

All-solid-state potentiometric sensor for iodide and cyanide based on a mixed AgI/Ag₂S/epoxy membrane

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An all-solid-state potentiometric sensor for iodide and cyanide ions was developed. A rigid and mechanically robust membrane was obtained by the dispersion of the mixed silver iodide/silver sulfide salt in epoxy. The developed sensor showed very good potentiometric characteristics to iodide ions and cyanide ions as exhibited by its Nernstian response and high linearity. Response times of less than a minute are common. The surface can be renewed by simple polishing to produce a reproducible surface.

Keywords: potentiometric sensor; iodide; cyanide; AgI/Ag₂S/epoxy membrane

INTRODUCTION

An all-solid-state approach to potentiometric sensors introduces technologically appealing features. In the conventional potentiometric sensor, an internal reference solution is in contact with the sensing membrane and an internal reference electrode. However, in the all solid-state potentiometric sensor, the internal solution is eliminated and the sensing membrane is placed in direct contact with a solid conducting substrate. The sensor is therefore robust and can be used in a variety of positions (horizontally, inverted, etc.). Further, its design has become simple, amenable to miniaturization and adaptable for mass production.

A variety of designs have been adopted for an all-solid-state potentiometric sensor. In the coated-wire electrodes, the sensing membrane, which consists of a polymer film containing an

electroactive species, is formed directly on an inert conducting wire [1]. In the crystal membrane sensor, the sensing membrane involves an electroactive inorganic salt, either pressed into a pellet or dispersed in an inert matrix [2].

Among the matrix used in the sensing membrane of potentiometric sensors is epoxy resin. The membrane based on epoxy resin is rigid, mechanically robust and durable. The surface can be renewed by simple polishing to expose a fresh surface for further sensing. Furthermore, the membrane is moldable before curing, so that it can be drilled or machined to a desired shape or size [3].

Epoxy resin, most often Araldite, was widely used in the 1970s as a binding agent of inorganic salts for the membrane of an ISE with an internal solution and reference electrode [4–7]. Metal-filled conductive epoxies [8] or graphite-filled epoxies

[9, 10] were also used for connecting the conducting wire to a pressed pellet. Machado and co-investigators [11] prepared tubular iodide and bromide selective sensors in which the membranes were formed by mixing the silver salts with Araldite epoxy and employing a silver internal contact. Likewise, flow-through halide electrodes based on epoxy resin heterogeneous membranes were developed by Alegret and co-investigators [12]. An all-solid-state silver-selective sensor was similarly constructed by the dispersion of silver sulfide in commercial epoxy resins [13].

This paper describes the fabrication and characterization of a potentiometric sensor for iodide and cyanide based on the dispersion of a mixture of silver sulfide and silver iodide in epoxy with a copper internal contact. This sensor will provide an inexpensive analytical device for the rapid and reliable measurement of these two ions in food materials and in environmental waters.

The quantitation of iodide ions and cyanide ions is based on the electrical potential generated from the interaction of the silver salts on the surface of the membrane with the ions in the test solution. The silver ions in the membrane distribute itself across the membrane-solution interface producing a charge difference between the membrane and the solution. The iodide ions or the cyanide ions in solution establish an equilibrium with the ions in solution and influences the magnitude of the electrical potential difference. Iodide and cyanide ions are sensed indirectly through the solubility product of the silver iodide and the complexation equilibrium of the silver cyanide complex.

MATERIALS AND METHODS

Materials. Araldite M and hardener HY5162, supplied by Ciba-Geigy, were used for the preparation of the membrane. The mixed electroactive salt was prepared by co-precipitation from equimolar (0.1M) solutions of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and NaI with excess AgNO_3 . The precipitate was vacuum filtered, washed with distilled water, oven dried and pulverized in an agate mortar.

Sensor fabrication. An epoxy mixture was prepared by mixing Araldite M and hardener HY5162 in a 1:0.4 w/w ratio. Then, six parts of the pulverized mixture of electroactive salts was dispersed in one part of the non-conductive epoxy mixture. A 3.5 mm diameter shielded cable was stripped on both ends to expose 4 mm length of copper wire. The cable was then immobilized to the syringe with epoxy. The sensing mixture was introduced at the open end of a 1-mL syringe and packed tightly (Fig. 1). The membrane was allowed to cure overnight at room temperature. The cured membrane was polished and conditioned in 10^{-3} M of the analyte before analysis.

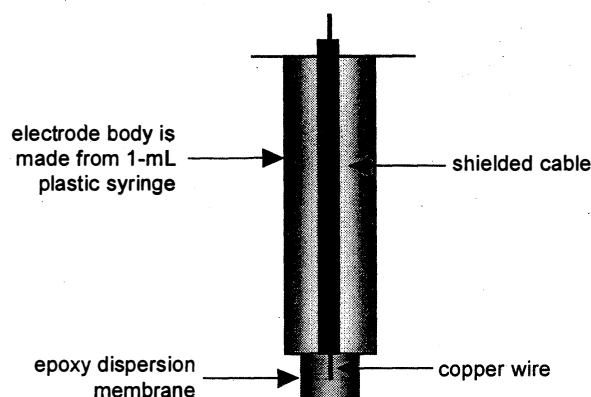


Fig. 1. Diagram of the epoxy dispersion sensor.

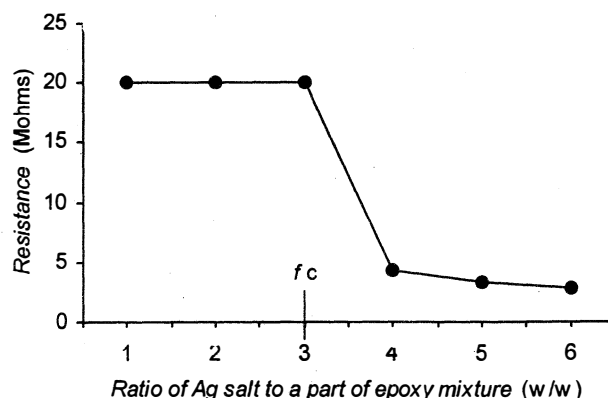


Fig. 2. Effect of mixed silver salt to epoxy weight ratio on the resistance of the sensing membrane.

Measurement procedure. The fabricated sensor and a silver-silver chloride reference electrode (Metrohm No. 6.0723.100) were connected to a digital pH/mV meter (Crisson GLP 22) and immersed in the test solution. The standard addition method was adapted in determining the potential response of the sensor to changes in the concentrations. All quantities in concentration were converted in activities for plotting the calibration curves.

Solutions of iodide ranging in concentration from 10^{-7} to 10^{-2} M were made by adding specified volumes of iodide solutions (10^{-4} to 1.0 M) to a stirred 25-mL water. The sensor signal at a particular concentration was monitored until its steady state response.

Similar volumes of cyanide solutions (10^{-4} to 1.0 M) were, likewise, added to a stirred 25-mL phosphate buffer solution (pH 11) to prepare cyanide solutions with concentrations ranging from 10^{-7} to 10^{-2} M. The sensor signal at a particular concentration was monitored till its steady state response. Because of the toxicity of hydrogen cyanide that can be evolved from cyanide solutions, the waste solutions were collected in a high-pH waste disposal medium.

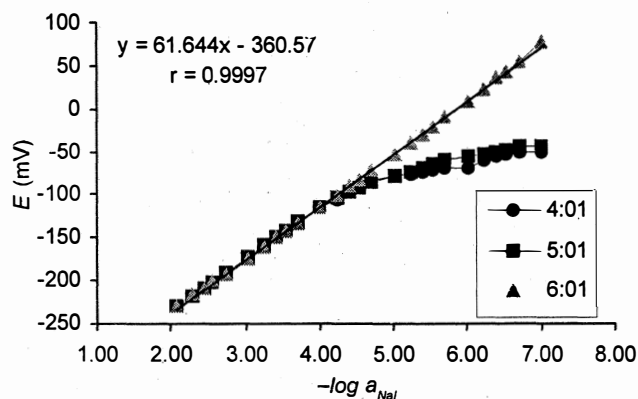


Fig. 3. Calibration curves of iodide sensors with varying w/w ratio of mixed silver salt to epoxy.

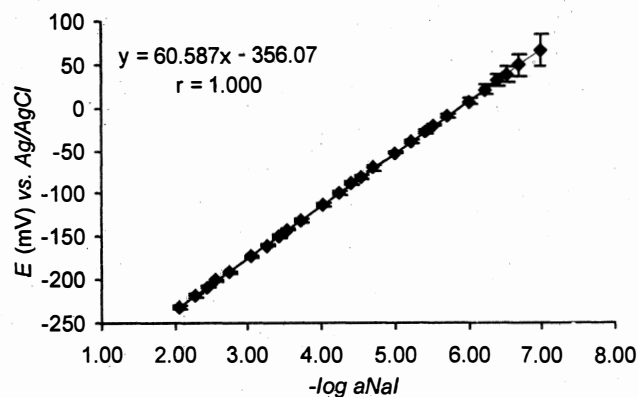


Fig. 4. Calibration curve ($n = 6$) at unbuffered of iodide solutions.

RESULTS AND DISCUSSION

Effect of silver salt mixture to epoxy weight ratio. The sensing membrane in a potentiometric sensor must be conductive. The presence of epoxy in the membrane could decrease the conductivity of the membrane by isolating the conducting particles of the silver salt from each other. The ratio of the weight of the silver salt to that of the epoxy was found to affect the electrical resistance of the membrane. As shown in Fig. 2, a steady increase in the weight fraction of the silver salt led to an abrupt decrease in resistance beyond the weight ratio of 3:1. This behavior corresponds to attainment of a percolation threshold point (f_c) wherein a continuous conducting path is formed by the contact of the conductor particles [12, 13]. Thus, only membranes with composition beyond this threshold point can be used in potentiometric sensors.

The composition of the sensing membrane influenced the performance of the iodide sensor (Fig. 3). The membrane with a composition of 6:1 w/w Ag salt:epoxy exhibited a high sensitivity (slope = $-61.644 \text{ mV}/\log a_{\text{NaI}}$) and excellent linearity ($r = 0.9997$) over a dynamic range of five orders (i.e., at a pNaI range of 2 to 7). Membranes with lower ratios (4:1 and 5:1 w/w Ag salt:epoxy) had the same performance characteristics, but over a narrower range (pNaI = 2 to 4). Thus, these membranes cannot be used to measure low levels of iodide ions. The presence of the epoxy serves as a barrier for the diffusion of the iodide ions to the silver salt, thus, decreasing its sensitivity.

Response characteristics of the sensor to iodide ions. The iodide sensor responded quite rapidly to the analyte at activities greater than 10^{-6} , attaining a steady state response within 30 sec. Longer response times of around 4–5 min were observed at activities lower than 10^{-6} . The presence of the epoxy polymer decreases the transport rate of the iodide ions to the silver salt

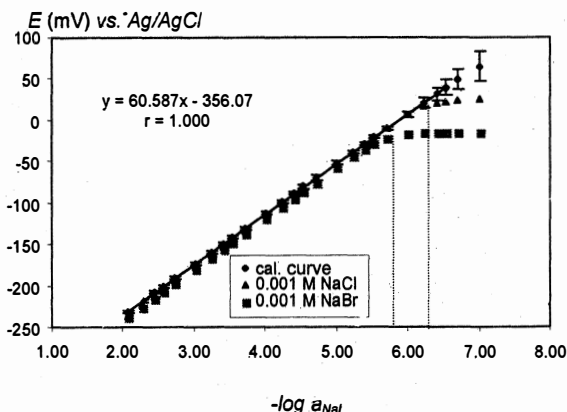


Fig. 5. Effect of interfering ions, Cl^- and Br^- , on the iodide response.

The response of the sensor to iodide ions was highly reproducible for iodide activities greater than 10^{-6} . Relative standard deviations (r.s.d.) of less than 1.0% were observed for ten replicate measurements.

The sensor response was not affected significantly by the ionic strength of the solution. The presence of electrolytes, such as KNO_3 , even at concentrations as high as 1 M did not alter the response of the sensor. Consequently, no ionic strength adapter was used in the measurement of the sensor response to iodide ions.

The sensor displayed a Nernstian response to iodide ions. The mean calibration curve based on six trials of the rigid sensor for iodide is shown in Fig. 4. The sensor exhibited high sensitivity ($m = -60.587 \text{ mV}/\log a_{\text{NaI}}$) with a very small relative standard deviation of the slope (r.s.d. = 0.622%) at a wide dynamic range (-2.0 to $-6.5 \log a_{\text{NaI}}$). The correlation coefficient of the curve was calculated to be 1.000. The two lowest iodide activities were excluded from the dynamic range due to their large relative standard deviation values (r.s.d. > 33%).

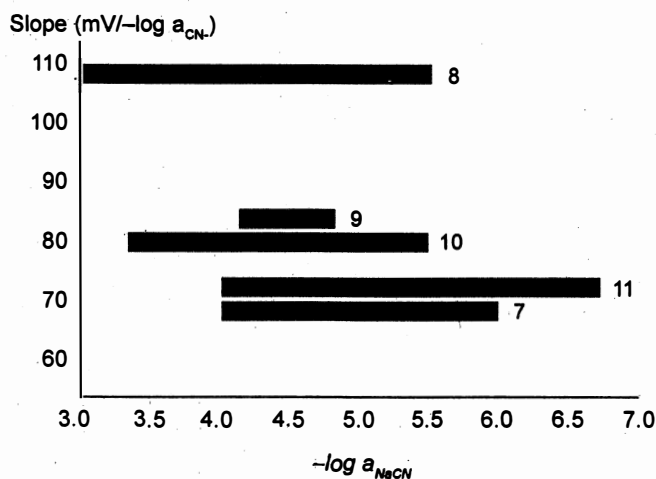


Fig. 6. Effect of pH on the dynamic working range of the cyanide sensor.

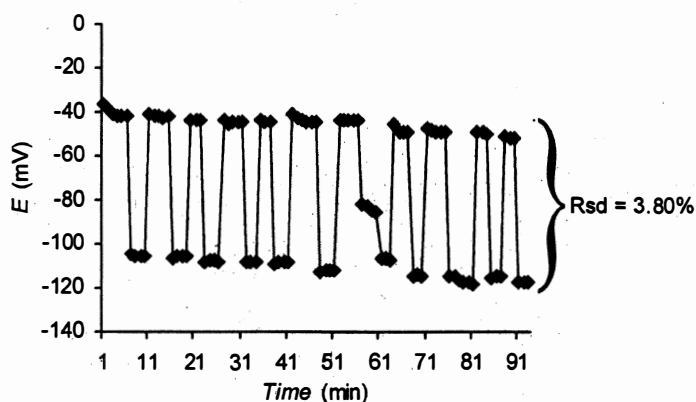
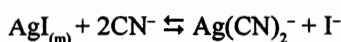


Fig. 7. Response of the epoxy-based sensor to cyanide on repeated exposure to -5.40 and $-4.41 \log a_{CN^-}$.

The sensor response, particularly to activities of iodide lower than 10^{-6} , was subject to interference by chloride and bromide ions. As shown in Fig. 5, the linearity of the calibration curve was significantly affected by bromide ions at activities corresponding to pNaI values greater than 5.53 and by chloride ions at activities corresponding to pNaI values greater than 6.22. Using the mixed-solution method for evaluating interference at a fixed concentration of the interfering ions (10^{-3} M bromide and 10^{-3} M chloride ions), the calculated selectivity coefficients were determined to be 1.00×10^{-3} for the chloride ions and 2.00×10^{-3} for the bromide ions.

Response characteristics of the sensor to cyanide ions. The response of the sensor to cyanide ions is due to the release of iodide ions into the solution as a result of the following complexation reaction occurring at the interface of the membrane (m) and the solution:



The released iodide establishes an equilibrium with the silver ion and generates a potential.

The pH of the solution affects the response of the sensor as it influences the amount of cyanide ions in solution. Hydrocyanic acid (HCN) approaches 100% dissociation at pH 12 (99.8%) with very minimal dissociation at pH 7 (0.8%).

The effect of pH on the sensor response was determined through the successive addition of a solution of cyanide into a buffer (pHs 7, 8, 9, 10, and 11) solution. Cyanide solutions buffered at pH 8 exhibited the highest slope with a wide working range, however, the variations on its calibration points were quite large (r.s.d. > 10%). On the other hand, cyanide solutions buffered at pH 11 exhibited good precision (r.s.d. < 5%) and high sensitivity ($m = -60.658$ mV/decade) at a pNaCN range of 4 to 6.5 (Fig. 6), thus, was chosen as the optimum pH condition.

The response time of the sensor to the cyanide ions is 15–20 sec slower than its response to the iodide ions. It takes around 45–50 sec to reach its steady state values for activities greater than pNaCN of 6 and longer response times are observed (5 min) for lower activities.

The sensor response on repeated exposures to high and low activities of cyanide ions was repeatable as shown in Fig. 7. A decrease in potential with time was observed but the relative standard of deviation in the potential differences between the high and low points is small (r.s.d. = 3.80%).

The sensitivity of the sensor to cyanide was greatly affected by the ionic strength of the solution as shown in Fig. 8. The presence of KNO_3 salt increased the sensitivity of the sensor and led to the decreased in the dynamic range. The greater the concentration of the KNO_3 salt in the solution, the higher was the slope accompanied by the narrowing of the dynamic range. This may indicate the sensitivity of the sensor to the KNO_3 .

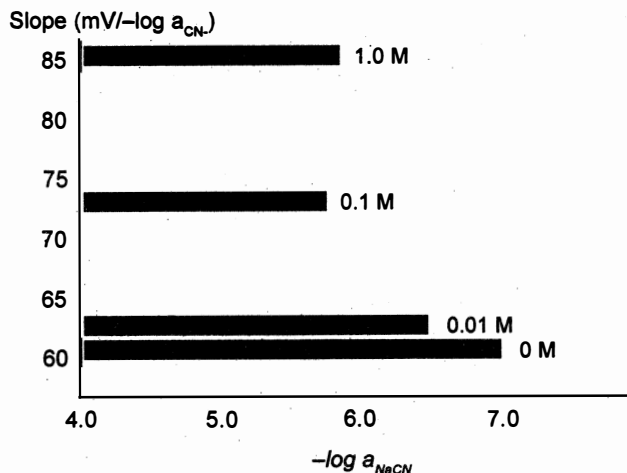


Fig. 8. Effect of ionic strength.

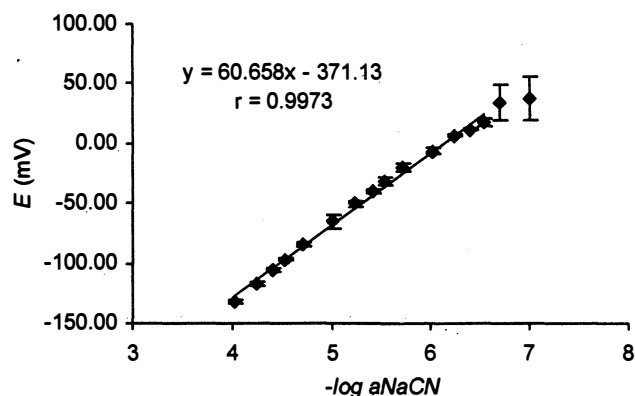


Fig. 9. Calibration curve of the cyanide sensor (pH 11, n = 6).

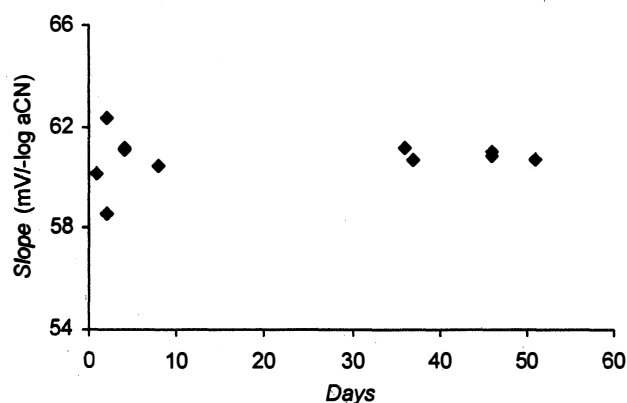


Fig. 10. Effect of time on the sensitivity of the epoxy based sensor.

salt. In the absence KNO_3 , the sensitivity of the sensor is Nernstian over a wide dynamic range, thus, all solutions were simply buffered at pH 11.

The epoxy-based membrane sensor exhibited a Nernstian slope ($m = -60.658 \text{ mV}/-\log a_{\text{NaCN}}$), a high correlation coefficient ($r = 0.9973$) from -4 to $-6.52 \log a_{\text{NaCN}}$ or 9.73×10^{-5} to $2.99 \times 10^{-7} \text{ M} [\text{NaCN}]$. The mean calibration curve based on six trials of the rigid sensor for cyanide ions is shown in Fig. 9. The sensor gave unstable responses at higher concentrations which can be attributed to the rapid poisoning of the membrane in the presence of a large amount of free cyanide ions since ionization of cyanide is almost complete at pH 11. The relative standard of deviation of the slope for six trials was 2.31% which indicated good reproducibility at its dynamic range.

The stability of the sensor was assessed by conducting calibration runs at random intervals. The sensor surface was polished and conditioned before each run. Figure 10 shows that the sensitivity of the sensor between runs are close to one another which indicates that a reproducible surface is obtained after each polishing. The sensor may be stored dry for almost

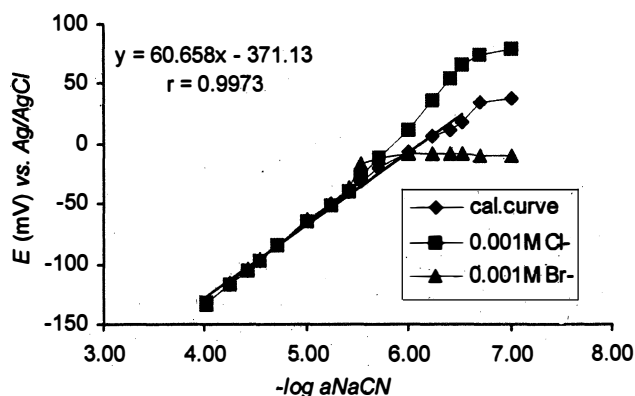


Fig. 11. Effect of interfering ions, Cl^- and Br^- on the response of the sensor.

two months without any deterioration in sensitivity. Therefore, the lifetime of the sensor is dependent on its 'reservoir', the bulk of the epoxy composite membrane.

The sensor response was greatly affected by the presence of bromide and chloride ions. These two interfering ions exerted greater interferences in the analysis of cyanide ions as compared to iodide ions as shown in Fig. 11. The calculated selectivity coefficients for bromide and chloride ions are 4.00×10^{-3} and 2.00×10^{-3} , respectively.

CONCLUSION

An all-solid state potentiometric sensor for iodide and cyanide based on an epoxy dispersion membrane was developed. The sensing membrane consisted of 6:1 w/w silver salt to epoxy. The sensor showed very good response characteristics to iodide and cyanide ions. However, the dynamic range in cyanide solutions is narrower than the iodide working range. Calibration runs in the absence of interfering ions are preferred due to the minimal interferences of bromide and chloride ions at very low activities of iodide and cyanide ions.

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