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Polarographic and Spectrophotometric Studies of the Spiro[indolin-pyridobenzopyrane] Complexes with the Heavy Metal Ions

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Abstract—By means of the cathode differential pulse polarography on a mercury drop electrode the reactions of Zn^{2+}, Cd^{2+}, and Pb^{2}+ ions with the spiro[pyridobenzopyranes] of the indoline series in DMSO were studied. Tetrabutylammonium perchlorate was used as the background electrolyte. It is found that well soluble heavy metal complexes of the spiro[indolin-pyridobenzopyranes] are formed in DMSO. The number of ligands, the step and the general stability constants of the obtained complex compounds are evaluated. The distribution curves of all the complexes under investigation are plotted. The spiropyrane complexes were also studied by means of the spectrophometric method. Good agreement of the results obtained by two different methods was established.

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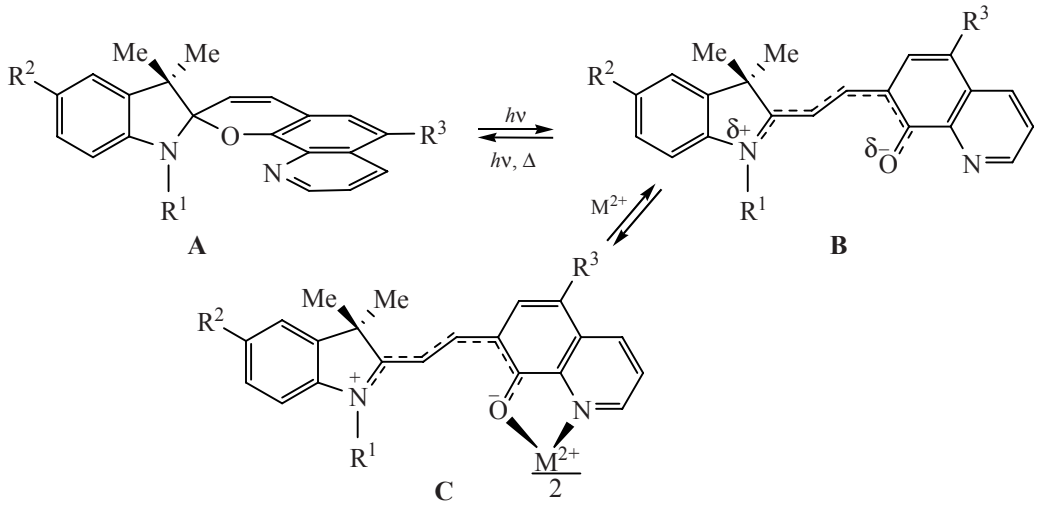
Development and synthesis of the polyfunctional molecular systems is the intensely unfolding direction acquiring great importance for the molecular electronics and sensorics [1, 2]. The bistable photochromic compounds such as spiropyranes, spirooxazines, chromenes containing the cation-recepting group are the typical examples of such molecules.

Photochromism of spiropyranes (Scheme 1) is connected with the thermally and photochemically reversible processes of heterolytic cleavage of the C_{spiro}–O bond and the subsequent *cis-trans* isomerization to the metastable merocyanine form **B** [3].

Great interest is attracted recently to the investigation of the spiropyrane isomerization caused by the definite chemical particles (specific substrates), in detail by metal cations [4]. Presence of partial negative charge on the oxygen atom of the merocyanine isomer **B** makes it a potential ligand in the reactions of complex formation with metal ions [5]. Bonding of the metal ion causes stabilization of one of the isomeric forms as well as alteration in its absorption and fluorescence properties as compared to the noncoordinated molecule.

Spiropyranes containing the corresponding functional analytical groups may be used as the fluorescent chemosensors (including the photodynamic ones when complex formation can be regulated by the transfer of molecule to the coordinationally active state or vice versa) for the qualitative and quantitative evaluation of metal ions having great importance for clinical practice, medicine, biology, and monitoring of the environment [6]. In this case the spiropyrane molecule as a rule contains the ionophoric fragment in *o*-position to the pyrane oxygen atom. The phenolate oxygen atom of the colored isomer takes part in the additional coordination of the metal cation. It was shown recently [7] that quinolinospiropyranes are the effective photodynamic fluorescent chemosensors for the series of metal cations. In the work presented the complex formation of spiro[indolin-pyridobenzopyranes] with Zn^{2+}, Cd^{2+}, and Pb^{2+} is studied by means of the differential impulse polarography.

Scheme 1.



[**I**]: $R^1 = CH_3$, $R^2 = H$, $R^3 = Cl$; [**II**]: $R^1 = CH_3$, $R^2 = H$, $R^3 = Br$; [**III**]: $R^1 = CH_2Ph$, $R^2 = H$, $R^3 = Br$; (**IV**): $R^1 = H_2CH_2COOH$; $R^2 = H$, $R^3 = Cl$; (**V**): CH_3, $R^2 = Cl$, $R^3 = Br$.

Main physicochemical characteristics of complex formation such as the number of ligands in complexes, the step and general stability constants are evaluated and on this basis the distribution curves of complexes under investigation are plotted. Results of the polarographic investigation of complex formation of the spiro[indolin-pyridobenzopyranes] were compared with the results obtained by means of the spectrophotometric analysis and by the methods of equilibrium shift and the crossing of curves. Both methods were used for investigation of the composition and stability of the mononuclear complex compounds.

Spiropyranes of the indoline series **I**–**V** exist in DMSO and another polar solvents as an equilibral mixture of the spirocyclic **A** and the merocyanine **B** forms (Scheme 1) that causes the existence of two signals on the polarogram with the peak potentials (E_p, V) in the range from –1.64 to –1.82 for the merocyanine form **B** and from –1.91 to –2.35 for the spirocyclic form **A**.

Table 1. Polarographic characteristics and the De Ford and Jume functions for the spiropyrane **IV** complex with zinc ions ($C^{2+}_{Zn} = 5\times10^{-4}$ M)

C_{IV}, M	E_p, V	ΔE_p, V	$F_0(x)$	$F_1(x)$	$F_2(x)$
0	–0.680	–	1	–	–
1×10^{-3}	–0.704	–0.024	6.49	5.49×10^3	4.63×10^6
2×10^{-3}	–0.716	–0.036	16.53	7.77×10^3	3.45×10^6
3×10^{-3}	–0.728	–0.048	42.10	1.37×10^4	4.28×10^6
4×10^{-3}	–0.734	–0.054	67.21	1.66×10^4	3.92×10^6
5×10^{-3}	–0.740	–0.060	107.26	2.13×10^4	4.08×10^6
Stability constants			K_0 1	K_1 858.00	K_2 4.00×10^6

For evaluation of the composition and the stability constants the De Ford and Jume method [8] was used. It is based on the Eq. (1) and is regarded as the modified Leden potentiometric method adapted for polarigraphy. Within the frames of this method the dependence $F_n(x)$ on the ligand concentration (C_L) was studied. In this case the solution must contain the excess of the complex-forming reagent because its concentration near the electrode surface must be equal to its concentration in solution $[x]_0 = [x]$. For evaluation of the step constants the series of The $F(x)$ functions was introduced.

$$F_0(x) = \exp\left(-\frac{nF}{RT}\,\Delta E_p\right). \qquad (1)$$

Here $\Delta E_p = (E_p)_{compl} - (E_p)_{free}$ is the difference in the potentials of peaks related to the complex and the free metal. Extrapolation of the graphical dependence $F_0(x)$ from $[x]$ to $[x] = 0$ gives the value $K_0 = 1$ which corresponds to the ordinate when $[x] = 0$. Extrapolation of the function $F_1(x) = [F_1(x) - 1]/C_L$ to $x = 0$ gives K_1 value. The function $F_2(x)$ for the evaluation of K_2 was introduced analogously. The polarographic characteristics, the calculated De Ford and Jume functions and the step stability constants of the spiropyrane **IV** complex with zinc cations are presented in the Table 1.

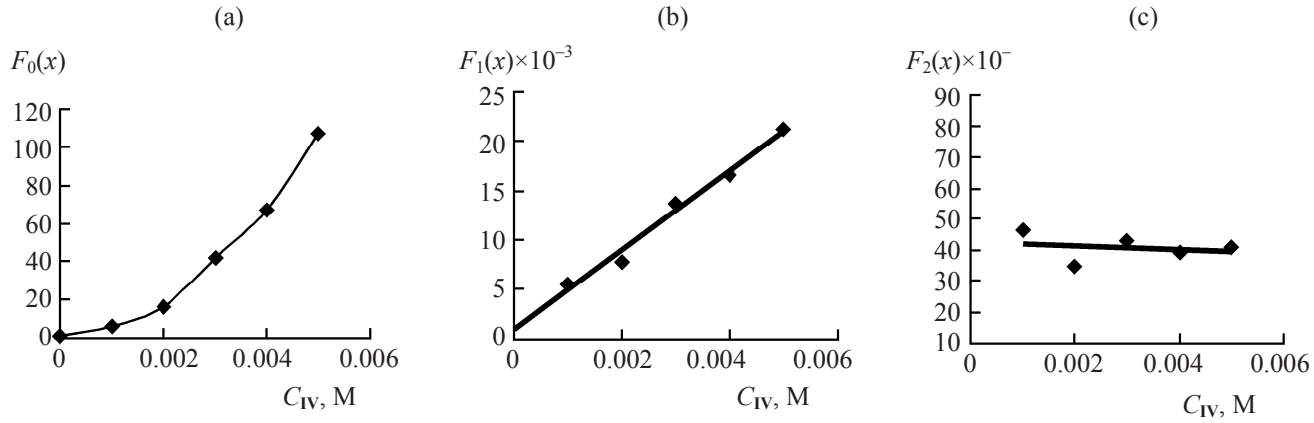


Fig. 1. Dependence of (a) $F_0(x)$, (b) $F_1(x)$, and (c) $F_2(x)$ on the concentration of ligand for the Zn^{2+}–spiropyrane **IV** system.

On the basis of these data for spiropyrane **IV** the $F_n(x)$ functions on the ligand concentration (C_L) were plotted (Fig. 1) and the distribution of Zn complexes depending on the concentration of spiropyrane **IV** in solution was shown (Fig. 2). Analogous results were obtained for all the spiropyrane complexes with Zn^{2+}, Cd^{2+}, and Pb^{2+}. The $F_1(x)$ function is linear in all the cases, and $F_2(x)$ is the straight line parallel to the abscissa axis that tells about the formation of complex of the 1:2 composition.

Values of the De Ford and Jume functions $F_n(x)$ (n = 0, 1, 2) at the zero concentration of ligand corresponds to the step stability constant of the corresponding complex (Table 2). The merocyanine form of spiropyridobenzopyranes under study forms intensively colored complexes with Zn^{2}+, Cd^{2+}, and Pb^{2+} containing two ligand molecules. The data obtained show that spiropyranes under investigation form stable complexes with the stability constant values characteristic of the chelate compounds. The second stability constants of complexes have large values while the first ones are so small that in some cases they can hardly be evaluated by means of the polarographic method. It permits to propose that the solution contains mainly the complex of the 1:2 composition. Its stability is caused by the chelating effect giving rise to two five-member rings.

From the distribution curves for each complex the concentration ranges containing mainly the complexes either of the 1:1, or of the 1:2 composition, or the free metal ion are selected (Table 3).

As is shown, the first stability constants of the cadmium-containing spiropyrane complexes under investigation are larger than that of the Zn^{2+} and Pb^{2+} ones. It may be proposed that stability of such complex is connected with more favorable steric conditions resulting from the increase in size of cadmium ion as compared to that of zinc one. The second stability constants of cadmium complexes are lower than the corresponding zinc ones that may be also explained by the stability of the 1:1 complexes making the transfer of monoligand complexes to the two-ligand ones less favorable.

For the comparison of the results obtained by means of the differential pulse polarography the Zn^{2+} and Pb^{2+} complexes of 3,3-dimethyl-1-(2-carboxyethyl)-6'-chlorospiro{indolin-2,2'-[3,2-*h*]pyrido[2*H*-1]benzo-pyrane} **IV** and Cd^{2+} complex of 6'-bromo-1,3,3-tri-methylspiro{indolin-2,2'-[3,2-*h*]pyrido-[2*H*-1]benzopy-rane} **II** were studied by the independent methods of the equilibrium shift and crossing

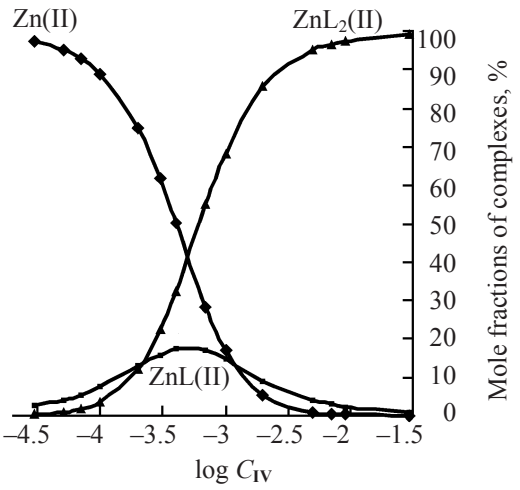


Fig. 2. Dependence of the distribution of zinc complexes on the logarithm of the spiropyrane **IV** concentration.

Table 2. Values of the step and general stability constants of complexes of the heavy metal ions with spiropyranes obtained by means of the differential pulse polarography

Metal ion	Spiropyrane	K_1	K_2	β_2
Zn^{2+}	**I**	10	1.23×10^{9}	1.23×10^{10}
	II	10	4.71×10^{5}	4.71×10^{6}
	III	8.25×10^{3}	5.00×10^{6}	4.12×10^{10}
	IV	8.58×10^{2}	4.00×10^{6}	3.43×10^{9}
	V	2.92×10^{3}	7.00×10^{6}	2.04×10^{10}
Cd^{2+}	**I**	8.59×10^{3}	4.00×10^{7}	3.44×10^{11}
	IV	3.07×10^{5}	9.68×10^{8}	2.98×10^{14}
	V	4.00×10^{6}	1.44×10^{8}	5.76×10^{14}
Pb^{2+}	**IV**	1.67×10^{3}	6.32×10^{6}	1.05×10^{10}

Table 3. The composition of spiropyrane complexes with Cd^{2+}, Zn^{2+}, and Pb^{2+} ions depending on the concentration of ligands

Spiropyrane	The spiropyrane concentration rangecontaining mainly		
	Cd^{2+}	complex of the 1:1 composition	complex of the 1:2 composition
I	$<1\times10^{-4}$ M	1×10^{-4}–2×10^{-4} M	$>2\times10^{-4}$ M
IV	$<3.2\times10^{-6}$ M	3.2×10^{-6}–3.2×10^{-4} M	$>3.2\times10^{-4}$ M
V	$<1.6\times10^{-7}$ M	1.6×10^{-7}–1.6×10^{-2} M	$>1.6\times10^{-2}$ M
	Zn^{2+}	complex of the 1:1 composition	complex of the 1:2 composition
I	$<3.2\times10^{-5}$ M	–	$>3.2\times10^{-5}$ M
II	$<1.6\times10^{-3}$ M	–	$>1.6\times10^{-3}$ M
III	$<1\times10^{-4}$ M	1×10^{-4}–2×10^{-3} M	$>2\times10^{-3}$ M
IV	$<5\times10^{-4}$ M	–	$>5\times10^{-4}$ M
V	$<2.5\times10^{-4}$ M	2.5×10^{-4}–5×10^{-4} M	$>5\times10^{-4}$ M
	Pb^{2+}	complex of the 1:1 composition	complex of the 1:2 composition
IV	$<4.6\times10^{-4}$ M	–	$>4.6\times10^{-4}$ M

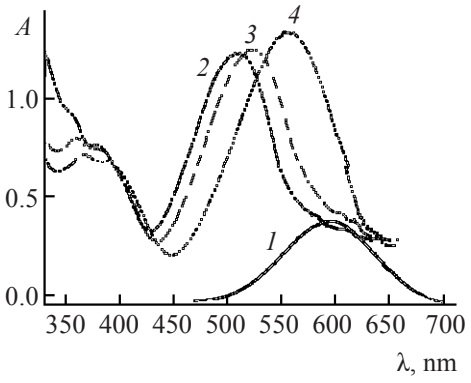


Fig. 3. The absorption spectra of spiropyrane **IV** solution in (*1*) DMSO and in the presence of (*2*) Zn^{2+}, (*3*) Cd^{2+}, and (*4*) Pb^{2+} ions. Concentration of the zinc, cadmium and lead salts 1×10^{-4} M.

of the spectrophotometric curves [9]. It occured that complex formation of the merocyanine form of spiropyranes with different metal ions is accompanied by change in coloration and hence by appearance of the charge transfer bands characteristic of complexes [10]. The λ_{max}, nm values of the open form of spiropyrane differ from that of its complexes with the heavy metal ions by 90–140 nm that permits to carry out the spectrophotometric studies of complex formation. In the Fig. 3 the electron absorption spectrum of the merocyanine form **IV** in DMSO is presented. The absorption band with λ_{max} 600 nm is connected with the formation of the open form **B** from the starting colorless spiro form **A**. Addition of Zn^{2+}, Cd^{2+}, and Pb^{2+} ions in the concentration 1×10^{-4} M to the solution of compound **IV** causes the immediate

alteration in the initial coloration followed by its increase in the course of 4–7 min. The open form takes part in the complex formation with metal ions that is accompanied by the characteristic spectral alterations. In the Fig. 3 the absorption spectra of complexes measured 7 min after the addition of Zn^{2+}, Cd^{2+}, and Pb^{2+} ions are presented.

Calculations of the stability constants for the systems Cd^{2+}–spiropyrane **II**, Zn^{2+}–spiropyrane **IV**, and Pb^{2+}– spiropyrane **IV** are presented in the Table 4. Stability of Cd^{2+}, Zn^{2+}, and Pb^{2+} complexes and the number of ligands in them were also evaluated by means of crossing of the spectral curves method. Results of this investigation carried out by three independent methods are presented in the Table 5. The results obtained by three independent methods are in good agreement with one another. The spiropyrane complexes are stable in time. They are characterized by the expressed absorption bands in the range 500–610 nm. It permits to use spiropyranes as the chelating agents, regarded as sensors for evaluation of the heavy metals. Noticeable selectivity of spiropyranes **I**, **IV** in relation to Cd^{2+}, Zn^{2+}, or Pb^{2+} ions was absent. The difference in λ_{max} of various complexes is about 15–30 nm. The cadmium and zinc complexes have approximately equal stability that tells about low selectivity of their coevaluation by means of the differential pulse polarography. Due to that new methods of their separation including the preliminary extraction or chromatography combined with the polarographic analysis must be probably developed.

Separate spectrophotometric methods can be also used. On the whole increase in the general stability constants β_2 of cadmium complexes as compared to zinc ones is observed. It shows that cadmiun ions are more subjected to complex formation. Hence, increase in sensitivity and selectivity of cadmium evaluation takes place.

EXPERIMENTAL

The measurements were carried out on a PA-2 polarograph in the differential impulse regime. The polarizational curves were registered on aXY Recorder-4103 self-recorder. The three-electrode thermostated cell containing working dropping mercury electrode, saturated calomel reference electrode with the potential +0.247 V, and an auxiliary platinum electrode was used.

Table 4. Spectrophotometric characteristics of complexes for the calculations of the stability constants and the number of ligands by means of the equilibrium shift method

Complex	$C_{sp}\times10^{-5}$, M	–log [L]	A	log $A/(A_{pr}-A)$
Cd^{2+} (2×10^{-5}, M)–spiropyrane **II**	1.0	5.000	0.095	–0.87
	2.0	4.699	0.350	–0.15
	3.0	4.523	0.540	0.32
	4.0	4.398	0.670	0.71
	5.0	4.301	0.800	–
	6.0	4.222	0.800	–
Zn^{2+} (2×10^{-5}, M)–spiropyrane **IV**	1.0	5.000	0.08	–0.54
	2.0	4.699	0.20	0.10
	3.0	4.523	0.22	0.39
	4.0	4.398	0.29	0.62
	5.0	4.301	0.36	–
	6.0	4.222	0.36	–
Pb^{2+} (4×10^{-5}, M)–spiropyrane **IV**	2.0	4.699	0.39	–0.16
	4.0	4.398	0.61	0.24
	6.0	4.222	0.76	0.57
	8.0	4.097	0.90	1.16
	1.0	4.000	1.05	–
	1.2	3.921	0.95	–
	1.4	3.854	0.95	–

Table 5. Comparison of general stability constants (β) and the calculated number of ligands (n) obtained by means of the differential impulse polarography and spectrophotometric methods

Method	General stability constant (β) and the number of ligands (n)		
	spiropyrane **IV**		spiropyrane **IV**
	Zn^{2+}	Pb^{2+}	Cd^{2+}
De Ford and Jume method (differential impulse polarogrophy)	3.43×10^{9} $n = 2.00$	1.05×10^{10} $n = 2.00$	3.51×10^{10} $n = 2.00$
The equilibrium shift method (spectrophotometric)	1.27×10^{9} $n = 1.95$	2.52×10^{9} $n = 2.05$	1.05×10^{12} $n = 2.58$
Crossing of the spectral curves method (spectrophotometric)	1.26×10^{10} $n = 2.00$	1.78×10^{10} $n = 2.20$	1.38×10^{11} $n = 2.12$

Spiropyranes of the indoline series **I–V** were investigated (Scheme 1). They were obtained according to the procedure [11]. Investigations were carried out using DMSO of the "chemically pure" grade purified ac-cording to the standard procedure.

Tetrabutylammonium perchlorate with the constant concentration 0.01 M was used as the background electrolyte. It was several times crystallized before use. Good reproducibility of the polarographic peaks was established at this smallest necessary background concentration. The crystallized cadmium perchlorate of the "chemically pure" grade, zinc nitrate hexahydrate of the "pure for analysis" grade, and lead nitrate of the "chemically pure" grade were used. The working solutions of compounds under investigation were prepared by dissolution of the weighted samples in DMSO. Under these conditions the ionic strength was constant.

Electrochemical cell was thermostated at 20°C. Before each polarographic evaluation the oxygen dissolved was removed from electrolyte by bubbling pure argon for 10 min. After that the peak potential was fixed.

In the course of spectrophotometric studies the optic density of solutions was measured on a Specord UV-VIS spectrophotometer in the 1 cm cuvettes. Measurements were carried out at 20°C in DMSO.

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