



Influence of hydrophobization of the polyazulene ion-to-electron transducer on the potential stability of calcium-selective solid-contact electrodes



Ning He^a, Lajos Höfler^b, Rose-Marie Latonen^a, Tom Lindfors^{a,*}

^a Åbo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry, Biskopsgatan 8, FIN-20500 Turku/Åbo, Finland

^b Budapest University of Technology and Economics, Department of Inorganic and Analytical Chemistry, Szt. Gellért tér 4, H-1111 Budapest, Hungary

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ABSTRACT

We introduce here electrosynthesized polyazulene (PAz) as a new ion-to-electron transducer material in solid-contact ion-selective electrodes (SC-ISEs). It is shown that the neutral form of PAz possesses high hydrophobicity (water contact angle: $126 \pm 14^\circ$) due to its aromatic carbon structure. This makes PAz attractive as a solid-contact (SC) material in SC-ISEs in combination with its high redox capacitance which is three times higher than for PEDOT-PSS. We have studied the electrochemical stability of PAz in direct contact with aqueous electrolyte solutions and applied it as the SC layer buried under a calcium-selective plasticized poly(vinyl chloride) ion-selective membrane (ISM). It is demonstrated that the hydrophobization of the PAz solid-contact at $E \leq 0.2$ V significantly improved the potential stability of the calcium-selective SC-ISEs which showed a potential drift of only 0.5 mV h^{-1} when the ISMs were for the first time contacted with 0.1 M CaCl_2 for 24 h. Simultaneous determination of the potential stability and the water uptake with the FTIR-ATR spectroscopy could not clearly prove the correlation between low water content at the PAz/substrate interface and the good potential stability obtained with the pre-hydrophobized SC-ISEs. This is due to the relatively uneven surface morphology of the PAz film making the evanescent standing wave of the IR beam to sense water not only in the PAz transducer layer, but also in the ISM. Hence, it is not possible to distinguish between the distribution of water in the ISM and the PAz solid-contact layer. The new SC material presented here was also characterized with cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy.

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1. Introduction

Over the past few decades, the synthesis and characterization of polyazulene (PAz) has attracted attention because of its electronic and optical properties [1–4]. The azulene monomer is a non-alternant aromatic hydrocarbon with a partial negative charge on the five-membered ring and a positive charge on the seven-membered ring of the monomer. Upon oxidative electrochemical [2,3] and chemical [1,5] polymerization, azulene monomers are linked together between C1 and C3 of the five-membered ring (Fig. 1) [6]. The electrochemically prepared PAz films possess a relatively high electrical conductivity of 10^{-2} to 1 S cm^{-1} [7]. The films show good stability in organic solvents, highly reversible redox and electrochromic properties [8] which have been utilized in supercapacitors [4], batteries [9] and electrochemical biosensors [10].

In this work, thin PAz films were used for the first time as the ion-to-electron transducer layer in calcium-selective solid-contact ion-selective electrodes (SC-ISE). We have studied the influence of hydrophobization of the PAz solid-contact layer on the potential stability of the SC-ISEs.

Plasticized poly(vinyl chloride) (PVC) based ion-selective membranes (ISMs) are commonly used in potentiometric ion-selective electrodes (ISEs) [11–14]. The PVC based ISMs are deposited directly on top of the electrically conducting substrate material (usually glassy carbon (GC), gold or platinum) in the coated-wire electrode (CWE) configuration [15] or on top of the solid-contact (SC) layer in the SC-ISE setup [16,17]. Because of the water uptake of the ISM, a thin aqueous layer or water pools may be formed at the ISM/substrate interface in CWEs or at the ISM/SC and SC/substrate interfaces in SC-ISEs [18,19]. The water accumulated in the thin water layer or the water pools will behave as small electrolyte reservoirs resulting in the transmembrane flux (re-equilibration) of primary and interfering ions between these reservoirs and the sample solution. This has shown to negatively influence the

* Corresponding author.

E-mail address: Tom.Lindfors@abo.fi (T. Lindfors).

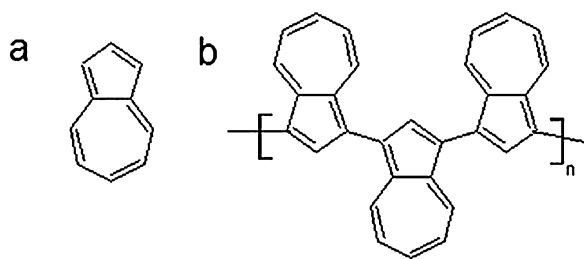


Fig. 1. The chemical structures of (a) azulene and (b) PAz.

long-term potential stability and the detection limit of the SC-ISEs and the CWEs [18]. Hence, it is crucial to be able to control the water uptake of both the SC layer and the ISM to be able to minimize the flux of water through the ISM to the transducer layer and to achieve SC-ISEs with superior response characteristics.

Different methods have been applied to eliminate the detrimental aqueous layer formation in the SC-ISEs. One approach relies on increasing the hydrophobicity of the outer ISM. Silicone rubber (SR) was introduced as the ISM matrix for K^+ -selective ISEs already in the 1970s [20] and recently it was shown by the FTIR attenuated total reflection (ATR) spectroscopy [13,14,21], and the coulometric Karl Fischer technique [21] that the water uptake of the SR based ISMs was much lower than for the ISMs based on plasticized PVC. The moisture cured SR membranes contained initially more water than the PVC membranes but it was assumed that this water is immobile in the SR matrix [21]. The lower water uptake of SR was shown to be beneficial in the SC-ISEs having an outer calcium-selective SR-ISM and a polyaniline (PANI) nanoparticle based SC [22]. With this combination of materials it was possible to achieve the detection limit of 10^{-9} M showing the advantage of the SR in lowering the detection limit of the SC-ISEs. Another approach to prevent the water layer formation is attributed to the use of hydrophobic SC materials. For example, a lipophilic redox-active self-assembled monolayer has been used as the SC layer to modify the electrode substrate surface resulting in better characteristics for some of the studied ISEs [18,19]. These two approaches relying on the hydrophobicity of both the ISM and the SC layer have been successfully combined. It was recently demonstrated that the water uptake was efficiently reduced in hydrophobic poly(methyl methacrylate)/poly(decyl methacrylate) by mixing it with the hydrophobic and electrically semiconducting poly(3-octylthiophene) (POT) which is often used as the transducer layer in SC-ISEs [23]. In another study, the SR based SC-ISEs with the detection limit of 10^{-8} M was prepared with POT as the hydrophobic and water-repellant ion-to-electron transducer layer [24]. In that study the water uptake, impedance spectra and potential stability of the SC-ISEs were simultaneously measured *in situ* with the hyphenated FTIR-ATR and electrochemical impedance spectroscopy (EIS) technique providing a broad spectrum of useful information about processes occurring in the ISM and the SC layer, especially during the initial contacting (24 h) of the SC-ISEs with the electrolyte solution [24,25]. The same hyphenated method was used in this work to study the relationship between the hydrophobicity of the PAz solid-contact layer and the potential stability of the SC-ISEs.

It has been shown that a reversible wettability of a polypyrrole film was achieved by modifying its electronic state by polarization of the film surface between its neutral and oxidized form [26]. In this work, we have polarized the PAz transducer layer at different potentials and studied how the hydrophobization of the SC material influenced the water contact angle (CA) of PAz and its water uptake in direct contact with 0.1 M $CaCl_2$, and its behavior as a buried ion-to-electron transducer layer under calcium-selective plasticized PVC membranes. We have used PVC based ISMs due to

their ability to solubilize most ionophores but also because their water uptake is higher than for the SR-ISMs. With ISMs having higher water uptake it is easier to study how the hydrophobization of the PAz solid-contact influences the potential stability of the SC-ISEs. Here we report that the polarization of PAz at $E \leq 0.2$ V resulted in SC-ISEs with a low potential drift (0.5 mV h^{-1}) upon the initial conditioning in 0.1 M $CaCl_2$. This is the first time PAz has been used as an ion-to-electron transducer in SC-ISEs and the paper focuses therefore on the basic characterization of PAz as the SC layer. In a follow-up study, we will report the application of the PAz-based SC-ISEs in potentiometric sensing.

2. Experimental

2.1. Chemicals

Azulene (99%), acetonitrile (ACN, 99.5%, anhydrous) and $CaCl_2$ were received from Aldrich and used without additional purification. High molecular weight PVC, bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTfPB), calcium ionophore IV (ETH 5234), and tetrahydrofuran, all of the selectophore grade, and tetrabutylammonium hexafluorophosphate (TBAPF₆, 99%) were purchased from Fluka and used as received.

2.2. Electropolymerization of PAz and its electrochemical characterization

For the SEM and CA measurements, the azulene was electrochemically polymerized in a three-electrode one-compartment cell on Pt sputtered ITO glass electrodes ($A = 1.0$ cm²; Pt layer thickness: 30 nm), while the electropolymerization was carried out on Pt sputtered ZnSe reflection elements ($A = 0.3$ cm²; Pt layer thickness: 15 nm) for the PAz film which were used in the FTIR and potential stability measurements. In the three-electrode cell, a coiled Pt wire and a Ag/AgCl wire served as the counter and the reference electrode (calibrated versus ferrocene/ferrocenium, $E_{redox} = 0.36$ V), respectively. All polymerizations were done in ACN solutions containing 0.01 M azulene and 0.1 M TBAPF₆ by potentiodynamic cycling between -0.6 V and 1.2 V with the scan rate of 50 mV s^{-1} (the Autolab PGSTAT 30 potentiostat equipped with the GPES software). The PAz film thickness was varied by the number of potential cycles. All solutions used for polymerization and characterization of the PAz films ($V = 3$ ml) were purged with nitrogen for 5 min before the experiments and the TBAPF₆ was dried under vacuum at 80 °C for 30 min prior to use. In the electropolymerization on the ITO substrates, the formed PAz films were washed in some cases with ethanol and dried with nitrogen gas after every second cycle. For the FTIR measurements, the PAz films were polymerized on ZnSe in the FTIR electrochemical cell under a constant flow of monomer solution (ca. 0.5 ml min^{-1}). In both cases, the electropolymerization resulted in a more compact and even PAz film morphology compared to the polymerization done in non-stirred quiescent solutions [27].

After the polymerization, the oxidation and reduction behavior of the PAz films was studied by cyclic voltammetry (CV) in a 0.1 M TBAPF₆-ACN solution by cycling the potential between -0.4 V and 1.0 V with the scan rate of 50 mV s^{-1} . The electrochemical impedance spectra were measured in 0.1 M TBAPF₆-ACN at 0.7 V (100 kHz–10 mHz; $\Delta E_{ac} = 5$ mV) with the Autolab potentiostat (PGSTAT 30) equipped with the frequency response analyzer (FRA).

To obtain PAz with different hydrophobicity, the oxidation state of the films was varied by polarizing them at -0.4 , 0.2 and 1.0 V for 5 min in 0.1 M TBAPF₆-ACN. After the polarization, the

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