores in the SR matrix.[19] Therefore, the composites of PVC and SR based membranes were developed and investigated in order to diminish ion diffusion in ISMs and at the same time to maintain the solubility of all membrane components. Furthermore, incorporating SR into the PVC membrane was found to increase the adhesion of membranes to the electrodes surface, and prolong significantly the lifetime of the electrodes.[20] An alternative approach to improve the performance of ISEs is to employ asymmetric or layered membranes.[21–23] Asymmetric cellulose triacetate membranes were employed to reduce the interference from salicylate on chloride-ISEs,[21] while bilayers of polyacrylate membranes were explored to lower the detection limit of K^+-ISEs.[23]

SC-ISEs using electrically conductive polymers (ECPs) as the solid contact often show some potential drift that may be caused by the sensitivities of ECPs to pH, O_2, CO_2, temperature, light[24,25] or by the water uptake of PVC based ISMs.[26–28] In order to improve the reproducibility of the standard potential (E^0) of SC-ISEs, different methods have been investigated. For example, hydrophobic poly(3-octylthiophene) and Ca^{2+}-poly(methyl methacrylate): poly(n-decyl methacrylate) based polymeric membrane matrix improved the reproducibility of standard potential to $E^0 \pm 6.7$ mV.[29] Electrochemical pre-polarization of a polyazulene solid contact before the deposition of the PVC-based ISM reduced the E^0 variation of four identical ISEs to $E^0 \pm 7.9$ mV.[30] The E^0 was also adjusted by electrochemical polarization of the SC-ISE and by short-circuiting of the SC-ISE with a reference electrode immersed in electrolyte solution.[31,32] Remarkably, the standard deviations of the standard potential of ISEs were reduced to less than 1 mV by using redox buffer species, such as cobalt (II/III)[24,33,34] and nanoclusters^0/nanocluster$^+$ in the solid contact.[35] Furthermore, it was reported that the selection of Au as the electronic contact exhibited a better reproducibility of the standard potential than glassy carbon substrates.[36] However, so far stabilization of E^0 by modifying the outer layer of the ion-selective membrane has not been reported.

In the present work we propose an alternative way to improve the stability of the standard potential of SC-ISEs by adding an outer layer of silicone rubber (SR) onto the plasticized PVC-based ISM. The effect of SR on the adsorption of bovine serum albumin at the electrode surface was studied as well.

EXPERIMENTAL

Chemicals. High molecular weight PVC, bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), hydrogen ionophore I (tridecylmethyl amine, TDA), potassium tetrakis(p-chlorophenyl)borate (KTpClPB), potassium ionophore I (valinomycin) and tetrahydrofuran (THF), all of selectophore grade, were purchased from Sigma-Aldrich. Room temperature vulcanizing silicone rubber (RTV 3140) was obtained from Dow Corning. PSS (Poly(sodium 4-styrenesulfonate), Mw ~70,000), EDOT (3,4-ethylenedioxythiophene, >97%), BSA (bovine serum albumin) and PBS (phosphate buffer saline) tablets were purchased from Sigma-Aldrich and used as received. Buffer solutions of pH 4, 7, and 10 were obtained from Oy FF-chemicals Ab. All aqueous solutions were prepared using deionized water (18.2 MΩ cm) obtained from ELGA ultra-pure water system.

Electrodeposition of PEDOT(PSS). Glassy carbon (GC) electrodes were used as electronic contact and substrate for preparation of ISEs. The GC electrodes were polished on a soft mesh using 0.3 µm Al_2O_3, after which the electrodes were rinsed with ultra-pure water. Electrodeposition of PEDOT(PSS) onto polished GC electrodes was carried out using an AUTOLAB General Purpose Electrochemical System (GPES). The electropolymerization was performed in a three electrode cell containing EDOT (0.01 M) and NaPSS (0.1 M) aqueous solution.[37] The GC electrode was used as working electrode (area 0.07 cm^2), a GC rod was used as counter electrode, and a single junction Ag/AgCl/3 M KCl served as reference electrode. A constant current of 0.014 mA was passed through the working electrode for a 714 s.[38] After electropolymerization, the GC/PEDOT(PSS) electrodes were rinsed with ultra-pure water and dried overnight in air.

SC-ISEs preparation. Three different membrane cocktail solutions were prepared with the following compositions: (i) 32.9 wt% PVC and 65.7 wt% DOS, 1 wt% valinomycin and 0.4 wt% KTFPB with the total mass of 100 mg of the membrane components dissolved in 1 ml THF, (ii) 100 wt% SR with the total mass of 50 mg dissolved in 1 ml THF and (iii) a 1:1 (v/v) mixture of cocktail solutions (i) and (ii). Three types of SC-ISEs were then prepared as schematically shown in Figure 1. The first electrode (**Figure 1** A) was based on cocktail (i) that was drop-casted by subsequent 30 µl, 30 µl and 40 µl portions of cocktail (i) solution onto GC/PEDOT(PSS). The other two types of SC-ISEs were prepared by the same procedure as in type (i) but replacing the last 40 µl portion of the cocktail (i) solution with cocktails (ii) or (iii). The three types of SC-ISEs studied in this work (**Figure 1**) will be denoted as K^+-ISE(i), K^+-ISE(i/ii) and K^+-ISE(i/iii). Analogously the three types of membranes will be denoted as ISM(i), ISM(i/ii) and ISM(i/iii).

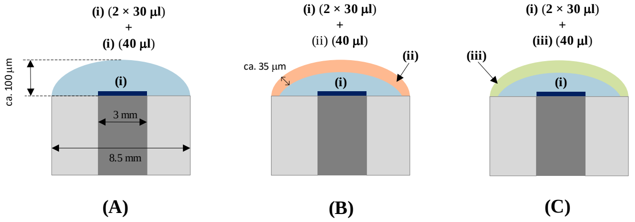

Figure 1. Schematic illustration of K^+-ISE(i) (A), K^+-ISE(i/ii) (B) and K^+-ISE(i/iii) (C)

The drop casting of the last portion of the ISM cocktail solutions (40 µl) was performed by equally distributing the membrane cocktail onto the whole surface area of the ISEs to ensure that the outer coating layer covered the whole surface of the electrodes. The interval time between each step of drop-casting was ca. 60 s. All membranes were dried in air for 72 h. The total thickness of all membranes was ca. 100 µm.

Optical microscopy and FTIR. Membranes for microscopy and FTIR studies were prepared in the same way as described in the previous section, but on a clean glass surface instead of GC. After the membrane was dried, it was detached from the glass surface and cut across to get its cross-section to be analyzed by optical microscopy. The cross-section image of the ISM(i/ii) membrane was recorded by Veho VMS-004 Discovery Deluxe USB Microscope. Using the same sample, the IR spectra of the ISM(i/ii) (on both sides of membrane) were measured by Fourier transform infrared spectroscopy (Bruker IFS66/S) equipped with a single reflection ATR microsampler (VideoMVP™). For comparison, FTIR spectra were also recorded for the individual membrane components (SR, DOS, valinomycin and KTFPB).

Null ellipsometry. An automated Rudolph ellipsometer was used to monitor the adsorption of BSA at the surface of bare SiO_2 and at SiO_2 coated with the three types of membranes studied. The instrumental setup, substrate cleaning process, experimental parameters and the sequence of procedures during the measurements and data treatment were the same as applied previously.[18] The PVC-based membrane ISM(i) was found to have poor adhesion to the SiO_2 substrate. To increase the adhesion of the ISM(i) onto the substrate, the SiO_2 was first modified with pure silicon rubber by dip coating the SiO_2 substrate into the THF solution of silicon rubber (0.5 mg ml^{-1}). Subsequently the substrates were left for solvent evaporation (10 h). Then, these SiO_2 substrates were used to immobilize ISM(i), ISM(ii) and ISM(iii) by dip coating the substrates into the diluted membrane cocktails (dry mass of 0.5%). All substrates were left for evaporation of the solvent for ca. 20 h in air. In the ellipsometric setup, the single substrate was vertically mounted into a glass trapezoid cuvette (Hellma, Germany) containing 5 ml of 10^{-2} M PBS, thermostated at 25 °C. Every time a newly produced substrate was used and the ellipsometric measurements were repeated three times for each substrate type.

Potentiometric measurement. The potentiometric response of the three different types of SC-ISEs was recorded using a 16-channel potentiometer (Lawson Labs Inc., input impedance = 10^{15} Ω) at room temperature (23 ± 2 °C). A double junction electrode (Ag/AgCl/3 M KCl/1 M LiOAc) was used as the reference electrode. Three identical SC-ISEs were used for each type of ISM. After conditioning overnight in 10^{-3} M KCl solution, the electrodes were calibrated from 10^{-3} to 10^{-9} M KCl by successive tenfold dilution using an automatic dilution system (711 Liquino and Dosino 700, Metrohom, Herisau, Switzerland). The selectivity coefficients of the electrodes were determined using the separate solution method. The measured potential was corrected for the liquid junction potentials and the activities were calculated according to the Debye–Hückel equation.[39,40]

Modified water layer test. A modified water layer test that was recently introduced by Lindner et al.[41] was used here to evaluate the effect of the coatings (ii) and (iii) on the penetration of CO_2 through the membrane and thereby identify the presence of water between the ISM and solid contact. To determine the water layer formation, CO_2 gas was used (which diffuses through the membrane) to alter the pH of the water-layer (if present). This method requires a pH-sensitive membrane. To assess water layer formation between ISM and the PEDOT(PSS), a pH-selective membrane was drop-cast on top of GC/PEDOT(PSS). The pH-selective membrane contained 3.9 wt% hydrogen ionophore I, 1.2 wt% KTpClPB, 64 wt% DOS and 31 wt% PVC, where a 200 mg dry mass of membrane components was dissolved in 2 ml of THF. The electrode preparation procedure was the same as for the K^+-selective electrodes, i.e. drop-casting of the outer layers (ii) and (iii) on the pH-selective membrane. Before use, the pH-selective SC-ISEs were conditioned in pH 4.0 for 24 h. The electrodes were examined for their Nernstian response in three pH buffers (pH 4.0, 7.0 and 10.0). Then the modified water layer test was run, where a 100 ml pH 7.4 buffer solution was prepared and was split into two equal 50 ml solution portions. While one 50 ml solution portion was kept at pH 7.4, the other one was purged with CO_2 gas to change the pH of the solution to pH 6.6. The electrodes were first immersed in pH 7.4 buffer solution and the potential was measured for ca. 10 min. The electrodes were then transferred to the pH 6.6 buffer solution and the potential was recorded for the same time. The potential was measured alternatively in the solutions pH 7.4 and pH 6.6. The pH of the solutions was measured using a combination pH glass membrane electrode (Metrohm).

RESULTS AND DISCUSSION

Reproducibility of electrode potentials. In this work, the influence of the protective SR coating on the standard potential reproducibility and potentiometric response of K^+-selective SC-ISEs were studied. The potentiometric responses were measured between 10^{-3} and 10^{-9} M KCl solutions, while the slopes were calculated from the linear range part of the calibration curve (10^{-3}-10^{-6} M). The calibration values for K^+-ISE(i), K^+-ISE(i/ii) and K^+-ISE(i/iii) (n=4) after conditioning in 10^{-3} M KCl solution are listed in **Table 1**. In the best case of each types, the standard deviation of E^0 was 28.3 mV for K^+-ISE(i) after 16 days conditioning, 1.9 mV for K^+-ISE(i/ii) and 7.9 mV for K^+-ISE(i/iii) after 1 day conditioning. It shows the high reproducibility of the standard potential of K^+-ISE(i/ii) was achieved on each day. The slope values were slightly improved in the case of K^+-ISE(i/ii) and K^+-ISE(i/iii) compared with K^+-ISE(i). The low detection limits which were all ca. 10^{-7} M, were not influenced by adding the coating layer. The potentiometric response for K^+-ISE(i), K^+-ISE(i/ii) and K^+-ISE(i/iii) (n=4) after conditioning in 0.001 M KCl solution for 8 days is shown in **Figure 2**

Table 1. The calibration values of K^+-ISE(i), K^+-ISE(i/ii) and K^+-ISE(i/iii) (n=4) after conditioning in 0.001 M KCl solution for 1, 4, 8 and 16 days.

Electrodes type	K^+-ISE(i)			K^+-ISE(i/ii)			K^+-ISE(i/iii)		
Time days	Slope mV/decade	E^0 mV	Detection limit x 10^{-7} M	Slope mV/decade	E^0 mV	Detection limit x 10^{-7} M	Slope mV/decade	E^0 mV	Detection limit x 10^{-7} M
1	53.5 ± 1.3	224.0 ± 30.3	1.8	55.0 ± 0.2	302.8 ± 1.9	1.4	53.1 ± 1.0	203.8 ± 7.9	1.1
4	56.6 ± 1.5	242.2 ± 34.0	2.2	57.2 ± 0.4	314.9 ± 5.2	2.3	58.4 ± 0.4	276.4 ± 22.2	1.4
8	55.9 ± 1.1	190.0 ± 35.3	1.8	57.3 ± 0.1	315.0 ± 3.5	1.5	57.1 ± 0.9	245.5 ± 19.7	1.0
16	55.3 ± 1.4	193.1 ± 28.3	1.8	56.8 ± 0.2	293.8 ± 11.0	1.3	56.5 ± 0.7	226.2 ± 25.8	0.9

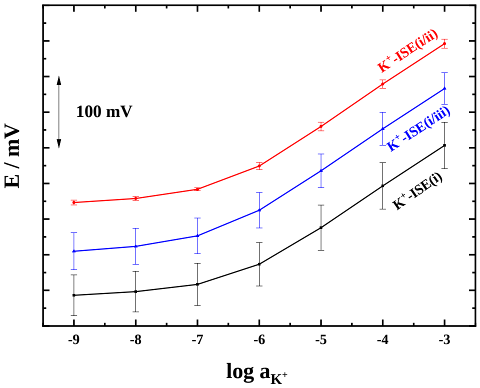

Figure 2. Potentiometric response for K⁺-ISE(i), K⁺-ISE(i/ii) and K⁺-ISE(i/iii) (n=4) after conditioning in 0.001 M KCl solution for 8 days.

The role of the protective coating layer. The microscope picture of the cross section of the ISM(i/ii) and the FTIR spectra taken on both sides of the SR layer is shown in **Figure 3**. Since the two layers (SR and PVC membrane) in ISM(i/ii) do not fuse with each other **Figure 3 A**, the protective SR layer could be easily peeled off and studied by FTIR for the presence of membrane components in the SR layer. The FTIR was performed in the wavenumber range of 1400-1900 cm^{-1} (bottom) for the SR coating (ii) on both sides (top and bottom). For comparison FTIR of pure SR, KTFPB, DOS and valinomycin (components of PVC-based membrane) were recorded. The FTIR spectra for top and bottom sides of SR in coating (ii) overlapped, indicating homogeneous distribution of membrane components in the entire membrane. The difference between the pure SR and SR coating (ii) was observed at ca. 1740 cm^{-1} in the IR spectrum (**Figure 3 B**, insert). This small peak was related to C=O stretching vibration in DOS. Furthermore, no evidence of lipophilic salt or the ionophore were found by FTIR, which is related to their low concentration, i.e. below the detection limit of the FTIR. However, the presence of the DOS in SR suggests that during membrane preparation there is a slow diffusion of the membrane components from the plasticized PVC layer (i) to the protective layer of SR (ii). Moreover, the ionophore and KTFPB are well soluble in the plasticizer, so the presence of DOS in SR indicates that ionophore and KTFPB are present there too. Moreover, a relatively long conditioning time for K⁺-ISE(i/ii) may be required owing to the transmembrane flux of membrane components from PVC to the protective coating layer, because the diffusion coefficients of moieties in SR is much lower than in PVC.[27,28]

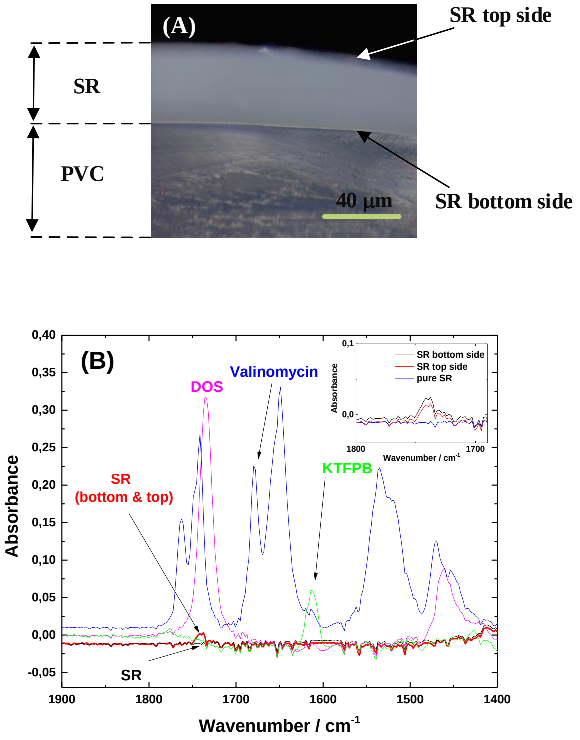

Figure 3. Cross-section microscopic image of the coating (ii) membrane **(A)** and FTIR spectra of SR, DOS, valinomycin, KTFPB and SR from coating (ii) on top and bottom sides **(B)**.

Additionally, to identify whether there is an ionophore in the protective SR coating (ii), the unbiased selectivity coefficient of all K⁺-ISEs to potassium over sodium and calcium were studied using the separate solution methods. As shown in **Table 2**. it was found that the unbiased selectivity coefficients for all types of K⁺-ISEs studied here are similar and comparable to the ones obtained using membranes of the same or similar compositions.[42,43] This confirms that the ionophore is present in the protective SR coating (ii), as the response of the sensor is governed by the selectivity coefficients typical of valinomycin based ISEs. However, the protective SR coating (ii) may slow down leaching of any membrane components from the ISM(i/ii) while the inner PVC layer (i) may act as a reservoir for the membrane components (ionophore, lipophilic salt and plasticizer).

Table 2. Selectivity coefficients (log $K_{K+,j}$) for K⁺-ISEs after conditioning in 0.01 M KCl solution (n= 4).

Ion-selective Electrodes	log $K_{K+,j}$	
	j = Na⁺	j = Ca²⁺
ISE(i)	**-4.41 ± 0.08**	**-5.17 ± 0.10**
ISE(i/ii)	**-4.81 ± 0.17**	**-5.22 ± 0.10**
ISE(i/iii)	**-4.56 ± 0.13**	**-5.13 ± 0.09**

Protein adsorption. Adsorption of protein (BSA) on ion-selective membranes were performed by means of null ellipsometry. The experimental procedures were previously reported.[18] The results of dynamic adsorption of BSA at the surface of bare SiO_2, plasticized PVC membrane (i) as well as SR coatings (ii) and (iii) are shown in Figure 4. Adsorption of BSA was done from a solution of 1 mg·ml^{-1} BSA in 0.01 M PBS. As shown in **Figure 4**, after the addition of 1 mg ml^{-1} BSA, the adsorption of protein on the bare SiO_2 surface was negligible. In similar experiments it was found that the amount of BSA at the surface of the plasticized PVC membrane (i) increased. In the case of the SR coating (ii), the BSA adsorption increased at the very beginning, slightly decreased after one minute and finally equilibrated at a constant value after 2.5 min. Interestingly, after 30 min the SR coating (ii) adsorbed the lowest amount of BSA (1.0 mg·m^{-2}), which is half of PVC-based membrane (2.15 mg·m^{-2}). Coating (iii) absorbed slightly more BSA than coating (ii), since coating (iii) contains 50% plasticized PVC. After washing off the unbound and loosely bound BSA by PBS solution at t = 35 min, the amount of BSA absorbed on the PVC-based membrane (i) slightly decreased from ca. 2.15 to 2.00 mg m^{-2}. However, for coatings (ii) and (iii) there was no obvious change in the adsorption when rinsing with PBS solution. The irreversible biofouling, especially for coating (ii), ought to benefit the potentiometric stability of ISEs employing such a SR coating when used in sample solutions with different concentrations of biomolecules.[18] Moreover, the adsorption of the BSA was found to be a rapid process, which was 95% complete already after 150 s of the adsorption experiment.

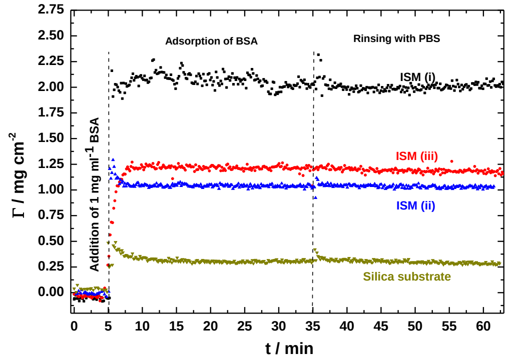

Figure 4. Adsorption of BSA (1 mg·ml^{-1}) in 10^{-2} M PBS at bare SiO_2 and SiO_2 coated with ISM(i), ISM(ii) and ISM(iii).

Modified water layer test. The potential of H^+-selective SC-ISEs with plasticized PVC membrane (i) and the two different SR coatings (ii) and (iii) were recorded in solutions of pH 7.4 and pH 6.6 (purged with CO_2) after 7 days of electrode conditioning. The results are shown in **Figure 5**. As CO_2 was introduced into the buffer solution, it can diffuse through the pH-selective ISM and influence the pH of any water layer present at the backside of the ISM. Since the ISM is pH-selective, this would lead to a biased potential or potential drift. The lower diffusion coefficient of water in SR than the PVC-based ISM is expected to slow down the water uptake of the SR-coated ISM[27]. Due to the low concentration of the buffer solution during conditioning (at pH 4 buffer), 7 days conditioning was decided to be applied. After the buffer solution was changed from pH 7.4 to pH 6.6, the potential jump was expected to be ca 47.5 mV (calculated from calibration slope) due to the change in pH. As shown in **Figure 5**, the potential drift was found to be minimal for the H^+-ISE with SR coating (ii) (0.14 mV/min), followed by coating (iii) (0.32 mV/min) and the PVC-based membrane without any coating (0.41 mV/min) at pH 7.4 buffer solution. The lower potential drift for the H^+-ISE with SR coating (ii) indicates less water uptake, compared to the other types of membranes studied. Thus, it can be concluded that the outer coating of SR is significantly slowing down the diffusion of water through the membrane.

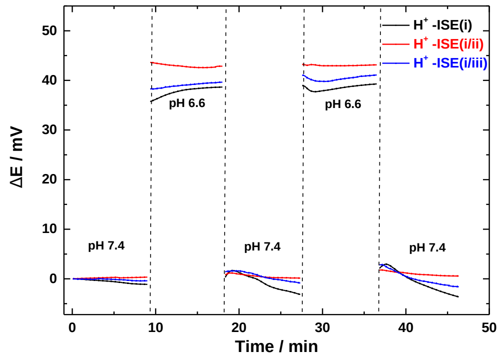

Figure 5. Potential drifts measured by modified water layer test of all type of H^+-ISEs after conditioning in pH 4.0 buffer solution for 7 days.

CONCLUSIONS

A new and simple approach was found to improve the reproducibility of the standard potential of potentiometric ion sensors. K^+-selective ISEs with a relatively stable standard potential (E^0 ± 3.5 mV) was obtained by adding a silicone rubber (SR) layer as an outer coating on a plasticized PVC-based membrane. The selectivity coefficients of valinomycin-based K^+-selective ISEs were not influenced by adding the outer SR layer when the ISE was pre-conditioned for a sufficiently long time. This indicates that the plasticizer, ionophore and lipophilic additives gradually diffuse from the inner plasticized PVC membrane to the outer SR coating. If the solubility of these active membrane components is lower in SR than in PVC, it can be hypothesized that the inner PVC-based membrane provides a constant supply of active membrane components to the outer SR membrane until an equilibrium is reached. This opens an interesting scenario where an inner membrane can act as a reservoir of active components, while the analytical performance is determined by the outer membrane. Furthermore, the SR coating was found to decrease protein adsorption compared to the plasticized PVC membrane.

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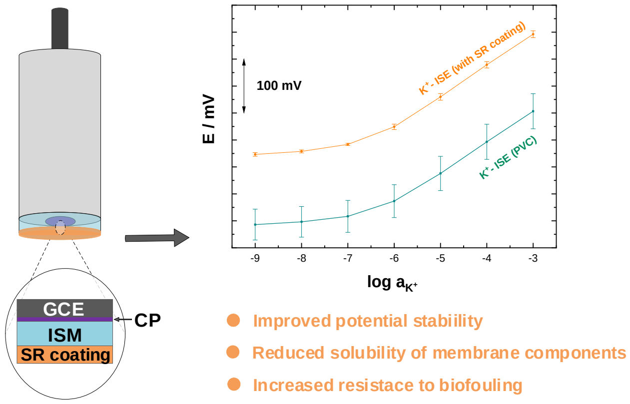
Graphical abstract



- Improved potential stability
- Reduced solubility of membrane components
- Increased resistace to biofouling