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Potentiometric sensing of iodide using polymeric membranes of microwave stabilized β-AgI

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ABSTRACT

A polymer based heterogeneous ion selective electrode (ISE) membrane was fabricated for the potentiometric sensing of iodide. The sensing element used for the preparation of the ISE membrane was microwave stabilized β-AgI. Because microwave energy was found to be beneficial for causing hysteresis at the phase transition temperature of AgI, an attempt has been made to prepare stable and conductive β-AgI crystals by post microwave irradiation under high pressure. A conventionally precipitated AgI based ISE was also fabricated for comparative studies. The β-AgI based ISE could respond to a wide range of iodide concentrations (1×10^{-8} to 1 M) within 60 s with a detection limit of 10 nM. The ISE gave stable response to iodide ions in a pH range of 2.0–8.0 and was highly selective in the presence of various interfering ions. The performance of the proposed iodide ISE in the analysis of natural and seawater samples was encouraging, and the determination of iodide in table salt and human urine samples was explained using the developed sensor.

1. Introduction

Iodide is essential for human health as it helps to ensure proper thyroid gland function and serves as an antiseptic for skin wounds and for the emergency disinfection of drinking and swimming pool waters. Even though the role of iodide is vital, an excess dosage can cause several health hazards, such as gastrointestinal irritation and ulceration, chemical pneumonitis, hypothyroidism, hemolytic anemia, acute renal failure and congenital goiter [1]. Pure iodine is also concern for human health as ^{291}I exists as a radionuclide even though it is found in low concentrations in nuclear effluents (long half-life of $\sim 10^7$ years) [2]. In aqueous environments, iodide is the dominant species of iodine, especially at low to neutral pH values, and it has a positive redox potential. Exposure to high doses of iodide may occur by the ingestion of drinking water, pharmaceuticals, and food; therefore, the determination of iodide is essential in our environmental analysis [3–5].

Various analytical methods reported for the determination of iodide reveal that most of these techniques are complicated and expensive for routine analysis. Electrochemical detection methods, such as amperometry, biamperometry, stripping voltammetry, and potentiometry, have been reported for the determination of iodide [6]. Among these electrochemical methods, the potentiometric determination of the iodide concentration via ion selective electrodes (ISEs) was one of the simplest methods used and widely agreed for the sensing of various ionic species [7]. ISEs form a group of simple and inexpensive electro-analytical tools because they possess unique characteristics, such as fast response, wide dynamic range, easy preparation method and simple experimental procedures [8,9]. ISEs have been widely used in the determination of ions in various fields of research, such as environmental science, life science, clinical science, diagnostics, pharmaceutical science, and water chemistry [10–12].

Pungor and Hollós-Rokosinyi founded an important era for developments in iodide sensing by fabricating the first iodide selective electrode in 1961 using a silver iodide precipitate incorporated into paraffin wax as the sensing membrane [13]. Similar iodide electrodes were later fabricated based on pressed pellets of AgI alone or with Ag_2S incorporated into paraffin wax or silicon rubber [14]. Later, polyvinyl chloride (PVC) membrane electrodes with complex carriers were developed with Nernstian slopes to ensure high selectivity and sensitivity [15–21].

Research in the area of iodide sensing by ISEs is in an advanced stage, and various ionophores incorporated into PVC membranes are currently used extensively. A comparison of the characteristics of some iodide ISEs, including commercially available ISEs, is shown in Table 1. Specific metal coordination complexes, as iodide ionophores, have been incorporated into the PVC matrix of the ISEs to obtain lower detection limits. By understanding the features and conductivity of the AgI crystal lattice, the scope of Pungor's strategy, which was based on conductive AgI, can be broadened so

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Table 1
Comparison of the characteristics of iodide ISEs, including the commercial ISEs.

Sensing element	Linear range (M)	pH	LOD (μM)	Response time (s)	Interference	Reference
Ionophore based iodide ISEs						
Triisobutyl phosphine sulphide complexes of Ag(I) and Hg(II)	1×10^{-5} to 10^{-3}	–	4–6	30–720	SCN^-, Br^-, Cl^-	[15,16]
Co(II)-Schiff base complex	4.8×10^{-7} to 2.3×10^{-2}	4–8	0.48	40	NO^{2-}, SCN^-, ClO^{4-}, Br^-	[17]
Ce-salen complex	8×10^{-6} to 5×10^{-2}	3–11	6	7	SCN^-	[18]
Thiopyrilium ion derivative	8×10^{-7} to 0.1	5.5–8.0	0.2	15	–	[19]
Co(II)-N,N′bis (salicylaldehyde-*n*-octyl) diimine	8.4×10^{-7} to 2.3×10^{-2}	4–8	0.47	40	OH^-	[20]
Fe(III)-Schiff base complex	3.4×10^{-5} to 0.1	3.5–8.5	5	–	–	[21]
Commercially available iodide ISEs						
Orion	5×10^{-8} to 1	–	0.05	20	–	
Omega	2×10^{-8} to 1	–	–	–	–	
Elit	9×10^{-8} to 1	–	–	<10	–	

that better sensing platforms may be designed. Silver iodide has a high ionic conductivity and exists in three polymorphs: γ-AgI (face-centered cubic at room temperature (RT)), β-AgI (hexagonal, can exist at temperatures up to 147 °C) and α-AgI (body-centered cubic, can exist at temperatures above 147 °C) [22]. The ionic conductivity of AgI is associated with the rapid motion of Ag^+ ions over a number of partially occupied sublattice sites and leads to Frenkel defects [23]. Attempts have made to stabilize the conductive forms of AgI by either temporary or permanent methods. Some studies reported the generation of a superionic α-phase at a lower temperature than the phase transition temperature of AgI under microwave (MW) heating [24,25]. The phenomenon was explained by a multi-phonon coupling of the electromagnetic field with the vibrational motions within the AgI crystal lattice. However, this effect was insufficient to account for the stabilization of α-AgI at extremely low temperatures once the MW irradiation was removed. It was also reported that for a few substances such as zeolites, the beneficial coupling of pressure with microwave heating had advantages over simple MW heating [26]. This coupling can offer conductivity enhancement for AgI and a better sensing performance compared to the low conductive form of AgI.

In this study, we fabricated a simple and low-cost heterogeneous polymer membrane based ISE by incorporating stable β-AgI crystals into PVC in the presence of the plasticizer dioctyl phthalate. A judicious amount of microwave power was used to stabilize the β-AgI by strongly coupling the lattice phonons with microwaves via the reorientation of electric dipoles under microwaves. The superior features of the current ISE compared with other PVC based heterogeneous ISEs allowed the routine monitoring and determination of iodide in environmentally relevant samples.

2. Experimental procedures

2.1. Reagents

Sodium iodide, a high molecular-weight PVC, *o*-nitrophenyloctylether (*o*-NPOE), dioctylphthalate (DOP) and sodium sulphide were obtained from Sigma Aldrich (St. Louis, MO, USA). All metal salts, including silver nitrate, potassium iodide, sodium nitrate, potassium chloride, potassium bromide, potassium nitrate, disodium oxalate, sodium carbonate, sodium sulphate, sodium dihydrogen phosphate, potassium thiocyanate and tetrahydrofuran (THF), were of analytical grade and used as received from Merck (Darmstadt, Germany). Iodide solutions of lower concentrations were freshly prepared by the aqueous dilution of defined volumes of a standard 10^{-1} M stock solution and were kept in amber-colored bottles. Deionized water was used the measurements and for the preparation of the sample solutions. The pH of the test solutions was appropriately adjusted with NaOH or HCl solution.

2.2. Instrumentation

Microwave preparations were completed in a START D microwave labstation with detachable temperature and pressure sensors (Milestone, Sorisole, Italy). The Milestone microwave reactor has a single magnetron with a rotating diffuser for homogeneous microwave distribution in the cavity (37 cm × 34.5 cm × 33.5 cm), with a maximum delivered power of 122 W in 1 W increments and an output power up to 1200 W. High pressure experiments were conducted in 100 mL PFA Teflon reaction vessels placed in a rotor block segment. The time, temperature, pressure and MW power of each experiment were monitored and controlled using the EasyWAVE software package. The temperature was controlled using a shielded thermocouple inserted directly into the reaction vessel, and the pressure inside the vessels was monitored using a pressure sensor (APC-55E). All potentiometric measurements were performed in a digital ion analyzer (model L1 126, ELICO, India) using the proposed ISE in conjunction with a calomel reference electrode (ELICO, India). X-ray diffraction patterns of AgI samples were taken using a Cu K_α X-ray source and the Philips PW 1710 diffractometer (the Netherlands). Scanning electron micrographs were obtained using a JEOL JSM-5600 LV instrument (SEM, Japan).

2.3. Procedures

2.3.1. Preparation of AgI by conventional precipitation

Silver iodide was precipitated from a 1:5 molar ratio mixture of KI and $AgNO_3$ by the dropwise addition into a Teflon vessel. The conventional precipitation of AgI was performed at room temperature and atmospheric pressure using the same molar ratio, and complete precipitation was allowed by incubating the mixture for 2 h with constant stirring. All preparations were performed in the dark to avoid the photodegradation of the AgI precipitate and its precursors.

2.3.2. Stabilization of β-AgI under microwave heating

Conventionally precipitated AgI and the mother liquor were subjected to MW irradiation at high temperatures in tightly closed Teflon vessels that were placed in the microwave cavity. Different temperatures and durations of irradiation were applied. Initially the system was allowed to attain the target temperature under a maximum MW power of 900 W for 10 min, followed by a constant and continuous MW power for 5 min. For 5 min constant time, various temperatures were applied: 75 °C, 120 °C, 147 °C and 190 °C. The AgI formed at 147 °C contained β-AgI but was not stable over time and gradually changed to its γ form. The AgI prepared at 190 °C contained the β form and was stable even after aging for several months. Another set of MW irradiation experiments were performed at a constant temperature of 190 °C for different periods of