Multi-ion and pH sensitivity of AgGeSe ion selective electrodes

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ABSTRACT

Many chalcogenide glasses have been found to combine benefits such as good chemical durability, selectivity, and reproducibility for applications as solid-state sensitive membranes of ion selective electrodes (ISEs). In previous works, we have shown that ISEs with ionic conductive AgGeSe membranes have good sensitivity to Ag^+ ions. In the present work, we explore the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$, $10 \leq x \leq 30$ (at%) system as candidate for ISEs applications detecting several other ions (K^+, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}). We evaluated ISEs fabricated with bulk as well as with thin film membranes. We found no dependence of the sensing properties on the Ag content of the ionic conductive membranes. Thin films exhibited the same properties than bulk membranes, indicating that these chalcogenide glasses have great potential for miniaturization. The ISEs showed a high response (Nernstian or super-Nernstian) to the presence of Hg^{2+}, Pb^{2+}, and Fe^{3+}, a low response (sub-Nernstian) to the presence of Cr^{3+}, and a total lack of response to the presence of Cd^{2+}, Ni^{2+}, Mg^{2+}, and K^+. We also tested how the pH of the solution affected the response of the ISEs. The potentials of the ISEs were practically constant in neutral or acidic solutions, while decreased drastically in basic solutions when the primary ion was not present. The latter phenomenon was caused by the slow dissolution of the membrane into the solution, meaning that long-term basic environments should be avoided for these ISEs. We concluded that ISEs with ionic conductive AgGeSe membranes are good candidates to integrate multi-electrode systems.

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1. Introduction

Chalcogenide glasses are being widely studied for membranes of ion selective electrodes (ISEs) because they usually exhibit better chemical durability, selectivity, reproducibility, and lifetime than polycrystalline chalcogenides [1]. The development of all-solid-state electrodes (i.e. with internal metal contact) and thin film deposition techniques (e.g. pulsed laser deposition, sputtering) have facilitated ISEs miniaturization [2,3]. This, in turn, has enabled the fabrication of electrode arrays by silicon-processing techniques leading to miniaturized electronic tongues [4–8]. ISEs used in arrays must exhibit: cross-sensitivity (i.e. different levels of sensitivity to different ions), stable and reproducible parameters, and good chemical durability [5,9].

$Ag_x(Ge_ySe_{1-y})_{100-x}$ (at%) glasses have a large miscibility gap with two separated phases: a Ag-rich and a Ag-poor amorphous phase [10]. When $x \leq 8$ at%, the AgGeSe system is a semiconductor. In previous works, we measured no response of electrodes with these membranes [11]. When $x \geq 8$ at%, the Ag-rich phase percolates, increasing the conductivity by seven orders of magnitude,

and the material becomes a fast ionic conductor [12]. Previously, we reported that ISEs with ionic conductive AgGeSe membranes are highly sensitive to Ag^+ and Cu^{2+} in aqueous solutions (with detection limits $\sim 10^{-7}$ M for both ions, and slopes ~ 65 mV/pAg and ~ 50 mV/PCu) [13,14]. We also found that AgGeSe-based bulk ISEs are sensitive to Fe^{3+}, and not sensitive to Mg^{2+} and Cd^{2+} [13].

In this work, we explored whether ISEs with ionic conductive $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ ($10 \leq x \leq 30$) membranes possess the characteristics required for electrode arrays used in electronic tongues. To this end, we measured the sensitivities to a relatively broad set of interfering ions, including alkali, alkaline and transition metals: K^+, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. With the goal of fabricating miniaturized devices in a future work, we compared the response of thin film membranes to response of larger bulk membranes. Finally, we tested how the pH of the solution may affect the response of these ISEs.

2. Experimental

Chalcogenide bulk glasses with compositions $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ ($x=10$, 15, 20, 25, and 30) were prepared by melt-quenching [15]. The high purity elements in the desired

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stoichiometry were sealed in quartz ampoules, evacuated to 10^{-6} mbar, heated to 950 °C and then kept in liquid state at that temperature for about 10 h. After this time, the liquid samples were rapidly quenched in an ice–water mixture.

Thin film chalcogenide membranes (300 ± 50 nm thick) were prepared by pulsed laser deposition (PLD) in an on-axis geometry [16]. A Nd:YAG pulsed laser ($\lambda = 355$ nm, 5 ns, 10 Hz) with a fluence of 5–8 J/cm^2 was used and bulk chalcogenide glasses were employed as targets.

Two types of all-solid-state ISEs were fabricated: using either bulk or thin film membranes. Bulk membrane ISEs were constructed by cutting the glasses into rectangular plates. Two opposing faces were polished until achieving mirror finish and a metal contact (either Au or Cr) was sputtered on one of the faces. The thin film ISEs were made first by sputtering the metal contact on a substrate (microscope slides) and then, depositing the chalcogenide film on top of the metal contact and the substrate (leaving part of the metal contact exposed). Cables were attached to the metal contacts with silver paint and then the electrical connections were insulated from the aqueous media by encapsulating in epoxy resin [14]. The response of the ISEs was studied by direct potentiometry [14] in aqueous solutions containing the ions: K^+, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, or Pb^{2+}, in the concentration range 10^{-8}–10^{-3} M. A double junction Ag/AgCl(sat.) reference electrode was used with KCl (4 M) in the inner container and KNO$_3$ (0.1 M) in the outer container. Nitrate salts were used as sources of all cations. Potential measurements were taken at room temperature (25 °C) with a high impedance millivoltmeter with 0.1 mV accuracy. KNO$_3$ (0.1 M) was used as supporting electrolyte in order to insure a constant ionic strength. All measurements in solutions of Hg^{2+} and Fe^{3+} were performed at pH=2 to prevent the formation of hydroxides [17–19].

Calibration curves were obtained by plotting the potential of the electrode vs the logarithm of the concentration. Values of the slope (S) and the detection limit (DL) were extracted from the calibration curves. Nernst's law should be expected under thermodynamic equilibrium and considering ion exchange between the solution and the membrane as the sensing mechanism. Accordingly, the Nernstian slopes observed for the calibration curves at room temperature are: 59.2 mV/decade for monovalent ions, 29.6 mV/decade for divalent ions, and 19.7 mV/decade for trivalent ions.

Selectivity coefficients were calculated by the "fixed interference method", according to the procedure recommended by IUPAC [20]. We used a constant concentration of each interfering ion (10^{-3} M) and changed the concentration of the primary ion (Ag^+) from 10^{-8} to 10^{-3} M.

The pH sensitivity was studied with a Hanna pH 211 pH-meter in the range 2–10 (with a 2-point calibration before each measurement). Two solutions were studied: (i) KNO$_3$ (0.1 M), and (ii) KNO$_3$ (0.1 M)+AgNO$_3$ (10^{-4} M). The pH of the solutions was changed by adding nitric acid or potassium hydroxide.

Surface images were obtained with a Field Emission-Scanning Electron Microscope (FE-SEM) Zeiss SUPRA 40 equipped with an in-lens detector of secondary electrons. The samples observed by FE-SEM of composition Ag$_{10}$(Ge$_{0.25}$Se$_{0.75}$)$_{90}$ were purposely fractured before introducing them into the FE-SEM chamber and the images were taken in the fractured zones. The fractured samples were observed as-fractured and after being submerged for 10 h in three different solutions: (i) potassium hydroxide at pH=10, (ii) potassium hydroxide+Ag(NO$_3$) (10^{-4} M) at pH=10, and (iii) Ag(NO$_3$) (10^{-4} M).

3. Results

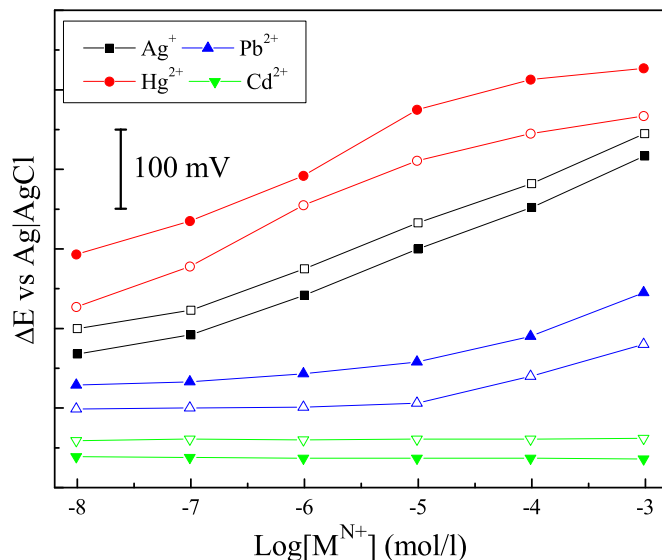We found that the studied electrodes exhibited stable and

Fig. 1. Calibration curves of bulk (solid) and thin film (hollow) ISEs for each of the ions. Hg^{2+} solutions were prepared at pH=2.

reproducible responses but these were very different in the presence of different ions. For each of the ions, all electrodes presented similar calibration curves, regardless of the membrane's composition or geometry.

Figs. 1 and 2 show the calibration curves for the studied ions. Since all the studied membranes (Ag$_x$(Ge$_{0.25}$Se$_{0.75}$)$_{100-x}$ with $10 \leq x \leq 30$) exhibited approximately the same slope and detection limit (within experimental error), their compositions are not reported in Figs. 1 and 2.

Table 1 presents the mean values and confidence intervals of the slope, detection limit and the logarithm of the selectivity coefficient of the ISEs for each of the studied ions. The mean values were calculated over electrodes of all membrane's compositions and geometries.

The electrodes showed a high response (Nernstian and super-Nernstian) to the presence of Hg^{2+}. Both bulk and thin film ISEs presented S-shaped calibration curves (Fig. 1). In the middle concentration range, 10^{-7}–10^{-5} M, a super-Nernstian slope of 70 mV/pHg was reached, while at higher concentrations ($> 10^{-5}$ M) the
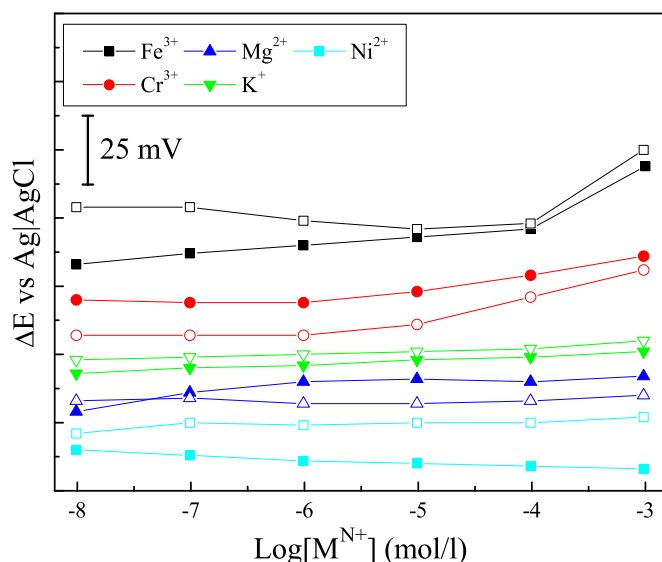

Fig. 2. Calibration curves of bulk (solid) and thin film (hollow) ISEs for each of the ions. Fe^{3+} solutions were prepared at pH=2.

Table 1

Values of the slope (S in mV/decade), detection limit (DL in mol/l) and logarithm of the selectivity coefficient (log ($K_{A,B}{}^{pot}$)) of bulk and thin film ISEs for each of the studied ions (primary ion: Ag^+). The selectivity coefficient was measured at a constant concentration (10^{-3} M) of each interfering ion.

Ion	S (mV/dec)	DL (M)	SC
Ag^+	56 ± 5	5×10^{-8}	–
Hg^{2+}	$70 \pm 10/28 \pm 5$	5×10^{-8}	2×10^{-4}
Pb^{2+}	44 ± 6	10^{-5}	10^{-6}
Fe^{3+}	25 ± 4	10^{-4}	6×10^{-5}
Cr^{3+}	8 ± 3	10^{-5}	10^{-6}
Cd^{2+}	–	–	10^{-6}
Ni^{2+}	–	–	10^{-6}
Mg^{2+}	–	–	10^{-6}
K^+	–	–	10^{-5}

slope was near-Nernstian (~ 28 mV/pHg). The shape of the curves depended on the time the membrane was immersed in the Hg^{2+} solution and on the cation concentration. As the immersion time elapsed, the slope in the middle concentration range decreased and the detection limit increased. Thus, a slow "poisoning" of the membrane led to a potential that was poorly reproducible and strongly dependent on the hydrodynamic conditions (i.e. stirring).

The response of the electrodes to the presence of Pb^{2+} and Fe^{3+} was: $S \approx 44$ mV/pPb, DL $\approx 10^{-5}$ for Pb^{2+}, and $S \approx 25$ mV/pFe, DL $\approx 10^{-5}$ M for Fe^{3+}, as can be seen in Figs. 1 and 2. As described in the experimental section, the response to Fe^{3+} was measured at pH=2 to prevent the formation of hydroxides. Legin et al. reported that the concentration of free Fe^{3+} at pH=2 is only half of the total amount of Fe in the solution [21]. Although the data Legin et al. presented had strong dispersion, their work warns that even at pH < 2, the amount of Fe^{3+} could be pH dependent.

The electrodes were poorly sensitive to Cr^{3+} ($S \approx 8$ mV/pCr, i.e.: sub-Nernstian behavior), and practically non-sensitive to Cd^{2+}, Ni^{2+}, Mg^{2+} or K^+.

The selectivity coefficients reported in Table 1 indicate that Hg^{2+} was the only ion to interfere-slightly-with the response of the ISEs to the primary ion (i.e. Ag^+). We observed no interference by the other studied ions.

The effect of the pH on the ISEs response was practically the same for all membrane's compositions and geometries (Figs. 3 and
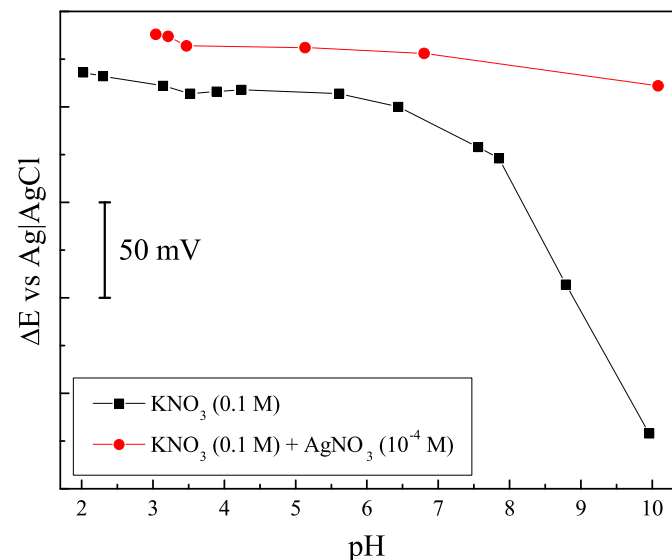
Fig. 4. Potential of thin film ISEs vs double junction Ag/AgCl(sat.) reference electrode (KCl(4 M)/KNO$_3$(0.1 M)) at room temperature (25 °C) in different solutions as a function of pH.
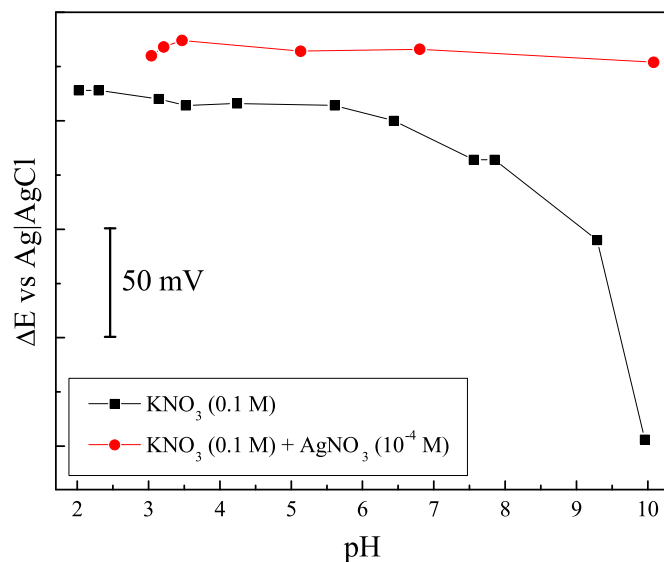
4). We first measured the potential of the electrodes in KNO_3 solution (0.1 M) with varying pH values (i.e. KNO_3 was the supporting solution in all calibrations). The ISEs response was stable throughout the pH range 2–6 and decreased in the pH range 6–10 (the decrease became more pronounced at higher pH values). Then, we studied the ISEs response in solution KNO_3 (0.1 M)+Ag(NO$_3$) (10^{-4} M) and found a relatively constant potential throughout all the tested pH range (pH=3–10).

We analyzed the surface of the membranes after the exposure to basic media by FE-SEM. In Fig. 5, we show two images of bulk $Ag_{10}(Ge_{0.25}Se_{0.75})_{90}$ glasses, one before (a) and one after (b) the immersion of the sample in potassium hydroxide solution at pH=10 for 10 h. In both images, two phases can be easily distinguished (a Ag-rich and a Ag-poor phase). These are a consequence of the spinodal decomposition during the synthesis of the glass [22,23]. The submersion of the glass in basic media modified the surface of the sample, increasing the roughness of the Ag-poor phase (Fig. 5b). We repeated the experiment with samples in potassium hydroxide+Ag(NO$_3$) (10^{-4} M) solution at pH=10 for 10 h and observed the same increase in roughness. Finally, we repeated the experiment with samples in Ag(NO$_3$) (10^{-4} M) (i.e.: not basic solution) for 10 h and found that the roughness did not change.

4. Discussion

We found no dependence of the sensing properties of the ISEs on the composition of the AgGeSe membranes. Thus, as long as the AgGeSe membrane is ionic conductive, Ag content does not affect the sensitivity, detection limit, selectivity or pH resistance. Also, thin films exhibited the same properties than bulk membranes, indicating that these chalcogenide glasses have great potential for miniaturization.

The ISEs showed a response to the presence of Hg^{2+} very different from the one predicted by Nernst's law. Similar characteristics were observed for ISEs in Hg^{2+} solutions by other authors [17,18,24,25]. While a detailed elucidation of the mechanism for Hg^{2+} super-Nernstian sensing is beyond the scope of the present paper, some authors reported that during the soaking of the membranes in Hg^{2+} solutions, a dual process of silver release (from the membrane) and mercury uptake (into the membrane)
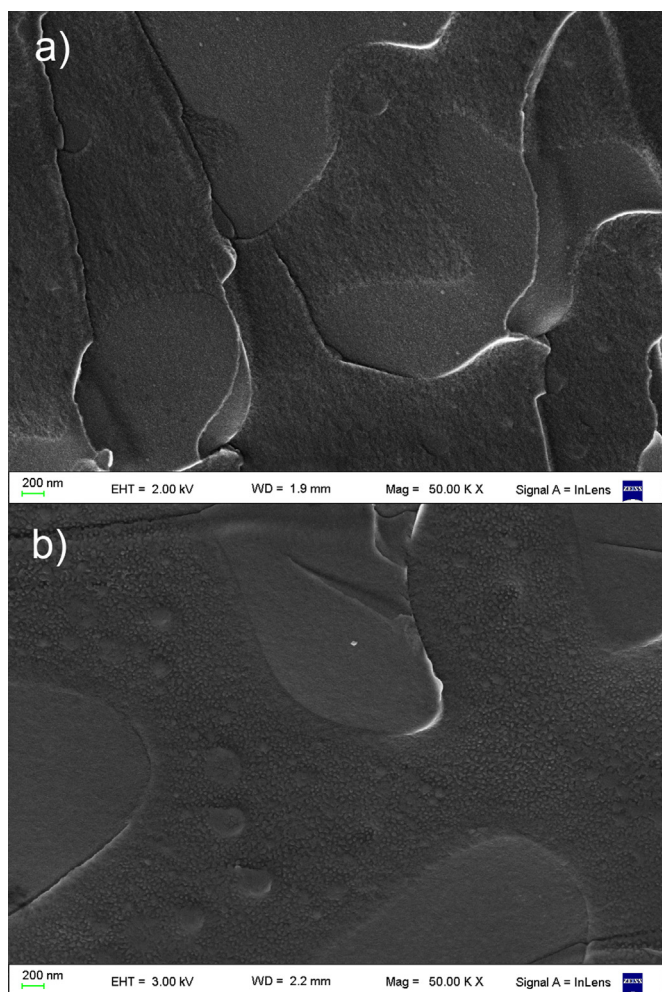
Fig. 3. Potential of bulk ISEs vs double junction Ag/AgCl(sat.) reference electrode (KCl(4 M)/KNO$_3$(0.1 M)) at room temperature (25 °C) in different solutions as a function of pH.

Fig. 5. FE-SEM images of $Ag_{10}(Ge_{0.25}Se_{0.75})_{90}$ bulk samples. Both images were taken at the same magnification. (a) Sample before treatment in basic media. (b) Sample after submersion in potassium hydroxide solution at pH$=$10 for 10 h.

takes place at the membrane/solution interface [17,18]. These authors argued that those ion-exchange processes might have been responsible for the observed Nernstian and super-Nernstian slopes of the electrodes and for the slow "poisoning" of the membrane.

Regarding the response of the electrodes to pH, we observed two types of response: when the primary ions (Ag$^+$) were present, the potential remained relatively constant throughout all the tested pH range (pH$=$3–10), indicating that formation of complexes (e.g. Ag$_2$O, AgOH) did not occur as can be predicted by the measurements of Biedermann et al. [26]. When the primary ions were absent, the potential remained constant only in the acidic region, but strongly decreased in the basic region.

Legin et al. proposed that this response of the electrodes to pH is related to the presence of anionic sites capable of proton exchange at the membrane's surface [5], although a slow dissolution of the membrane in basic media [27] could also explain this behavior.

To investigate whether the dissolution of the chalcogenide membrane was in fact occurring in basic media, we submerged $Ag_{10}(Ge_{0.25}Se_{0.75})_{90}$ bulk samples in potassium hydroxide solution at pH$=$10 for 10 h. We then observed by FE-SEM that, as a consequence of this treatment, the roughness of one of the phases had increased (Fig. 5b). Therefore, we propose that the response of the electrodes to high pH is governed by the dissolution of the chalcogenide glass by the basic solution [27]. Further investigations will be carried out in order to attain a better understanding of the dissolution process.

When the primary ions (Ag$^+$) were present, we measured an almost-constant potential throughout all the tested pH range (pH$=$3–10). The surface analyses of these samples revealed the same roughness change as in the previous samples (i.e.: submerged in basic solution without primary ions), indicating that the dissolution process of the membrane took place regardless of the presence of the Ag$^+$ ions. This phenomenon has been discussed by other researchers [5,28,29] and has been explained as follows: the response to the primary heavy metal cation is the main potential-generating mechanism and overcomes the other possible mechanisms [5] (e.g.: the dissolution of the membrane).

Both pH studies (with and without primary ions in the solution) indicate that AgGeSe membranes for ISEs applications should avoid long-term exposure to basic environments.

5. Conclusions

We fabricated ion selective electrodes (ISEs) with sensitive membranes of compositions $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ ($10 \leq x \leq 30$), both in bulk and thin film geometries, and measured their response to the presence of K$^+$, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. The Ag content of the ionic conductive membrane (i.e.: ≥ 8 at% of Ag) did not affect any of the sensing properties. Thin films exhibited the same response than bulk membranes, indicating that these chalcogenide glasses have great potential for miniaturization. The ISEs exhibited a range of cross-sensitivity to the studied ions. They responded with high sensitivity to Hg^{2+} throughout all the tested concentration range, but under continuous measurement, this sensitivity decreased and became stirring dependent due to a "poisoning" effect on the membrane. At middle and high concentrations ($> 10^{-5}$ M), they were highly sensitive to Pb^{2+} and Fe^{3+}, while poorly sensitive to Cr^{3+}. They showed a total lack of response to Cd^{2+}, Ni^{2+}, Mg^{2+}, and K$^+$.

In the absence of primary ions (Ag$^+$), the pH of the solution did not affect the potential of the ISEs in the acidic region, but a strong potential decrease took place in the basic region. Even though some researchers have proposed that the driving mechanism is the response to H$^+$ [5], we believe that the reduction of the potential is caused by the slow dissolution of the membrane into the solution.

When primary ions were present even at low concentrations (10^{-4} M), the potential remained relatively constant throughout all the tested pH range (pH$=$3–10), showing that the response to Ag$^+$ ions is the main mechanism that determines the potential of the electrodes.

Bearing in mind that electrodes with ionic conductive AgGeSe membranes should avoid long-term exposure to basic environments, we conclude that these membranes are good candidates to integrate multi-electrode arrays (which would also include other chalcogenide-based as well as polymer-based ISEs).

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