



Thermodynamics of nickel(II) and iron(III) complexation with nicotinamide in aqueous ethanol and aqueous dimethyl sulfoxide



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ABSTRACT

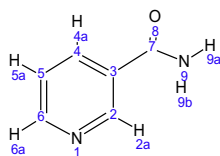
The complexation of Ni(II) and Fe(III) with nicotinamide in aqueous ethanol and aqueous dimethyl sulfoxide was directly studied by calorimetry at $T = 298.15$ K and ionic strength value 0.25 (NaClO_4). The results of thermochemical study were discussed using solvation-thermodynamic approach basing on the accounting of reagents solvation. The absence of contact ion pairing between Ni^{2+} and ClO_4^- was observed by IR-spectroscopy at ionic strength value 0.25. Nicotinamide was found to replace the water molecule within cation coordination sphere by means of UV-Vis spectroscopy.

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1. Introduction

Pyridinecarboxamide-3 (nicotinamide, B_3 vitamin) is known as agent preventing pellagra together with nicotinic acid [1]. In the living tissues both these compounds are included in composition of NAD and NADP coenzymes. The nicotinamide also effects on protein and RNA biosynthesis [2].

The nicotinamide is used as hydrotropic agent in pharmaceutical chemistry. It increases the solubility of nifedipine, indometacin, halofantrine and some others [3–6]. Nicotinamide is the active component of a number of multivitamins [7].



On the other hand, nicotinamide is promising compound for synthesizing the metal complexes with greater biological activity

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than free ligand [8]. The comprehensive information about characteristics of bond between metal ion and biologically active ligand, about methods of these characteristics determination and about applicability of obtained conclusions for prediction of substance biological activity could be found in works [9–12]. The change of structural, hydrophilic/hydrophobic etc. properties of biologically active ligands forming the complexes with metal ions could provide the pharmaceutical bioavailability. The increase of it is due to the facilitation of drug infiltration through the lipophilic barriers (biological membranes and etc.) [8].

Nickel acts in a few of biological reactions having significance in vital functions of some protozoa and bacteria [13]. The metal provides the molecular hydrogen oxidation and is included in urease composition (in fungi and plants as well [14]). In the same time, the harmful (in particular, allergenic [15] and carcinogenic [16,17]) effect of nickel compounds on human health must be noted.

When being in heme composition, Fe^{3+} ion is involved in oxygen transfer [18]. Another biological function of iron is participating in the ATP synthesis [19].

In the recent work [20], the antibacterial and antifungal effects of ten transition metal ion (including Ni^{2+} and Fe^{3+}) complexes of nicotinamide were investigated. The coordination compound formed with the nickel(II) ion has a more intense action than that

formed by iron(III) ion, which is more effective than unbound nicotinamide, when being used versus such fungi as *Aspergillus flavus* and *Candida albicans*, such Gram(+) bacteria as *Staphylococcus aureus* and *Bacillus subtilis*, and such Gram(–) bacteria as *Escherichia coli*, *Pseudomonas aeruginosa*.

The development of the novel antimicrobial agents such as d-metal ions complexes with biologically active ligands is obligatory because pathogenic microorganisms become resistant towards medicines being already designed and it becomes a really challenging problem [21].

Complex of iron(III) with nicotinamide is analogous to ferramidum drug (dinicotinamide complex of iron(II) chloride), which is used for treatment of iron deficiency [1]. Due to the development necessity of new methods of anemia treatment, the compounds containing iron ion in both of oxidation numbers are of great interest nowadays [22–25]. The design of iron containing drugs should suggest a good ferrous or the ferric complexes lypophilicity providing an effective gastrointestinal absorption [26]. So, the study of Fe³⁺ ion complexation with nicotinamide is of significance not only from point of view of coordination chemistry but also from point o view of medicine.

In these cases one should know the thermodynamics of complex formation processes in water and mixed water-organic solvents. The solvent as active participant of chemical reaction significantly effects on is rate, direction, mechanism and becomes a forceful means of chemical process control.

The study of solvent composition influence on complexation processes is an important theme in inorganic chemistry and physical chemistry of solutions. It is determined by coordination equilibria significance in aqueous and non-aqueous solvents and is of theoretical interest for defining the causal relationship between solvation and complexation processes.

The aim of presented paper is to study the influence of aqueous ethanol and aqueous dimethyl sulfoxide solvent composition on reaction exothermicity of nickel(II) and iron(III) complexation with nicotinamide. To reach this goal, the solvation-thermodynamics approach accounting the contribution of thermodynamic functions of ligand, central ion and complex into the thermodynamic characteristic change of reaction transfer is used.

Note the absence of literature data on heat effects of nickel(II) complexation with nicotinamide (L) either in aqueous media and in mixed solvents. The changes of enthalpy of nicotinamide coordination by iron(II) ion were determined earlier in water and aqueous ethanol [27].

2. Experimental

2.1. Materials

The nicotinamide of 'highly pure' grade (Merk Group, Darmstadt, Germany) was used without additional purification. The sodium perchlorate (Reakhimkomplekt, Slavgorodnee, Russia) of 'pure' mark was purified by double recrystallization and dried at 120 °C until its weight becomes constant. The ethanol of 'rectified' grade (Arzamaspir, Arzamas, Russia) was distilled with metallic sodium at atmospheric pressure (0.097 to 0.104) MPa. The dimethyl sulfoxide (Reakhimkomplekt, Staraya Kupavna, Russia) of 'chemically pure' mark was purified *via* distillation in 0.25 atm. vacuum. The remaining water content were measured using gravimetric method in case of ethanol (1.04 weight%) and using C. Fischer method [28] in case of DMSO (0.20 weight%). All the mixed solvents were prepared by weighting the accurate amounts of organic component (taking into account the remaining water content within it) and deaerated bidistilled water with error 0.01 g.

The nickel(II) perchlorate was synthesized of nickel(II) carbonate of 'pure' grade (Reakhimkomplekt, Slavgorodnee, Russia) and

perchloric acid of 'pure for analysis' mark (Reakhimkomplekt, Slavgorodnee, Russia). The Ni²⁺ ion concentration was controlled *via* chelatometry and photometry measuring the optical density of its aqua complex at $\lambda = 400$ nm [29].

The iron(III) perchlorate was synthesized of iron(III) sulfate of 'pure' grade (Reakhimkomplekt, Slavgorodnee, Russia) and perchloric acid of 'pure for analysis' mark (Reakhimkomplekt, Slavgorodnee, Russia) using the way of preparation described in paper [30]. The iron(III) concentration was controlled using photometry basing on optical density of its thiocyanate complex at $\lambda = 490$ nm [31].

All the data on the used chemicals are presented in table 1.

2.2. Apparatus and procedures

2.2.1. Calorimetry

The enthalpy changes of complexations and dilutions were obtained using ampoule calorimeter with isothermal shell. The calorimetric setup was virtually the same as that described in [32]. The main elements of the calorimeters are the calorimetric cell, the thermostating system, and the units for measuring temperature, current, and the time of calibration. The calorimetric cell consisted of the following construction elements: a reaction glass, a non-inductive rod-type calibration heater, a thermistor, a propeller blade mixer with an ampoule holder, and a brass cover into which the reaction glass was placed. The amount of heat for each calorimetric experiment (the main period) was measured comparatively [33], and current calibration was performed (the final period).

All the measurements were made at ionic strength value 0.250 ± 0.001 (NaClO₄) and temperature 298.15 ± 0.01 K.

In order to determine the heat effect of nickel(II) complexation with nicotinamide in aqueous ethanol and aqueous dimethyl sulfoxide, the 35.02 ml aliquot containing the $0.04165 \text{ mol} \cdot \text{l}^{-1}$ Ni(ClO₄)₂ at pH 5.1 and the indifferent electrolyte (NaClO₄) was placed into the calorimetric cell. There was the solution of $(0.06061 \text{ to } 0.2366) \text{ mol} \cdot \text{l}^{-1}$ nicotinamide(L) and the indifferent electrolyte in the sealed glass ampoule ~0.8 ml volume. The concentration conditions of experiments were optimized *via* mathematical planning using RRSU program [34]. According to calculations, the media acidity of pH = 5.1, which was created by HClO₄ addition and controlled *via* potentiometry, prevents the hydrolysis of nickel(II) ions ($\text{p}K_{\text{hydr}} = 9.86$ [35]) and the ligand protonation. Thus, the following processes contribute the common heat effect of mixing:



and the dilution of ligand solution on the calorimetric cell volume which is measured in the separate experiment.

The equilibrium constants of both of chemical processes were taken from papers [36,37]. The nickel(II) and nicotinamide concentrations were selected in order to minimize the yield of NiL₂²⁺ (it did not exceed 3% in our experiment). The resulting value of enthalpy change of coordination reaction is calculated as follows:

$$\Delta H_1 = \frac{q_{\text{mix}} - q_{\text{dil}}}{\alpha}, \quad (3)$$

where ΔH_1 is the enthalpy change of nickel(II)-nicotinamide complexation, q_{mix} is heat of mixing of solutions containing metal ion and ligand, q_{dil} is heat of ligand dilution on the calorimetric cell volume, and α is yield of monoligand complex.

The results of calorimetric study of coordination process of Ni²⁺ and nicotinamide at different compositions of binary solvents are given in tables 2 and 3.

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