

Hydrogen bonds and molecular complexes in solutions of cellulose nitrate

Yu. M. Mikhailov,* N. V. Chukanov, and V. S. Smirnov

*Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.*

Fax: +7 (096) 515 3588. E-mail: yummm@icp.ac.ru

Intermolecular hydrogen bonds in the systems based on cellulose nitrate and a number of low-molecular solvents were studied by IR spectroscopy. The majority of the systems under study are characterized only by redistribution of intensities of the spectral bands corresponding to the pure polymer accompanied by their minor shift. In this case, acceptors of cellulose nitrate become sterically accessible for the redistribution of hydrogen bonds, and only an insignificant portion of them forms hydrogen bonds with a solvent. New spectral bands in the IR spectra were observed only for solutions containing diethyldiphenyl carbamide, suggesting the formation of a molecular complex.

Key words: molecular complex, hydrogen bond, cellulose nitrate, low-molecular solvent, polymer solution, IR spectrum.

The formation of molecular complexes is a classical evidence for a complex structure of solutions of organic compounds, including polymers, and reflects the plurality of their energetically favorable states.^{1–4} Many assumptions on the formation of molecular complexes of cellulose nitrate (CN) have been advanced.^{5–9} In all known cases, conclusions on the complex formation were based on XDA data. For example, in the CN–acetone,⁵ CN–dibutyl phthalate (DBP),⁷ and CN–ethyl acetate⁹ systems, structural complexes have been observed under certain conditions. The formation of a structural complex, for example, in the CN–DBP system, has been observed when an excess of a low-molecular substance penetrated into the oriented polymer fiber.⁷ In other cases for the same system, only ordering of the structure accompanied by a decrease in the partial entropy of the solvent has been observed.⁸

In the CN–ethyl acetate system, the complex is formed during the sorption of the solvent vapor.⁹ The structural complex is not recovered after melting of the complex under the action of new portions of the sorbed solvent followed by its complete desorption and repeated sorption. Moreover, the possibility of the formation of a complex with ethyl acetate depends on the thickness of the CN film.

Complex formation in these systems has not been confirmed by the calorimetric^{10,11} and sorption¹² methods.

In almost all X-ray studies of the structure of CN solutions, the formation of complexes was attributed to the intramolecular hydrogen bonds formed.^{7,9} The IR spectroscopic study of CN solutions indicates^{13,14} changes occurred in the system of hydrogen bonds (HB) as compared to the pure CN. However, these conclusions are based only on the analysis of integral shifts of the

band of the hydroxyl group of CN. At the same time, neither new spectral bands indicating the complex formation nor distinct regularities of the formation of HB have been observed for any of the systems studied.

In this work, we examined the fine structure of IR spectra of several solutions of CN, including those for which the formation of structural complexes has been observed previously^{5–9}; the specific features of intermolecular HB in these systems were also considered.

Experimental

Cellulose nitrate with a nitrogen content of 13.1 wt.% characterized by a mean numerical molecular weight of $\sim 2.5 \cdot 10^5$ and a polydispersity coefficient of ~ 5.0 was studied. Its binary solutions with the following thermodynamically compatible low-molecular substances with low vapor densities were studied¹⁵: dibutyl phthalate, triallyl isocyanurate (TAIC), methacryl(bis-triethylene glycol) phthalate (MGP-9), and diethyldiphenyl carbamide (DEDPC). All substances were chemically pure grade and used without additional purification. The components were combined by the preparation of 2–3% solution of the polymer in ethyl acetate, from which films 10–50 mm thick on Teflon supports were obtained by casting. The residual content of ethyl acetate in the films was not higher than 0.3 wt.%.

IR spectra were recorded on a Specord IR-75 spectrophotometer with a spectral width of the gap of $2.5\text{--}4.0\text{ cm}^{-1}$ in the $3100\text{--}3800\text{ cm}^{-1}$ frequency region and of 2.0 cm^{-1} at frequencies lower than 1500 cm^{-1} . Films of CN solutions were analyzed both on KRS-5 supports and without them. Spectral data were processed by the SHAPE program package. As a result, a set of individual spectra was obtained, whose sum gave an experimental envelope of IR spectra. The shape of individual contours is described by the Voigt function.¹⁶ The correct solution of the problem of separation of bands is provided by the fact that the number of individual bands is not higher than the total number of maxima and inflection points

of the initial envelope. The value of the mean-square deviation is the second criterion. Different starting sets of bands (determined by the methods of moments, second derivative, and others) result in different mean square deviations, from which we preferred the least deviation.

Results and Discussion

The IR spectrum of pure CN contains five bands in the region of stretching vibrations of OH groups (Fig. 1, *a*). One of them, with a maximum at 3670–3680 cm^{-1} , is assigned to free hydroxyl groups, and the

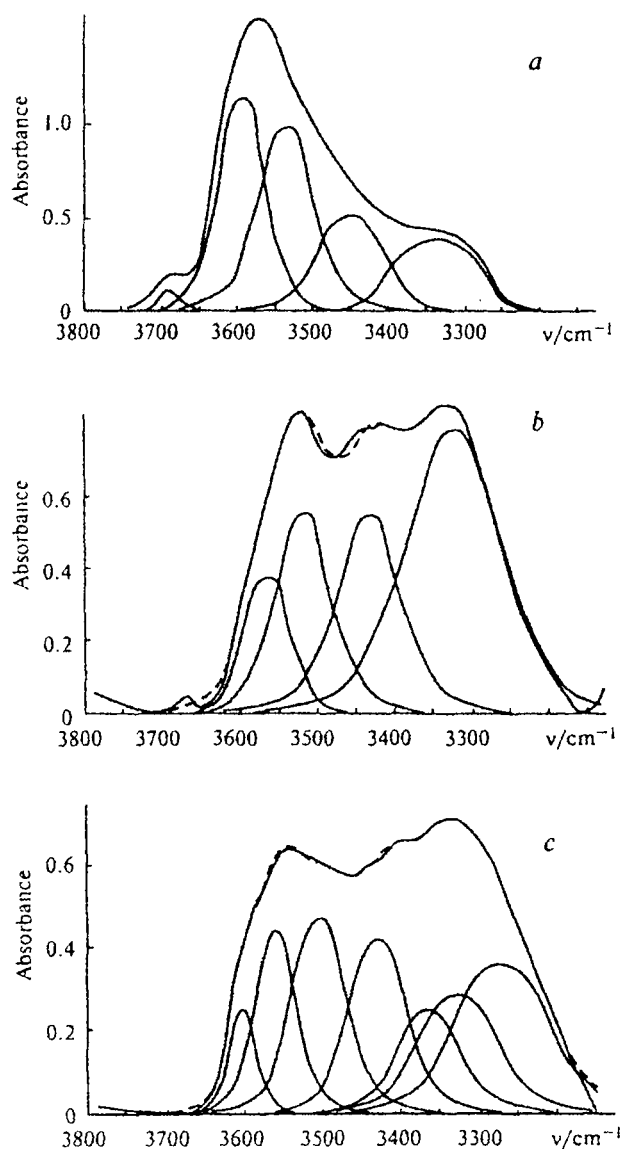


Fig. 1. Experimental IR spectra and their individual contours in the starting CN (*a*) and in solutions containing 29 wt.% DBP (*b*) and 33 wt.% DEDPC (*c*). Envelopes reproduced by the combination of individual contours are shown by dotted lines.

remaining four bands are attributed to the groups involved in HB with different stabilities. The presence of free OH groups has been detected previously¹⁷ for CN and other cellulose derivatives. Most likely, four types of HB correspond to four types of acceptors of HB. It can be assumed that they are the nitroester groups of two types ($\nu_1 = 3591 \text{ cm}^{-1}$ and $\nu_2 = 3532 \text{ cm}^{-1}$), the ester group of the β -glucoside bond ($\nu = 3445 \text{ cm}^{-1}$), and the hydroxyl groups (the strongest bond, $\nu = 3328 \text{ cm}^{-1}$). For all systems studied, except for CN–DEDPC, no new bands were observed in any of the spectral regions. The effects of DBP, TAIC, and MGP-9 on changes in the spectra of solutions are similar. In this case, as shown by DBP (Fig. 1, *b*), the intensity is redistributed, and the bands are insignificantly shifted relative to those of pure CN. The shift of the bands to the low-frequency spectral region indicates strengthening of hydrogen bonds and is accompanied by their broadening. The correlation between the width at the half-height and the position of the maximum of these bands was observed (Fig. 2), which confirms the correctness of the approach chosen for the separation of bands.¹⁸ The values of shifts of the bands of OH-stretching vibrations were used to estimate the energy of HB from the correlation dependence obtained¹⁹ for intramolecular HB in solutions of organic compounds. The results of this estimation are presented in Tables 1 and 2.

The validity of this approach can be substantiated, in our case, by the fact that steric hindrances for the formation of intermolecular HB are not so considerable for polymer solutions as those for the formation of intramolecular HB by molecules of low-molecular compounds and in the case of solids with a high crystallinity.

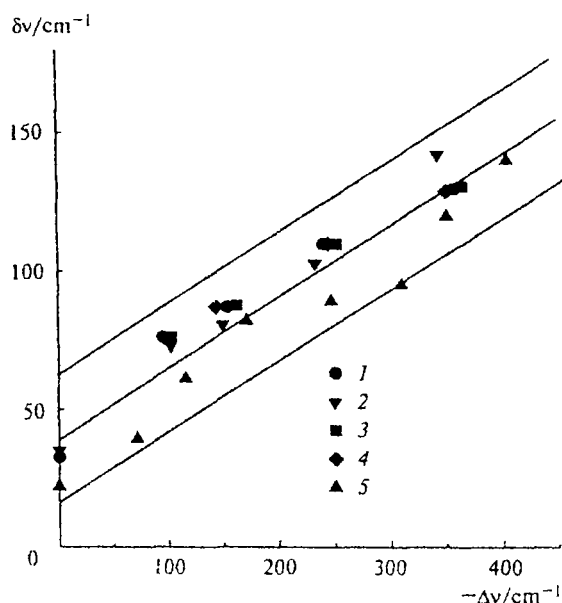


Fig. 2. Correlation between the shift of the spectral band relative to the band of free hydroxyl ($\Delta\nu$) and its width ($\delta\nu$) for solutions of low-molecular substances in CN: 1, CN; 2, DBP; 3, TAIC; 4, MGP-9; and 5, DEDPC.

Table 1. Spectral parameters of CN and CN—low-molecular solvent systems in the region of stretching vibrations of hydroxyl groups

System	Content of solvent (wt.%)	ν/cm^{-1}	Intensity of band (rel. units)	Bond energy /kcal mol ⁻¹
CN	0	3591	0.73	2.3
		3532	0.65	3.5
		3445	0.34	4.6
		3328	0.27	5.6
		3567	0.44	2.7
CN—DBP	29.0	3519	0.66	3.6
		3436	0.65	4.6
		3325	0.92	5.7
		3576	0.53	2.7
CN—TAIC	25.0	3517	0.79	3.6
		3427	0.53	4.7
		3314	0.58	5.8
		3581	0.29	2.7
CN—MGP-9	29.0	3515	0.73	3.7
		3434	0.76	4.6
		3328	0.46	5.7

Table 2. Spectral parameters of the CN—DEDPC system

Band	ν	$\Delta\nu$	$\delta\nu$	ΔR	E	Acceptor of hydrogen bond
	cm^{-1}			/nm	/kcal mol ⁻¹	
1*	3675	0	22	0	0	Absent
2	3600	75	41	0.0015	2.0	—Ph
3*	3559	116	61	0.0030	2.9	—O—NO ₂
4*	3503	172	82	0.0035	3.6	(—O—NO ₂)'
5*	3427	248	89	0.0058	4.7	—C—O—C—
6	3362	313	95	0.0070	5.4	N
7*	3323	352	120	0.0080	5.9	—OH
8	3269	406	140	0.0090	6.3	C=O

Note. The following designations are used: $\Delta\nu$ is the shift of the band, $\delta\nu$ is the line width, ΔR is the shortening of the distance between the acceptor and the O atom, and E is the bond energy.

* Fixed bands of CN.

In addition, CN is a semirigid chain polymer with a considerable length of the kinetic segment within which the formation of HB is impossible, and HB between different segments do not differ from intermolecular HB. It is most likely that the configuration of HB in the systems studied is close to the energetically most favorable configuration, since in the opposite case, positions of bands assigned to different HB would change strongly with the composition of the system. In fact, these effects are insignificant, despite the fact that weak changes in the stability of the one-type HB occur when the composition of solutions is varied, which is indicated by the scatter of points on the correlation dependence of broadening on the shift of the band.

An increase in the concentration of solvents up to the average region of compositions in all systems results in the redistribution of intensities of spectral bands in favor of stable HB. This is related, most likely, to the fact that an increase in the mobility of fragments of macromolecules facilitates the formation of more favorable configurations. Both the stability of HB increases with each type of acceptors and the fraction of HB with the strongest acceptors. For example, at a high content of DBP in solutions (~90 wt.%), one intense band at 3418 cm⁻¹ predominates in the spectrum. This is most likely a shifted band of pure CN ($\nu = 3445$ cm⁻¹), which is shifted (at the DBP content of 50 wt.% and 29 wt.%) to 3423 cm⁻¹ and 3436 cm⁻¹, respectively.

Along with the changes indicated, the shift of the band of the carbonyl group from 1710 cm⁻¹ to 1721 cm⁻¹ was observed for low concentrations of DBP (~3 wt.%) only. For solutions containing more than 10 wt.% of the low-molecular component, no similar spectral changes indicating that DBP participates in the formation of HB were observed. The intensity of the band in the IR spectrum corresponding to free hydroxyl groups decreases as the concentration of the solvent increases. This is most likely related to the involvement of them in the HB system due to an increase in the mobility of fragments of macromolecules in the solution.

A more complex character of the interaction of the components (Fig. 1, c) is observed in the systems containing DEDPC. In this case, several new bands were observed in the region of stretching vibrations of OH groups along with the shifted bands of CN. A correlation dependence, which virtually coincides with that presented in Fig. 2, between the parameters of these bands and bands of stretching vibrations of OH groups bound to DEDPC is also observed.

The HB parameters estimated from the correlation presented previously¹⁴ and acceptors assumed on the basis of their energies of formation are presented in Table 2. The data on shortening of the distance between the acceptor and oxygen atom, which were calculated from the known²⁰ correlation, are also given.

The results obtained, in particular, the presence of new bands in the region of stretching vibrations of O—H, suggest the formation of a complex in the CN—DEDPC system, which is also confirmed by the appearance of a new band at 1462 cm⁻¹ (Fig. 3). Note that the intensity of the absorption bands of CN in the region of 1430–1480 cm⁻¹ is noticeably lower than those for pure DEDPC and its solution with CN, and even under the assumption of a noticeable contribution of the bands of CN to the spectrum of the solution, the latter cannot be described by the superposition of spectra of the components.

Thus, of all the systems studied, only CN—DEDPC solutions exhibit the formation of a molecular complex along with the enhancement of HB of CN. In other cases, solutions are formed in which acceptors of CN become, most likely, sterically accessible predominantly

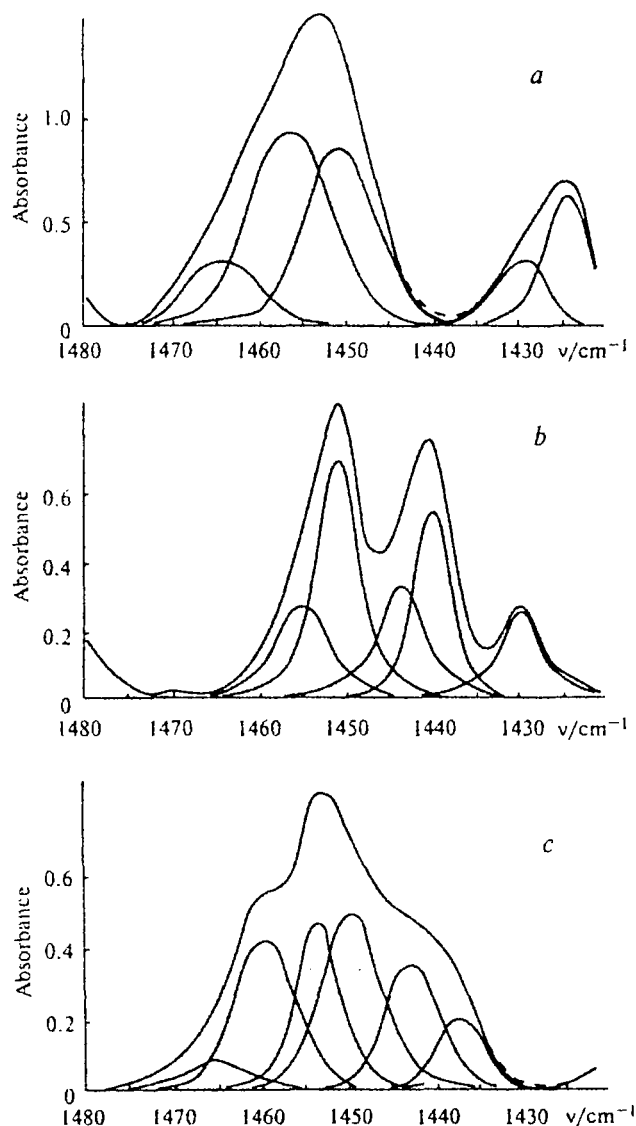


Fig. 3. Experimental IR spectra and their individual contours in the region of 1480–1420 cm^{-1} for CN (a), DEDPC (b), and a 29% solution of DEDPC in CN (c).

for the redistribution of HB, and only an insignificant portion of them forms HB with solvents.

It can be assumed that the difficult formation of the structural complex of DBP with CN (observed previously⁷ on the basis of the reflection of the starting polymer in the region of existence of the complex) is

related to the facts revealed above. As a whole, the instability observed from the effect of structural formation is most likely due to the plurality of hierarchic levels of the structural arrangement of CN solutions, the manner of their formation, and the dependence on ordering the of the starting polymer.

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