Electrolytic nickel plating is a widespread process in galvanotechnics. This is predetermined by the presence of a complex of valuable properties of nickel-based galvanic precipitation. Thus, machine-building industry constantly demands corrosion-resistant, hard, and wear-resistant coatings. Modern electrotechnical production requires plastic, non-strained protective coatings, which can be soldered. Development of hydrogen energy generation initiates improvement of the technologies for obtaining catalytically-active materials. High decorative characteristics of nickel coatings render leading positions to nickel plating in finishing the fittings, accessories, car emblems, jewelry production. Nickel dispersions are used in the manufacture of complex metal parts using 3D printers.

One of the directions of development of electrochemical nickel plating is the use of electrolytes containing carboxylic acids. High buffer properties of carboxylic acids damp changes in pH of the electrolyte near the electrode. This enables enhancement of the working density of nickel deposition current. In addition, in the presence of carboxylic acids in the electrolyte, nickel ions bind in complexes. The latter is used to control the speed of the charge and crystallization conditions of the cathode sediment.

Thus, there is no doubt about the relevance of studying special features of chemical and electrochemical stagnation...
es of electroreduction of monosubstituted forms of nickel aqua-complexes with carboxylic acids as the basic component of the complex nickel plating electrolytes.

2. Literature review and problem statement

Kinetic characteristics of nickel ions electroreduction and the properties of the obtained precipitation are determined, first of all, by the composition of the nickel plating electrolyte. The need to intensify the process of nickel deposition led the scientific community to explore the new types of electrolytes. One of the variants to modify the process is to use complex electrolytes. During alloys electrodeposition, the presence of complexes is required for the convergence of stationary potentials of the separation of components of the alloy [1, 2]. The introduction of carboxylic acids to the nickel plating electrolyte affects the kinetics of electroreduction of nickel ions. The process of deposition of nickel-based coatings is largely dependent on the buffer properties of electrolyte [3–5] and the stability of complex ion compounds [6].

The electrodeposition of nickel from aqueous solutions is accompanied by a parallel course of hydrogen evolution reaction. The result is an increase in the pH of a near-electrode layer. The elevated pH values may lead to the formation of insoluble hydroxide nickel compounds [7]. The introduction of such compounds to the cathode sediment has a negative impact on the quality of nickel coatings. Authors of [8] showed that the use of sodium citrate as a buffer supplement makes it possible to obtain fine-crystalline compact nickel precipitation at high current output values. Authors of [9] proposed sodium gluconate as the buffer additive. To increase the limit current density of the nickel deposition, authors of [10] introduced amber acid to the nickel plating electrolyte. In the amber-acid electrolyte almost all acid is associated with a nickel complex [NiH(Succ)\textsuperscript{2+}]. High buffer capacity of solutions is provided by the dissociation of these compounds.

One of carboxylic acids that are often used in electrolytes for the electrodeposition of metals and alloys is glycine (H\textsubscript{2}Gly) [11–14]. In [15], authors studied buffer properties of acetate, sulfate and chloride glycine-containing nickel plating electrolytes. It was shown that different forms of amino acid and background anions act in a solution as two buffer systems. Buffer properties of the electrolyte are the additive magnitude of the action of these systems.

Authors of [16] note that in addition to the buffer action, carboxylic acids affect the kinetics of electrodeposition of nickel through complex-formation. It was established that the electrolyte composition of nickel form monosubstituted nickel(II) aqua-complexes; this will make it possible to conduct predictable optimization of compositions of the complex nickel plating electrolytes in order to ensure high performance of the process of nickel electrodeposition.

To achieve the set aim, the following tasks have been solved:

- using a quantum-chemical modeling, to identify the nature of intermediates and to determine thermodynamically possible pathways of electroreduction of monosubstituted nickel aqua-complexes with propionic and acrylic acids;
- to establish kinetic peculiarities of nickel electrodeposition in the presence of propionic and acrylic acids, and to compare empirical data to the results of quantum-chemical calculations.

3. The aim and objectives of the study

The aim of present work was to establish influence of the nature of carboxylic acid on the chemical and electrochemical stages of the process of electroreduction of monosubstituted nickel(II) aqua-complexes. This will make it possible to conduct predictable optimization of compositions of the complex nickel plating electrolytes in order to ensure high performance of the process of nickel electrodeposition.

To achieve the aim, the following tasks have been solved:

4. Materials and methods for research into nickel electrodeposition from the complex electrolytes

Quantum-chemical simulation was performed using non-empirical methods of the software WinGAMESS [18]. Cluster systems were calculated using the spin-unlimited Hartree-Fock method. The central atom of a metal was described by the basis 6-31G**, atoms of the ligands – by the basis 6-311G. We employed a hybrid B3LYP method from the density functional theory, which includes five functionals: exchange functionals by Becke, Slater, Hartree-Fock, as well as LYP and VWN5 correlation functionals [19]. During modelling, we optimized the examined ions surrounded by a first solvate shell and estimated energies of the optimized complexes. Next, the energies were refined taking into consideration the solvation using a polarization continuum model [20].

Using the DFT theory, in particular the hybrid potential B3LYP, significantly improves the convergence of results [20]. The application of the heavier full-electron basis 6-31G of the central atom markedly worsens the correlation convergence of results. More accurate results were obtained when using a central atom of the basis CRENBL ECP. For \textit{Ni}\textsuperscript{2+} cation, we calculated energies in the high-spin and low-spin states.

Polarization measurements were carried out using the potentiostat PI-50-1 (Belarus) in a set with the programmer PR-8 (Belarus). Electrochemical studies were conducted in a three-electrode glass cell. We used the USB-oscilloscope (Ukraine) as a recording device, connected to a Pentium Celeron computer (USA). We used a gold working electrode during research. The end of the gold rod, pressed in Teflon, with a cross-sectional area of 0.4 cm\textsuperscript{2} served as the electrode. The preparation of the electrode before the research involved polishing by a suspension of magnesium oxide and washing with bidistilled water.

Empirical studies were conducted in the electrolytes containing, as a background, a single molar solution of sodium perchlorate. The source of nickel ions was nickel.
perchlorate. To prepare the solutions we used chlorine acid (60%) and nickel carbonate of the qualification (p. a.). Propionic (HPr) and acrylic (HAc) acids were in conformity with the qualification (pur.). PH values of the solutions were brought to the preset value with a solution of sodium hydroxide. Acidity of the solutions was controlled using the universal ionomer EV-74 (Belarus).

5. Results of research into nickel electrodeposition from the electrolytes containing propionic and acrylic acids

To establish the role of complexation in the process of nickel electrodeposition, we examined propionic and acrylic acids. Dissociation constants of these acids are $1.34 \times 10^{-3}$ and $5.53 \times 10^{-5}$, respectively [21]. Therefore, the buffer properties of solutions of propionic and acrylic acids are close. Unification of the pH magnitude of a near-electrode layer makes it possible to run a comparative analysis of the impact of these acids on the kinetics of nickel electrodeposition from the standpoint of structure and electrochemical behavior of the corresponding complexes with nickel.

Results of the energy estimation of possible structures of monosubstituted nickel(II) aqua-complexes are shown in Fig. 1, a. The introduction of anions of propionic acid to the composition of an aqua-complex results in the offset of energy values towards negative side for the particles containing four molecules of water in the inner coordination sphere. Thus, the dominant form of the system is the pentaligand complexes of nickel.

Thus, the energy of complex $[\text{Ni}^{2+}(\text{H}_2\text{O})_4\text{Pr}^-]$ exceeds the energy of complex $[\text{Ni}^{2+}(\text{H}_2\text{O})_3\text{Pr}^-]$ by the magnitude equal to $33.61 \text{kJ/mol}$. At the same time, a difference in the energies of complexes $[\text{Ni}^{2+}(\text{H}_2\text{O})_3\text{Pr}^-]$ and $[\text{Ni}^{2+}(\text{H}_2\text{O})_4\text{Pr}^-]$ is $111.06 \text{kJ/mol}$.

It should be noted that a decrease in the coordination number of energetically favorable form of nickel aqua-complexes is not the consequence of bidentate of the carboxyl group of the propionate ion (Fig. 2, a).

The highest occupied molecular orbital is shown in the transient particles and in the intermediate.

Assume that an incomplete electroreduction of complex $[\text{Ni}^{2+}(\text{H}_2\text{O})_4\text{Pr}^-]$ with a participation of one electron occurs with the formation of transitional particle $[\text{Ni}^{2+}(\text{H}_2\text{O})_3\text{Pr}^-]^*$ (Fig. 2, b). The quantum-chemical calculation shows that the total charge of water molecules changes from $+0.120$ to $-0.427$ (Table 1). Therefore, there occurs the acceptance of charge by water molecules.

**Table 1**

| Structure element | $z$=+2, $n$=4 | $z$=+1, $n$=4 | $z$=+1, $n$=3 | $z$=0, $n$=3 | $z$=0, $n$=1 |
|------------------|--------------|--------------|--------------|--------------|--------------|
| Ni               | +1.526       | +1.309       | +1.318       | +0.507       | -0.247       |
| H$_2$O           | +0.015       | -0.108       | -0.040       | -0.021       | +0.038       |
| H$_2$O$_2$       | +0.049       | -0.102       | +0.128       | -0.102       | -          |
| H$_2$O$_3$       | +0.015       | -0.108       | -0.06        | +0.226       | -          |
| H$_2$O$_4$       | +0.041       | -0.109       | -            | -            | -          |
| H$_2$O$_5$       | -            | -            | -            | -            | -          |
| Pr               | -0.646       | -0.882       | -1.346       | -1.610       | -0.791       |
| $\Sigma q(\text{H}_2\text{O})$ | +0.120 | -0.427       | +0.028       | +0.103       | +0.038       |

According to the estimated data (Table 1), the electron is localized on a nickel ion in the case of dehydration of the inner coordination sphere of transition particle $[\text{Ni}^{2+}(\text{H}_2\text{O})_3\text{Pr}^-]^*$. This process is energetically favorable and proceeds with heat release (Fig. 1, b):

$$[\text{Ni}^{2+}(\text{H}_2\text{O})_4\text{Pr}^-]^- \rightarrow [\text{Ni}^{2+}(\text{H}_2\text{O})_3\text{Pr}^-]^* + \text{H}_2\text{O} \Delta E = -25.47 \text{kJ/mol}.$$
Also, energetically favorable is the process of reduction of the intrasphere water molecules of the transient particle:

\[
\begin{align*}
[Ni^{2+}(H_2O)_6]^+ + e^- & \rightarrow [Ni^{2+}(H_2O)_6]^{2+} + H_2O \\

E & = -124.6 \text{ kJ/mol.}
\end{align*}
\]  

(5)

It is energetically possible to bind acrylic acid in molecular form into a complex:

\[
\begin{align*}
[Ni^{2+}(H_2O)_6] + HAk & \rightarrow [Ni^{2+}(H_2O)_6(HAk)] + H_2O \\

E & = -48.4 \text{ kJ/mol.}
\end{align*}
\]  

(6)

At pH 3–4, nickel plating electrolyte is dominated by the complexes of nickel with acrylate-ions (Fig. 4, a). The transfer of the first electron to the external unoccupied orbital of acrylate complex \([Ni^{2+}(H_2O)_6(Ak)]\) results in the following transformations. The bond of acrylate-ion with the carboxyl oxygen is strengthened (Ni-O distance is reduced from 2.032 Å to 1.886 Å). The energy of bond with one intrasphere water molecule is somewhat increased.

Transitional structure \([Ni^{2+}(H_2O)_6(Ak^2-)]\) (Fig. 4, b) retains the geometry of the starting complex \([Ni^{2+}(H_2O)_6(Ak)]\). The assimilated electron is localized on the vinyl fragment of acrylate-ion.

Dependent on the multiplicity, the magnitudes of charges on central atoms somewhat change. However, the charge on nickel in the transition complex (+1.473) is close to the corresponding magnitude in complex \([Ni^{2+}(H_2O)_6(Ak)]\) (+1.650).

According to the energy chart (Fig. 3, b), a steady intermediate is particle \([Ni^{+}(H_2O)_6(Ak)]\). The cleavage of three molecules of water at its formation makes it possible for the electron to take one of the orbitals of \(Ni^{2+}\) ion and to convert it into the reduced form of \(Ni^{2+}\) (Fig. 4, c).

The charge of the central atom of the formed intermediate \([Ni^{+}(H_2O)_6(Ak)]\) reduces to +0.645, while the charge localized on acrylate-ion becomes equal to –0.54.

The process of restructuring the inner coordination sphere of the partially reduced nickel complexes is accompanied by an additional release of energy:
When transferring the second electron to intermediate \( \text{Ni}^2+ (\text{H}_2\text{O})_6 \text{(Ak)} \), the charge is localized not on the orbitals of nickel, but on the vinyl fragment of acrylate-ion. An analysis of structures with a lower coordination number of nickel did not reveal more energetically favorable variants than \( \text{Ni}^2+ (\text{H}_2\text{O})_6 \text{(Ak)} \).

\[
\begin{align*}
\text{Ni}^2+ (\text{H}_2\text{O})_6 \text{(Ak)} & \rightarrow \text{Ni}^0 (\text{H}_2\text{O})_6 \text{(Ak)} +3\text{H}_2\text{O} \Delta E=–78.3 \text{kJ/mol.} \\
\end{align*}
\]

6. Discussion of results of research into nickel electrodeposition from the electrolytes containing propionic and acrylic acids

Experimental data on nickel electrodeposition in the presence of propionic and acrylic acids indicate exponential dependence of the potential on current density. Consequently, discharging of nickel ions in the investigated range of potentials proceeds in accordance with the equation of a delay discharge, which is typical for the electrodeposition of nickel [3]. Voltammograms, linearized in semi-logarithmic coordinates, are shown in Fig. 5. The introduction of the examined carboxylic acids to the electrolyte containing nickel ions leads to a decrease in the kinetic constraints for the isolation of nickel.

A possible reason is a varying degree of blocking the cathode surface with hydroxide nickel compounds in the examined electrolytes. This process is most pronounced in the surface of cathode with hydroxide nickel compounds in the examined carboxylic acids, is very difficult. This is possibly due to the blocking of nickel from the electrolyte, not containing carboxylic acids, is very difficult. This is possibly due to the blocking of nickel from the electrolyte containing nickel ions leads to a decrease in the kinetic constraints for the isolation of nickel.

When transferring the second electron to intermediate \( \text{Ni}^2+ (\text{H}_2\text{O})_6 \text{(Ak)} \), the charge is localized not on the orbitals of nickel, but on the vinyl fragment of acrylate-ion. An analysis of structures with a lower coordination number of nickel did not reveal more energetically favorable variants than \( \text{Ni}^2+ (\text{H}_2\text{O})_6 \text{(Ak)} \).

\[
\begin{align*}
\text{Ni}^2+ (\text{H}_2\text{O})_6 \text{(Ak)} & \rightarrow \text{Ni}^0 (\text{H}_2\text{O})_6 \text{(Ak)} +3\text{H}_2\text{O} \Delta E=–78.3 \text{kJ/mol.} \\
\end{align*}
\]

Fig. 5. Voltammograms of nickel isolation at pH 3 from the electrolyte: 1 — 1 M \( \text{NaClO}_4 \)+0.1 M \( \text{Ni(ClO}_4)_2 \); 2 — 1 M \( \text{NaClO}_4 \)+0.1 M \( \text{Ni(ClO}_4)_2 \)+0.1 M \( \text{HPr} \); 3 — 1 M \( \text{NaClO}_4 \)+0.1 M \( \text{Ni(ClO}_4)_2 \)+0.1 M \( \text{HAk} \)

Special features of the electron structure of transient particles of the propionate nickel complexes indicate the possibility of electroreduction of intrasphere water molecules. This may occur because the transformation stage of transient particles into intermediate is slow. The electroreduction of water leads to an increase in the pH of a near-electrode layer. Under these conditions, it is possible that the insoluble hydroxide compounds of nickel are formed. The latter may block the cathode surface and inhibit the isolation of nickel.

During nickel electrodeposition from the acrylate complexes, the electroreduction of intrasphere water molecules is not energetically favorable. Therefore, in this case, a change in the pH of a near-electrode layer will be smaller. The specified comparison seems justified because buffer properties of the examined acids are close.

Thus, to interpret experimental data on the kinetics of nickel electrodeposition from the electrolytes containing carboxylic acids, we applied results of the quantum-chemical calculations. We noted a satisfactory correlation between the effects observed in the experiment and those expected based on the simulation. The advantage of using quantum-chemical calculations is the possibility to establish the nature of intermediate particles whose detection in situ is difficult. At the same time, reliability of the simulation results depends on taking into consideration the maximum quantity of influencing factors. Consequently, empirical and estimated data are complementary.

7. Conclusions

1. By using quantum-chemical calculations, it was established that the coordination number of the nickel acrylate complex is six. For the case of the propionate nickel complex, an energetically favorable form is the pentaligand complex.

2. It was found that during electroreduction of the propionate nickel complex the charge is localized on the water molecules of an intermediate particle. This can lead to the electroreduction of an intrasphere molecule of water, which is accompanied by an increase in the pH of the electrolyte. In the acrylate complex, the localization of a charge occurs on the vinyl fragment of acrylate-ion. Electrochemical reaction of reduction of the coordinated water molecules in such a particle is not energetically favorable.

3. Voltammetric studies have shown that the isolation of nickel from the electrolyte, not containing carboxylic acids, is very difficult. This is possibly due to the blocking of the cathode surface with insoluble hydroxide compounds of nickel. In the absence of a buffer additive, pH of the near-electrode layer increases due to the occurring reaction of hydrogen evolution. The introduction to the electrolyte of the examined carboxylic acids partly reduces this effect. Acrylic acid contributes to the greater activation of nickel isolation than propionic acid. Because the buffer properties of these acids are close, the observed difference in the kinetics of nickel electrodeposition is explained by the peculiarities of electron structure of the transient particles containing acrylate- and propionate-ions.

References

1. Karakurkchi, A. V. Electrochemical deposition of Fe–Mo–W alloy coatings from citrate electrolyte [Text] / A. V. Karakurkchi, M. V. Ved', I. Yu. Yermolenko, N. D. Sahhnenko // Surface Engineering and Applied Electrochemistry. – 2016. – Vol. 52, Issue 1. – P. 43–49. doi: 10.3103/s1068375516010087

2. Karakurkchi, A. V. Functional properties of multicomponent galvanic alloys of iron with molybdenum and tungsten [Text] / A. V. Karakurkchi // Functional materials. – 2015. – Vol. 22, Issue 2. – P. 181–187. doi: 10.15407/fm22.02.181

3. Danilov, F. I. Kinetics of nickel electroplating from methanesulfonate electrolyte [Text] / F. I. Danilov, I. V. Sknar, Yu. E. Sknar // Russian Journal of Electrochemistry. – 2011. – Vol. 47, Issue 9. – P. 1035–1042. doi: 10.1134/s1023193511090114
4. Danilov, F. I. Electrodeposition of nickel-based nanocomposite coatings from cerium(III)-ion-containing methanesulfonate electrolytes [Text] / F. I. Danilov, Yu. E. Sknar, I. G. Tkach, I. V. Sknar // Russian Journal of Electrochemistry. – 2015. – Vol. 51, Issue 4. – P. 294–298. doi: 10.1134/s1023193515040023

5. Danilov, F. I. Kinetics of electrodeposition of Ni–ZrO2 nanocomposite coatings from methanesulfonate electrolytes [Text] / F. I. Danilov, Yu. E. Sknar, N. V. Amirulloeva, I. V. Sknar // Russian Journal of Electrochemistry. – 2016. – Vol. 52, Issue 5. – P. 494–499. doi: 10.1134/s1023193516050037

6. Mech, K. Influence of organic ligands on electrodeposition and surface properties of nickel films [Text] / K. Mech // Surface and Coatings Technology. – 2017. – Vol. 315. – P. 232–239. doi: 10.1016/j.surfcoat.2017.02.042

7. Balakai, V. I. Alkalization of the near-cathode layer in electrodeposition of nickel from a chloride electrode [Text] / V. I. Balakai, A. V. Arzumanova, K. V. Balakai // Russian Journal of Applied Chemistry. – 2010. – Vol. 83, Issue 1. – P. 65–71. doi: 10.1134/s1070427210010143

8. Li, C. Nickel electrodeposition from novel citrate bath [Text] / C. Li, X. Li, Z. Wang, H. Guo // Transactions of Nonferrous Metals Society of China. – 2007. – Vol. 17, Issue 6. – P. 1300–1306. doi: 10.1016/s1003-6326(07)60266-0

9. Rudnik, E. Effect of gluconate addition on the electrodeposition of nickel from acidic baths [Text] / E. Rudnik, M. Wojnicki, G. Wloch // Surface and Coatings Technology. – 2012. – Vol. 207. – P. 375–388. doi: 10.1016/j.surfcoat.2012.07.027

10. Sedoikin, A. A. The role of migration mass transfer in the electrodeposition of nickel from sulfate-chloride and chloride solutions containing succinic acid [Text] / A. A. Sedoikin, T. E. Tsupak // Russian Journal of Electrochemistry. – 2008. – Vol. 44, Issue 3. – P. 319–326. doi: 10.1134/s1023193508030099

11. Ibrahim, M. A. M. Role of Glycine as a Complexing Agent in Nickel Electrodeposition from Acidic Sulphate Bath [Text] / M. A. M. Ibrahim, R. M. Al Radadi // Int. J. Electrochem. Sci. – 2015. – Vol. 10. – P. 4946–4971.

12. Mosavat, S. H. Electrodeposition of nanocrystalline Zn–Ni alloy from alkaline glycinate bath containing saccharin as additive [Text] / S. H. Mosavat, M. E. Bahrololoom, M. H. Shariat // Applied Surface Science. – 2011. – Vol. 257, Issue 20. – P. 8311–8316. doi: 10.1016/j.surfcoat.2011.03.017

13. Nagai, T. Relationship between film composition and microhardness of electrodeposited Ni–W–B films prepared using a citrate–glycinate bath [Text] / T. Nagai, K. Hodouchi, H. Matsubara // Surface and Coatings Technology. – 2014. – Vol. 253. – P. 109–114. doi: 10.1016/j.surfcoat.2014.03.022

14. Ergeneman, O. Morphology, structure and magnetic properties of cobalt–nickel films obtained from acidic electrolytes containing glycine [Text] / O. Ergeneman, K. M. Sivaraman, S. Pané, E. Pellicer, A. Teleki, A. M. Hirt et. al. // Electrochimica Acta. – 2011. – Vol. 56, Issue 3. – P. 1399–1408. doi: 10.1016/j.electacta.2010.10.068

15. Dolgikh, O. V. The influence of the nature of background anions on the buffer capacity of glycine-containing electrolytes for nickel electroplating [Text] / O. V. Dolgikh, V. T. Zuen, N. V. Sotskaya // Russian Journal of Physical Chemistry A. – 2009. – Vol. 83, Issue 9. – P. 939–944. doi: 10.1134/s0036024409060120

16. Taranina, O. A. Electrodeposition of nickel from sulfate solutions in the presence of aminoacetic acid [Text] / O. A. Taranina, N. V. Evreinova, I. A. Shoshina, V. N. Narayev, K. I. Tikhonov // Russian Journal of Applied Chemistry. – 2010. – Vol. 93, Issue 1. – P. 58–61. doi: 10.1134/s107042721001012x

17. Sotskaya, N. V. Nickel electroplating from glycine containing baths with different pH [Text] / N. V. Sotskaya, O. V. Dolgikh // Protection of Metals. – 2008. – Vol. 44, Issue 5. – P. 479–486. doi: 10.1134/s0033173208050123

18. Foresman, J. B. Solvent Effects. 5. Influence of Cavity Shape, Truncation of Electrostatics, and Electron Correlation on ab Initio Reaction Field Calculations [Text] / J. B. Foresman, T. A. Keith, K. B. Wilberg, J. Snoonian, M. J. Frisch // The Journal of Physical Chemistry. – 1996. – Vol. 100, Issue 40. – P. 16098–16104. doi: 10.1021/jp960488j

19. Cramer, C. J. Density functional theory for transition metals and transition metal chemistry [Text] / C. J. Cramer, D. G. Truhlar // Physical Chemistry Chemical Physics. – 2009. – Vol. 11, Issue 46. – P. 10757. doi: 10.1039/b907148b

20. Seredyuk, V. A. Estimation of reliability of quantum-chemical calculations of electronic transitions in aqua complexes of transition metals [Text] / V. A. Seredyuk, V. F. Vargulyuk // Russian Journal of Electrochemistry. – 2008. – Vol. 44, Issue 10. – P. 1105–1112. doi: 10.1134/s1023193508100042

21. Rabinovich, V. A. Quick reference [Text] / V. A. Rabinovich, Z. Ya. Khavin, A. A. Potekhin, A. I. Efinov (Eds.). – 3-e izd., pererab. i dop. – Leningrad: Himiya, 1991. – 432 p.