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The Formation of Nickel(II) Chloride Ammine Complexes in the Pores of Modified Fibers of Cellulose Cloth

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Abstract—A sorbent was synthesized as a cellulose cloth, the fibers of which have nanopores with walls made of cellulose chains and ethanol cyclams. The formation of $(NH_4)_2[NiL(NH_3)_2Cl_2]$ complexes where L^{2-} is the $CH-(O^-)-CH-(O^-)$ glucopyranose group was established by chemical analysis and IR and UV/Vis spectroscopy. Using small-angle X-ray scattering and measurement of the partial free space and adsorption capacity, the complex formation in the $[Ni(NH_3)_6]Cl_2$ concentration range of up to 0.43 mol/L was found to occur in nanopores with the sorption constant $K_{sorb} = 15.8$. The limiting content of the complexes is 2.63 mmol/g and their effective radius is 0.45 nm. In the concentration range of 0.43–0.91 mol/L, the complexation occurs on the fiber surface, $K_{sorb} = 1.85$. The effective radius of the complexes is 0.5 nm.

Keywords: complex formation, nickel, ammonia, chloride, pores, cloth, cellulose, polyvinyl chloride, cyclam

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INTRODUCTION

Cellulose cloths possessing extensive surface of fibers and inner pores are promising for the development of readily accessible materials suitable for absorption of metal complexes from solutions with transportation into appropriate media. In [1, 2], it is demonstrated that a porous structure can be formed on the fiber surface by grafting polyvinyl chloride (PVC) cyclam derivatives to the cellulose chains that form the fiber surface and to the fibril surface inside the fibers [1–3]. A material made of porous cellulose cloth (CC) with mesopores on the surface and inner nanopores formed from the fibril wall chains cross-linked by cyclam networks is described in [4]. CC can withdraw Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) chloride ammine complexes from solutions, the metal uptake of the material reaching 2.5 mol/kg. CC can serve as a bridge for transfer of complexes from concentrated solutions to various media. Cellulose chains of pore walls possess $-CH-(OH)-CH-(OH)-$ groups translatable from cyclopyranoses (H_2L). The formation of complexes with $M^{n+} : L^{2-}$ ratio of 1 : 1, where M^{n+} is the complexing metal ion, is sterically feasible inside a pore. The L^{2-} anion can be coordinated by the reaction $MA_jX_i + H_2L = MLA_{j-2}X_i + 2HA$, where A is a ligand that can be protonated, e.g., NH_3. The complex formation in the mesopores occurs at the interface. The complexes can get into nanopores only from mesopores through holes in common walls. In a nanopore, complexes are located in a space confined by the pore walls; therefore, the effective radius of the complexes would be smaller than that on the surface. The structure of the ligand contour of the pores predetermines the possibility of relay migration of complexes in CC like along the bridge. In this connection, it is of interest to elucidate the characteristic features of formation of metal chloride ammine complexes in CC. As a model, we used the $[Ni(NH_3)_6]Cl_2$ complex with a saturated inner sphere. According to [5], on sorption of $[Ni(NH_3)_6]Cl_2$ in the porous structure of ethanol cyclam PVC derivatives, Cl^- ions enter the inner sphere. The UV/Vis spectra in the region of Ni^{2+} *d–d* transitions provide conclusions about the nature of Ni^{2+} environment in the complexes and the shape of Ni^{2+} polyhedra [6, 7].

The goals of this study are to perform the interaction of CC with $[Ni(NH_3)_6]Cl_2$ solutions of various concentrations under conditions where the CC region located in the solution is much smaller than the CC length; to determine the $Ni^{2+} : NH_3 : Cl^-$ stoichiometric ratios in the CC complexes by chemical analysis; to determine the inner sphere composition and the structure of complexes by IR and UV/Vis spectroscopy; to trace the pore filling depending on the proportion of complexed L^{2-} and the filling of surface

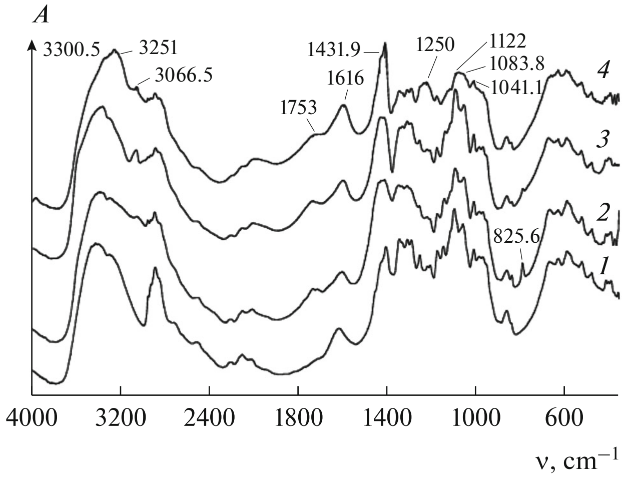

Fig. 1. IR spectra: (*1*) initial CC, (*2–4*) CC containing (*2*) 1.23, (*3*) 2.63, and (*4*) 3.92 mmol/g of the complexes.

fibrils by small-angle X-ray scattering (SAXS) and to measure the adsorption capacity; to determine the partial volumes of the complexes in the pores and on the surface; and to estimate the effective radii of the complexes.

EXPERIMENTAL

The reagents and materials included cotton gauze of 1.45 g/cm^3 density containing 97–97.5% cellulose washed by procedure [2], SG-7 PVC resin (containing 88.4% PVC and 9–10% phthalic acid esters as an additive), benzyl alcohol, ethanolamine, NaOH, nickel chloride hexahydrate, ammonium chloride, 25% aqueous ammonia, benzene, and hexane. All compounds were high-purity grade or reagent grade chemicals.

The cellulose material was synthesized as described in [2–4]. A gauze sample was impregnated with a 14% solution of PVC in benzyl alcohol containing 0.5% NaOH by repeated compression in a press up to 3–3.5 atm and pressure discharge until a constant weight was attained. The impregnated sample was transferred into an identical solution preheated to 110–130°C, kept for 1 h, washed with hot benzyl alcohol, placed into a 92% solution of ethanolamine preheated to 95–105°C, kept for 1 h, and washed with hot water. CC looked like a light yellow-colored gauze. The samples of 10 m length and 5 cm width were formed. The composition of CC was established by procedures [1–3]. The partial pore volume (free space) was measured by a reported procedure [4]. Structural parameters of the inner pores were determined by SAXS. The SAXS intensity was measured on a tailored SAXSess diffractometer (AntonPaar) using monochromatic CuK_α radiation. The measurements were carried out in vacuum in the transmission mode (the scattering vector range was 0.1–28 nm^{-1}) [8]. The following CC characteristics were established: the mole mass fraction of ethanol cyclams (20.9%), mass fraction of cellulose (79.1%), content of ethanol amine groups (0.185 mmol/g), pore partial volume (free space volume) (0.54 cm^3/cm^3), static adsorbed capacity of benzene vapor (0.43 mmol/g), and the inner pore width with the assumption that the pores were disk-shaped (~2 nm).

The diffuse reflectance spectrum (DRS) of CC was recorded on a Perkin-Elmer 2000 FT IR spectrometer (Fig. 1). The DRS exhibited characteristic cellulose bands at 3421 and 3300 cm^{-1} corresponding to hydrogen bond vibrations, the ν(CH) compound band at 2897 cm^{-1}, the >CH–OH bands at 1430 and 1376 cm^{-1}, and bands at 900 and 876 cm^{-1} due to the glycoside group [9–11].

Solutions of $[Ni(NH_3)_6]Cl_2$ were prepared in 1 M NH_4Cl. The total ammonia concentration was found as $\overset{\circ}{c}_{NH_3} = 6\overset{\circ}{c}_{Ni} + [NH_3]$, where $\overset{\circ}{c}_{Ni}$ is the total concentration of Ni(II) complexes and $[NH_3]$ is the equilibrium ammonia concentration, which was chosen to be 0.1 mol/L, where the complexes $[Ni(NH_3)_6]Cl_2$ predominate.

A CC sample of at least 10 cm length was wetted in a 1 mol/L solution of NH_4Cl, wiped with filter paper, and hanged above a beaker with a $[Ni(NH_3)_6]Cl_2$ solution in such a way that one end of the sample was immersed into the solution by not more than 3 mm. After the fabric contact with the solution, the colored front moved along CC. The interaction was terminated after the cloth became uniformly stained. The cloth was dried at 120–125°C to a constant weight.

The Ni^{2+} content was determined by sample titration with a solution of Trilon B with murexide, NH_3 was quantified by sample titration with HCl with bromthymol blue, and Cl^- was determined by argentometric titration (table). An increase in the $[Ni(NH_3)_6]Cl_2$ concentration was found to result in higher $c(Ni^{2+})$. For $[Ni(NH_3)_6]Cl_2$ concentrations of up to 0.43 mol/L, sorption is described by the equation: $c(Ni^{2+}) = 2.63 - c(Ni^{2+})/15.5c\{[Ni(NH_3)_6]Cl_2\}$, where 2.63 mmol/g is the Ni^{2+} content at $[Ni(NH_3)_6]Cl_2$ concentration of up to 0.43 mol/L and 15.5 is the sorption constant in this concentration range. For $[Ni(NH_3)_6]Cl_2$ concentrations of 0.43–0.91 mol/L, sorption is described by the equation $c(Ni^{2+}) = 4.48 - [c(Ni^{2+}) - 2.63]/1.85c\{[Ni(NH_3)_6]Cl_2\}$, where 4.48 mmol/g is the limiting sorption capacity of CC, and 1.85 is the sorption constant in the $[Ni(NH_3)_6]Cl_2$ concentration range of 0.43–0.91 mol/L.

The composition of the inner sphere was determined for samples with $c(Ni^{2+})$ = 1.23 (**I**), 2.63 (**II**), and 3.92 mmol/g (**III**) by UV/Vis and IR spectroscopy. The DRS of samples **I**, **II**, and **III** are summarized in Fig. 1. The content of complexes affects the spectral pattern at 3500–3300 cm^{-1}. According to [11], the spectra of 3*d*-metal ammonia complexes exhibit ν(N–H) bands at ~3300 cm^{-1}. In our case, they were superimposed onto the bands of cellulose hydrogen bonds. This affected the spectral pattern in this region. In other regions of cellulose bands, the spectra of **I**, **II**, and **III** largely resemble the spectrum of CC. This indicates that the formation of complexes did not affect the structure of elementary fibrils and CC fibrils. A 3056 cm^{-1} band for the ν(N–H) mode of NH_4^+ appeared in the spectrum. Its intensity was higher in the spectrum of **II** than in the spectrum of **I**, while in the case of **III**, it was greater than for **II**.

The UV/Vis spectra of CC **I**, **II**, and **III** were recorded on a Perkin-Elmer Lambda 35 spectrometer in the range of 400–900 nm, which includes the $^3A_{2g} \to {}^3T_{1g}(F)$ (500–900 nm) and $^3A_{2g} \to {}^{1'}A_{1g}(G)$ (400–500 nm) bands typical of Ni(II) complexes (Fig. 2). According to [4, 5], the $^3A_{2g} \to {}^3T_{1g}(F)$ transition wavenumber for octahedral Ni(II) complexes is determined by the Jorgensen's rule of average environment [4, 5]. The $^3A_{2g} \to {}^3T_{1g}(F)$ transition is observed for complexes with tetragonal distortion of the octahedral field [5]. In the 400–900 nm range, the spectrum of CC contains no bands. The $^3A_{2g} \to {}^3T_{1g}(F)$ transition wavenumbers of 13650 (**I**), 13700 (**II**), and 13720 cm^{-1} (**III**) correlate with those for diammine acid complexes [9, 10]. In the spectrum of **I**, a band at 22200 cm^{-1} is present in the $^3A_{2g} \to {}^{1'}A_{1g}(G)$ transition region. This band is absent in the spectra of **II** and **III**. In all cases, the coordination number of Ni is 6. It follows from the table that component ratios in the complexes are $Ni^{2+} : NH_3 = 1 : 2$ and $Ni^{2+} : Cl^- = 1 : 2$; this corresponds to a bidentate coordination of L^{2-}. Since simultaneous coordination of two L^{2-} in one sphere is sterically impossible, each L^{2-} anion functions as a bidentate ligand. The coordination of H_2L is accompanied by formation of the NH_4^+ cation. In this case, the complex can be described by the formula $(NH_4)_2[NiL(NH_3)_2Cl_2]$.

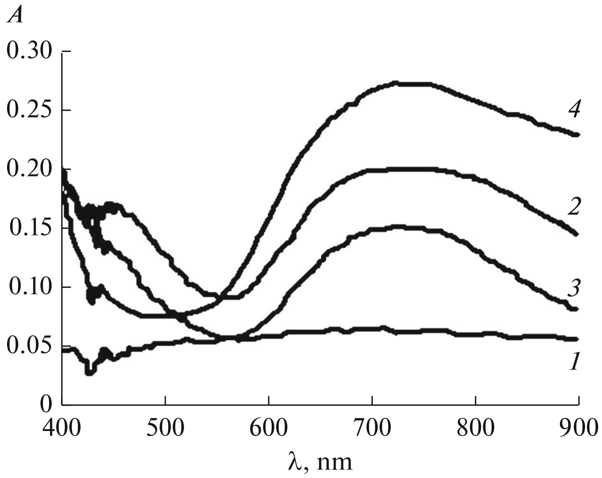

Fig. 2. UV/Vis spectra of (*1*) initial CC, (*2–4*) CC containing (*2*) 1.23, (*3*) 2.63, and (*4*) 3.92 mmol/g of the complexes.

According to the SAXS data, the inner pores are partially (in **I**) or completely (in **II**) filled. Hence, if sorption occurs in the $[Ni(NH_3)_6]Cl_2$ concentration range of up to 0.43 mol/L, the complexes are formed in the pores. The adsorption capacity c_{ad}(**III**) = 0.35 mmol/g; it is 0.07 mmol/g lower than that of CC. This indicates that after inner pores have been filled, the complexation occurs on the fibril surface.

The partial volumes of the complexes in the pores and on the surface were measured and the effective radius of the complexes was estimated in the following way. The partial volumes of the voids in **II** and **III** were measured: V_{void} = 48 (**II**) and 44 (**III**) vol %. The volume of the voids in CC is composed of the pore volume and the space between the fibrils and fibers. The $NiL(NH_3)_2Cl_2$ complexes at a concentration of 2.63 mmol/g occupy the volume $V_{comp} = V_{void}(CC) - V_{void}$(**II**) = 0.06 cm^3/g. These values were used to calculate the effective radius $r^0_{comp} \approx 0.45$ nm. Complexes with a concentration of 1.29 mmol/g on the extended surface occupy $V_{surf} = V_{void}$(**II**) − V_{void}(**III**) =

Dependence of Ni^{2+}, NH_3, and Cl^- contents in CC on the $Ni(NH_3)_6]Cl_2$ concentration in the solution

$c\{[Ni(NH_3)_6]Cl_2\}$, mol/L	$c(Ni^{2+})$, mmol/g	$c(NH_3)$, mmol/g	$c(Cl^-)$, mmol/g
0.0912	1.69	3.41	3.5
0.1825	2.05	4.07	4.1
0.365	2.48	4.98	4.94
0.4663	2.78	5.59	5.56
0.5475	3.64	7.21	7.27
0.730	3.81	7.57	7.60
0.9125	3.92	7.82	7.85

0.04 cm^3/g. These values imply the effective radius of ~0.5 nm.

RESULTS AND DISCUSSION

We found that the formation of the complexes $(NH_4)_2[NiL(NH_3)_2Cl_2]$ is more energetically favorable upon sorption in the pores than on the surface. Considering the effective radius of the complex, a 2 nm wide disk-shaped pore can accommodate up to two complexes. Evidently, packing in the pores is close to the limit and is tighter than that on the surface. Hence, the complex formation in the pores is accompanied by greater entropy increase than that on the surface.

The investigation data made it possible to propose a sorption and complexation mechanism for CC. The length of the CC section that occurs in contact with a $[Ni(NH_3)_6]Cl_2$ solution is much smaller than the whole CC length. In the case of solutions with concentrations of up to 0.43 mol/L, the complexes $[Ni(NH_3)_6]Cl_2$ at the interface react with H_2L on the surface to be converted to $(NH_4)_2[NiL(NH_3)_2Cl_2]$. The CC surface involves chains from adjacent walls. Therefore, upon ligand exchange $(NH_4)_2[NiL'(NH_3)_2Cl_2] + H_2L'' \rightarrow (NH_4)_2[NiL''(NH_3)_2Cl_2] + H_2L'$, where H_2L' and H_2L'' are surface groups, the complexes migrate from the surface into the pores. They move in the pores via a similar reaction owing to pressure exerted by the solution of $[Ni(NH_3)_6]Cl_2$ on the interface in the contact area. Apart from H_2L, the pore walls contain $-CH_2-OH$ groups and glycoside groups of cellulose, which can react with NH_4^+ and with coordinated NH_3 and Cl^-. On the one hand, this affects the uniformity of distribution of the complexes in the pores and, on the other hand, this gives rise to stress in the pores and fibrils, which counteracts the pressure exerted by $[Ni(NH_3)_6]Cl_2$. Hence, an equilibrium is established when the pressures on both sides of the interface become equal. As noted above, the UV/Vis spectrum of **I** in CC exhibits the ${}^3A_{2g} \rightarrow {}^{1'}A_{1g}(G)$ transition band characteristic of complexes with a tetrahedrally distorted inner sphere. It is likely that in **I**, the complexes are extended to form a chain. They are affected by not only $-CH_2-OH$ and glycoside groups, but also by the $>C-OH$ groups of free H_2L, which induces the distortion of the inner sphere. On further filling of the pores, the number of free H_2L decreases, and the complexes are arranged as two chains. In **II**, the effects of $-CH_2-OH$ and glycoside groups become equal for each complex and the inner spheres become less distorted. After the pores have been filled at $[Ni(NH_3)_6]Cl_2$ concentrations exceeding 0.43 mol/L, a porous layer of $[NiL(NH_3)_2]Cl_2$ grows on the surface.

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