The association and complexation equilibria in the system D-glucitol—nickel(II)—water

A. V. Rubanov and F. V. Devyatov*

Kazan (Volga Region) Federal University,
18 ul. Kremlevskaya, 420008 Kazan, Russian Federation.
Fax: +7 (843) 238 7901. E-mail: ARubanov@rambler.ru

A joint study using polarimetry, spectrophotometry, and mathematical modeling revealed the formation of 1 : 1, 2 : 1, and 4 : 4 outer-sphere complexes of nickel(II) ions with neutral D-glucitol (H_6Glc-ol), *viz.*, $\{[Ni(H_2O)_n] \cdot (H_6Glc\text{-}ol)_{aq}\}^{2+}$, $\{[Ni(H_2O)_n]_2 \cdot (H_6Glc\text{-}ol)_{aq}\}^{4+}$, and $\{[Ni(H_2O)_n]_4 \cdot [(H_6Glc\text{-}ol)_{aq}]_4\}^{8+}$ in a weakly acidic medium. In aqueous solutions, D-glucitol forms tetramers. For each form, the constant of formation and the specific optical rotation was calculated.

Key words: D-glucitol, nickel(II), aqueous solution, optical activity, association, tetramer, cluster, outer-sphere complexation, equilibrium constants, mathematical modeling.

At present, D-glucitol ((2*S*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol; H_6Glc-ol; **1**) and other polyols are widely used in pharmacy and cosmetology as well as hydrophilic cosolvents for liquefaction of pigments, dyes, polymers, and vitamins that stabilize compositions and impart them attractive appearance. However, in chemistry of coordination compounds the properties of compound **1** as a ligand have been poorly studied[1] because its donor groups possess weak acidic properties (pK = 13.46).[2] In this connection, it is believed that ligand **1** is poorly competitive with water molecules for positions in the first coordination sphere of the ion of a complex-forming agent in aqueous solutions. Therefore, it is assumed that complexation occurs only at rather high pH values corresponding to deprotonation of the ligand and (simultaneously) hydrolysis of a cation. The latter makes the problem and methodology of complexation studies much more complicated. There are preliminary data[3] on the existence of a 1 : 1 Ni^{II} complex with the molecular form of **1** even at weakly acidic pH values, but the nature of this interaction remains unclear.

In a correct description of complexation, it is first of all necessary to know the state of the ligand **1** and to take into account possible intermolecular associative interactions depending on the concentration of **1**.

Since compound **1** is an optically active hexaatomic alcohol, its state in solution as well as the involvement in complexation can be characterized by polarimetry. The angle of rotation (α) of the polarization plane of plane-polarized light depends on the concentration (C) and on the nature of the optically active substance[4]:

$$[\alpha]^T_\lambda = \alpha \cdot 100/(l \cdot C), \quad (1)$$

where $[\alpha]^T_\lambda$ is the specific rotation (deg mL g^{-1} dm^{-1}), λ is the wavelength (nm) at which the measurement is carried out, T is the temperature (°C), α is the observed rotation (deg), l is the optical path length (dm), and C is the concentration of the optically active substance (g (100 mL)$^{-1}$).

The conformational state and, therefore, the optical activity of compound **1** may change owing to the interaction with a certain component of the system. Each conformer is characterized by its own $([\alpha]^T_\lambda)_i$ value; therefore, $[\alpha]^T_\lambda$ is an additive quantity[5]:

$$[\alpha]^T_\lambda = \sum_{i=1}^{N} ([\alpha]^T_\lambda)_i \cdot \alpha'_i, \quad (2)$$

where α'_i is the contribution of the ith conformer.

This allows polarimetry to be used in the studies on the solvation state and complexation of optically active ligands.[5,6]

The published $[\alpha]^T_\lambda$ values for compound **1** in water refer to particular concentrations. For instance, the value −2.0 (see Ref. 7) was calculated from Eq. (1) for a solution with C = 9 g (100 mL)$^{-1}$ at 20 °C. However, the hydration numbers of polyols are not constants; they abruptly increase on dilution of solutions and can be as high as 25 at a carbohydrate concentration of 0.32 mol.%.[8] As the polyol concentration increases, the hydration number tends to the limiting value for a given polyol; this is a consequence of structural changes, *viz.*, the formation

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1555—1559, August, 2010.
1066-5285/10/5908-1594

of molecular associates of polyols. From Eq. (2) it follows that the value cited (Ref. 7) is the sum of the contributions of all conformers of molecule **1** ignoring association. In this connection, for detailed studies of the optical activity of compound **1** are required in a wide range of concentrations at 25 °C using mathematical methods for processing the experimental data to obtain a quantitative description of association.

In addition, it was found[9] that the relaxation efficiency coefficient[10] of a complex with the neutral form of **1** appeared to be about 17% higher than that of Ni^{II} aqua ion (**2**). The theory of NMR[10] predicts, in particular, such an increase owing to the change in the shortest distance between a proton and a paramagnetic (in this case, the distance should shorten by 2.6% only). This is possible if an outer-sphere complex is formed; here, one or more hydrogen bonds between the intra-sphere water molecules of the aqua ion **2** and hydroxyl groups of compound **1** are involved in the interaction. Thus, one should establish the type (intra-sphere or outer-sphere) of the interactions of compounds **2** and **1** in weakly acidic and neutral regions of pH values.

Experimental

Nickel nitrate $Ni(NO_3)_2$ ("analytically pure" grade), and ligand **1** twice recrystallized from aqueous ethanol were used. The amount of crystallization water was calculated based on the results of elemental analysis. The concentration of aqua ion **2** was determined trilonometrically. All measurements were carried out at a constant temperature of 25.0±0.1 °C. The optical activities of the solutions were determined on a P3002RS Automatic Digital Polarimeter (A. Krüss Optronic GmbH, Germany) Selected operating characteristics of the instrument are as follows: angle range from –45° to +45°, accuracy 0.002°, a 589-nm Na lamp as the source of radiation. The cell length was 20 cm.

Electronic absorption spectra and the optical densities were recorded on a Perkin—Elmer Lambda EZ-210 spectrophotometer in 1-cm cells. The accuracy of the optical density measurements was at least 0.001.

Proton activities were determined on a pH-150M high-resistance potentiometer with an accuracy of 0.02 pH units. The pH-meter was calibrated against standard buffer solutions.

The particle size (effective hydrodynamic diameter) was determined by dynamic light scattering on a Zetasizer Nano ZS (Malvern Instruments Ltd) instrument. Signals were analyzed using the software supplied with the equipment. The measurement error was at most 10%.

Complexation was studied by the shift of equilibrium technique using a series of solutions with different metal : ligand ratio at a constant concentration of **1** (0.1 mol L^{-1}).

The dependences of the experimental $[\alpha]_D^{25}$ values on the concentration of compounds **2** and **1** were processed by mathematical modeling using the CPESSP (Complex formation Parameters of Equilibria in Solutions with Solid Phases) software.[11] The program executes an iterative procedure to minimize the functional F:

$$F = \sum_{k=1}^{N} [(Q_{k,\mathrm{exp}} - Q_{k,\mathrm{calc}}) \cdot \omega_k]^2, \quad (3)$$

where $Q_{k,\mathrm{exp}}$ and $Q_{k,\mathrm{calc}}$ are the experimentally measured characteristics of a solution in the kth experiment and its theoretical value, respectively, N is the number of experiments, and ω_k is the root-mean-square error. One has

$$Q_{\mathrm{calc}} = f(\beta_{i...n}, \alpha'_{i...n}, \chi_{i...n}, \xi_{i...n}), \quad (4)$$

where β_i and χ_i are the constant of formation and the physicochemical parameter of the ith complex, α'_i is its content, and ξ_i is the matrix of the stoichiometric coefficients.

The reliability of the results obtained was estimated from the F-test[12]:

$$F_{\mathrm{cr}} = \sigma^2/\sigma^2_{\mathrm{exp}} \le F_{\upsilon 1,\upsilon 2,p}, \quad (5)$$

where σ and σ_{exp} are the dispersions of the theoretical and experimental data, respectively; υ_1 and υ_2 are the numbers of the degrees of freedom in the numerator and denominator in Eq. (5), respectively; and p is the specified significance level of the F-test. Since

$$\sigma^2 = F_{\mathrm{min}}/(N - 2n), \quad (6)$$

Eq. (5) takes the form:

$$F_{\mathrm{cr}} = F_{\mathrm{min}}/(F_{\upsilon 1,\upsilon 2,p} \cdot \sigma^2_{\mathrm{exp}}(N - 2n) \le 1. \quad (7)$$

Meeting the inequality (7) implies that the solution found is true with a probability close to $1 - p$.[13]

Results and Discussion

Changes in the $[\alpha]_D^{25}$ values of the aqueous solutions of ligand **1** with an increase in its concentration (Fig. 1) substantiate the conclusions[8] about the effect of the degree of hydration and associative equilibria on the structural state of **1** in solution.

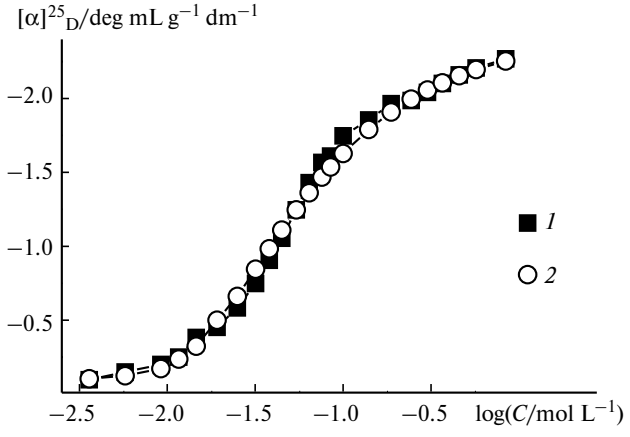


Fig. 1. The $[\alpha]_D^{25}$ values plotted *vs.* molar concentration of **1**: experimental data (*1*) and results of calculations using the mathematical model (*2*).

Mathematical modeling of the experimental dependence of $[\alpha]_D^{25}$ on the concentration of compound **1** using the CPESSP program (see Fig. 1) made it possible to correctly describe the totality of processes by the equilibrium

$$4\ H_6Glc\text{-}ol_{aq} \overset{K_e}{\rightleftharpoons} \{H_6Glc\text{-}ol_{aq}\}_4, \qquad (8)$$

where

$$K_e = [\{H_6Glc\text{-}ol_{aq}\}_4]/[H_6Glc\text{-}ol_{aq}]^4. \qquad (9)$$

We also calculated the constant K_e of equilibrium (8) and the $[\alpha]_D^{25}$ values for all conformers (Table 1).

Initially, the model included various forms of **1** with different degrees of association (n = 2—6) and successive transitions from one form to another. However, such models appeared to be incorrect with respect to the F-test (7). The calculated content of each form is plotted *vs.* the content of compound **1** in water is given in Fig. 2.

When comparing the $[\alpha]_D^{25}$ values calculated in this work with the published data,[7] one should take into account the fact that the optical activity of the monomeric form of **1** is 27 times lower than that of the corresponding tetramer (see Table 1). For instance, for $[\alpha]_D^{25} = -2.0$ (*c* 9, H_2O)[7] the concentration corresponds to a 0.4945 *M* solution of **1** (log*C* = −0.306) with a tetramer content of 83% (see Fig. 2). Then, having substituted the necessary values (see Table 1) into Eq. (2) and ignoring the temperature correction, one gets $[\alpha]_D^{25} = -2.03$.

Table 1. Polarimetric and thermodynamic characteristics of the system **1**—H_2O

Form	logK_e	$[\alpha]_D^{25}$/deg mL g^{-1} dm^{-1}
$H_6Glc\text{-}ol_{aq}$	—	−0.09(±0.04)
$\{H_6Glc\text{-}ol_{aq}\}_4$	1.02(±0.07)	−2.43(±0.01)

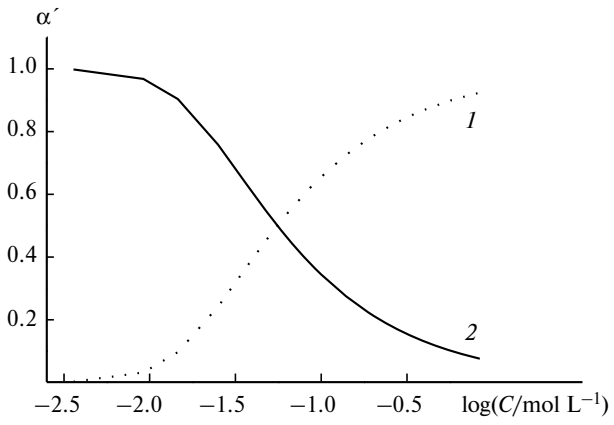


Fig. 2. Content (α′) of tetramer (*1*) and monomer (*2*) plotted *vs.* molar concentration of **1**.

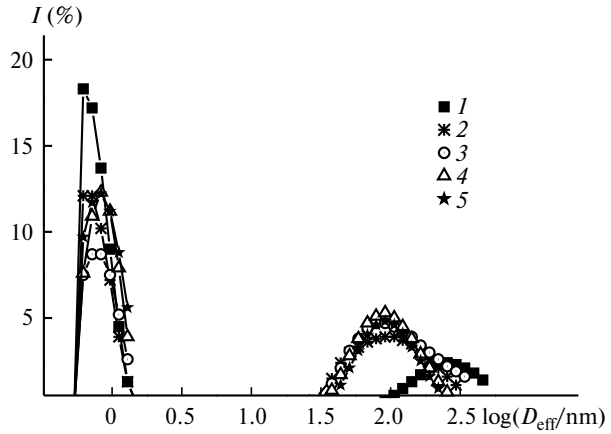


Fig. 3. Particle diameter (D_{eff}) distribution obtained by dynamic light scattering in the system **1**—water at C(**1**) = 0.0108 (*1*), 0.1628 (*2*), 0.3241 (*3*), 0.4818 (*4*), and 0.6503 mol L^{-1} (*5*).

At first glance, the formation of a tetramer and the absence of other forms of compound **1** of different degree of association is somewhat unexpected. However, polyatomic alcohols can form helices comprising four and six units.[14] To obtain reliable information on the processes and on the degree of association of compound **1** in water, we studied the distribution of the effective hydrodynamic diameters D_{eff} of particles at different concentrations (Fig. 3) was obtained by dynamic light scattering.

There are only two (!) well-defined peaks in the whole concentration range studied (see Fig. 3). The peaks indicate the existence of two types of particles with the diameters of nearly 1 nm (this is comparable with the size of the monomer; the length of molecule **1** calculated using the HyperChem7.5 program is 0.89 nm) and 100 nm (associate). But for the curve *1* (see Fig. 3) with the minimum concentration of ligand **1** the second peak corresponds to larger particles. Most likely, this is due to an increase in the size of the hydration sphere of **1** and, therefore, to a looser packing of monomers **1** in the associate.[11] In addition, the intensities of the peaks are also different, *viz.*, the content of tetramer **1** is about 5% (see Fig. 2) and therefore the intensity is lower; as the concentration of **1** increases, the content of tetramers abruptly increases (see Fig. 2). But the curves *2*—*5* (see Fig. 3) show no clearly defined dependences of the peak intensities on the concentration of **1** because the content of the tetramer of **1** at such concentrations (see Fig. 3) changes from 80 to 85% (see Fig. 2). Thus, these results confirm the correctness of mathematical modeling of polarimetric data and the validity of Eq. (8). Since all hydroxyl groups of polyols[14] are involved in the formation of OH...O bonds about 0.27 nm long,[11] ligand **1** can form a stable associate-type structure with quite a "rigid" spatial coordination of the hydrogen bonds. In addition, a medium associated through H-bonds can represent a pseudopolymeric structure and form a three-dimensional network of H-bonds.[15]

Thus, the hydrodynamic diameter of about 100 nm corresponds to a self-assembling cluster comprising helical tetramers of **1** and water molecules from the hydration shells of the tetramer and corresponding monomers.

$$n\,(H_6Glc\text{-}ol_{aq})_4 + m\,H_2O \overset{K_e}{\rightleftarrows} \{(H_6Glc\text{-}ol_{aq})_{4n}\cdot m\,H_2O\} \quad (10)$$

The numbers n and m characterizing the size of a "coil" vary within a rather narrow range (see Fig. 3). This is most likely due to the presence of a thermodynamically stable associate, whose "core" has a well-defined structure stabilized by the steric and conformational effects of polar groups of the solvent and ligand **1**. The constant K_e of the equilibrium (10) can be determined by mathematical modeling only if the parameters n and m are known. Therefore, additional methods of investigation are required.

To reveal the character of the interaction **2**—**1** in the weakly acidic region of pH values, we recorded a series of electronic absorption spectra at different concentrations (Fig. 4).

From Fig. 4 it follows that the positions of maxima of spectral bands are independent of the metal : ligand ratio and that the absorption intensity is proportional to the chromophore concentration. This indicates an unchanged state of the first coordination sphere of the complex-forming agent and, therefore, no covalent bonding between compound **2** and the oxygen atoms of the hydroxyl groups in ligand **1** and no noticeable hydrolysis of the cation. The latter is also suggested by the dependences of pH values on the concentration of salt **2** in the absence and in the presence of **1** (Fig. 5).

Thus, one of a few chances to confirm or reject the formation of a complex of **2** with **1** under the specified conditions is to carry out a polarimetric study of this system, which allows one to monitor the conformational state of the ligand.

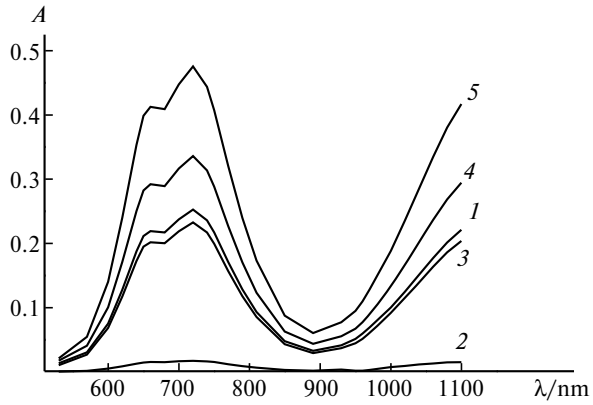


Fig. 4. Electronic absorption spectra of the system $Ni(NO_3)_2$—**1**—H_2O at different Ni : **1** ratios: 1 : 0 (*1*), 0.01 : 1 (*2*), 1 : 1 (*3*), 1.5 : 1 (*4*), and 2 : 1 (*5*); $C(\mathbf{1}) = 0.1$ mol L^{-1}.

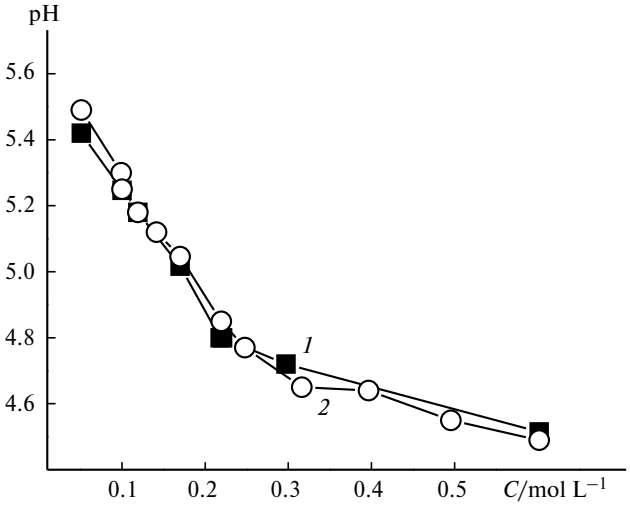


Fig. 5. pH values plotted *vs.* concentration of Ni^{II} in the systems $Ni(NO_3)_2$—H_2O (*1*) and $Ni(NO_3)_2$—**1**—H_2O (*2*).

Since the $[\alpha]_D^{25}$ value of ligand **1** is small, reliable data can only be obtained at sufficiently high concentrations of the optically active substance. We chose a decimolar concentration of compound **1**. According to our study, at this concentration it exists as a mixture of monomers and tetramers in a 1 : 2 ratio (see Fig. 2).

Changes in $[\alpha]_D^{25}$ (**1**) upon the addition of **2** (Fig. 6) indicate structural rearrangements in associates of **1**. This can occur in the case of specific interactions (H-bonding) of the metal aqua ions with the functional groups in **1**, *i.e.*, outer-sphere complexation.

The results of mathematical modeling using experimental data are shown in Table 2 and in Fig. 7.

$$K_e = [\{Ni_n(H_6Glc\text{-}ol)_m\}^{2n+}]/[Ni^{2+}]^n[H_6Glc\text{-}ol]^m \quad (11)$$

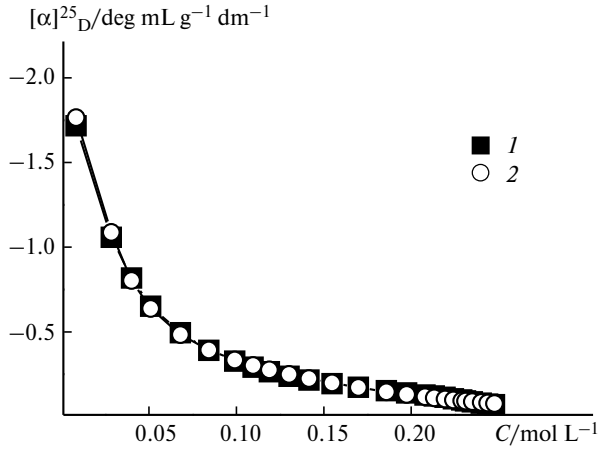


Fig. 6. Experimental (*1*) and theoretical (*2*) dependences of $[\alpha]_D^{25}$ values on the concentration of Ni^{II} in the system $Ni(NO_3)_2$—**1**—H_2O at $C(\mathbf{1}) = 0.1$ mol L^{-1}.

Table 2. Polarimetric and thermodynamic characteristics of the system Ni^{II}—**1**—H_2O

Form	Composition		$\log K_e$ ±(0.03—0.06)	$-[\alpha]_D^{25}$ /deg mL g^{-1} dm^{-1} ±(0.002—0.01)
	n	*m*		
$\{(Ni_{aq})\cdot(H_6Glc\text{-}ol_{aq})\}^{2+}$	1	1	0.71	0.078
$\{(Ni_{aq})_2\cdot(H_6Glc\text{-}ol_{aq})\}^{4+}$	2	1	2.26	0.003
$\{(Ni_{aq})_4\cdot(H_6Glc\text{-}ol_{aq})_4\}^{8+}$	4	4	6.86	0.051

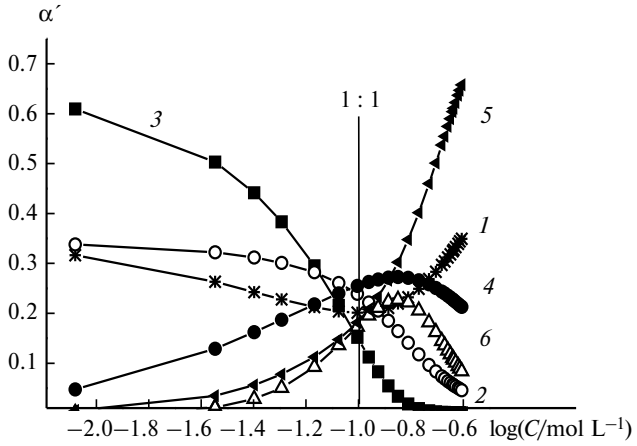
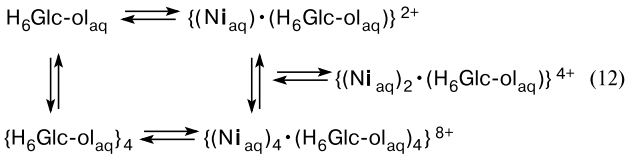


Fig. 7. The content (α´) of different forms plotted *vs.* molar concentration of Ni^{II} in the system $Ni(NO_3)_2$—**1**—H_2O at $C(\mathbf{1}) = 0.1$ mol L^{-1}: Ni^{II}_{aq} (*1*), $H_6Glc\text{-}ol_{aq}$ (*2*), $\{H_6Glc\text{-}ol_{aq}\}_4$ (*3*), $\{(Ni_{aq})\cdot(H_6Glc\text{-}ol_{aq})\}^{2+}$ (*4*), $\{(Ni_{aq})_2\cdot(H_6Glc\text{-}ol_{aq})\}^{4+}$ (*5*), and $\{(Ni_{aq})_4\cdot(H_6Glc\text{-}ol_{aq})_4\}^{8+}$ (*6*).

In modeling we considered a variety of chemically reasonable associates with variable M : L ratio (M : L = 1—4 in different combinations). In all cases, except for those mentioned above, the models obtained were incorrect with respect to the F-test (7).

The stability constants (11) of the outer-sphere complexes appreciably increase with an increase in "nuclearity" (see Table 2). This may be a consequence of the overall polarization effect of metal aqua ions on the ligand conformation and on the network of H-bonds in the nearest environment (of the cluster).

The state of the system in the concentration range studied (see Fig. 7) can be described by the following reaction scheme (12).



(12)

From Fig. 7 it follows that at the equimolar ratio M : L the binuclear and tetranuclear complexes are accumulated in nearly equal amounts. This may suggest that the ligand clusters execute a strong "structural control" (the monomer is almost not consumed) in the formation of outer-sphere complexes. As the metal concentration increases, the entropy contribution due to breakdown of associates also increases. This leads to abrupt accumulation of the binuclear form $\{(Ni_{aq})_2\cdot(H_6Glc\text{-}ol_{aq})\}^{4+}$.

Thus, one can suggest that the nature of the interaction of nickel(II) ions with D-glucitol in weakly acidic aqueous solutions is mainly due to hydrogen bonds and the outer-sphere complexes represent polymolecular associates. The role of the center of association is most probably played by the tetramer of D-glucitol whose hydrated form is the building block of the cluster (diameter is about 100 nm). Metal aqua ions only embed into the network of H-bonds of the cluster and thus gradually destroy it as the content of the complex-forming agent increases. The composition and strength of associates first of all depends on the conformational state (degree of hydration) of the ligand. A specific feature of this system is an efficient H-bonding between two nickel(II) ions within the same D-glucitol molecule at metal : ligand ratios exceeding 1 : 1. Structural studies of such associates require the use of additional methods of investigation.

References

1. Yu. E. Alekseev, A. D. Garnovskii, Yu. A. Zhdanov, *Usp. Khim.*, 1998, **67**, 723 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1998, **67**, 723].
2. I. Pedruzzi, E. A. Borges da Silva, A. E. Rodrigues, *Separation and Purification Technology*, 2008, **63**, 600.
3. A. V. Rubanov, F. V. Devyatov, *Tez. dokl. Nauch. konf. molodykh uchenykh, aspirantov i studentov NOTs KGU "IMaterialy i tekhnologii XXI veka"* [*Abstrs Conf. of Young Researchers, Post-Graduates Students, and Students "Materials and Technologies of the 21st Century"*] *(Kazan, February 14—15, 2003)*, Kazan, 2003, 73 (in Russian).
4. V. M. Potapov, *Stereokhimiya* [*Stereochemistry*], Khimiya, Moscow, 1988, 464 pp. (in Russian).
5. F. V. Devyatov, A. R. Mustafina, S. G. Abdullina, V. P. Gubskaya, S. G. Vul´fson, I. A. Nuretdinov, Yu. I. Sal´nikov, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1054 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1993, **43**, No. 6].
6. F. V. Devyatov, K. A. Ignat´eva, *Uch. zap. Kazan. gos. un-ta* [*Proc. Kazan State Univ.*], 2006, **148**, No. 1, 42 (in Russian).
7. *Beilsteins Handbuch der organischen Chemie*, Berlin Verlag von Julius Springer, Berlin, 1941, **1**, p. 605.
8. P. P. Shah, C. J. Roberts, *J. Phys. Chem. B*, 2007, **111**, 4467.
9. F. V. Devyatov, A. V. Rubanov, Yu. I. Sal´nikov, *Tez. dokl. XXI Mezhdunar. Chugaevsk. konf. po koordinats. khimii* [*Abstrs XXI Int. Chugaev Conf. on Coord. Chem.*] *(Kiev, June 10—13, 2003)*, Kiev, 2003, 239 (in Russian).
10. A. A. Popel´, *Magnitno-relaksatsionnyi metod analiza neorganicheskikh veshchestv* [*Magnetic Relaxation in Analysis of Inorganic Compounds*], Khimiya, Moscow, 1978, 224 pp. (in Russian).

11. Yu. I. Sal´nikov, A. N. Glebov, F. V. Devyatov, *Poliyadernye kompleksy v rastvorakh* [*Polynuclear Complexes in Solutions*], Izd. Kazan State Univ., Kazan, 1989, 288 pp. (in Russian).
12. E. S. Shcherbakova, I. P. Gol´dshtein, E. N. Gur´yanova, *Usp. Khim.*, 1978, **47**, 2134 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1978, **47**, No. 12].
13. E. S. Shcherbakova, A. A. Bugaevskii, I. K. Karpov, *Matematicheskie voprosy issledovaniya khimicheskikh ravnovesii* [*Mathematical Problems in Studies of Chemical Equilibria*], Izd. Tomsk State Univ., Tomsk, 1978, 232 pp. (in Russian).
14. A. N. Anikeeva, G. M. Zarubinskii, S. N. Danilov, *Usp. Khim.*, 1976, **1**, 106 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1976, **1**].
15. R. P. Tiger, M. A. Levina, S. G. Entelis, M. A. Andreev, *Kinet. Katal.*, 2002, **43**, 709 [*Kinet. Catal.* (*Engl. Transl.*), 2002, **43**].

Received June 18, 2009;
in revised form January 28, 2010