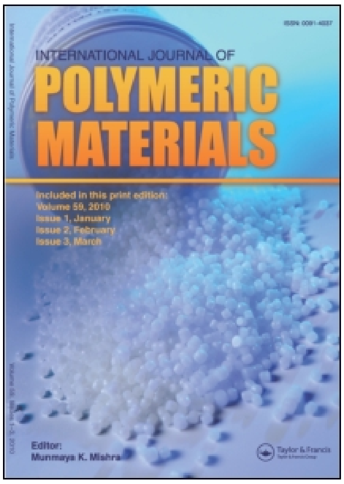

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Influence of Solvent on the Structure of Cellulose and its Derivatives in Solution

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The influence of solvents on the structure of cellulose and its derivatives in solution are reviewed.

KEY WORDS Cellulose, derivatives, structure solutions.

The theory for flexible polymer molecules in dilute solutions is based on extensive experimental data, whilst data on the conformational and hydrodynamic parameters in solutions of cellulose are often ambiguous.[1,2]

The rigidity of a cellulose chain can vary noticeably due to solvation in non-aqueous solvents and formation of complex polymer-solvent.[3] Both an increase and decrease in the chain rigidity can occur depending on the complex formed.

1. MODELS OF THE CONFORMATIONAL CHARACTERISTICS OF CELLULOSE AND ITS DERIVATIVES[4,5]

Analysis of the structure presupposes an interrelation between the distance between the ends of the polymer chain h, radius R and molecular characteristics: molecular mass M and contour length L. Freely-jointed, rotary-isomeric and persistent mechanisms are the most widely used models in polymer physics.[5]

In the freely-jointed chain model developed by Kuhn[6] and Mark,[7] a real chain is substituted by an "equivalent" one that consists of T straight-linear segments of length A; whose spatial orientations are mutually independent. The condition of "equivalence" presupposes selection of N and A values ($L = NA$) at which the linear dimensions of the freely-jointed chain corresponds to those of a real chain molecule. The length of the segments into which the chain is divided serves as a measure of the equilibrium rigidity of the chain and is called the Kuhn segment.

Due to thermal motion, macromolecules in solutions are able to assume an infinitely large number of "momentary" conformations.[8] The average-square distance between the chain ends $\langle h^2 \rangle$ and the average-square inertion radius $\langle R^2 \rangle$ are characteristics of the statistical sizes of a molecule. Linear statistical sizes of freely-joint chain have the following correlations:

$$\langle h^2 \rangle = LA, \qquad \langle R^2 \rangle = (LA)/6. \tag{1}$$

Eyring[9] considered the simplest model: a chain consisting of an arbitrary number of links $-n$ with length $-l$, the latters being joint and rotating with respect to each other under valent angle $\pi - \theta$. For a long enough chain ($n \rightarrow \infty$):

$$\langle h^2 \rangle = nl^2(1 + \cos\theta)/(1 - \cos\theta), \tag{2}$$

$$\langle R^2 \rangle = \{(nl^2)/6\}(1 + \cos\theta)/(1 - \cos\theta), \tag{3}$$

From Equations (2) and (3) the chain with free rotation at fixed valent angle becomes a Gaussian chain,[10] since its linear dimensions grow proportionally to the contour length (nl).

Polypeptides,[11] cellulose derivatives,[12] DNA[13] contain only a small number of Kuhn segments in the chains.

Realization of flexibility takes deformability into account in the persistent chain model.[14] This model takes into account the short-range action of elements that constitute the chain. Transition to a continuous worm-like chain ($l \rightarrow \infty$), the curvature is constant along its entire length and determined by the persistence length q. The size of the worm-like chain is determined by Porod's equation[15]:

$$\langle h^2 \rangle = 2q^2(L/q - 1 + e^{-L/q}). \tag{4}$$

In the limit, its linear dimensions approximate to the Gaussian distribution, the persistent length being equal to half-length of the Kuhn segment of the "equivalent" Gaussian chain: $A = 2q$. In the limit the short worm-like chain, its form approaches the stick-like one: $h^2 = L^2$.

Bogdanetskii[16] carried out analysis of the temperature coefficient of the characteristic viscosity $dln[\eta]/dT$ for rigid-chain polymers using the worm-like cylinder model of Yamakava-Fujii[17] reflected by the $dln(\langle R^2 \rangle dM)_\infty/dT$ parameter. Data for this parameter for ethylcellulose, nitrate, tributyrate and tricarbanilate of cellulose have been measured.[17]

2. HYDRODYNAMIC AND CONFORMATIONAL CHARACTERISTICS OF CELLULOSE AND ITS DERIVATIVES

The translatory and rotary friction exhibited on diffusion, sedimentation and viscosimetry of polymer solutions, are the main methods for the structure of polymeric molecules. The quantitative interpretation of experimental data on a molecular level is possible on the base of the interrelation between the conformational characteristics of the molecules and their hydrodynamic properties in solutions. The translatory and rotary motion is described using hydromechanics laws. Most investigators[18-21] believe that a worm-like cylinder reflects the hydrodynamic behaviour of a rigid-chain polymer in solution. A cylinder is bent so that its axial line can be described by an equation of a worm-like chain. Description of the intrinsic viscosity $[\eta]$ of a solution of rigid-chain molecules based on the model of a worm-like cylinder developed by Yamakava. Initial calculations[17] of $[\eta]$ were carried out taking into account the semi-spheric form of the worm-like cylinder, Yamakava obtained the expression below for $L/A > 2.278$

$$M/[\eta] = \Phi_{\infty}^{-1}(M_L/A)^{3/2}M^{1/2}\varphi(L, d, A) \qquad (5)$$

where $M_L = M/L$, $\Phi = 2.87 \cdot 10^{23}$ mol^{-1}, and

$$\varphi = 1 - [C_1(A/L)^{1/2} + C_2(A/L) + C_3(A/L)^{3/2} + C_4(A/L)^2] \qquad (6)$$

Coefficients C_1, C_2, C_3 and C_4 depend on d/A and are represented by a polynomial series.[21] Introduction of a complex functional dependence of φ on L, d and A is caused by the necessity of taking into account the influence of the effects of "excess" volume and "leakage" of the macromolecules on their hydrodynamic properties.

The "leakage" of a chain means the equality of the resistance that is experienced by it when moving within solvent to the sum of the resistances that could be experienced by all its elements, if each of them moved in the absence of the rest. In this sense, a completely stretched chain possesses the highest leakage. When the chain molecule folds up into a ball, there screening of the segments that are inside the ball is equivalent to a decrease in the hydrodynamic interaction. For cellulose and its derivatives with molecular masses $\sim 10^5 - 10^6$ g·mol^{-1} the effect of leakage has a substantial influence on the viscosimetric behaviour.

The effects of excluded volume takes into account the limitation of the number of the chain elements occurring due to mutual non-overlap; resulting in increasing linear dimensions of the macromolecular coil:

$$\langle h^2 \rangle = \alpha \langle h^2 \rangle_{\theta}^{1/2} \qquad (7)$$

where α is the degree of swelling of a coil; and $\langle h^2 \rangle_{\theta}^{1/2}$ its linear dimensions in absence of the volumetric effect. The influence of the excluded volume effect on the hydrodynamics of molecules increases with increase in their length and decrease in the equilibrium rigidity: while the macrochain rolls up into a coil, the number of the intramolecular contacts increases—the volumetric effects are growing.

Selection of the θ-conditions under which the volumetric effects are compensated for by mutual attraction between the chain elements, for a number of polymers is rather difficult.[23] Estimation of the equilibrium rigidity of a chain not perturbed by volumetric effects, becomes simpler when investigating the hydrodynamic properties of low-molecular fractions of polymers. Mark-Kuhn equation for a non-perturbed chain

$$|\eta|_0 = K_{\theta}M^{1/2} \qquad (8)$$

predicts the linear increase in intrinsic viscosity with $M^{1/2}$

$$[\eta]_{\theta}/M^{1/2} = K_{\theta} = \Phi_{\infty}(LA/M)^{3/2}. \qquad (9)$$

Solvent non-ideality results in a rapid increase in the macromolecular dimensions with increase in molecular mass. Stockmayer and Fixman[24] takes into account the dimensions of the perturbed chain:

$$[\eta]/M^{1/2} = \Phi_\infty(LA/M)^{3/2} + 0.51\Phi_\infty BM^{1/2}. \tag{10}$$

Extrapolation of the dependence of experimental values of $[\eta]/M^{1/2}$ on $M^{1/2}$ at condition $M = 0$ allows using Equation (10) determination of $(A/M_L^{3/2})$.

Acceptability of the Stockmayer-Fixman method for the estimation of the non-perturbed length of the Kuhn segment is confirmed in Reference 10: $[\eta]/M^{1/2}$ at $M = 0$ for polyvinylcinnamate in solution corresponds precisely to $[\eta]/M_\theta^{1/2}$ obtained by direct measurement in a θ-solvent.

With increasing rigidity of the chain, the influence of volumetric effects on the macromolecular dimensions becomes weaker: smaller number of the intramolecular contacts corresponds to lower degree of coiling.[10] Tsvetkov gives data on the negative temperature coefficients of the intrinsic viscosity of solutions of cellulose derivatives.

Application of formula (5) to estimate the non-perturbed dimensions of rigid-chain polymeric molecules is rather difficult: dependence of $M/[\eta]$ on $(L/A)^{1/2}$ is not monotonous. With increasing L/A, expression (5) degenerates into an asymptotic function described by[25]

$$M/[\eta] = \Phi_\infty(M_L/A)^{3/2}M^{1/2} + 2.2\Phi_\infty^{-1}(M_L^2/A)[l_n(A/d) - 0.755], \tag{11}$$

which is correct for long worm-like spherocylinders ($L/A > 20$).

Representation of experimental data in the form $M/[\eta] = f(M^{1/2})$ allows definition of the length of Kuhn segment if M_L is known:

$$\partial(M/[\eta])/\partial M^{1/2} = (M_L/A)^{3/2}\Phi_\infty^{-1}. \tag{12}$$

Values of the hydrodynamic diameter d are determined from the point at which the straight line cut the ordinate axis, using A that is calculated formula (12).

High equilibrium rigidity of macromolecules limits the applicability of the extrapolation formula (11) to the region of highly-molecular fractions of polymers. With increasing skeleton rigidity of a chain, the deviation from the properties of Gaussian coil becomes noticeable at larger molecular masses, and the deviation from linear dependence (11) is marked at higher $M^{1/2}$. Figure 1 shows the dependence $M/[\eta] = f(M^{1/2})$ for fractions of cellulose nitrate. Cellulose nitrate with lower values of the degree of substitution possesses a lower equilibrium rigidity (Table II). Noticeable deviations from linearity begin at $M^{1/2} > 400$. For samples with higher equilibrium rigidity, cellulose nitrate with $\gamma = 2.4$, it is impossible linear dependence is observed (11) over the entire M region. Such an expression was obtained in Reference 26.

$$(M^2/[\eta])^{1/3} = \Phi_\infty^{-1/3}(M_L/A)^{1/2}M^{1/2} + (k/4.65A_0)(M_L/3\pi)(l_n[A/d] - 1.065), \tag{13}$$

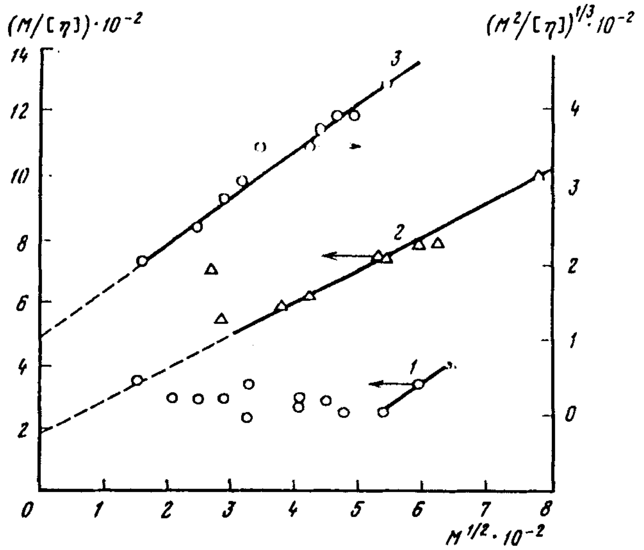

FIGURE 1 Dependences of $M/[\eta]$ (1, 2) and $M^2/[\eta]^{1/3}$ (3) on $M^{1/2}$ for the solutions of cellulose nitrate fractions[10]: 1, 3—the sample with degree of substitution 2.4 in ethylacetate (No. 15 from Table II); 2—the sample with degree of substitution 1.4 in system DMAA-6% LiCl (No. 22 from Table II).

TABLE I

Magnitudes of molecular masses and intrinsic viscosities of the cellulose samples with various degrees of polymerization (DP)

DP of cellulose	$M \cdot 10^{-3}$	$[\eta], \frac{\text{dl}}{\text{g}}$	$A \cdot 10^4, \frac{\text{cm}^3}{\text{g} \cdot \text{mol}}$
150	21.0	1.86	36
150	24.3*		
600	91.0	7.84	31
600	97.2*		
755	122.0*		
750	140.0	8.81	27
810	147.0*		
810	165.0	9.81	24

M* are the labelled magnitudes of the molecular mass of the cellulose samples.

where A_0 is the hydrodynamic invariant for a given polymer-solvent system; k is the Boltzmann constant.

Expression (13) allows interrelation of $[\eta]$ and M in the form $M^2/[\eta]^{1/3} = f(M^{1/2})$ (Figure 2). The equilibrium rigidity can be determined from the slope (13):

$$\partial(M^2/[\eta])^{1/3}/\partial M^{1/2} = (M_L/A)^{1/2} \cdot \Phi_\infty^{-1/3} \tag{14}$$

at M_L and $\Phi_\infty = 2.87 \cdot 10^{23}$ mol^{-1}. The intersection of the straight line (13) on the ordinate axis, allows calculation of the chain diameter d.

Calculation of the monomeric link projection on the chain direction $\lambda = M_0/M_L$, obtained when analysing its chemical structure. Experimental determination

TABLE II

Length of the statistical Kuhn segment and chain diameter (*d*) of cellular and its derivatives

No.	Polymer: cellulose and its derivatives	Molecular characteristic of polymer	Solvent	Determination conditions	*A*, Å	*d*, Å	Reference
1	2	3	4	5	6	7	8
1	cellulose	$\gamma = 0$	cadoxen		76	8.0	[40]
2	cellulose	$\gamma = 0$	cadoxen		142		[41]
3	cellulose	$\gamma = 0$	cadoxen		100	16	[42]
4	cellulose	$\gamma = 0$	cadoxen		91	7	[44]
5	cellulose	$\gamma = 0$	DMAA + LiCl	$C_{LiCl} = 5\%$	200		[27]
6	cellulose	$\gamma = 0$	FeTNa		120	28	[42]
7	cellulose	$\gamma = 0$	FeTNa		144		[43]
8	cellulose	$\gamma = 0$	cadoxen		50–150		[45]
9	cellulose	$\gamma = 0$	FeTNa		120–250		[45]
10	cellulose	$\gamma = 0$	DMAA + LiCl		165–250		[45]
11	cellulose	$\gamma = 0$	$CF_3COOH—C_2H_4Cl_2$		170		[1]
12	cellulose	$\gamma = 0$	N-methylmorpholene-N-oxide		70–100		[45]
13	nitrate	$\gamma = 2.0$	ethyl acetate		102	9.5	[46]
14	nitrate	$\gamma = 2.3$	ethyl acetate		160	8	[47]
15	nitrate	$\gamma = 2.4$	ethyl acetate		236	11	[48]
16	nitrate	$\gamma = 2.58$	ethyl acetate	25°C	250	17	[49]
17	nitrate	$\gamma = 2.7$	ethyl acetate		254	18.6	[49]
18	nitrate	$\gamma = 2.7$	ethyl acetate		200		[51]
19	nitrate	$\gamma = 3$	ethyl acetate		236		[43]
20	nitrate	$\gamma = 2.7$	butyl acetate		260		[51]
21	nitrate	$\gamma = 1.9$	methylethylketone		113	10.5	[52]
22	nitrate	$\gamma = 1.14$	DMAA + LiCl	$C_{LiCl} = 6\%$	106	8.5	[48]
23	nitrate	$\gamma = 2.55$	acetone		200	21	[42]
24	nitrate	$\gamma = 2.55$	acetone		176		[53]
25	nitrate	$\gamma = 2.9$	acetone		332		[53]
26	nitrate	$\gamma = 2.91$	acetone		260	26	[42]
27	nitrate	$\gamma = 3$	acetone		264		[41]
28	ethyl	$\gamma = 2.27$	ethyl acetate		175	12	[54]
29	ethyl	$\gamma = 2.6$	bromoform		204		[51]

TABLE II (*Continued*)

1	2	3	4	5	6	7	8
30	ethyl	$\gamma = 2.6$	DMFA		280		[51]
31	ethyl	$\gamma = 2.75$	acetone		168	9.5	[55]
32	cyanoethyl	$\gamma = 2.6$	acetone		250	8.3	[56]
33	hydroxyethyl		water		182		[57]
34	hydroxyethyl		water		100	29	[42]
35	ethylhydroxyethyl		water		100	29	[42]
36	ethylhydroxyethyl		water		180		[57]
37	hydroxypropyl		DMAA	25°C	130		[38]
38	hydroxypropyl		DMAA	70°C	90		[38]
39	acetoxypropyl		dimethyl phthalate	25°C	150	4	[28]
40	acetoxypropyl		dimethyl phthalate	105°C	88	10	[28]
41	acetoxypropyl		dimethyl phthalate	150°C	58	16	[28]
42	carbanilate	$\gamma = 2.3$	ethyl acetate		154	13	[58]
43	carbanilate	$\gamma = 3$	cyclohexanone	73°C		77	[59]
44	carbanilate	$\gamma = 3$	cyclohexanone		160		[60]
45	carbanilate	$\gamma = 3$	dioxane		245		[60]
46	carbanilate	$\gamma = 3$	dioxane + methanol		245		[61]
47	carbanilate	$\gamma = 3$	DMSO		338		[62]
48	carbanilate	$\gamma = 3$	anisole	94°C	65		[59]
49	carbanilate	$\gamma = 3$	acetone		205		[60]
50	acetate		trifluoroethanol		111		[41]
51	acetate		acetone		119		[41]
52	acetate	$\gamma = 2.2$	DMFA		230		[63]
53	acetate	$\gamma = 2.87$	chloroform		170		[63]
54	acetate	$\gamma = 3$	acetic acid	25°C	150		[64]
55	acetate	$\gamma = 3$	acetic acid	60°C	90		[64]
56	acetate	$\gamma = 0.49$	DMAA		60	24	[42]
57	acetate	$\gamma = 2.46$	DMAA		100	36	[42]
58	acetate	$\gamma = 2.92$	DMAA		120	34	[42]
59	carboxymethyl	$\gamma = 0.9$	cadoxen	26°C	120	24	[65]
60	carboxymethyl	$\gamma = 0.9$	cadoxen + water	26°C	170	34	[65]
61	butyrate	$\gamma = 2.9$	methylethylketone		200	7.0	[66]
62	benzoate	$\gamma = 2.2$	dioxane		180	40	[67]
63	benzoate	$\gamma = 3$	chloroform		216		[51]

TABLE II (*Continued*)

1	2	3	4	5	6	7	8
64	monophenyl acetate	$\gamma = 2.2$	benzene		110	40	[67]
65	dimethyl phosphonocarbamate	$\gamma = 2.0$	water + NaCl	$C_{NaCl} = 0.2$ M	165	9.0	[69]
66	xanthate		water + DMSO	$C_{DMSO} = 90\%$	108		[41]
67	caproate		dioxane		95		[41]
68	methylol		DMSO		320		[69]
69	methyl		water		182		[57]
70	phenyl carbamate	$\gamma = 1.9$	DMFA		170		[51]
71	monophenyl acetate	$\gamma = 2.5$	ethyl acetate		180		[51]
72	NaCMC		water + NaCl	$J \to 8$ mol/l	100	30	[42]
73	NaCMC	DP 120	water + NaCl	$J = 0.1$ mol/l	254		[70]
74	NaCMC	DP 112	water + NaCl	$J = 0.1$ mol/l	249		[70]
75	NaCMC	DP 98	water + NaCl	$J = 0.1$ mol/l	224		[70]
76	NaCMC	DP 81	water + NaCl	$J = 0.1$ mol/l	208		[70]
77	NaCMC	DP 55	water + NaCl	$J = 0.1$ mol/l	165		[70]
78	NaCMC	DP 120	water + NaCl	$J = 0.34$ mol/l	190		[70]
79	NaCMC	DP 112	water + NaCl	$J = 0.34$ mol/l	177		[70]
80	NaCMC	DP 98	water + NaCl	$J = 0.34$ mol/l	148		[70]
81	NaCMC	DP 81	water + NaCl	$J = 0.34$ mol/l	132		[70]
82	NaCMC	DP 55	water + NaCl	$J = 0.34$ mol/l	124		[70]

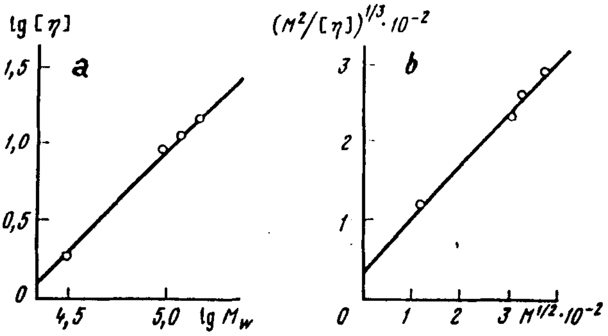

FIGURE 2 Dependences of lg[η] on lg M_w (a) and of $(M^2/[\eta])^{1/3}$ on $M^{1/2}$ (b) of the solutions of cellulose in mixture CF_3COOH—$C_2H_4Cl_2$ ($X_{C2H4Cl2}$ = 0.3 mol.fr.).

of λ is possible for polymers with very high rigidity. Nitrates for which λ is 5.1 ± 0.1 Å 10,21 meet this requirement better than other cellulose derivatives.[27–29]

Determination of the hydrodynamic and conformational parameters in non-aqueous solution of cellulose in mixtures of trifluoroacetic acid with chlorinated hydrocarbons.[1]

The interrelation between molecular mass and intrinsic viscosity[30] have experimentally determined the molecular-mass characteristics and intrinsic viscosities of non-aqueous solutions of cellulose in mixtures of trifluoroacetic acid (CF_3COOH) with chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2), 1,2-dichlorethane ($C_2H_4Cl_2$). Measurements for diluted solutions of cellulose with degrees of polymerization from 150 to 910 determined by sedimentation and viscosimetry. Sedimentation analysis of non-aqueous solutions of cellulose in mixtures of CF_3COOH, CH_2Cl_2, $CHCl_3$ and $C_2H_4Cl_2$. Cellulose concentrations were varied from 0.08 to 0.25 g/dl.[32] Viscosity was determined using a capillary viscosimeter at 298 ± 0.1 K for a series of solutions over the same concentration interval. The intrinsic viscosity was determined by extrapolation to zero of η_{spec}/C and ln η_{rel}/C dependences.

A selection of non-destructive solvents was used to determine the molecular-mass characteristics of cotton and wood cellulose. The optimum ratio of components in the mixtures of CF_3COOH with $CHCl_3$, $C_2H_4Cl_2$ were chosen taking into account the solubility of cellulose and self-association in non-aqueous solvents[33] and equal 0.3 mol. fraction of chlorinated hydrocarbons in mixtures with acid.

Sedimentation analysis of cellulose 0.1% mass. in CF_3COOH and its mixtures with CH_2Cl_2, $CHCl_3$ and $C_2H_4Cl_2$ are shown in Reference 30. The average molecular mass was calculated by extrapolation at infinite dilution of the effective molecular mass using the expression[34]:

$$(1/\bar{M})_{corr} = 1/\bar{M}_w + A_2C + \cdots \qquad (15)$$

The values of M_w were corrected for polydispersity taking the polydispersity coefficient into account according to equation:

$$\bar{M}_w^{corr} = \bar{M}_w(a + 1)\Gamma(a + 1)/K, \qquad (16)$$

where a is the exponent of the Mark-Kuhn-Houwink equation; Γ is the gamma-function; $K = 2 \div 7$.

The specific partial volume $\bar{V}$, is necessary to calculate the average molecular mass from the sedimentation data, and was determined picnometrically. The magnitudes of $\bar{V}$ and ρ at 298 K were 0.586 cm^3/g and 1.393 g/cm^3, respectively.

Table I carries the values of the molecular masses and intrinsic viscosities.

The viscosity of cellulose solutions in CF_3COOH decreases due to degradation.[35] Examination of the solutions of cellulose (degree of polymerization 600 and 810) in $CF_3COOH—C_2H_4Cl_2$ indicate that the viscosity properties of the solutions do not change over 2 months.

A persistent chain model was used to estimate the non-perturbed dimensions of cellulose in non-aqueous solution. Figure 2b can be described, by equation $(M^2/[\eta])^{1/3} = f(M^{1/2})$. The intersection, $A_\eta = 34$, and tangent $B_\eta = 0.65$ were used to calculate the value of the Kuhn segment (A), diameter of macromolecule (d) and other conformational parameters in agreement with equations[28]:

$$d_r/A_0 = 0.5B_\eta^4\bar{V}/A, \tag{17}$$

$$lg\ d_r = -0.173 + \lg(d_r^2/A_0), \tag{18}$$

$$A_0 = 0.46 - 0.53 \lg d_r, \tag{19}$$

$$M_L = A_\eta\Phi^{1/3}/A_0, \tag{20}$$

$$h^2/M = (N_\eta\Phi_0^{1/3})^{-2}; \qquad A = h^2M_L/M. \tag{21}$$

The conformational parameters are: $A = 170 \cdot 10^{-8}$ cm, $d = 5.5 \cdot 10^{-8}$ cm.

The magnitude of the Kuhn segment and second virial coefficients (Table I) indicate that cellulose is a semi-rigid-chain polymer.

Papkov[36] identified the concentration C^*, corresponding to a sharp increase in $\eta_{spec}/C = f(C)$, the concentration at which the ineration centres of the macromolecules become comparable with the dimensions of the macromolecules themselves. Estimation of C^* using the geometric dimensions of the macromolecules:

$$d \sim (2.5M/C^*)^{1/3}10, \tag{22}$$

where d is the diameter of a sphere (Å); C^* is the upper concentration boundary of the diluted solution (g/100 cm^3). For rigid-chain polymers, Papkov assumes $d \approx \langle h^2\rangle^{1/2}$ and determines the equilibrium rigidity $A = 2q$ using Porod's formula (4).

Iteratively calculated values of the intrinsic viscosities using the functional dependence of Yamakava (5), allows the connection of $[\eta]$ with the molecular characteristics of polymer (M_L, A, d, L).

Bianchi with co-authors,[27] have studied cellulose in N,N-dimethylacetamide-LiCl mixture, and assumed the projection length of glucopyranose chain to equal 5.14 Å. Variation of the hydrodynamic diameter between 4.5 to 6 Å, and the persistent length from 70 to 140 Å indicates the worm-like cylinder with $q = 110 \pm 10$ Å is the best model (Figure 3).

3. INFLUENCE OF THE MOLECULAR CHARACTERISTICS OF CELLULOSE AND ITS DERIVATIVES ON THE EQUILIBRIUM RIGIDITY IN SOLUTION

The values of the diameters and lengths of Kuhn segments of cellulose and its derivatives are compiled in Table II.[40–70]

The data obtained by different authors differ noticeably from each other, the magnitude of the equilibrium rigidity for cellulose in cadoxen lie within 76 to 142 Å limits.[40–44] A values for different cellulose derivatives are hardly comparable with each other due to the differences in the degree of substitution γ and nature of solvents.

Values of the Kuhn segment lengths are 100–300 Å, and are an order of magnitude higher than those for flexible polymers. The flexibility of cellulose and its derivatives is determined by the hindered rotation of the pyranose rings around the bridge bonds OC_1 and OC_4. Hydrogen bonds play an essential role in these interactions. IR-spectroscopy data,[71] indicates that cellulose molecules in the crystalline state from intramolecular hydrogen bonds $(O_3'O_5)$ and (O_2O_6'). The influence of $(O_3'O_5)$ H-bond on the conformation of cellulose acetates in solutions is the foundation of Shakhparonov's analysis.[40,44,72]

Figure 4 indicates the dependence of the equilibrium rigidity A on the degree of substitution γ in cellulose derivatives. Substitution of cellulose creates additional

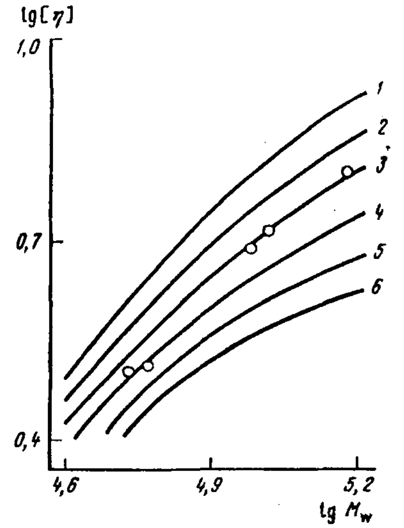

FIGURE 3 Comparison between experimental and calculated values of the intrinsic viscosity of cellulose in DMAA-LiCl mixture. The curves correspond to the theoretical dependence $[\eta]$ – M_w for the worm-like cylinders with d = 5.8 Å, M_L = 162/5.14 D/Å, and the magnitude of the persistent length 140 (1), 120 (2), 110 (3), 100 (4), 90 (5) and 80 Å (6). Circles denote experimental $[\eta]$ of monodisperse samples of cellulose in DMAA-5% LiCl mixture.

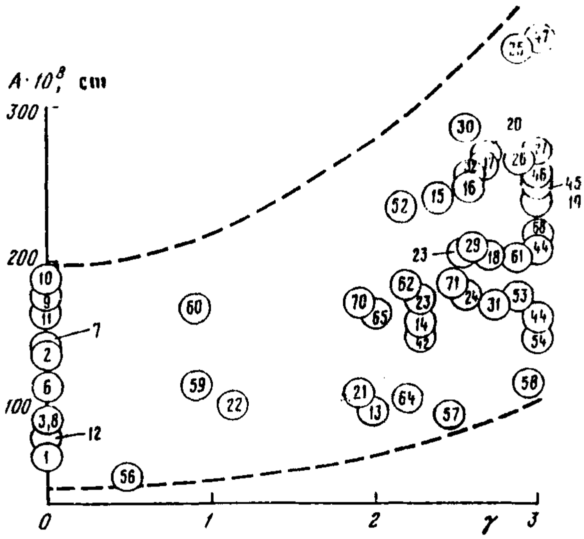

FIGURE 4 Dependence of the length of the statistical Kuhn segment on the degree of substitution of hydroxyl groups of glucopyranosic cycle in the cellulose derivatives. Numbering of the experimental points corresponds to that in Table II.

steric hindrances to the mutual rotation of pyranosic rings. Cellulose carbanilate (R = —CO—NH—C_6H_5 ethyl- (R = —C_2H_5) and nitrate (R = —NO_2) with similar degrees of substitution ($\gamma = 2.3$) in ethyl acetate, have equilibrium rigidities which do not differ within experimental error (154, 175 and 160 Å in References 58, 54 and 47.

Introduction of substituents into the glycopyranosic chain, results in a change in H-bonds. Increase in the degree of substitution causes an increased skeletal rigidity. Burchard[12,62] suggested that secondary cyclization of cellulose carbanilate by hydrogen bonds formation $>\mathrm{NH} \rightarrow \mathrm{O{=}C}<$ explains a high rigidity of the chain, A = 338 Å for the cellulose carbanilate in DMSO.[68] In the second case, the increase in the degree of substitution is accompanied by extreme changes in the chain rigidity. Introduction of acetyl groups into cellulose results in increased rigidity due to formation of hydrogen bonds $—\mathrm{OH} \rightarrow \mathrm{O{=}C}<$. The number of hydrogen bonds formed by acetyl and hydroxyl groups is a maximum at $\gamma^* < 3$; γ^* value depend substantially on the distribution of substituents along the chain. According to Shakhparonov's data,[72] the maximum rigidity for cellulose acetate in dichloromethane is achieved at $\gamma^* = 2.90$, [$\gamma = 2.70$, $[\eta] = 285$ cm^3/g; $\gamma = 2.90$, $[\eta] = 350$ cm^3/g; $\gamma = 3.0$, $[\eta] = 275$ cm^3/g]. Introduction of methanol and change of composition of the mixed solvent on the base of dichlormethane was used[72] to qualitatively estimate the number of intramolecular bonds. Introduction of methanol caused destruction of the (O_3O_5) bond. Sato[42] studying the hydrodynamic behaviour of substituted acetates in dimethylacetamide and indicated a double increase in their skeleton rigidity when the degree of substitution increased from 0.49 to 2.92.

Figure 5 shows the dependence of the equilibrium rigidity of cellulose nitrates in a series of solvents. A considerable increase in A, more than 200%, occurs on double-substitution of cellulose nitrates was considered by Pearson and Moore.[73] For nitrate $\gamma = 2.9$ in acetone $A = 332$ Å[42,53]; nitrate with $\gamma = 2.91$ in acetone possesses $A = 260$ Å. The chain rigidity of cellulose nitrate increases insignificantly in the solvent series: acetone < ethyl acetate < methylethylketone < dimethylacetamide + 6% LiCl (Figure 5).

The influence of solvent of the conformation was analyzed by Kamide and Saito.[74] They indicated an increase in rigidity of cellulose diacetate $\gamma = 2.46$ in changing to the more polar solvents (Figure 5). The equilibrium rigidity of polyelectrolytes (sodium salt of carboxymethylcellulose) decreases with increase in the ionic strength of solvent[42,70]: for NaCMC in the aqueous solution of sodium chloride, $A = 254$ Å at $I = 0.1$ mol/l; $A = 190$ Å at $I = 0.34$ mol/l; $A = 100$ Å at $I \rightarrow \infty$. Taking into account the dielectric permeability of the aqueous solution of sodium chloride decreases its ionic strength, in agreement qualitatively with the conclusion of Kamide and Saito.[70]

4. THE INFLUENCE OF MIXED SOLVENTS ON THE CONFORMATIONAL PARAMETERS OF CELLULOSE DERIVATIVES AND THE PHASE TRANSITIONS

The tendency to exhibit lyotropic mesomorphism is determined by the degree of anisodiametry of the macromolecules.

There are two methods of calculation of conformational parameters; persistent length q and hydrodynamic diameter d of macromolecules. The first is a linear

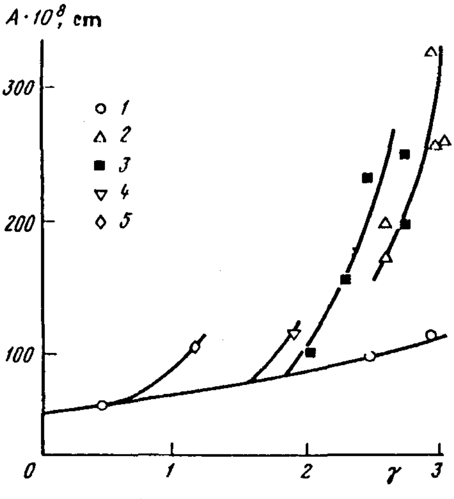

FIGURE 5 Dependence of the equilibrium rigidity of glycopyranosic chain on the degree of substitution for the cellulose acetates in DMAA (1) and nitrates in acetone (2), ethyl acetate (3), methylethylketone (4) and DMAA-6% LiCl mixture (5).[94]

dependence between the intrinsic viscosity and the molecular mass $[\eta]$, $M = f(M^{1/2})$.[91] Determination of q and d comes from the tangent of the straight line and intersection along the ordinate axis. The second method[75] involves the variation of q and d using the theoretical expression of Yamakava and Fuji for the intrinsic viscosity of worm-like cylinders.

The axial ratio is known to influence the critical concentrations for formation of LC-phase in solution. Equations for the intrinsic viscosity of Yamakava-Fuji[17] (23) and Khokhlov-Semyonov[5] (24) for the critical concentrations for formation of the LC-phase allows determination of q and d of macromolecules:

$$[\eta] = \Phi(L/A)^{3/2}A^3M^{-1}, \tag{23}$$

$$V_2^* = \frac{d}{A}\,\frac{3.34 + 11.3(L/A) + 4.06(L/A)^2}{(L/A)(1 + 0.387L/A)}, \tag{24}$$

where Φ is the viscosimetric constant; L is the contour length of a chain; $A = 2q$ is the Kuhn segment.

The calculations used earlier[95] can be used for the critical concentration and intrinsic viscosities of diluted CTA solutions in the mixed solvent. Two assumptions are made:

—equality between the molecular masses of CTA samples initially and in solutions;

—the magnitude of the projection of a monomeric link onto the direction of glycopyranosic chain is assumed to equal 5.15 Å.[78]

In conformity with the above assumptions: $M_w = 1.84\cdot 10^5$ and $L = 3.35\cdot 10^3$ Å. The values of q and d obtained from the calculations are given in Tables II and III.[95]

TABLE III

Values of persistent length q (Å) and hydrodynamic diameter d (Å) of CTA macromolecules in mixed solvents CF_3COOH—CH_2Cl_2 over 283–303 K interval

	$X_{CH2Cl2} = 0.00$ m.f.		$X_{CH2Cl2} = 0.13$ m.f.		$X_{CH2Cl2} = 0.25$ m.f.	
T, K	q	d	q	d	q	d
283	58	2.4	55	2.1	74	2.7
288	57	2.4	49	2.0	73	2.7
293	54	2.4	44	1.8	72	2.8
298	54	2.4	39	1.6	68	2.7
303	51	2.3	34	1.5	65	2.6
313	48	2.3				
318	47	2.2				

	$X_{CH2Cl2} = 0.36$ m.f.		$X_{CH2Cl2} = 0.47$ m.f.		$X_{CH2Cl2} = 0.67$ m.f.	
T, K	q	d	q	d	q	d
283	83	2.0	71	2.5	77	3.0
288	78	2.2	68	2.5	76	3.4
293	76	2.4	66	2.5	76	3.7
298	72	2.6	64	2.5	72	4.0
303	70	2.8	62	2.5		

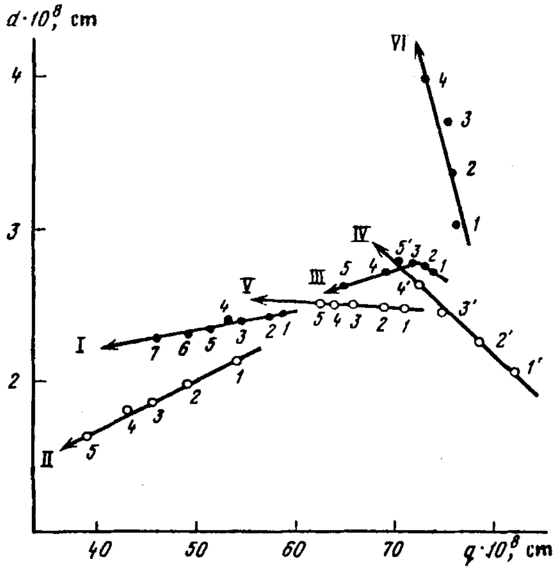

FIGURE 6 Diagram of axial ratios of CTA macromolecules in mixed solvent $CF_3COOH—CH_2Cl_2$ with compositions: 0.00 (I), 0.13 (II), 0.25 (III), 0.36 (IV), 0.47 (V), 0.67 (VI) mol.fr. of CH_2Cl_2 at temperatures: 283 (1), 288 (2), 293 (3), 298 (4), 303 (5), 313 (6) and 318 K (7).

TABLE IV

Values of the intrinsic viscosity (cm^3/g) and Martin's constants for HOPC solutions in some solvents

	Water		Ethanol		DMAA		Dichlormethane	
T, K		K_M		K_M		K_M		K_M
288	219	0.28	334	0.10	288	0.21	358	−0.03
293	204	0.35	302	0.16	235	0.16	369	−0.03
298	187	0.42	330	0.18	—	—	284	−0.03
303	158	0.52	308	0.15	221	0.19		
313	113	0.94			198	0.22		
318					167	0.35		

TABLE V

Values of Kuhn segment for HOPC molecules in some solvents[85]

	Kuhn segment, Å			
T, K	Water	Ethanol	DMAA	Dichlormethane
288	210	370	220	410
293	190	320	230	430
298	170	370	—	460
303	160	330	240	250
308	140	330	210	
313	100	130	190	
318	90		150	

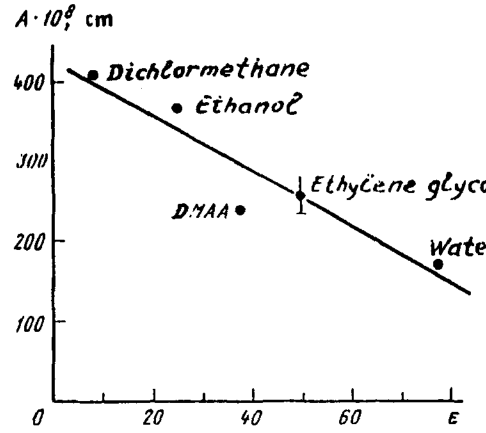

FIGURE 7 Dependence of equilibrium rigidity of HOPC chain on solvent dielectric permeability.

The calculated values agree with literature data[42]: the cellulose acetate with $\gamma = 2.92$ in DMAA is characterized by $A = 120$ Å.

Increase in the dichlormethane content in the mixture with CF_3COOH leads to an increasing equilibrium rigidity of CTA. The temperature increase and the equilibrium rigidity decreases with increasing temperature. Temperature does not practically influence the d value in mixtures with dichlormethane content below 0.4–0.5 mol. fraction. In the systems with high dichlormethane content in the mixtures with trifluoroacetic acid, the persistent length of CTA molecules exceeds 70 Å, and the hydrodynamic diameter grows with increasing temperature (Figure 6).

The mixed solvents of dichlormethane with CF_3COOH 0.4–0.5 mol. fraction is interesting not only from the point of view of the anomalous dependence of d on T, but also the peculiarities of the phase transitions of systems based on cellulose triacetate.[81] Rheological studies by Saito[82] were used to estimate the phase structure. This approach presupposes the identity between the temperatures at which the minimum and maximum viscosities are achieved, and the appearance of anisotropic and disappearance of the isotropic phase in solution. In CF_3COOH the transition of CTA into a highly oriented state occurs through a narrow corridor which limits the co-existence of the isotropic and anisotropic phases. One maximum is observed in CTA solution. With increasing CH_2Cl_2 concentration above 0.5 mol. fraction in mixtures with CF_3COOH, two maxima in the concentration dependence, whilst there is only one maximum in the temperature dependence. As temperature increases, the first maximum degenerates into a shoulder, and the second is displaced into a region of higher polymer concentration. The complicated character of the concentration dependence of viscosity reflects a series of phase transitions over the temperature interval between the ternary (T_t) and critical (T_c) points.[5] The axial ratio $A/d < 50$ testify to this supposition.[5]

5. INFLUENCE OF THE DIELECTRIC PROPERTIES OF SOLVENTS ON EQUILIBRIUM RIGIDITY OF CELLULOSE DERIVATIVES

Criteria have been developed to allow selection of solvents for observation of the lyotropic LC-state. Experimental measurements of hydroxypropylcellulose (HOPC) in non-aqueous solutions (M_w = 120000, degree of substitution 3) is carried out in water, ethanol, dimethylacetamide (DMAA) and dichloromethane.[85]

Dependence of the reduced viscosity is non-linear as predicted by Martin's equation:

$$\frac{\eta_{spec}}{C} = [\eta] e^{K_M [\eta] C} \tag{25}$$

is observed to a greater degree for HOPC solutions in dichlormethane and DMAA than for those in water and ethanol. The non-linear character of $\eta_{red}/C = f(C)$ in the region of low HOPC concentrations is carried out by extrapolation to infinite dilution from the region $4 \cdot 10^{-3} - 1 \cdot 10^{-2}$ g/cm^3 (Table IV).[85]

Since HOPC is a semi-rigid-polymer, the segment rigidity of polyglucosidic chain is carried out in agreement with the Yamakava-Fuji equation. Calculation of the HOPC chain diameter—$d = 12.8 \cdot 10^{-8}$ cm—are given in Table V.[57]

Figure 7 shows the dependence of the Kuhn segment value of HOPC solutions on solvent dielectric permeability. The tendency to decrease the segment rigidity of HOPC chain with increasing polarity of solvent is obvious.[87,88]

Kamide and Saito[74] showed for cellulose diacetate (degree of substitution 2.46) an increase in the equilibrium rigidity when going from tetrahydrofurane to more polar acetone and DMAA. A clear interrelation between solvation and mesomorphism in non-aqueous solutions is found out.

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