

Application of Tetra Cyclohexyl Tin(IV) as an Anionic Carrier for the Construction of a New Salicylate Membrane Sensor

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A new tin complex namely tetracyclohexyl tin(IV) (TCHT) was synthesized and used as the ion carrier for the construction of a highly selective salicylate sensor. This sensor shows a Nernstian response to salicylate ions over a very wide concentration (1.0×10^{-7} - 1.0×10^{-1} M) in a pH range of 5.5-10.5. The optimum selectivity and response could be obtained for a membrane incorporating 30% PVC, 61% BA, 3% of cationic additive (HTAB) and 6% of TCHT. The response time of the electrode is very short in the whole concentration range (15 s). The electrode also shows an excellent discriminating ability for salicylate ions with respect to the most common organic and inorganic anions including chloride, sulfate, nitrate, nitrite, cyanide, sulfite, iodide, thiocyanate, phosphate, acetate, oxalate, citrate, and tartarate ions. The detection limit of the proposed sensor is 8.0×10^{-8} M. The electrode was successfully used for determining the concentration of salicylate ion in synthetic serums.

Keywords: Salicylate ion selective electrode; PVC membrane; Tetra cyclohexyl tin(IV).

INTRODUCTION

Electrodes using a plasticized PVC membrane incorporating derivatives of vitamin B12, Co(III), Sn(IV), Mo(IV) and Mn(III) porphyrin complexes, Schiff's base complexes, pyrylium and thiopyrylium derivatives and electropolymerized Co(II) porphyrin derivative films demonstrated potentiometric anion selectivity sequences which deviated from the Hofmeister pattern.¹⁻¹⁴ These deviations resulted from the direct interactions between the central metal and the analyte ions. Thus, this unusual anion selectivity behavior was based on the properties of the central metal and the chemical environment around the central metal. Many organometallic compounds have been synthesized, some of which have been applied in many fields, and especially in the construction of anion selective electrodes, since the 1960s. Although these electrodes exhibited unusual responses to respective anions (e.g., chloride, nitrate, dibasic phosphate and salicylate), the research on new carriers for improvement of the potentiometric response characteristics of these electrodes is of considerable interest in order to be applied for the analysis in actual samples.

Salicylate and its analogues, including acetylsalicylate (aspirin), are available to the public in a wide variety of formulations. The most widely used analytical method for the detection of salicylate is based on the Trinder reaction in which sample salicylate reacts with ferric ions to form a colored complex in acid solution.¹⁵ Since similar complexes can be formed under the same experimental conditions, this method always lacks adequate selectivity over many common anions. Polymeric membrane electrodes based on quaternary ammonium salts of salicylate suffer from the same problem.^{16,17} Electrodes prepared by incorporating Mn(III) and Sn(IV) porphyrin complexes into PVC membranes exhibited high selectivity towards salicylate, but it is necessary to improve some potentiometric response characteristics such as linear range, detection limit and sensitivity.¹⁸ In this work, we wish to report a salicylate-selective electrode based on the newly synthesized tetra cyclohexyl tin(IV). The results indicate that electrodes based on TCHT offer a wide linear response range, high selectivity and high sensitivity to salicylate, and can be used in a wide pH range of 5.0-10.5. The novel electrode has been used for the determination of trace amounts of

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salicylate ion in biological samples with satisfactory results.

EXPERIMENTAL SECTION

Reagents

Reagent grade benzyl acetate (BA) and hexadecyltrimethylammonium bromide (HTAB) were purchased from Fluka Company, ortho-nitrophenyloctyl ether (NPOE) and high relative molecular weight PVC were purchased from Aldrich Company and tetrahydrofuran (THF) was purchased from Merck Company and all were used as received. The sodium and potassium salts of all anions used, all from Merck Company, were of the highest purity available and were used without any further purification except for vacuum drying over P_2O_5 . Triply distilled de-ionized water was used in all experiments.

Synthesis of tetra cyclohexyl tin

TCHT (Fig. 2) was synthesized according to a method as follows.

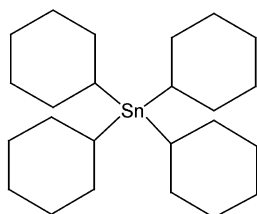


Fig. 1. The structure of TCHT.

Place 14.4 g of 0.6 M magnesium into a three-necked flux attached to a condenser and a mechanical stirrer. To this, add 25 cc of ether and 0.02 g of iodine as an activator. Then, add to the flux dropwise 71 g of 0.06 M chlorocyclohexan dissolved in 100 cc of ether and boil at the boiling point for 1 h. Afterwards, add 32.5 g of 0.125 M stannic chloride dissolved in 100 cc xylene to the flux content (which is called Grignard reagent) and boil it for 1.5 h and then for 2 h. Cool it and after the addition of 50 cc of water, separate the aqueous and organic phases. Add 20 cc of 10% HCl to the aqueous phase and again separate the aqueous and organic phases. Mix the organic phase with the former organic phase. After solvent distillation, 47.8 g of tetra cyclohexyl tin is obtained, based on acetic chloride, with a boiling point of 260-264 °C and 85% yield.

Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg PVC, 61 mg of plasticizer BA, 3 mg of additive HTAB, and 6 mg of ionophore TCHT in a glass dish of 2 cm in diameter. The mixture was completely dissolved in 3 mL of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube with an outer diameter of 5 mm was dipped into the mixture for about 5 s, during which a nontransparent membrane of about 0.3 mm thickness was formed on its tip.

The tube was then pulled out from the mixture and kept at room temperature for about 1 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M sodium

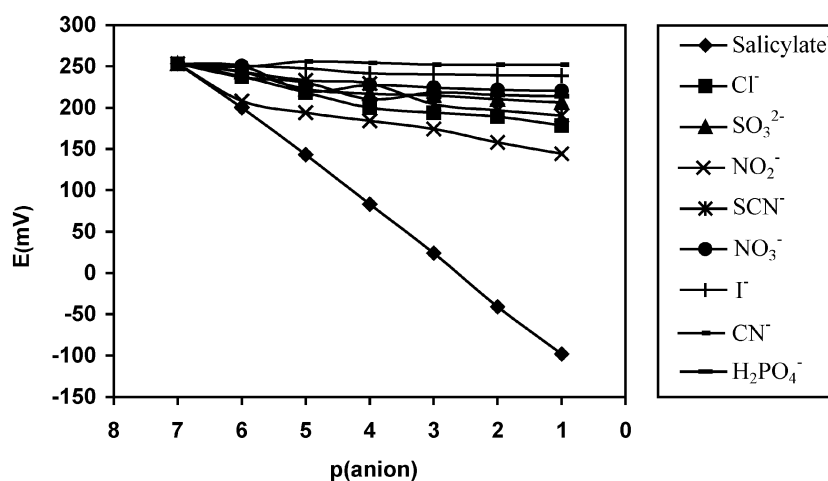


Fig. 2. Response behavior of the TCHT-based membranes towards different anionic species.

salicylate) before being conditioned for 8 h by soaking in a 1.0×10^{-2} M sodium salicylate. The internal reference electrode used in the electrode was a silver/silver chloride reference electrode.

EMF measurements

The EMF measurements were carried out with the following cell assembly:

Ag-AgCl/internal solution (1.0×10^{-3} M sodium salicylate + 1.0×10^{-3} M sodium chloride)/PVC membrane/test solution/Hg-Hg₂Cl₂, KCl (satd).

RESULTS AND DISCUSSION

To have an assessment about the selective behavior of this complex toward different anionic species, the first studies were made using the TCHT-based sensor on a large number of organic and inorganic anions. The results of these studies, as plotted in Fig. 2, show the selective behavior of TCHT-based sensors toward salicylate, with respect to the other anions tested. Based on the results we decided that the construction of a TCHT-based salicylate selective sensor is feasible.

Optimization of the membrane composition

It is well known that some important features of the PVC-based membranes, such as the nature and amount of ionophore, the plasticizer properties, the plasticizer/PVC ratio and, especially, the nature of additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes.¹⁹⁻²⁷ Table 1 summarizes results of the composition optimization studies performed in this work. As can be seen from Table 1, between two solvent media-

tors used (BA and NPOE), BA with a much lower polarity than NPOE, shows better sensitivity (nos. 4, 6). This is due to the ability of BA for the extraction of salicylate ions with a lipophilic property, from aqueous solution to the organic membrane phase. As can be seen from Table 1, the sensitivity of the sensor is affected by the amount of ionophore in the membrane which is investigated in membranes no. 1 to no. 3. Increasing the amount of TCHT, up to a value of 6%, results in the best sensitivity (no. 2). As can be seen among the membranes no. 1, no. 2 and no. 3, which are constructed in an absence of additive, further increasing the amount of TCHT from 6% in membrane no. 1 to 7% in membrane no. 3, decreases the potential response, most probably due to inhomogeneities caused by the saturation of the membrane solvent.

Since the presence of lipophilic positively charged additives improves the potentiometric behavior of certain selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity,²⁷⁻³¹ the addition of 3% HTAB, in membranes no. 4 and no. 5, will increase the sensitivity of the electrode response considerably so that the membrane electrode demonstrates a Nernstian behavior compared to membranes no. 1 to no. 3. However, the membranes with the composition of 30% PVC, 6% TCHT, 3% HTAB, 61% BA show a nice Nernstian potential response. The potential response of the electrode with the optimum composition and response behavior is shown in Fig. 3.

Dynamic response time

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the salicylate concentration in solution, over a concentration range of 1.0×10^{-2} - $1.0 \times$

Table 1. Optimization of the membrane ingredients

No.	% Composition				Slope (mV/decade)
	TCHT	Plasticizer	Additive	PVC	
1	5	BA, 65	-	30	31.9 ± 0.1
2	6	BA, 64	-	30	40.4 ± 0.4
3	7	BA, 63	-	30	37.5 ± 0.2
4	6	BA, 61	HTAB, 3	30	59.0 ± 0.3
5	6	BA, 62	HTAB, 2	30	57.7 ± 0.3
6	6	NPOE, 61	HTAB, 3	30	39.3 ± 0.2
7	-	BA, 68	HTAB, 2	30	17.4 ± 0.5

10^{-7} M.

The actual potential versus time trace is shown in Fig. 4. As seen, in the whole concentration range the membrane electrodes reach their equilibrium responses in a very short time (15 s).

Calibration curves and statistical data

The potential responses of the proposed sensor at varying concentrations of salicylate ions show a linear response in the range of 1.0×10^{-1} - 1.0×10^{-7} M. The slope of

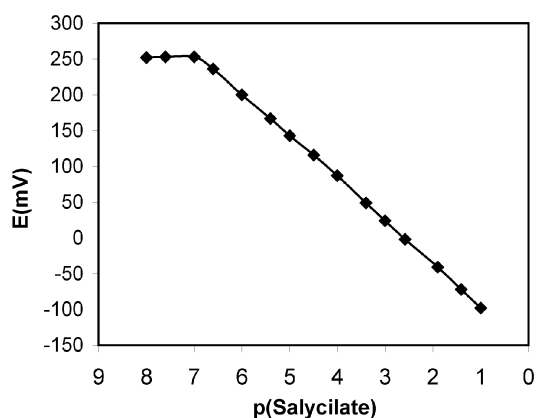


Fig. 3. Calibration curve of the sensor with the optimum composition (No. 4).

the calibration graph was 59.0 ± 0.3 mV per decade of the activity of salicylate ions. The limit of detection as determined from the intersection of the two extrapolated segments of the calibration graphs was 8.0×10^{-8} M. The standard deviation of ten replicate measurements is ± 0.4 mV.

Lifetime of the sensor

The membrane electrodes prepared could be used for at least 2 months without any measurable divergence. The lifetimes of the sensors were tested over a period of 70 days. During this period, the electrodes were in daily use over an extended period of time (one hour per day), and the results are given in Table 2. As can be seen from Table 2, after 8 weeks a very slight gradual decrease and increase in the slopes and detection limit was observed, respectively. This is due to the leaking of membrane ingredients from membrane to the solution. Thus, the membrane electrode prepared could be used for at least 2 months without any measurable divergence.

Effect of pH on potential response of the sensor

The potential response of the membrane sensor was investigated in the pH range of 4.0-11.0, using a 1.0×10^{-4} M solution, and the results are shown in Fig. 5. As can be

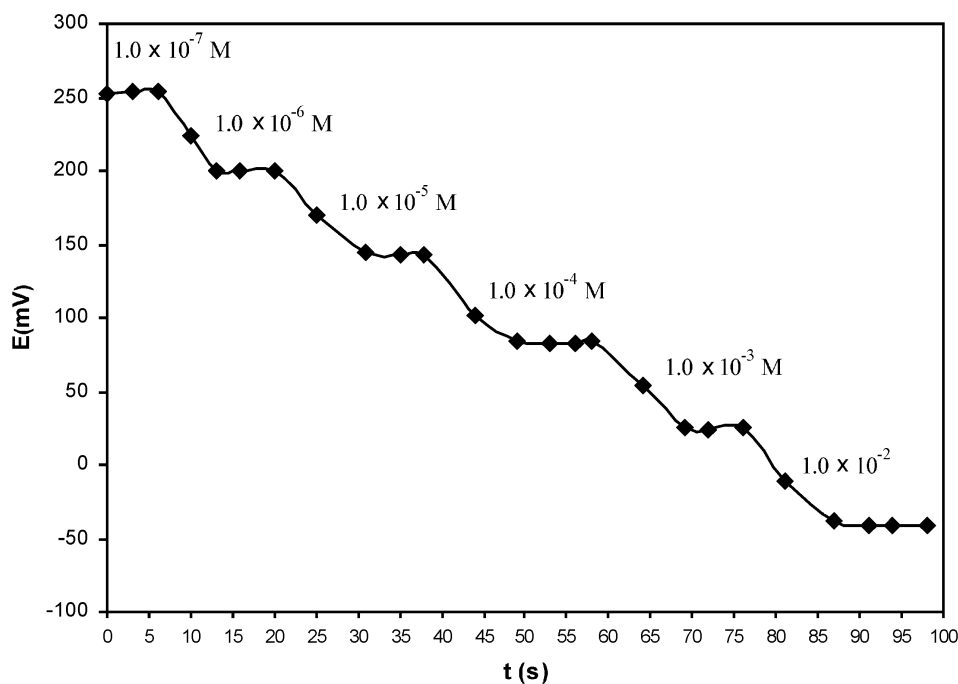


Fig. 4. Response time of the TCHT-based sensor by 10 fold changes in the concentration of the test solution.

Table 2. The lifetime of the salicylate membrane sensor

Week	Slope (mV per decade)	DL
First	59.0 ± 0.2	8.0 × 10 ⁻⁸ M
Second	58.8 ± 0.3	8.3 × 10 ⁻⁸ M
Third	58.5 ± 0.3	8.6 × 10 ⁻⁸ M
Fourth	58.4 ± 0.5	8.8 × 10 ⁻⁸ M
Fifth	58.3 ± 0.6	9.0 × 10 ⁻⁷ M
Sixth	58.1 ± 0.3	9.2 × 10 ⁻⁷ M
Seventh	58.0 ± 0.4	9.2 × 10 ⁻⁷ M
Eighth	57.8 ± 0.2	9.5 × 10 ⁻⁷ M
Ninth	55.1 ± 0.5	4.5 × 10 ⁻⁶ M
Tenth	50.4 ± 0.7	8.5 × 10 ⁻⁶ M

seen, the potential remains constant in the pH range of 5.0–10.5. At lower pH values, a drift in the potential was observed. This is due to the decrease of concentration of free salicylate ions at pH lower than 7.0. At higher pH values the drifts that are observed are due to the interferences of the OH⁻ and their competition with salicylate ions.

Selectivity of the sensors

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients, K_{sel} . In this work, we determined selectivity coefficients with the separation solution method (SSM) and matched potential method (MPM).^{32–34}

According to the MPM, a specified activity (concentration) of primary ions ($A = 1.0 \times 10^{-6} - 1.0 \times 10^{-4}$ M of salicylate) is added to a reference solution (1.0×10^{-6} M of salicylate) and the potential is measured. In a separate experiment, interfering ions ($B = 1.0 \times 10^{-3} - 1.0 \times 10^{-2}$ M)

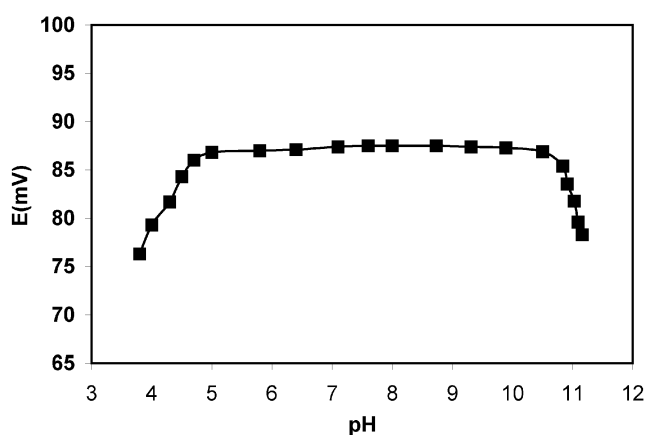


Fig. 5. The potential behavior of the salicylate sensor with pH of the test solution.

are successively added to an identical reference solution, until the measured potential matches the one obtained before by adding primary ions. The selectivity coefficient, $K_{\text{AB}}^{\text{Pot}}$, is determined as

$$K_{\text{AB}}^{\text{Pot}} = \Delta A / A_{\text{B}}$$

where, $\Delta A = a'_{\text{A}} - a_{\text{A}}$; that a_{A} is the initial primary ion activity and a'_{A} is the activity of A in the presence of interfering ion, a_{B} . The resulting values are shown in Table 3. As can be seen, for all anions used, the selectivity coefficients are smaller than 7.0×10^{-5} .

The IUPAC commission of 1976 recommended the use of two different procedures to determine the Nicolskii coefficients of ISEs, namely the so-called separate solution method (SSM). The SSM involves the measurement of two separate solutions, each containing a salt of the determined ion only. The Nicolskii coefficient is then calculated from the two observed emf values.

The experimental conditions employed and the resulting values for the electrode are given in Table 3. As seen, for all diverse ions used, the selectivity coefficients of the electrode are in the order of 4.0×10^{-5} or smaller, indicating they would not significantly disturb the functioning of the salicylate ion-selective electrodes. It is also worth noticing that the potentiometric response of the proposed sensor was found to be insensitive to the nature of the cations used.

Table 3. Selectivity coefficient of various interfering ions ($M^{\text{n-}}$) for the salicylate-selective electrode with the best membrane composition by SSM and MPM

$M^{\text{n-}}$	K_{sel}	
	SSM	MPM
SCN ⁻	7.5×10^{-6}	8.5×10^{-6}
I ⁻	4.0×10^{-6}	3.5×10^{-6}
NO ₃ ⁻	3.0×10^{-6}	5.0×10^{-6}
NO ₂ ⁻	7.5×10^{-6}	8.5×10^{-6}
Cl ⁻	8.5×10^{-6}	1.0×10^{-5}
SO ₃ ²⁻	7.2×10^{-6}	6.5×10^{-6}
H ₂ PO ₄ ²⁻	2.1×10^{-6}	4.0×10^{-6}
CN ⁻	2.0×10^{-6}	3.5×10^{-6}
SO ₄ ²⁻	3.5×10^{-5}	5.0×10^{-5}
C ₂ O ₄ ²⁻	4.0×10^{-5}	7.0×10^{-5}
CH ₃ COO ⁻	2.5×10^{-5}	4.5×10^{-5}
Tartrate	1.7×10^{-5}	7.0×10^{-5}
Citrate	2.5×10^{-5}	5.0×10^{-5}

Table 4. Composition of simulated serum

Compound	Concn. (mM)	Compound	Concn. (mM)
D,L-alanine	0.41	D,L-methionine	0.034
L-arginine	0.21	L-phenylalanine	0.16
L-aspartic acid	0.88	L-serine	0.16
L-cysteine	0.071	D,L-tryptophan	0.085
glycine	0.14	NaHCO ₃	8.0
L-histidine	0.14	NaCl	88.8
L-lysine	0.20	Citric acid	0.17

Analytical applications

The high degree of salicylate selectivity exhibited by the sensor makes it potentially useful for monitoring free salicylate ions in biological samples such as urine and serum. For therapeutic drug monitoring, determining the free concentration of a drug is claimed to be physiologically more relevant than determining its total concentration. In this regard, experiments were performed to determine the feasibility of using the sensor to measure salicylate in a synthetic serum sample. The measurements were conducted with the samples containing 1.8×10^{-5} - 1.2×10^{-3} M of salicylate. The composition of the synthetic serum is given in Table 4. The concentration of each component was chosen to match its normal level in human serum.³⁵ The results obtained by the potentiometric method are in good agreement with those of the colorimetric method, as shown in Table 5. As seen in this table, the salicylate concentrations obtained indicate that the constituents of the synthetic

Table 5. Recovery test of salicylate added to synthetic serum sample

Amt. added (mmol/L)	Amt. found (mmol/L)	Colorimetry (mmol/L)
0.018	0.019	0.017
0.025	0.024	0.026
0.052	0.053	0.051
0.088	0.089	0.087
0.150	0.153	0.151
0.230	0.227	0.235
0.560	0.564	0.557
0.710	0.720	0.715
1.200	1.205	1.197

serum sample do not interfere in any way with the detection of salicylate. It is interesting to note that the monitoring of salicylate concentration in biological samples by the proposed sensor at a very low level of 0.0180 mM is superior to all previously reported methods.³⁶⁻⁴⁰ Therefore, the pro-

Table 6. Comparison of the different evaluation parameters of the THCT-based sensor with other previously reported salicylate sensors

Ref.	Response time	Detection limit	Linearity range	Major interfering anions ($\log k_{A,B} > -2.15$)	Slope
[26]	~10 s	5.0×10^{-6} M	1.0×10^{-5} M 1.0×10^{-1} M	SCN ⁻ , ClO ₄ ⁻	-59.2
[36]	< 10 s	4.0×10^{-5} M	2.0×10^{-4} M 1.0×10^{-2} M	Acetyl salicylate	-55
[37]	10 s	1.0×10^{-6} M	2.5×10^{-6} M 1.0×10^{-1} M	SCN ⁻ , ClO ₄ ⁻ , I ⁻	-57.4
[38]	-	2.5×10^{-6} M	4.0×10^{-6} M 1.0×10^{-1} M	SCN ⁻ , ClO ₄ ⁻	-57.05
[39]	20-30 s	8.0×10^{-7} M	1.0×10^{-6} M 1.0×10^{-1} M	-	-59.2
[40]	120 s	4.0×10^{-5} M	1.0×10^{-4} M 1.0×10^{-2} M	SCN ⁻	-55 to -60
This work	< 15 s	8.0×10^{-8} M	1.0×10^{-7} M 1.0×10^{-2} M	-	-59.0

posed sensor could be used for the determination of salicylate in serum samples with very low concentrations.

Comparison of the performance of the salicylate sensors

Table 6 compares the response time, detection limit and selectivity coefficients of the proposed sensor with those of the best salicylate-selective electrodes reported in the literature.^{26,36-40} As it is obvious immediately, the proposed sensor in the terms of detection limit and dynamic range is superior to the previously reported salicylate membrane sensors.

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