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> PHYSICAL CHEMISTRY OF SOLUTIONS =

Nickel(II) Complexes with 2-Hydroxyethyliminodioacetic Acid in Aqueous Solutions of Dicarboxylic Acids

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Abstract—The equilibria in binary and ternary systems containing a nickel(II) salt, 2-hydroxyethyliminodiacetic acid, and dicarboxylates were studied by spectrophotometric and potentiometric methods with NaClO₄ as the supporting electrolyte at I = 0.1 and $T = 20 \pm 2^{\circ}$ C. The molar and protic composition and the pH regions of existence of the complexes were determined, the stability constants of complexes containing the same or different ligands were determined. The fractional distribution of the complexes as the function of acidity was elucidated. The experimental data were treated using mathematical models to estimate the possibility of existence of a broad range of complex species in solution and to distinguish the species that are sufficient to take into account for reproducing the experimental results.

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Nickel(II) compounds (chlorides, sulfates, phosphates, formates, and so on) find wide use in various fields of industry as tanning extracts, nickel-plating electrolytes, phosphate etching materials, and so on. 2-Hydroxyethyliminodiacetic acid, which forms complexes with many metals, is used as an effective complexing agent. The ability of this compound to form metal ion complexes of various composition, charge, and stability and its high water solubility served as prerequisites for the use of this chelating agent as an effective eluent in the separation of lanthanides [1–4].

Dicarboxylic acids are used in various fields of industry including the production of varnishes and paints, synthetic fibers, and food products, while dicarboxylic acid amides (dipeptides) coordinated to micronutrient metals are known as biologically active medicinal agents [5].

Nickel is also a biologically active metal. The excessive "technology-induced" nickel(II) compounds that get into the body are toxic for the metabolism and carcinogenic for cells [6].

Recent years have seen advantageous development of studies into metal coordination compounds containing chelating agents. The formation of chelates in the presence of additional ligands often markedly enhances their functional activity, which may be caused by electron density redistribution, increase in the stability of the complex species, increase in the reactivity, formation of new structural entities, etc.; this considerably extends the scope of their application.

Thus, it appears pertinent to study the quantitative characteristics of the reactions of nickel(II) with 2-hydroxyethyliminodiacetic acid (H_2 Heida) in the presence of saturated dicarboxylic acids (oxalic

(H₂Ox), malonic (H₂Mal), and succinic (H₂Suc) acids), as this would open up the way for developing complexing compositions with a pre-specified set of properties.

The complexes of 2-hydroxyethyliminodiacetic acid with nickel(II) were studied repeatedly by various methods. A potentiometric study at I = 0.1 and T = 20 [7], 25 [8, 9], and 30°C [10] showed the presence of [NiHeida] (log β = 9.28 [7], 9.15 [8], 9.33 [9], 9.50 [10]) and [NiHeida₂]²⁻ complexes (log β = 14.25 [7], 14.18 [9], 14.65 [10]). According to spectrophotometry at I = 0.1 (NaClO₄) and T = 20°C, the [NiHeida] (log β = 9.52) and [NiHeida₂]²⁻ (log β = 13.90) complexes exist [11].

Nickel(II) complexes with dicarboxylic acids have also been repeatedly studied but the results are quite contradictory as regards both the composition and the stability constants of the complexes. To our knowledge, no data on different-ligand nickel(II) complexes with H_2 Heida and dicarboxylic acids are present in the literature.

For understanding of the complexation processes in ternary systems, knowledge of the processes that occur in the corresponding binary systems is needed. Since the published data on the Ni(II) complexes containing one sort of the ligands are contradictory, we studied in detail the complexation in binary systems under identical experimental conditions in order to determine more precisely the composition and the stability constants of Ni(II) complexes with these reagents. Nickel(II) dicarboxylates were studied previously [12]. Also a review of publications dealing with Ni(II) dicarboxylates was presented [12]. Here we report the study of the Ni(II) $-H_2$ Heida system.

α

EXPERIMENTAL

The complexation was studied by spectrophotometry. The absorbance of the solutions was measured on SF-26 and SF-56 spectrophotometers using a tailormade Teflon cell with guartz walls and 5-cm thick absorption layer. This cell allows for simultaneous measurement of the solution pH and absorbance. The wavelengths were adjusted at 380–420 nm with an error of ± 0.1 nm. All A = f(pH) curves were obtained by spectrophotometric titration. Doubly distilled water was used as the reference solution. The hydrogen ion activity was measured on an I-160 ion meter with an ES-10601/7 working electrode and an ESR-10101 reference electrode. The instrument was calibrated against standard buffer solutions prepared from volumetric concentrates (fixanal) and tested at the UPKP-1 bench. The desired pH was created by adding analytical grade NaOH or HClO₄ solutions. The constant ionic strength ($I \approx 0.1$) was maintained by an analytical grade solution of NaClO₄. In the case of a large excess of dicarboxylic acids, all equilibrium constants were calculated for the basic ionic strength. The studies were performed at $t = 20 \pm 2^{\circ}$ C. A nickel(II) perchlorate solution was prepared by dissolving reagent grade nickel(II) oxide in perchloric acid. Solutions of the chelating agents and dicarboxylic acids were prepared by dissolving exact weighed amounts of reagent grade chemicals (AO Reachim) in distilled water. The mathematical treatment of the results was done by CPESSP [13] and Sol-Eq[14] software.

RESULTS AND DISCUSSION

The absorption spectrum of nickel(II) hexaaqua complex exhibits three absorption bands: 400 (${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}, P$), 714 (${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}, F$), and 1111 nm (${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$).

The investigation of the complexation in binary and ternary systems was based on the fact that the absorption spectra and the absorbance of solutions of Ni(II) perchlorate change in the presence of the chelating agent and dicarboxylic acids. In addition, we constructed theoretical models of the complexation for ternary systems neglecting the different-ligand complexation. A comparison of the theoretical A =f(pH) curves and the experimental values revealed deviations associated with the formation of differentligand complexes. The working wavelength was chosen at 400 nm where the proper absorbance of the ligand is insignificant at various pH, while the complexes show a considerable hyperchromic effect. The pattern of the A = f(pH) curves constructed for the binary and ternary systems indicates that the complexation occurs over a broad pH range for all of the systems.

It is quite a challenge to describe the equilbria in binary and, especially, in ternary systems containing various hydroxy complexes and various protonated forms of polydentate ligands. Since the values of the stability constants to be determined depend on the set



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Fig. 1. Absorbances (*A*) and mole fractions (α) of nickel(II) complexes vs pH for the Ni(II)–Heida system: (*I*) experimental curve A = f(pH), (*2*) Ni²⁺, (*3*) [NiHeida], (*4*) [NiHeida₂]²⁻, (*5*) [Ni(OH)Heida]⁻; $c_{\text{Ni}} = 4 \times 10^{-3}$, $c_{\text{Heida}} = 8 \times 10^{-3}$ mol/L.

of species chosen to describe the system, choosing the appropriate set of complex species is of prime importance. In the software we used, the expedience of including one or another metal complex or ligand species was determined based on minimization of the Fisher criterion, which takes into account the discrepancy between the experimental and theoretical absorbances (A) for each component of the system. This software provides a fairly reliable estimate of the equilibrium system parameters and the stoichiometry and thermodynamics of the chemical processes. The chemical equilibria in the binary and ternary systems were described using a modification of the ion pair model. This model implies the possible existence of a broad range of complexes and associates in the solution.

By mathematical treatment of the A = f(pH)curves, the composition of the complex species and the types of acid-base equilibria in binary and ternary systems were determined. The pH regions of existence of the complexes were derived from the diagrams of distribution of the species as a function of pH. This is exemplified in Fig. 1, which shows the experimental dependence of absorbance and mole fraction distribution curves (α) of various complexes vs pH for the Ni(II)-H₂Heida system.

As follows from Fig. 1, the A = f(pH) curve has three buffer areas corresponding to the formation of three complexes. The first one is formed at 1.0 < pH <3.6 and exists at 3.6 < pH < 5.0. The second complex is formed at 5.0 < pH < 8.6 and exists at 8.6 < pH <10.0. When pH > 10.0, the third complex manifests itself. The mole fractions of the complexes that are

Complex	pH regions of existence	pH _{opt}	logβ	The maximum mole fraction of the complex for pH_{opt} , %
[NiHeida]	1.0-12.0	3.6-4.7	9.33 ± 0.05	98
[NiHeida ₂] ^{2–}	>3.7	8.6-11.6	14.20 ± 0.06	94
[Ni(OH)Heida] ⁻	>10.0		12.05 ± 0.11	
[NiHeidaHOx] ⁻	0.6-4.8	2.0	16.92 ± 0.12	23
[NiHeidaOx] ^{2–}	>1.8	7.2	13.47 ± 0.18	85
[NiHeida ₂ Ox] ^{4–}	>5.9	9.5-11.3	16.50 ± 0.20	60
[Ni(OH)HeidaOx] ³⁻	>11.2		15.39 ± 0.23	
[NiHeidaHMal] ⁻	1.0-7.0	3.5	16.15 ± 0.19	77
[NiHeidaMal] ^{2–}	>2.7	6.2	11.36 ± 0.63	85
[NiHeida ₂ Mal] ^{4–}	>5.1	9.1-12.0	14.73 ± 1.30	32
[Ni(OH)HeidaMal] ^{3–}	>10.6		12.17 ± 0.68	
[NiHeidaHSuc] ⁻	2.5-6.5	4.6	13.83 ± 0.79	4
[NiHeidaSuc] ^{2–}	>3.3	5.9	9.77 ± 0.26	39
[NiHeida ₂ Suc] ^{4–}	>5.4	8.5-12.5	13.44 ± 0.47	6

Some characteristics of identical- and different-ligand nickel(II) complexes with 2-hydroxyethyliminodiacetic acid and dicarboxylic acids at I = 0.1 (NaClO₄) and $T = 20 \pm 2^{\circ}$ C

formed in the Ni(II)– H_2 Heida systems and the relevant stability constants are summarized in the table. Note that the initial pH for the formation of most complexes is rather clear-cut; however, the final pH of the existence of one or another complex is not always established because it is located in a highly alkaline region (pH > 12).

The complexes formed in binary and ternary systems were identified taking into account three monomeric nickel(II) hydrolysis constants [15], two dissociation constants for each dicarboxylic acid [16, 17], and three dissociation constants of 2-hydroxyethyliminodiacetic acid [18, 19]:

H ₂ Ox	H_2Mal	H ₂ Suc	H ₂ Heida
_	_	_	1.60
1.54	2.73	4.00	2.20
4.10	5.34	5.24	8.73
	H ₂ Ox - 1.54 4.10	$\begin{array}{ccc} H_2Ox & H_2Mal \\ - & - \\ 1.54 & 2.73 \\ 4.10 & 5.34 \end{array}$	H_2Ox H_2Mal H_2Suc 1.542.734.004.105.345.24

Note that that the yield of nickel(II) complexes with either identical or different ligands depends not only on the medium acidity but also on the ligand concentration. The full yield of different-ligand complexes is not achieved even with considerable excess of the ligands. It was also found that for the formation of different-ligand complexes, the ligand concentration should not be lower than their concentration in the complexes with identical ligands. Figure 2 shows the A = f(pH) curves for the acid– base equilibria in the binary and ternary systems comprising oxalic or malonic acid. In both cases, the formation of complexes with identical or different ligands occurs over a broad pH range. In the Ni(II)– H₂Heida–H₂Ox system, H₂Ox functions obviously as the primary ligand, while in other systems, this role is played by H₂Heida. This is indicated by the curves of absorbance and fractional distribution of the complexes vs pH.

In the 1 : 2 : 2 Ni(II) $-H_2$ Heida $-H_2$ Ox system (Fig. 3a), [NiHOx]⁺ and [NiOx]complexes exist in a highly acidic medium. At pH 2.3, the complex [NiHeidaHOx]⁻ is formed in 52% yield; then it is deprotonated to give [NiHeidaOx]²⁻. The yield of the latter complex reaches 94% at pH 6.0. Simultaneously with the different-ligand complex, nickel oxalate $[NiOx_2]^{2-}$ exists at 1.2 < pH < 6.0 (yield 35% at pH 4.0). On further decrease in the acidity, the complex [NiHeidaOx]^{2–} adds one more H₂Heida molecule to give mixed dichelate $[NiHeida_2Ox]^{4-}$. This species is accumulated at 6.0 < pH < 14.0, the highest yield being 38% (at 10.0 < pH < 11.0). The formation of $[NiHeida_2Ox]^{4-}$ is possible only through partial cleavage of the chelate rings of the nickel dichelate. At pH >11.0, this complex is hydrolyzed and the complex [Ni(OH)HeidaOx]³⁻ is accumulated in 59% yield (at pH 13.8).

As the oxalic acid concentration increases fivefold (Fig. 3b), the fraction of [NiHeidaHOx]⁻ decreases



Fig. 2. Absorbance of solutions vs pH for nickel(II) in the systems (a) Ni(II)–H₂Heida–H₂Ox and (b) Ni(II)–H₂Heida–H₂Mal for (1) Ni(ClO₄)₂ and its complexes with (2) H₂Heida, (3) H₂Ox, (4) H₂Mal, (5) H₂Heida + H₂Ox, and (6) H₂Heida + H₂Mal; (7, 8) theoretically calculated curve neglecting the different-ligand complexation. The compositions are 2 (2, 3, 4), 1 : 2 : 25, (6, 8) 1 : 2 : 100; $c_{Ni} = 4 \times 10^{-3}$ mol/L, $\lambda = 400$ nm.



Fig. 3. Distribution of nickel(II) complexes vs. pH for the Ni(II)–H₂Heida–H₂Ox system for (a) 1 : 2 : 2 and (b) 1 : 2 : 10 compositions: (1) Ni²⁺, (2) [NiHOx], (3) [NiOx], (4) [NiHeidaHOx]⁻, (5) [NiHeida], (6) [NiOx₂]²⁻, (7) [NiHeidaOx]²⁻, (8) [NiHeida₂Ox]⁴⁻, (9) [NiHeida₂]²⁻, (10) [Ni(OH)HeidaOx]³⁻, (11) Ni(OH)₃⁻; $c_{Ni} = 4 \times 10^{-3}$ mol/L, $\lambda = 400$ nm.

but simultaneously the fractions of $[NiHeida_2Ox]^{4-}$ (56% at pH 10.0) and $[Ni(OH)HeidaOx]^{3-}$ (80% at pH 13.8) increase. The mole fractions of other species change little. It was also noted that an increase in the content of H₂Heida in the system entails even greater accumulation of $[NiHeidaHOx]^-$ and $[NiHeida_2Ox]^{4-}$. For example, when the composition is 1 : 5 : 5, the yields of these complexes are 65% (at pH 2.3) and 72% (at pH 10.0), respectively.

The formation of different-ligand complexes in the $Ni(II)-H_2Heida-H_2Mal$ system also depends appreciably on the malonic acid concentration. When the com-

ponent ratio is 1 : 2 : 10, the yields of the [NiHeidaH-Mal]⁻, [NiHeidaMal]^{2–}, and [NiHeida₂Mal]^{4–} complexes are 46% (pH 4.0), 65% (pH 6.0), and 11% (9.0 < pH < 12.0), respectively. A fivefold increase in the concentration of the secondary ligand results in the yields of these complexes being 76, 84, and 31%, respectively, at the same pH values (Fig. 4a, where H₂Dik stands for any dicarboxylic acid).

The different-ligand complexation in the Ni(II)– H_2 Heida– H_2 Suc occurs only with large excess of succinic acid, the yields still being low. For example, for 1 : 2 : 100 component ratio, the yields of the [NiHeidaHSuc]⁻,

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Fig. 4. Distribution of nickel(II) complexes vs. pH for the Ni(II)-H₂Heida-H₂Mal and Ni(II)-H₂Heida-H₂Suc systems for (a) 1: 2: 50 and (b) 1: 2: 100 compositions: (1) Ni²⁺, (2) [NiHDik]⁺, (3) [NiHeida], (4) [NiHeidaHDik]⁻, (5) [NiMal], [NiMal₂]²⁻, (7) [NiHeidaDik]²⁻, (8) [NiHeida₂]²⁻, (9) [NiHeida₂Dik]⁴⁻, (10) [Ni(OH)HeidaMal]³⁻, (11) Ni(OH)₃⁻; (11); $c_{Ni} = 4 \times 10^{-3}$ mol/L, $\lambda = 400$ nm.

[NiHeidaSuc]^{2–}, and [NiHeida₂Suc]^{4–} complexes are 4, 39, and 6% for pH 4.5, 6.0, and 9.0–13.0, respectively (Fig. 4b). It also follows from the Figure that over a broad pH region, succinic acid solutions contain mainly the nickel chelates [NiHeida] and [NiHeida₂]^{2–}.

A comparison of the stability constants of neutral nickel(II) chelate dicarboxylates results in the following series of complexes in the order of increasing stability constants:

$$\begin{split} \left[\text{NiHeidaSuc}\right]^{2-} &< \left[\text{NiHeidaMal}\right]^{2-} \\ &< \left[\text{NiHeidaOx}\right]^{2-}, \\ \left[\text{NiHeida}_2\text{Suc}\right]^{4-} &< \left[\text{NiHeida}_2\text{Mal}\right]^{4-} \end{split}$$

< [NiHeida₂Ox]^{4–}.

The decrease in the stability of mixed nickel(II) complexes is obviously related to the structure of dicarboxylates. A decrease in the number of methylene groups in the dicarboxylic acid molecules is known to suppress their complexing ability.

Since in the $[NiHOx]^+$ and [NiOx] complexes predominate in the Ni(II)-H₂Heida-H₂O system in highly acidic media, the different-ligand complexation process can be represented as follows:

$$[NiHOx]^+ + Heida^{2-} \rightleftharpoons [NiHeidaHOx]^-.$$

In solutions of H_2Mal and H_2Suc , the opposite process takes place, i.e., dicarboxylic acid (H_2Dik) adds to nickel chelate:

 $[NiHeida] + HDik^{-} \rightleftharpoons [NiHeidaHDik]^{-}.$

The subsequent reaction may follow two pathways: $[NiHeidaHDik]^{-} \rightleftharpoons [NiHeidaDik]^{2-} + H^{+}$ or

$$[NiHeidaHOx]^{-} + Ox^{2-}$$

$$\rightleftharpoons [NiOx_2]^{2-} + Heida^{2-} + H^+.$$

In the pH region of formation of nickel dichelate, one more mole of hydroxyethylimino diacetate adds according to the equations

$$[NiHeidaDik]^{2^{-}} + Heida^{2^{-}}$$
$$\rightleftharpoons [NiHeida_{2}]^{2^{-}} + Dik^{2^{-}},$$
$$[NiHeidaDik]^{2^{-}} + Heida^{2^{-}} \rightleftharpoons [NiHeida_{2}Dik]^{4^{-}}$$

The yields of complexes formed according to these equations are different for different systems. At the same pH values, two-ligand complex predominates in some systems and the different-ligand complex is the major product in other systems.

The latter complex is hydrolyzed in highly alkaline media

$$[NiHeida_2Dik]^{4-} + OH^{-}$$
$$\rightleftharpoons [Ni(OH)HeidaDik]^{3-} + Heida^{2-}.$$

The character of equilibria in these systems and the composition and stability of the resulting complexes can be interpreted by considering the structures of the hydrated nickel(II) ion and the ligands, the symmetry, and the type of bonds. In view of the fact that the Ni(II) coordination number is 6 and the chelating agent and dicarboxylic acids are tri- and bidentate ligands, respectively, the structure of some complexes can be represented by the following skeletal schemes:





REFERENCES

- 1. L. Wolf and I. Massonne, J. Prakt. Chem. 4, 178 (1956).
- 2. L. Wolf and I. Massonne, J. Prakt. Chem. 5, 14 (1957).
- 3. L. Wolf and I. Massonne, J. Prakt. Chem. 5, 288 (1957).
- N. M. Dyatlova, V. Ya. Temkina, Yu. F. Belugin, et al., Zh. Neorg. Khim. 10, 1131 (1965).
- 5. P. Karrer, *Organic Chemistry*, Ed. by M. N. Kolosov (Elsevier, Amstrerdam, 1938).
- 6. L. K. Sadovnikova, D. S. Orlov, and I. N. Lozanovskaya, *Ecology and Environmental Protection upon Chemical Pollution* (Vyssh. shkola, Moscow, 2006) [in Russian].
- G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, Helv. Chim. Acta 38 (5), 1147 (1955).
- 8. J. F. Felcman and J. J. da Silva, Talanta **30** (8), 565 (1983).
- M. Jones and L. Pratt, J. Chem. Soc., Dalton Trans. 13, 1207 (1976).
- S. Chaberek, R. Courtny, and A. Martell, J. Am. Chem. Soc. 74 (20), 5057 (1952).

- 11. V. I. Kornev and V. A. Valyaeva, Zh. Fiz. Khim. **52** (7), 1815 (1978).
- V. I. Kornev, M. G. Semenova, and D. A. Merkulov, Russ. J. Coord. Chem. 35 (7), 519 (2009).
- Yu. I. Sal'nikov, F. V. Devyatov, N. E. Zhuravleva, and D. V. Golodnitskaya, Zh. Neorg. Khim. 29, 2273 (1984).
- 14. L. D. Pettit and K. J. Powell, The IUPAC Stability Constants Database. Academic Software, version, 5. 83 (2008).
- 15. Yu. Yu. Lur'e, *Handbook of Analytical Chemistry* (Khimiya, Moscow, 1979).
- 16. A. E. Martell and R. M. Smith, *Critical Stability Constants* (Plemum Press, New York, 1974), Vol. 3.
- A. K. Iain, R. C. Charma, and G. K. Chaturvedi, Pol. J. Chem. 52 (2), 259 (1978).
- B. N. Karadakov and Khr. R. Ivanova, Koord. Khim. 4 (9), 1365 (1978).
- 19. S. Eberle and I. Bayat, Inorg. Nucl. Chem. Lett. 5 (4), 229 (1969).