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Determination of Salicylate ion by Potentiometric Membrane Electrode based on Zinc Aluminium Layered Double Hydroxides-4(2,4-dichlorophenoxy)Butyrate Nanocomposites

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A new salicylate ion sensor based on zinc aluminium layered double hydroxides-4(2,4-dichlorophenoxy) butyrate (Zn/Al-DPBA) nanocomposite was developed. Three plasticisers with different polarity, namely 2-nitrophenyloctylether (2-NPOE), tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl) adipate (BEHA) were used to study the performance characteristic of the sensor. The membrane electrode having compositions 7:30:60:3 (Zn/Al-DPBA:PVC: 2-NPOE:NaTPB) exhibited excellent Nernstian slope of 58.8 ± 1.0 mV/decade in the concentration range of 1.0 x 10^{-5} to 1.0 x 10^{-1} M. It had a detection limit of 3.9 x 10^{-6} M and was able to give a constant potential response in the pH range of 4.0 to 12.0 at 25 ± 1 ºC. The proposed sensor was easy to develop, low cost, showed fast response time (within 11-35 s) and can be used up to 4 months without any divergence in potential. The electrode was used for the determination of salicylate in pharmaceutical samples and the results were comparable with those obtained with high performance liquid chromatography method.

Keywords: Salicylate, Ion selective electrode, Potentiometry, Nanocomposite, Ionophore

1. INTRODUCTION

Salicylate, acetylsalicylic acid (aspirin) and their derivative compounds are often used as fungicidal and antimicrobial agents in pharmaceuticals preparation (external use), as well as in the treatment of inflammatory processes as antipyretic and analgesic drugs (internal use). Salicylate was used in food and beverages preservation, but it has been banned since the sixties in several countries

due to its toxicity [1-3]. In blood, the salicylate becomes toxic when its concentration is higher than 2.2 x 10^{-3} mM (300 mg/L). The effective therapeutic range is between 1.1 x 10^{-3} to 2.2 x 10^{-3} mM (150-300 mg/L), which is very close to the toxicity level. The salicylate concentration values higher than 4.3 x 10^{-3} mM (600 mg/L) are regarded as lethal [2,4]. Therefore, an effective method is required to monitor the salicylate level in the serum.

The conventional method for the determination of salicylate is based on Trinder reaction, in which the salicylate ion reacts with ferric ion to form a coloured complex in an acidic solution. This method lacks adequate selectivity for the formation of other similar complex [5]. Analytical techniques such as high performance liquid chromatography (HPLC) [6-8], fluorometry [9], phosphorimetry [10], luminescence [11], biomimetic [12], UV spectrophotometry [13,14], gas chromatography-mass spectrometry (GCMS) [15] and flow injection atomic absorption spectrometry [16] have also been used for this purpose. However, many of these techniques display drawbacks such as time consuming and complex sample pre-treatment procedure.

Ion selective electrode (ISE) is widely used for the determination of ionic species in aqueous environment. This technique offers excellent selectivity, fast response time, low cost, simple design and development [17-19]. However, there are only a few reports on the use of potentiometric method for salicylate determination in the pharmaceuticals formulations [20-24]. Studies have shown that layered double hydroxides have great potential to be used as ionophores for the development of anion potentiometric sensors [25-27]. As further discussed by Ballarin et al. [25], these materials are able to behave as anion exchangers.

To our knowledge, there is so far, no report in the literature describe the development of ISE using zinc aluminium layered double hydroxides-4(2,4-dichlorophenoxy) butyrate (Zn/Al-DPBA) (Fig. 1) nanocomposite as an ionophore. The ultimate aim of this work is to develop an ISE based on Zn/Al-DPBA nanocomposite for potentiometric determination of salicylate ion (Sal^-).

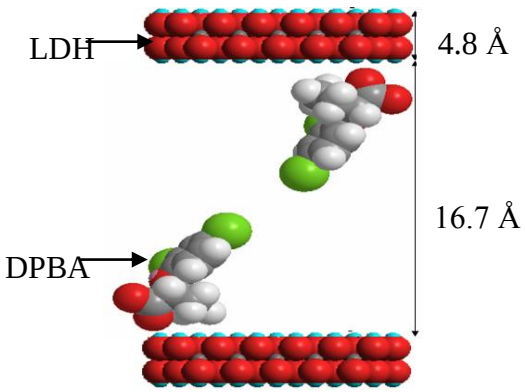

Figure 1. The proposed arrangement of DPBA intercalated into LDH inorganic interlayer

2. EXPERIMENTAL

2.1. Apparatus

The potentiometric measurements were carried out on solutions magnetically stirred at 25 ± 1 ºC, using a digital pH/ion meter (Orion 720A) with a sensitivity of 0.1 mV. A Ag/AgCl electrode (SCE) of BASi, MF-2052 (USA) with a fibre junction was used as the external reference electrode. The pH value was measured using a glass-pH electrode (Orion 915600).

2.2. Chemicals and reagents

All chemicals were of analytical-reagent grade purity and used without further purification. High molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyloctylether (2-NPOE), tris(2-ethylhexy) phosphate (TEHP) and bis(2-ethylhexyladipate) (BEHA) were obtained from Fluka (Switzerland), while sodium tetraphenylborate (NaTPB) was supplied by Sigma-Aldrich (USA). Potassium and sodium salts of all anions and tetrahydrofuran (THF) were purchased from Merck (Germany). The Zn/Al-DPBA nanocomposite was synthesised according to the same procedure outlined by Hussein et al. [28]. The pH adjustments were made with a Britton Robinson buffer and sodium hydroxide solution. Stock standard solution of 1.0×10^{-1} M sodium salicylate (NaSal) was prepared freshly in distilled deionised water. The stock solution was further diluted to the required concentrations before use.

2.3. Preparation of salicylate membrane

The membrane solutions were prepared by dissolving varying amounts of ionophore (Zn/Al-DPBA), PVC, plasticiser and NaTPB in THF. The mixture was stirred and air bubbles were removed. The solution was transferred into a flat bottom glass plate of 2 cm diameter, covered with a filter paper and left overnight to allow slow evaporation of the solvent at room temperature. The membrane was detached from the glass plate, cut to suitable sizes and attached to one end of a glass tube with Araldite® glue for 4 days. The glass tube was filled with the internal solution (1.0×10^{-2}M NaSal). The electrode was conditioned by soaking in 1.0×10^{-3} M Sal^- for 24 h before use.

2.4. Electrode conditioning and EMF measurement

A conditioning procedure was adopted to avoid the exposure of the electrode membrane to a relatively preferred ion prior to measurement of specific target ion [29-31]. This procedure is crucial for the determination of unbiased selectivity coefficients [31]. Before starting the measurements, the electrode was preconditioned in the magnetically stirred water until a steady potential was obtained. The performance of the electrode was investigated by measuring its potential in sodium salicylate solutions ranged from 1.0×10^{-7} to 1.0×10^{-1} M. The data were plotted as observed potential vs. the

logarithm, on the salicylate concentration [32]. The electrochemical system for this electrode can be represented as follow:

Ag|AgCl, KCl (3M)|internal solution NaSal(1.0×10^{-2}M)||PVC membrane|test solution|Pt

3. RESULTS AND DISCUSSION

The selectivity, sensitivity, lifetime and linearity of the ISEs depend on the nature of the ionophore, properties of the plasticiser and composition of the membrane [19,33-35]. The amounts of the ionophore and additive used, as well as the PVC ratio have great influence on the sensitivity and selectivity of ISE for salicylate ion [36-38].

In this study, three plasticisers with different polarity, 2-NPOE, TEHP and BEHA were used to study the performance characteristic of the sensor. The potential responses of the salicylate membranes are given in Table 1. Membrane No.1 was developed without addition of plasticiser and NaTPB. This membrane showed linearity in the concentration range of 1.0×10^{-5} to 1.0×10^{-2} M and gave a Nernstian slope of 48.5 ± 1.0 mV/decade. When BEHA and 2-NPOE were added the Nernstian slopes were increased to 52.3 ± 1.0 and 58.8 ± 1.0, respectively.

Table 1. Optimized membrane composition and their potentiometric response properties in salicylate selective electrode

Membrane No.	PVC (mg)	Ionophore (mg)	Plasticizer (mg)	Additive (mg)	Slope (mV/decade) ± 1.0	Linear range (M)	Limit of detection (M)	Response time (s)	Lifetime (month)
1	30	7	without	without	48.5	1.0×10^{-5} – 1.0×10^{-2}	7.9×10^{-6}	40–72	4
2	30	7	without	3	56.0	1.0×10^{-5} – 1.0×10^{-2}	7.5×10^{-6}	11–35	4
3	30	7	60(2NPOE)	without	50.5	1.0×10^{-4} – 1.0×10^{-1}	2.8×10^{-5}	11–35	4
4	30	7	60(2NPOE)	3	58.8	1.0×10^{-5} – 1.0×10^{-1}	3.9×10^{-6}	11–35	4
5	30	7	60(BEHA)	without	43.6	1.0×10^{-5} – 1.0×10^{-2}	5.6×10^{-5}	11–35	4
6	30	7	60(BEHA)	3	52.3	1.0×10^{-5} – 1.0×10^{-2}	6.3×10^{-6}	11–35	4
7	30	7	60(TEHP)	without	21.0	1.0×10^{-3} – 1.0×10^{-1}	5.6×10^{-4}	11–35	4
8	30	7	60(TEHP)	3	49.6	1.0×10^{-4} – 1.0×10^{-1}	6.3×10^{-5}	11–35	4

Meanwhile, addition of TEHP did not cause significant effect on potential response of the membrane. From Table 1, the weight ratio (plasticiser:PVC) of 2.0 produced maximum sensitivity. The application of 2-NPOE has resulted in greater potentiometric response, better sensitivity and linearity of calibration plots as compared to TEHP and BEHA. The nature of the plasticiser influences both the mobility of the ionophore and its complex. Furthermore, plasticizers were applied to the polymer matrix in order to decrease its viscosity and to provide mobility of the membrane constituents

within the membrane phase. The ionophore membrane selectivity depends on the dielectric constant of the membrane phase [39]. The effectiveness of plasticisers to improve sensor characteristics has also been investigated using different concentrations of plasticisers having different dielectric constants (ε): TEHP (ε =4.8),dibutyl butyl phosphonate, DBBP (ε =4.6), dibutyl phthalates, DBP (ε =6.4), 2-NPOE (ε =24), 1- chloronaphthalene, CN (ε =5), dioctyl phthalate, DOP (ε =5), and PVC(ε =3.9). The addition of plasticizers improves the working concentration range [40–43].

The plasticiser 2-NPOE (ε=24) is a more effective solvent mediator in preparing the salicylate selective electrode because it has high dielectric constant and polarity as compared to BEHA (ε= 4) and TEHP (ε= 4.8). Besides that, the 2-NPOE has the nitroaromatic group and octylphenyl ester as that can act electron withdrawing group (NO_2 or CN) and their position on the phenyl ring has been varied. The phenyl ethers were selected for transportation studies because of their high polarity to attract the ionophore.

Membrane No.4 with composition of 30 mg PVC, 60 mg 2-NPOE, 7 mg Zn/Al-DPBA and 3 mg NaTPB exhibited a wide working concentration range of 1.0×10^{-5} to 1.0×10^{-1} M and produced the best Nernstian slope of 58.8 ± 1.0 mV/decade. As shown in Table 1, the potential response of the membrane was improved by NaTPB addition, an anion excluder [44]. Xu et al. [45] recommended the use of NaTPB in detecting Sal^-. This additive reduces the membrane resistance and interference from sample anions [46-48]. Therefore, NaTPB enhances the response behaviour and selectivity.

As recommended by the International Union of Pure and Applied Chemistry (IUPAC), the limit of detection (LOD) was calculated from the intersection of two extrapolated segments of the calibration curve (Fig. 2). The LOD for membrane No.4 was found to be 3.9×10^{-6} M, while membranes No.6, No.8 and No.1 had a LOD value in the range of between 6.3×10^{-6} M, 6.3×10^{-6} M and 7.9×10^{-6} M respectively. Of membranes studied, membrane No.4 showed highest sensitivity. This may be due to the phenyl ethers group that was selected for transportation studies because of the latter high polarity in the chemical structure of the 2-NPOE.

The effect of pH on potential response of the membranes was studied over the pH range of 3.0 to 12.0 at salicylate ion concentration of 1.0×10^{-2} M (Fig. 3). As shown in Fig. 3, the potential response for membrane No.4 remains constant between pH 4.0 and 12.0. Meanwhile, membranes with BEHA and TEHP addition showed a constant response within pH range of 6.0 to 11.0 and 7.0 to 11.0, respectively. In basic medium, more OH^- ions are available to compete with salicylate ions for interaction with the ionophore. At low pH values, H^+ ions will protonate Zn/Al-DPBA which will lead to a significant reduction in its ability to interact with salicylate ions. 2-NPOE had a significant effect on membrane's ability to retain pH effect on potential response. It was apparent that membrane No.4 was able to produce a constatnt potential response over pH value of 4.0 to 12.0.

The response times of the electrode were measured after successive immersions of the electrode in a series of salicylate solutions which ranged from 1.0×10^{-5} to 1.0×10^{-1} M and results of this study are shown in Fig.4. The ISE without plasticized and NaTPB addition membrane No.1 showed a response time of 40-72s. The response time reduced to 11-35s when the NaTPB and plasticiser were added. Ballarin et al. [25] developed an ISE based on layered double hydroxides (LDH) or hydrotalcite for salicylate determination and obtained a response time of 1-6 minutes. The proposed ISE response time is 11-35s, therefore, the latter sensor is better than the former sensor. It is

important to note that the potential can be recorded from low to high concentration of salicylate, or vice versa. It was apparent that the sensing behaviour was not affected by this procedure.

The lifetime of each membrane electrode depends on the one or more of component in the structure loss, while contacting with aqueous solution. Zn/Al-DPBA nanocomposite which is used as an ionophore has sufficient liphophilicity to prevent leaching of the membrane matrix into the aqueous solution surrounding the membrane electrode. Zhang et al. [49] and Maria de los et al. [50] note that the application of liphophilicity ionophore and plasticiser may result in stable potentials and long lifetimes. In order to investigate stability, the electrode membranes were tested over a period of 4 months. During this period the membrane electrodes were used daily and were stored in 1.0×10^{-3} M Sal^- solution when not in use. Before any measurements, the membrane electrode was conditioned in 1.0×10^{-3}M Sal^- for 30-40 minutes. No significant change in performance of the electrode (slope, linear range) was observed during this period.

The potentiometric selectivity coefficient $K_{A,B}^{pot}$ is defined as the ability of an ISE to distinguish between ions in the same solution, and it has been regarded as the most important

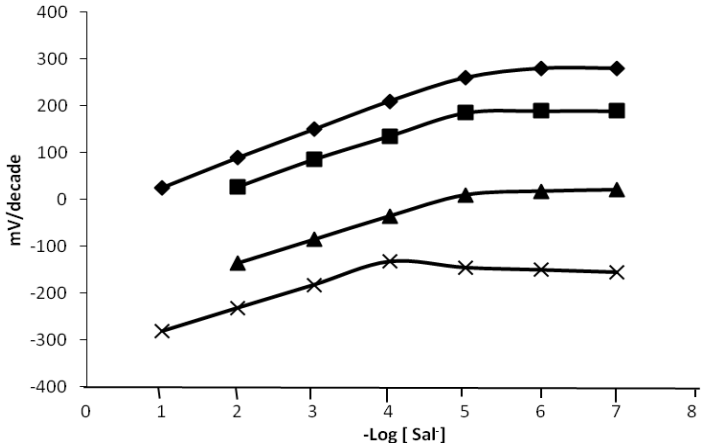

Figure 2. Calibration graph for the potentiometric response of the salicylate selective electrode (♦) 2-NPOE, (■) BEHA , (▲) control and (×) TEHP

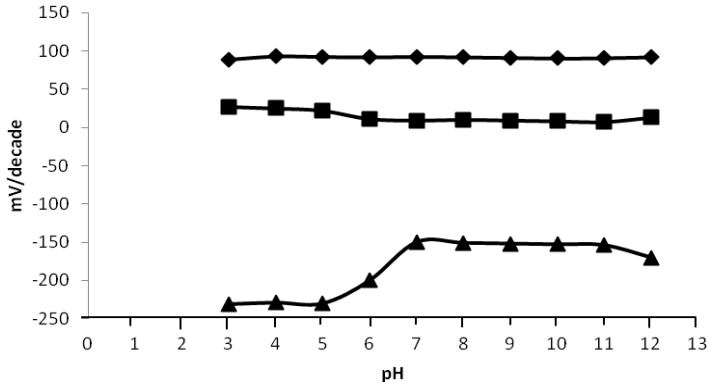

Figure 3. The pH responses of the membrane electrode at 1.0×10^{-2} M Salicylate concentration (♦) 2-NPOE, (▲) TEHP and (■) BEHA

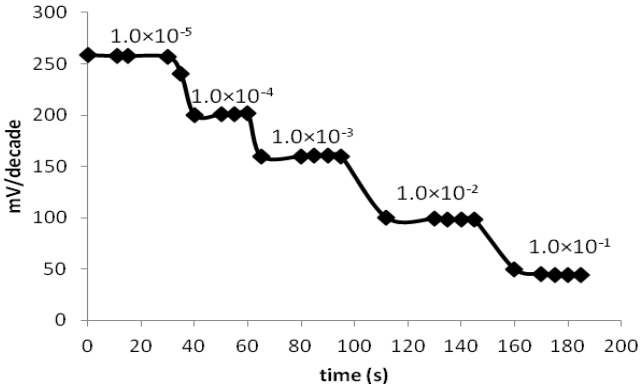

Figure 4. Respons time of the membrane electrode (No.4) for salicylate with change of the concentration from 1.0×10^{-5} to 1.0×10^{-1}M

characteristic of an ISE [44]. In order to realize the level of interference caused by these ions in the performance of electrode, a mixed method was carried out [51–53]. In all experiments conducted, the potential response was observed at the optimum pH 9.5. The selectivity values $K_{A,B}^{pot}$ were evaluated using the 'fixed interference method' (FIM) [54-58]. According to FIM, the potentials were measured in a fixed interfering ion concentration (1.0×10^{-2} M) and a series of varying salicylate ion concentrations (1.0×10^{-7} to 1.0×10^{-1} M). The $K_{A,B}^{pot}$ values are summarised in Table 2. From Table 2, membrane No. 4 demonstrates high selective response toward salicylate ion over other anions with a selectivity sequence order of $SCN^->SO_3^{2-}>SO_4^{2-}=CrO_4^{2-}>NO_3^->Cr_2O_7^{2-}=PO_4^{3-}>Br^->CH_3COO^->Cl^->I^->CO_3^{2-}>OH^->HPO_4^{2-}$. The sequence order obtained is not in good agreement with the so-called Hofmeister selectivity sequence, $R^->ClO_4^->SCN^->I^->NO_3^->Br^->NO_3^->NO_2^->Cl^->OAC>HCO_3^->SO_4^{2-}>HPO_4^{2-}$ [29]. This might be due to specific interaction of the anions with the central metal atom in the ionophore used. Ballarin et al. [25] point out that the membranes containing hydrotalcite (HT) as the ionophore does not have a significant selectivity towards the intercalated anion. Therefore, the membrane No.4 has an anti-hofmeister series. As discussed by Isa et al. [44], the $K_{A,B}^{pot}$ value of less than one indicates high selectivity toward the analyte than the interfering ion. Therefore, the interfering ions studied did not interfere the determination of salicylate using membrane No. 4. Based on the $K_{A,B}^{pot}$ values listed in Table 2, it is clear that the proposed membrane sensor is reliable.

Table 2. Selectivity of coefficients determined by use of the fixed interference method for the salicylate-selective electrode (membrane No. 4)

Interfering ion	$K_{A,B}^{pot}$	Interfering ion	$K_{A,B}^{pot}$
NO_3^-	4.0×10^{-2}	Br^-	1.6×10^{-2}
SO_3^{2-}	2.0×10^{-2}	CO_3^{2-}	4.0×10^{-3}
SO_4^{2-}	2.5×10^{-2}	CH_3COO^-	3.2×10^{-2}
SCN^-	1.0×10^{-2}	$Cr_2O_7^{2-}$	1.0×10^{-2}
OH^-	1.6×10^{-4}	$Cr_2O_4^{2-}$	2.5×10^{-2}
Cl^-	1.0×10^{-3}	HPO_4^{2-}	4.0×10^{-4}
I^-	3.2×10^{-3}	PO_4^{3-}	1.0×10^{-2}

It is necessary to compare the potentiometric parameters obtained from this study with values from other reported ISEs, since this will suggest the effectiveness of Zn/Al-DPBA nanocomposite as an inonophore for salicylate ISE. The potentiometric parameters of the proposed electrode are comparable with those of salicylate ISE electrodes as shown in Table 3. As can be seen from the table, the proposed Sal-ISE is considerably improved with respect to those of the previously reported salicylate- ion selective electrodes.

Table 3. Comparison of the potentiometric parameters of the proposed Sal-selective electrode with the other Sal- selective electrode

Reference number	Ionophore	Concentration range (M)	Detection limit (M)	Slope (mV/decade)	pH range	Response time (s)	Life time (month)
[59]	New Schiff base tetraneclear copper complex of O-vannlin-methionine $(Cu(II)_4$-TVM)	1.5×10^{-6}-1.0×10^{-1}	8.0×10^{-7}	-56.3	3.0–8.0	20-30	3
[60]	1,8-bis(salicylaldiminato)-3,6-dioxaoctane copper	1.0×10^{-6}-1.0×10^{-1}	8.0×10^{-7}	-58.1	4.0-8.0	30-40	2
[61]	Tin(IV) tetraphenylporphyrin	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-5}	-55.0	2.7-7.8	5-10	2
[62]	Chiral salen Mn(II) complex	1.0×10^{-5}-1.0×10^{-1}	7.2×10^{-6}	-58.1± 0.5	7.0-10.2	30	3
The proposed Sal^- ISE	Zinc aluminium 4-(2,4-dichlorophenoxy)butyric acid	1.0×10^{-5}-1.0×10^{-1}	3.9×10^{-6}	-58.8± 1.0	4.0-12.0	11-35	4

Table 4. Determine of salicylate in different aspirin tablet samples (n=3): comparison of potentiometric results with HPLC method

Aspirin sample (mg/tablet)	Proposed electrode (ISE) (wt.%)	HPLC (wt.%)
100	8.5±0.2	8.3±0.2
300	8.9±0.3	8.8±0.2
500	9.3±0.2	9.5±0.3

The proposed electrode was applied to determine salicylate ion in pharmaceutical sample. The data were compared with the high performance liquid chromatography (HPLC) using the standard addition method. Table 4 shows that the proposed electrode indicated a good agreement between the potentiometric and HPLC method.

4. CONCLUSIONS

This work highlights the applicability of Zn/Al-DPBA nanocomposite as an inonophore for

salicylate ISE. The properties of this material are supposed to be responsible for the potentiometric behavior of the membrane based on the Zn/Al-DPBA having a divalent anion in the interlayer that should display a better selectivity. Furthermore, Zn/Al-DPBA acts as ionophore in order to develop an ion selective electrode sensitive to the anion 'entrapped' in the clay structure. Zn/Al-DPBA's best performance in the ion selective electrode depends mainly on the electrostatic interaction between the brucite-like plane and the exchangeable anions. The membrane electrode with plasticizer 2-NPOE displays a good performance because of the influence of the high dielectric constant. The anions selectivity obtained from this study was in the order of $SCN^->SO_3^{2-}>SO_4^{2-}=CrO_4^{2-}>NO_3^->Cr_2O_7^{2-}=PO_4^{3-}>Br^->CH_3COO^->Cl^->I^->CO_3^{2-}>OH^->HPO_4^{2-}$.

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