

НЕОРГАНИЧЕСКАЯ И АНАЛИТИЧЕСКАЯ ХИМИЯ

УДК 546.289 + 546.328 + 535.24

CHARACTERIZATION OF α -8 MOLYBDOGERMANIC ACID ACCORDING TO ITS REACTION WITH BASIC DYE NEUTRAL RED

E. Kh. HAIRIYAN

M.G. Manvelyan Institute of General and Inorganic Chemistry NAS RA
10, d. 2, Argutyan Str., Yerevan, 0051, Armenia
Fax: (374 10) 231275, E-mail: mirferd@rambler.ru

It was shown that basic dye neutral red (NR), reacting with molybdo germanic heteropolyacid (MGA) at pH 2.4–4.0, leads to the stabilization of α -8-molybdo germanic heteropolyacid (8-MGA) in the form of less water soluble ion association with NR. The substitution level of MGA in the products, which was determined by the acidity of the reaction with NR, is equal to 4 (pH -0.4 ± 0.1) and 8 (pH 0.2 ± 0.85), and in the case of masking of the surplus molybdenum(VI), it is equal to 8 (pH 0.2 ± 5.0). In accordance with experimental results, it has been demonstrated that the eightfold basicity of 8-MGA involves both “strong” and “weak” basicity. The formation chemistry, the structure of 8-MGA, and the conditions for its high stability in aqueous solutions have been discussed.

Figs. 6, tables 3, references 17.

Introduction. Basic dyes, due to their structural characteristics and nature, selectively react with various series of molybdenum heteropolyacids (HPAs). It has been established that the compositional variations in the products depend both on the nature of the basic dye used and on the acidity of the performed reaction. This information is of significance in demonstrating the stabilization of the practically yet not described molybdo germanic heteropolyacids (MGAs) belonging to the series containing eight Mo atoms in the form of ion association with characteristically different basic dyes [1-5]. In all cases, it was found that, even when the acidity was reduced up to pH 6.0, the substitution level of MGA was equal to four[1]. MGAs belonging to other series form both tetra- and octa-substituted complex compounds, depending only on the nature of the basic dye used [6-9]. The investigations presented herein on reactions of MGA with the basic dye neutral red reveal new properties of 8-MGA.

Results and Discussion

Earlier we showed that the acidity for the quantitative formation MGA, which was confirmed by light absorption of MGA–basic dye compounds, is practically independent on the used basic dye and is observed in the quite wide range of acidity $\text{pH} = 1.4\div 4.2$ [6]. During the establishment of the optimal conditions for MGA–NR compounds, MGA was initially obtained at $\text{pH} = 2.4\div 4.0$ (referred to as the initial acidity, pH_i). It was found that the quantitative formation of MGA–NR compounds is impossible to investigate directly under the conditions of quantitative formation of MGA because of the interaction of NR with the available surplus isopolymolybdate ions in the solution. This obstacle was eliminated in two ways:

(a) by gradually increasing the acidity after the quantitative formation of MGA and studying the reaction of NR with MGA (outside the optimal acidity interval for the formation of MGA).

(b) by masking the incoherence of isopolymolybdate ions in MGA through the use of sodium oxalate and studying the reaction of MGA with NR both in the optimal acidity intervals for the quantitative formation of MGA and under less acidic **conditions** (referred to as the final acidity, pH_f).

The dependence of light absorption on pH_f is shown in Figure 1, in which the data was obtained at constant values of pH_i and constant concentrations of molybdate ions and NR.

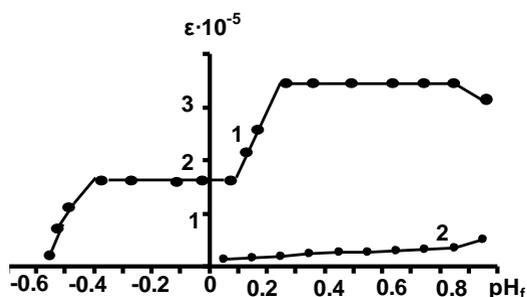


Fig. 1. Dependence of molar coefficient of light absorption on pH_f in acetone solutions containing MGA–NR compounds (curve 1) and isopolymolybdate ions (curve 2). $[\text{Ge}^{\text{IV}}] = 1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $[\text{NR}] = 1.7 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $[\text{MoO}_4^{2-}] = 1.2 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$; $\text{pH}_i = 2.5$; $\ell = 0.1 \text{ cm}$ (ℓ : path length)

The dependence of light absorption on acidity in the process of obtaining $\text{MGA} \cdot n\text{NR}$ is characterized by two plateaus at the intervals $\text{pH} = -0.4\div 0.1$ and $0.2\div 0.85$. In the first case the molar coefficient of light absorption is $1.62 \cdot 10^5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, in the second case it is $3.2 \cdot 10^5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. It has been experimentally established that in both cases Ge^{IV} is quantitatively bound in the compound $\text{MGA} \cdot n\text{NR}$.

The results on the optimal acidity for the formation and separation of $\text{MGA} \cdot n\text{NR}$ compounds when the surplus isopolymolybdate ions are masked by using sodium oxalate are given in (Fig. 2).

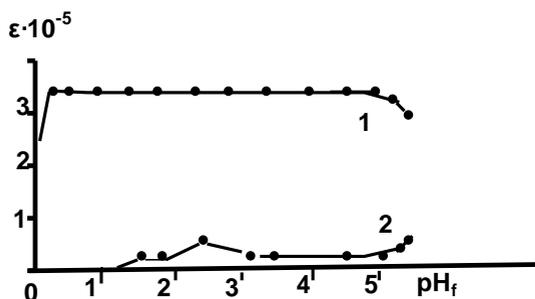


Fig. 2. Dependence of ϵ on pH_f in acetone solutions containing MGA-NR compounds (curve 1) and isopolymolybdate ions (curve 2) with use of $\text{C}_2\text{O}_4^{2-}$ ions to disguise excess molybdenum(VI). $[\text{Ge}^{\text{IV}}] = 1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $[\text{NR}] = 1.7 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $[\text{Mo}^{\text{VI}}] = 1.2 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$; $\text{pH}_i = 2.2$; $[\text{C}_2\text{O}_4^{2-}] = 0.01 \text{ mol} \cdot \text{l}^{-1}$; $\ell = 0.1 \text{ cm}$ (ℓ : path length).

The application of sodium oxalate makes it considerably possible to move the optimal pH interval towards less acidic values, and, in accordance with this, to obtain the MGA·nNR compounds under the conditions of acidity required for the quantitative formation of MGA ($\text{pH}_f = 0.6 \div 4.2$), as well as enabling the acidity to be reduced up to $\text{pH}_f = 5.0$. Under these conditions, the molar absorption coefficient of the compounds was constant at a value of $\epsilon = 3.2 \cdot 10^5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. In the above-mentioned optimal concentrations ($\text{pH}_i = 2.6$; $[\text{Mo}^{\text{VI}}] = 1.2 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$, $\text{pH}_f = -0.3$ or 3.0 when using $0.01 \text{ mol} \cdot \text{l}^{-1} \text{ Na}_2\text{C}_2\text{O}_4$) the formation of MGA·nNR compounds was studied in relation with the concentration of NR and molybdate ions (Table 1).

Table 1

The optimal conditions for obtaining MGA·nNR compounds in the absence (entries 1, 2) and presence (entry 3) of masking agent; $\text{pH}_i = 2.6 \div 3.0$.

Entry	MGA·nNR	pH_f	$[\text{C}_2\text{O}_4^{2-}]$ ($\text{mol} \cdot \text{l}^{-1}$)	$[\text{MoO}_4^{2-}] \cdot 10^3$ ($\text{mol} \cdot \text{l}^{-1}$)	$[\text{NR}] \cdot 10^4$ ($\text{mol} \cdot \text{l}^{-1}$)	Molar absorptivity at 530 nm ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)
1	MGA·4NR	$-0.4 \div 0.1$	–	0.96–5.0	1.0–2.0	$1.62 \cdot 10^5$
2	MGA·8NR	$0.2 \div 0.85$	–	0.96–5.0	1.7–4.5	$3.2 \cdot 10^5$
3	MGA·8NR	$0.2 \div 4.6$	0.01	0.96–7.0	1.7–6.0	$3.2 \cdot 10^5$

It is obvious that the use of oxalate ions also notably improves the concentration conditions for the formation and separation of MGA·nNR compounds.

The quantitative relation of NR and MGA in the reaction products was established by the method of isomolar series, in which experiments were performed at different acidities and total concentrations of Ge^{IV} and NR (Figures 3 and 4).

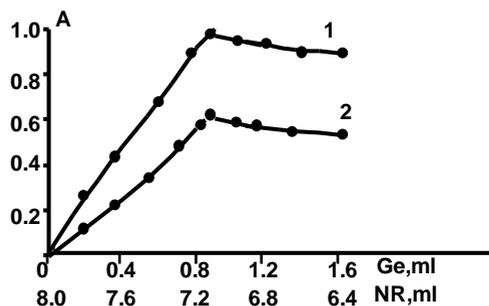


Fig. 3. Isomolar diagram of the system MGA-NR [$v(\text{Ge}^{\text{IV}})/v(\text{NR}) = 1:8$]. $\text{pH}_i = 2.6$; $[\text{Mo}^{\text{VI}}] = 1.2 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$; $[\text{C}_2\text{O}_4^{2-}] = 1 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$; $\ell = 0.3 \text{ cm}$ (ℓ : path length); $\text{pH}_f = 1.5$ or 4.0; $[\text{Ge}^{\text{IV}}] + [\text{NR}] = 2 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ (curve 1); $1 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ (curve 2).

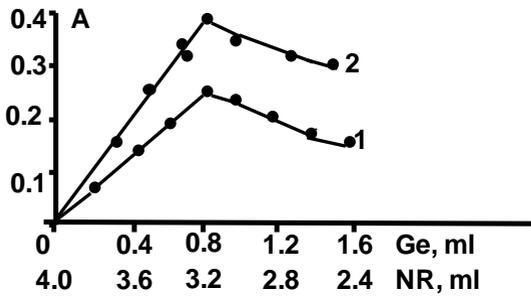


Fig. 4. Isomolar diagram of the system MGA-NR $[v(\text{Ge}^{\text{IV}})/v(\text{NR}) = 1:4]$; $\text{pH}_i = 2.6$; $[\text{MoO}_4^{2-}] = 1.2 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$; $l = 0.1 \text{ cm}$ (l : path length); $\text{pH}_f = -0.3$; $[\text{Ge}^{\text{IV}}] + [\text{NR}] = 2 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ (curve 1); $4 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ (curve 2)

On the basis of the given data, it follows that NR forms two ion associations with structurally different outer coordination spheres, which are related with the acidity of the performed reaction: $\text{MGA} \cdot 4\text{NR}$ ($\text{pH}_f = -0.4 \pm 0.1$) and $\text{MGA} \cdot 8\text{NR}$ ($\text{pH}_f = 0.2 \pm 0.8$ or 0.2 ± 5.0 when surplus molybdate ions are masked). Analogous data were obtained also by experimental analysis (Table 2) and according to the relation $\varepsilon_{\text{MGA} \cdot n\text{NR}}/\varepsilon_{\text{NR}}$ (Table 3).

Table 2

The results of experimental analysis of $\text{MGA} \cdot n\text{NR}$ compounds for content of NR, Ge^{IV} , and Mo^{VI} (the number of parallel experiments is 6, $P = 0.95$)

MGA·nNR	pH _i	Number of moles determined experimentally			$v(\text{NR})/v(\text{Ge})/v(\text{Mo})^{[\text{a}]}$
		NR ($\text{mol} \cdot 10^7$)	Ge ^{IV} ($\text{mol} \cdot 10^7$)	MoO ₄ ²⁻ ($\text{mol} \cdot 10^7$)	
MGA·4NR	2.6	4.00 ± 0.03	1.01 ± 0.01	8.00 ± 0.01	3.99:1.00:8.01
MGA·8NR	2.6	8.00 ± 0.02	1.02 ± 0.02	8.05 ± 0.05	7.84:1.00:7.88
MGA·4NR	3.2	4.00 ± 0.02	1.00 ± 0.01	8.04 ± 0.01	4.00:1.00:8.00
MGA·8NR	3.2	8.00 ± 0.03	1.01 ± 0.01	8.05 ± 0.05	7.92:1.00:7.97
MGA·4NR	3.8	4.02 ± 0.02	1.00 ± 0.01	8.04 ± 0.01	4.02:1.00:8.04
MGA·8NR	3.8	8.04 ± 0.01	1.02 ± 0.01	8.00 ± 0.02	7.88:1.00:7.84

For determination of the content of Mo^{VI} , the MGA–basic dye precipitate was dissolved in 0.5 mL concentrated H_2SO_4 and Mo^{VI} was determined in the obtained solution by using the sulfocyanitic method [10]. Supposing that the interspherical content of MGA, thereby also the content of the reaction product, can change as pH_i changes, the compounds $\text{MGA} \cdot n\text{NR}$ were distinguished by three different but optimal pH_i values. In the obtained sulfate solution NR was decomposed by boiling with hydrogen peroxide for a long time. The calibration graphic was obtained under the same conditions.

The results show that in all cases the formation and separation of the ion association on the basis of MGA belonging to the series containing eight molybdenum atoms do not depend on pH_i .

**Relation of $\epsilon_{\text{MGA}\cdot n\text{NR}}$ and ϵ_{NR}
(the number of parallel experiments is 6, $P = 0.95$).**

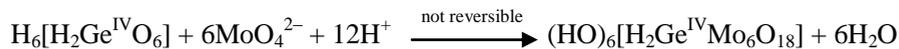
Composition according to isomolar diagram	Molar absorptivity at 530 nm ($l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)		$n = \epsilon_{\text{MGA}\cdot n\text{NR}}/\epsilon_{\text{NR}}$
	$\epsilon_{\text{MGA}\cdot n\text{NR}} \cdot 10^{-5}$	$\epsilon_{\text{NR}} \cdot 10^{-5}$	
MGA·4NR	1.62 ± 0.01	0.40 ± 0.01	4.05
MGA·8NR	3.21 ± 0.02	0.40 ± 0.01	8.02

At $\text{pH}_i = 2.4\text{--}4.0$ the α form of MGA is obtained. The formation of the association complex with four associated NR cations under the comparably acidic conditions shows the existence of “strong” basicity in α -8-MGA, which is equal to four. It is obvious that this basicity of α -8-MGA was realized by using the reagent we had used earlier[1,4] and does not depend on the acidity of the performed reaction.

When NR was used, it was established that association complex $[\text{GeMo}_8\text{O}_{30}]\cdot 8\text{NR}$ formed first at reduced acidity of the performed reaction. Without doubt it is evident that “weak” basicity also exists for α -8-MGA and it is equal to four, which we had not observed previously when using other basic dyes. According to our previous observations, the availability of “strong” and “weak” basicity, which in both cases is equal to four, is also characteristic for α -MGAs belonging to series containing higher numbers of molybdenum atoms[6–9]. Therefore, the basicity of α -MGA does not depend on the content of inner coordination spheres. α -MGAs containing less than eight molybdenum atoms, which are stable in solution and can react with the basic dye, were not obtained by us and also not described in the literature. Therefore, as it was earlier presented by us, the formation of heteropolyacid (HPA) occurs only on the basis of the proposed $\text{H}_{12-n}\text{X}^n\text{O}_6$ acid (where X is the central heteroatom, n its valency) and does not depend on the composition of the inner sphere.

The composition of the inner coordinated network has been suggested by us on the basis of the “core” where the atoms of molybdenum(VI) have sublayered distribution [11–13]. In addition to this, we suppose that the contents of heteropolyacid “cores” in the α and β forms are different [14, 15].

The β -core is formed on the basis of the supposed saturated acid $\text{H}_6[\text{H}_2\text{Ge}^{\text{IV}}\text{O}_6]$ resulting from coordination. Condensation of six hydrogen atoms of this acid with molybdic acid results in the formation of the rigid compact structure with a cavity shown in Figure 5, where the Ge atom at the center is surrounded by six oxygen atoms in an octahedral environment. This involves six atomic cycles (one of which is shown in Figure 5 with bold lines).



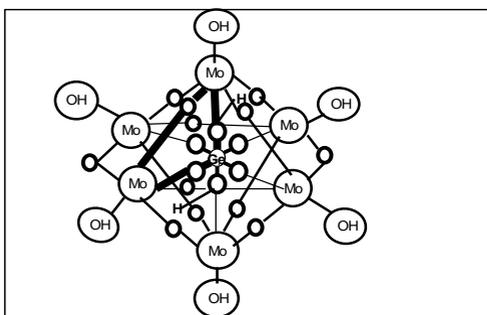
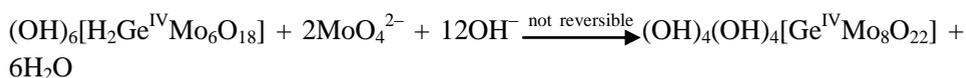


Fig. 5. Proposed core structure of β -6-MGA

It is known that β -MGA is converted irreversibly into the more stable α -form in solvents, especially when the acidity is reduced. This behavior most probably results from the structure of the β -MGA core. At reduced MGA concentrations and reaction acidity, two hydrogen atoms of the inner sphere in this β -“core” can separately participate in the condensation reaction with molybdate ions and then, as a result of condensation between one OH group of this new connected molybdate and one of the six OH groups in the β -core, can form six-atomic supplementary and stable closed rings (whose total number is 2) on the basis of the β -core.



As a result, the packed rigid structure shown in Figure 6 is formed. In this structure, the germanium atom is centered in an octahedral environment and is surrounded by oxygen atoms included in eight units with six atoms. This causes the high stability of the “core”.

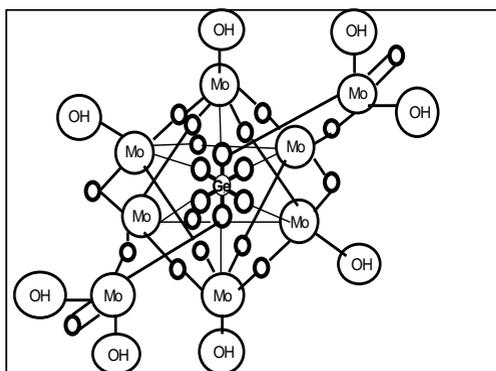
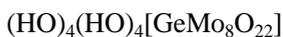


Fig. 6. Proposed core structure of α -8-MGA.



As it is obvious from the presented structure, the presence of eight connected OH groups in the “core” stipulate the basicity of the core. In this case, the basicity of α -8-MGA, which is eight, involves four “strong” (connected with molybdenum

atoms through six oxygen atoms) and four “weak” types of basicity (connected with molybdenum atoms through five oxygen atoms) [16-19].

There is no doubt that the demonstrated α -8-MGA “core”, which exists in the real form, can be synthesized as a separate, stable form of MGA in the solution. The growth of α -MGA from α -8-MGA to α -12-MGA more probably occurs in the stages of the condensation reaction as a result of the presence of four OH groups with “strong” basicity and with use of one of two OH groups of molybdic acid (HO–MoO₃H). In these cases, a second superficial layer of α -MGA appears which might contain from one up to four atoms of molybdenum (VI). These atoms are not connected with each other because of the distance between them, and they are mobile. This certainly determines the presence of chemical equilibrium between the eight-basic α -MGAs of the series containing various numbers of molybdenum atoms: from α -8-MGA up to α -12-MGA. Each one of these forms can be stabilized as a less water soluble complex compound, as a result of its selective interaction with the basic dye, which was experimentally demonstrated by using basic dyes of various characteristics.

In addition, the suggested structure of the α -MGA core may become a key for understanding the formation of dimers and then polymers (conglomerates) by accepting that this occurs by the condensation of OH groups directly related with the core.

Conclusion. In this paper, the formation of MG–NR compounds is discussed and proposals for their structure are presented. These results are important because they can help understand the chemistry of heteropoly compounds in solution, which was unknown up to now. On the other hand, on the basis of such results, it will be possible to synthesize in aqueous solution new biologically active types of polyoxometalates and/ or heteropoly compounds, which can help understand the mechanism of action of polyoxometalates on living organisms, which would be very useful in modern medicine.

Experimental part

Reagents: A solution of Ge^{IV} (0.005 M, pH 7.2) was prepared by dissolving the appropriate weight of GeO₂ (especially pure) in distilled water, adding a small portion of sodium hydroxide solution and further diluting as required.

The following reagents were used: sodium molybdate (pure; 0.024 M), NR (pure; 0.1% aqueous solution), sodium oxalate (pure; 0.2 M), nitric acid (especially pure; s. g. 1.41), acetone (pure). All solutions were kept in polyethylene bottles.

Preparation and Separation of MGA–NR Compounds: To a solution (containing a definite amount of Ge^{IV}) in a conical centrifuge tube was added a definite amount of molybdates followed by nitric acid until the optimum acidity (referred to as the initial acidity, pH_i) required for the quantitative formation of MGA was reached, and the volume was made up to 5 ml with distilled water.

The solution was stirred and left for 10–15 min for the formation of the maximum amount of MGA. Then the optimum acidity (called the final acidity, pH_f) for the separation of MGA–NR was established, and a certain amount of oxalate solution (if necessary) and the reagent dye were added, and the volume was completed to 10 ml with distilled water. After mixing and formation of a considerable amount of precipitate, the mixture was centrifuged, the solution was carefully decanted, and the pH of the solution was measured. The precipitate was washed in a test tube with water (2 ml), then separated by centrifuging and dissolved in acetone (10 ml). The degree of combination of Ge^{IV} in MGA and then in MGA–NR was estimated from the absorbance of the acetone solution.

A blank test was performed to check the formation of isopolymolybdate salts of NR. The absorbance of the solution was measured at 530 nm in 1 mm cells. Solid compounds were separated by centrifuging for 1–2 min at 3000 rpm.

**α-8-ՄՈՒԻԲԴՈՎԵՐՄԱՆԱԿԱՆ ԹԹՎԻ ԲՆՈՒԹԱԳԻՐԸ ԸՍՏ ՉԵԶՈՔ
ԿԱՐՄԻՐ ՆԻՄՆԱՅԻՆ ՆԵՐԿԱՆՅՈՒԹԻ ՆԵՏ ՆՐԱ ՌԵԱԿՑԻԱՅԻ**

Է. Ք. ՆԱՅՐԻՅԱՆ

Սպեկտրոֆոտոմետրիկ եղանակով հաստատվել է, որ չեզոք կարմիր (ՉԿ) հիմնային ներկանյութը, փոխազդելով մոլիբդոդեքսանական հետերոպոլիթիթի (ՄԳԹ) հետ, ստացված pH 2.4÷4.0 միջակայքում, առաջացնում է n(ՉԿ)·8ՄԳԹ, ջրում դժվարալուծ կոմպլեքսային ասոցիատներ: ՄԳԹ-ի տեղակայման աստիճանը ստացված կոմպլեքսային ասոցիատներում պայմանավորվում է ՉԿ-ի հետ ունեցող ընթացման թիթվոլոթյամբ և հավասար է 4-ի, երբ միջակայրի թիթվոլոթյունը (2.5M HNO₃ ÷pH 0.1) և 8-ի, երբ (pH 0.2÷0.85) և (pH 0.2÷5.0) օքսալատով մոլիբդենի ավելցուկի քողարկման պայմաններում: Դա ևս մեկ ապացույց է ՄԳԹ-ի ութի հավասար հիմնայնություն, ինչպես նաև նրա “ուժեղ” և “թուլ” հիմնայնություն առկայություն:

ՉԿ-ի և ՄԳԹ-ի քանակների հարաբերությունը փոխազդեցության արգասիքներում հաստատվել է իզոմոլյար սերիաների եղանակով, պինդ ֆազերի քիմիական անալիզի, ինչպես նաև կոմպլեքսային միացություն և ՉԿ-ի մարման մոլյար գործակիցների հարաբերությունը: Բերված տվյալներից հետևում է, որ թիթվոլոթյունից կախված՝ ըստ արտաքին կոորդինացիոն սֆերայի, առաջանում է 2 տարբեր բաղադրություն կոմպլեքսային ասոցիատներ՝ ՄԳԹ·4ՉԿ (pH -0.4÷0.1) և ՄԳԹ·8ՉԿ (pH 0.2÷0.85) կամ (pH_պ 0.2÷5.0) մոլիբդատի ավելցուկի քողարկման դեպքում:

Հաստատվել է նաև, որ բոլոր դեպքերում անկախ թիթվոլոթյունից, կոմպլեքսային ասոցիատները առաջանում են ըստ Mo(VI)-ի ութերորդ շարքի ՄԳԹ-ի հիմքի վրա: Ռեակցիայի զգայնությունը բարձր է: $\varepsilon = 1.75 \cdot 10^5$, երբ pH_պ -0.4÷0.1 և $\varepsilon = 3.2 \cdot 10^5$, երբ pH_պ 0.2÷5.0:

ХАРАКТЕРИСТИКА α -8-МОЛИБДОГЕРМАНИЕВОЙ КИСЛОТЫ ПО ЕЕ РЕАКЦИИ С ОСНОВНЫМ КРАСИТЕЛЕМ НЕЙТРАЛЬНЫМ КРАСНЫМ

Э. Х. АЙРИЯН

Институт общей и неорганической химии им. М.Г. Манвеляна
НАН Республики Армения
Армения, 0051, Ереван, ул. Аргутяна, 2 пер., д. 10
Факс: (374 10)231275, E-mail: mirferd@rambler.ru

Спектрофотометрическим методом установлено, что основной краситель нейтральный красный (НК), реагируя с молибдодгерманиевой гетерополикислотой (МГК), полученной при pH 2.4÷4.0, приводит к стабилизации 8-МГК в виде мало растворимых в воде комплексных ассоциатов. Степень замещенности МГК в продуктах обуславливается кислотностью проведения реакции с НК и равна 4 (pH - 0.4÷0.1) и 8 (pH 0.2÷0.85) и в случае маскировки избытка Mo(VI) pH (0.2÷5.0). Тем самым доказывается восьмиосновность 8-МГК, а также наличие “сильной” и “слабой” ее основностей.

Соотношение количеств НК и МГК в продуктах реакции было установлено методом изомольярных серий, поставленных при различных кислотностях и суммарной концентрации Ge(IV) и НК, препаративным анализом и по отношению $\epsilon_{\text{МГК}\cdot\text{НК}}/\epsilon_{\text{НК}}$.

Из приведенных данных следует, что в зависимости от кислотности проведения реакции НК с МГК образует два различных по составу внешней координационной сферы комплексных ассоциата – МГК·4НК (pH -0.4÷0.1) и МГК·8НК (pH 0.2÷0.85) или (pH 0.2÷5.0) в условиях маскировки избытка Mo(VI). Было установлено также, что во всех случаях, независимо от pH_{КА}, комплексный ассоциат образуется и выделяется на основе МГК 8-ого ряда по молибдену.

Чувствительность реакции высокая: $\epsilon = 1.75 \cdot 10^5$ при pH -0.4÷0.1 и $\epsilon = 3.2 \cdot 10^5$ при pH_{КА} 0.2÷5.0.

REFERENCES

- [1] *Mirzoyan F.V., Tarayan V.M., Hairiyani E.Kh., Grigoryan N.A.* // *Talanta*, 1980, v. 27, p. 1055.
- [2] *Mirzoyan F.V., Tarayan V.M., Petrossian A.A.* // *Zh. Neorg. Khim.*, 1984, v. 29, p. 1997; online INIST–CNRS 2007.
- [3] *Mirzoyan F.V., Sarkisyan N.P., Petrossian A.A.* // *Ukr. Khim. Zh.*, 1987, v. 53, p. 391.
- [4] *Mirzoyan F.V., Petrossian A.A., Hairiyani E.Kh., Karapetyan A.A., Sarkisyan Zh.V.* // *J. Anal. Chem.*, 2000, v. 55, p. 258.
- [5] *Mirzoyan F.V., Hairiyani E.Kh., Mirzoyan L.A., Ohanyan N.A.* // *Chemical Journal of Armenia*, 2000, v. 53, p. 50.
- [6] *Mirzoyan F.V., Tarayan V.M., Hairiyani E.Kh.* // *Arm. Khim. Zh.*, 1979, v. 32, p. 106.
- [7] *Mirzoyan F.V., Tarayan V.M., Hairiyani E.Kh.* // *Anal. Chim. Acta*, 1981, v. 124, p. 185.
- [8] *Mirzoyan F.V., Tarayan V.M., Hairiyani E.Kh.* // *Zh. Anal. Khim.*, 1984, v. 39, p. 2010.
- [9] *Hairiyani E.Kh., Mirzoyan F.V.* // *Zh. Neorg. Khim.*, 1987, v. 32, p. 381; online 2007 INIST–CNRS.
- [10] *Zaitchikova L.B.* // *Zavod. Lab.*, 1949, v. 15, p. 1025.
- [11] *Mirzoyan F.V., Hairiyani E.Kh., Karapetyan A.A., Vartapetyan L.M.* Conversion Potential of Armenia and ISTC Programs, International Seminar, Yerevan, 2–7 October 2000, 113.

- [12] *Mirzoyan F.V.* International Conference of Chemistry and Chemical Technology, Yerevan 2007, p. 25.
- [13] *Mirzoyan F.V.* / Armenian Patent 2008, AM20080170.
- [14] *Mirzoyan F.V.* International Polyoxometalate Symposium, Jacobs University, Bremen, Germany, 2009.
- [15] *Bayanov V.A.* Thesis "Kinetics of germanomolybdc heteropolyanions in aqueous solutions" PhD in Chem., Saint Peterburg, Saint-petersburg State Electrotechnical University "LETI" after V.I. Ulyanov (Lenin), 2015, p. 111.
- [16] *Dubovik D.B., Tikhomirova T.I., Ivanov A.V., Nesterenko P.N., Shpigun O.A.* // J. Anal. Chem., 2003, v. 58, p. 802.
- [17] *Fedotov M.A., Maksimovskaya R.I.* // Journal of Structural Chemistry, 2006, v. 47, p. 961.
- [18] *Long De-Liang, Burkholder E., Cronin L.* // Chem. Soc. Rev., 2007, v. 36, p. 105.
- [19] *Wang X., Liu J., Pope M.T.* // Dalton Trans., 2003, p. 957.