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MULTIFUNCTIONALITY OF NITROGEN OXIDE COMPOUNDS AS A BASIS FOR PREPARATION OF PRACTICALLY IMPORTANT CELLULOSE MATERIALS

In the Laboratory of Physical Chemistry and Modification of Cellulose, over many years, a multitude of physical and chemical transformations of cellulose (Cel) under the action of nitrogen oxide compounds (N_2O_4, NO_2, N_2O_3, HNO_3) was studied, including determination of conditions for stimulating each type of reaction; namely, oxidation, nitrosation, nitration, hydrolytic cleavage or adduct formation. About 100 of our publications are summarized in a review [1] covering mainly fundamental aspects of this area. The amount of information accumulated thus far allowed rational approaches to be outlined concerning preparation of a number of practically important materials using nitrogen oxide compounds. Owing to multifunctionality of the latter with respect to Cel, it is often possible to do with a single reagent for a simultaneous or sequential performing several operations of chemical or structural modification of Cel. In preparation of carboxylated microcrystalline Cel, for example, using gaseous nitrogen oxide(IV) enables oxidation and hydrolytic dispersion of Cel to be performed, as well as enhancement of stability and whiteness of the final product.

Not only chemical and structural modification of Cel with nitrogen oxide compounds is of practical significance, but also participation of the latter in the process of preparation of Cel itself. High solubility of nitrates, which are mineral components of vegetal tissues, along with high reactivity of HNO_3 with respect to lignin, provides the opportunity of selective extraction of radionuclides in the course of nitric acid delignification of contaminated straw of annual plants and preparation of radionuclide-free Cel and nitrolignin. These results contribute to the development of a prospective technology for rehabilitation and deactivation of radionuclide-polluted territories. The proposed version of utilization of radionuclide-contaminated straw of technical agrocultures has won support from international scientific community.

In this review, examples are discussed of efficient use of nitrogen oxide compounds for the preparation of such practically important materials as completely or partially substituted Cel acetates soluble in organic solvents, water-soluble polysaccharide sulphates of low degree of substitution, powder forms of Cel hydrate and carboxylated Cel in structurally disordered or microcrystalline form, as well as for isolation of radiation-free Cel and nitrolignin from radionuclide-contaminated agricultural residues.

1. NITROSATION OF CELLULOSE AND OTHER POLYSACCHARIDES AS A METHOD OF «CHEMICAL ACTIVATION» FOR PREPARATION OF ACETO- AND SULPHOESTERS

Partial nitrosation of Cel in acetic acid (AA) may be of practical interest as an effective preactivation method in the preparation of cellulose acetates [2, 3]. The high reactivity of cellulose nitrite in the homogeneous transesterification reactions with acetylating agents is known [4]. This property of Cel nitrite is clearly manifested under usual acetylation conditions as well, when the reaction starts under heterogeneous conditions and ends up by a complete dissolution of the final product in the acetylating mixture (reaction up to a «clear field»).

The proposed activation procedure reduces to brief treatment of Cel with a solution of N_2O_4 in glacial AA and subsequent displacement of the free nitrogen oxides from the fibre by the same acid. The traditional industrial schemes for the activation of Cel are also based on the treatment of the fibre with AA. In Table 1, comparative data are given on Cel acetylation after activation using the conventional and the proposed methods. The activating mixture AA–N_2O_4 of composition 80:20 provides an extremely rapid conversion of Cel into the corresponding acetate with a virtually complete degree of substitution (DS). In this mixture, formation of an adduct of Cel trinitrite with AA takes place [1] and, as a result of this, very extensive swelling of the fibre occurs that complicates removal of free nitrogen oxides from it in the final stage of activation.

Table 1

Results of acetylation by the methylene chloride method of cotton Cel activated at 20 °C with AA or the N_2O_4–AA mixture

Activation conditions	Reaction time until attainment of a «clear field»/min	DS of Cel acetate	DP of Cel acetate
Initial Cel – native			
1 h, 80 % AA	180	2.85	740
20 min, N_2O_4–AA mixture (20:80)	7	2.86	400
5 min, N_2O_4–AA mixture (5:95)	30	2.92	650
Initial Cel – mercerized			
1 h, 80 % AA	180 (no homogenization)	1.62	
5 min, N_2O_4–AA mixture (5:95)	50	2.90	

Note: Acetylating mixture: acetic anhydride-acetic acid-methylene chloride (30:10:60 vol. %), catalyst – perchloric acid (~1 % of mass of C), liquor ratio 10 ml g^{-1}, temperature 26 °C.

The addition of small amounts of N_2O_4 (5 vol. %) does not induce excessive swelling of the fibre, so that the activation process occurs simply and rapidly, enabling nevertheless an appreciable increase in reactivity and higher DP of the final product to be achieved. After such activation, even mercerized cellulose that is well-known by its low reactivity in acetylation, is acetylated almost completely.

The proposed method of Cel activation provides a smooth and uniform reaction process, owing to which carrying out the reaction in acetone up to the «clear field» point makes it possible to obtain partially substituted Cel acetates (DS = 2,12 – 2,26; DP = 420–590), soluble in acetone, dioxane, DMF, AA and other solvents [3]. The properties of these products are similar to those of the secondary Cel acetates obtained via a two-stage scheme: complete acetylation of Cel – partial homogeneous hydrolysis. The known methods for the direct synthesis of such materials [5] are based on the acetylation of Cel in the presence of large amounts of H_2SO_4 (15 % – 25 % of the mass of Cel) and on the reaction being carried out in dioxane. While being more complex, these methods are based on the same principle of 'chemical activation'– by sulphate formation in this case. The mixed esterification of Cel leads to homogenization of the reaction mixture in early stages of the reaction and to uniformity of the substitution by acetyl groups that provides solubility in organic solvents of partially substituted Cel acetate. In order to isolate C acetate in a pure form and impart thermal stability to it, a special operation involving the saponification of the sulphate ester groups is carried out [5]. Preparation of similar materials based on partially nitrosated Cel is performed using the conventional acetylating mixture and does not require any additional stabilization procedures.

Biological activity is the property of not only expensive and difficult-to-isolate polysaccharide derivatives (heparin, chondroitin sulphate, etc.), but also of the sulphates of readily available polysaccharides (Cel, dextran, mannan, chitosan) [6]. An efficient procedure for a uniform conversion of polysaccharides into sulphates is the homogeneous transesterification of the respective nitrites using SO_3 in the DMF-N_2O_4 system [4]. As an alternative to the highly toxic and corrosive SO_3 in preparing sulphate esters, we have proposed [7–9] using its «stored» forms – salts of acids $H_2S_nO_{2n+1}$ (n = 1, 2) or $H_2S_nO_{3n+1}$ (n = 1–3) that generate SO_3 when acted upon by the reaction medium. Along with the system homogenization due to formation of the nitrosoester, the presence of N_2O_4 ensures sulpating activity of the potential SO_3 source.

Reactants stimulating sulphate formation can act as oxidants, or can participate in exchange processes, or can combine the oxidizing and exchange functions, depending on the type of sulphur-containing compound employed. The first role is assumed when SO_2 is converted into the sulphating complex of SO_3 with the solvent [10]. The role of N_2O_4 is not confined to only nitrosation of the polysaccharide and generation of SO_3. The equilibrium DS with respect to sulpho-groups depends on the N_2O_4/SO_3 ratio, decreasing as the latter grows.

Thus, apart from the known instability of the sulphate esters in acid media, account must be taken also of the desulphating activity of N_2O_4, i.e. the existence in the reaction systems of equilibrium between the sulphate and nitrite ester substituents in the polysaccharide:

$$R\text{–}OH + N_2O_4 \rightleftharpoons R\text{–}ONO + HNO_3$$

$$R\text{–}ONO + HNO_3 + SO_3 \longrightarrow R\text{–}OSO_3H + N_2O_4 \qquad (1)$$

When salts of $H_2S_nO_{3n+1}$ are used as a source of sulphur, the reactive sulphating agent is generated *in situ* as a result of exchange reactions involving HNO_3 and N_2O_4.

$$Na_2SO_4 + 2HNO_3 \underset{}{\overset{}{\rightleftharpoons}} H_2SO_4 + 2NaNO_3 \xrightarrow{N_2O_4} SO_3 + HNO_2 + HNO_3\ (NOSO_3OH + HNO_3) - 2HNO_3$$

$$2NOSO_3OH \xrightarrow{DMF} N_2O_3 + H_2S_2O_7 \bullet DMF; \qquad (2)$$

$$H_2S_2O_7 \rightleftharpoons H_2SO_4 + SO_3$$

The SO_3 evolved from the salts shifts the equilibrium (1) towards the formation of sulphate ester. Owing to homogeneity and equilibrated nature of the process, the displacement of nitrite by sulphate ester groups takes place uniformly. The Cel sulphates being obtained are completely soluble in water even at DS 0.2, which cannot be realized with any other known sulphate formation process.

A mixed type of activating influence of N_2O_4 and HNO_3 is manifested with respect to salts of acids $H_2S_nO_{2n+1}$:

$$Na_2SO_3 + 2HNO_3 \rightleftharpoons 2NaNO_3 + H_2SO_3 \xrightarrow{HNO_3\ (N_2O_4)} H_2SO_4 + HNO_2\ (N_2O_3) \qquad (3)$$

It follows from equations (2) and (3) that in the case of using salts with tetravalent sulphur both exchange and oxidation reactions take place. The latter lead to heating of the system and to acceleration of the reaction. Salts with hexavalent sulphur are preferable because the equilibrium is established slowly and without heating in this case, thus creating mild conditions for the synthesis, which prevent degradative transformations of macromolecules. The overall synthesis time is reduced as a result of combination of stages involving dissolution of the starting material and its conversion into sulphate on simultaneous introduction of the polymer and the salt into the DMF-N_2O_4 mixture. At the appropriate DS, the mannan and dextran sulphates synthesized in this way exhibit a distinct anticoagulant activity while being non-toxic even when applied in large doses (2–5 g kg^{-1}) [11].

The studies outlined above resulted in the development of an anti-aterosclerotic drug on the basis of mannan sulphate, which is now marketed under the name «Ronasan».

2. THE KNECHT COMPOUND AS AN ALTERNATIVE TO ALKALINE CELLULOSE FOR PREPARATION OF STRUCTURALLY AND CHEMICALLY MODIFIED POWDER FORMS OF CELLULOSE

Practical importance of Cel mercerization phenomenon based on intracrystallite swelling in alkali hydroxide solutions is well-known. The intracrystallite swelling of native Cel can also be caused by HNO_3 at concentrations close to 68.4 %, the value corresponding to azeotrope composition [12]. As a result of the swelling, crystalline phase of an additive compound, the Knecht compound (KC), is formed. Although this compound has been known for a long time [13, 14], its features remain yet obscure under many aspects [1].

On the basis of the X-ray diffraction data obtained by Andress [14], in combination with the current concepts concerning formation of Cel adducts [15], the crystalline phase of KC can be regarded as a result of insertion and stoichiometric 'fixation' of HNO_3 between the least interlinked (101) planes of the three-dimensional lattice of Cel (Fig. 1). The movement of these planes apart from one another along the large ac diagonal on the cell projection is accompanied by a decrease in the angle β, without affecting significantly the $(10\bar{1})$ and (002) planes. The (101) reflection on the X-ray diffraction pattern of the new phase is displaced towards smaller diffraction angles. According to Gess [16], KC is an oxonium-like compound by its nature, being a product of addition of HNO_3 to the oxygen of the glucoside group of Cel. Under the action of water, the polymorph Cel II is regenerated from KC, and this fact, being similar to behaviour of the alkaline Cel, allows the whole procedure to be considered as an acid version of 'mercerization' [17, 18].

The HNO_3 ability to form the Knecht additive compound with C becomes clearly apparent at the concentration of 68 % [19]. This tendency increases with increasing concentration of HNO_3. At the same time, an active accumulation of the HNO_3 pseudo form ($HO–NO_2$), which provokes nitration of Cel [20], starts from the concentration of ~ 69 % on. Hence, the stimulation of phase transformation by increasing the HNO_3 solution concentration is complicated by nitrating ability of the acid at concentrations above 69 %.

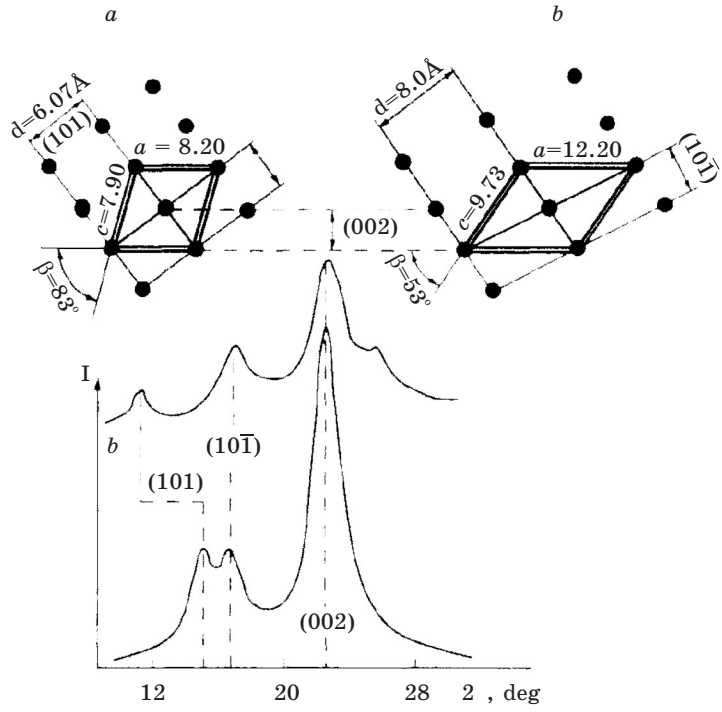

Fig. 1. Schematic illustration of the transformation of Cel-I unit cell (*a*) into KC unit cell (*b*) and the corresponding changes in the diffractogram

Lower temperatures are known to favour the process of traditional mercerization of Cel. This is usually explained by differences in temperature coefficients for the formation reaction rate and hydrolysis rate of alkaline Cel (the latter value is greater) [20]. The experimental results obtained in our studies give evidence of a peculiar effect of temperature on nitric acid «mercerization» process occuring in Cel of different origin and morphology [17, 18]. When cotton Cel (cotton Cel) is taken as starting material, the temperature dependence is similar to that observed for traditional mercerization, i.e. temperature decrease from 20 °C to 0 °C stimulates the polymorphic transformation (Fig. 2). However, a complete transformation of the starting material into the polymorph-II is not reached under these conditions. As compared to the initial cotton Cel, phase transformations are substantially slower in cotton microcrystalline Cel (cotton MCCel).

The above conditions of interaction with HNO_3 being applied to wood sulphite Cel (WCel) cause its complete and relatively rapid transformation into the polymorph-II. Unlike cotton Cel, this process occurs more rapidly at 20 °C, not at 0 °C. The anomalous character of temperature dependence is more pronounced in samples with a conventional (amorpho-crystalline) morphology (Fig. 2*a*). Wood microcrystalline Cel (WMCCel), unlike cotton MCCel, is «mercerized» at an unexpectedly high and almost temperature-independent rate, up to a conversion degree of ~ 60 %. (Fig. 2*b*). It is at the final stage only that a somewhat slower polymorphic transformation is observed at 0 °C as compared with that at 20 °C. The highest activity of sulphite WCel was noted in the traditional mercerization with NaOH solutions too, while cotton Cel and Ramie Cel were categorized among the least active [21].

It is obvious that the true dependence of the permutoid (according to Mark) reaction rate on temperature is reflected in experiments with cotton Cel, whose degree of chemical purity is superior to that of technical grade WCCel of any production methodology. The following Cel contents are found in its raw materials: up to 98 % in cotton seed fluff, and no more than 55 % in wood tissue. The destructive

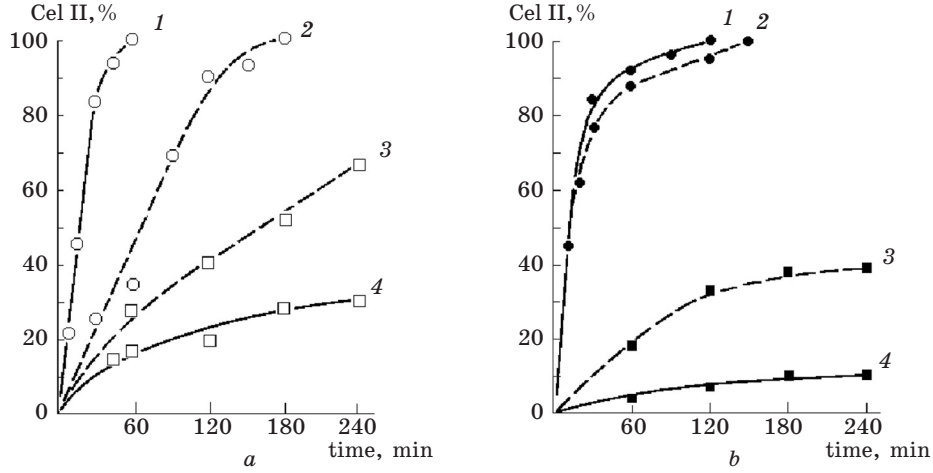

Fig. 2. Degree of transformation into polymorph-II of fibrous (*a*) and microcrystalline (*b*) form of WCel (*1*, *2*) and cotton Cel (*3*, *4*) as Function of interaction with 68.5 % HNO_3 at 20 °C (*1*, *4*) and 0 °C

transformations caused by hard pulping conditions used for the removal of large quantities of lignin and hemicelluloses from the wood tissue exert negative influence on porous capillary system and reactivity of the fibres being isolated. Dense deposits of unremoved low-molecular fractions (consisting mainly of hemicelluloses) prevent the reagent penetration through the capillary system and make diffusional mechanism prevail over the capillary one [20, 22]. Thus, there are reasons to think that the HNO_3 transfer towards WCel crystallites at lower temperatures occurs under conditions of larger diffusional inhibition than it is seen in the case of CCel. This can be associated with a decreased ability of the acid to overcome the hemicellulose deposits due to its weaker hydrolytic activity at lower temperatures. The crystallite transformation is 'retarded' correspondingly, and this is seen on the X-ray patterns. Sound confirmation of this point of view is the fact that WMCCel is 'mercerized' at 0 °C more rapidly than the initial Cel. The most probable cause of this acceleration is weakening of the diffusional factor influence on the process kinetics as a result of 'liberation' of crystallites from the structurally disordered binding material. In the traditional mercerization, the reagent penetration is favoured by the hemicellulose solubility in alkaline media. Furthermore, the swelling of Cel in 68–69 % HNO_3 is not so extensive as in NaOH solutions [17]. Microphotographs shown in Fig. 3 enable a comparison to be made between transversal dimensions of the cellulose fibre on swelling in 68.5 % HNO_3 with that swollen in 18 % NaOH. It is apparent that the alkaline medium caused a two-fold greater thickening of the fibre as compared with the nitric acid one.

The incapability of the two cotton Cel morphological forms to be «mercerized» completely under conditions providing complete «mercerization» of the corresponding WCel forms (Fig. 2) is in agreement with the idea [21] about the influence of crystallite dispersity and imperfectness on the depth of phase transformations associated with the formation of additive compounds. The crystallites of cotton Cel are considerably larger and more perfect than the crystallites of WCel, and this fact, together with a relatively small swelling of Cel in 68–69 % HNO_3, makes WCel more suitable for the nitric acid 'mercerization'.

During the nitric acid «mercerization», the conventional (amorpho-crystalline) Cel undergoes a considerable depolymerization (Fig. 4). A rapid decrease in DP of the initial Cel at the beginning of its interaction with 68.5 % HNO_3 is followed by a slow degradation of molecular chains. The rate of hydrolytic cleavage of the

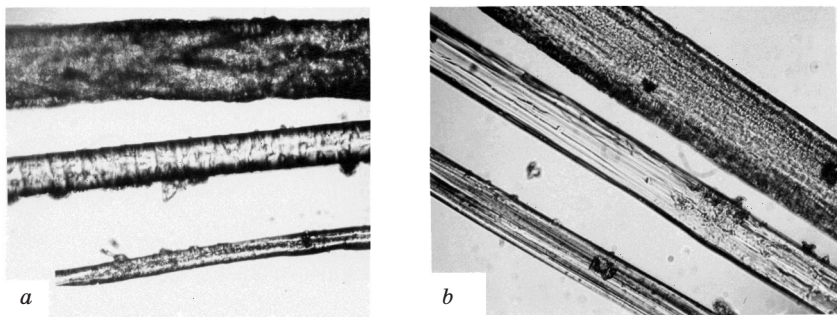

Fig. 3. Optical microphotographs of flax Cel (*a*) and Cel hydrate (*b*) fibres. From the bottom upwards: initial fibre swollen in 68.5 % HNO_3 solution; fibre swollen in 18.5 % NaOH solution

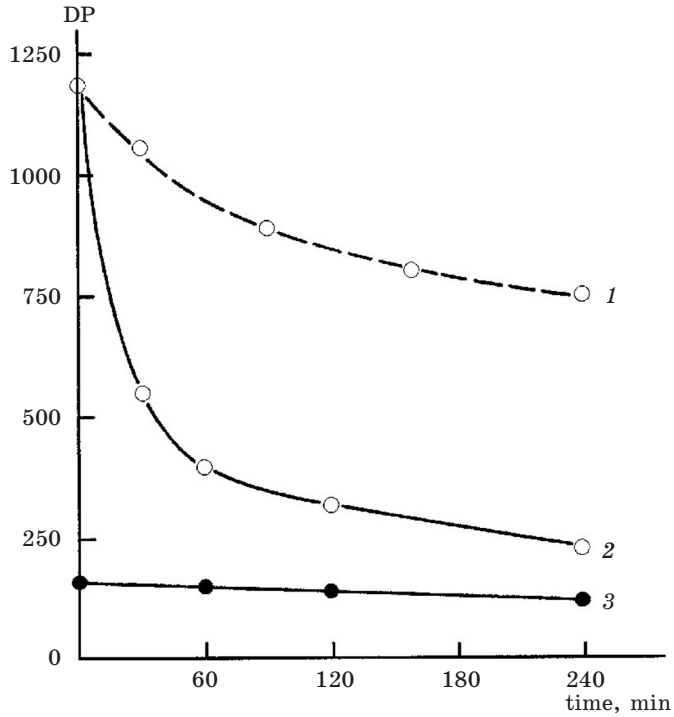

Fig. 4. Changes in DP of initial WCel (*1*, *2*) and WMCCel (3) during mercerization at 20 °C (*2*, *3*) and at 0 °C (*1*, *3*)

macromolecules strongly depends on the 'mercerization' temperature (Fig. 4). A complete polymorphous transformation of WCel at 20 °C (reaction with HNO_3 for 1 h) is accompanied by an about three-fold decrease in DP (that initially was ~1200), while at 0 °C (reaction with HNO_3 for 3 h) the DP value decreases 1.5 times only. Unlike the initial Cel, its microcrystalline form remains resistant to hydrolysis under conditions of intracrystallite swelling as well. As a probable cause of preventing from the development of destructive transformations, a high stoichiometry may be noted in the reaction of 68.5 % HNO_3 with Cel macromolecules organized into crystallites [14, 23].

According to [14], one molecule of HNO_3 falls to the share of two anhydroglucose units of Cel. During the period of complete 'mercerization' of WMCCel at both 20 °C and 0 °C, the initial DP value remains virtually invariable.

The IR spectra of 'mercerized' Cel reveal prominent features making the difference between the Cel-II polymorph and Cel-I polymorphs [24]. There are no signs of oxidative transformations (1700–1800 cm^{-1}), but characteristic bands of nitroester groups are present (1650, 1280, 850 and 750 cm^{-1}). The rate of bound nitrogen accumulation in Cel depends strongly on the temperature at which the reaction with HNO_3 takes place (Fig. 5). The effect of the initial material morphology on the esterification process is small. In the course of complete 'mercerization' at both 20 °C (reaction with HNO_3 for 1h) and 0 °C (reaction with HNO_3 for 3h), the ordinary Cel accumulates approximately equal amounts of nitrogen: 0.7 to 0.8 % (DS_{-ONO_2} = 0.08–0.09).

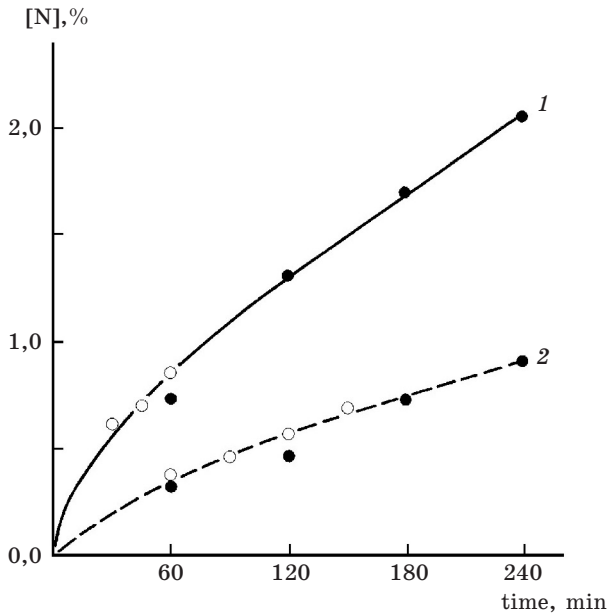

Fig. 5. Bound nitrogen accumulation kinetics reflecting the course of reaction of the initial WCel (o) and WMCCel (•) with 68.5 % HNO_3 at 20 °C (*1*) and 0 °C

In the case of nitric acid 'mercerization' of WMCCel, the influence of esterification on the physical structure of the products becomes appreciable. We noticed that WMCCel «mercerized» at 0 °C (interaction with HNO_3 for 2.5 h) is significantly superior in crystallinity to the same WMCCel «mercerized» at 20 °C (interaction with HNO_3 for 2 h) The latter one is notable for its two-fold higher bound nitrogen content (~ 1.3 %; $DS_{\text{-ONO}_2} = 0.15$). If the «mercerization» time is increased up to 4 h, the amount of bound nitrogen rises to ~ 2 % ($DS_{\text{-ONO}_2} = 0.25$).

In X-ray diffraction patterns of the products, a gradual «degeneration» of the crystallite scattering with increasing degree of esterification is observed, and it is hardly perceptible at $DS \geq 0.25$. At the same time, the X-ray diffraction pattern of WMCCel «mercerization» product obtained at 0 °C during 4 h displays a quite distinct crystallite scattering of Cel-II (Fig. 6), because the bound nitrogen content in this case does not exceed 0.9 % ($DS_{\text{-ONO}_2} = 0.1$). An obvious correlation can be discovered between the degree of esterification and the degree of decrystallization of the «mercerized» WMCCel. We think the main cause of structural disorganization of WMCCel during its nitric acid «mercerization» is associated with its partial esterification under conditions of intracrystallite swelling, which entails disturbance in structural regularity. It should be emphasized that a well-defined decrystallization effect can only be observed in the case of WMCCel, when the entire nitrating potential of HNO_3 is used up solely for the crystalline phase of Cel. Manifestation of this effect is favoured, in our opinion, by a relatively small chain length of WMCCel molecules, which is comparable in size with a segment of ordinary Cel.

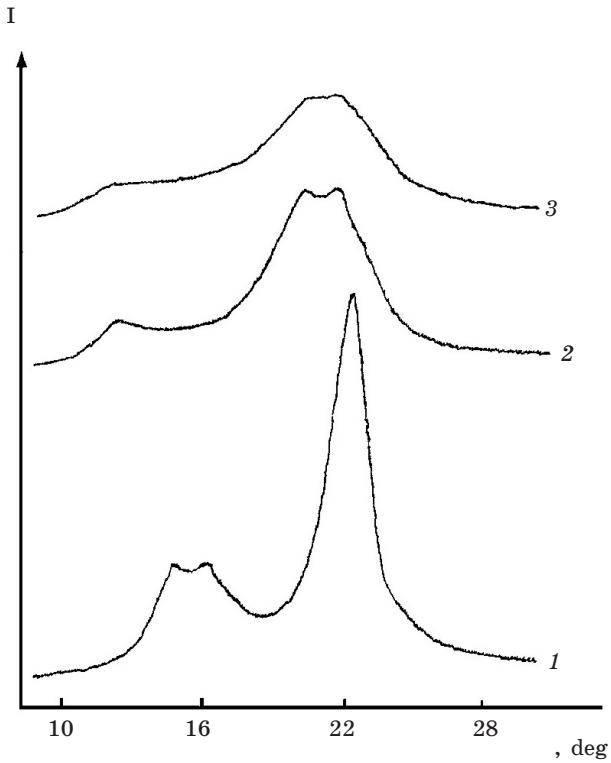

Fig. 6. X-ray diffractograms of WMCCel (*1*) and products of its «mercerization» during 4 h at 0 °C (*2*), and during 3 h at 20 °C (*3*)

It follows from the aforesaid that the combination of complex-forming and hydrolytic functions of HNO_3 makes it possible to realize a non-traditional, purely acidic WCel processing scheme to afford powder WCel-II forms having microcrystalline or amorpho-crystalline morphology [25–27].

During the non-traditional preparation of material with the microcrystalline morphology (WMCCel-IIn), WCel was first treated with nitric acid of concentration 68.5 % for 3 h at 0 °C and liquor ratio of 20 ml/g. The swollen Cel was then pressed off until a ca. 3-fold weight increase was reached. As a result of the press-off procedure, at least 60 % of initial acid volume is usually recovered. This acid, after appropriate fortification and compensation for losses, can be re-used for the polymorphic transformation of Cel. To the pressed-off fibrous mass, a quantity of water was added necessary to form 2.0 to 2.5 N HNO_3 solution from the concentrated acid absorbed by the fibres. As a result of the dilution procedure, the KC formed decomposes to yield Cel-II, which is then hydrolysed with boiling 2.0–2.5 N HNO_3 down to its «level-off DP» value (1 h, liquor ratio ca. 10 ml/g).

Samples of powder wood Cel-II (WPCel-IIn) having amorpho-crystalline morphology were prepared according to the purely acidic scheme from Cel previously hydrolysed down to the «level-off DP». The hydrolysis was carried out using boi-

ling 2.5 N HNO_3 at a liquor ratio of 10 ml/g during 1 h. The WMCCel-I thus obtained was converted into the Cel-II polymorph using 68,5 % HNO_3, as above.

In order to perform a comparative characterization of the Cel-II powder forms obtained by the purely acidic method, WMCCel-IIt and WPCel-IIt samples of similar structures have also been prepared according to the traditional scheme. In the traditional procedure, the polymorphic transformation was performed as a conventional mercerization of native Cel with 18 % NaOH solution during 1 h at 0 °C and at liquor ratio of 20 ml/g. The hydrolysis, washing and drying conditions were identical for all the samples prepared, the only difference being the way of converting native cellulose into hydrated cellulose.

The final powder product yield is mainly determined by the material mass loss during the hydrolysis of cellulose fibres down to the «level-off DP» value. Such losses are the most appreciable in the course of hydrolysis of Cel-II whose crystalline structure is less perfect than that of Cel-I. Accordingly, the WMCCel-IIn and WMCCel-IIt samples are obtained in yields of 72–75 %, with respect to the initial Cel mass, whereas the yields of WMCCel-I, WPCel-IIn and WPCel-IIt amount to 83–85 %.

Weak absorption bands characteristic of nitro ester groups were present in the spectrum of WPCel-IIn only, because 68.5 % HNO_3 which is known to possess a nitrating ability was used in the final preparation stage of this sample. According to the chemical analysis data, this preparation contains ca. 8 nitro ester groups per 100 cellulose elementary units. In the course of preparation of WMCCel-IIn, the treatment of cellulose fibres with 68.5 % HNO_3 is followed by the procedure of its hydrolytic cleavage, as a result of which the major part of nitro ester groups introduced during the first stage is removed from the fibre together with the amorphous binding component [25].

X-ray diffractograms of the prepared samples are shown in Fig. 7. When comparing angular positions of reflections in the X-ray diffractograms 2 and 4 with those in X-ray diffractograms of similar samples but prepared using a traditional mercerization procedure (3 and 5), it can be concluded that the action of 68.5 % HNO_3 results in a virtually complete polymorphic conversion of the native crystalline structure.

At the same time, however, there are reasons to suspect the presence of some «residual nativity» in WMCCel-IIn, because the most intense reflection in its diffractogram is (002), which is characteristic of Cel-I (curve *1*), and not of Cel-II (curves *3*, *5*). This is probably due to the fact that the polymorphic conversion occurs under conditions of a considerably less extensive swelling of Cel in the nitric acid medium as compared to the alkaline one. During the process of polymorphic transformation under the action of HNO_3, the Cel fibres undergo a significantly greater decrystallization than they do under common mercerization with a NaOH solution. This difference in crystallinity is retained also after the cellulose hydrolysis down to its «level-off DP». The crystallinity index of WMCCel-IIn is 0.44, whereas that of WMCCel-IIt amounts to 0.57 (Table 2). The polymorphic transformation of WMCCel-I under the action of HNO_3 is accompanied by the most profound decrystallization, the causes of which have been discussed above. The X-ray diffractogram of WPCel-IIn sample, curve 4, is typical of Cel-II with a very low degree of structural order: its crystallinity index is 0.23 against 0.45 for WPCel-IIt.

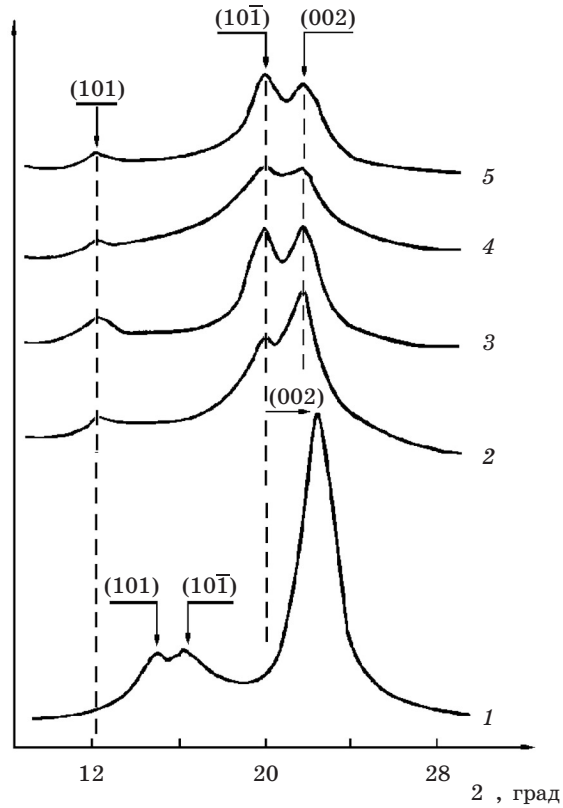

Fig. 7. X-ray diffraction pattern of Cel powder:
1 – WMCCel-I, *2* – WMCCel-IIn, *3* – WMCCel-IIt,
4 – WPCel-IIn; *5* – WPCel-IIt

Table 2

Some characteristics of cellulose powder forms

Sample	DP	Crystallinity index	WRV, %	I_2 sorption value, mg/g
WMCCel-I	170	0.67	58	19.9
WMCCel-IIn	50	0.44	107	76.3
WMCCel-IIt	50	0.57	105	27.0
WPCel-IIn	150	0.23	155	261.4
WPCel-IIt	160	0.45	208	119.1

Scanning electron microscopy photographs shown in Fig. 8 demonstrate particle dispersity and surface morphology of WMCCel-IIt and WMCCel-IIn. The observed particles represent aggregates of individual microcrystals. When comparing microphotographs *b* and *d*, it is seen that the way of polymorphic transformation of the initial Cel affects substantially the morphology of particles formed on

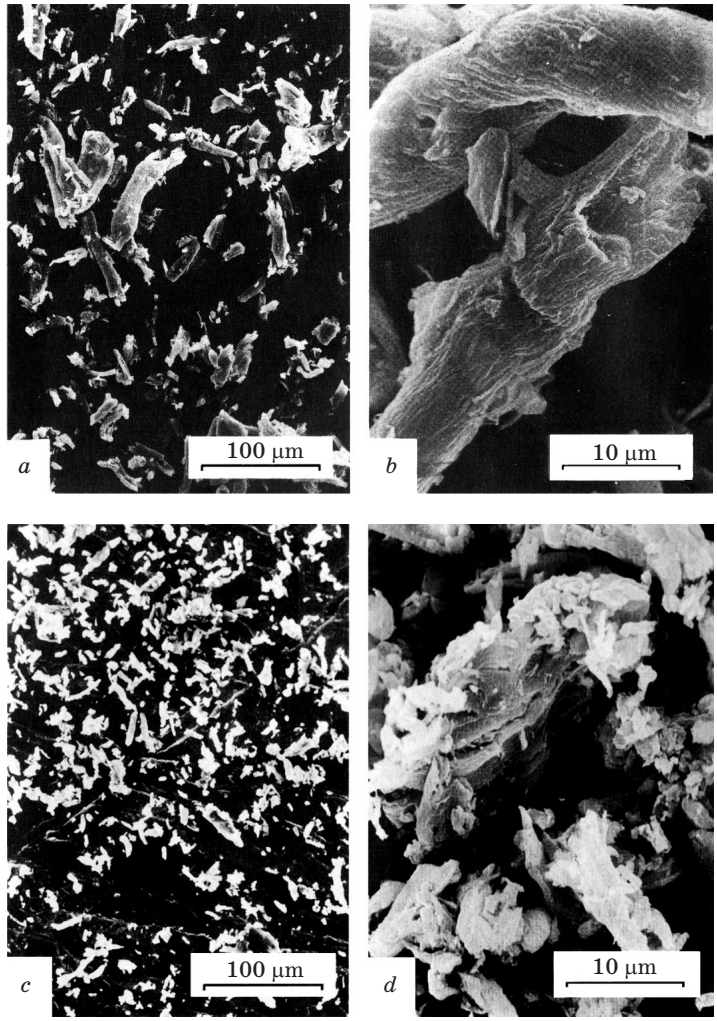

Fig. 8. Scanning electron microphotographs:
a, *b* – WMCCel-IIt; *c*, *d* – WMCCel-IIn

subsequent hydrolysis of the fibre down to the «level-off DP». The WMCCel-IIt particles obtained in the course of traditional mercerization of Cel retain a relatively «smooth» surface relief characteristic of the initial fibre. The particles of WMCCel-IIn obtained by purely acidic preparation technology are characterized by a developed surface relief reflecting the factors of not only transversal but also longitudinal cleavage of the fibre.

One can judge about dimensions of individual crystallites being constituents of samples with microcrystalline morphology from the value of «level-off DP» that is determined by longitudinal dimensions of the crystallites (Table 2). Based on the mean «level-off DP» value of 170 for WMCCel-I, the anhydroglucose unit length for Cel (5.15 Å), and the stretched conformation of macromolecules in mic-

rocrystals, the estimated mean longitudinal dimension of microcrystals of this native material is ca. 900 A. The conversion of Cel-I into Cel-II is accompanied by considerable changes in dispersity and morphology of crystallites [25, 27]. The «level-off DP» value of both WMCCel-IIn and WMCCel-IIt is ca. 50, which means a more than 3-fold decrease in crystallite length as compared to WMCCel-I.

In the course of preparation of both WPC-IIn and WPC-IIt by the polymorphic transformation of WMCCel-I using both alkaline and acidic reagents, the mean DP value of 170, that is characteristic of native microcrystals, remains almost unchanged, while the crystallite dimensions and crystallinity of the material as a whole decrease significantly (Table 2). The crystallite length is not determined by the DP value any more (the latter is greater). The microcrystalline structure of Cel-I transforms into a usual amorpho-crystalline structure of Cel-II with a small DP value.

We have found that the polymorphic transformation of Cel by the nitric acid method, unlike the traditional one, is accompanied by the appearance of numerous longitudinal microfissures in the fibre. The largest of these are visible quite well with the aid of a scanning electron microscope on both the side surfaces of WPCel-IIn particles and on the cross-sections of fibrous fragments (Fig. 9). Their formation must promote the enhancement of sorption properties of the material.

The prepared WCel-II powder forms differ from WMCCel-I by their considerably higher hydrophilicity and sorption activity (Table 2). The hydrophilic properties of Cel powders were evaluated according to their water-retaining value (WRV). This index reflects the water-retaining ability of a final product sample washed until neutral but not dried. Microcrystalline forms of Cel-II prepared by the both methods are characterized by comparable WRVs that are substantially inferior to those of the respective amorpho-crystalline forms. The most hydrophilic is the sample with an amorpho-crystalline morphology prepared by the traditional method (WPCel-IIt), in spite of the fact that its crystallinity index is higher

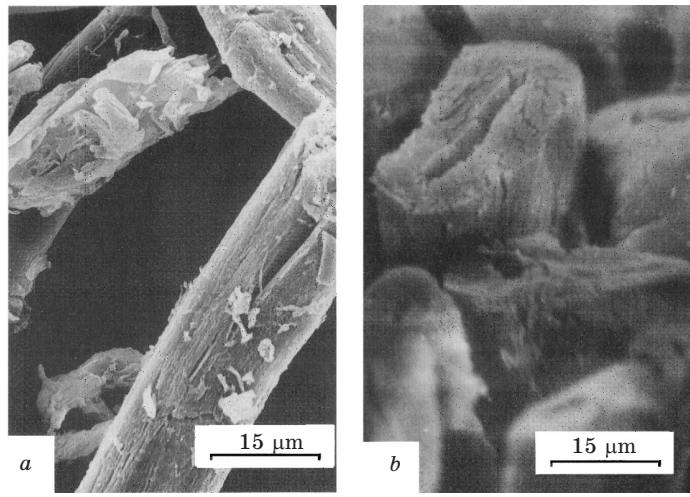

Fig. 9. Scanning electron microphotographs:
a – WPCel-IIn, *b* – cross-section of cotton Cel fibres treated with 68.5 % HNO_3

than that for the respective sample prepared by the purely acidic scheme (WPCel-IIn). There is no rigorous correlation between indices of crystallinity and those of hydrophilicity for the samples, whereas the influence of the morphological factor on the WRV is rather important.

The WCel-II powder forms prepared according to the purely acidic scheme manifest a more than two-fold superiority to their traditionally prepared analogues in sorption ability with respect to iodine (Table 2). Here too, the highest sorption activity is found for the samples possessing the amorpho-crystalline morphology. The iodine sorption values measured for these samples are 3–4 times higher as compared to the samples with microcrystalline morphology.

Similar effects are observed for Congo red dye sorption as well (Fig. 10). The Congo red sorption isotherms for WMCCel-I and WMCCel-II samples agree within experimental error (Fig. 10, curve *1*). It should be noted that the iodine sorption values for these samples are rather close too (Table 2). The sorption activity of the WMCCel-IIn sample towards the dye is somewhat higher than that for the two samples mentioned earlier, but the difference in the limit sorption values is small (curves *1* and *2*). Hence, with respect to voluminous molecules, the microcrystalline forms of Cel-I, as well as those of Cel-II of different preparation techniques, display similar li-

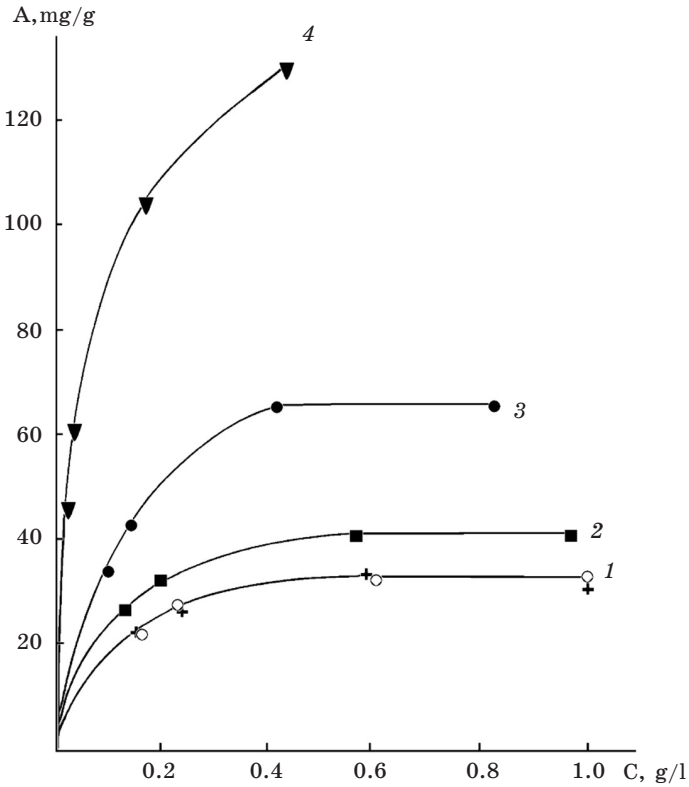

Fig. 10. Isotherms of Congo red sorption by Cel powder forms:
1 – WMCCel-I and WMCCel-IIt; *2* – WMCCel-IIn;
3 – WPCel-IIt; *4* – WPCel-IIn

mit sorption values. The most efficient sorption of Congo red (and that of iodine) is observed for the WPCel-IIn sample (curve *4*), being markedly superior to that for all the other samples in this respect. Within the same morphological form of powder material, an interrelation is observed between its crystallinity index and sorption ability with respect to both iodine and Congo red. The lower crystallinity of a sample, the more active it is as sorbent (Table 2 and Fig. 10). However, the superior sorption qualities of WPCel-IIn among all other samples are probably due to not only its low crystallinity, but to a more developed surface of its particles due to microfissure formation too. In the course of preparation of WMCCel-IIn samples, the micro-cracking effect is partially leveled during hydrolytic degradation of the fibre to form microcrystal aggregates in the final stage of the process. This effect is present in its most pronounced form in cases when the final stage is the polymorphic transformation of pre-dispersed fibres under the action of nitric acid (WPCel-IIn sample). In our opinion, just the micro-cracking effect, along with low crystallinity, provide the high sorption ability of this sample.

In the course of Cel oxidation with nitric acid, the KC adduct is capable of playing the role of a reactive «matrix» [28]. It is apparent that the structural state of Cel corresponding to KC should be superior to the initial one as regards activity and uniformity of reaction because the reagent taking part directly in oxidation of Cel is incorporated into crystal lattice of the latter.

The most rational method for obtaining carboxylated powder Cel (CPCel) based on the use of the same reagent for both oxidation and dispersion of the C fibre has been proposed in [29]. It consists in the treatment of Cel with 60 % HNO_3 in the presence of sodium nitrite that serves to generate nitrogen(IV) oxide acting as a catalyst of the oxidation process taking place in the system. In that way, a considerable oxidation degree (12 % to 14 % of COOH groups by mass)[1] can be obtained within 30 h at room temperature.

The oxidized fibres, after pressing-off the excess of the reaction medium and introducing the appropriate amount of water, are converted into a powder state by means of partial hydrolysis with diluted HNO_3 formed at the reflux temperature.

The course of oxidation of the KC obtained on the basis of flax Cel (97 % of α-Cel, DP=1800) under the stated conditions is depicted by the curve 1 in Fig. 11. Pre-activation of the initial Cel consisted in its treatment with 68.5 % HNO_3 for 1 h. After that, water was added to the system in a quantity necessary to form 60 % HNO_3, as well as $NaNO_2$ (1.4 g per 1 g of Cel). Except for the pre-activation stage, the reaction conditions were the same as in [29].

It is apparent that the carboxyl group accumulation occurs at a virtually constant rate throughout the whole time interval studied, suggesting a uniformity of oxidation within the bulk of the fibre. Appropriate conditions for a uniform reaction are created probably owing to a relatively high stability of KC towards 60 % HNO_3 at 18 °C. Within 10 h, 15.1 % of COOH groups are formed. According to [29], more than 30 h are needed to attain such level of oxidation. The material oxidized at 18 °C retains its initial fibrous form while somewhat increasing its mass due to the reaction. Just as in [29], an additional treatment is required to transform the fibres into a powder state.

[1] When the C-6 atoms of all anhydroglucose units are oxidized, the COOH group content is 25.57 %, by mass.

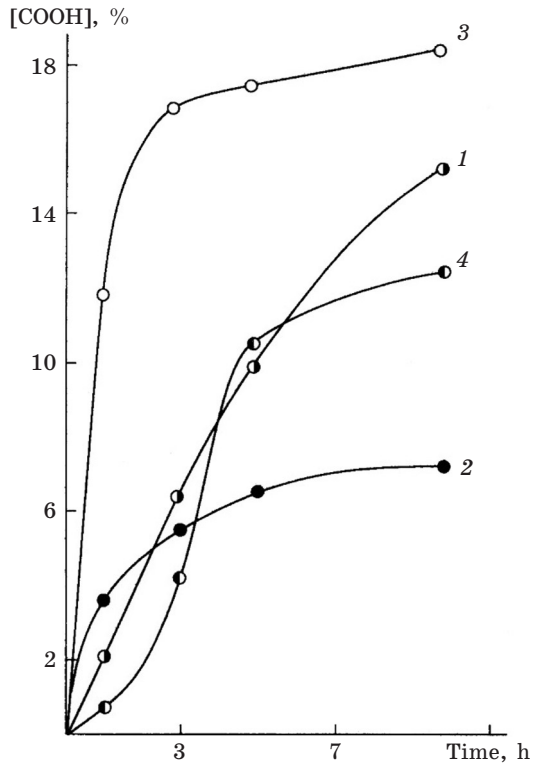

Fig. 11. Accumulation of carboxyl groups upon oxidation of (*1*) the KC with 60 % HNO_3 at 18 °Cel in the presence of $NaNO_2$; (*2*) Cel-I with 55 % HNO_3 at 70 °C; and the KC with 55 % HNO_3 at (*3*) 70 °C and (*4*) 50 °C

Initiation of the oxidative transformation by increasing the reaction temperature makes the use of $NaNO_2$ unnecessary, and allows the fibre oxidation and degradation processes to be combined into one, thus avoiding the separate stage of partial hydrolysis that involves a technologically complicated operation of pressing-off the oxidized fibrous mass from an excess of toxic and corrosive medium. In the single-stage version, the reaction temperature and acid concentration should be balanced in such a way that, while maintaining sufficiently high rates of Cel oxidation, excessive stimulation of hydrolysis and nitration be avoided, the latter being also very sensitive to the temperature and concentration factors.

In a series of experiments performed in order to find out acceptable conditions for a single-stage process for preparing CPCel from flax cellulose, the best results were obtained with 55 % HNO_3 at 70 °C and liquor ratio of 15 ml/g (Fig. 11, curve *2*). As one can see, the process character is typical for heterogeneous transformations of Cel, the depth of which is limited by the poor accessibility of the crystalline «component» of the fibre to the reagent. In this material, only 7.4 % of the COOH groups are accumulated after 10 h of reaction. The yield of oxidized powder mass is 80 %, which is equal to that of chemically unchanged microcrystalline Cel

(MCCel) obtained from the fibre by a usual hydrolysis procedure with boiling diluted mineral acid down to the «level-off» DP.

For the adduct of Cel with HNO_3, the rate and degree of oxidation increase sharply under these conditions (Fig. 11, curve *3*). After 1 h, the content of COOH groups is already 11.9 %; after 10 h, it reaches 18.3 %. However, the rate of hydrolysis is also high, hence an acceptable yield of CPCel cannot be obtained in this case; it amounts to 48 % after 1 h of reaction and is only 20 % after 10 h. The high rate and degree of hydrolytic degradation of the macromolecules promote oxidation because the hydrolysis products act as reducing agents, i.e. they assist (along with temperature) the formation of nitrogen oxide(IV) in the system. The major portion of the starting material undergoes deep hydrolysis and passes into solution already in the initial stages of the process, thus strongly promoting oxidation. As a result of this, the majority of COOH groups (about 17 %) is formed during the first 3 h at a nearly constant rate, and then the oxidation rate drops sharply, and only slight contribution is made to the development of oxidation process during the following 7 h of reaction. There is a synchronism in the decrease of oxidation and hydrolytic cleavage rates. The slow stage corresponds to after-oxidation of a relatively small amount of the material having structural organization that provides hydrolytic stability. As a whole, the increase in accessibility of the initial fibre structure due to pre-activation is so high that at 70 °C the major portion of the macromolecules undergoes a deep hydrolytic cleavage. The high rate and degree of oxidation of the activated Cel at 70 °C are achieved at the expense of the yield of the desired product.

The activation energy of heterogeneous acid hydrolysis of Cel is rather high (about 150 kJ [30]), therefore, the rate of this reaction stage is strongly temperature-dependent. For example, on decreasing the temperature by 20 °C, the yield of oxidized powder mass after treatment of KC for 10 h is 80 %. The rate and degree of oxidation decrease correspondingly because the factors that promote oxidation are weakened (Fig. 11, curve *4*). Oxidation is decelerated not only in the final stage, as it was seen in the cases discussed above, but also at the very beginning of oxidation. This is probably due to a slow accumulation of the required amount of nitrogen oxide(IV) in the system at 50 °C. Nonetheless, the degree of KC oxidation at 50 °C is much higher than that of common Cel at 70 °C. The content of COOH groups is 10.5 % after 5 h and 12.3 % after 10 h (cf. Curves *2* and *4*, Fig. 11). These reaction conditions are unlikely to be optimal, but it is apparently possible, by varying temperature and concentration, to select conditions that would provide a sufficiently high degree of oxidation of KC and a good yield of powdered oxidized Cel. According to chemical analysis data, the total carbonyl group content of the CPCel obtained on the basis of KC does not exceed 2 %, which is typical for the Cel oxidized at the 6-th carbon atom. The bound nitrogen content is also small (< 0.4 %).

The character of variation of the substrate accessibility during the reaction should also be considered as one of the major causes of different behaviour of KC in the experiments discussed. The KC oxidation proceeded in HNO_3 of lower concentration than that needed for this adduct to be formed. The concentration gradient alone would cause the KC to decompose gradually. Increasing the temperature, changing the chemical composition of macromolecules, their degradation, and other factors should also exert influence on this process. These circumstances affect the final product structure too.

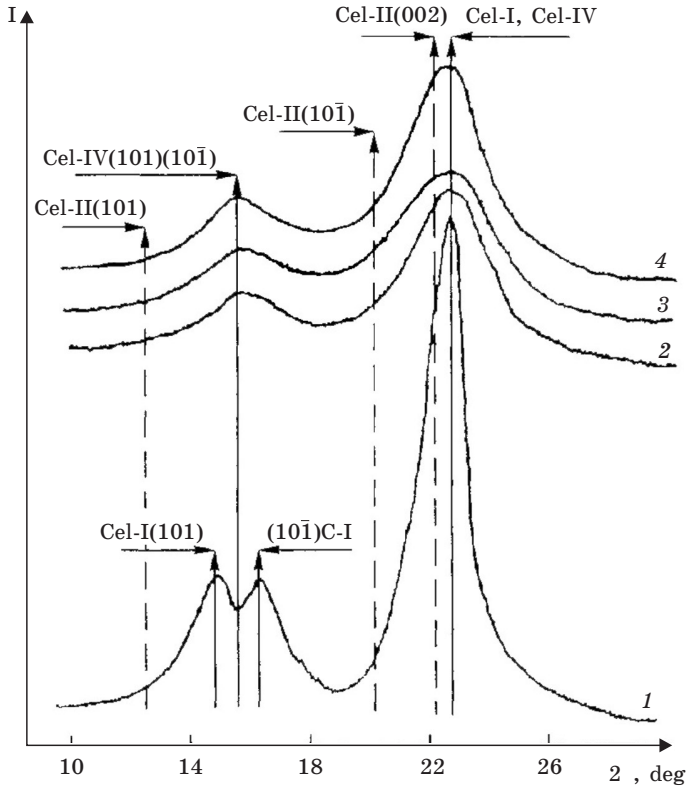

Fig. 12. X-ray diffraction pattern of the oxycellulose samples containing (*1*) 7.4, (*2*) 15.1, (*3*) 18.3 and (*4*) 12.3 % of carboxyl groups

The KC decomposition with water is known to involve a mercerization-like effect, i.e. the formation of Cel-II. In our case, the system where KC was formed (68.5 % HNO_3) was diluted with a relatively small amount of water, to reduce the acid concentration down to the level required (55–60 %), and thereafter the conditions promoting oxidation were created. In the diffractograms of CPCel obtained on the basis of KC (Fig. 12, curves *2–4*), there are no signs of reflections characteristic of Cel-II. According to angular positions of reflections, these diffractograms can be attributed to partially decrystallized Cel-I or Cel-IV. There are known examples of formation of Cel-IV in the systems given [31]. However, blurred appearance of diffractograms of the CPCel samples obtained on the basis of KC does not allow a specific Cel modification to be attributed to them.

The particles of CPCel samples thus obtained are characterized by low stability toward mechanical stress in either in dry or wet state. The latter circumstance allows a high degree of dispersity to be attained immediately after the powder wash-out from HNO_3, and, if necessary, the process could be ended with the formation of a uniform colloidal dispersion having consistency of a paste or ointment based on an aqueous-organic dispersion medium (ethanol, glycerol, acetone, etc.).

3. COMBINATION OF THE OXIDATIVE AND ACID-HYDROLYSING FUNCTIONS OF NITROGEN OXIDE(IV) AS A METHOD FOR PREPARING CARBOXYLATED MICROCRYSTALLINE CELLULOSE

Preparation of cation-exchanger enterosorbents based on carboxylated Cel capable, in particular, of binding and removing radionuclides and heavy metals from the human organism is a topical and promising trend in cellulose chemistry.

Of the cellulose-based sorbents, microcrystalline Cel (MCCel) deserves a particular attention in this respect. MCCel is a product of hydrolytic cleavage of cellulose down to the so-called «level-off DP» (150–220 monomer units, depending on the kind of initial cellulose). As a result of hydrolysis, the fibres are liberated from the structurally disordered component and impurities contained therein. A disruption of the fibrous structure of the material takes place, which is converted into a finely dispersed powder consisting of particles that are aggregates of microcrystals. The distinguishing features of MCCel are high degree of chemical purity, highly ordered supramolecular structure and a unique capability of forming stable tixotropic gels. Hydrogels are formed by applying hard shear stress conditions to 5–20 % aqueous dispersions of MCCel [32]. MCCel is widely used as filler or thickener substance in the manufacture of many medical products. It is used as a dietary additive, and as a means of removing sludge from the gastrointestinal tract; the latter application is due to high sorption capacity of MCCel in combination with some «abrasive» effect. A disadvantage of MCCel as enterosorbent is its lack of ionogenic groups present in such well-known enterosorbents as pectin or marine algae polysaccharides (laminarin, carrageenan).

Features of the proposed method for preparing carboxylated MCCel (CMCCel) are as follows [33]:

Air-dry Cel was treated with gaseous nitrogen(IV) oxide in a specially-made reactor. The process was conducted at room temperature during the time necessary for attaining the required degree of Cel oxidation. Then a calculated quantity of water was filled into the reactor fitted with a reflux condensor, and the reactor content was heated to boiling temperature to convert the carboxylated cellulose fibres into CMCCel. Reaction of water with the excess nitrogen oxides sorbed by Cel leads to formation of nitrous and nitric acids, which play the role of catalysts in the hydrolytic process of Cel destruction. Thus, nitrogen(IV) oxide is, in fact, fulfilling both oxidative and acid-hydrolyzing functions. Under conditions we used in our experiments, approximately 4 % HNO_3 was formed in the system. The hydrolysis process was continued until a complete conversion of the fibre into a uniform finely dispersed mass was attained. The latter was repeatedly pressed-out and washed with water on a Schott filter until complete removal of nitrate and nitrite ions, as checked by reaction with diphenylamine. A part of the obtained CMCCel was dried at 60 C, ground in a mortar, and fractions were taken out that passed through a 100 μm sieve. Another part of the wet CMCCel was used for hydrogel preparations.

Preparation of a material that possesses both ion-exchanger properties and the properties of MCCel imposes certain requirements on the first stage of the process: carboxylation of Cel fibres. The Cel fibre crystallinity, and consequently the CMCCel yield, depend on the degree of carboxylation. If the degree of oxidation is small (up to ca. 5 % w/w COOH groups, γ~18,3)[1], the Cel crystallinity incre-

[1] γ is the number of COOH groups per 100 anhydroglucose units

ases to some extent due, in particular, to the refining effect. The increase in crystallinity may be also caused by the removal of largely destroyed macromolecular fragments of Cel present in amorphous areas, together with hemicelluloses, during the wash-out procedure.

A deeper oxidation of Cel decreases its crystallinity owing to disruption in regularity of the macromolecules. The higher the degree of oxidation, the greater is the decrystallization, because the reaction acquires an intracrystallite character. The MCCel yield in the reaction of Cel hydrolysis down to the «level-off DP» is directly associated with crystallinity of the starting material. For this reason, it is always higher for cotton Cel than for WCel irrespective of its origin or method of manufacture. The CMCCel yield from oxidized Cel containing 5 % of COOH groups is ca. 80 %, i.e. it is virtually the same as the MCCel yield from WCel. From oxidized Cel containing 13.5 % of COOH groups (γ= 49.3), a powder material of low crystallinity is obtained in a yield of ca. 60 %. Thus, to obtain CMCCel, it is rational to oxidize the starting fibre to a relatively low carboxyl group content, e.g. 5 %, that is equal to the free carboxyl group content of pectins. In this case, the ion-exchanger properties, the properties due to the microcrystalline morphology, and the final product yield are well-balanced. It should be pointed out that the COOH group content in the oxidized Cel fibre and in the CMCCel prepared thereof agree within the error limits for the barium acetate analytical method, in spite of the fact that significant amounts of structurally disordered material were removed from the fibre in the course of hydrolysis. This observation can possibly be accounted for as follows:

As it has already been pointed out, the hydrolytic cleavage of oxidized Cel takes place in an oxidizing medium. In the initial stage of the hydrolytic process, evolution of brown vapours of NO_2 from the reaction mixture is observed. Under such hydrolysis conditions, «afteroxidation» of Cel is possible, in particular, of carbonyl groups present. This may be the cause of equal carboxyl group content in oxidized fibrous Cel and in the CMCCel prepared from it, and of enhanced stability of CMCCel. For example, the temperature at which thermal decomposition starts for CMCCel containing 3.5 % of COOH groups (γ = 12.7) is by 32 °C higher than the corresponding value (175 °C) for its precursor, fibrous Cel with the same degree of carboxylation. The observed difference in thermal stability (196 °C vs. 163 °C) remains after 4 h exposition of the samples to UV light, which causes the both starting decomposition temperatures to decrease by ca. 12 °C. Among factors that contribute to the enhanced stability of CMCCel, its content of nitroester groups should be mentioned, which is inferior as compared to its precursor, carboxylated fibrous Cel. Cel oxidation with nitrogen(IV) oxide is always accompanied by accumulation of nitroester groups in small amounts, which lower chemical stability of the material [34]. Unlike Cel oxidation, nitration of Cel depends substantially on the diffusion factor; therefore, the nitroester group accumulation takes place primarily in easily accessible areas of the fibre, which are then removed in the course of hydrolysis. It should be noted that nitrogen oxide compounds are capable of Cel bleaching [35]. Under the reaction conditions employed, the enhancement of bleaching after conversion of the starting Cel into CMCCel is seen quite distinctly.

Conversion of the acid CMCCel form (H-CMCC) into its sodium salt (Na-CMCCel) facilitates preparation of homogeneous, stable tixotropic hydrogels. To prepare similar gels from MCCel, special high-speed (ca. 20000 rpm) shear blendors are necessary. It is

only under severe shear stress conditions that the disaggregation of MCCel microcrystals is possible, which is necessary for a stable hydrogel to be formed. To facilitate gel formation, after Cel hydrolysis and washing the MCC obtained, addition of water-soluble Na-carboxymethylcellulose in amounts of 8–10 % w/w has been proposed [32]. Such an additive envelops the microcrystals, playing the role of a «barrier» compound.

To prepare Na-CMCCel gels, there is no need for high-speed blendors any more. It is noteworthy that, in the case of Na-CMCC salts, an easy gel formation occurs already with a ~2 % COOH group content ($\gamma = 7.2$). Under our experimental conditions, cream-like hydrogels with pH 6.5 to 7.0 were obtained containing 10 ± 0.5 % w/w of Na-CMCCel.

Convincing evidence of completeness of salt formation is obtained when comparing IR spectra of dry samples of H- and Na-CMCCel. On neutralization, an intense band at 1730 cm^{-1} in H-CMCCel spectrum due to the stretching C=O vibration of the carboxyl group disappears almost totally; instead, an intense band at 1610 cm^{-1} is seen, characteristic of carboxylate anion [34].

Na-CMCCel hydrogels have a distinctly marked tixotropy. After a certain time, they become structured and lose fluidity, which reappears on shaking. During two years of storage, we did not observe any signs of layer separation in the hydrogels. On drying thin layers of the hydrogels, brittle mat films are formed, easy to reduce into powder that we used in our experiments along with the hydrogels themselves.

In Fig. 13, curve *1*, X-ray diffractograms of H-CMCCel with carboxyl group contents of 2.5 % and 4.8 % ($\gamma = 9.1$ and 17.5) and of the respective Na salts (cur-

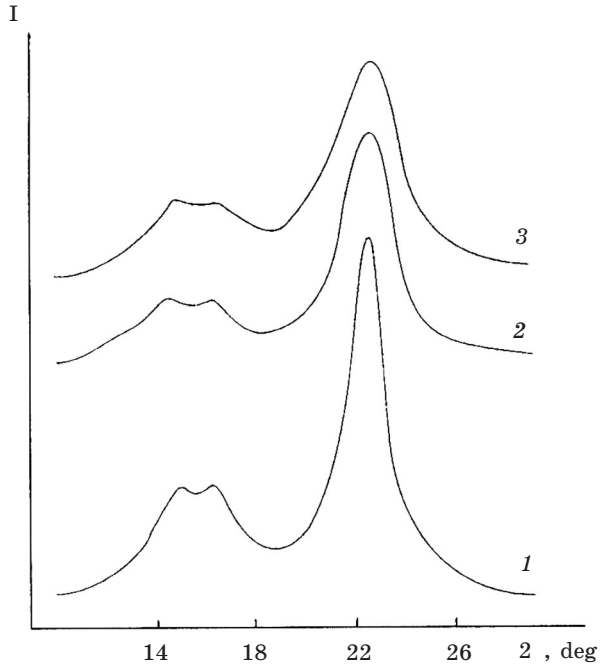

Fig. 13. X-ray diffraction pattern of CMCCel samples: *1* – H-CMCCel with 2.5 % and 4.8 % COOH group content; *2* – Na-CMCCel with 2.5 % COOH group content; *3* – Na-CMCCel with 4.8 % COOH group content

ves *2* and *3*) are shown. The X-ray patterns of the both samples containing the H-form are almost identical, and correspond to the native modification of Cel (Cel-I) with highly ordered supramolecular structure. The crystallinity index for H-CMCCel samples is 0.66, being somewhat higher than that for the starting cellulose (0.64). These data are convincing evidence of carboxyl group localization in the intercrystallite areas on the microcrystal surface.

Conversion of the H-form of CMCCel into the Na-form causes a significant decrease in size of microcrystals, which is the more pronounced, the higher is oxidation degree of CMCCel. This is seen from the broadening of reflections of Cel-I on X-ray patterns of Na-CMCCel, accompanied by a corresponding decrease in their intensities (Fig. 13, curves *2* and *3*). The crystallinity index for Na-CMCCel ($\gamma = 9.1$) goes down to 0.62, and that for Na-CMCCel ($\gamma = 17.5$) – to 0.60. Nevertheless, the core of particles forming the disperse phase of Na-CMCCel hydrogel remains crystalline.

The decrease in microcrystal size and crystallinity may be explained by a strong hydrophilization of the microcrystal surface as a result of salt formation, and by formation of a «water-soluble» fraction of Na-CMCCel from a certain part of oxidized molecules of the surface layer. Most probably, the fraction in question is a colloid-soluble, sol-like one. This fraction, playing the role of a «barrier» between microcrystals, assures the ease of their disaggregation on dispersing the aqueous suspension into the state of hydrogel. It should be noted that O. A. Battista, in his well-known monograph [32], pointed out prospective character and practical significance of topochemically modified MCCel.

Table 3

Sorption values (mg/g) measured for various sorbents and various periods of time using neutral 0,02 % solutions of methylene blue

Sorbent	Duration of sorption, hours	
	3	72
«Ankir» brand MCCel	~ 1.0	4.2
«Medetopect» brand pectin-containing product	24.0	26.5
CMCCel with 3.0 % COOH group content	31.6	32.6

To assess sorptive activity of various CMCCel samples as compared to one another and to commercial enterosorbents available, a bulky organic cation – methylene blue (MB) – was selected as the agent to be sorbed. Of commercially available enterosorbents of polysaccharide nature, «Ankir» brand (Russia) cotton MCCel, and «Medetopect» brand apple pectin-based product were tested. The sorption results are presented in Table 3. According to the experimental conditions, maximum sorption value for the dye from its 0.02 % solution should be 33.3 mg/g. Based on the average period of time that food stays in the stomach, we suggested that the results obtained after sorption period of 3 hours would be the most representative. As seen from Table 3, irrespective of sorption duration, MCCel binds the dye rather poorly, in spite of the fact that its surface is negatively charged [32]. Sorption ability of the acid form of CMCCel with 3 % COOH group contant ($\gamma = 10.9$) is distinctly higher than that of the pectin-based product. During 3 hours, it binds up 95 % of MB, whereas only 72 % binding could be achieved with the «Medetopect» product.

In the case of «Medetopect» product, about 20 % of non-bound dye are still present in solution after 72 h of sorption duration. This value is 10 times as high as the corresponding result obtained with a CMCCel sample.

In Fig. 14, dye sorption isotherms are shown for the samples of H- and Na-CMCCel taken in different forms (powder or hydrogel), and with different degree of carboxylation. All the sorption isotherms are described by the Langmuir equation. As seen, Na-CMCCel hydrogels have the highest sorptive ability, calculated on the basis of dried substance. This can be naturally explained by the maximum accessibility of active sorption centres in the hydrogels. The overwhelming part of the dye is sorbed according to the cation-exchange mechanism. An almost two-fold difference in the degree of oxidation (γ = 9.1 and 17.5) accounts for the corresponding two-fold difference in maximum MB sorption values measured for the two Na-CMCCel gels (195 and 390 mg/g). Maximum MB sorption value for the Na-CMCCel gel (γ = 9.1) makes 109 % of the total exchange capacity (TEC), and the respective value for the Na-CMCCel gel (γ = 17.5) makes 115 % of the TEC. The fact of exceeding the 100 % TEC value may be due to a contribution of physical sorption to the MB binding.

Powder Na-CMCCel samples have significantly lower sorptive ability as compared to gels because the active surface of the sorbent grains is not maximally exposed

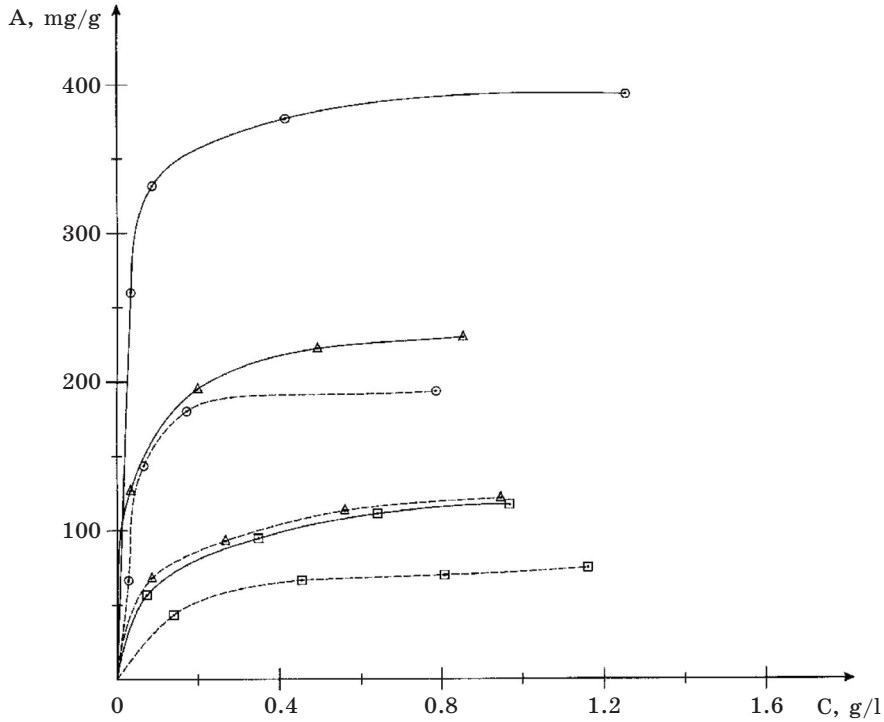

Fig. 14. Isotherms of methylene blue sorption by CMCCel samples containing 4.8 % of COOH groups (solid curves) and 2.5 % of COOH groups (dotted curves). □ – H-CMCCel in powder form; Δ – Na-CMCCel in powder form; o – Na-CMCCel in hydrogel form

in this case. It would be logical to assume the presence of shielding effects as well, exerted by bulky MB molecules already sorbed which prevent access of further molecules to many of the active centres available. The difference in carboxylation degree of powder Na-CMCCel samples (γ = 9.1 and 17.5) results in about two-fold difference in maximum sorption values, similarly to that observed in the case of gels. For these samples, the TEC is filled up to 69 % and 72 %, respectively.

As regards sorption capacity, the salt CMCCel forms have obvious advantages over the acid ones. This logically follows from their higher degree of ionization. It should also be taken into account that interaction of Na-CMCCel macroions with MB in its hydrochloride form results in formation of NaCl salt, whereas the reaction product in the case of H-CMCCel is HCl – a strong acid that shifts the ion exchange equilibrium toward the starting compounds.

The dependence of maximum sorption value on the degree of carboxylation is not so pronounced for H-CMCCel as it is in the case of Na-CMCCel. Maximum MB sorption values for the acid CMCCel forms with 2.5 % and 4.8 % COOH group content are 80 and 118 mg/g, respectively. The TEC fill is higher for the sample with lower degree of carboxylation (48 % vs. 34 %). This fact can be explained by higher degree of dissociation of the former.

In that way, the proposed method of structural chemical modification of cellulose using exclusively a «one-pot reagent» makes it possible to obtain practically valuable materials with microcrystalline morphology, enhanced stability, whiteness and gel-forming ability, and a marked ion-exchanger activity. The aforementioned properties are evidence of a promising character of these preparations as a basis for creation of sorbents for health care applications.

As a result of extended studies of combined oxidative-hydrolytic action of a number of nitrogen- and iodine-containing reagents (nitric acid, periodic acid, nitrogen oxides, etc.) on Cel and properties of the derivatives obtained, methods for preparation of novel Cel-based sorbents with a promising potential of application in medicine have been developed [33, 36]. The range of the sorbents being obtained covers both medications for emergency use as antidotes in cases of poisoning with heavy metals or radionuclides (mainly highly-carboxylated products) [36] and remedies for prevention of chronic intoxications, including the «drug diseases», capable of long-term removal of endogenous toxins or toxic substances from the human organism (mainly low- and medium-carboxylated Cel-based substrates) [37]. New C-based entersorbents in hydrogel form that have now passed clinical testing in gastroenterology and detoxication therapy possess ulcer-enveloping anti-ulcerogenous action superior to that of aluminium-based antacid medications. The latter have the disadvantage of containing aluminium that has undesirable side effects, particularly on long-term use, with a potential of developing «aluminium dementia», Alzheimer disease, etc. Studies of the named enterosorbent gels revealed their innocuous character and their ability to manifest the so-called «parachute effect» – a property highly appreciated by detoxication therapy clinicians. This effect consists in an increase of sorptional ability of a medication in distal areas of the gastrointestinal tract. Other advantages of the new enterosorbent gels include their compatibility with remedies used for similar purposes, e.g. with varous strains of useful microflora, activated carbon, etc. The stabilizing effect of Cel component contributes to increase the shelf life of the final products while significantly decreasing the side effects [37].

Furthermore, these products can be used not only as the main active components, but as a basis for creation of various sustained release drug forms containing other active agents, designed for either internal or external use. For example, cytarabine and its analogues used in ophtalmological practice proved to possess an enhanced efficacy in the form of CMCCel-based eye ointments that we have developed recently [38]. The modified Cel-based enterosorbents of this kind were shown to synergetically enhance the effects of lithium cations as applied in psychiatry, narcology, immunology and cardiology, while suppressing undesired side effects. Active component release studies performed with antibiotics encapsulated in granules of oxidized Cel suggest a potential for the development of corresponding *per os* forms with prolonged action [39].

4. NITRIC ACID DELIGNIFICATION AS A METHOD FOR OBTAINING RADIONUCLIDE-FREE CELLULOSE AND NITROLIGNIN FROM RADIONUCLIDE-CONTAMINATED VEGETAL MATERIAL

Over recent years, a major effort in scientific activity of the Laboratory of Physical Chemistry and Modification of Cellulose at the RIPhChP BSU is focused on the use of nitrogen oxide compounds to enhance efficacy of delignification of straw from various agrocultures. The Cel content of straw from such plants as cereals, rape, and soya is on the same level as that of wood of deciduous species (ca. 50 %). In the case of flax fibres, it attains the value of 80 %. An enormous interest in the low-cost and annually renewable raw materials for obtaining fibrous products is actually manifested worldwide [40–43]. Studies in this area are now on the upgrade. Straw Cel is now produced in thousands of industrial plants [41]. The worldwide consumption of non-wood materials for cellulose production has increased by more than 50 % from 1983 to 1994, and an increase by more than 120 % is forecasted for the year 2010 [43]. Currently, about 12 % of Cel produced worldwide are obtained from annual plants [42].

Owing to features of their morphological structure, the stems of annual plants are the best material for delignification involving HNO_3 [44]. High reactivity of HNO_3 toward lignin determines the main advantages of the process: high rate, moderate temperature, and atmospheric pressure. The two-stage nitric acid method for delignification of vegetal material is actually a modified version of the single-stage alkaline soda method that is widely used. The latter consists in treating the plant material with an alkali solution under relatively hard conditions, whereupon lignin is removed in the form of its soluble derivatives of phenolate type. A pre-treatment of the raw material with HNO_3 solution results in selective nitration and oxidation of lignin, which markedly enhance its solubility during the subsequent alkaline extraction in the second stage.

This has allowed, in particular, a chemical «cottonization» of flax raw material to be performed, rendering it suitable as a substitute for cotton in its conventional application areas (textile industry, etc.). The data obtained in the course of pilot trials of the fibrous product manufactured from this material provide evidence of its high quality and suitability for production of staple fibre yarn. This area of activity appears to be very topical for Belarus where shortages of cotton

raw material are now a problem. We have reported [45–47] the nitric acid delignification conditions for winter rye straw allowing Cel to be isolated in a high yield (up to 50 %), with low residual lignin content (1.7 % vs. 23.5 % in the starting raw material), pentosan content (up to 16.5 % vs. 22.2 % in the starting raw material) and high α-Cel content (up to 90 %). Physico-mechanical tests of the experimental samples have shown that the nitric acid straw Cel can be efficiently used in compositions with WCel for the manufacture of various kinds of paper and cardboard products.

The most significant and promising results have been obtained in experiments on nitric acid delignification of vegetal material grown on radionuclide-polluted territories [48, 49]. It has been discovered that during the delignification process carried out under specific conditions a most complete separation of radioactive mineral components from the plant tissue is achieved. A comparison of deactivating capability was made between the nitric acid method and the alkaline soda one that is most commonly used. The starting materal was winter rye straw from Khoyniki region that had suffered from the Chernobyl accident. Its contamination level for ^{137}Cs was 470 Bq/kg, and for ^{90}Sr – 25 Bq/kg. The final Cel half-product isolated from this raw material using the nitric acid method had the contamination level of 30 Bq/kg for ^{137}Cs and 2.5 Bq/kg for ^{90}Sr. The respective indices for the product treated according to the alkaline soda method were 282 Bq/kg and 15 Bq/kg. When comparing these results it becomes clear that, as regards deactivating ability, the nitric acid version of treatment is superior to the alkaline soda one by an order of magnitude. The high deactivating capability of the nitric acid method was confirmed in experiments with model highly-contaminated raw material – meadow grasses (65500 Bq/kg in ^{137}Cs and 3790 Bq/kg in ^{90}Sr). Treatment of these under conditions of nitric acid delignification allows the radioactivity level of the final solid residue to be reduced more than 200 times for ^{137}Cs and more than 250 times – for ^{90}Sr, with respect to the initial values. Along with this, it is important to note that the major part of radionuclides is extracted, in a practically selective manner,in the first stage of acid treatment, and the lignin extracts obtained in the second stage are of a relatively low activity. The high selectivity of radionuclide extraction is probably due to good solubility of nitric salts being formed. Liquid radioactive waste will be localized in the initial stage of the process. Then, they can be concentrated, converted into some solid state form using one of the known technologies and safely disposed of. In this connection, the technology of extracting radionuclides from liquids by means of widely used industrial sorbents (ceolites) appears to be acceptable. The nitric acid delignification can be performed using both commercial and the so-called «missile» nitric acid that contains such additives as N_2O_4, I_2, HF and H_3PO_4 and is the main component of missile fuel. After nuclear missile disarmament of Republics of the former USSR, large quantities of unclaimed 'missile' nitric acid were left on their territories. Storage of this material in concentrated form in the absence of special conditions is rather dangerous, whereas its utilization is problematic and expensive. In the periodic press, there were several communications about leakage of this oxidant from depositories in the Far East of Russia. Even these relatively minor episodes of leakage involved human casualties and pollution of air and water resources over large territories. The proposed version of utilization of nitric acid solutions in a diluted form will not entail technological or environmental problems.

The obtained results are in direct relation to the development of rational technologies for rehabilitation and deactivation of territories polluted with radionuclides and heavy metals as a result of technogenous accidents, military tests or hostilities, and terrorist attacks.

The post-Chernobyl experience has shown that essentially two types of agricultural technologies are acceptable on polluted territories.

The first one, the so-called agrotechnical or agrochemical counter-measures, is based on a regular heavy application of various fertilizers into the soil. This promotes competitive absorption of cations – analogues of radionuclides – by the plants, leaving radionuclides themselves in the soil and decreasing thereby the radionuclide uptake by the plants being used as fodder or for food production [50, 51]. However, the costs required are quite high, and no soil deactivation is achieved According to [52], any counter-measures undertaken at present, i.e. after a long time after the Chernobyl disaster has broken out, are economically unjustified in ^{137}Cs pollution zones with less than 370 kBq.m^{-2}.

Technologies of the second type, which are less studied but very promising, are based on cultivation of technical (non-nutritional) plants whose seeds are raw material for obtaining radionuclide-free products. In Belarus, on territories with pollution density of 370 to 555 kBq.m^{-2} of ^{137}Cs, and 37 to 55 kBq.m^{-2} of ^{90}Sr, the culture of rape has already been introduced, and radionuclide-free oil was extracted from its seeds [51, 53]. Average accumulated radionuclide level of the rape seeds as compared to the rape straw is 1.5 times lower for ^{137}Cs, and 2.6 times lower for ^{90}Sr [53]. After oil extraction, the radionuclide content of the oilcake becomes doubled whereas almost none is found in the rape oil [53]. In an effort to recover for rural economy 500,000 ha of soil contaminated with strontium and caesium, sowing all these territories with rape is planned in Belarus. Studies are also underway aimed at improvement of soya and flax cultivation technologies on these territories with a view to obtain competitive products from the respective seeds. Along with obtaining radionuclide-free products, a phytodeactivation of contaminated soil, i.e. progressive purification due to radionuclide uptake by the plants, is achieved using this technology [54]. A large interest in phytodeactivation technologies is actually manifested in many countries.

Agrotechnical products are not intended for nutritional purposes. Therefore, the efficiency of technologies of the second type should be evaluated primarily from the point of view of economical and environmental expediency, and not using directly the deactivation coefficient, as is generally done in the case of the first type technologies [51]. One can admit an arbitrarily high deactivation coefficient value provided that radionuclides cannot come into a human organism some other way, say, by inhalation of contaminated smoke. Nevertheless, the production residues in the form of straw where the major part of radionuclides is accumulated are disposed of by incineration. In the course of this procedure, certain amounts of radionuclides are usually dispersed into the environment with the smoke particles, even if special equipment is used [55]. Thus, a problem of utilization of contaminated straw from the technical agriculture plants does exist. For example, after harvesting rape seeds, up to 5 t of contaminated straw per hectare is left as residues.

Obtaining radionuclide-free Cel and nitrolignin from the straw of technical agrociltures is profitable from economical and ecological point of view. This ap-

proach opens additional possibilities in reducing costs for rehabilitation and deactivation of polluted territories by increasing the range of commercial products being in a stable demand on the market. Cel value is 4–5 times higher than that of the energy obtained on combustion of the same quantity of Cel-containing material. Bringing nitrolignin into contaminated soil will enrich it with humin-like substances and prevent wind erosion and radionuclide transportation with the dust. It will reduce to a minimum the secondary contamination, prevent radionuclide transportation through the «nutritional chain» and provide a progressive deactivation of the soil.

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