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A Zn(II) ion-selective electrode based on chalcogenide As_2Se_3–Sb_2Se_3–ZnSe and $GeSe_2$–ZnSe–ZnTe glasses

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Abstract

Zn(II) ion-selective electrodes with chalcogenide glassy As_2Se_3–Sb_2Se_3–ZnSe and $GeSe_2$–ZnSe–ZnTe membranes were developed. Basic analytical characteristics such as stability, linearity, slope of the electrode function, limits of detection, effect of pH on the electrode potential and response time were studied with varying glass compositions. A structural mechanism for explanation of the dependencies obtained is suggested.

1. Introduction

Ion-selective electrodes (ISE) with functional membranes consisting of polycrystalline chalcogenides have been widely used during the last three decades. Recently, chalcogenide glasses have been recommended as exhibiting several advantages compared to the corresponding chalcogenide crystals. For example, they have shown higher stability against dissolution in the electrolyte and chemical attack in corrosive media and better selectivity in the presence of some interfering ions [1, 2]. They have therefore been successfully applied as membrane materials for metal ion detection such as Ag^+ [3], Cu^{2+} [4, 5] and Fe^{3+} [6]. Chalcogenide glasses are also convenient model materials for the study of ionic sensitivity processes and the relationship between these processes, the chemical stability of the membrane surface and the bulk transport properties such as ionic and electronic conductivity. A new theoretical interpretation of the phenomena observed in glassy electrodes has been discussed in [7].

Research into Ge(As)–Zn–Se(Te) glasses is a matter of interest for finding the optimal possibilities of Zn^{2+} ISE. The aim of this study is to determine the correlation between the composition based on As_2Se_3–Sb_2Se_3–ZnSe (ASZ) and $GeSe_2$–ZnSe–ZnTe (GZZ) glasses and the analytical characteristics, as well as to investigate the mechanism which governs the ionic sensitivity of chalcogenide glass sensors. The glass-forming regions in both systems have been described in a previous paper [8].

2. Experimental details

The required weights of the components totalling roughly 4 g were flame-sealed into a quartz ampoule under a vacuum of 10^{-3} Pa. The sealed tube was then placed in a rocking furnace and heated at 850 °C (for ASZ) and 950 °C (for GZZ). The final stage was water quenching with an average cooling rate of 2–5 K s^{-1} [8]. The glassy state and uniformity of the samples were checked by X-ray diffraction and electron microscopy.

The compositions chosen for ISE from both studied systems were noted in Figure 1. Eight groups of ISE (with three samples of each group) were studied. The membranes (1–3 mm thick) were prepared by cutting, burnishing and polishing of the glassy samples obtained. They were constructed with an inner liquid junction. The sensor element was fixed with epoxy resin to the edge of a PVC tube (the electrode body). The contact between the membrane and the inner reference electrode (Ag/AgCl) was achieved through an electrolyte containing 10^{-3} M KCl. The electrode function was measured using an electrochemical cell of the type:

$$\text{Hg, } Hg_2Cl_2 \mid \text{KCl(saturated)} \parallel \text{Solution} \mid \text{ISE} \mid \text{KCl} \mid \text{AgCl, Ag}$$

A standard calomel electrode was used because of its stable potential. The additional potential as a result of the asymmetry of the cell had no influence on the slope of the electrode function.

The cell was calibrated under a conventional working regime, the solutions for calibration being prepared by consecutive dilution of 1 M $Zn(NO_3)_2$ with bidistilled water. The potential was measured under constant stirring (150 rev min^{-1}) in solutions of progressively increasing concentration. The pH effect was studied by adding a small amount of concentrated HNO_3 or solid

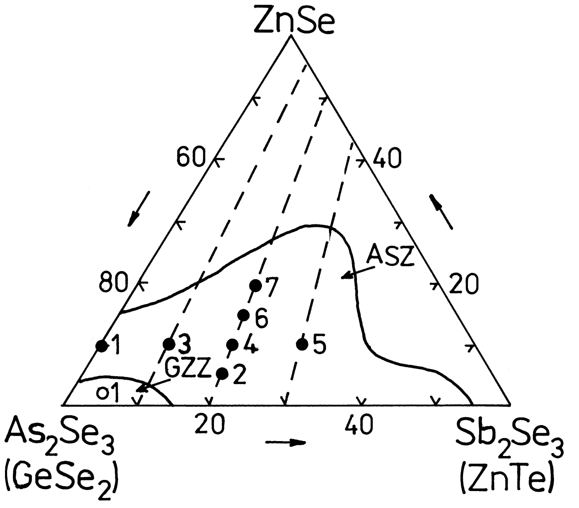


Fig. 1. Glass-forming regions in the As_2Se_3–Sb_2Se_3–ZnSe and $GeSe_2$–ZnSe–ZnTe systems and the compositions studied.

KOH to the solution containing the potential-determining ion. For stabilization of the Zn^{2+}-centres, conditioning was achieved by immersion of the electrodes in 10^{-3} M $Zn(NO_3)_2$ solution. The limits of detection were determined in a standard solution of Zn(II) in the range 10^{-1} to 10^{-6} M $Zn(NO_3)_2$ at a constant stirring rate of 150 rev min^{-1} and pH 3.

3. Results

3.1. *Stability, linearity (L) and slope of the electrode function (S)*

For studying the reproducibility of the electrode function, three electrodes of each membrane composition were used and tested with regard to their ageing time (three months). The following parameters were determined: linear range (L) and slope (S) of calibration curves, and time (τ) to reach stable values of the electrode potential (E). The electrode function was measured on nonconditioned and conditioned (15 and 30 min, respectively) ISE. The nonconditioned ISE from the ASZ system were characterized with significant instability, $\tau = 150$–200 s, low values of L and S, especially at small ZnSe concentrations.

Conditioning for 15 min stabilized and improved the parameters of the electrode function. The slope of the electrode functions varied in the limits $S = 22$–41 mV dec^{-1} and the linearity $L = 10^{-5}$ to 10^{-1} M Zn(II). More of the investigated ISE exhibited a higher S value than the theoretical value (S_{theor}) from the Nernst equation. That is, they have a supernernstian slope:

$$E = E_o + S_{theor} \log a_A = E_o + \left(\frac{59.52}{z}\right) \log a_A \qquad (1)$$

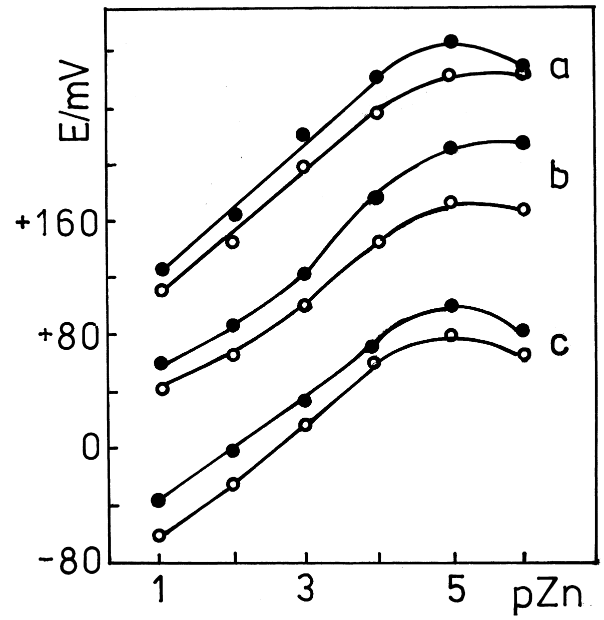


Fig. 2. Limits of the electrode function of Zn(II) ISE (conditioning 15 min): (a) Compositions of 2, 4, 6, 7 ASZ, (b) compositions of 1, 3, 4, 5 ASZ and (c) composition 1 GZZ.

where E_o is the standard potential, $S_{theor} = S/z(S = 10^3 RT \ln 10/F$, R is the universal gas constant, F is the faradaic constant, z is the charge of the determining ion), and a_A is the activity of the determining ion. In Figure 2 the limits, within which the electrode function of the investigated Zn(II) ISE is confined, are given.

Figure 3 shows the influence of the membrane composition on L and S of the electrode function, at $m = \text{const.}$ ($m = [Sb_2Se_3]/([Sb_2Se_3] + [As_2Se_3])$ (a) and $z = \text{const.}$ ($Z = [ZnSe]$) (b), respectively. As a detail, Figure 4 illustrates the variation of S depending on z(a) and m(b). Increasing the content of the active component (ZnSe in this case) at $m = \text{const.}$) results in higher S (Figures 3(a), 4(b)) but L remains constant. A similar dependence is observed at lower m (at $z = \text{const.}$) but L decreases by a decade (Figures 3(b), 4(a)).

The electrode function for the GZZ system is presented in Figure 5. Since the glass-forming region in this system is very narrow, the influence of the membrane composition on the electrode characteristics is not specified.

It was established by testing the ISE after 90 days that S rapidly decreases and the electrode function stabilizes around values typical for a two-valence anion. L remains almost constant for the GZZ system and decreases by a decade for the ASZ one.

3.2. *Limits of detection (LD)*

For as-prepared electrodes, LD has values of $(2.0$–$5.8) \times 10^{-6}$ for the ASZ system, 5.0×10^{-6} M Zn(II) for the GZZ system and, after 90 days, $(1.4$–$5.5) \times 10^{-6}$ and 5.0×10^{-7} M Zn(II), respectively (Table 1). Increasing

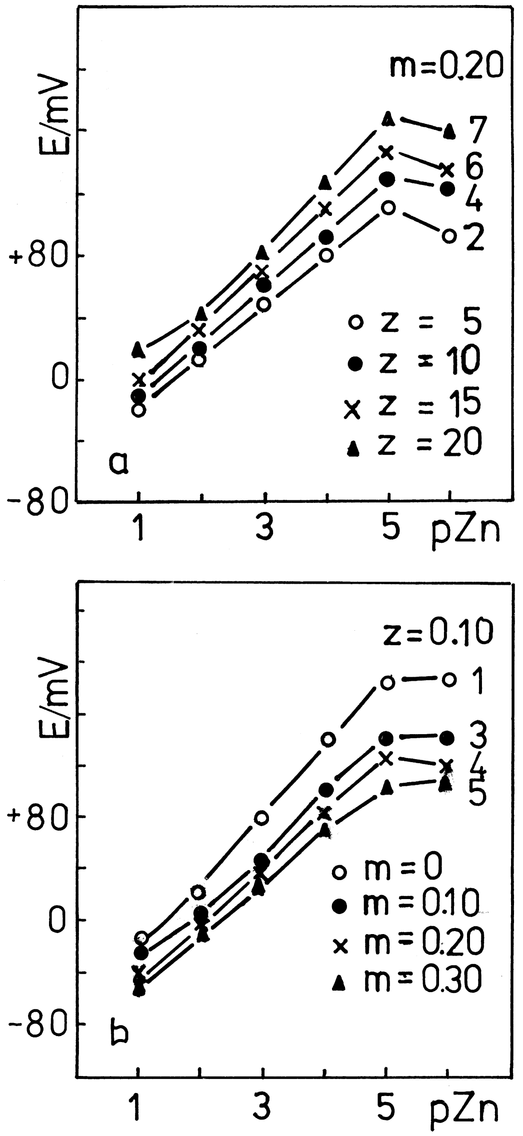


Fig. 3. Electrode function of Zn(II) ISE (conditioning 15 min): (a) Compositions of 2, 4, 6, 7 ASZ and (b) compositions of 1, 3, 4, 5 ASZ.

the content of the active component (ZnSe), at $m =$ const. leads to a decrease in LD. Analogous regularity is observed at lower m and constant ZnSe content. The ISE of the groups 1 ASZ and 7 ASZ exhibit the best values of this parameter (Table 1).

3.3. *Effect of pH on the electrode potential*

The electrode potential of ISE does not depend on $[H^+]$ in the range from $(pH)_{min}$ to $(pH)_{max}$ (Figure 6(a) and (b)). Both limits depend on the concentration of the Zn^{2+} ions in the solution and on the chemical composition of the membrane. $(pH)_{min}$ is 3–4 for the ASZ system and 2–3 for the GZZ, the values being higher with decreasing Zn^{2+} concentration. At $pH < (pH)_{min}$, the polymer matrix of the membrane dissolves (Figure 6(a) and (b), zone A), $(pH)_{max}$ being 6–7 and 5–7 for the ASZ and GZZ systems, respectively. At $pH > (pH)_{max}$, the chalcogenide glass dissolves and $Zn(OH)_2$

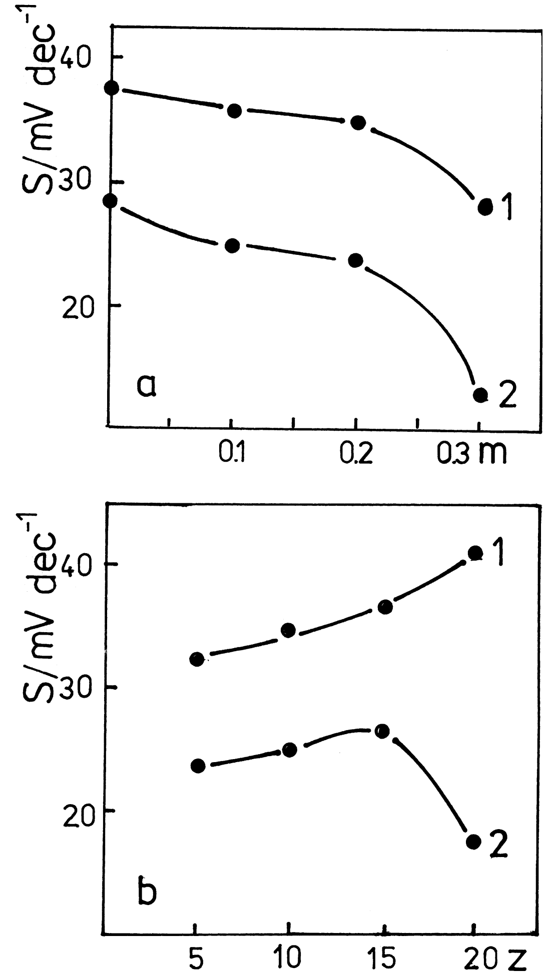


Fig. 4. Slope of the electrode function depending on m (a), z (b): after 0 (1) and 90 (2) days.

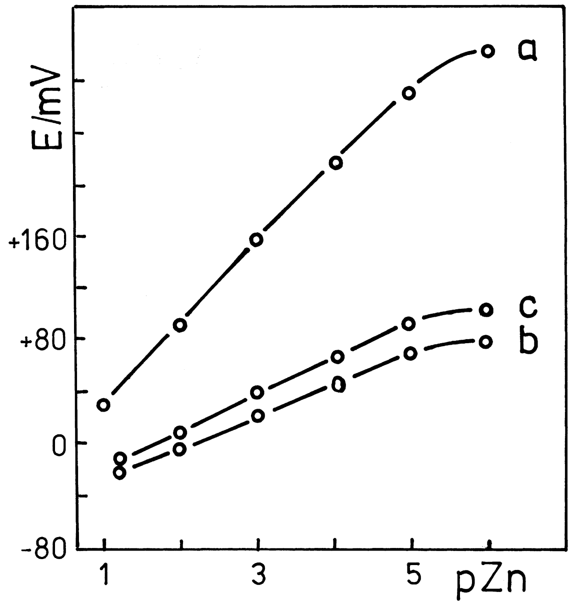


Fig. 5. Electrode function of Zn(II) ISE (conditioning 15 min): after 0 (a); 90 days (b); 90 days, polished surface (c).

Table 1. Analytical characteristics of the electrodes

Sample	Testing after 0 days			Testing after 90 days		
	S/mV dec^{-1}	L/M Zn(II)	LD/M Zn(II)	S/mV dec^{-1}	L/M Zn(II)	LD/M Zn(II)
1ASZ	38.0	10^{-1}–10^{-5}	4.0×10^{-6}	28	10^{-2}–10^{-5}	1.8×10^{-6}
3ASZ	36.0	10^{-1}–10^{-5}	4.4×10^{-6}	25	10^{-2}–10^{-5}	3.6×10^{-6}
4ASZ	35.0	10^{-1}–10^{-5}	5.0×10^{-6}	23	10^{-3}–10^{-5}	4.5×10^{-6}
5ASZ	28.0	10^{-1}–10^{-5}	5.8×10^{-6}	13	10^{-2}–10^{-5}	5.5×10^{-6}
2ASZ	32.5	10^{-1}–10^{-5}	5.2×10^{-6}	24	10^{-1}–10^{-5}	3.2×10^{-6}
4ASZ	35.0	10^{-1}–10^{-5}	5.0×10^{-6}	25	10^{-3}–10^{-5}	3.0×10^{-6}
6ASZ	36.5	10^{-1}–10^{-5}	3.9×10^{-6}	26	10^{-3}–10^{-5}	2.0×10^{-6}
7ASZ	41.0	10^{-2}–10^{-5}	2.0×10^{-6}	18	10^{-2}–10^{-5}	1.4×10^{-6}
1GZZ	40.0	10^{-1}–10^{-5}	5.0×10^{-6}	17	10^{-1}–10^{-5}	5.0×10^{-7}

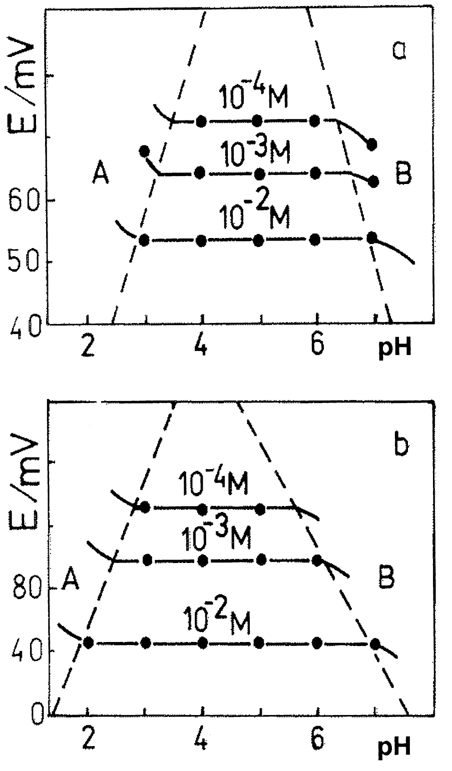


Fig. 6. pH dependence of the electrode potential of ISE: (a) ASZ and (b) GZZ.

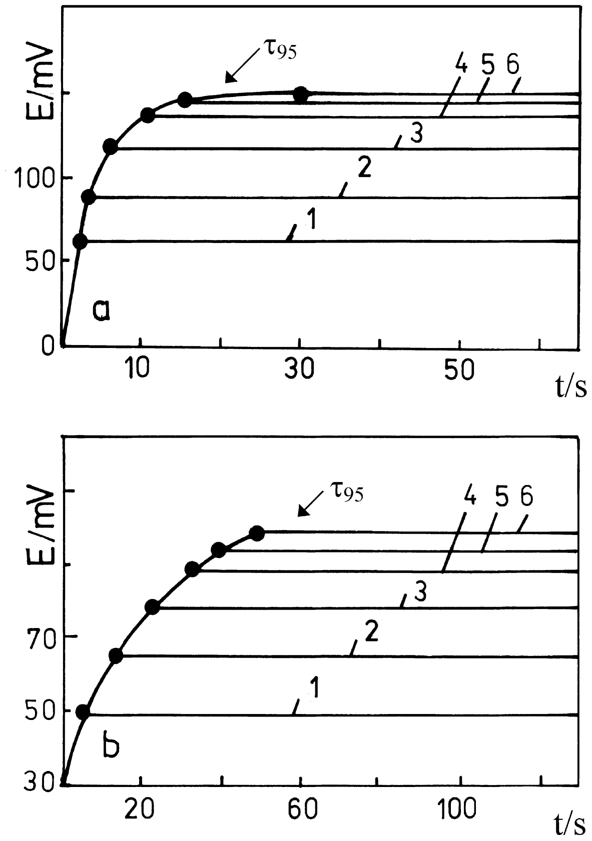


Fig. 7. Dependence of response time on membrane composition: (a) ASG; (b) GZZ; and solution concentration: (1) 10^{-1}, (2) 10^{-2}, (3) 10^{-3}, (4) 10^{-4}, (5) 10^{-5} and (6) 10^{-6} M Zn(II).

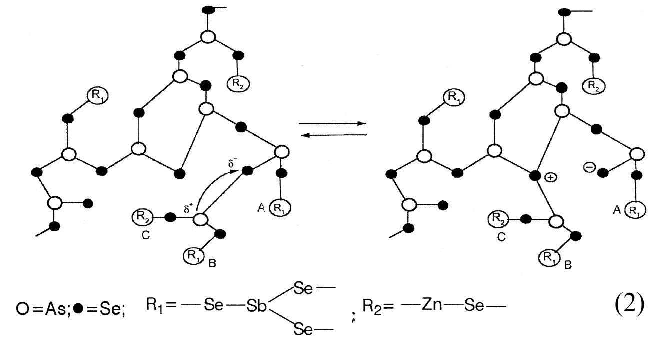
sediment is deposited (Figure 6(a) and (b), zone B) which prevents effective functioning of the ISE.

3.4. *Response time (τ_{95})*

This parameter was determined in the concentration range 10^{-6}–10^{-1} M Zn(II) at pH 4. $\tau_{95} \approx 2$–30 s for the ASZ system and $\tau_{95} \approx 5$–50 s for the GZZ system (Figure 7(a) and (b)).

4. Discussion

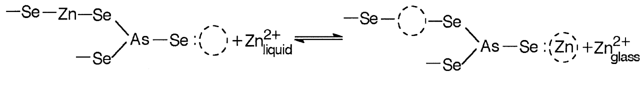
During the synthesis of the chalcogenide ASG glasses, Zn atoms occupy positions A, B or C in positive- and negative-charged centres of Scheme 2:



(2)

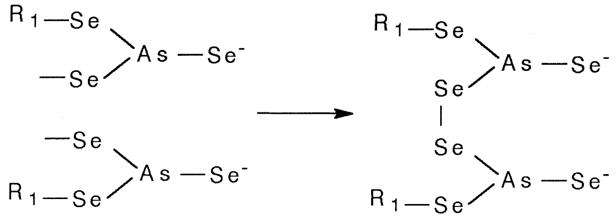
$$[(2R_1R_2 4(AsSe_{3/2})] \longleftrightarrow [R_1R_2Se(AsSe_{2/2})_3]^+ + R_1AsSe_{2/2}Se^-$$

At the beginning of the measurement, the exchange process $\mathrm{Zn}^{+}_{\mathrm{liquid}} \leftrightarrow \mathrm{Zn}^{+}_{\mathrm{glass}}$ occurs, following Scheme 3:



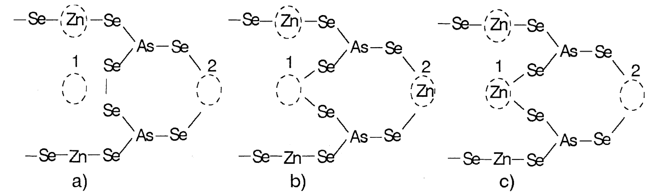
This is, probably why the initial electrode function has a slope typical of a univalent anion (Figure 2), i.e. opposite to the slope of a univalent cation (~59 mV dec^{-1}).

Due to secondary processes (diffusion, crystallization, phase transition *etc.*) or external treatment (electric or magnetic fields, heating, light exposure, conditioning *etc.*), the defects might be extracted from the basic matrix of the glass and diffuse in its volume, creating new defect centres. The negative-charged $(\mathrm{AsSe}_{3/2}\mathrm{R}_1)^-$ defects for the ASZ system have smaller sizes than the positive-charged $[\mathrm{Se}(\mathrm{AsSe}_{2/2})_3\mathrm{R}_1\mathrm{R}_2]^+$ defects and can interact with each other, for example, according to Scheme 4:



$$2\,(\mathrm{AsSe}_{3/2}\mathrm{R}_1)^- \rightarrow [\mathrm{Se}_2(\mathrm{AsSe}_{2/2})_2(\mathrm{R}_1)_2]^{2-}$$

Structural changes of the defective centre in the working regime of ISE are illustrated by Scheme 5:



a) b) c)

Before conditioning, two spatial free positions, (1) and (2), exist (case (a)). After conditioning, Zn^{2+} ions coming from the solution occupy position (2) in the defect centre, which is accompanied by bond breaking between the two bridged Se atoms (case (b)). This results in creation of two new bonds. During the measurement cycle, the Zn^{2+} ions occupy position (1), while Zn^{2+} ions in position (2) pass into solution (case (c)). Again, two free bonds are formed. This consecutive process of occupation and delivery of the active positions (1) and (2) in the defect centre repeats continuously, ensuring a permanent working regime of the ISE. The relative value of S decreases during the working regime and the stabilization of the electrode function to values typical for a two-valent ion (Table 1, Figures 2–4) can be explained by the assumption for creation of the double-ionized defects (Scheme 5 (b) and (c)). External influences (dirt, sediment, dissolution, oxidation *etc.*) lead to blockage or exhaustion of the membrane surface, which can be restored by polishing and so continues to work by repeated conditioning, following the above mechanism.

In addition, Scheme 5 also suggests the possibility for creation of ISE for detection of Zn(II)-ions on the basis of non-Zn containing chalcogenide glasses. In this case the chalcogenide membrane has to be preliminarily conditioned in a Zn-salt solution [4]. Besides, Zn(II) ISE can be sensitive to other Me(II) ions available in the solution. Consequently, Zn(II) ISE can be used as an element from a multisensor system for simultaneous detection of several Me(II) ions [9].

5. Conclusions

(i) New Zn(II) ISE with chalcogenide glassy $\mathrm{As}_2\mathrm{Se}_3$–$\mathrm{Sb}_2\mathrm{Se}_3$–ZnSe and GeSe_2–ZnSe–ZnTe membranes are developed. (ii) The comparison of the results of the studied ISE shows that compositions with higher ZnSe content (maximal values of z) and with higher GeSe_2 content (minimal values of m) are convenient for practical applications. (iii) In particular, 1 ASZ and 7 ASZ exhibit the best parameters: for 1ASZ, $S = 38$ mV dec^{-1}, $L = 10^{-5}$–10^{-1} M Zn(II), $LD = 4.0 \times 10^{-6}$ M Zn(II); for 7 ASZ, S=41 mV dec^{-1}, L = 10^{-5}–10^{-2} M Zn(II), $LD = 2.0 \times 10^{-6}$ M Zn(II). In both cases, $(\mathrm{pH})_{\mathrm{min}}$ 3–4, $(\mathrm{pH})_{\mathrm{max}}$ 6–7, $\tau_{95} = 2$–30 s in the concentration range 10^{-6}–10^{-1} M Zn(II).

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