AN INVESTIGATION OF THE FORMATION OF MOLECULAR COMPLEXES OF O-(3,5-DINITROBENZOYL)-O-ACETYLCELLULOSE WITH *n*- AND π-DONORS

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Soluble O-(3,5-dinitrobenzoyl)-O-acetylcellulose was synthesized, and the formation of molecular complexes with *n*- and π-donors was investigated. The formation of complexes obeys the Langmuir adsorption isotherm adjusted for macromolecules. The formation of molecular complexes with low-molar mass compounds of the type of heterocyclic compounds, aromatic amines and condensed hydrocarbons was confirmed by electric resistance measurements. The largest decrease in the specific resistance by 2—3 orders of magnitude was observed with indole and phenothiazine, while the specific resistance of the other types of donors decreased by 1—2 orders of magnitude. A decrease in the activation energy took place with all types of complexes.

In our preceding paper[1] we described the synthesis and electric properties of acetal prepared from 4-nitrobenzaldehyde and 2-hydroxyethylcellulose and of an amino derivative obtained by reduction of the respective acetal. Electric resistance measurements of the synthesized derivatives showed that their temperature dependence obeys a relation which is valid for semiconductors. The specific resistance values of the synthesized derivatives depend on the character of the chromophore present; high resistance values were obtained only in those cases where the derivative contained only the nitroaryl group. The partial reduction of the nitro group to an amino derivative caused a decrease in the electric resistance, which with respect to the chemical structure of the polymer was attributed to the formation of intra- or intermolecular charge-transfer complexes[2].

The formation of *n*- and π-charge-transfer complexes on cellulose derivatives has been discussed in refs[3,4]. While trinitrobenzyl and trinitrophenyl ethers of cellulose[3] form only *n*-complexes with aromatic amino compounds, Snyder and Welch[4] synthesized insoluble 3,5-dinitrobenzoylcellulose of natural cotton, which in addition to *n*-complexes gives also rise to π-complexes with various low-molar mass donors.

In this paper we report results of an investigation of the formation of charge--transfer complexes and of the specific electric resistance of newly synthesized

O-(3,5-dinitrobenzoyl)-O-acetylcellulose. The synthesis was carried out by employing a modified method according to ref.[4]. By this procedure, a nitro derivative of acetylcellulose soluble in the usual organic solvents was prepared.

EXPERIMENTAL

O-Acetylcellulose with the degree of substitution (D_A) 1·1 (Lachema) and with the average viscosity degree of polymerization (P_η) 194 was used in the synthesis (ref.[5]).

Electron absorption spectra were recorded with a Specord UV-VIS (Zeiss, Jena) spectrophotometer in 1,4-dioxan in 1 cm quartz cells. Infrared spectra were recorded with an IR-71 (Zeiss, Jena) spectrophotometer on films cast from a tetrahydrofuran solution on NaCl plates.

Acetylcellulose (5 g) was dissolved in 50 cm^3 of N,N-dimethylformamide. To the solution thus obtained, 30 cm^3 of pyridine and 10 g (0·043 mol) of 3,5-dinitrobenzoylchloride was added with stirring. After the whole amount of chloride had been added, the reaction mixture was heated to mild reflux. Under such conditions, condensation lasted 7 h. After that, the reaction mixture was left to cool to room temperature, and O-(3,5-dinitrobenzoyl)-O-acetylcellulose thus formed was precipitated into a water–ethanol mixture at the ratio 3 : 1. The cream-coloured polymer was dissolved in N,N-dimethylformamide and reprecipitated three times into methanol, filtered off and dried in vacuo to constant mass. The yield was 4·3 g of the product with the degree of substitution D_{NB} 0·59, $v_{as}(NO_2)$ at 1 535 and $v_s(NO_2)$ at 1 340 cm^{-1}, readily soluble in N,N-dimethylformamide, 1,4-dioxan, ethyl methyl ketone, and tetrahydrofuran.

The complexes were prepared by using a method described in ref.[4]. Perfectly homogenized O-(3,5-dinitrobenzoyl)-O-acetylcellulose (800 mg) was added to 20 cm^3 of the organic solvent containing a calculated quantity of the donor dissolved in it and undissolved cellulose. Carbon tetrachloride was used in the investigation. After the establishment of equilibrium (24 h) the polymer complex was removed by filtration and washed with 1 cm^3 of pure solvent, in order to remove the free donor on the surface of the polymer sample. The amount of the donor bound to O-(3,5-dinitrobenzoyl)-O-acetylcellulose was determined gravimetrically, up to a constant mass of the dried polymer complex. The mass was determined with an analytical balance WA 35, PRL-TA 14 (Poland). The error of determination did not exceed $\pm 0·5\%$. The results were treated by the least squares method ($r^2 = 0·92 \sim 0·97$).

The d.c. resistance of the samples was measured in the temperature range between 22 and 120°C (at $10 \sim 12$ various temperatures). Pressed powder samples were used. The sandwich electrodes were made from vacuum deposited gold. All measurements took place in argon atmosphere. Preparation of the samples and the apparatuses used have been described in detail in ref.[1]. The results were treated by the last squares method ($r^2 = 0·95 \sim 0·99$).

RESULTS AND DISCUSSION

The synthesis of soluble aromatic acetylcellulose nitroester is based on a condensation reaction between 3,5-dinitrobenzoyl chloride and acetylcellulose with a reduced degree of substitution of acetyl groups. According to our results, acetylcellulose with the degree of substitution used is satisfactory for this purpose. We had intended to prepare nitroester with a high degree of substitution of nitroaromatic chromophores. Table I shows that a change in the conditions of condensation had no considerable effect on the degree of substitution of nitroaromatic groups on the polymer chain,

neither due to an increased chloride content nor due to extension of the reaction time. This is obviously casued by the fact that the more reactive positions on the gluco-pyranoside units 2 and 3 are already partly occupied by acetyl groups, which sterically hinders the approach of larger charge-transfer chloride molecules.

The formation of charge-transfer complexes was studied using a method reported in ref.[4]. According to this method, the amount of the bound donor may be described by using the modified Langmuir equation[6], which has also been widely used in the investigation of binding of low-molar mass compounds to macromolecules[7]:

$$\frac{1}{f} = \frac{1}{nKc}\frac{1}{n}, \tag{1}$$

where f means the fraction of the total number of moles of the 3,5-dinitrobenzoyl acceptor on cellulose, attacked by the given donor, n is a constant characterizing the accessible positions on the cellulose acceptor with respect to the total number of positions present in 1 mole of the nitropolymer acceptor, c is the concentrtion of the donor in mol dm^{-3} dissolved in the solvent used, and K is the equilibrium constant (mol^{-1}).

The linear dependence of complex formation was checked for indole, anthracene, pyrene, and N,N-dimethylaniline. O-(3,5-dinitrobenzoyl)-O-acetylcellulose with D_{NB} 0·78 was used in the investigation. The results obtained are summarized in Table II and Fig. 1. Fig. 1 shows that the presence of acetyl groups along with 3,5-dinitrobenzoyl chromophores on the cellulose chain does not affect the shape of the absorption isotherm of the formation of complexes of compounds under study. A parallel experiment in which pure acetylcellulose was used did not confirm an increase in mass due to the complex formation with the same donors. The dependence also allow us to infer that the value of the equilibrium constant depends on the

TABLE I

Effect of conditions of the reaction between acetylcellulose (D_A 1·1; 5 g) and 3,5-dinitrobenzoyl-chloride (pyridine, reflux) on the degree of nitrobenzoylation (D_{NB})

Chloride mmol	Reaction time h	Product	
		% N	D_{NB}
43	7	4·10	0·59
43	10·5	4·18	0·61
64	10·5	5·39	0·78

type and size of the donor. The determined different n values may be explained by the fact that the nitrobenzoyl acceptor is probably bound in various positions of the glucopyranoside unit. Since the acceptor may be chemically bound in positions 1, 2, 3, 4, or 6, the number of accessible sites also varies, similarly to the number of independently equal acceptor particles in the macromolecule needed for the formation of a complex with the donor.

TABLE II

Formation of complexes of O-(3,5-dinitrobenzoyl)-O-acetylcellulose with selected donors (symbols defined in the text at Eq. (*1*), Δm means increase in mass)

c mmol dm^{-3}	Δm %	$f \cdot 10^2$	Colour of complex	n	K mol^{-1}
Donor : indole					
8	4·2	18·2			
10	6·8	19·9			
20	8·6	25·0	yellow	0·38	149·5
30	9·2	26·8			
40	10·5	28·8			
Donor : N,N-dimethylaniline					
10	3·1	8·7			
12	4·1	11·6			
20	5·2	14·7	brown-red	0·20	119·5
30	5·9	16·5			
40	6·4	17·9			
Donor : anthracene					
8	1·9	3·8			
10	2·3	4·2			
20	3·6	6·9	light yellow	0·18	34·2
30	4·5	8·6			
40	5·8	11·0			
Donor : pyrene					
8	2·0	3·2			
10	2·3	4·0			
20	3·6	6·4	light yellow	0·24	19·8
30	4·5	9·3			
40	5·8	10·9			

Figs 2 and 3 show the electron absorption spectra of charge-transfer complexes of O-(3,5-dinitrobenzoyl)-O-acetylcellulose for indole and N,N-dimethylaniline. Addition of the donors just mentioned displaces the right shoulder of the absorption spec-

FIG. 1

Dependence of $1/f$ for complexes of the donor with O-(3,5-dinitrobenzoyl)-O-acetylcellulose on the reciprocal concentration of the donor: *1* indole, *2* N,N-dimethylaniline, *3* pyrene, *4* anthracene
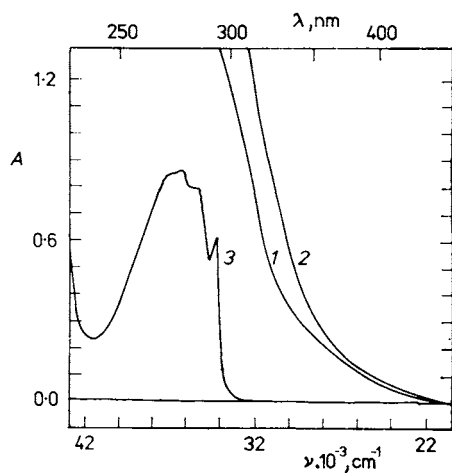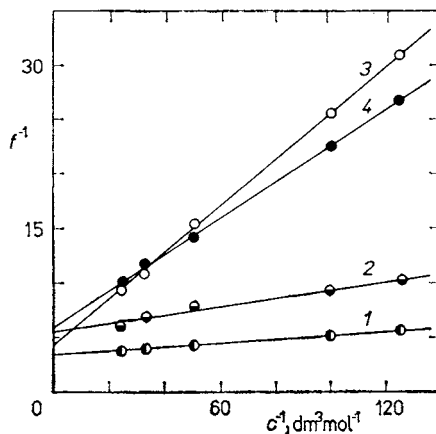
FIG. 2

Electron absorption spectra (solutions in 1,4-dioxan): *1* O-(3,5-dinitrobenzoyl)-O-acetylcellulose (0·1%), *2* 0·1% solution of O--(3,5-dinitrobenzoyl)-O-acetylcellulose with $7 . 10^{-2}$ cm^3 of a $3 . 10^{-3}$ mol dm^{-3} indole solution added, *3* indole $2·37 . 10^{-2}$ mol . . dm^{-3}
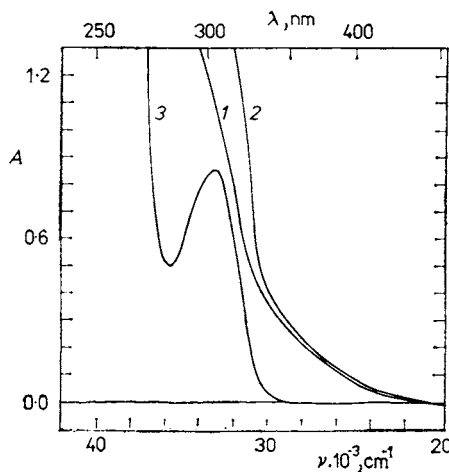
FIG. 3

Electron absorption spectra (solutions in 1,4-dioxan): *1* O-(3,5-dinitrobenzoyl)-O-acetylcellulose (0·1%), *2* 0·1% solution of O--(3,5-dinitrobenzoyl)-O-acetylcellulose with $0·045$ cm^3 of a $3 . 10^{-3}$ mol dm^{-3} N,N--dimethylaniline solution added, *3* N,N-dimethylaniline, $4·5 . 10^{-5}$ mol dm^{-3}

trum in the bathochromic direction, which is also reflected in a change of colour of the polymer complex (Table II).

The results of measurements of the temperature dependence of electric resistance (Table III) indicate that the temperature dependence of electric resistance satisfies a relation valid for semiconductors[8],

$$\varrho = \varrho_0 \exp\left(\Delta E/kT\right), \tag{2}$$

in which ΔE is the activation energy of free charge carriers needed for reaching the conductivity band in the case of extrinsic semiconductors, or half the width of the forbidden band in the case of intrinsic semiconductors, ϱ_0 is the material constant, k is the Boltzmann constant and T is the absolute temperature.

By comparing the ϱ and ΔE values of O-(3,5-dinitrobenzoyl)-O-acetylcellulose one can see that the changes are not important. Much larger changes are observed when complexes with condensed aromatic hydrocarbons having the character of π-donors are formed. In this case the electric resistance decreases by $2-3$ orders of magnitude with respect to the individual components alone. The ΔE values also

TABLE III

Specific resistance (25°C) and activation energy values of complexes of O-(3,5-dinitrobenzoyl)-O-acetylcellulose (DNBC). f is defined in the text (starting donor concentration 70 mmol dm^{-3}, cf. Table II)

Compound (donor)	ϱ_{25} Ωm	ΔE eV	Complexes with DNBC		
			f	ϱ_{25}, Ωm	ΔE, eV
AC[a]	$3\cdot27 \cdot 10^{17}$	0·97	—	—	—
DNBC	$1\cdot98 \cdot 10^{17}$	1·10	—	—	—
Indole	—	—	63·1	$2\cdot83 \cdot 10^{14}$	0·83
Phenothiazine[b]	$4 \cdot 10^9$	0·80	98·0	$1\cdot29 \cdot 10^{15}$	0·44
Fluorene	—	—	72·4	$4\cdot76 \cdot 10^{15}$	0·71
Chrysene[b]	$4 \cdot 10^{17}$	$1\cdot02 - 1\cdot10$	21·6	$1\cdot05 \cdot 10^{16}$	0·83
Pyrene[b]	$5 \cdot 10^{15} - 10^{18}$	$1\cdot02 - 1\cdot10$	57·3	$4\cdot93 \cdot 10^{15}$	0·64
Anthracene[b]	$7 \cdot 10^{13} - 10^{20}$	$0\cdot75 - 1\cdot35$	30·7	$2\cdot11 \cdot 10^{15}$	0·82
B[c]	—	—	30·3	$9\cdot50 \cdot 10^{16}$	0·97
D[d]	—	—	96·3	$7\cdot12 \cdot 10^{16}$	0·92
T[e]	—	—	62·0	$3\cdot60 \cdot 10^{17}$	1·04

[a] O-Acetylcellulose (D_A 1·1). [b] Data for ϱ_{25} and ΔE of donors taken from ref.[8]. [c-e] 4,4′-Bis-(dimethylamino) derivatives of [c] benzophenone (B), [d] diphenylmethane (D), and [e] triphenyl-methane (T).

decrease. The decrease in both ϱ and ΔE values is obviously connected with the formation of charge-transfer complexes[2]. In the case of heterocyclic compounds — indole and phenothiazine — the measured specific resistance values are lower by 2−3 orders of magnitude, compared with pure O-(3,5 dinitrobenzoyl)-O-acetylcellulose. The ΔE values are also lower. Formation of complexes with compounds of the type of substituted anilines brought about a decrease in electric resistance by approximately one order of magnitude, compared with pure O-(3,5-dinitrobenzoyl)--O-acetylcellulose. There was also a small decrease in the ΔE values.

A comparison of changes in the recorded specific resistance and changes in the UV spectrum allows us to infer that binding of the donors under investigation to O-(3,5--dinitrobenzoyl)-O-acetylcellulose proceeds via formation of weak complexes. O-(3,5-dinitrobenzoyl)-O-acetylcellulose forms complexes with both π- and n-donors. According to the specific resistance values measured, the strongest complexes are formed by indole and phenothiazine, weaker complexes are formed by condensed aromatic hydrocarbons, while the weakest are those obtained with substituted anilines as model compounds of various leuco-compounds. This fact is obviously connected with steric hindrances of relatively large molecules of the last group of compounds arising in the process of complex formation. In this case the higher values of a quantity defined as the fraction of the total number of moles of the 3,5-dinitrobenzoyl acceptor on the cellulose chain attacked by the donor probably do not characterize only the complex actually formed: the sample contains also molecules bound in some other way.

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