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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Complexing of Chromium(III) and Aluminum(III) Cations with Phosphorus-Containing Cellulose-Based Fibrous Sorbent

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Abstract—Sorption of Al^{3+} and Cr^{3+} cations from sulfuric acid solutions with a cellulose phosphate-based fibrous sorbent was examined.

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Modification of cellulose ethers/esters is aimed primarily at improving their strength characteristics and increasing the stability in solutions. A possible way to affect the mechanical and physicochemical properties of the modified cellulose fibers lies in adsorption by them of cations (Al^{3+}, Cr^{3+}, Cd^{2+}) acting as cross-linkers with respect to the macromolecule. Such treatment of these sorbents is more efficient than grafting side chains to the polysaccharide macromolecules [1].

This study concerns sorption of the Al^{3+} and Cr^{3+} cations with low-substituted cellulose phosphate (CP). It is biocompatible with human body tissues, capable of biodegradation, and suitable as a sorbent of medicinal substances and resolving surgical suture thread material. The relationships in sorption of single-, double-, and triple-charged metal cations with high-substituted cellulose phosphate were described in [2, 3], where a quantitative model of the sorption process was presented. The structure of complexes involving some double- and triple-charged cations and cellulose phosphate was discussed earlier [3, 4], but still remains to be convincingly established.

Here, we examined sorption of aluminum(III) and chromium(III) from sulfuric acid solutions with cellulose phosphate fibers and determined the composition and structure of the complexes formed by the metals with the sorbent acting as polymeric ligand.

EXPERIMENTAL

Phosphoric acid esters of cellulose based on modified rayon ("Khimvolokno" Production Association, Svetlogorsk) and cotton (Groniteks Joint-Stock Company, Grodno) fibers were prepared by the procedure described in [5]. For esterification of the cellulose fibers served an aqueous solution of orthophosphoric acid (chemically pure grade) and carbamide (pure grade) with the concentration of 0.5 and 3.33 M, respectively. The liquor ratio was 10 ml g^{-1}.

The cellulose phosphate samples were identified from the content of phosphorus [6] and nitrogen [7] and based on the results of potentiometric titration with 0.05 M NaOH against the background of 0.05 M NaCl. Table 1 lists the main characteristics of the samples examined.

Sorption of Al^{3+} and Cr^{3+} cations with the cellulose phosphate samples from 0.01–0.20 M solutions of their sulfuric acid salts was carried out under static conditions for 24 h at 298 K and the liquor ratio of 100 ml g^{-1}. To adjust pH of the solution of the metal salts we added the necessary amount of barium hydroxide which reacts with sulfuric acid to form virtually insoluble barium sulfate. The degree of swelling was determined gravimetrically [8].

The CP samples containing metal cations were washed with water and dried in a vacuum desiccator above phosphorus(V) oxide at 323 K under residual

Table 1. Physicochemical characteristics of cellulose phosphate samples

Sample	Content of indicated species			Degree of swelling, g g^{-1}	Static exchange capacity, mg-eq g^{-1}			$pK_{0.5}$	
	nitrogen, %	carbamate groups, mmol g^{-1}	phosphorus, %		1[a]	2[a]	total	1[a]	2[a]
Rayon fiber	0.26	0.19	0.90	0.39	0.3	0.3	0.6	2.9	7.0
Cotton fiber	0.33	0.24	0.90	0.73	0.3	0.3	0.6	3.1	7.0

[a] In two steps.

pressure of 0.10 kg-force cm^{-2}. The content of adsorbed Al^{3+} and Cr^{3+} cations in the adsorbent phase was determined by the procedure described in [9]. We monitored pH of the initial and equilibrium solutions with an HI 9321 pH-meter using combined and glass electrodes.

The IR spectra of cellulose phosphates and their salt forms were recorded on a Thermo Nikolet FT-IR Nexus spectrophotometer.

The composition of the complexes was determined by potentiometric titration with and without metal cations in CP. For the experimental technique and calculation of the structure of the resulting complexes, see [10]. The initial concentration of the metals salts in solution was 0.1 M.

Cellulose phosphate contains phosphoric acid groups, as well as carbamate and hydroxy groups; its structure can be presented as

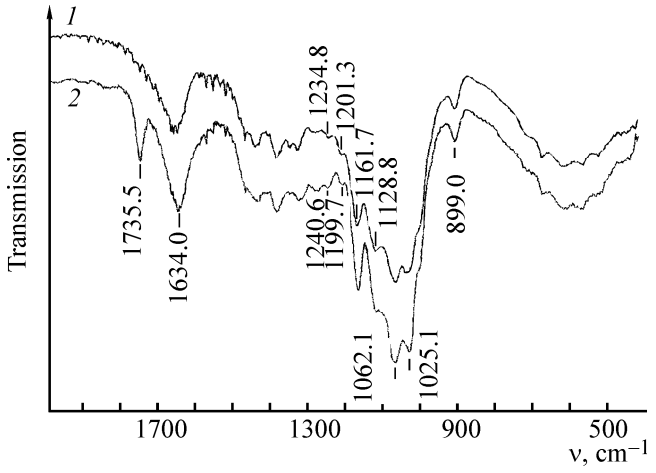
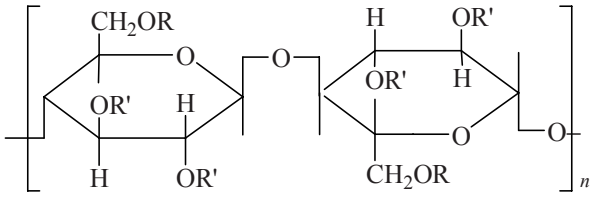


Fig. 1. IR spectra of (*2*) CP and (*1*) its salt form with aluminum; (ν) wave number.



R = H, $PO(OH)_2$, $CONH_2$, R' = H, $CONH_2$.

The presence of phosphoric acid and carbamate groups in CP was confirmed by elemental analysis, potentiometric titration, and IR spectroscopic data (Fig. 1). By contrast to the initial cellulose, the CP samples exhibit an IR absorption band of carbonyl group (C=O) near 1735 cm^{-1}. According to published data [5, 11], this suggests the presence of carbamate groups in these samples. The absorption bands with maxima at 1025–1065 and 1200 and 1240 cm^{-1} can be assigned to the stretching vibrations of the P–O–C and P=O groups, which suggests the presence of phosphoric acid groups in CP [3, 5, 11].

Figure 2 shows the isotherms of sorption of the Al^{3+} and Cr^{3+} cations from solutions of sulfuric acid salts with CP based on rayon (Fig. 2, curves *1, 2*) and cotton (Fig. 2, curve *3*) fibers. Also, for comparative assessment of the selectivity of the sorption properties of the cation exchangers, we presented the isotherms of sorption of these metal cations with carboxy-containing cellulose sorbent (monocarboxy cellulose, MCC) with nearly identical exchange capacity. It is seen that the maximal sorption capacities for the cations with CP of different origin are nearly identical. Specifically, it corresponds to the exchange capacity in the first step (EC_1) and is achieved at the salt concentration in solution $c \geq 0.1$ M. It should be noted that CP exceeds the carboxy-containing cation exchanger in sorption selectivity with respect to triple-charged cations. Also, the selectivity series for sorp-

tion of the cations of both metals with the cation exchangers at pH 1.7–1.9 are different: Cr(III) ≈Al(III) for CP, and Cr(III) <Al(III) for MCC.

A decrease in pH of the equilibrium solutions relative to the initial solutions suggests proceeding in the systems of interest of ion exchange involving CP. In acid media (pH_{eq} 1.7–1.9) ca. 10% of strongly acidic groups of CP occur in the ionized state. Hence, the content of the cations absorbed by CP significantly exceeds that of the ionized groups of the sorbent. Thus the sorption of triple-charged cations with CP is underlain by simultaneous Coulomb and coordination interactions.

The participation of phosphoric acid groups of CP in coordination bonding with Al^{3+} and Cr^{3+} is confirmed by the IR spectroscopic data. In the IR spectrum of the interaction product of CP with Al^{3+} cations (Fig. 1) the absorption bands of the P=O group (1200–1240 cm^{-1}) change in intensity, and the maximum of the absorption band at 1240 cm^{-1} shifts to lower frequencies. Saldadze and Kopylova-Valova [10] and Bobritskaya et al. [12] attributed these changes in the bands associated with the stretching vibrations of the P=O of group to the coordination bonding between the metal and oxygen in the phosphoric acid group. Similar changes are also characteristic of the IR spectrum of the interaction product of CP with Cr(III).

Table 2 shows that, with increasing pH of the equilibrium solution to 3.5, the sorption capacity of CP with respect to triple-charged cations tends to increase. At the same time, the above-mentioned features of sorption of Cr(III) and Al(III) cations with cellulose cation exchangers containing different functional groups are preserved. Sorption of $Al^{3+}$and Cr^{3+} with CP cations tends to enhance with increasing pH of solutions of their salts because of an increase in the concentration of deprotonated phosphoric acid groups in the sorbent phase, which favors ion exchange and complexing.

To elucidate the composition of the complexes formed during sorption of triple-charged cations, we carried out potentiometric titration of cellulose phosphate in the presence of Al^{3+} and Cr^{3+} cations in the sorbent. The potentiometric titration data (Fig. 3, Table 3) suggest that the complexes formed in sorption of Cr(III) and Al(III) from their sulfuric acid solutions contain at least two metal cations per phosphoric acid group. Formation of complexes in which one ligand (L) is bound by two metal cations [copper, iron(III), etc.] was mentioned by Bobritskaya et al. [12]. We showed earlier [13] that sorption of triple-charged metal cations with MCC samples involves formation of Cr(III):COO^- = 1:2 and Al(III):COO^- = 1:1 complexes. Clearly, the difference in the composition

Table 2. Sorption capacity of phosphorylated and oxidized cellulose [12] with respect to chromium and aluminum cations in relation to pH

Sample	Metall cation	pH_{eq}	Amount of absorbed cations $\bar{c}_M$, mmol g^{-1}
CP	Cr^{3+}	1.8	0.32
		2.7	0.36
		3.0	0.43
	Al^{3+}	1.8	0.28
		2.5	0.35
		3.5	0.47
MCC	Cr^{3+}	2.1	0.13
		2.5	0.22
		3.2	0.24
	Al^{3+}	2.1	0.17
		3.0	0.29
		3.7	0.42

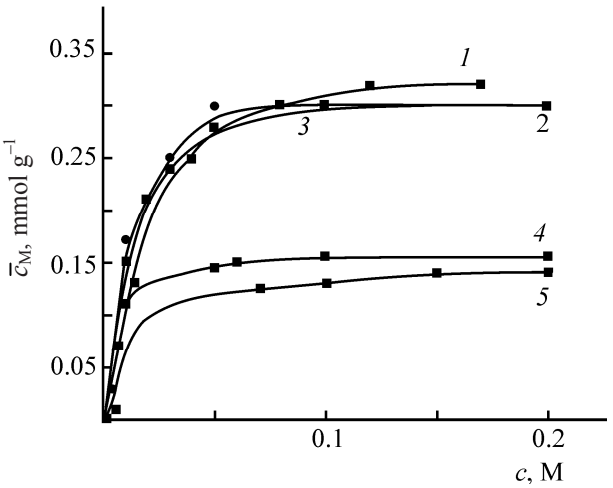


Fig. 2. Isotherms of sorption of (*1, 5*) chromium and (*2–4*) aluminum cations with CP in the form of (*1, 2*) rayon and (*3*) cotton fibers and (*4, 5*) MCC (EC = 0.7 mg-eq g^{-1}) in the form of rayon fibers. ($\bar{c}_M$) Content of metal cations in the CP phase, mmol g^{-1}, and (c) content of metal cations in solution, M.

Table 3. Experimental potentiometric titration data for CP in the presence of chromium and aluminum salts

Metall cation	pH_{eq}	[L], mol l^{-1}	c_M, mmol g^{-1}	Q, g g^{-1}	n = L:M
Cr^{3+}	2.6	0.61	0.28	0.22	1:2
	2.7	0.89	0.38	0.22	1:2
	2.8	0.94	0.40	0.20	1:2
Al^{3+}	2.7	0.51	0.28	0.25	1:2
	2.9	0.69	0.36	0.23	1:2
	3.0	1.06	0.43	0.19	1:2

of the complexes can also affect the selectivity of sorption of triple-charged cations with cellulose cation exchangers containing cabroxy and phosphoric acid groups.

The composition of the resulting complexes varies with the structure of the cellulose sorbents; this concerns both the ionic state of the cations in the external solution and the structure of the cation exchanger.

The equilibrium solutions of chromium sulfate and aluminum sulfate after sorption of cations with MCC and CP have nearly identical acidities (within 1.6–2.1). Over this pH range the chromium and aluminum cations occur in aqueous solutions mainly as mononuclear aqua $[M(H_2O)_6]^{3+}$ and hydroxo $[M(OH)\cdot(H_2O)_5]^{2+}$ complexes [14]. Also, Cr(III) and Al(III) sulfates proper are complex compounds containing one sulfo group in the inner coordination sphere [15], for which reason aqueous solutions can contain the following complex ions:

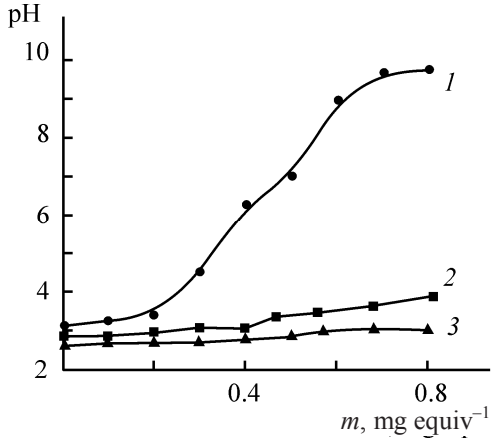
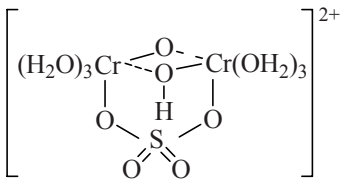


Fig. 3. Curve of potentiometric titration of CP (*1*) without and with (*2*) Al^{3+} and (*3*) Cr^{3+} cations. Ionic strength of 0.5 was achieved by adding Na_2SO_4 into solutions. (*m*) Amount of the added alkali.

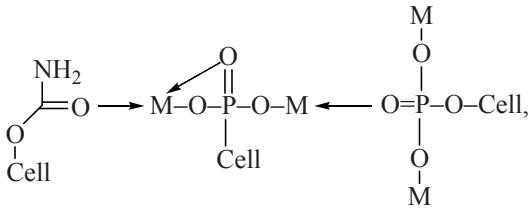


Identical compositions of the aqueous solutions of the sorbates when sorbed with both cation exchangers (CP, MCC) suggest that the observed differences in the sorption capacities and compositions of the resulting complexes are associated with the structural features of the sorbents (dibasic phosphoric acid groups, presence of carbamate groups in phosphorylated cellulose).

To analyze possible participation of the carbamate groups in sorption interactions between CP and metal cations, we examined the IR spectra of the salt forms of CP in the region corresponding to vibrations of the carbonyl group (Fig. 1). In the IR spectra of all the salt forms of CP the band at 1735 cm^{-1} either decreases in intensity (Cr form of CP) or totally disappears (Al form of CP). This suggests participation of the carbamate groups in coordination bonding with metal cations [3, 10].

Bobritskaya et al. [12] carried out IR and ESR spectroscopic examinations and revealed formation of M:–$OPO(O^-)_2$ = 2:1 complexes in sorption of multiple-charged metal cations with phosphate-containing sorbent prepared by phosphorylation of a polyvinyl alcohol–polyacrylonitrile copolymer with oxyethylidene diphosphonic acid. This suggests that a weakly acidic group of phosphoric acid ester of cellulose can form an additional coordination bond with chromium and aluminum cations without releasing a proton into the external solution. Ermolenko et al. [2] reported on participation of the second hydroxy group of the phosphoric acid group of CP in complexing with Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{2+}, Fe^{2+}, Fe^{3+}, and Cr^{3+} cations.

Comparison of published data with our experimental results suggests the following plausible structure of the complexes formed by the metal cations and phosphorylated cellulose:



where Cell is the cellulose matrix, and M = Cr^{3+}, Al^{3+}; the charges of the complex cations and ligand groups of the cation exchanger are omitted.

This structure visualizes ionic bonding between the metal cations and protonated first hydroxy group and the donor-acceptor bonding with the phosphoryl oxygen atom and oxygen atoms of the carbonyl and second hydroxy group of CP. The unutilized positive charge of the metal cations is balanced by the sulfate ions contained in the ion-exchanger phase.

Formation of such compounds promotes cross linking of the macromolecules of the modified cellulose. This substantially decreases the degree of swelling of chromium- and aluminum-containing CPs relative to that of the initial CP sample (Tables 1, 2).

CONCLUSIONS

(1) Cellulose phosphates in the form of rayon and cotton fibers exhibit high, approximately identical selectivities in sorption of triple-charged aluminum and chromium cations.

(2) Potentiometric titration data suggest formation of M(III):–$OPO(O^-)_2$ = 2:1 coordination compounds in the cellulose phosphate phase at pH within 2.6–3.0. Sorption of the Cr^{3+} and Al^{3+} cations on cellulose phosphate promotes cross linking of the macromolecules of the modified polysaccharide and causes the water-retaining power of the fibers to decrease.

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