
APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

New Polymeric Chemical Sensors for Determination of Lead Ions

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Abstract—New polymeric electrochemical sensors for determining the content of lead were suggested. As the active substance of the polymeric membranes of the sensors was used *N,N'*-tetrabutylidipicolinamide, the compound exhibiting a high extractive capacity for heavy metal ions. The selectivity of the sensors with respect to lead ions in the presence of copper, cadmium, and zinc in a considerable excess was studied.

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The development of modern methods of analytical chemistry is aimed in many respects to devise instruments and approaches that provide fast, accurate, and reliable chemical analysis of samples in the real-time mode. Analytical methods of this kind are in high demand both in the industry, for monitoring of various technological processes, and in ecological inspection of natural samples. A particular place among important tasks for chemists-analysts is occupied by the problem of lead determination. This circumstance is due both to the wide occurrence of this element in various technological processes and to its high toxicity for living organisms.

Various methods exist for determination of lead: complexometry, electrogravimetry, spectrophotometry, and atomic absorption spectrometry. As a rule, most of these techniques involve complicated and prolonged sample preparation, large amount of expendable materials, need to use the labor of highly skilled personnel, and high-cost the equipment. Apparently, only a limited number of analytical methods enable automated on-line measurements. As an attractive instrument satisfying the requirements of rapidity and reliability of determination, simplicity of use, and possibility of measurement automation may serve chemical sensors and, in particular, ion-selective electrodes (ISEs).

A comparatively large number of various types of ISEs for determination of lead have been developed. These include chalcogenide glass electrodes [1, 2], widely used sensors with polycrystalline sulfide membranes, and also ISEs with membranes based on various organic

complexing agents. Among these types of ISEs, the last variety of sensors is the subject of the largest number of publication, which is due to the apparent advantages of polymeric materials. ISEs of this kind enable controlled variation of their electrochemical characteristics via modification of the chemical structure of the active substance of the membrane, ionophore, capable of selective complexation with target ions. In addition, it is possible to control the sensor properties by varying the ratio between the membrane components, ionophore, and ion-exchange additive, and by changing the polarity of the plasticizer-solvent. In recent years, the researchers' interest in film-type electrochemical sensors has been steadily growing, principal theoretical concepts of operation of such sensors have been revised, it has been shown that electrodes of this type provide exceedingly low detection limits, concepts of the selectivity coefficients have been reconsidered, and potentiometric techniques with external current flows have been developed [3–5].

A major disadvantage of solid-state PbS ISEs is the membrane poisoning by Hg^{2+} , Ag^+ , and Cu^{2+} ions. This circumstance has initiated a search for new substances-ionophores for PVC-plasticized membranes. However, analysis of published data shows that a large number of polymeric film electrodes for determination of lead developed by now have the same disadvantages: their selectivity with respect to lead in the presence of copper and cadmium ions is, as a rule, low. This circumstance strongly restricts the variety of the possible practical applications of sensors of this kind, because lead, copper,

and cadmium ions are frequently simultaneously present in real solutions.

The sensitivity of polymeric sensors to Pb^{2+} or PbA^+ , where A is an anion (commonly OH^- , acetate, or nitrate anion), depends not only on the composition of the sensor membrane, but also on the solution pH and anion concentration. Because magnitudes of the electrode responses may be typical of single- or double-charged cations, or may have intermediate values, the selectivity coefficients should be interpreted with great care.

The first of the suggested film electrodes for lead were sensors based on diamides of oxo and dioxo carboxylic acids [6], which give a Nernst response to PbA^+ . The selectivity of these electrodes is rather high. Introduction of ionic additives into the membrane results in a slope of the electrode function, equal to 35.3 mV dec^{-1} , which presumably corresponds to a mixed response to Pb^{2+} and PbA^+ . The problem associated with the influence of silver and mercury ions is reliably solved if diphenyl methyl-*N*-phenyl hydroxamic acid is used as a ionophore [7]. Sensors based on this compound give a theoretical response to Pb^{2+} (28.5 mV dec^{-1}); nitrate solutions with pH 5–6 were used in the study. A rather large number of studies have been concerned with various crown ethers [8–12]. Of interest among the most recent studies are those devoted to use of diporphyrin xanthenes [13]; membranes containing these compounds, plasticized with *o*-nitrophenyl octyl ether, provide a Nernst response of the sensors in the range 2.6×10^{-6} – $1.0 \times 10^{-1} \text{ M}$, the selectivity of the sensors is rather high, but their working pH range is rather narrow (4.5–7.5).

It should be noted that none of the presently suggested materials for lead-selective electrodes is ideal and versatile; practical use of these electrodes inevitably involves problems associated with the membrane poisoning by various components of the solutions and with the insufficient selectivity to some component. As a rule, the determination of lead is the most strongly affected by cadmium, copper, and silver ions.

It seems promising to use substances with high extraction capacity, serving as extractive agents in liquid extraction, for creating ISEs reversible toward ions of metals, including lead. Examples of successful extension of the fundamental aspects of liquid extraction to development of chemical sensors have been reported [14–17]. A large promise for use as sensor materials is shown by various diamides of dibasic organic acids, which is due to their structural diversity, strong

complexing properties, and high chemical stability even in corrosive media [17].

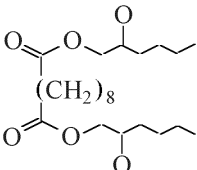
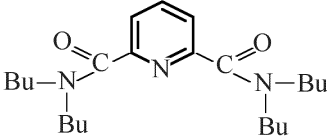
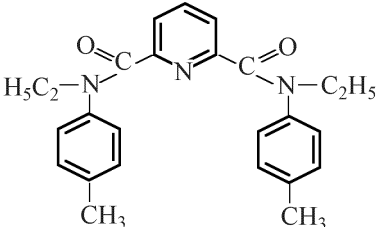
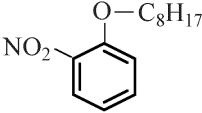
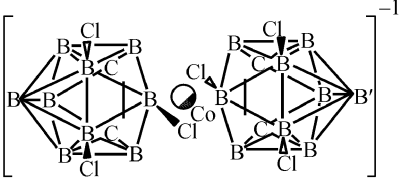
The extractive agents of this class, studied in most detail, are diamides of malonic and diglycolic acids. These extractive agents have a high extraction capacity for actinides and lanthanides, and new extractive techniques for nuclear waste processing have been developed on their basis. Previously, the authors have studied sensors based on *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), with addition of various anionic modifiers. The new sensors exhibited a high sensitivity to trivalent lanthanides and a widely varying selectivity [17].

Recently, studies of a new class of diamides, derivatives of pyridine-2,6-dicarboxylic (dipicolinic) acid, have been commenced. Their extractive properties depend on substituents at amide nitrogen atoms. Diamides substituted with only alkyl substituents show high extraction capacity for tetra- and hexavalent actinides (e.g., U and Th), but do not extract trivalent actinides and lanthanides. Dipicolinediamides having both alkyl and aryl substituents have a considerably higher extraction capacity and effectively extract uranium, actinides, lanthanides [18], and some fission products (e.g., Pd [19]). It should be noted that solutions of dialkyldiaryldipicolinediamides extract americium better than europium. The separation coefficient $D_{\text{Am}}/D_{\text{Eu}}$ reaches a value of 6. As the structure of substituents changes, the extraction selectivity with respect to light lanthanides also changes [20].

With diamides (of any structure) used in a mixture with chlorinated cobalt dicarbollide (CCD), a considerable synergetic effect was observed. Diamide–CCD mixtures effectively extract cesium, actinides, and rare-earth elements from nitric acid solutions [21]. It should be noted that the dramatic increase in the extractive capacity upon addition of CCD to dipicolinediamides results in that the extraction capacities of dialkyldiaryldiamides and tetraalkyl-substituted diamides become closer. Sensors based on diethylditolylidipicolinediamide exhibit a fairly high sensitivity to REE [22].

In this study it was suggested to use *N, N'*-tetrabutyl dipicolinediamide as a neutral ligand for binding lead in the membrane phase. As a cation-exchange additive served CCD, a hydrophobic anion with properties of a strong acid. CCD is widely used in liquid extraction to improve the extractive behavior of reagents and acts as a cation-exchange compound, similarly to the tetraphenyl borate anion conventionally used in ionometry.

Table 1. Structural formulas of membrane components

Structural formula	Compound
$(-\text{CH}_2-\text{CHCl}-)_n$	Poly(vinyl chloride)
	Di-(2-ethylhexyl) sebacate
	<i>N,N'</i> -Tetrabutyl-dipicolindiamide
	<i>N,N'</i> -Diethyl- <i>N,N'</i> -dithiolyl-dipicolinediamide
	<i>o</i> -Nitrophenyl octyl ether
	Chlorinated cobalt dicarbollide

EXPERIMENTAL

Dipicolinediamides, including *N,N'*-diethyl-*N,N'*-dithiolyl-dipicolinediamide (EtT) and *N,N'*-tetrabutyl-dipicolinediamide (TBu) were synthesized at Khlopin Radium Institute by the known procedure [23]. CCD in the H^+ -form was provided by Catchem company (Czech Republic). All the other components used to fabricate sensor membranes in this study were purchased from Fluka (Switzerland). Inorganic salts and organic solvents of chemically pure grade were purchased from Reaktiv company (St. Petersburg). All the solutions were prepared using double-distilled water.

In this study, film-type polymeric sensors with a solid contact were fabricated. Poly(vinyl chloride) (PVC) served as the matrix of the membranes. As solvents-

Table 2. Compositions of sensor membranes

Composition no.	Component	Content, wt %	Molality (relative to the membrane mass), mol kg^{-1}
1	PVC	33.0	
	<i>o</i> -NPOE	66.0	
	CCD	0.1	0.002
	TBu	0.9	0.02
2	PVC	33.0	
	DOS	66.0	
	CCD	0.1	0.002
	TBu	0.9	0.02
3	PVC	32.8	
	DOS	65.6	
	CCD	0.3	0.010
	TBu	1.3	0.050
4	PVC	32.8	
	<i>o</i> -NPOE	65.6	
	CCD	0.3	0.010
	TBu	1.3	0.050
5	PVC	32.9	
	DOS	65.8	0.010
	TBu	1.3	0.050
6	PVC	32.9	
	<i>o</i> -NPOE	65.8	0.010
	TBu	1.3	0.050

plasticizers served di(2-ethylhexyl) sebacate (DOS) and 2-nitrophenyl octyl ether (*o*-NPOE). CCD was used as a cation-exchange additive. The structural formulas of membrane components are presented in Table 1. A total of 12 different membrane compositions were prepared from EtT and TBu with CCD. It was found in further experiments that EtT-based sensors have, on the whole, somewhat lower sensitivity and, therefore, TBu-based sensors will be considered in what follows, unless otherwise stated.

Sensor membranes were fabricated on the basis of two different plasticizer-solvents (DOS and NPOE), with different concentration ratios between the neutral ligand and the cation-exchange additive (CCD and TBu), and also TBu-based membranes containing no CCD [24]. The compositions of the sensor membranes are listed in Table 2.

To weighed portions of the membrane components was added a freshly distilled tetrahydrofuran (THF) and the mixture was agitated with a magnetic stirrer to

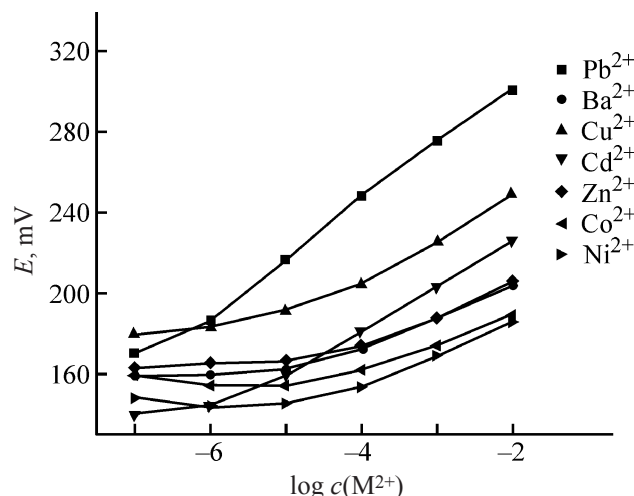
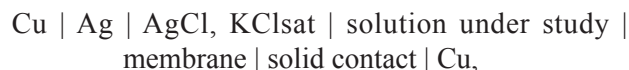


Fig. 1. Typical calibration dependences for the sensor with composition 4 in solutions of various metal cations. (E) Potential and (c) concentration.

complete dissolution. The resulting mixture was poured into a flat-bottomed Teflon weighing bottle and kept there until THF completely evaporated (~48 h). Discs 7 mm in diameter were cut from the thus obtained membrane and a solid contact composed of a composite current-conducting material was deposited onto one of its sides. Upon deposition of the composite material, a layer with mixed conductivity is formed on the membrane surface (ionic in the membrane material and electronic in the composite component of this layer). A current shunt (copper wire) was inserted into the deposited composite. The assembly was allowed to stand to complete drying of the composite current-conducting material, and then the membrane was glued into a plastic electrode case. After drying of the glue, the sensors were soaked in a lead nitrate solution for 2 days before the first measurement. Between measurements, the sensors were stored in air.

At least three sensors with membranes of each type were fabricated. The numerical values of various parameters, presented below, are obtained by averaging over sensors of a given type.

Potentiometric measurements were performed in a galvanic cell:



with a multichannel electronic digital voltmeter with a high input resistance, connected to a personal computer for data acquisition and processing. An EVL 1M 3.1 silver chloride electrode served as reference.

The sensitivity of the sensors was studied by the method of calibration measurements in the concentration range 10^{-7} – 10^{-2} M. The slopes of the linear portions of the electrode functions were calculated for the concentration range 10^{-6} – 10^{-3} M.

The selectivity coefficients were determined by the methods of mixed solutions (MMS) and bi-ionic potentials (BIP).

The pH values of solutions were monitored using an ESL 43-07 standard pH-glass electrode preliminarily calibrated against standard buffer solutions. All measurements were made at room temperature.

The sensitivity of the sensors was studied using the calibration method with a set of standard solutions of various cations (Cu^{2+} , Zn^{2+} , Pb^{2+} , Co^{2+} , Cd^{2+} , Ni^{2+} , etc.) in the concentration range 10^{-7} – 10^{-2} M. The sensitivity was found as the slope of the linear portion of the electrode function $E = f(\log a)$, calculated by the least-squares method (the theoretical value under the normal conditions is 29.6 mV dec^{-1} for double-charge cations). The slopes were, as a rule, calculated in the concentration range 10^{-6} – 10^{-4} M, in which the activity coefficients are close

Table 3. Slopes of the electrode functions of the sensors (Average sensitivity determination error $\pm 2 \text{ mV}$)

Composition no.	Cation								
	Mg^{2+}	Ca^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ba^{2+}	Pb^{2+}
1	4	5	5	5	14	7	15	5	35
2	3	4	3	5	13	5	13	5	44
3	2	5	10	14	11	5	23	12	51
4	4	7	7	9	15	8	20	10	37
5	4	6	7	8	15	8	19	8	37
6	2	3	7	11	9	4	20	10	55

to unity, and, therefore, the ion concentrations were not recalculated to activities. The standard electrode potential was found by extrapolation of the linear portion of the calibration dependence to a value $\log a = 0$.

Figure 1 shows, for the example of sensors with composition 4, typical calibration dependences obtained; averaged data on the sensitivity of the materials under study are listed in Table 3.

As follows from these data, all the sensors under study exhibit high sensitivity to lead ions. Attention should be given to the fact that the slopes of the electrode functions of the sensors, measured without pH fixation, markedly exceed the theoretical value of 29.6 mV dec^{-1} and fall within the range $35\text{--}51 \text{ mV dec}^{-1}$. The super-Nernst values of the slopes of the electrode function can be explained in terms of the theory of the phase boundary potential. These slopes are probably observed because the activity of metal ions in the sensor membrane phase does not have a constant value, necessary for a Nernst response to be observed, and depends on the composition of a solution under study. In addition, such a result may be due to a mixed response of the sensors to M^{2+} and compounds of the MOH^+ type, which, as is known, can exist in solutions of transition metals. The slopes of the electrode functions of the sensors for other double-charged ions are substantially smaller than the theoretical values, which indicates that the membrane compositions are insensitive to these ions.

Because lead ions are hydrolyzed in aqueous solutions, which leads to a change in pH, various substances, 0.01M solution of potassium nitrate and nitric acid solutions with pH 2 and 3, were studied to reveal the effect of pH and fix the ionic strength. It can be seen from the data in Table 4 that determination of lead in strongly acidic solutions with pH 3 and lower is impossible because of the strong protonation of the ionophore.

The effect of the CCD cation-exchange additive on the sensor properties of the membranes is seen in the calibration curves measured in potassium nitrate. The CCD-containing composites 3 and 4 show a higher electrode sensitivity than composites 5 and 6, which contain no cation-exchange additive. Also noteworthy is the high selectivity of the sensors to lead in the presence of high concentrations of potassium ions. This single-charged cation has no effect on the determination of lead, and the calibration dependences of the sensors in a 0.01 M solution of potassium nitrate have the same outward appearance and detection limit as those in purely aqueous solutions of lead.

Table 4. Sensitivity of the sensors to Pb^{2+} in various media

Composition no.	0.01 M KNO_3	Without pH fixation	pH = 2	pH = 3
1	26 ± 3	34 ± 3	-1 ± 1	-1 ± 1
2	21 ± 3	44 ± 5	2 ± 1	2 ± 1
3	36 ± 2	51 ± 5	6 ± 1	11 ± 1
4	29 ± 3	37 ± 4	15 ± 1	1 ± 1
5	18 ± 5	41 ± 6	2 ± 1	0 ± 1
6	19 ± 5	31 ± 4	0 ± 1	39 ± 3

The selectivity of the membranes was studied by the method of bi-ionic potentials. The sensor potentials were measured in millimole solutions of metal salts; the data obtained were used to calculate by the known procedure the logarithms of the selectivity coefficients with respect to lead ions (Table 5).

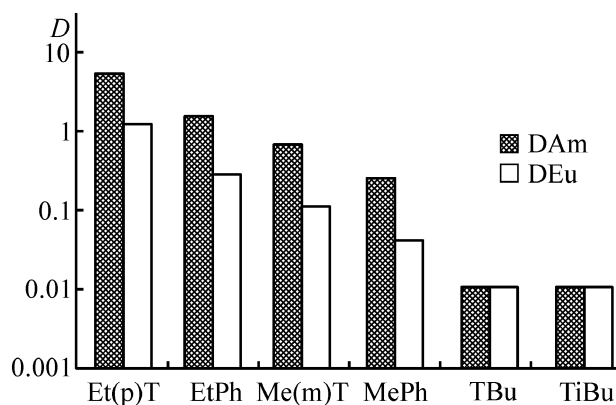


Fig. 2. Distribution coefficients D of metals in relation to the diamide structure in extraction from 3 M HNO_3 . Extractive agent: 0.1 M dipicolinediamide in *meta*-nitrobenzotrifluoride.

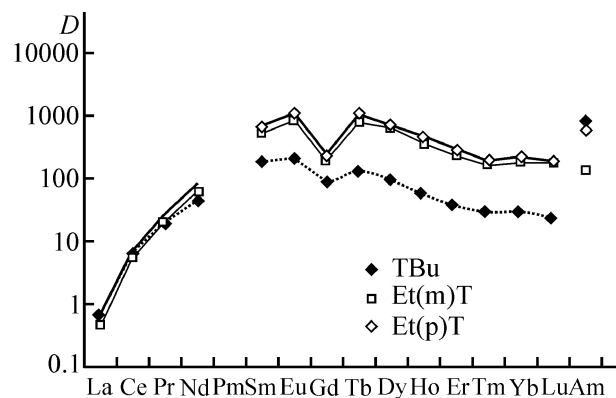


Fig. 3. Distribution coefficients of metals in relation to the diamide structure. Extractive agent: 0.02 M CCD + 0.01 M dipicolinediamide in phenyl trifluoromethyl sulfone.

Table 5. Logarithms of the selectivity coefficients of the sensors $\pm 0.2 \log K_{\text{Pb}^{2+}/\text{M}^{2+}}^{\text{sel}}$

Com- position no.	Cation					
	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ba^{2+}
1	-3.7	-3.9	-1.8	-3.2	-3.0	-2.6
2	-4.9	-5.1	-3.4	-4.8	-4.5	-3.8
3	-4.8	-4.7	-3.0	-4.2	-3.7	-2.8
4	-3.7	-3.8	-1.8	-3.2	-2.7	-3.3
5	-3.9	-3.8	-1.4	-3.2	-3.6	-2.0
6	-3.4	-3.4	-1.2	-2.8	-3.3	-2.3

Table 6. Lower detection limits of the sensors $\log c(\text{M}^{2+})$

Com- position no.	Cation		
	Cu^{2+}	Cd^{2+}	Pb^{2+}
1	-5.1 ± 0.1	-5.0 ± 0.1	-6.5 ± 0.1
2	-5.2 ± 0.1	-5.1 ± 0.1	-6.4 ± 0.1
3	-5.3 ± 0.1	-5.2 ± 0.1	-6.1 ± 0.1
4	-5.0 ± 0.1	-5.0 ± 0.2	-6.4 ± 0.1
5	-5.0 ± 0.1	-5.1 ± 0.1	-6.5 ± 0.1
6	-5.3 ± 0.2	-5.2 ± 0.2	-5.9 ± 0.1

It can be seen that the sensors developed are distinguished by high selectivity to lead ions in the presence of other double-charged ions. The most pronounced disturbing influence on the determination of lead is exerted by cobalt and nickel cations. Lead can be determined with a number of sensor composites in the presence of a more than 1000-fold excess of zinc. The selectivity to lead is also rather high in the presence of cadmium. The data obtained for the selectivity of the sensors open up wide prospects for practical application of the electrodes developed for solution of real analytical problems.

The lower detection limits of the sensors for various metals were found from the calibration dependences by the procedure recommended by IUPAC. Because the sensors developed show a noticeable sensitivity only to cations of lead, copper, and cadmium, the results obtained in determining the lower detection limit are given only for these ions (Table 6).

The lower detection limits of the sensors for double-charged metal cations were in the range $6.5\text{--}5.0 \text{ pM}^{2+}$. The lowest values were observed for lead ions with sensors of compositions 1 and 5.

It is of interest to compare the sensor characteristics obtained with extraction data for similar substances and

Table 7. Structural formulas of dipicolinediamides

Structural formula	Compound
	TB, TBu tetra-butyl-dipicolinediamide
	TIB, TBu tetra-butyl-dipicolinediamide
	Me(m)T <i>N,N'</i> -dimethyl- <i>N,N'</i> -dimetatolyl-dipicolinediamide
	DEDP, EtPh <i>N,N'</i> -diethyl- <i>N,N'</i> -diphenyl-dipicolinediamide
	MePh <i>N,N'</i> -dimethyl- <i>N,N'</i> -diphenyl-dipicolinediamide
	Et(p)T <i>N,N'</i> -diethyl- <i>N,N'</i> -di- <i>para</i> -tolyl-dipicolinediamide
	Et(m)T <i>N,N'</i> -diethyl- <i>N,N'</i> -di- <i>meta</i> -tolyl-dipicolinediamide

mixtures. The extractive properties of dipicolinediamides depend on the structure of a diamide. Previously, the extraction capacity of diamides with different substituents at the amide nitrogen atom have been studied (Table 7).

It can be seen in Fig. 2 that tetraalkyl-substituted dipicolinediamides almost do not extract europium and americium. At the same time, dipicolinediamides containing both alkyl and aryl substituents [Et(p)T, EtPh, Me(m)T, MePh] effectively extract americium and europium.

The distribution coefficients increase upon introduction of alkyl substituents into the phenyl ring, but they are

considerably larger for all dialkyldiaryl diamides than those for tetraalkyl substituents.

When diopicolinediamides are used in a mixture with CCD, a strong synergetic effect is observed. Figure 3 shows data on extraction of REE and americium with mixtures of CCD with tetrabutyl diamide and two dialkyldiaryldiamides of dipicolinic acid. Irrespective of their structure, all the diamides extract metals rather effectively; however, the extraction capacity of all the mixtures for light REE (La–Nd) is nearly the same and differences in this property are only observed for REE from Sm to Lu. However, for these metals, too, the difference is somewhat smaller than that in extraction with pure diamides. The frequently occurring dependence is observed in this case: a higher extraction capacity leads to a lower selectivity.

In the case of chemical sensors, the described extraction dependences are not observed in an explicit form. Sensors based on tetraalkyldipicolindiamide (TBU) show a higher sensitivity to lead cations than sensors based on a dialkylditolyl derivative (EtPh), and introduction of the CCD cation-exchange additive does not have such a pronounced effect on the response of the sensors as that in the case of extraction with a mixture of CCD and a diamide. However, as shown previously [22], high sensor sensitivities to metal cations in an acid medium can be obtained in determining various REE with EtPh-based sensors. Thus, despite the apparent usefulness of extraction data in development of new chemical sensors, the patterns observed in liquid extraction (distribution coefficients and their dependence on the position of a metal in the Periodic system) cannot be always directly extended to be used in development of sensor membranes with prescribed characteristics. Presumably, it is necessary, on passing from extractive systems to polymeric plasticized membranes, to take into account the effect of the difference in characteristics of solvents (diluent in extraction and solvents of plasticizers for sensor membranes) and the presence of PVC in the membrane.

CONCLUSIONS

(1) New polymeric electrochemical sensors were developed on the basis of *N,N'*-tetrabutyl-dipicolinediamide with a matrix of poly(vinyl chloride) plasticized with di(ethylhexyl) sebacate and *o*-nitrophenyl octyl ether, and chlorinated cobalt dicarbollide as ion-exchange

additive, for determining lead ions; the electrochemical characteristics of the sensors fabricated were studied.

(2) It was found that the new sensors have a high sensitivity to lead ions in a wide concentration range. The slope of the linear portion of the electrode function of the sensors in lead ion solutions is 30–55 mV dec⁻¹, depending on the membrane composition. The selectivity of the sensors to lead ions in the presence of Cu²⁺, Cd²⁺, and Zn²⁺ was studied. Logarithms of the selectivity coefficients fall within the range -2.2 ± 1 . In addition, it was found that the new sensors have a low detection limit (6.5–5.0 pM²⁺). The data obtained make it possible to recommend these polymeric ion-selective membrane electrodes for accomplishing various analytical tasks involving determination of lead.

(3) It was demonstrated that there are no direct quantitative correlations between the behavior of ligands in liquid extraction and in sensor membranes. However, data on the extractive behavior of various ionophores enable preliminary selection of promising membrane-active compounds for use in chemical sensors.

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