Effect of Titanium Tetrachloride Used for Obtaining Powdered Cellulose on the Acid-Base Properties of Its Suspensions

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Abstract

For the first time a pK spectroscopy technique was applied to study the influence of Lewis acids upon changing the acid-base properties of cellulose suspensions. Basing on the cellulose pK spectra obtained before and after the modification in the solution of titanium tetrachloride, it was demonstrated that the action of titanium tetrachloride on the cellulose results in weakening the bonds between hydrogen ions and appropriate acid-base groups, thereby the number of these groups remain unchanged. The powdered cellulose obtained under the influence of titanium tetrachloride differs from the original (fibrous) one in a high ion exchange capacity.

Key words: powdered cellulose, MCC, cellulose suspension, Lewis acid, titanium tetrachloride, ion-exchange capacity, pK spectroscopy

INTRODUCTION

The condition of environmental objects at the present stage of the development of science is being studied with the use of chemical, physical and mathematical methods. In particular, the pK spectroscopy technique is promising for studying equilibria in complicated naturally occurring systems whereon there are no reliable data concerning the functional composition, whereas the classical methods of analysis are difficult to apply the and do not always provide adequate information about the structure. The method of pK spectroscopy allows one to plot so-called pK spectrum as a bar graph basing on the potentiometric titration of samples [1–3], which plot represents the relative molar fraction of acid-base groups inherent in the sample under studied depending on a conditional dissociation constant pK. Thus, the pK spectrum can serve as a complete pictorial characteristic of the acid-base properties of the object under investigation.

The theory for the method of pK spectroscopy was formulated as applied to the studies on the acid-base properties of suspensions, solutions and hydrosols. To date, this method is successfully used in order to study various homogeneous and heterogeneous systems such as acid-base catalysts and ion exchange resins [4, 5], sols and suspensions of minerals [2, 6–8], soil suspensions [9–11], aqueous solutions of the mixtures of organic acids [12], emulsion fir extract [13]. For studying the molecular suspensions of biopolymers such as cellulose, we first used this method.

Cellulose is attributed to naturally occurring polyelectrolytes. Resulting from breaking cellulose macromolecules the average polymerization level (PL$_{av}$) of the cellulose exhibits a decrease, the fibres of the cellulose are transformed into powder. Depending on the conditions of depo-

lymerisation one could obtain either partially destructed or fine powdered cellulose, whereas depending on the depolymerisation mode of the cellulose fibres the cellulose surface exhibits either increasing or decreasing the content of ionogenic groups. Usually, in order to perform the conversion of cellulose fibres into powder, one uses hydrolytic or oxidation-hydrolytic destruction techniques. It is well known [14, 15] that the microcrystalline cellulose (MCC) obtained in such a manner loses some ionogenic groups in the course destruction. In this work we demonstrated using the pK spectroscopy a difference between acid-base properties of cellulose suspensions and its degradation products obtained in two different ways.

MATERIALS AND METHODS

Analytical methods

The polymerization level of the cellulose was determined from the viscosity in an aqueous solution of cadmium ethylene diamine complex using an Ostwald capillary viscometer with a capillary diameter equal to 0.82 mm [16]. The lignin content was determined with 72 % H_2SO_4 solution according to Komarov modification [17]. The exchange capacity of cellulose was characterized by the milligram equivalents of ions absorbed by 1 g of a sample, basing on data resulting from potentiometric acid-base titration in accordance with the procedure described in [18].

Starting materials

We used unbleached softwood cellulose pulp from Mondi Syktyvkar OJSC (Russia) before and after treatment by a solution of titanium tetrachloride in hexane. As a reference sample we obtained powdered cellulose (PC) from the same raw material using a "classic" hydrolysis procedure currently applied in the industry for MCC production [19].

In order to obtain the PC a weighed sample portion of fibrous cellulose (FC) (12.0 g) dried at 105 °C, was placed into a conical flask to fill with 250 cm^3 of a freshly prepared solution of titanium tetrachloride in hexane with the concentration equal to $4.5 \cdot 10^{-3}$ mol/dm^3. We used commercial pure grade $TiCl_4$, purified *via* simple distillation [20]. The reaction was performed at 23 °C during 20 min. The reaction mixture was then transferred onto a glass filter; the solution was filtered with further washing out the Lewis acid residues using the same solvent and dried.

The hydrolytic treatment of cellulose was performed in accordance with a "classical" method in 2.5 M HCl solution during 90 min at the temperature of boiling the liquid [19].

RESULTS AND DISCUSSION

Lewis acids exhibit a high destructing action with respect to the acetal bonds of carbohydrates [21]. In the course previous studies, we found that the action of Lewis acids on cellulose solutions results in obtaining a fine PC powder within a short period of time [22–27]. The destruction of macromolecular chains to the limiting PL value occurs intensely to be almost completed within the first 5–20 min from the beginning of the reaction.

Resulting from the action of hexane $TiCl_4$ solution on the cellulose solution, a sample of modified PC was obtained [24–28]. Table 1 demonstrates some of the physical and chemical properties of the samples under investigation.

Unbleached cellulose pulp represents a complicated naturally occurring composite material that involves alongside with the main com-

TABLE 1

Physicochemical properties of cellulose samples

Cellulose samples	Treatment	PL$_{av}$	Lignin content, %	Soluble fraction (pH 11), %	ρ_{bulk}, g/cm^3
Fibrous cellulose	–	1260	5.74	0.69	–
Microcrystalline cellulose	HCl–H_2O	170	5.61	0.73	0.054
Powdered cellulose	$TiCl_4$–C_6H_{14}	200	3.80	4.46	0.076

ponent (cellulose) any other accompanying substances such as lignin and hemicellulose. In connection with this fact, studying the composition and amount of ionogenic groups in the cellulose depolymerisation products represent a complicated task. In order to accomplish the mentioned task, we used the technique of pK spectroscopy.

Cellulose chemical conversion occurs mainly in a heterogeneous environment. Studying the ability of cellulose and its depolymerisation products with respect to ion exchange was carried out basing on the data concerning the potentiometric titration of suspensions thereof [26, 28]. The titration curves are presented in Fig. 1.

The amount of hydrogen ions adsorbed representing the value of the Gibbs adsorption (G_H) at the interface cellulose–aqueous solution was determined *via* calculation using the following formula

$$G_H = [(C_{HCl}V_0 - C_{NaOH}V) - [H^+](V_0 + V)]/ m \qquad (1)$$

where C_{HCl} is the concentration of a strong monobasic acid (HCl), added to the cellulose suspension prior to the titration, mmol/cm^3; V_0 is the volume of an aliquot taken for the titration cm^3; C_{NaOH} is the titrant concentration mmol/cm^3; V is the volume of NaOH added in this point of the titration curve, cm^3; m is the mass of the cellulose in the aliquot, g.

Basing on the results of GH value calculation, we plotted this value depending on pH for each samples (Fig. 2). The Gibbs adsorption value for hydrogen ions (G_H) is equal (accurate within a constant G_0) to the total adsorption of all the hydrogen ions from the solution on the surface of cellulose particles. The value of G_0 represents the amount of hydrogen ions adsorbed on the boundary layer of the surface
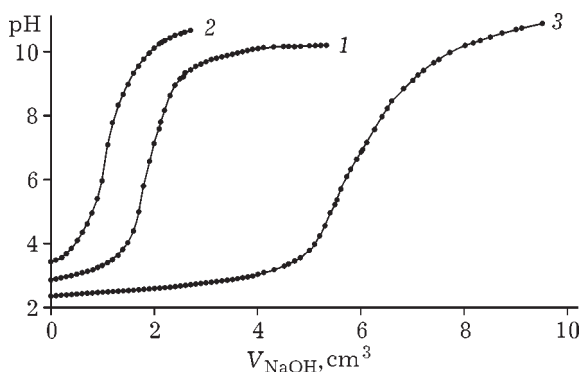

Fig. 1. Potentiometric titration curves for the suspensions of fibrous (*1*), microcrystalline (*2*) and powdered (*3*) cellulose.
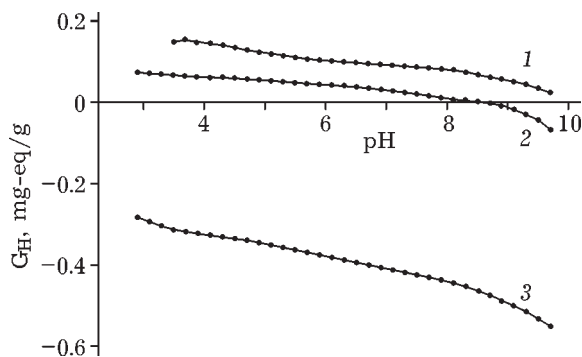

Fig. 2. Gibbs adsorption value (G_H) for the suspensions of fibrous (*1*), microcrystalline (*2*) and powdered (*3*) cellulose depending on pH.

under study, which amount is not dependent on the solution pH of and includes both hydrogen ions corresponding to the zero charge point of the sorbent surface under study, and hydrogen ions those cannot be titrated under experimental conditions (e. g., hydrogen ions inherent in the OH groups of hydroxo complexes characterized by strongly basic properties). The G_H and G_0 values can be either positive or negative depending on the position of the dividing surface of the sample. Thus, the complete adsorption value for hydrogen ions on the surface under study could be written as it follows:

$$G_H + G_0 = \sum_i G_i \frac{1}{1 + 10^{pH - pK_i}} \qquad (2)$$

where G_i is the exchange capacity of the i-th acid-base group; pK_i is the dissociation constant exponent characterizing this group, ΣG_i being the full exchange capacity of the cellulose sample with respect hydrogen ions.

The summation in eq. (2) is performed for all the acid-base groups reversible with respect to hydrogen ions on the surface of the suspension under investigation. It is assumed therein that all the acidic groups are basic monobasic.

The data obtained for the PC suspension indicate that there is a strong specific interaction between the Ti^{4+} ions present in the system and the surface of the particles in the suspension. As a result, the point of zero charge of the surface is strongly shifted toward lower pH values, and Γ_H becomes negative [29, 30] (see Fig. 2).

The lowest values of $\pm G_H$ are exhibited by a sample of MCC, since the cellulose after hydrolytic degradation represents a powder-like material with a small amount of ionic groups
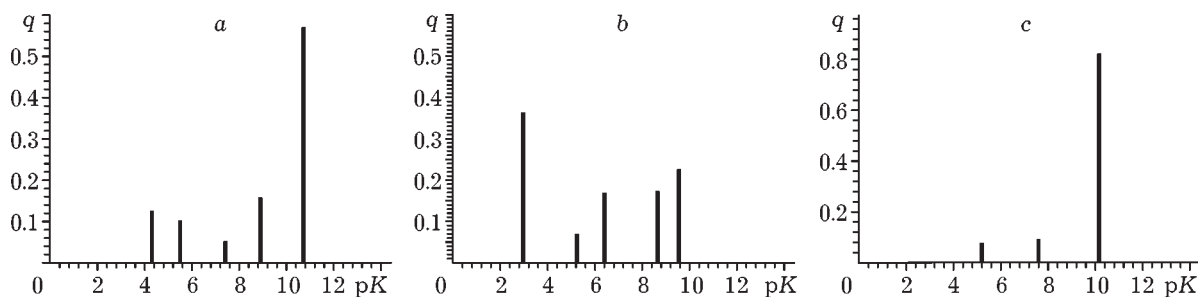
Fig. 3. pK spectra of fibrous (*a*), microcrystalline (*b*) and powdered (*c*) cellulose.

on the surface as to compare with FC obtained in the solution of titanium tetrachloride.

With the help of computer processing the potentiometric titration data using specially developed software we obtained pK spectra for each sample of cellulose (Fig. 3). The values of q are equal to the relative molar fractions of corresponding acid-base groups. The difference in the number of peaks on the histograms (cellulose pK spectra) indicates that there occurs the formation of different amount of ionic groups depending on the method of treatment.

The pK spectra obtained for the suspensions of fibrous powdered cellulose (see Fig. 3, *a*, *b*) exhibit an equal number of acid-base groups [28], however in the case of the PC there is shifting all the bands toward lower the pK values observed. This corresponds to a weaker bond between hydrogen ions and corresponding acid-base groups. The effect observed is correlated with an increased chemical reactivity of the PC under obtaining, which, to all appearance, could be connected with breaking cellulose chains and, consequently, with decreasing the polymerization level [23, 25, 26, 31]. The microcrystalline cellulose as a product of the hy-

drolytic processing of FC is depleted with ionic groups as to compare with the latter (see Fig. 3, *c*): the histogram of MCC pK spectrum demonstrates only three peaks to present.

Figure 4 presents data concerning the total exchange capacity of the cellulose with respect to hydrogen ions for the three samples under investigations such as CC, PC and MCC. The values of the total exchange capacity with respect to hydrogen ions (G) for the PC are higher than those for CC and MCC (see Fig. 4). For the PC obtained resulting from the action of titanium tetrachloride on unbleached softwood cellulose pulp, the total exchange capacity of ΣG_i = G = 0.37 mg-eq/g.

Comparing the values of the total exchange capacity (G) for the samples under study, which values were calculated in two ways, indicates a greater informativity of the computer processing of potentiometric titration data due to taking into account the boundary layer of the surface adsorption G_0 on the surface of the samples.

CONCLUSION

1. For the first time using a pK spectroscopy technique we studied the acid-base properties of naturally occurring composite material suspensions such as unbleached softwood cellulose pulp.

It has been found that the use of low $TiCl_4$ concentrations in solution for cellulose treatment results in breaking the cellulose macromolecules and weakening the bonds between hydrogen ions and corresponding acid-base groups, thereby the number of these groups remain unchanged.

2. It is demonstrated that the influence of $TiCl_4$ hexane solution upon the cellulose results in obtaining powdered cellulose contains more ionogenic groups than the MCC.
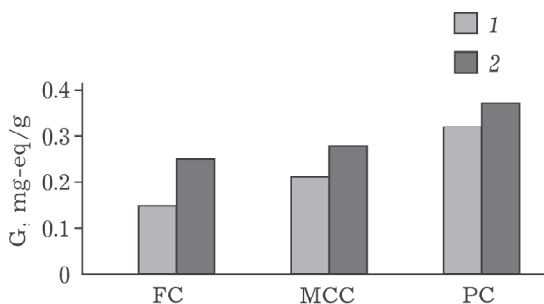

Fig. 4. Total cellulose ion exchange capacity with respect hydrogen ions (G), calculated in different ways: *1* − as described in [18]; *2* − using a computer data processing.

3. The impact of $TiCl_4$ on unbleached softwood cellulose pulp results in obtaining powdered cellulose that differs from the other cellulose samples under investigation by high values of the total exchange capacity.

REFERENCES

1 Ryazanov M. A., Ryazanov A. M., Zlobin D. A., *Izv. Vuzov. Khim. i Khim. Tekhnol.*, 43, 5 (2000) 150.

2 Ryazanov M. A., Dudkin B. M., *Kolloid. Zh.*, 65, 6 (2003) 831.

3 Ryazanov M. A., Nauch. Konf. "Fizicheskaaya Khimiya Poverkhnostnykh Yavleniy i Adsorbtsii" (Thesises), Ivanovo, 2010, pp. 57–60.

4 Ryazanov M. A., Dudkin B. M., Nenev N. A., Savina O. A., IV Vseros. Konf. "Primeneniye pK-Spektroskopii pri Izuchenii Kislotno-Osnovnykh Kharakteristik Poverkhnostey Sorbentov" (Thesises), Syktyvkar, 2002, pp. 196–203.

5 Ryazanov M. A., Filippov D. V., Kravchenko A. V., Ulitin M. V., *Zh. Fiz. Khim.*, 84, 3 (2010) 460.

6 Ryazanov M. A., Dudkin B. M., *Kolloid. Zh.*, 66, 6 (2004) 807.

7 Ryazanov M. A., Dudkin B. N., *Phys. Chem. Surf. Phenomena*, 83 (2009) 2318.

8 Ryazanov M. A., Dudkin B. M., Loukhina I. V., Turova O. V., *Kolloid. Zh.*, 67, 6 (2005) 823.

9 Ryazanov M. A., Lodygin E. D., Beznosikov V. A., Zlobin D. A., *Pochvovedeniye*, 8 (2001) 934.

10 Shamrikova E. V., Ryazanov M. A., Vanchikova E. V., *Chemosphere*, 65 (2006) 1426.

11 Shamrikova E. V., Vanchikpova E. V., Ryazanov M. A., *Pochvovedeniye*, 11 (2007) 1309.

12 Ryazanov M. A., *Khim. Rast. Syrya*, 2 (2010) 109.

13 Bely V. A., Chukicheva I. Yu., Khurshkainen T. V., Sadykov R. A., Ryazanov M. A., Saltysova E. B., *Butlerovskiye Soobshcheniya*, 25, 4 (2011) 54.

14 Petropavlovskiy G. I., Gidrofilnye Chastichno Zameshchennye efiry Tsellyulozy i Ikh Modifikatsiya Putem Khimicheskogo Sshivaniya, Nauka, Leningrad, 1988.

15 Sharkov V. V., Lukanina T. L., Izucheniye Struktury Poroshkovykh Tsellyuloz i Kompozitsionnykh Materialov, Poluchennykh v Laboratornykh i Promyshlennykh Usloviyakh (Otchet po NIR), VNPOBumprom, Leningrad, 1985.

16 Bolotnikova L. S., Danilov S. N., Samsonova T. I., *Zh. Prikl. Khim.*, 1 (1966) 176.

17 Obolenskaya A. V., Elnitskaya Z. P., Leonovich A. A., Laboratornye Raboty po Khimii Drevesiny i Tsellyulozy, Ekologiya, Moscow, 1991.

18 Ayvazov B. V., Praktikum po Khimii Poverkhnostnykh Yavleniy i Adsorbtsii (High School Book), Vyssh. Shkola, Moscow, 1973.

19 Battista O. A., Smith P. A., *Ind. Eng. Chem.*, 54, 9 (1962) 20.

20 Karyakin Yu. V., Angelov I. I., Chistye Khimicheskiye Veshchestva, Khimiya, Moscow, 1974.

21 Sarybaeva R. I., Afanasiev V. A., Zaikov V. E., Shchelokhova L. S., *Usp. Khim.*, XLVI (1977) 1395.

22 Frolova S. V., Struktura i Fiziko-Khimicheskiye Svoystva Tsellyulozy, Destruktirovannoy Kislotami Lyuisa (Candidate's Dissertation in Chemistry), Ivanovo, 2009.

23 Frolova S. V., Demin V. A., *Zh. Prikl. Khim.*, 81, 1 (2008) 152.

24 Torlopov M. A., Frolova S. V., Demin V. A., *Chem. Sustain. Dev.*, 15, 4 (2007) 491.
URL: http://www.sibran.ru/English/csde.htm

25 Torlopov M. A., Frolova S. V., *Khim. Rast. Syrya*, 3 (2007) 63.

26 Kuvshinova L. A., Frolova S. V., Demin V. A., Nauch.-Prakt. Konf. Professorsko-Prepodavatelskogo Sostava Syktyvkarskogo Lesnogo Instituta po Itogam Nauch.-Issled. Raboty v 2009 Godu (Proceedings), SLI, Syktyvkar, 2010.

27 Kuvshinova L. A., Demin V. A., in: Khimiya i Tekhnologiya Rastitelnykh Veshchestv (Treatises of Komi NTs UrO RAN, No. 176), Syktyvkar, 2005, pp. 24–31.

28 Frolova S. V., Kuvshinova L. A., Ryazanov M. A., Nauch. Konf. "Fizicheskaaya Khimiya Poverkhnostnykh Yavleniy i Adsorbtsii" (Thesises), Ivanovo, 2010, pp. 60–63.

29 Zhukov A. N., *Kolloid. Zh.*, 58, 2 (1996) 280.

30 Frolova S. V., Kuvshinova L. A., Kuchin A. V., RU Pat. No. 2478664, 2013.