ANALYSIS OF THE STRUCTURE OF CARBOHYDRATES WITH USE OF THE REGULARIZED DECONVOLUTION METHOD OF VIBRATIONAL SPECTRA

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Abstract

The infrared spectra of polysaccharides (amylose and cellulose) as well as of their constituent monosaccharides (α- and β- D-glucose) and the results of their deconvolution are presented. The number of bands separated upon deconvolution in the 1200-920 cm^{-1} spectral range exceeds the number of visualized absorption maxima in the room temperature spectra by a factor of more than two. It is shown that the results of deconvolution of the IR spectra of monosaccharides are in good agreement with the data of normal coordinate analysis of these compounds in the crystalline state. The manifestation in IR spectra of the investigated monosaccharides of factor group splitting of a number of nondegenerate fundamental vibrational modes of molecules in the crystalline state has been found. It has been shown that the glycosidic linkage formation in polysaccharides with 1→4 glycosidic linkage is characterized by the appearance of new absorption bands in the 1175-1140 cm^{-1} spectral range, as compared to the infrared spectra of their constituent monomers. In the 1000-970 $см^{-1}$ range, in the deconvolved IR spectrum of cellulose, absorption bands, which are not observed in the monomer spectrum, are separated. The number of bands in the above region remains unchanged for amylose, as compared to the spectrum of monomer α-D-glucose.

Keywords: ***Vibrational spectroscopy; factor-group splitting; glycosidic linkage; carbohydrates; deconvolution***

1. Introduction

In analyzing the composition and structure of complex chemical compounds various spectroscopic methods, including vibrational (IR and Raman) spectroscopy have been successfully used. However, analytical potentialities of the method of vibrational spectroscopy are restrained, to a great extent, by the low resolution of bands in the spectra of complex substances. The number of visualized absorption maxima in such spectra is considerably smaller than the actual number of individual components. This fact considerably hampers interpretation of vibrational spectra of these compounds as well as the establishment reliable spectral-structural correlations.

The effective way for solving this problem is the use of corresponding methods for mathematical treatment of vibrational spectra. These methods make it possible to reveal the fine structure of the bands in complex spectra and to determine the characteristics of individual components, which allows a more precise interpretation of them.

The aim of the present work is to obtain new data on the influence of the structure of carbohydrates on the formation of their vibrational spectra using the regularized method of deconvolution.

2. Experimental

IR spectra of monosaccharides α- and β-D-glucose were registered at room temperature on a Nicolet Protege 460 FT-IR spectrometer, IR spectra of polysaccharides amylose and native cotton cellulose- on a Jasco Model IR-810 spectrophotometer. Powdered samples

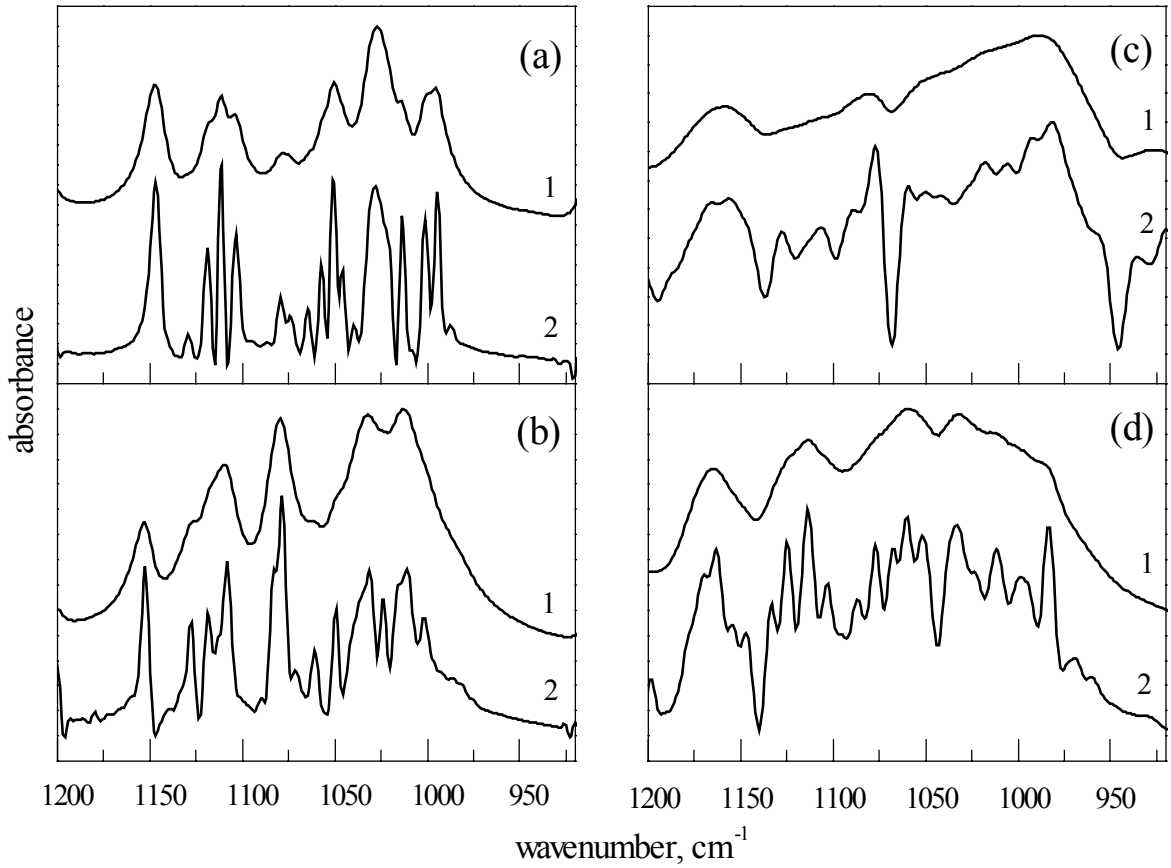

Fig.1. IR spectra of α-D-glucose (a), β-D-glucose (b), amylose (c), cellulose (d) (1) and the results of their deconvolution (2).

were dispersed in KBr pellets and recorded with an instrumental resolution of 2 cm^{-1} and an averaging of 256 scans on the FTIR spectrometer and with a resolution of 3 cm^{-1} on the Jasco spectrophotometer.

Deconvolution of IR spectra of carbohydrates being investigated has been performed using the regularized method of deconvolution [1,2].

3. Results and discussion

Fig. 1 shows the IR spectra of monosaccharides α- and β-D-glucose, polysaccharides amylose and cellulose in the 1200-920 $см^{-1}$ range and the results of their deconvolution.

From Fig. 1 it is seen that the use of the regularized method of deconvolution permits a considerable resolution enhancement in IR spectra of the investigated carbohydrates. The number of individual bands separated as a result of deconvolution in the 1200-920 cm^{-1} range is more than doubled compared to the room temperature spectra of these compounds.

The monosaccharides being investigated crystallize in the orthorhombic system with the space-group symmetry $P2_12_12_1$. Each unit cell contains four molecules. Due to the presence of several molecules in the crystalline cell one can observe in the IR spectra of monosaccharides the factor group splitting of nondegenerate fundamental vibrational modes into components corresponding different symmetry species. The values of such splittings are small and this makes it impossible to resolve them in the room temperature IR spectra.

The number of bands observed in the deconvolved spectra of α- and β-D-glucose in the 1200-920 см$^{-1}$ range considerably exceeds maximum number of frequencies calculated for the isolated molecule model. The indicated increase in the number of observed frequencies in the range under investigation is explained by the fact that the majority of the bands exhibit, as a result of deconvolution, splitting into components with different intensities, the separation between whose maxima is $\Delta\nu = 5\text{-}10$ см$^{-1}$ (Fig. 1). In the case under consideration, there are no vibrations whose degeneracy can be removed under the action of the crystal's static field. However, in the IR spectra of monosaccharides, the so-called correlation-field effect can manifest itself, leading to the factor-group splitting of the fundamental vibrational modes of the molecules in the crystalline cell. With regard for the factor group splitting, the number of experimental bands observed in the deconvolved IR spectra of the investigated monosaccharides is in good agreement with the data of normal coordinate analysis for these compounds in the crystalline state.

The use of the regularized method of deconvolution made it possible to establish new spectral characteristics of polysaccharides amylose and cellulose with 1→4 glycosidic linkage in 1200-920 см$^{-1}$ range. For this purpose a comparative analysis of the deconvolved IR spectra of amylose and cellulose and their corresponding monomers α- and β-D-glucose has been carried out (Fig. 1). Comparison of spectral curves in Fig. 1 shows that in the 1140 - 1000 cm^{-1} range all the bands that are observed in both room temperature and deconvolved spectra of polysaccharides are also present in the spectra of their monomers, while in the 1175-1140 and 1000-920 cm^{-1} ranges, as a result of deconvolution, new bands are separated, as compared to the spectra of constituent monomers. These ranges are close to the previously mentioned in work [3] regions where stretching vibrations ν(CO) C-O-C glycosidic bridge in oligosaccharides manifest themselves.

In the room temperature IR spectra of amylose and cellulose in the 1175-1140 cm^{-1} range the broadening and the high-frequency shift of the bands at 1165 and 1158 см$^{-1}$ are observed, as compared to the spectra of monosaccharides (Fig. 1). The results of deconvolution showed that the indicated spectral changes are due to the appearance in this range of additional absorption bands with the formation of glycosidic linkage. This fact confirms the attribution of the bands in the range under consideration to the stretching vibrations of C-O-C glycosidic linkage.

In the IR spectra of the investigated polysaccharides, characteristic distinctions because of the difference in glycosidic linkage configuration have been established. Thus, as it can be seen from Fig. 1, characteristic of cellulose with β (1→4) glycosidic linkage is the appearance of several absorption bands in the 1000-970 cm^{-1} range instead of a single weak band observed in the IR spectrum of monomer β-D-glucose. For amylose (α configuration of the glycosidic linkage), as compared to the monosaccharide α-D-glucose, the number of absorption bands in the given region remains unchanged. Besides, comparison of the results of deconvolution shows that in the IR spectra of amylose and cellulose, as opposed to their constituent monomers, there are several components in the 970-920 cm^{-1} range (Fig. 1). This fact can be indicative of nonequivalence of 1 → 4 glycosidic linkages in the molecules of the investigated polysaccharides.

4. Conclusions

The use of the regularized method of deconvolution has made it possible to achieve a considerable resolution enhancement in the IR spectra of the investigated mono- and polysaccharides. The number of vibrational frequencies separated as a result of

deconvolution exceeds the number of visualized absorption maxima in the room temperature IR spectra by factor more than two. This permits a more detailed analysis of these spectra.

The results of deconvolution of the IR spectra of α- and β-D-glucose are in a good agreement with the data of normal coordinate analysis of these compounds in the crystalline state. The presence in the experimental spectra of monosaccharides of a number of additional bands compared with the number of calculated vibrational modes of one type of symmetry can be due to the factor group splitting of the fundamental modes of several molecules in the crystalline cell, which should be taken into account when interpreting the vibrational spectra.

It has been established that the characteristic of polysaccharides with $1 \rightarrow 4$ glycosidic linkage is the appearance of new absorption bands in the 1175-1140 cm^{-1} spectral range as compared to the spectra of their constituent monomers, which can be a spectroscopic manifestation of glycosidic linkage formation. This fact can be used in identifying different structural transformations of polysaccharides with participation of glycosidic linkage.

The distinctions between the IR spectra of amylose and cellulose in the 1175-1140 and 1000-970 cm^{-1} regions are attributed to the difference in the glycosidic linkage configuration. Characteristic of cellulose with β configuration of glycosidic linkage is the appearance in the above ranges of several absorption bands instead of one band observed in the spectrum of monomer β-D-glucose. In the 1000-970 cm^{-1} frequency range, as compared to the α-D-glucose spectrum, the number of bands in the spectrum of amylose (α configuration of the glycosidic linkage) remains unchanged.

The results obtained can be used in investigating the vibrational spectra of carbohydrates with the aim of solving various practically important problems of molecular spectral analysis.

References

[1] D.K. Buslov and N.A. Nikonenko, Appl. Spectrosc. 51 (1997) 666.
[2] D.K. Buslov and N.A. Nikonenko, Appl. Spectrosc. 52 (1998) 613.
[3] M. Kačuráková and M. Mathlouthi, Carbohydr. Res. 284 (1996) 145.