Complex formation of molybdenum (V) with 1-phenyl-2,3-dimethylpyrazoline-5-thion in 4 mol/L HCl medium at 273-338 K

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Abstract. The process of complexation of molybdenum (V) with 1-phenyl-2,3-dimethylpyrazolin-5-thione in a 4 mol/l HCl medium in the temperature range 273-338 K was studied by the potentiometric method. It has been shown that the reduced form of the 1-phenyl-2,3-dimethylpyrazolin-5-thione molecule is involved in the complex formation reaction. Using the data of potentiometric studies, the change in the energy value (ΔE) of the $(NH_4)_2[MoOCl_5]^{2-}$-1-phenyl-2,3-dimethylpyrazolin-5-thione-4 mol/l HCl system, the equilibrium concentrations of 1-phenyl-2,3-dimethylpyrazolin-5-thione, formation function values, step and general stability constants of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V) formed in HCl solutions in the temperature range 273-338 K. The stability constants of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V) were refined using the Bjerrum graphical method. The temperature coefficient method was used to estimate the thermodynamic functions of complex formation processes in the $(NH4)2[MoOCl5]$-1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/L HCl system. The domains of dominance and the maximum yield of each complex form are found. It has been established that in the studied system $(NH_4)_2[MoOCl_5]$-1-phenyl-2,3-dimethyl-pyrazolin-5-thione - 4 mol/l HCl during the interaction of the MoO^{3+} ion with 1-phenyl-2,3-dimethylpyrazolin- 5-thione in the entire temperature range of the experiment forms 5 mononuclear coordination compounds containing from one to five coordinated molecules of the organic ligand. It was found that with increasing temperature, the values of the general stability constants of coordination compounds decrease, which confirms the exothermicity of the reaction of formation of oxochloro-1-phenyl-2,3-dimethylpyrazoline-5-thione compounds of molybdenum (V). The experimentally found values of enthalpy made it possible to assume that the reaction of complex formation between the MoO^{3+} ion and the molecules of nitrogen- and sulfur-containing heterocyclic 1-phenyl-2,3-dimethylpyrazolin-5-thione proceeded exothermically spontaneously. Based on the above equations, all calculations were carried out using a computer in the Excel programming language, Borland Delphi, Windows 7 operating system.

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1 Introduction

Molybdenum is a rare polyvalent bioactive metal of group VI of the periodic system.+4, and +6 are the most typical and stable oxidation states.

In nature, it is in these oxidation states that its various ore minerals are distributed, formed in the hydrothermal (molybdenite) and oxidized (powellite, molybdite, wulfenite, etc.) zones. In addition to the main minerals, molybdenum is included in various polymetallic sulfide ores and minerals as an isomorphic impurity [1, 2]. Some natural compounds of molybdenum (V) containing vital trace elements such as nitrogen, sulfur, phosphorus, etc., are parts of vitamins and hormones, participate in catalytic, redox reactions of biochemical processes, in maintaining the activity of xanthine oxidase, dehydrogenase, and sulfide oxidase enzymes. These enzymes are directly involved in the catabolism of purines and sulfur-containing amino acids. Molybdenum is an indispensable metal component for many enzymes and is involved in carbon, nitrogen, and phosphorus metabolism, in the synthesis of chlorophyll, and increases the intensity of the photosynthesis process. The enzyme nitrate reductase also contains molybdenum, with the participation of which nitrates are reduced to ammonia in plants. Molybdenum plays an important role in the processes of nitrogen fixation from the atmosphere by nodule and free-living bacteria. Although the need for plants in molybdenum is much less than in boron, zinc, copper, and manganese, legumes, cauliflower and white cabbage, lettuce, spinach, radishes, mustard, citrus fruits, and beets most of all feel the lack of this trace element. The presence of molybdenum in the soil positively affects the growth and yield of wheat, oats, flax, corn, tomatoes, potatoes, and buckwheat. Under its influence, the quality of products is significantly improving, and the protein content in grain and hay of legumes, vitamins, and sugars in vegetables increases. At the same time, an excess of molybdenum (more than 1 mg/kg of plant dry matter) does not reduce plant productivity but accumulates in various products, which leads to endemic gout in humans and toxicosis in animals. The best accumulators of molybdenum are legumes. If the molybdenum content in the soil is too high, the plants grow slowly, and the leaves become red-yellow, covered with spots with a brown tint. Signs of a moderate lack of molybdenum in plants are outwardly similar to signs of nitrogen starvation. With a significant deficiency of molybdenum, bright yellow-green or pale orange spots appear between the veins of old leaves, mainly on the upper side. At the same time, young leaves curl inward in the form of spoons; growth points die off, leaf veins remain light green, plant growth is weakened, flowering is delayed, etc. [3,4].

Being a polyvalent d-transition metal in various oxidation states, molybdenum can form binary and coordination compounds. It forms stable compounds in the highest oxidation state (VI) since low oxidation states are unstable and disproportionate even under normal conditions. [1,4]. In this regard, the synthesis and study of the properties of coordination compounds of molybdenum in the lowest oxidation state is an important task since, in the process of complexation, often low oxidation states of polyvalent metals are stabilized, which makes it possible to obtain new previously unknown coordination compounds [5,6].

The literature provides much information on the synthesis and study of cluster and coordination compounds of molybdenum in the + 6 oxidation state with complex biologically active organic ligands. And in [7], mononuclear and binuclear coordination compounds of molybdenum in the +5 oxidation state with such bioactive organic ligands as thiosemicarbazide and imidazole derivatives were synthesized and studied. The composition and properties of the obtained compounds are identified and confirmed by elemental and X-ray phase analysis and methods. IR spectroscopy [8], potentiometry, conductometry, and thermogravimetry [9].

Among organic ligands, such heterocyclic compounds as pyrazolone derivatives containing donor atoms of nitrogen, sulfur, phosphorus, etc., deserve special attention. They

exhibit high biological and catalytic properties. For example, pyrazolone derivatives such as analgin, antipyrine, 1-phenyl-2,3-dimethylpyrazolin-5-thione, orysol, dithiopyrilmethane, etc. exhibit antipyretic, bactericidal, antitumor, antiallergic, catalytic properties and are widely used in the pharmaceutical and medical industries for manufacturing of various drugs [10,11]. Among the pyrazolone derivatives, some compounds exhibit luminescent, growth-regulating, and herbicidal properties and are used in the national economy [7,12].

It is known that most of the pyrazolone derivatives are more or less toxic substances. However, the coordination of these ligands to metal ions can significantly affect both their biological and catalytic activity and the properties of complexing metal ions.

The literature contains data on coordination compounds of ions of some d-transition metals with various pyrazolone derivatives. In papers published between 1974 and 1996. data are given on the synthesis and study of the composition and properties of coordination compounds of bismuth (III), iron (III), copper (II), mercury (II), osmium (IV), and other metals with 1-phenyl-2,3-dimethylpyrazoline-5-thione, dithiopyrilmethane and some other pyrazolone derivatives. It is reported that the composition and structure of the obtained coordination compounds were established by elemental analysis, IR, and UV spectroscopy. It has been shown that 1-phenyl-2,3-dimethylpyrazolin-5-thione is monodentate coordinated with the studied metal ions through the sulfur atom of the thione group. The authors of [13-15] studied the processes of complexation of rhenium (V), iron (III), and copper (II) with 1-phenyl-2,3-dimethylpyrazolin-5-thione in HCI solutions by potentiometric titration. And HBr of various concentrations at temperatures of 273-338 K. It has been shown that 1-phenyl-2,3-dimethylpyrazolin-5-thione forms five complex forms with rhenium (V) ions, and with iron (III) and copper (II) ions in solutions of hydrohalic acids, four complex particles are formed. Based on the studies carried out by these authors, the equilibrium concentrations of the studied ligand, the formation functions, and the stepwise and general stability constants of the complexes were found, and the thermodynamic functions of the complex formation processes were calculated.

By the beginning of our research, there was practically no information in the scientific literature on the study of the processes of complex formation of molybdenum (V) with 1-phenyl-2,3-dimethylpyrazolin-5-thione in solutions of hydrohalic acids. In [16,17], we were the first to study the processes of complex formation of molybdenum (V) with 1-phenyl-2,3-dimethylpyrazolin-5-thione in solutions of 6 mol/l HCI at 273, 288, 298, and 338 K.

The purpose of this work was a systematic study of the process of complex formation of molybdenum (V) with 1-phenyl-2,3-dimethylpyrazolin-5-thione in a medium of 4 mol/l HCI at 273-338 K, determination of the formation function, stepwise and general stability constants, the region dominance, yield maxima and determining the effect of temperature on a given process and the stability of the complexes formed, the calculation of the values of the thermodynamic functions of the complex formation reaction.

2 Experimental part

The starting compounds were: $(NH_4)_2[MoOCl_5]$ grade "pure" synthesized and purified by us according to the procedure described in [5], 1-phenyl-2,3-dimethylpyrazolin-5-thione and HCI were qualified as "pure grade". The content of molybdenum in the composition $(NH_4)_2[MoOCl_5]$ was determined by the gravimetric method, and chloride ions by the Mohr method in the form of hardly soluble AgCI [17,18]. The initial concentrations of molybdenum (V) and 1-phenyl-2,3-dimethylpyrazolin-5-thione were equal, respectively: $C_{mo}=1.10^{-2}$, $C_L= 1.10^{-3}$ mol/l.

The study of the complexation process was carried out by potentiometric titration using a voltage comparator P-3003M1, in the temperature range of 273-338 K, using a redox

ligand electrode based on 1-phenyl-2,3-dimethylpyrazolin-5-thione and its oxidized form. The required concentration of the oxidized and reduced form (Ox/Red) of 1-phenyl-2,3-dimethylpyrazolin-5-thione was created by oxidation of its part in a medium of 4 mol/l HCl 0.1 with a normal solution of iodine in ethanol. A platinum plate served as the indicator electrode, and a silver chloride electrode was used as the reference electrode. Buffer solutions with known pH values were used to calibrate the potentiometric setup [19,20].

The potential of the system $[MoOCl_5]^{2-}$ - 1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCl was established within 10-15 min at 273-338 K. The temperature in the potentiometric cell was maintained using a water thermostat; the accuracy of maintaining the temperature was ± 0.1 0C. At each temperature, potentiometric titration was carried out 4-5 times. Statistical processing of the obtained results was carried out according to the procedures [21] and Dörfel's [20]. At each titration point, the equilibrium concentration of 1-phenyl-2,3-dimethylpyrazolin-5-thione and the formation function (ñ) were determined using equations 1 and 2:

$$lg[L] = \frac{E_{init.} - E_i}{1.983 \cdot 10^{-4} \cdot T} + lgC_L^{\ init} + \frac{1}{2}lg\frac{V_{init.}}{V_{tot.}}$$

$$\overline{n} = \frac{C - [L]}{MoO^{3+}} \qquad (2)$$

where: $E_{init.}$ is the initial equilibrium potential of the system in the absence of molybdenum (V); E_i is the equilibrium potential of the system at a given titration point; C_L is initial analytical concentration of 1-phenyl-2,3-dimethylpyrazolin-5-thione; T is the temperature of the experiment; V_{out}/V_{total} are the ratio of the initial volume of the system to the total.

All calculations on potentiometric determination, the equilibrium concentration of 1-phenyl-2,3-dimethylpyrazolin-5-thione, formation functions, evaluation of step and general stability constants and their refinement, the maximum yield of mole fractions of complex particles formed in solution 4 mol/l HCl, ΔH, ΔS and ΔG values were performed using a computer in the Excel programming language, Borland Delphi, Windows 7 operating system, based on the above equations, with values of ñ equal to 0.5; 1.5; 2.5; 3.5; 4.5 [22].

3 Results and discussion

As noted, by the method of potentiometric titration, we studied the process of complexation of molybdenum (V) with 1-phenyl-2,3-dimethylpyrazolin-5-thione in a 4 mol/l HCl medium in the temperature range of 273–338 K; therefore, the formation of the protonated form of this organic ligand in an acidic medium was to be expected. It is known that many nitrogen- and sulfur-containing organic compounds, including heterocyclic pyrazoline and its derivatives, as well as aromatic amines, exhibit weak basic properties [11]. In this regard, apparently, their basic properties prevent the process of protonation, as a result of which their solvated molecules can be formed in an acidic medium. Therefore, considering the data of [10-14], it can be stated that the complexation reaction most likely involves not protonated molecules of 1-phenyl-2,3-dimethylpyrazolin-5-thione but its neutral solvated form. The study of the composition of the resulting complex compounds suggests that in the $[MoOCl_5]^{2-}$ - 1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCl system, the complexing agent is the molybdenyl ion MoO^{3+} contained in the composition of the initial $(NH_4)_2[MoOCl_5]$ rather than the molybdenum (V) ion.

The conducted potentiometric studies have shown that when titrating a solution of $(NH_4)_2[MoOCl_5]$ with 1-phenyl-2,3-dimethylpyrazolin-5-thione dissolved in 4 mol/l HCl,

the potential (E) of the system under study: $[MoOCI_5]^{2-}$ - 1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCI at all intervals of the studied temperatures (273-338K) decreases. A decrease in the value of the system's potential can be stated in favor of the formation of new oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione coordination compounds of molybdenum (V).

Table 1 shows the experimental data obtained during the potentiometric titration of the system: $[MoOCI_5]^{2-}$-1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCl at 318 K, which we used to determine the function formation of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione coordination compounds of molybdenum (V), by the graphic method of Bjerrum [23].

Table 1. Values of equilibrium concentrations of molybdenum (V) ions, 1-phenyl-2,3-dimethylpyrazolin-5-thione, and functions of formation (ñ) of complexes at 318 K: $C_{Mo(V)}^{ref}$=0.060 mol/l, C_L=0.035 mol/l until the ligand is oxidized with iodine solution

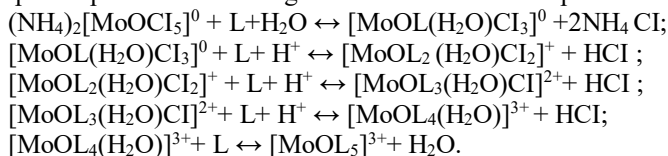| №	ΔE, mV	C_L=0.035	$C_{Mo(v)}$=0.060	Lg[L]	ñ
		mol/l			
1	2	3	4	5	6
1	25.0	0.040	0.007	2.13	4.80
2	26.0	0.039	0.007	2.15	4.49
3	27.0	0.038	0.008	2.17	4.22
4	28.0	0.038	0.008	2.18	3.98
5	29.0	0.037	0.008	2.20	3.77
6	30.0	0.037	0.009	2.22	3.58
7	31.0	0.036	0.009	2.24	3.41
8	32.0	0.036	0.009	2.26	3.26
9	34.0	0.035	0.010	2.30	2.99
10	36.0	0.034	0.011	2.34	2.77
11	37.0	0.033	0.011	2.36	2.56
12	38.0	0.032	0.012	2.38	2.39
13	39.0	0.031	0.012	2.40	2.24
14	41.0	0.031	0.012	2.44	2.19
15	43.0	0.030	0.013	2.47	2.01
16	45.0	0.029	0.014	2.51	1.86
17	47.0	0.028	0.014	2.55	1.73
18	49.0	0.027	0.015	2.59	1.62
19	50.0	0.026	0.016	2.61	1.52
20	52.0	0.025	0.016	2.66	1.40
21	53.0	0.024	0.017	2.68	1.30
22	54.0	0.023	0.018	2.71	1.17
23	55.0	0.022	0.018	2.73	1.07
24	56.0	0.020	0.019	2.76	0.98
25	57.0	0.020	0.020	2.79	0.90
26	59.0	0.019	0.020	2.83	0.84
27	60.0	0.018	0.021	2.86	0.79
28	61.0	0.017	0.021	2.88	0.74
29	62.0	0.016	0.022	2.90	0.70
30	63.0	0.016	0.022	2.93	0.65
31	64.0	0.015	0.023	2.96	0.59
32	65.0	0.014	0.023	2.99	0.55
33	66.0	0.013	0.024	3.02	0.51
34	68.0	0.013	0.024	3.06	0.48
35	69.0	0.012	0.025	3.09	0.45

Using the experimental data, curves were plotted for the formation function (ñ) of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V) on the inverse logarithm of the equilibrium concentration of the ligand (-lg[L]) in a medium of 4 mol/l HCl in the range of 273-338 K (Fig. 1).
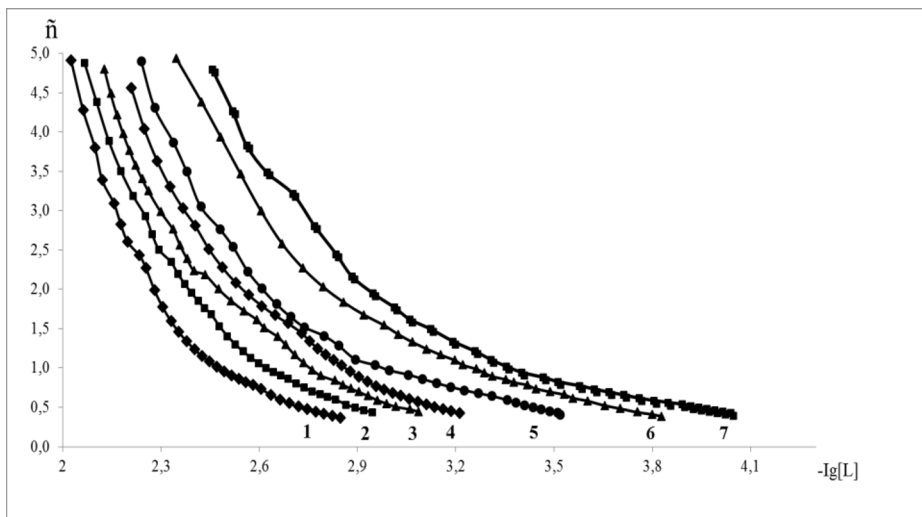
Fig. 1. Curves of formation of 1-phenyl-2,3dimethylpyrazolin-5-thione complexes of molybdenum (V) in medium of 4 mol/l HCl at 273-338 K.

Fig. 1 shows that the dependence of ñ on -lg[L] for all formed complexes in the range of 273-338 K is non-linear [24]. There are five sections on the complex formation curves that correspond to certain ranges of equilibrium concentrations of 1-phenyl-2,3-dimethylpyrazolin-5-thione, indicating that in the process of interaction of the molybdian-ion (MoO^{3+}), which is present in the solutions of the initial $(NH_4)_2[MoOCl_5]$, with 1-phenyl-2,3-dimethylpyrazolin-5-thione, in a medium of 4 mol/l HCl, stepwise complexation occurs.

Using the Bjerrum method, based on data on the dependence of ñ on -lg[L], the number of complex particles formed in a solution of 4 mol/l HCl was found. It was found that when an excess of a solution of 1-phenyl-2,3-dimethylpyrazolin-5-thione is added to the system under study, the slope of the dependence curves ñ on -lg[L] at temperatures of 273, 288, 298, 308, 318, and 338, respectively, is: 0.049, 0.051, 0.053, 0.055, 0.057 and 0.059 V/mol^{-1}, which corresponds to the sequential addition of five solvated molecules of 1-phenyl-2,3-dimethylpyrazolin-5-thione to the MoO_3^+ ion (curves 1,2,3,4,5). Based on the potentiometric titration data obtained in the system $[MoOCl_5]^{2-}$ - 1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCl, we assumed the sequential formation of five oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complex particles of molybdenum (V), containing in the inner coordination sphere, in addition to the organic ligand and the halide ion, also coordinated water molecules. The stepwise formation of molybdenum(V) complexes proceeds according to the reaction schemes presented below:

$(NH_4)_2[MoOCl_5]^0 + L + H_2O \leftrightarrow [MoOL(H_2O)Cl_3]^0 + 2NH_4Cl$;

$[MoOL(H_2O)Cl_3]^0 + L + H^+ \leftrightarrow [MoOL_2(H_2O)Cl_2]^+ + HCl$;

$[MoOL_2(H_2O)Cl_2]^+ + L + H^+ \leftrightarrow [MoOL_3(H_2O)Cl]^{2+} + HCl$;

$[MoOL_3(H_2O)Cl]^{2+} + L + H^+ \leftrightarrow [MoOL_4(H_2O)]^{3+} + HCl$;

$[MoOL_4(H_2O)]^{3+} + L \leftrightarrow [MoOL_5]^{3+} + H_2O$.

Using the obtained data of the process of stepwise complexation in the $[MoOCl_5]^{2-}$ - 1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCI system, at half-integer values of the formation function (ñ), by the Bjerrum graphical method [23] we found the stepwise stability constants of five oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V). The values of the general stability constants were determined by us using the program proposed by E.I. Kapustin [25]. The values of total ($lg\beta_i$) and average stability constants (pK_i) of oxochloro-1-phenyl-2,3-dimethylpyrazoline-5-thione complex particles found from the formation curves (Fig. 1) are presented in Table. 2 and 3.

Table 2. Values of the general stability constants ($lg\beta_i$) of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V), found in a medium of 4 mol/l HCl, by the Bjerrum graphical method at 328 K.

T, K	$lg\beta_1$	$lg\beta_2$	$lg\beta_3$	$lg\beta_4$	$lg\beta_5$
328	3.04	2.62	2.37	2.23	2.14

TABLE 3. Stepwise stability constants of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V) found in 4 mol/L HCl at 328 K

T, K	K_1	K_2	K_3	K_4	K_5
328	1.09×10^3	4.16×10^2	3.34×10^2	1.69×10^2	1.38×10^2

From the data of Tables 2 and 3, it can be seen that with increasing temperature, there is a decrease in the value of both general and stepwise stability constants formed by oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V).

Table 4. Average values of the overall stability constants of 1-phenyl-2,3-dimethylpyrazolin-5-thione complexes at 328 K

| T, K	pK_1	pK_2	pK_3	pK_4	pK_5
328	3.21±0.36	2.69±0.16	2.42±0.10	2.18±0.10	1.87±0.56

The -Lg[L] values found in each part of the complexation curve show how much and to what extent the values of the stability constants of oxochloro-1-phenyl-2,3-dimethylpyrazoline-5-thione complexes of molybdenum (V) differ from each other. When analyzing the ratios of the stepwise stability constants of the resulting complex particles, it was found that the value of K_1 is 2.57 times greater than the value of K_2, and the value of K_2 is 1.65 times greater than the value of K_3. At the same time, the value of K_3 exceeds the value of K_4 by 1.51 times, and the fourth formation constant is greater than the fifth constant by 1.20 times. We refined the stability constants of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complex particles formed in a 4 mol/L HCl medium at a temperature of 328 K using the equation:

$$\bar{n} = \frac{\beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4 + \beta_5[L]^5}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \beta_4[L]^4 + \beta_5[L]^5} \quad (3)$$

where β is the general stability constant; [L] is the equilibrium concentration of 1-phenyl-2,3-dimethylpyrazolin-5-thione. Equation (3) was solved using the program developed by Kapustin in the programming language Excel Borland Delphi [23], operating system Windows 7.

A, the equation $P_{4y}=0$ was solved by the bisection method. For all values of c, from 0.1 to 5.0, the equilibrium concentrations of 1-phenyl-2,3-dimethylpyrazolin-5-thione-[L] were found with a step of 0.1. The curves for the formation of oxochloro-1-phenyl-2,3-

dimethylpyrazolin-5-thione complexes of molybdenum (V) were built based on experimentally found and refined values of the stability constants (Fig. 2).
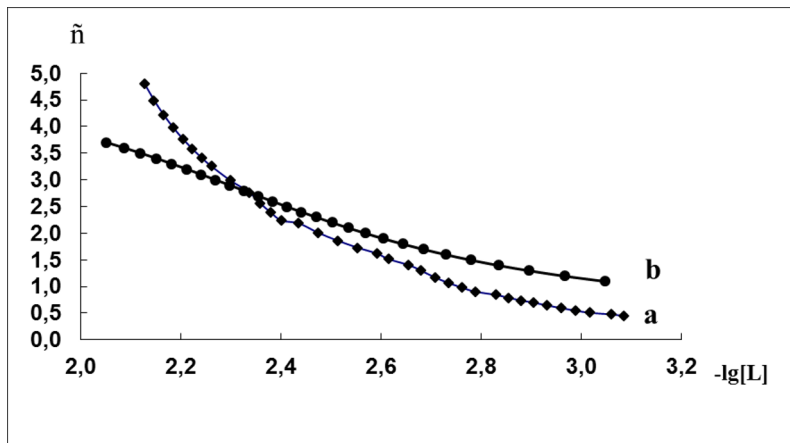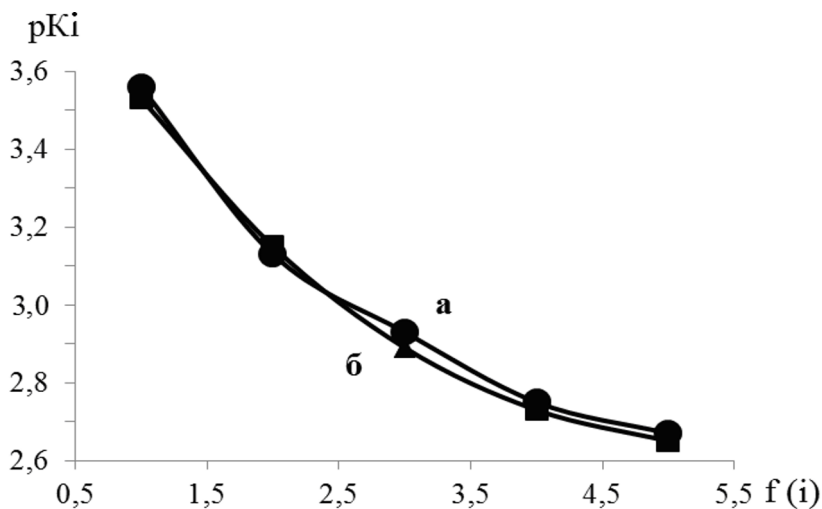

Fig. 2. Curves of the formation of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V): a is according to the experiment; b is refined (after data processing).

Using these formation curves (Fig. 2 a and b), we found the refined pK_i^* values, with half-integer values of the formation function (ñ), which turned out to be respectively equal: $pK_1^*=-Ig[L]_{n=0.5}=3{,}21$; $pK_2^*=-Ig[L]_{n=1.5}=2{,}69$; $pK_3^*=-Ig[L]_{n=2.5}=2{,}42$; $pK_4^*=Ig[L]_{n=3.5}=2{,}18$; $pK_5^*=-Ig[L]_{n=4.5}=1{,}87$.

It can be seen that the refined values of pK_1^*, pK_2^*, and pK_3^* are slightly different and have greater values compared to the experimentally found pK_1-pK_5. At the same time, it can be seen that compared with the refined values of pK_1^*-pK_3^*, the values of pK_4^* and pK_5^* are comparatively smaller than those found experimentally.

Fig. 3 shows the dependence of pK_i values on the number of coordinated molecules (i) of 1-phenyl-2,3-dimethylpyrazolin-5-thione.


Fig. 3. Dependence curve $pK_i = f(i)$ for oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V): a - according to experimental data; b - refined (after data processing).

It can be seen from the data in Fig. 3 that with an increase in the number of coordinated molecules of 1-phenyl-2,3-dimethylpyrazolin-5-thione (i) to the MoO^{3+} ion, the pKi values decrease, which is probably due to the steric hindrance created by the entry of subsequent bulk solvated molecules of heterocyclic 1 -phenyl-2,3-dimethylpyrazolin-5-thione (i) into the inner coordination sphere of complex particles.

To determine the area of the dominance of complex particles formed in the system: $[MoOCl_5]^{2-}$-1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l-HCI using the refined values of the stepwise stability constants, we plotted the diagrams of the distribution curves of the complexes at a temperature of 328 K (Fig. 4) and found the maximum share of the yield of equilibrium oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V).
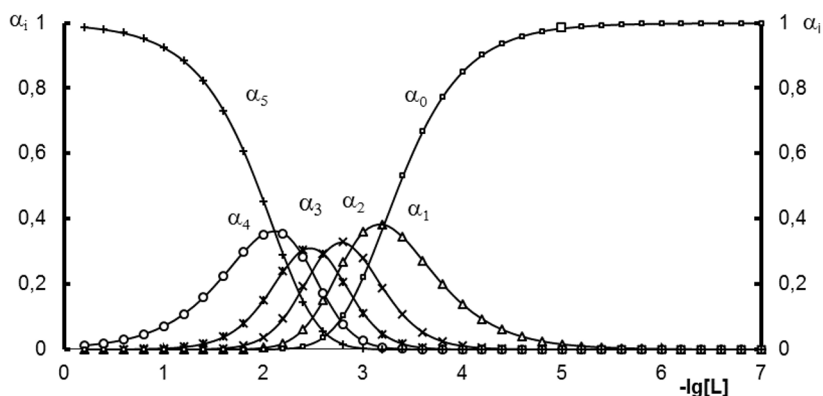
Fig. 4. Distribution curves of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V) in a medium of 4 mol/l HCI (328 K): α_0 - $(NH_4)_2[MoOCI_5]$; α_1 - $[MoOL(H_2O)CI_3]^0$; α_2 - $[MoOL_2(H_2O)Cl_2]^{1+}$; α_3 - $[MoOL_3(H_2O)Cl]^{2+}$; α_4 - $[MoOL_4(H_2O)]^{3+}$; α_5 – $[MoOL_5]^{3+}$.

An analysis of the dependence of the distribution function on temperature shows that the yield of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes Mo(V) decreases with increasing temperature of the experiment, which is probably due to the exothermic process of formation of new complexes. The construction of distribution diagrams for oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complex particles and their analysis made it possible to reveal the dominance area of each of them depending on the concentration of the reagents involved in the complexation reaction and the temperature of the experiment.

Tables 5 and 6 present the values of the maximum yield of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of Mo(V) formed at temperatures of 328 K in a medium of 4 mol/l HCI found from the distribution curves (Table 5) and the value of the equilibrium concentration (table 6) of the investigated heterocyclic organic ligand (-lgL).

Table 5. Yield maxima (αimax) and -lg[L] of 1-phenyl-2,3-dimethylpyrazolin-5-thione complex species in 4 mol/l HCl at 328 K.

| Compositionofthecompound	Yield maxima ($α_i^{max}$) of complexes, 328 K	Values -lg [L] at$α_i^{max}$
$[MoOL(H_2O)CI_3]^0$	0.37	3.20
$[MoOL_2(H_2O)CI_2]^+$	0.33	2.80
$[MoOL_3(H_2O)CI]^{2+}$	0.29	2.60
$[MoOL_4(H_2O)]^{3+}$	0.34	2.20
$[MoOL_5]^{3+}$	0.20	0.20

Table 5 shows that with an increase in the number of coordinated molecules of the studied ligand to the molybdenyl ion (MoO)$^{3+}$, the maximum yield of complex particles (αimax) formed in a 4 mol/l HCl medium in the temperature range from 273 to 338 K naturally shifts to towards higher values of the equilibrium concentration of 1-phenyl-2,3-dimethylpyrazolin-5-thione. The revealed fact indicates a decrease in the stability of four and five substituted mononuclear oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione coordination compounds of molybdenum (V) due to the presence of many molecules that are not involved in the process of complex formation.

It can also be stated that the coordination of large amounts of organic ligand molecules in the inner coordination sphere of the complex ion probably creates certain obstacles to forming a stable coordination bond.

To confirm the probability of the formation of complex particles of molybdenum (V) with 1-phenyl-2,3-dimethylpyrazolin-5-thione in solutions of hydrohalic acids, it was necessary to calculate the thermodynamic values of the complexation process in the temperature range of 273-338K. Calculation of thermodynamic valuesΔH (change in enthalpy), SΔ (change in entropy) of the reaction of complex formation in solutions, was carried out taking into account the experimentally found values of lgβi according to the equation:

$$lgB_i = -\frac{\Delta H}{R \cdot 298.15 \cdot 2.3} + \frac{\Delta S}{R \cdot 2.3}\left[\frac{1}{298.15} - \frac{1}{T}\right] \qquad (4)$$

There are two unknowns in equation 4, so the values HΔ and SΔ were found by a graphical method using the dependence of pK$_i$ on 1/T (Fig. 5).
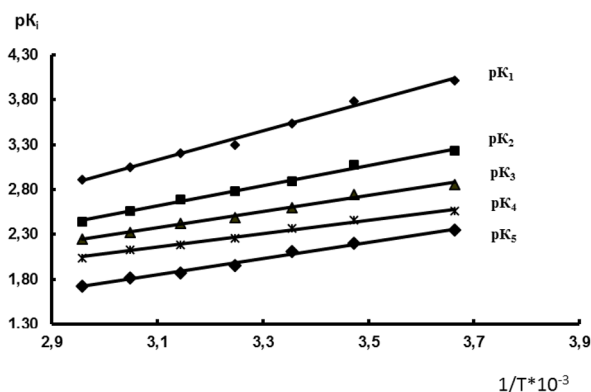
Fig. 5. Dependence of pK$_i$ on 1/T for oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V) forming in a medium of 4 mol/l HCl at 273-338 K: 1-[MoOL(H$_2$O)CI$_3$]^0; 2-[MoOL$_2$(H$_2$O)CI$_2$]$^+$; 3-[MoOL$_3$(H$_2$O)CI]$^{2+}$; 4- [MoOL$_4$(H$_2$O)]$^{3+}$; 5- [MoOL$_5$]$^{3+}$.

The value of HΔ was determined by the tangent of the slope of the straight lines, the dependence pK$_i$ =1/T·10-3, and the value of SΔ were determined by the segment cut off by this straight line on the y-axis. The change in the value of the isobaric-isothermal potential (ΔG) was calculated using the Gibbs equation: $\Delta G = \Delta H - T \cdot \Delta S$(Table 6).

Table 6. Values of thermodynamic functions of the process of formation of oxochloro-1-phenyl-2,3-dimethylpyrazolin-5-thione complexes of molybdenum (V) in a medium of 4 mol/l HCl at 273-338 K.

Reactionscheme	-ΔG, kJ/mol	-ΔH, kJ/mol	ΔS, J/(mol K)
$[MoOCl_5]^{2-}+L+H_2O\rightarrow[MoOL(H_2O)Cl_3]^0$	22.93 ± 1.08	31.26 ± 3.86	36.92 ± 12.67
$[MoOL(H_2O)Cl_3]^-+L\rightarrow[MoOL_2(H_2O)Cl_2]^+$	18.42 ± 1.25	21.68 ± 2.27	17.16 ± 7.44
$[MoOL_2(H_2O)Cl_2]^++L\rightarrow[MoOL_3(H_2O)Cl]^{2+}$	16.31 ± 0.68	14.45 ± 7.31	1.77 ± 23.97
$[MoOL_3(H_2O)Cl]^{2+}+L\rightarrow[MoOL_4(H_2O)]^{3+}$	14.60 ± 0.62	14.43 ± 1.53	3.43 ± 5.04
$[MoOL_4(H_2O)]^{3+}+L\rightarrow[MoOL_5]^{3+}$	13.40 ± 3.98	17.41 ± 1.93	-18.60 ± 6.35

It can be seen from the data in Table 6 that all oxochloroaqua-1-phenyl-2,3-dimethylpyrazoline-5-thione complexes formed in a 4 mol/l HCl solution are enthalpy-stable compounds. However, during the formation of a $[MoOL_5]^{3+}$ complex particle containing five coordinated molecules of 1-phenyl-2,3-dimethylpyrazolin-5-thione, an increase in the value ofΔH occurs, i.e., exothermicity of complexation reactions. It is also seen that at all stages of the formation of 1-phenyl-2,3-dimethylpyrazolin-5-thione complexes, the value of SΔhas a negative value, which can be explained by a decrease in the number of particles in the studied system $[MoOCl_5]^{2-}$- 1-phenyl-2,3 - dimethylpyrazolin-5-thione - 4 mol/l HCl, due to the addition of subsequent molecules of the organic ligand to the ion of the complexing agent MoO^{3+}. Table data. 6 also show that the formation of all 1-phenyl-2,3-dimethylpyrazolin-5-thione Mo(V) coordination compounds is accompanied by heat release, since the value of HΔhas a negative value and indicates a spontaneous exothermic complex formation reaction between MoO^{3+} and solvated molecules with 1-phenyl-2,3-dimethylpyrazolin-5-thione in a medium of 4 mol/l HCl at 273-338K.

4 Conclusions

For the first time, the process of complex formation in the $[MoOCl_5]^{2-}$ -1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCl system at 273-338 K was studied by potentiometric titration. The number and composition of the complexes formed in the studied system were established.

The stepwise and general stability constants of the five complex particles formed are found, and the regions of their dominance and the yield maxima of each complex form are determined.

It is shown that with increasing temperature, the values of the general stability constants of coordination compounds decrease. Changes in the values of the thermodynamic functions of the complex formation reaction were revealed by the temperature coefficient method. Based on the experimentally found values of enthalpy, the spontaneous occurrence of the complex formation reaction between the MoO^{3+} ion and the molecules of nitrogen- and sulfur-containing 1-phenyl-2,3-dimethylpyrazolin-5-thione is assumed.

Based on the conducted potentiometric studies of complexation processes in the system $[MoOCl_5]^{2-}$-1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCl, the formation of five mononuclear 1-phenyl-2,3-dimethylpyrazolin-5-thionic coordination compounds in a 4 mol/l HCl medium over the entire temperature range of the experimenter.

It has been shown that complex particles containing from 1 to 2 coordinated molecules of 1-phenyl-2,3-dimethylpyrazolin-5-thione are the most stable compared to complex

particles containing more than three attached molecules of 1-phenyl-2,3-dimethylpyrazolin-5-thione. It was also found that under the chosen experimental conditions, the first two complex compounds are formed with the highest yield compared to the rest.

Based on the data of a potentiometric study, the regions of existence and the maximum yield of each complex particle were established, and their stability constants were calculated, which made it possible to develop methods for obtaining new one- and two-substituted coordination compounds of molybdenum(V) with 1-phenyl-2,3-dimethyl-pyrazoline-5-thione in hydrochloric acid solutions. It has been established that the main complexing agent in the studied system $[MoOCl_5]^{2-}$ - 1-phenyl-2,3-dimethylpyrazolin-5-thione - 4 mol/l HCl is the $(MoO)^{3+}$ molybdenyl ion.

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