DOI: 10.6060/ivkkt.20186109-10.5778

УДК: 547.461.4-386: 54 – 162.37

УСТОЙЧИВОСТЬ КООРДИНАЦИОННЫХ СОЕДИНЕНИЙ ИОНОВ НЕКОТОРЫХ d-МЕТАЛЛОВ С АНИОНОМ ЯНТАРНОЙ КИСЛОТЫ В ВОДНО-ЭТАНОЛЬНЫХ РАСТВОРИТЕЛЯХ

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В статье проведен обзор данных по комплексообразованию ионов никеля (II), кобальта (II) и меди (II) с анионом янтарной кислоты в водно-органических растворителях. Собственные данные сопоставлены с результатами, приведенными в литературе для комплексов d-металлов с анионами малеиновой и янтарной кислот. Состав и устойчивость координационных соединений в водно-этанольных растворителях были исследованы методом потенциометрического титрования. Исследование влияния состава водно-этанольного растворителя на устойчивость координационных соединений M^{2+} с анионом янтарной кислоты, а также на значения pK ступенчатой диссоциации янтарной кислоты проводили при ионной силе 0,1, которая создавалась перхлоратом натрия при температуре 298,15 ± 0,10 K. Установлено, что устойчивость монолигандных комплексов ионов Ni^{2+}, Co^{2+} и Cu^{2+} с анионом янтарной кислоты увеличивается с ростом содержания этанола в растворителе. В водных растворах ион Cu^{2+} образует более устойчивые комплексы с анионами янтарной и малеиновой кислот, чем ионы Ni^{2+} и Co^{2+}. В растворителе вода-этанол такое соотношение сохраняется для комплексов этих ионов с янтарной кислотой, однако в растворителе вода-изопропанол устойчивость комплексов никеля (II) и кобальта (II) с янтарной кислотой примерно одинакова. Увеличение устойчивости комплексов d-металлов с анионами малеиновой и янтарной кислот обусловлено дестабилизацией лиганда при переходе от воды к водно-этанольным растворителям. Изменение в сольватном состоянии лиганда является основным вкладом в изменение устойчивости комплексов d-металлов с лигандами аминного, глицинатного и ацетатного типа в водно-органических растворителях.

Ключевые слова: реакции комплексообразования, устойчивость комплексов, ионы d-металлов, смешанные растворители, янтарная кислота

STABILITY OF COORDINATION COMPOUNDS OF SOME d-METAL IONS WITH SUCCINIC ACID ANION IN AQUEOUS-ETHANOL SOLVENTS

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The paper provides an overview of own data on complexation of nickel (II), cobalt (II) and cooper (II) ions with succinic acid anion in water-organic mixed solvents. Proper data are compared with data reported in literature for d-metal complexes with anions of maleic and succinic acids. The effect of aqueous ethanol solvent compositions on the stability of coordination compounds of M^{2+} with succinic acid anion as well as on pK values of stepwise succinic acid dissociation was carried out by a potentiometric titration at ionic strength of 0.1 maintained with sodium perchlorate at 298.15 ± 0.10 K. Mono ligand complexes of Ni^{2+}, Co^{2+} and Cu^{2+} ions with succinic acid anion become stronger when ethanol content rises. In aqueous solutions Cu^{2+} ion forms stronger complexes with succinic and maleic acid anions than Ni^{2+} and Co^{2+} ions. In the studied water - ethanol solution this ratio is maintained for complexes with succinic acid anion, but a water-isopropanol solvent exerts leveling effect on the stability of complexes of nickel (II) and cobalt (II). An increase in the stability of complexes of d-metal with anions of maleic and succinic acids is due to the destabilization of the ligand with increasing ethanol concentration. The principal contribution of the changes in the solvation state of ligand is a typical for the stability changes of d-metal complexes with amine, glycinate, and acetate type ligands in water-organic mixed solvents.

Key words: complex formation reactions, complex stability, d-metal ions, mixed solvents, succinic acid

Для цитирования:
Тукумова Н.В., Усачева Т.Р., Thuan Tran Thi Dieu, Шарнин В.А., Giancola C. Устойчивость координационных соединений ионов некоторых d-металлов с анионом янтарной кислоты в водно-этанольных растворителях. *Изв. вузов. Химия и хим. технология.* 2018. Т. 61. Вып. 9-10. С. 15–22

For citation:
Tukumova N.V., Usacheva T.R., Thuan Tran Thi Dieu, Sharnin V.A., Giancola C. Stability of coordination compounds of some d-metal ions with succinic acid anion in aqueous-ethanol solvents. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 9-10. P. 15–22

INTRODUCTION

Quantitative account of the solvent composition influence on the complex formation reactions is the scientific basis of the selection of the solvent to obtain new complexes with prescribed thermodynamic properties. The estimation of the influence of mixed solvent composition on the thermodynamic solvation parameters of reagents and products (ΔG, ΔH, ΔS), and the derivation of proper relationships between their solvation parameters and those of reaction, allow to devise predictive models for complex formation reactions. Studies of the complex formation reaction of *d*-metal ions with amine, carboxylate and crown-ethers [1-8] as well as molecular complexes of crown-ether with amino acids and peptides [9, 10] have revealed several general rules governing thermodynamics of reactions and solvation of the reagents in aqueous-organic solvents. These rules have shown the possibility of predicting the thermodynamic parameters of complex formations in different media according to a change in the solvation state of ligands.

The study of complex formations between d-metal and bioligand in solvents is important to understand an impact of different media on the interactions in living systems. In particularly a wide practical application of succinic acid (fig.1) requires comprehensive study of its interactions in solutions [11].

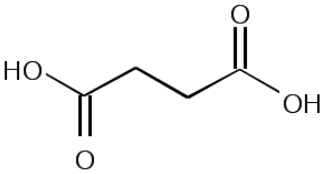

Fig. 1 Structural formula of succinic acid
Рис. 1. Структурная формула янтарной кислоты

Succinic acid anions are capable to forming coordination compounds with ions of microelements, which play an important role in the biological processes. For this purpose, this paper provides an overview of own data on complex formation of Ni^{2+}, Co^{2+} and Cu^{2+} ions (M^{2+}) with succinic acid anions in water-organic mixed solvents [12-16]. Proper data are compared with data reported in literature for akin compounds [3, 4, 7, 8, 17-22].

DISCUSSION

The effect of aqueous ethanol solvent compositions on the stability of coordination compounds of M^{2+} with succinic acid anion as well as on pK values of stepwise succinic acid dissociation was carried out by a potentiometric titration at ionic strength of 0.1 maintained with sodium perchlorate at 298.15 ± 0.10 K. [12-16]. The content of ethanol in mixed solvent was 0.0, 0.1, 0.3, 0.5 and 0.7 mole fractions. Succinic acid did not dissolve at larger ethanol concentrations. The stability of coordination compounds was studied at the ratio $M^{2+} : H_2L = 1:1$. Mathematical treatment of experimental data was performed using PHMETR universal software destined to calculate equilibria with arbitrary number of chemical processes in solution [23].

The following reactions for a system containing succinic acid (H_2L), $M(ClO_4)_2$ and $NaClO_4$ are supposed: acid–base equilibria of H_2L (1, 2), reaction of M^{2+} with the products of dissociation of succinic acid (3–5) and with hydroxide ion (6), as well as water dissociation (7).

$$H_2L \Leftrightarrow H^+ + HL^- \quad (1)$$
$$HL^- \Leftrightarrow H^+ + L^{2-} \quad (2)$$
$$M^{2+} + HL^- \Leftrightarrow [MHL]^+ \quad (3)$$
$$M^{2+} + L^{2-} \Leftrightarrow [ML] \quad (4)$$
$$M^{2+} + 2L^{2-} \Leftrightarrow [ML_2]^2 \quad (5)$$
$$M^{2+} + OH^- \Leftrightarrow MOH^+ \quad (6)$$
$$H_2O \Leftrightarrow H^+ + OH^- \quad (7)$$

The pK values of stepwise succinic acid dissociation reports the Table 1. The pK values for both steps increase monotonically with the increase of EtOH content in solution.

Table 1

Values of pK for succinic acid dissociation at T = 298.15K and I =0.1 ($NaClO_4$) in aqueous – ethanol solutions [16]

***Таблица 1.* Значения pK диссоциации янтарной кислоты при T = 298,15K и ионной силе I =0,1 ($NaClO_4$) в водно-этанольных растворителях [16]**

mol.fr.	pK_1	pK_2
0.0	4.04 ± 0.02	5.48 ± 0.04
0.1	4.22 ± 0.05	5.96 ± 0.04
0.3	4.73 ± 0.04	6.02 ± 0.04
0.4	5.05 ± 0.06	6.44 ± 0.02
0.5	5.17 ± 0.06	6.57 ± 0.04
0.7	5.63 ± 0.06	7.00 ± 0.02

There are no literature data on the values of hydrolysis constants for M^{2+} (pK_{MOH+}) in aqueous-ethanol solutions (eq.6). The yield of MOH^+ particles in water did not exceed 1%. Therefore the literature data $pK_{NiOH+} = 9.86$, $pK_{CoOH+} = 8.96$ and $pK_{CuOH+} = 9.86$ [24] obtained in aqueous solutions were used in PHMETR calculation in H_2O-EtOH solvents. We recalculated the equilibrium constant for the reaction (7) at zero ionic strength [25] by equation with one individual parameter for ionic strength 0.1 and taking into account the process of water ionization in aqueous - ethanol solvents [26]. The mathematical treatment of experimental data showed that the process (4) prevails at all range of ethanol concentrations. Increasing of pH lead to an increase the [ML] species yield. The maximal yields of $[MHL]^+$ and $[ML_2]^{2-}$ species were not exceed 3%, which no provides a possibility to obtain reliable of $lg\beta_{[MHL]}{}^+$ and $lg\beta_{[ML2]}{}^{2-}$ values under these conditions.

Values of $lg\beta_{[NiL]}$, $lg\beta_{[CoL]}$ and $lg\beta_{[CuL]}$ at different content of ethanol are given in the Table 2. The literature data on $lg\beta_{[NiL]}$ and $lg\beta_{[CoL]}$ in water are rather contradictory. The experimental conditions are completely consistent with ours only in the paper [17], but the $lg\beta_{[NiL]}$ value is given without an error and it is significantly different from our result. In the papers [18-22] a nitrate background electrolyte is used.

Table 2

Stability of mono-ligand complexes of Ni^{2+}, Co^{2+} and Cu^{2+} ions with succinic acid anion in aqueous – ethanol solutions at T = 298.15K and I =0.1

***Таблица 2.* Устойчивость моно-лигандных комплексов ионов Ni^{2+}, Co^{2+} и Cu^{2+} с анионом янтарной кислоты в водно-этанольных растворителях при T = 298,15K и I =0,1**

X_{EtOH}, mol.fr.	$lg\beta_{[NiL]}$	$lg\beta_{[CoL]}$	$lg\beta_{[CuL]}$
0.0	1.96 ± 0.06 ($NaClO_4$) [15] 1.60 (NaClO4) [17] 3.17 ± 0.02 ($NaNO_3$) [18] 3.12 ± 0.09 ($NaNO_3$) [19] 1.71 ± 0.03 (KNO_3) [20]	1.64± 0.02 ($NaClO_4$) [15] 1.62 ± 0.03 (KNO_3) [20] 1.50 ± 0.02 (KNO_3) [21] 2.97 ± 0.02 ($NaNO_3$) [18] 1.80 ± 0.06 ($NaNO_3$) [22]	2.98±0.02 ($NaClO_4$) [16] 2.61 [33] 2.59 [34] 3.02 ± 0.01 (KNO_3) [20] 3.20 ($NaNO_3$) [19]
0.1	2.53±0.04 [15]	1.87 ± 0.04 [15]	3.78 ± 0.02[16]
0.3	3.02±0.04 [15]	2.67 ± 0.04 [15]	5.20 ± 0.04[16]
0.4	3.33±0.04 [15]	3.20 ± 0.04 [15]	6.01 ± 0.06[16]
0.5 [15]	3.65±0.04	3.41 ± 0.06	-
0.7 [15]	4.23±0.06	3.60 ± 0.02	-

In aqueous solutions Cu^{2+} ion forms stronger complexes with succinic and maleic acid anions than Ni^{2+} and Co^{2+} ions. This fact is in the agreement with the Irving-Williams series ($Zn^{2+} < Cu^{2+} > Ni^{2+} > Co^{2+}$). In the studied water - ethanol solution this ratio is maintained for complexes with succinic acid anion, but a water-isopropanol solvent exerts leveling effect on the stability of complexes of nickel (II) and cobalt (II) [14] (Fig. 2).

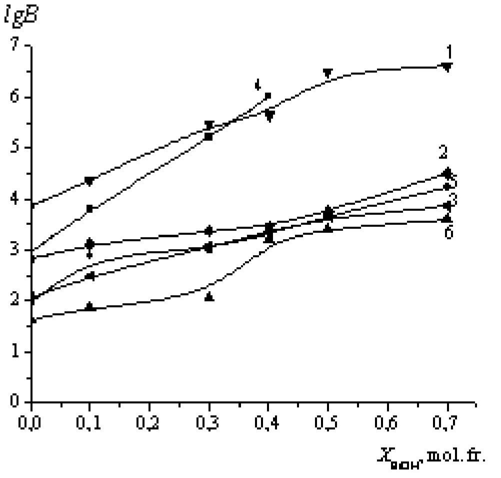

Fig. 2. Dependenses of the logarithm of the stability constants of coordination compounds of cooper (1), nickel (2), and cobalt (3) ions with maleic acids anions [12,13] and cooper (4), nickel (5), and cobalt (6) ions with succinic acids anions [15,16]

Рис. 2. Зависимость логарифма константы устойчивости координационных соединений ионов меди (1), никеля (2) и кобальта (3) с анионами малеиновой кислоты [12,13], ионов меди (4), никеля (5) и кобальта (6) с анионами янтарной кислоты [15,16]

Increase in the content of ethanol in solution leads to the growth of [ML] complexes stability (Table 2.). Aqueous-ethanol solvent has similar effect on the stability of mono ligand Cu^{2+}, Co^{2+}, Ni^{2+} complexes with ethylenediamine [7], as well as with anions of maleic acid [13], aminoacetic acid [6, 3], acetic acid [4, 27], and with ammonium ion [8, 5].

That solvent influences solvation and complex formation equilibria of ions and individual molecules is a well known fact. In this way, the reactivity of each participant strongly depends on the chemical nature and the composition of mixed solvents. When the solution medium is a mixture of two or more solvents, the phenomenon of preferential solvation may take place, in which the solvation shell of the solute has a composition different from that of the bulk solvent mixture, and models for its calculation have been proposed [28, 29].

It is noticed, that solvatecomplex of metals make a basis of coordination chemistry as they are present at all stages of transformation of complexes of metals at solutions. The effects of mixed solvent composition and of the preferential solvation on the change in the solvation state of metal ions have been studied in [29 - 32].

Universal interpretation of the coordination compound stability changes in mixed solvents is the application of a solvation approach which takes into account all changes in reagent's solvation states [28]. Thereby, the influence of the solvent composition changes on the thermodynamic reaction parameters and the reagent's solvation (Z) can be quantitatively described by the equations:

$$\Delta_{tr}Y_r = \Delta_r Y_{(s)} - \Delta_r Y_{(H_2O)} \qquad (8)$$

$$\Delta_{tr}Y\,(Z) = Y(Z)_{\,(s)} - Y(Z)\,Y(Z)_{(H_2O)} \qquad (9)$$

where $\Delta_r Y_{(s)}$ and $\Delta_r Y_{(H_2O)}$ are the thermodynamic parameters (ΔG, ΔH, $T\Delta S$) of a complex formation reaction, and $Y_{(s)}$ and $Y_{(H_2O)}$ are the thermodynamic parameters of reagents solvation in mixed solvent and in H_2O, respectively.

The solvent influence on the reaction thermodynamic parameters changes can be also expressed in terms of the solvation contributions ($\Delta_{tr}Y$) of all participants by the equation:

$$\Delta_{tr}Y_r = \Delta_{tr}Y([ML]) - \Delta_{tr}Y(L^{2-}) - \Delta_{tr}Y(M^{2+}) \qquad (10)$$

To apply eq. (10), the solvation thermodynamic parameters of reagents ($\Delta_{tr}Y(M^{2+})$, $\Delta_{tr}Y(L^{2-})$) and complex $\Delta_{tr}Y([ML])$ must be known.

The equation (9) and the data of the Table 2 were used to calculate the Gibbs energy transfer values form water into water-ethanol mixtures ($\Delta_{tr}G^0_r$) for the [CuL], [CoL] and [NiL] complex formation reactions. A complete analysis of the reagents solvation contributions into the $\Delta_{tr}G^0_r$ by the equation (10) is not possible now due to the absence of $\Delta_{tr}G^0$ values for succinic acid anion ($\Delta_{tr}G^0(L^{2-})$), and also those for Co^{2+} ($\Delta_{tr}G^0$ (Co^{2+})). The $\Delta_{tr}G^0_r$([NiL]) and $\Delta_{tr}G^0_r$([CoL]) values are close each other form 0.0 up to 0.5 mole fractions of ethanol (Fig. 3). The value of $\Delta_{tr}G^0_r$([NiL]) is more exothermic than $\Delta_{tr}G^0_r$([CoL]) at the 0.7 ethanol mole fraction.

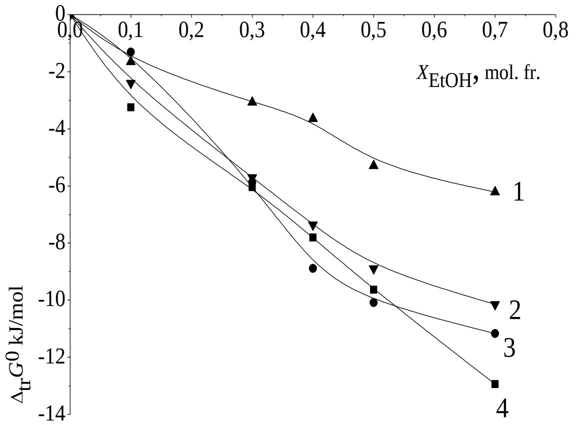

Fig. 3. Dependence of Gibbs energy changes for the transfer of formation reactions of coordination compounds of Ni^{2+} (1, 4) and Co^{2+} (2, 3) ions with maleic acid anion (1 [13], 2 [12]) and with succinic acid anion (3, 4) [15] from water into aqueous ethanol solutions

Fig. 3. Зависимость изменения энергии Гиббса при переносе реакции образования координационных соединений ионов Ni^{2+} (1, 4) и Co^{2+} (2, 3) с анионом малеиновой кислоты (1 [13], 2 [12]) и с анионом янтарной кислоты (3, 4) [15] из воды в водно-этанольные растворители

The Gibbs energy changes for the [NiL] and [CuL] complex formation reaction and for the Ni^{2+} and Cu^{2+} ions solvation in H_2O-EtOH mixtures are presented in Fig. 4 and Fig.5. The solvation-thermodynamic analysis of the cooper acetate (II) complex formation reaction in aqueous ethanol showed that the contribution from the acetate ion desolvation $\Delta_{tr}G^0(Acet^-)$ into $\Delta_{tr}G^0_r$ is about 10 kJ/mol at the transfer from water to H_2O-EtOH solvent with 0.3 mole fraction of EtOH [27].

In accordance with an additive method it can be estimate a solvation contribution of the succinic acid anion as a double contribution from acetate ion solvation ($2\Delta_{tr}G^0$ ($Acet^-$)). The contributions from the Ni^{2+} and Cu^{2+} solvation state are not favor to increasing the stability of their complexes with maleic and succinic acid anions.

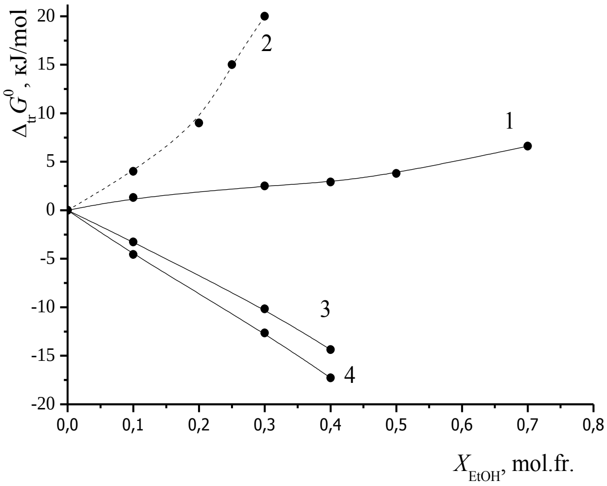

Fig. 4. Thermodynamic characteristics of Cu^{2+} complexation with succinic (L^{2-}) and maleic (Y^{2-}) acid anions in water-ethanol solvents:1 – $\Delta_{tr}G^0$ (Cu^{2+}) [29]; 2 – double contribution from acetate ion solvation ($2\Delta_{tr}G^0$ ($Acet^-$)) assumed as succinic acid anion contribution;3 – $\Delta_{tr}G^0_r$ for [CuY] complex formation [16]; 4 – $\Delta_{tr}G^0_r$ for [CuL] complex formation [16]

Рис. 4. Термодинамические характеристики комплексообразования Cu^{2+} с анионами янтарной (L^{2-}) и малеиновой (Y^{2-}) кислот в водно-этанольных растворителях: 1 – $\Delta_{tr}G^0$ (Cu^{2+}) [29]; 2 – удвоенный сольватационный вклад ацетат-иона ($2\Delta_{tr}G^0$ ($Acet^-$)), принятый равным сольватационному вкладу аниона янтарной кислоты; 3 – $\Delta_{tr}G^0_r$ для реакции образования комплекса [CuY] [16]; 4 – $\Delta_{tr}G^0_r$ для реакции образования комплекса [CuL] [16]

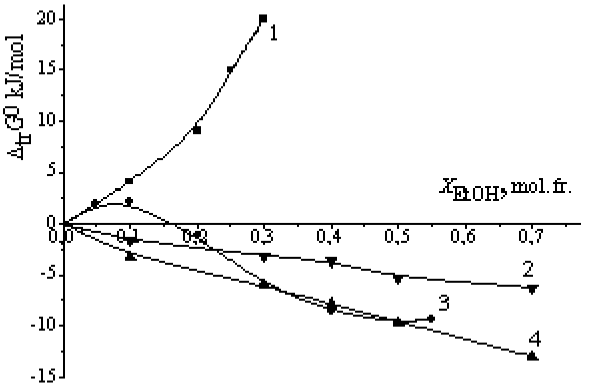

Fig. 5. Thermodynamic characteristics of Ni^{2+} complexation with succinic (L^{2-}) and maleic (Y^{2-}) acid anions in water-ethanol solvents:1 – double contribution from acetate ion solvation ($2\Delta_{tr}G^0$ ($Acet^-$)) assumed as succinic acid anion contribution; 2 – $\Delta_{tr}G^0_r$ for [NiY] complex formation [13]; 3 – $\Delta_{tr}G^0$ (Ni^{2+}) [29]; 4 – $\Delta_{tr}G^0_r$ for [NiL] complex formation [15]

Рис. 5. Термодинамические характеристики комлексообразования Ni^{2+} с анионами янтарной (L^{2-}) и малеиновой (Y^{2-}) кислот в водно-этанольных растворителях:1 – удвоенный сольватационный вклад ацетат-иона ($2\Delta_{tr}G^0$ ($Acet^-$)) принятый равным сольватационному вкладу аниона янтарной кислоты; 2 – $\Delta_{tr}G^0_r$ для реакции образования комплекса [NiY] [13]; 3 – $\Delta_{tr}G^0$ (Ni^{2+}) [29]; 4 – $\Delta_{tr}G^0_r$ для реакции образования комплекса [NiL] [15]

CONCLUSIONS

It can be assumed that an increase in the stability of complexes of cooper, cobalt and nickel with anions of maleic and succinic acids with increasing ethanol concentration is due to the destabilization of the ligand. The principal contribution of the changes in the solvation state of ligand is a typical for the stability changes of *d*-metal complexes with amine [7], glycinate [3], and acetate [4] type ligands in water-organic mixed solvents.

This study was performed at the Research Institute of Thermodynamics and Kinetics of Chemical Processes of the Ivanovo State University of Chemistry and Technology.

ACKNOWLEDGMENT

Dr. T.R. Usacheva and prof. C. Giancola thank the University of Naples Federico II for the financial support of their collaboration contributed to the preparation of this paper.

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Поступила в редакцию 17.04.2018
Принята к опубликованию 15.05.2018

Received 17.04.2018
Accepted 15.05.2018