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Effect of structure and properties of membrane active substance on analytical performance of ion-selective electrodes

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Abstract: The potential creating properties of a group of acidic chelating compounds are presented. The studies have been carried out by the constructing of new ion-selective electrodes based on PVC membranes doped with the studied compounds, and determining the basic analytical parameters of the electrodes. The usefulness of eight out of nine investigated compounds in the preparation of the membrane phase electrodes selective for cobalt, zinc and cadmium has been shown. It has been also found that the acidic properties of ionophore have an essential influence on the analytical parameters of the constructed electrodes. The response mechanism of the obtained electrodes has been investigated by simultaneous spectrophotometric-potentiometric measurement of membranes used in electrodes. It has been found that during the conditioning of electrode, a complex of active substance with primary ion is formed in the membrane phase, then the membrane composition is established and remains unchanged in the next measurements.

Keywords: ion-selective electrode, acidic chelating ionophore, PVC membrane, potentiometry, spectrophotometry

1. Introduction

Ion-selective electrodes have been studied for more than four decades, and are now routinely employed for direct potentiometric measurements of various ionic species in environmental, industrial and clinical samples (De Marco et al., 2007; Bakker et al., 2001; Lewenstam et al., 1997). The research on ion selective electrodes is concerned with the search for new chemical compounds (Solsky, 1990; Baker et al., 2002; Agrawal et al., 2008) that could be used for construction of ion selective electrodes characterized with the desirable analytical parameters. Owing to their versatility that allows a wide range of selectivities for metal ions, especially heavy metal ions, use of chelating agents as a sensing material seems to be attractive for designing liquid membrane ISEs for heavy metal ions (Gupta et al., 2011; Bakker et al., 1999; Bühlman et al., 1998). Recently, we succeeded in the preparation of new ion-selective electrodes sensitive to zinc, cadmium and cobalt using different chelating ionophores (Wardak, 2008; Wardak et al., 2004a; Wardak et al., 2004b; Dumkiewicz et al., 2002; Dumkiewicz et al., 2000a). In this paper we present the collected results of research involving the potential creating properties of the compounds described previously as well as new compounds.

The aim of this paper is to search for the influence of the acidifying character of ionophore, used for membrane preparation, on the analytical properties of the obtained electrodes based on them. Both, the investigated compounds and their complexes with metal ions are coloured. This allowed us to perform spectrophotometric studies, which in turn made possible the optimization of the conditioning time of the electrodes and monitoring of the complexation process in the membrane.

2. Materials and methods

2.1. Reagents

During the study mentioned reagents were used: tributylphosphate (TBP), dibutylphthalate (DBP), zinc chloride - (Merck, Germany), tris(2-ethylhexyl) phosphate (TEHP) - (K&K Laboratories, ICN), low

molecular weight poly(vinyl chloride) (PVC) (Aldrich, USA), 2-nitrophenyl octyl ether (NPOE), other reagents were purchased from Fluka. As chelating active substances of electrodes, the following compounds were used:

- 1,2,4 triazole derivatives: I - 3-(2'-hydroxynaphthylazo-1')-1,2,4 triazole; II - 3-(3',4' dihydroxyphenylazo-1')-1,2,4 triazole; III - 3-(2',4' dihydroxyphenylazo-1')-1,2,4 triazole;
- 3-mercapto 1,2,4 triazole derivatives: IV - 3-mercapto-5-(2'-hydroxynaphthylazo-1')-1,2,4 triazole; V - 3-mercapto-5-(3',4' dihydroxyphenylazo-1')-1,2,4 triazole; VI - 3-mercapto-5-(2',4' dihydroxyphenylazo-1')-1,2,4 triazole;
- 1,3,4 thiadiazole derivatives: VII - 2-(2'-hydroxynaphthylazo-1')-1,3,4 thiadiazole; VIII - 2-(3',4' dihydroxyphenylazo-1')-1,3,4 thiadiazole; IX - 2-amino-5-(2'-hydroxynaphthylazo-1')-1,3,4 thiadiazole.

These compounds were synthesized in the Department of Drug Chemistry, Medical University in Lublin. They are derivatives of 1,2,4 triazole and 1,3,4-thiadiazole which practically does not dissolve in water but dissolves relatively well in plasticizers as well as in methanol, cyclohexanone, dimethylformamide, amines and tetrahydrofuran. They are acidic chelating agents with weak acidic properties. Their chemical structures as well as values of dissociation constants (pK_a) are shown in Fig. 1 (Zareba, 1989). The compounds form stable chelating complexes with metal cations which have metal:ligand ratio of 1:2 or 1:1. These complexes are chromatic and insoluble in water but soluble in organic solvents.

All stock aqueous solutions of $1 \times 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$ were prepared by dissolving the weighted amount of corresponding salts in distilled, deionized water. Working solutions in the concentration ranging from $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ to $1 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ were prepared by appropriately diluting stock solutions.

2.2. Apparatus

The equilibrium potential of the studied electrodes was measured versus the Orion 90-02 reference electrode filled with Orion 90-00-01 solution: $1.7 \text{ mol} \cdot \text{dm}^{-3} \text{ KNO}_3 + 0.64 \text{ mol} \cdot \text{dm}^{-3} \text{ KCl} + 0.06 \text{ mol} \cdot \text{dm}^{-3} \text{ NaCl} + 1 \text{ cm}^3 \cdot \text{dm}^{-3} \text{ 37\% HCHO}$. The measurements were carried out at room temperature in the solutions stirred with a mechanical stirrer by means of a Multifunctional Computer Meter CX 721 Elmetron (Poland). This device enables the recording of EMF changes vs. time. An Orion 81-72 glass electrode was used to pH measure. Spectrophotometric measurements were performed with SPEKORD M40 (Carl Zeiss, Jena) spectrophotometer combined with a computer.

2.3. Construction of the electrode and membrane preparation

The major component of the electrode is a potential determining membrane phase based on plasticized PVC, which is in direct contact with an Ag/AgCl electrode and placed in a cylindrical Teflon container screwed onto the electrode body. The electrode membrane phase consists of two layers placed in a Teflon holder: the inner layer containing plasticized PVC (without ionophore) in which the Ag/AgCl electrode is placed and the outer layer contacting with the tested solution and containing the active substance apart from the inner layer components. The electrode construction and membrane preparation were described in earlier papers (Wardak, 2008; Wardak et al., 2004a, Dumkiewicz et al., 2000b). The electrodes were conditioned in $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ of primary ions solution to saturate PVC membrane in these ions.

2.4. Cell for spectrophotometric and potentiometric measurements

Simultaneous spectrophotometric and potentiometric measurements were made using a specially constructed teflon cell (Fig. 2). It consists of one working cell and one reference cell. The internal reference Ag/AgCl electrode is placed in the reference cell whereas the reference Ag/AgCl with a double salt bridge is placed in the working cell. Primary ion solution of the adequate concentration and NaCl solution of $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ concentration were poured using a syringe into the working cell and the reference cell, respectively. The reference cell with Ag/AgCl electrode placed in NaCl solution together with the membrane correspond to ion-selective electrode, but the working cell with reference Ag/AgCl with a double salt bridge placed in primary ion solution correspond to sample solution and reference electrode. Thus this is a typical potentiometric system with ion-selective electrode.

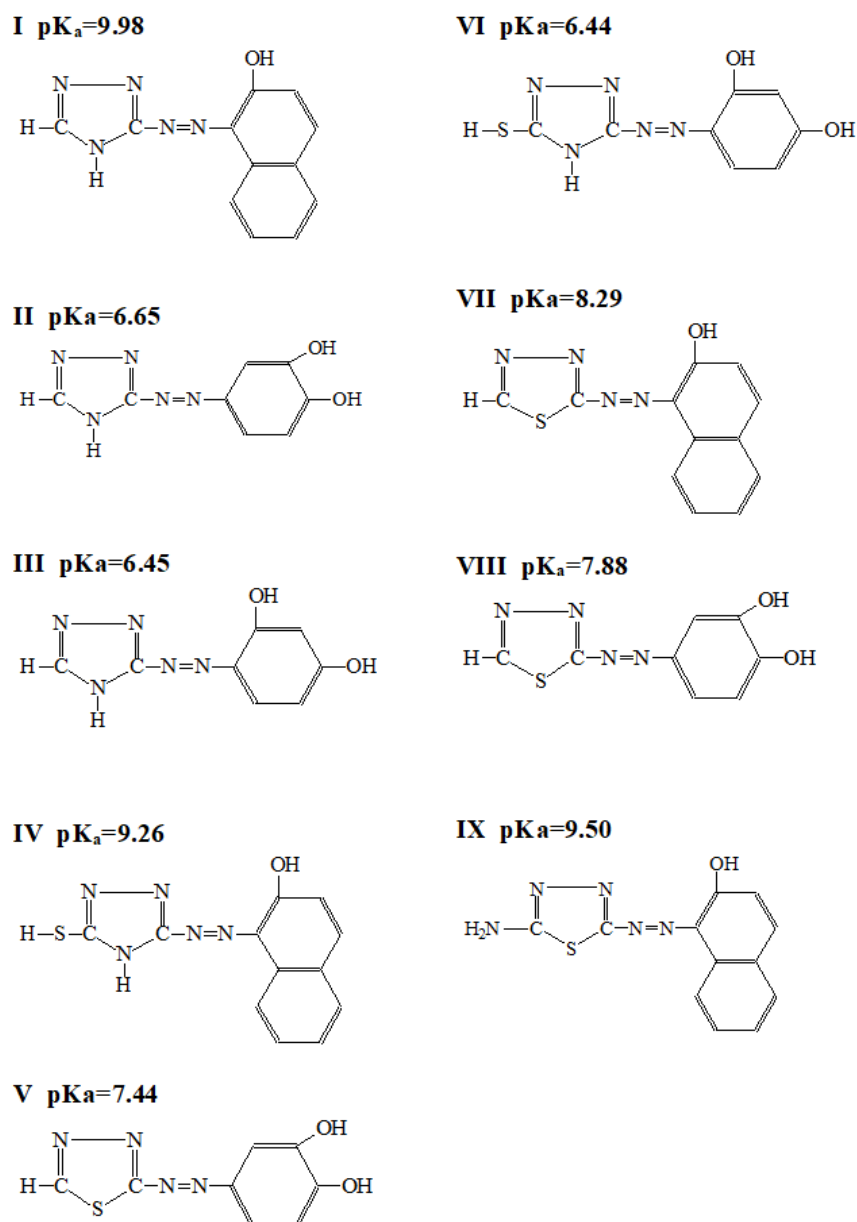


Fig. 1. Structures of ionophores used in this work and the values of their dissociation constants: I - 3-(2'-hydroxynaphthylazo-1')-1,2,4 triazole; II - 3-(3',4' dihydroxyphenylazo-1')-1,2,4 triazole; III - 3-(2',4' dihydroxyphenylazo-1')-1,2,4 triazole; IV - 3-mercapto-5-(2'-hydroxynaphthylazo-1')-1,2,4 triazole; V - 3-mercapto-5-(3',4' dihydroxyphenylazo-1')-1,2,4 triazole; VI - 3-mercapto-5-(2',4' dihydroxyphenylazo-1')-1,2,4 triazole; VII - 2-(2'-hydroxynaphthylazo-1')-1,3,4 thiadiazole; VIII - 2-(3',4' dihydroxyphenylazo-1')-1,3,4 thiadiazole; IX - 2-amino-5-(2'-hydroxynaphthylazo-1')-1,3,4 thiadiazole

Two identical cells were used in the investigations. One was placed on the measuring light beam while the other was placed in the reference beam. Light fell perpendicularly to the membrane surface. Both the membrane thickness and solutions concentration were the same. The only difference was that the membrane in the reference cell did not include the active substance. The membranes used for spectrophotometric measurements were prepared in the following way: the membrane components (the same as in the electrode outer layer) were weighted and precisely mixed. Then THF was added and mixed again until clear solution was obtained. From this solution membranes were poured to a glass ring of 34 mm diameters placed on a glass plate and left for free evaporation of the solvent. Then the membranes were dried for 3 hours at 313K. Similarly, another membrane was prepared which has the same composition without the active substance. Circles of the diameter equal to the diameter of the measured cell (22 mm) were cut from membranes made in this way.

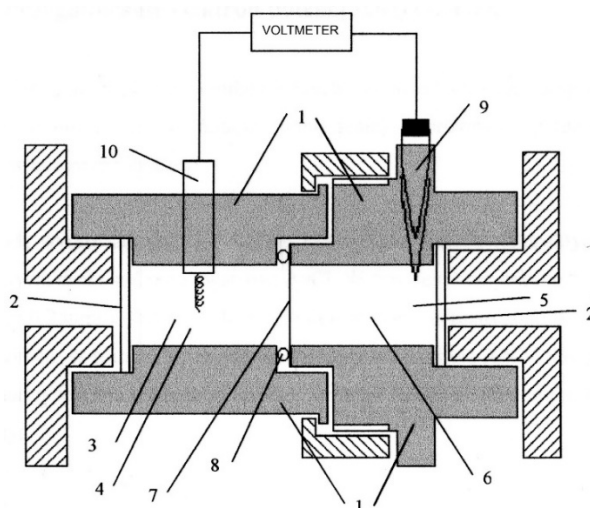


Fig 2. Measurement cell scheme: 1 - teflon housing, 2 - polyacryl window, 3 - reference chamber, 4 - NaCl solution, 5 - working chamber, 6 - primary ion solution (ZnCl_2 , CdCl_2 or CoCl_2), 7 - membrane, 8 - ring gasket, 9 - reference electrode, 10 - internal reference electrode

2.5. Procedures

In order to examine the potential creating properties of the studied compounds, the ion selective electrodes were constructed and their analytical parameters were estimated. Before the first measurement the electrodes were conditioned for at least 12 hours in $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ of primary ion solution, in order to saturate PVC membrane with these ions. Between measurements electrodes were stored in air. They were conditioned in $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ of primary ion solution during 30 min on the beginning of the measurements once a day. The electrode characteristics for all studied membrane sensors were determined in the primary ions solutions of the concentration 1×10^{-1} - $1 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$. The obtained results were interpreted and the detection limits, characteristic slope and measuring range were determined.

The response time of the examined electrodes was established by injecting the concentrated standard solutions into the stirred primary ion solution. Simultaneously, EMF changes of the studied electrode/reference electrode system were recorded.

The pH dependence of the electrode potential was investigated over the pH range of 3.0-9.5. For this purpose, $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 solution or $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ NaOH solution was added to that containing primary ion at the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. After each addition, the pH was measured and as soon as the electrode response was stable, the EMF of the studied electrode/the reference electrode system was read.

The prepared electrode analytical usefulness time was tested by measuring characteristic slopes of the electrodes kept in air. The measurements were made systematically, usually every three days, in freshly prepared CdCl_2 , ZnCl_2 or CoCl_2 solutions. The selectivity of the studied membrane electrodes was evaluated by establishing its selectivity coefficients in reference to the interfering ions by the separate solution method (by extrapolating the response functions to $a_i = a_j = 1 \text{ mol} \cdot \text{dm}^{-3}$ (Bakker et al., 2000)).

Spectrophotometric investigations of the membranes were performed in the following way:

- by measuring the dependence of absorbances of the studied membranes vs. the wave length (spectral measurements);
- by measuring the dependence of absorbances of the studied membranes vs. time with fixed wave length (kinetic measurements).

Simultaneously with kinetic measurements, also EMF studies of the cell formed by the examined membrane, and of the electrodes placed on both its sides, were performed. The aim of those measurements was to observe the time of potential formation against the time during which the complexation equilibrium is established in the membrane. This allowed us to optimize the time of electrodes conditioning in potentiometric measurements and to monitor the complex formation in the membrane.

3. Results and discussion

3.1. Potentiometric results

The potential creating properties of studied compounds were estimated based on electrodes performance having these compounds as an active substance in the polymeric membrane. The analytical parameters of obtained electrodes, determined from potentiometric measurements, are presented in Tables 1 and 2.

Table 1. The analytical parameters of electrodes based on the studied ionophores

Iono-phore	Primary ion	Plasticizer	Life time (month)	pH range	Measuring range (mol · dm ⁻³)	Characteristic slope (mV/decade)	Response time (s)
I	Cd(II)	DBF TBP	6.0	3.9-8.5	8.8x10 ⁻⁶ - 1.0x10 ⁻²	30.9	10
II	Cd(II)	DOA TBP	4.0	5.0-8.0	6.6x10 ⁻⁶ - 1.0x10 ⁻¹	30.2	20
	Ca(II)	NPOE TBP	3	5.1-7.9	4.5x10 ⁻⁵ - 1.0x10 ⁻¹	29.0	25
III	Cd(II)	TEHP TBP	7.0	4.3-8.5	5.9x10 ⁻⁶ - 1.0x10 ⁻¹	28.5	10
IV	Cd(II)	TEHP TBP	4.5	4.5-8.7	1.0x10 ⁻⁵ - 1.0x10 ⁻¹	27.0	20
V	Cd(II)	TEHP TBP	3.5	5.5-8.5	2.2x10 ⁻⁵ - 1.0x10 ⁻¹	28.6	40
VI	Zn(II)	DBF TBP	1.5	4.0-7.5	5.3x10 ⁻⁶ - 1.0x10 ⁻¹	29.0	30
VII	Zn(II)	TEHP TBP	1.5	4.5-7.8	5.6x10 ⁻⁶ - 1.0x10 ⁻¹	29.0	10
VIII	Cd(II)	DBF TBP	7	4.6-9.0	7.9x10 ⁻⁶ - 1.0x10 ⁻¹	29.8	20
IX	Co(II)	TEHP TBP	6	4.3-9.0	1.3x10 ⁻⁶ - 1.0x10 ⁻¹	30.1	10

Table 2. The selectivity coefficient values log K^{Pot_I/J} for electrodes based on studied compounds, determined by the separate solution method

Iono-phore	Primary ion	log K ^{Pot_I/J}											
		Cd ²⁺	Zn ²⁺	Ca ²⁺	Mg ²⁺	Ba ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Fe ²⁺	Mn ²⁺	K ⁺	Na ⁺
I	Cd(II)	0	-0.69	-2.03	-2.48	-2.26	-1.74	-2.58	-1.33	-1.28	-1.47	-3.39	-3.12
II	Cd(II)	0	-0.85	-0.60	-0.85	-1.17	-1.11	-1.32	-0.85	-0.97	-0.54	-1.82	-2.64
	Ca(II)	-0.26	-0.77	0	-	-	-0.33	-0.62	-	-	-	-1.15	-1.25
III	Cd(II)	0	-1.37	-1.58	-2.13	-1.58	-1.50	-1.85	-1.39	-1.46	-1.37	-2.12	-3.21
IV	Cd(II)	0	-1.10	-1.05	-2.12	-1.79	-1.17	-2.52	-1.70	-1.70	-1.66	-2.25	-3.03
V	Cd(II)	0	-1.00	-1.17	-1.28	-1.11	-1.25	-1.65	-1.30	-1.02	-1.16	-2.44	-2.30
VI	Zn(II)	-0.51	0	-0.76	-1.35	-1.14	-1.15	-1.35	-0.92	-0.65	-1.17	-3.02	-2.22
VII	Zn(II)	-0.41	0	-0.89	-1.52	-1.27	-0.51	-0.51	-0.60	-0.94	-0.51	-2.88	-2.24
VIII	Cd(II)	0	-1.46	-2.48	-1.74	-1.74	-1.74	-2.31	-1.50	-1.90	-1.59	-3.04	-2.25
IX	Co(II)	-1.22	-2.50	-2.1	-2.35	-2.02	0	-2.3	-1.3	-	-2.00	-3.30	-3.24

Analysis of data presented in Tables 1 and 2 allows us to conclude that the tested compounds exhibited the greatest affinity towards Cd²⁺ ions (I, II, III, IV, V, VIII), and Zn²⁺ ions (VI, VII). Moreover, the cadmium electrodes are less selective to zinc (the highest values of selectivity coefficients) and conversely, the zinc electrodes are the most sensitive to cadmium. This is probably due to similar structure of both ions. Only ionophore IX was selective to Co²⁺ ions. The cobalt electrode based on

ionophore IX is also the most sensitive to Cd^{2+} ions. The greatest differentiation in affinity occurs within the scope of derivatives 1,3,4 thiazazole. Compounds VII and IX, containing naphthol group, exhibited high affinity to zinc and cobalt, respectively. The change of sulphur atom in the heterocyclic ring into the nitrogen atom results in an increase of affinity to cadmium (ionophores I and IV). In order to explain and predict the interactions between ligands and cations of metals, the HSAB theory of "hard" and "soft" acids and bases is frequently used, as formulated by Pearson (Pearson, 1963; Basolo and Pearson, 1973). According to this theory, the cadmium ion is a soft acid, whereas the zinc and cobalt ions are medium hard acid. The hardness of complex-forming ligands is due to the presence of non-metal atoms in their donor groups. The hardness of bases decreases together with a decrease of their electron negativities. Thus, the change of a rather hard sulphur atom into a less hard nitrogen atom results in an increase of affinity of ligands to a soft acid, i.e. the cadmium ion. The electrodes containing in their membrane nonspecific ligand II are not selective (the high values of selectivity coefficients) and their sensitivity to the given ions depends on the kind of plasticizer used for membrane preparation (Tables 1 and 2). All the electrodes exhibit theoretical or near theoretical slope of characteristic, short response time 10-50 s, typical measuring range of 1×10^{-5} - 1×10^{-1} mol · dm⁻³ and life time from 1.5 to 7 months. It has been observed that the influence of hydrogen ions on the electrode response (lower value of pH range, see Table 1) is dependent on the acidity of ionophore and it is higher when the ionophore acidic character is stronger. It was observed especially for particular group of ionophores i.e. 1,3,4 thiazazole derivatives, 1,2,4 triazole derivatives and 3-mercapto 1,2,4 triazole derivatives. This dependence is shown in Fig. 3.

The influence of hydrogen ions vs. ionophore acidity constant point to different mechanisms of interaction of the studied ionophores. Ionophores of stronger acidic character (II, III, VI) behave like typical ion exchangers – they dissociate in the membrane phase and the active potential creating form is the ionophore anion which forms complexes with metal ions from the sample phase. The ionophores are more sensitive to the presence of hydrogen ions, which can be explained by their influence on the ionophore dissociation and thus on the main ion extraction from the sample phase to the membrane phase. In the case of ionophores of weak acidic properties (I, IV, V, VII, VIII, IX), the neutral undissociated ionophore form (neutral carrier) is a predominant potential creating form, therefore the electrodes based on these ionophores are less sensitive to the hydrogen ions as compared to ionophore from the same group.

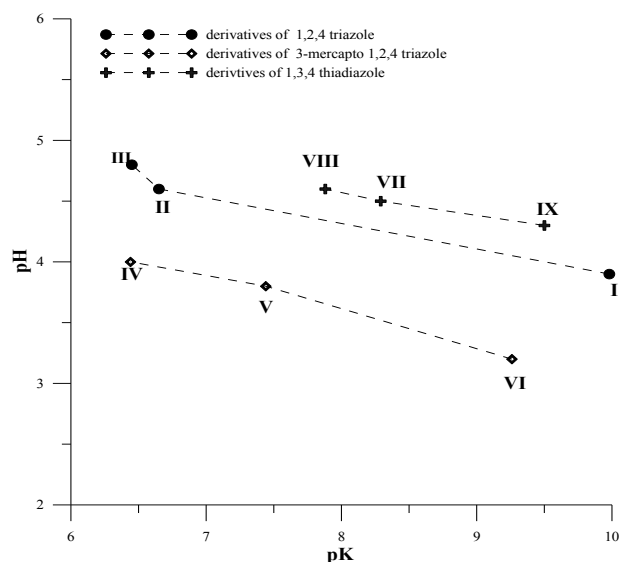


Fig. 3. Dependence of lower value of limit pH range of electrodes vs. dissociation constant of ionophore

3.2. Spectrophotometric-potentiometric research of electrode membranes

The performed investigations allowed us to define the presence of complex in the membrane, which is formed during the conditioning of the electrode. The exemplary absorption spectra obtained for membrane containing ionophore IV is presented in Fig. 4. As it can be seen the course of the spectra of membranes before and after the conditioning in the solution of the main ion are significantly different,

which proves the complex interaction of the main ion with the ligand immobilized in the membrane. The spectra of the membrane after the conditioning are characterized by one or two peaks shifted upfield as compared to the peak in the spectrum of membrane before the conditioning. Their shape depends on the ligand structure. For ligands containing the naphthol group, two distinct peaks are obtained after the conditioning, whereas for the remaining ligands only one peak of varying shape is noted.

As a result of the performed investigations of simultaneous measurement of potential and absorbance (Fig. 5), during the formation of the metal-ligand complex a potential is generated on the membrane-solution interphase. Metal cations, which form a complex with the ionophore in the membrane phase, pass to the membrane. From the course of curves presenting the dependence of absorbances of membranes vs. time, it can be stated that the complex is formed gradually, attaining the equilibrium state after a time ranging from 4000 s to 8000 s.

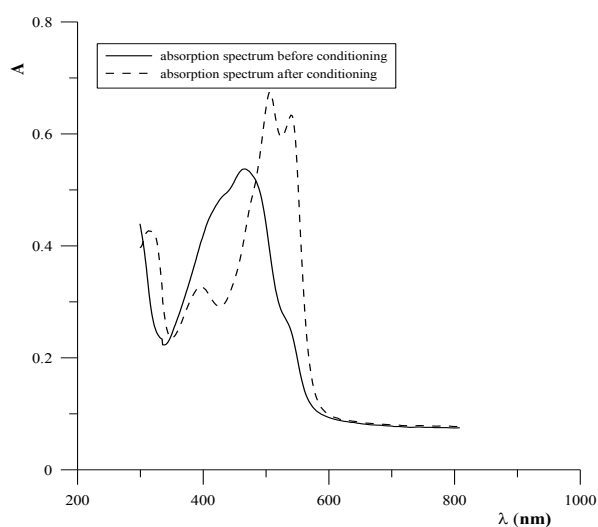


Fig. 4. Absorption spectra of membrane containing ligand IV, before and after conditioning in $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ CdCl_2 solution

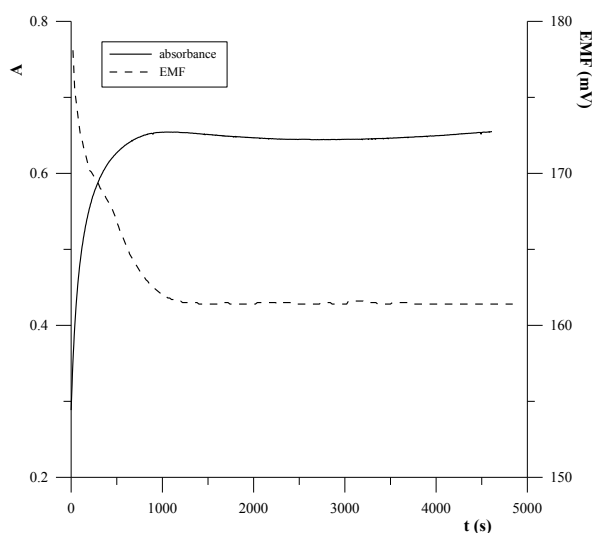


Fig. 5. Dependence of the membrane absorbance vs. time, and the EMF vs. time for the membrane containing ligand IV determined in $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ CdCl_2 solution. Absorbance measurement was done with analytical wave length of the complex $\text{Cd}(\text{L}_{\text{IV}})_2$ – 539.6 nm

Figure 6 presents the results of successive simultaneously performed potentiometric and spectrophotometric measurements of the membrane originally containing ligand IV, after the conditioning in CdCl_2 solution. The CdCl_2 solution was introduced into the working chamber in successive doses of increasing concentration. As can be seen in the picture, the membrane absorption

measured at the analytical wave length for the $\text{Cd}(\text{L}_{\text{IV}})_2$ complex is practically constant – the composition of membrane established during the process of conditioning remains unchanged. The curve presenting the EMF dependence vs. time of the cell formed by the membrane (after conditioning) and of the electrodes placed at its both sides, is analogical to the curve of ion-selective electrode response. The EMF value depends only on the composition of the water phase and increases together with an increase of concentration of cadmium ions. Similar results were obtained for other studied compounds.

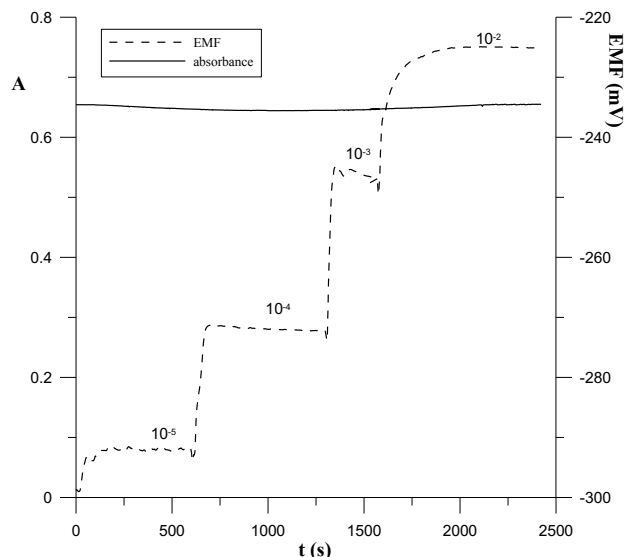


Fig. 6. Dependence of the membrane absorbance vs. time and the EMF vs. time for the membrane containing complex $\text{Cd}(\text{L}_{\text{IV}})_2$ (membrane with ligand IV after conditioning) determined in CdCl_2 solutions in the concentrations range of 1×10^{-5} – 1×10^{-2} mol·dm $^{-3}$. Absorbance measurement was done with analytical wave length of the complex $\text{Cd}(\text{L}_{\text{IV}})_2$ – 539.6 nm

4. Conclusions

As a result of the performed investigations electroactive properties of a group of chelating azo compounds possessing characteristics of a weak acid were determined. The following compounds: I, III, IV, V, VIII exhibit the greatest affinity to cadmium ions whereas compounds VI, VII and compound IX exhibited the greatest affinity to zinc and cobalt ions, respectively. It allows one to obtain ion-selective electrodes sensitive to the Cd^{2+} , Zn^{2+} and Co^{2+} ions and having good analytical parameters. The electrodes containing compound II in the membrane are characterized with poor selectivity which seriously limits their analytical usefulness. Moreover, the properties and mechanism of functioning of the obtained electrodes depend on the type of ionophore applied in the electrode membrane, and also on a large extent on its dissociation constant. Spectrophotometric measurements showed that during the conditioning of electrodes a ionophore – metal ions complex is formed in the membrane phase. The equilibrium of the reaction of complex formation is established slowly during the time ranging from 1 h to 2.5 h. The simultaneously formed potential at the membrane – solution interphase is established during the same (or a slightly shorter) time. The membrane composition is established during the conditioning and remains unchanged during further measurements.

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