Novel Triiodide PVC-Based Membrane Sensor Based on a Charge Transfer Complex of Iodine and Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone

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In this study a novel triiodide ion-selective electrode based on a charge transfer complex of iodine and Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone (ICT), as a membrane carrier was prepared. The electrode has a linear dynamic range between $1.0 \times 10^{-2}$ and $5.0 \times 10^{-7}$ M, with a Nernstian slope of 58.99 ± 0.3 mV decade $^{-1}$ and detection limit of $3.0 \times 10^{-7}$ M. The potentiometric response of the proposed sensor is independent of the pH of the solution in the pH range of 3.0-10.0. The electrode possesses the advantages of short conditioning time, fast response time, and especially, very good selectivity over a large number of common organic and inorganic anions. The electrode can be used for at least 6 months without any considerable divergences in the potentials. It was used as an indicator electrode in potentiometric titration of triiodide with thiocyanate.

Key Words : Triiodide ion-selective electrode, PVC membrane, Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone, Potentiometry

Experimental Section

Reagents. Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), acetophenon (AP), o-nitrophenylacetyl ether (NPOE), iodine, tetrahydrofuran (THF), hexadecyltrimethylammonium bromide (HTAB), and high relative molecular weight PVC (all from Merck) were used as received. The potassium and sodium salts of all anions used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P$_2$O$_5$. Doubly distilled deionized water was used throughout.

Synthesis of Complex. The ITC was synthesized in three steps including the synthesis of 2,3-butanedihydrazone, the synthesis of Schiff’s base and finally the synthesis of the charge transfer complex.

Step one, the synthesis of 2,3-butanedihydrazone: To a boiling solution of 11.63 g of aqueous hydrazine (0.24 M) in 100 mL of methanol, were added 75 mL of biacetyl (0.12 mol, 10.33 g), over a period of 120 minutes. Refluxing was continued for an additional 60 minutes. Then 200 mL of water were added and the methanol was removed by distillation. After cooling the resulting aqueous solution in an ice-bath, white crystals of the product were formed. These were filtered, washed with a little water, recrystallized from 100 mL of hot methanol, and dried in vacuum, m.p 158-159°C (reported 158°C); yield ~54%. Anal. Calcd. for C$_{10}$H$_{14}$N$_2$: C, 42.16; H, 8.71; N, 49.08. Found: C, 42.16; H, 8.71; N, 49.74. IR (KBr, cm$^{-1}$): 3330, 3180 (N-H); 1580 (C=N).

Step two, the Schiff’s base preparation: 2,3-Butanedihydrazone (1.14 g, 0.01 mol) was dissolved in 50 mL
Novel Triiodide Membrane Sensor

ethanol and then transferred into a 250 mL three necked flask. Under reflux 2.75 g (0.02 mol) of 2-hydroxyacetophenone in 80 mL of ethanol were added drop wise to the flask. The stirred mixture was kept reacting for 3 h under reflux, and then cooled to room temperature. The solid product was filtered, and the product was recrystallized from chloroform. Yield ~68%. Anal. Caded. For C₂₀H₂₂N₄O₄: C, 68.55%; H, 6.33%; N, 15.99. Found: C, 68.41%; H, 6.26%; N, 9.24%. IR (KBr, cm⁻¹): 3443 (νO-H); 1608, 1575 (νC=N).

Step three, preparation of the triiodide complex: I₂ and the obtained Schiff’s base were separately dissolved in chloroform and were mixed with each other in mol ratio of 4:1 (I₂/Schiff’s-base). The mixture was placed in refrigerator for 24 h and the precipitated complex was then separated from solvent by filter paper. Then the precipitate was recrystallized, and after one day, the complex was separated from the solvent by filter paper.

Electrode Preparation. The general procedure to prepare the PVC membrane was to mix thoroughly 63 mg of BA, 30 mg of powdered PVC, 2 mg of HTAB, and 5 mg of ICT in 5 mL of fresh THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at the room temperature for about 12 h. The tube was then filled with an internal filling solution of 1.0 × 10⁻³ M triiodide (1.0 × 10⁻³ M I₂ + 1.0 × 10⁻³ M I⁻). The electrode was finally conditioned by soaking in 1.0 × 10⁻³ M triiodide solutions for 12 h. A silver/silver chloride wire was used as an internal reference electrode.

EMF Measurements. All EMF measurements were carried out with the following assembly: A Corning ion analyzer 250 pH/mV meters was used for the potential measurements at 25.0 ± 0.1 °C. The EMF observations were made relative to a double-junction saturated calomel electrode (SCE, Philips), with its chamber filled with an ammonium nitrate solution. The activities were calculated according to the Debye-Hückel procedure.

Results and Discussion

It is well established that the selective interaction between a given analyte anion and a lipophilic carrier within the membrane is essential for the development of anion-selective polymeric membranes exhibiting anti-Hofmeister potentiometric selectivity patterns. In the case of the transition metal complexes, organometallic and metalloporphyrin compounds, the anion selectivity is mainly governed by the specific interaction between the central metal and anions rather than the lipophilicity of the anions or simple opposite charge interactions with anions.

In the case of triiodide sensor, charge transfer complex, ion-pair association, and Mn (III)-porphyrin derivatives, have been used as specific ion carriers. These reported triiodide sensors, exhibited Nernstian behaviors, and relatively good selectivities. Thus, at first, ICT was used as an ion carrier in the construction of anionic membrane sensors, for a wide variety of common organic and inorganic anions, with different lipophilicities. The potential responses of various anion-selective electrodes based on the charge-transfer complex used, are given in Figure 2. As can be seen, with the exception of triiodide, all anions tested, show negligible responses in the concentration range of 5.0 × 10⁻⁷-1.0 × 10⁻² M. This can be due to their very weak interactions
with the membrane. Figure 2 shows that among various anions tested, iodide exhibits a stronger response than other anions, at higher concentrations. This is most probably to some extent, due to the oxidation of iodide to triiodide ion. However, the triiodide membrane sensor revealed a Nernstian potential response in a wide concentration range (5.0 × 10⁻² - 1.0 × 10⁻² M).

It is well known that the membrane composition, and especially in some cases, the nature of the additive may have a significant influence on the sensitivity and selectivity obtained for a given ionophore. The performance characteristics of several membranes having ingredients of different proportions are summarized in Table 1. It is seen that membrane No. 3 with an optimized composition of 30% PVC, 63% BA, 5% ICT and 2% HTAB results in the best sensitivity and selectivity for the electrode response is shown in Figure 4. As seen, the response times of the PVC membrane for low concentrations of triiodide solutions, each having a 10-fold difference in concentration, was also investigated. A potential-time plot from the intersection of the two extrapolated segments of the calibration graph, was 3.0 × 10⁻⁷ M.

The critical response characteristics of the electrode were assessed according to IUPAC recommendation. The EMF responses of the PVC membrane at varying concentrations of triiodide ion are shown in Figure 3. Figure 3 indicates a rectilinear range from 5.0 × 10⁻² to 1.0 × 10⁻¹ M. The slope of the calibration curve was 58.99 ± 0.2 mV per decade of triiodide concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 3.0 × 10⁻⁷ M.

The average time required for the membrane electrode to reach a potential response within ± 1 mV of the final equilibrium value after successive immersions into a series of triiodide solutions, each having a 10-fold difference in concentration, was also investigated. A potential-time plot for the electrode response is shown in Figure 4. As seen, the response times of the PVC membrane for low concentrations (10⁻⁶), and high concentration of triiodide ions, are less than 12, and 10 s respectively. The standard deviation of 9 replicate measurements is ± 0.4 mV.

The pH dependence of the potential response of the

<table>
<thead>
<tr>
<th>Number</th>
<th>Composition %</th>
<th>Slope (mV decade⁻¹)</th>
<th>Linear Dynamic Range</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>PVC</td>
<td>Plasticizer</td>
<td>HTAB</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>BA, 64</td>
<td>2</td>
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<td>30</td>
<td>BA, 61</td>
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<td>9</td>
<td>30</td>
<td>NB, 63</td>
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Figure 3. Calibration curves of triiodide electrode based on ICT. (No. 3).
proposed electrode in the pH range of 1.0-13 was also tested, and the results are shown in Figure 4. As can be seen, the potential response remains constant over the pH range of 3.0-10.0. In highly alkaline media, the potential decreases sharply, most probably due to the disproportionation reaction between $\text{I}_2^-$ and OH$^-$ that results in the formation of hypooxide and iodide, both of which are insensitive to the membrane electrode. At pH values lower than 3.0, the electrode potential rises sharply. This is probably due to simultaneous response of the electrode to oppositely charged $\text{H}_2\text{O}^+$ and $\text{I}_3^-$ ions.

One of the most important characteristics of an anion-selective membrane electrode is its relative response, for the primary anion over other anions present in solution, which is usually expressed in terms of potentiometric selectivity coefficient. In this work, the matched potential method was used for the determination of the selectivity coefficients. According to this method, a specified activity (concentration) of the primary ion ($A = 10^{-4}$ M of triiodide) is added to a reference solution ($5.0 \times 10^{-7}$ M of triiodide), and the potential is measured. In a separate experiment, interfering ions ($B = 10^{-2}$-10$^{-4}$ M) are successively added to an identical reference solution, until the measured potential matches the one obtained before the addition of primary ions. The matched potential method selectivity coefficient, $K_{\text{SELM}}$, is then given by the resulting primary ion to interfering ion activity (concentration) ratio. The resulting values are given in Table 2.

From the data given in Table 2, it is immediately obvious that the proposed triiodide membrane sensor is highly selective with respect to most common organic and inorganic anions such as fluoride, chloride, bromide, iodide, nitrate, nitrite, sulfate, sulfite, and thiocyanate. Table 2 reveals that, the selectivity coefficients for all anions tested are $10^{-5}$ or smaller (except iodide and thiocyanate with $10^{-4}$), which seems to indicate that these anions have negligible disturbances on the functioning of the triiodide membrane electrode. The surprisingly high selectivity of the membrane electrode for triiodide ion over other anions used, most probably arises from the strong tendency of the carrier molecule SB for triiodide ion in the form of the (SBE-)$\text{I}_3^-$ adduct, as well as the kinetically, and thermodynamically, favored salt molecule matrix reaction between iodide ion and iodine, which results in the formation of a stable $\text{I}_3^-$ ion in solution.

Table 3, compares some of the selectivity coefficients, detection limits, and linearity concentration ranges of the best previously reported triiodide ion-selective electrodes based on different ion-carrier with those obtained for the proposed triiodide electrode based on ICT. As is immediately obvious from Table 3, not only in terms of detection limit and working concentration range, but also in terms of selectivity coefficients, the proposed triiodide sensor is superior to those reported for other triiodide ion-selective electrodes.

The proposed triiodide membrane sensor was found to work well under laboratory conditions. It was successfully used as an indicator electrode to the titration of 25.0 mL of a $1.0 \times 10^{-4}$ M triiodide solution with a $1.0 \times 10^{-2}$ M sodium thiosulfate solution and the resulting titration curve is shown in Figure 6. As can be seen, the amount of triiodide ions in solution can be determined with the electrode.

It is worth mentioning that the membrane electrode may

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**Figure 4.** Dynamic response time of the triiodide electrode for step changes in Concentration of $\text{I}_3^-$: A) $1.0 \times 10^{-5}$ M, B) $1.0 \times 10^{-4}$ M, C) $1.0 \times 10^{-3}$ M, D) $1.0 \times 10^{-2}$ M.

**Table 2.** Selectivity coefficient of various interfering anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>$K_{\text{SEL}}$</th>
</tr>
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<tbody>
<tr>
<td>Br$^-$</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>$&lt; 10^{-5}$</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>$&lt; 10^{-5}$</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>$2.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>$3.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>CN$^-$</td>
<td>$4.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>SO$_3^{2-}$</td>
<td>$1.7 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

**Table 3.** Comparison some of the selectivity coefficients, and detection limit, and linearity concentration range

<table>
<thead>
<tr>
<th>Reference</th>
<th>LDR</th>
<th>DL</th>
<th>$K_{\text{SCN}}$</th>
<th>$K_I$</th>
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<td>$8.0 \times 10^{-6}$ - $5.0 \times 10^{-3}$</td>
<td>$5.0 \times 10^{-6}$ M</td>
<td>$1.20 \times 10^{-3}$</td>
<td>–</td>
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<tr>
<td>26</td>
<td>$7.0 \times 10^{-6}$ - $2.0 \times 10^{-3}$</td>
<td>$3.0 \times 10^{-6}$ M</td>
<td>$5.01 \times 10^{-3}$</td>
<td>–</td>
</tr>
<tr>
<td>27</td>
<td>–</td>
<td>–</td>
<td>$2.51 \times 10^{-3}$</td>
<td>$1.00 \times 10^{-2}$</td>
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<tr>
<td>29</td>
<td>$7.9 \times 10^{-6}$ - $1.0 \times 10^{-1}$</td>
<td>$6.0 \times 10^{-6}$ M</td>
<td>$2.50 \times 10^{-4}$</td>
<td>$6.00 \times 10^{-2}$</td>
</tr>
<tr>
<td>30</td>
<td>$1.0 \times 10^{-5}$ - $1.0 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-6}$ M</td>
<td>$3.09 \times 10^{-3}$</td>
<td>$&lt; 10^{-4}$</td>
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<tr>
<td>This Work</td>
<td>$5.0 \times 10^{-7}$ - $5.0 \times 10^{-2}$</td>
<td>$3.0 \times 10^{-7}$ M</td>
<td>$1.50 \times 10^{-4}$</td>
<td>$3.00 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
possibly be used for the determination of ozone, after the oxidation of iodide to triiodide ion. The use of a triiodide ion-selective electrode for this purpose might be simpler than the use of disposable ozone sondes based on the coulometric oxidation of the iodide to triiodide ion, which are usually used for the determination of ozone.

References