



# Application of polyaniline for potentiometric recognition of salicylate and its analogues



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## ABSTRACT

Presented work proves usability of polyaniline (PANI) as a receptor for potentiometric detection of salicylates. The potentiometric selectivity of PANI-coated membranes based on tridodecylmethylammonium chloride (TDDMACl) towards salicylate is at least as good as the selectivity of membranes based on “conventional” specific supramolecular receptor systems such as Sn(IV) and Al(III) phthalocyanates. X-ray diffraction (XRD) and electric impedance spectroscopy (EIS) techniques are used to insight into the phenomena leading to improvement of salicylate-selectivity of PANI. These studies reveal the relative role of sodium chloride during the PANI polymerization that leads to preparing of partially crystalline polymer and decreasing of the “bulk” resistance of membrane. The “bulk” resistance change is attributed to introduction of the electronic conductivity into the system PANI/Salicylate. Determination of acetylsalicylate in pharmaceutical preparations with recovery at about 98–100% is reported. Additionally, the ability to detect  $(0.11 \pm 0.01) \times 10^{-3}$  M of salicylate present in a synthetic serum sample is demonstrated.

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## 1. Introduction

Potentiometric detection based on ion-selective electrodes (ISEs) is a simple method that offers great advantages such as high speed of measuring process, reasonable selectivity, wide linear dynamic range and low cost. Because of their selectivity, small size, portability and low cost, the potentiometric sensors are instruments being successfully applied in both chemical and clinical analyses. In contrast to the first impression, the development of potentiometric sensor is not easy due to the necessity to design a receptor capable of providing selective complex analyte of interest. An illustrative example can be the development of sensors for potentiometric detection of salicylate and its analogues, including acetylsalicylate (aspirin). The reliable salicylate-selective potentiometric sensor attracts lasting interest in the field of both medical and pharmaceutical applications [1]. A number of synthetic receptors based on guanidinium [2], metalloporphyrins [1], metallophthalocyanates [3], metallosalophenes [4], and metallocenes [5] have been proposed. Their selectivity is based on a biomimetic approach [2], a specific coordination of salicylate to metal center [1,3,4] or a specific interaction of salicylate with  $\pi$ -electron accepting system of receptor [5].

Conducting polymers (CPs) have found widespread use in the development of sensor technology [6] and in biomedical engineering [7,8]. Polyaniline (PANI) has proven useful for electrochemical detection of biologically active molecules, such as anticancer drugs [9], immunosuppressives [10], antibiotics [11]. The corresponding electrodes were often covered with a PANI composite [12], nanostructured PANI [13] or PANI immobilized onto silver nanoparticles/carbon multiwalled nanotubes [14]. Special attention was also paid to the dimensional CPs that exhibit unique properties such as greater conductivity and more catalytic activity [13,15]. These materials can be combined with metallic and semiconducting supports and open new perspectives for a development of sensor surface and properties [14,16,17]. Example of such biosensor can be polyphenol biosensor based on silver nanoparticles/carbon multiwalled nanotubes/PANI [14]. In contrary to earlier enzyme sensors, it has no leakage of enzyme during reuse and is unaffected by the external environment due to the protective PANI microenvironment.

Based on the above-mentioned trends, the purpose of this contribution is to introduce a new kind of receptor system for the potentiometric detection of salicylate and its analogues. The key innovation lies in replacing specific supramolecular receptor with a conducting polymer, specifically PANI. The salicylate-selectivity of PANI as a receptor of potentiometric sensor is discussed. The relations between PANI structure and its sensing properties are analyzed. Finally, applicability of proposed potentiometric sensor

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**Table 1**  
Potentiometric characteristics for uncoated (A) and PANI-coated (B, C) membranes.

Membrane (composition)	Chloride	Acetate	Benzoate	Salicylate
	Slope, mV/decade* Linear range, M	Slope, mV/decade* Linear range, M	Slope, mV/decade* Linear range, M	Slope, mV/decade* Linear range, M
A (TDDMACI)	-39 (6.4) $2 \times 10^{-3}$ – $2 \times 10^{-2}$	-53 (9.8) $2 \times 10^{-4}$ – $2 \times 10^{-2}$	-45 (3.5) $2 \times 10^{-4}$ – $2 \times 10^{-2}$	-59 (2.3) $2 \times 10^{-4}$ – $2 \times 10^{-2}$
B (TDDMACI/PANI)	-64 (3.1) $4 \times 10^{-6}$ – $2 \times 10^{-2}$	-68 (6.8) $2 \times 10^{-4}$ – $2 \times 10^{-2}$	-67 (3.8) $4 \times 10^{-6}$ – $2 \times 10^{-2}$	-76 (4.0) $4 \times 10^{-6}$ – $2 \times 10^{-2}$
C (TDDMACI/PANI + NaCl)	-52 (0.7) $4 \times 10^{-6}$ – $2 \times 10^{-2}$	-58 (6.1) $2 \times 10^{-4}$ – $2 \times 10^{-2}$	-60 (1.0) $4 \times 10^{-6}$ – $2 \times 10^{-2}$	-62 (1.6) $4 \times 10^{-6}$ – $2 \times 10^{-2}$

\* The values of relative standard deviation for slope of set of sensors ( $n=3$ ) based on tested membranes are given in parentheses

in two areas of practical interest is demonstrated: measuring of salicylate in a synthetic serum and monitoring of acetylsalicylate in drugs.

## 2. Experimental

### 2.1. Reagents

Poly(vinyl chloride) (PVC) of high molecular weight, 2-nitrophenyl octyl ether (NPOE), tridodecylmethylammonium chloride (TDDMACI), tetrahydrofuran (THF, stored over a molecular sieve) were purchased from Fluka (Selectophore grade, Switzerland). Aniline (>99%) and 2-[4-(2-hydroxyethyl)-1-piperazino]-ethanesulfonic acid (HEPES) were obtained from Sigma-Aldrich (Germany). Acids and various inorganic/organic salts of analytical grade used in the potentiometric measurements were bought from Lachema (Czech Republic). The commercial tablets of aspirin C (Bayer Bitterfeld GmbH, Greppin, Germany Herbacos-Bofarma, s.r.o.), acylpyrin (Zentiva, a.s., Czech republic), acylcoffin (Hlohovec, Slovak republic) used in this study were purchased at a local drugstore in Prague. All standard solutions and buffers were prepared using distilled water.

### 2.2. Preparation of membranes and deposition of polyaniline

The membranes were prepared by dissolving 3 mg of TDDMACI, 32.3 mg of NPOE and 64.7 mg of PVC in 1.0 mL THF at ambient temperature. The prepared membrane mixture was deposited onto a metallic ring of 16 mm internal diameter resting on a glass plate, and dried in air.

The oxidation polymerization of aniline was carried out with 10 ml of aqueous solution of aniline (0.08 M) and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (0.08 M) in 1.5 M HCl at 0 °C in the presence of TDDMACI-based membrane immersed in the reaction medium. When specified, 3.3 M NaCl was added in the polymerization mixture [16,17]. Uncoated membrane is referred to as membrane A. The membranes coated with PANI in the absence or in the presence of NaCl are referred to as membranes B and C, respectively. After polymerization, the PANI-coated membrane was removed, rinsed with 1.5 M HCl aqueous solution [18], treated ultrasonically for 10 min in 1.5 M HCl aqueous solution and dried at ambient temperature.

### 2.3. Potentiometric measurements

A disk of 10-mm diameter was punched from ion-selective membranes prepared as described above, glued onto a polymeric ring of 8 mm internal diameter with a PVC/THF paste, and mounted in the electrode body for potentiometric measurements. All measurements were carried out at ambient temperature with cell of the following type:

Ag; AgCl; 3 M KCl || sample solution | membrane | inner filling solution; AgCl; Ag.

An aqueous solution of  $10^{-3}$  M corresponding sodium salt was used as the inner filling of the electrode. Prior to the potentiometric experiment, the electrodes were soaked in a solution of  $10^{-3}$  M corresponding sodium salt. The potentiometric response ( $\Delta E$ ) was measured with digital ion-meter PHI 04 MG (Labio, Czech Republic). The potentiometric response of the prepared membranes toward chosen analytes (Table 1) was observed by adding 2  $\mu\text{L}$ , 10  $\mu\text{L}$ , 100  $\mu\text{L}$ , 1 mL and 10 mL of the corresponding sodium salt solution (0.1 M) into 50 mL of stirred water solution ( $\text{pH } 5.5 \pm 0.3$ ). After the potentiometric measurements the PANI-coated membranes were regenerated in 0.02 M NaOH for 10 min and then washed with distilled water for 1 min.

The values of potentiometric selectivity coefficients ( $\log K^{\text{Pot}}_{I,J}$ ) were determined by the separate solution method (SSM) [19] with the primary ( $I = \text{salicylate}$ ) and interfering ( $J = \text{chloride, acetate, benzoate}$ ) ions at concentration being 0.01 M in aqueous solution at  $\text{pH } 5.5 \pm 0.3$  (Table 2).

A program ACD/LogP DB was used to calculate the logarithm of partition coefficient ( $\log P$ ) values for a series of studied carboxylates.

### 2.4. Electric impedance spectroscopy measurements

All electric impedance spectroscopy (EIS) measurements were carried out using Potentiostat/Galvanostat M263 (PAR, Princeton, USA) connected with Lock-in amplifier 5110 (EG&A, Wellesley, USA). Measurements were realized in the frequency range of 0.1 MHz–0.01 Hz in 0.01 M testing aqueous solution in a shielded cell. The cell consisted of two acryl cuvettes ( $10 \times 10 \times 45$  mm) separated by membrane of 0.785  $\text{cm}^2$  area. The experimental membrane was glued between the two compartments of the measuring cell using mixture of PVC and THF. Before EIS measurements both sides of the fixed membrane were soaked overnight in 0.01 M aqueous solution of the tested analyte. Both cell compartments were filled with sodium salt of the studied analyte. The electrodes were placed into both compartments.

**Table 2**  
Comparison of potentiometric selectivity coefficients ( $\log K^{\text{Pot}}_{\text{Salicylate},j}$ ) for the membranes obtained in this work with the ones described in the literature.

Membrane	Chloride	Acetate	Benzoate
Membrane A (TDDMACI)	–	–1.9	–1.6
Membrane C (TDDMACI/PANI + NaCl)	–3.0	–3.4	–2.1
Aliquat 336S [26]	–1.96	<–2.7	–1.15
Sn[TPP]Cl <sub>2</sub> [1]	–3.8	–3.9	–1.4
Sn (IV) phthalocyanate [3]	–1.53	–1.84	–1.12
Al(III) phthalocyanate [3]	–1.85	–1.7	–1.12

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