

INTERACTIONS AT THE MOLECULAR LEVEL AND THEIR  
SPECTROSCOPIC MANIFESTATIONS IN THE DEXTRAN-WATER  
SYSTEM

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The influence of sorbed water on the IR spectrum of dextran has been studied as a function of the degree of hydration of the polymer. By analyzing the pattern of spectral changes it has been established that the water molecules are present in the bound state. Features of the specific interactions of water molecules with different active groups in the polymeric matrix are described. It has been found that the tendency to form large clusters of water is low in hydrated dextran and is shown only at vapor pressures close to saturated.

The main qualitative features of the sorption of water vapor by polymers have been established as a result of numerous investigations. The further development of the problem of the interaction of the polymers with sorbed water requires a deepening of our knowledge and an understanding of the specific nature of the molecular processes taking place, and also determinations of the limits of their action in relation to each concrete polymer.

The study of features of the hydration of polysaccharides the macromolecules of which differ only by their structure is of great interest, since together with a consideration of processes at the molecular level in a given system, in systematic investigations the possibility appears of establishing the influence of the distribution of polar groups of identical structure in the chain on the nature of the interaction of water with the polymer. In the present paper, which reports a continuation of IR-spectroscopic investigations of polysaccharide-water systems [1-4], we give the results of a study of the intermolecular interactions and states of water in dextran as functions of the degree of hydration of the polymer.

Figure 1 shows the IR spectra of a dextran film obtained at various degrees of hydration of the polymer. As a measure of the degree of hydration in this figure is given the relative humidity of the medium in which the sample was conditioned. The presence of sorbed water in polysaccharides can be judged from the band of the deformation (scissoring) vibrations of the water molecules located in the 1600-1660  $\text{cm}^{-1}$  region, which are not masked by the absorption bands of these polymers. As can be seen from Fig. 1, the residence of a previously dried dextran film in humid media leads to the appearance in this region of spectral frequencies of an absorption band the intensity of which is determined by the humidity of the medium.

A comparison of the spectra of dextran in the dry and the hydrated states shows that the most considerable spectral changes in the sorption of a film of water appear in the region of characteristic vibrations of OH group (3000-3700  $\text{cm}^{-1}$ ). Thus, when water enters a polymeric matrix, a broadening of the absorption band of the stretching vibrations of the hydroxyls, and increase in its intensity, and a shift of the maximum from 3400  $\text{cm}^{-1}$  for a sample in the dry state to  $\sim 3360 \text{ cm}^{-1}$  at high degrees of hydration of the polymer are observed. Such a marked dependence of the spectral pattern in the frequency interval of 3000-3700  $\text{cm}^{-1}$  on the degree of hydration of the polymer is not unexpected and is explained by the fact that in this region of the spectrum not only the OH groups of the polymer but also the water molecules absorb.

A study of the behavior of the bands of the OH-stretching vibrations usually gives rich information on features of intermolecular interactions with the participation of OH groups. However, in the case of hydrated polysaccharides neither the absorption bands of the hydroxyls of the polymer nor the absorption bands of water can be indicators of intermolecular

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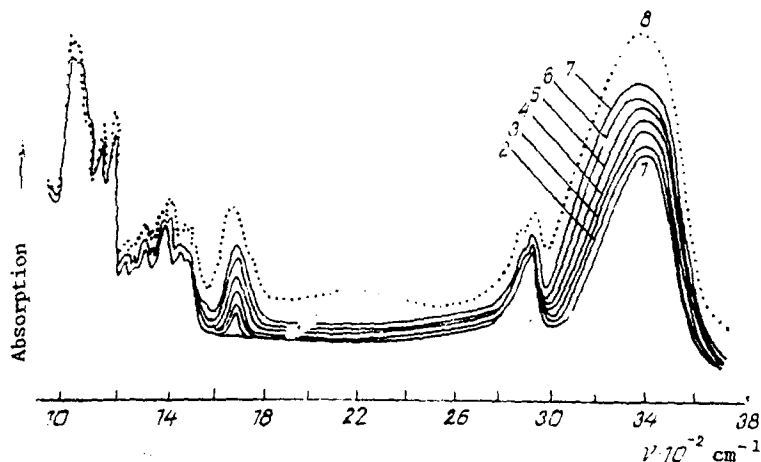


Fig. 1. IR spectra of a dextran film hydrated in  $H_2O$  vapor. Relative humidities (%): 0 (1); 7 (2); 11 (3); 33 (4); 52 (5); 75 (6); 84 (7); and 98 (8).

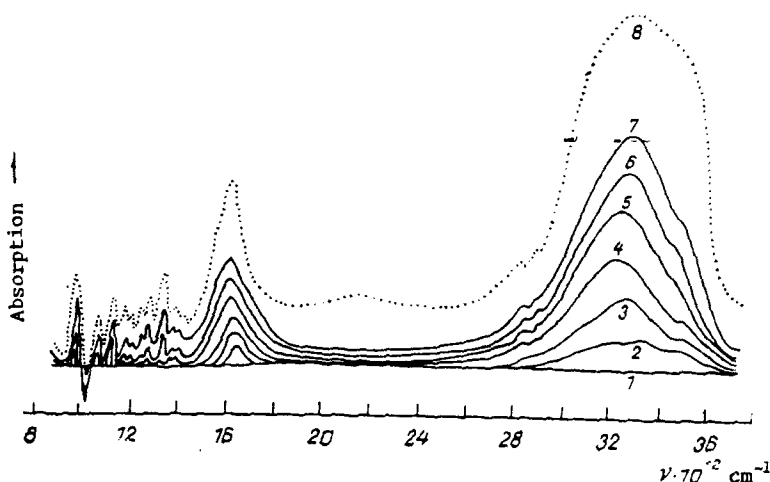


Fig. 2. Differential IR spectra obtained in the hydration of a dextran film in  $H_2O$  vapor. Relative humidities (%) 0 (1); 7 (2); 11 (3); 33 (4); 52 (5); 75 (6); 84 (7); and 98 (8).

interactions, because of their overlapping. Therefore, in an investigation of the sorption of water by polysaccharides a differential method of recording the spectra of a moist sample relative to a dry sample under the conditions of the same optical thickness of the film has been proposed [1]. This method permits the spectrum of the water sorbed by the polymer and also other changes due to its interaction with water to be isolated.

Figure 2 shows a series of such differential spectra obtained under various conditions of hydration of the sample. Analysis of the pattern of spectra changes shows that in the initial stage of the hydration of the polymer three broad overlapping absorption bands appear in the region of characteristic vibrations of the OH groups, with maxima close to 3270, 3365, and 3535  $cm^{-1}$ . We may note, however, that the bands at 3270 and 3365  $cm^{-1}$  are resolved (observed as individual maxima) only in the spectrum taken on the hydration of the film in the medium with the lowest humidity. In the spectra obtained at higher degrees of hydration of the polymer, these form either a single broad band with a maximum at a frequency of 3300  $cm^{-1}$  or a band with an unsymmetrical contour having a maximum at a frequency of  $\sim 3270$   $cm^{-1}$  and an inflection close to 3365  $cm^{-1}$ .

Before considering the question of the interpretation of the absorption bands detected, assuming that they are due mainly to the absorption of water, it must be mentioned that the hydration of dextran does not lead to the appearance of absorption bands in the spectral region of 3600-3800  $cm^{-1}$ . If it is considered that the bands of the symmetrical and antisymmetrical vibrations of free unperturbed water molecules appear at frequencies of  $\sim 3657$  and 3756

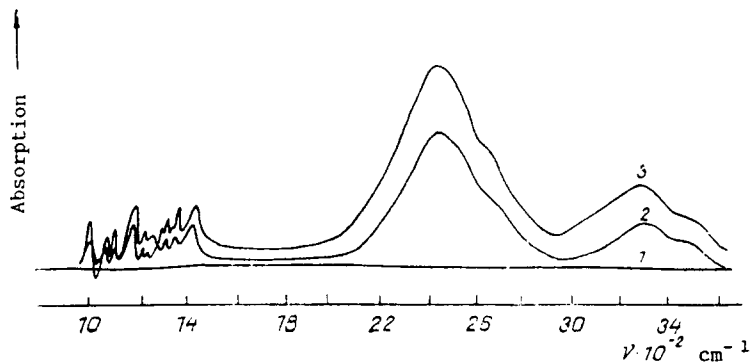


Fig. 3. Differential IR spectra obtained in the hydration of a dextran film in HDO vapor. Relative humidities (%): 0 (1); 42 (2); and 84 (3).

$\text{cm}^{-1}$  [5], this experimental result unambiguously shows that the absolute majority of the sorbed water molecules in the polymeric matrix are present in the bound state at both low and high degrees of hydration of the polymer. The position in the spectrum of the bands observed on differential recording (a considerable low-frequency shift) shows that the water molecules interact with the active groups in the polymeric matrix through hydrogen bonds. Furthermore, both OH groups in the water molecule participate in the formation of hydrogen bridges. This permits the assumption that in this interaction water molecules exhibit primarily proton-donating properties.

As is known, a water molecule can form up to four hydrogen bonds, being simultaneously a donor of protons and a donor of electrons (H-bonds with the participation of the unshared pairs of electrons of the oxygen atom). On the formation of H-bonds through a hydrogen atom, the low-frequency shift of the band of the stretching vibrations of water molecules may reach several hundreds of reciprocal centimeters. At the same time, participation in the formation of hydrogen bridges of the oxygen atom of a water molecule causes only a slight perturbation of its OH bonds. In this case the shifting of the bands of the stretching vibrations does not exceed a few reciprocal centimeters [5, 6]. It is therefore difficult to draw an unambiguous conclusion concerning the participation of the oxygen atoms of the molecules of water sorbed by the polymer in the initial stage of hydration in the formation of the H-bonds with the active groups of the macromolecules, since it does not appear possible to detect the weak additional perturbation of the OH bonds from the available spectroscopic results. However, it must be borne in mind that in the initial stage of sorption the polymer is present in the vitrified state and molecular (conformational) motion is limited. In view of this, the possibility of such an arrangement of the polar groups of the macromolecules as could provide the conditions for the formation by a water molecule of four hydrogen bonds with them appears unlikely. We may note that in literature sources reports have been found repeatedly that on the formation of H-bonds in many organic and inorganic compounds water reveals proton-donating properties [5].

The maximum close to  $3270 \text{ cm}^{-1}$  is present in a spectral region that is specific for the absorption of the first overtone of the scissoring vibrations of the water molecule. The marked increase in the intensity of the band in comparison with that characteristic for the overtone may be a consequence of Fermi resonance. As is known, deuteration eliminates Fermi-resonance interaction and the band of the overtone practically disappears. Figure 3 shows a differential spectrum obtained on the hydration of a dextran film in HDO vapor. The procedure for performing such experiments for polymers containing hydroxy groups has been given in [1]. The maximum at a frequency of  $3270 \text{ cm}^{-1}$  is not observed in the spectrum of the isotope-substituted form, which confirms its assignment to an overtone.

The most interesting distinguishing feature of the differential spectrum obtained in the process of sorption of half-heavy water by polymers is the appearance in place of the maximum at  $3270 \text{ cm}^{-1}$  of a broad band with a frequency of the maximum of  $3000 \text{ cm}^{-1}$ . Apparently, in the hydration of the film in  $\text{H}_2\text{O}$  vapor this band is masked by the neighboring overtone band. Absorption bands at  $3535$  and  $3365 \text{ cm}^{-1}$  (shoulder) are observed in the spectrum of the isotope-substituted form without fundamental changes.

Earlier [2], the spectroscopic manifestations of the hydration of xylan, the elementary units of the macromolecule of which contain no  $\text{CH}_2\text{OH}$  groups and are linked by  $\beta$ -1,4-glycoside bonds, were investigated. A comparison of the spectroscopic results obtained from hydrated dextran and hydrated xylan shows that the band at  $3000\text{ cm}^{-1}$  is not observed in the corresponding xylan spectra. This result permits the assumption that, most probably, this band is due to the absorption of the OH bonds of water molecules forming hydrogen bridges with the oxygen atoms of the  $\alpha$ -1,6 glucosidic bonds and the primary hydroxy groups located at the ends of the chains. The spectroscopic manifestation of the process of interaction (greatest low-frequency shift of the band) unambiguously shows that here the interactions of the water molecule form the strongest hydrogen bonds.

An additional argument in favor of such assignment of the band at  $3000\text{ cm}^{-1}$  may be the following considerations. It is known that the lowest acidity and the highest reactivity in polysaccharides (at least, in cellulose) are possessed by the primary hydroxy groups at  $\text{C}_6$ . The interaction between water and a polymer can be represented as an acid-base interaction where the water fulfils the role of the acid and the hydroxyls of the polymer, being electron donors, that of the base. Therefore, it must be expected that the water molecules interacting with the primary hydroxyls will give stronger H-bonds than those interacting with the secondary hydroxyls. It must be mentioned that an indeterminacy exists relative to the spectroscopic manifestation of the interaction of the OH group at  $\text{C}_4$  with water. Therefore an unambiguous assignment of the band at  $3000\text{ cm}^{-1}$  will be possible only after additional investigations on model compounds.

According to the literature [2], the stretching vibrations of water molecules interacting with the secondary hydroxyls at  $\text{C}_2$  and  $\text{C}_3$  are characterized by two absorption bands with maxima at  $3380$  and  $3350\text{ cm}^{-1}$ . The difference between the frequencies of the maxima of these bands amounts to  $\sim 170\text{ cm}^{-1}$ . A similar difference in the frequencies of the maxima has been reported for the pair of bands at  $3365$  and  $3535\text{ cm}^{-1}$  in the spectrum of hydrated dextran. On the basis of these facts it may apparently be suggested that the absorption bands at  $3365$  and  $3535\text{ cm}^{-1}$  are due to the stretching vibrations of a water molecule forming hydrogen bonds with the secondary hydroxyls of the elementary unit of the extran macromolecule. The small low-frequency shift of the maxima of these bands relative to those observed in the spectrum of xylan may be due to features of the structure of the extran macromolecule which apparently lead to an intensification of the proton-accepting capacities of the secondary hydroxyls.

It is interesting to note that the replacement of  $\text{H}_2\text{O}$  molecules by the unsymmetrical HDO molecules in the sorption of vapors by dextran is not accompanied by a change in the frequencies of the maxima of the bands of the OH-stretching vibrations (compare Figs. 2 and 3). If we start from the known situation [6] that the cause of the analogy in the spectral distributions is connected with the loss by water molecules of their original symmetry, then the results obtained indicate that, on interaction with the accessible groups, water molecules form predominantly unsymmetrical associates with nonequivalent perturbation of the two OH-bonds by hydrogen bridges.

As can be seen from Fig. 2, an increase in the amount of sorbed water in the polymer is accompanied by a rise in the intensity of all the bands located in the frequency region of  $3000$ - $3600\text{ cm}^{-1}$ . Calculation of the optical densities of the bands was not performed in view of their pronounced overlapping. Since the bands observed in the spectral region being analyzed are due predominantly to the absorption of water molecules interacting with the polymeric matrix (with the exception of the band at  $3270\text{ cm}^{-1}$ ), it can be stated that at all the humidities shown in the figure the water molecules find active group accessible for interaction.

At the present time, it is considered as generally accepted that at a certain content water in polymers forms clusters [7]. Complexes in which water molecules are bound to one another by hydrogen bridges have been studied repeatedly from IR spectra. As a rule, they are represented by a broad absorption band with a maximum close to  $3420\text{ cm}^{-1}$  [5]. However, a comparison of the spectra given in Fig. 2 shows that the spectroscopic indications of the formation of such hydrate structures in a dextran film can be detected only on the hydration of the polymer in media with humidities close to the maximum. Thus, in the dextran-water system, apparently, in contrast to other polysaccharides [2-4], not only in the initial stage of sorption but also at high degrees of hydration of the polymer, interaction of the water molecules with the polymeric matrix predominates. Probable reasons for the observed features of the interactions at the molecular level in hydrated dextran may be the adequate activity

of the groups of the macromolecules as a consequence of the amorphous state of the polymer and the lowering of the glass temperature and the corresponding increase in molecular mobility during the sorption of water, leading to the appearance of new accessible groups and, possibly, a free rotation of the oxygen atom of the glucosidic bond around the C-C bond. It must also be borne in mind that, according to the spectroscopic results, the energy of the hydrogen bonds formed by water molecules with the hydroxyls and, in the first place, with the oxygen atom of the glucosidic bond is somewhat higher than in clusters with H<sub>2</sub>O...H<sub>2</sub>O interaction. Therefore the first interaction may prove to be competitive with the second, which is partially confirmed by the dominance in intensity of the absorption band at 3000 cm<sup>-1</sup>.

#### EXPERIMENTAL

The work was carried out on dextran - a polysaccharide in the macromolecule of which, in contrast to other polysaccharides the elementary units of anhydroglucopyranose are linked by the less rigid  $\alpha$ -1,6-glucosidic bonds. The molecular mass of the polymer was 40,000, which ensured a lower degree of branching of the macromolecules through  $\alpha$ -1,3- and  $\alpha$ -1,4-glucosidic bonds.

The spectral measurements were performed on films obtained from a solution of the polymer in dimethyl sulfoxide and cast on fluorite substrates. The choice of DMSO as solvent is due to the fact that, in the preparation of films from aqueous solution, in the drying process the solution contracts to a drop on all available water-insoluble substrates. The problem therefore arose of choosing a solvent for improving the wetting of the substrate. A vacuum drying chest (at a pressure of 13.3 Pa) was used for eliminating the solvent. Because of the brittleness of thin films ( $d \sim 0.6 \mu\text{m}$ ) they were not removed from the substrate. Before hydration the films were dried in a vacuum desiccator over phosphorus pentoxide for two days. The conditions for the hydration of the samples in H<sub>2</sub>O and HDO vapors, their hermetic sealing, and the recording of the spectra (including differential spectra) have been given in [1, 2].

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