Conformation of carboxymethylcellulose in cadoxen–water solutions

P. N. Lavrenko*, O. V. Okatova and V. N. Tsvetkov
Academy of Sciences of the USSR, Institute of Macromolecular Compounds, Leningrad, USSR

H. Dautzenberg and B. Philipp
Academy of Sciences of the GDR, Institute of Polymer Chemistry 'Erich Correns', Teltow-Seehof, GDR

(*Received 4 November 1988; revised 20 March 1989; accepted 30 March 1989*)

Diffusion, sedimentation and viscosity of carboxymethylcellulose (CMC) ($DS=0.9\pm0.1$, $28\,000\leqslant M\leqslant380\,000$) were studied in cadoxen–water systems over a wide range of solvent composition. The results were interpreted according to the theory of hydrodynamic properties of worm-like chains. The equilibrium rigidity of CMC in cadoxen–water was shown to be comparable to that of unsubstituted cellulose in the same solvent. On dilution of the cadoxen–CMC system with water, no charge effects became visible up to a dilution ratio of 10 parts by weight of water per 1 part by weight of cadoxen, but the equilibrium rigidity increased considerably. The conformational parameters of CMC were compared to those of other cellulose derivatives and some synthetic polymers.

(Keywords: carboxymethylcellulose; polyelectrolyte effects; rigidity of polymers in solution)

INTRODUCTION

In addition to its technical importance as a water-soluble polymer, carboxymethylcellulose (CMC) with a degree of substitution (*DS*) up to 1.0 is of interest as a water-soluble model for cellulose, still resembling the properties of the original polymer to a considerable extent[1,2]. For both areas, a detailed knowledge of the molecular properties of the macromolecules in solution is required. Relevant studies in aqueous solution, however, can be impeded by chain aggregation, microgel formation and polyelectrolyte effects. Addition of NaCl to the solution[3,4] may largely suppress polyelectrolyte effects due to an increase in ionic strength, but, on the other hand, may favour chain aggregation due to salting out. As shown by us[5], cadoxen, i.e. an aqueous solution of Cd^{2+}–ethylenediamine complex known as a good solvent for unsubstituted cellulose[6], proved to be suitable for preparing a CMC solution with a rather molecular state of dispersion showing no disturbing polyelectrolyte effects. These remain sufficiently suppressed even after diluting the system with a rather large amount of water, as demonstrated by our results[5]. Based on the methods outlined in these previous publications, this paper summarizes our results on the molecular conformation of CMC in cadoxen–water solutions obtained by diffusion, sedimentation and viscosity measurements, and gives an interpretation on the basis of current hydrodynamic and statistical theories. Special attention was given to conformational changes with increasing water content of the system.

EXPERIMENTAL

Samples of CMC with a *DS* of 0.9 ± 0.1 and a molar mass *M* between 28 000 and 380 000 have been used. All CMC samples were prepared based on linters as cellulose starting material. In the case of sample 12, hydrolytically degraded linters (microcrystalline cellulose) was employed. Alkalization and after that carboxymethylation with monochloroacetate were performed in a medium composed of sodium hydroxide, water and ethanol or isopropanol, respectively. Degradation down to the degree of polymerization (*DP*) wanted was brought about either by alkaline-oxidative chain splitting in the reaction medium or by acid hydrolysis of CMC under mild conditions in acetone–water mixture (in that way samples 9 and 13 were obtained from sample 6). For sample 1, the molar mass distribution $\bar{M}_z/\bar{M}_w$ was determined in the usual way from sedimentation boundary spreading and found to be 1.4. As solvents, a cadoxen solution (6 wt% Cd, 28 wt% ethylenediamine, no sodium hydroxide) prepared according to ref. 6 and subsequently denoted as 'cadoxen' as well as various mixtures of this solution with water (denoted as 'cadoxen–water') have been employed. Relevant properties of these various solvents are listed in *Table 1*. Solutions of CMC in cadoxen with a polymer concentration between 0.03 and $0.3\,g\,dl^{-1}$ were prepared at a temperature of about 8°C and kept for one day before starting the measurements. The solutions in cadoxen–water were obtained by dissolving the Na–CMC sample in water and adding the appropriate amount of cadoxen. This procedure proved to be equivalent to that of dissolving the sample in cadoxen and subsequently diluting with water[5].

The viscometric measurements were performed in an Ostwald-type viscometer at 26°C with an average velocity gradient of:

$230\,s^{-1}$ in cadoxen
$360\,s^{-1}$ in cadoxen–water $(1+10)$
$393\,s^{-1}$ in cadoxen–water $(1+100)$

---

* To whom correspondence should be addressed

0032-3861/90/020348-05$03.00

The intrinsic viscosity $[\eta]$ was calculated from the reduced viscosity η_{sp}/c according to the Huggins equation:

$$\eta_{sp}/c = [\eta] + [\eta]^2 K'c \qquad (1)$$

in various solvents (*Table 2*). The Huggins constants K' were close to those reported[7]. Translational diffusion was investigated at 26°C in a scanning diffusiometer DAK-4[8] with a polarizing interferometric system of registration[9] employing Teflon cells with an optical length of 3.0 mm[10]. The procedure of evaluation of the 'symmetric' as well as the 'asymmetric' diffusiograms was reported in detail in our previous publication[5]. The diffusion coefficient D was obtained from the rate of 'dispersion' $\overline{\sigma^2}$ of the interferogram according to:

$$\overline{\sigma^2} = 2Dt \qquad (2)$$

where t means time. No dependence of D on polymer concentration was found up to $c_{pol} \leqslant 0.06\,\mathrm{g\,dl^{-1}}$. The refractive index increment was calculated from the area under the interferometric curve of the diffusiogram, amounting to an average of $0.11 \pm 0.01\,\mathrm{cm^3\,g^{-1}}$ in cadoxen and $0.15 \pm 0.01\,\mathrm{cm^3\,g^{-1}}$ in cadoxen–water (1 + 10).

The velocity of sedimentation of the dissolved polymer was obtained in an analytical ultracentrifuge MOM 3180 (Hungary) employing a double-sector or a single-sector cell, respectively, at a rotor speed of 45 000 or 65 000 rpm, respectively. The sedimentation coefficient s was calculated in the same way as in ref. 11. The dependence of s on polymer concentration was taken into account by extrapolation to $c \rightarrow 0$ according to:

$$1/s = (1/s_0)(1 + k_s c) \qquad (3)$$

($s_0 = \lim_{c \to 0} s$, k_s = parameter of concentration dependence of s) with an average value of $k_s/[\eta] = 1.0$ in cadoxen and of 0.84 ± 0.01 in cadoxen–water (1 + 10).

Table 1 Characteristics of cadoxen–water mixtures (by weight) at 26°C

Solvent	ρ_0 ($\mathrm{g\,cm^{-3}}$)	$\eta_0 \times 10^2$ ($\mathrm{g\,cm^{-1}\,s^{-1}}$)	n_D[a]
Cadoxen	1.050	4.02	1.394
Cadoxen–water (1 + 1)	1.024	1.77	1.354
Casoxen–water (1 + 10)	1.003	1.02	1.339
Cadoxen–water (1 + 100)	1.000	0.93	1.333
Cadoxen–water (1 + 500)	0.997	0.87	1.333

[a] n_D = refractive index

The densities of the Na-CMC (sample 1)/cadoxen–water (1 + 10) solutions of different Na-CMC concentration ($(0.125\text{–}1.08) \times 10^{-2}$ g/g) were determined with the digital density measurement equipment DMA 02D, Fa. Paar AG, Graz (Austria), as well as in a pycnometer (volume 12.67 cm^3) before and after dialysis. Dialysis was performed simultaneously for 7 days against the solvent using a cellophone membrane as in ref. 12. Dialysed solutions gave the same results as non-dialysed ones. The factor $(1 - \bar{v}\rho_0)$, with $\bar{v}_0$ being the partial specific volume of CMC and ρ_0 being the solvent density, was found to be 0.52 ± 0.02.

Hence, the molar mass of our CMC samples was calculated from diffusion and sedimentation data in cadoxen–water (1 + 10) using the value of 0.52 in combination with the Svedberg equation:

$$M_{SD} = (RT/(1 - \bar{v}\rho_0)(s_0/D) \qquad (4)$$

Here R is the gas constant and T is absolute temperature.

The hydrodynamic parameters of CMC/cadoxen–water (1 + 10) given in *Table 2* were used for the calculation of the hydrodynamic parameter A_0 defined by the equation[13]:

$$A_0 = (D\eta_0/T)(M[\eta]/100)^{1/3} \qquad (5)$$

wherein η_0 = solvent viscosity.

The average value of $A_0 = (3.36 \pm 0.09) \times 10^{-10}$ erg deg^{-1}mol$^{-1/3}$ falls into the range of A_0 values $(3.5 \pm 0.8) \times 10^{-10}$ erg deg^{-1} mol$^{-1/3}$ reported for cellulose derivatives in water and in aqueous buffers[13].

RESULTS AND DISCUSSION

The gradual suppression of the strong polyelectrolyte effect encountered in aqueous solutions of CMC by stepwise addition of cadoxen to the system was treated in detail elsewhere[5]. Our results obtained on this point, which are of relevance for a discussion of molecular conformation of CMC in solution, can be summarized as follows.

In the viscosity measurements linear η_{sp}/c vs. c plots were obtained already in cadoxen–water (1 + 500). On further addition of cadoxen to the system, $[\eta]$ decreases continuously according to *Figure 1*, obviously mainly due to coil contraction caused by the increase in ionic strength. The changes are more pronounced the higher the molar mass of the samples.

In the diffusion measurements, D was expected to increase on addition of cadoxen due to a suppression of charge-induced coil expansion. Obviously, however, this

Table 2 Hydrodynamic characteristics of the CMC samples in cadoxen and mixtures of cadoxen with water (by weight) at 26°C

		$[\eta] \times 10^{-2}$ ($\mathrm{cm^3\,g^{-1}}$)				
Sample no.	$M_{SD} \times 10^{-3}$ ($\mathrm{g\,mol^{-1}}$)	Cadoxen	Cadoxen–water (1 + 10)	Cadoxen–water (1 + 100)	$S_0 \times 10^{13}$ (s)	$A_0 \times 10^{10}$ (erg deg^{-1} mol$^{-1/3}$)
1	380	4.7	7.7	10	5.7	3.46
2	260	3.1	4.9	–	4.8	3.27
4	230	2.7	4.65	6.9	4.9	3.50
6	120	2.1	3.2	–	3.3	3.30
9	55	1.3	1.6	–	2.6	3.44
12	57	0.80	1.1	1.3	2.9	3.29
13	28	0.48	0.82	–	2.0	3.26

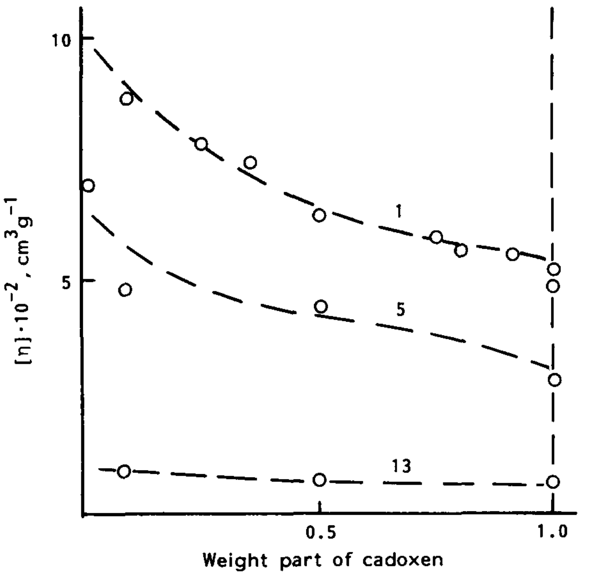

Figure 1 Dependence of the intrinsic viscosity on weight fraction of cadoxen in cadoxen–water solvent at 26°C for CMC samples 1 and 13 (see *Table 2* for specifications) and an additional sample 5 of $M = 260\,000$ (see ref. 5)

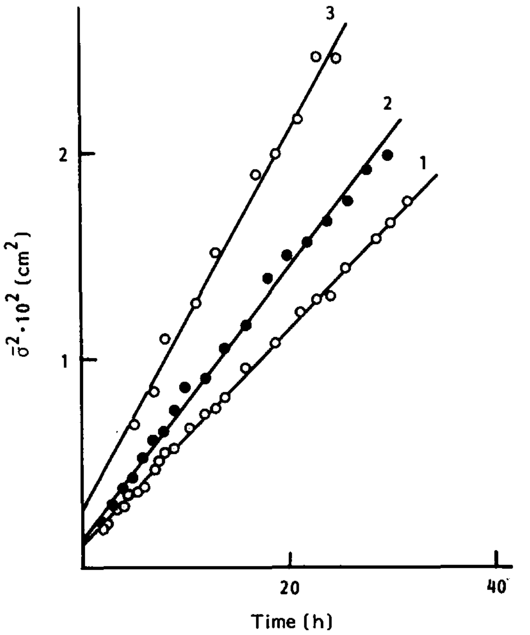

Figure 2 Dependence of diffusion curve dispersion on time for CMC (sample 1) in mixture of cadoxen–water with proportions: (1) 1+10, (2) 1+100 and (3) 1+500

influence is overcompensated by the suppression of the counteracting charge effect caused by the different thermal mobility of macroion and counterions (electrostatic charge effect), as D actually decreases on addition of cadoxen. This is demonstrated in *Figure 2*, showing the dependence of the rate of dispersion of the diffusion curve on the cadoxen content of the system. From a practical point of view, a cadoxen content of 1 part per 10 parts of water proved to be sufficient to suppress charge effects and to secure a molecular state of dispersion of the CMC in solution. After assessing the conditions for a valid evaluation of diffusion, sedimentation and viscosity measurements on CMC solutions without disturbing charge effects, the dependence of the hydrodynamic parameters of CMC in cadoxen–water solutions on molar mass of the polymer will now be discussed with respect to chain conformation.

Because dialysis did not change the results of density measurements we can assume that we determined the real value of $(1-\bar{v}\rho)$. Therefore, using M_{SD} values determined according to equation (4), we can calculate the values for $(M_x/M)\ (1-\bar{v}_x\rho)$ in Vink's expression[12] for the complex-forming solution:

$$M_{SD} = \frac{RT}{(M_x/M)(1-\bar{v}_x\rho)} \frac{(S_0)_x}{D_x} \qquad (6)$$

Here the index 'x' indicates the values belonging to the complex. With $M_{SD}(1+10)$, $(S_0)_x$ and D_x we obtained $(M_x/M)(1-\bar{v}_x\rho) = 0.69$ for cadoxen and $(M_x/M)(1-\bar{v}_x\rho) = 0.65$ for cadoxen–water(1+1). The value 0.69 is used below for characterizing the equilibrium rigidity of the CMC molecule in non-diluted cadoxen.

The relation between molar mass and hydrodynamic parameters of a dissolved polymer is usually described by the empirical Mark–Kuhn equations:

$$[\eta] = K_\eta M^\alpha \qquad (7)$$

$$S_0 = K_s M^\gamma \qquad (8)$$

A logarithmic plot of these functions for CMC in cadoxen and in cadoxen–water is presented in *Figure 3*, showing a linear dependence in the range of M investigated. Thus, equations (7) and (8) can be applied with the values of K_η,α and γ given in *Table 3*. In every case the values of M_{SD} obtained from sedimentation–diffusion data in mixture cadoxen–water (1+10) were used.

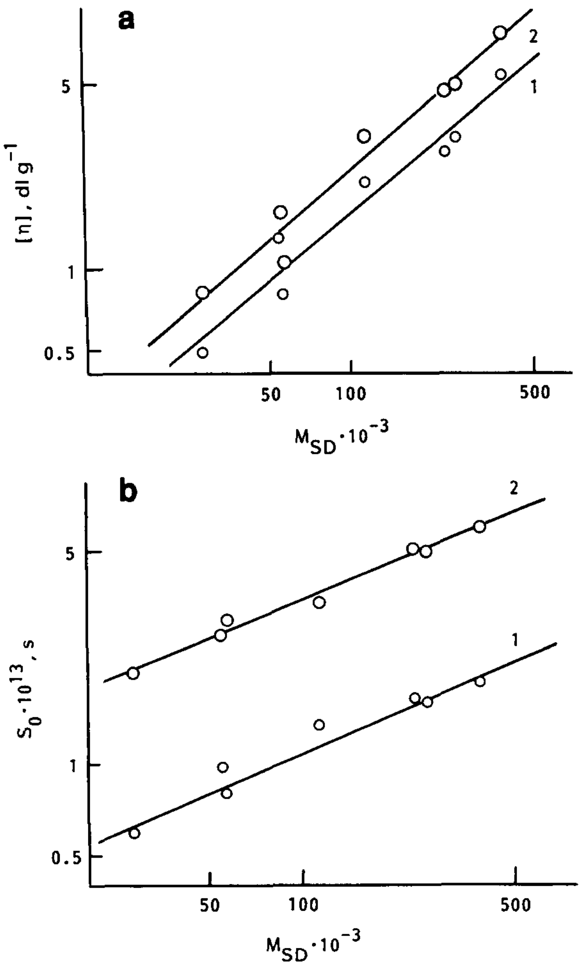

Figure 3 Logarithmic dependences of (a) $[\eta]$ and (b) S_0 on molecular weight M for CMC at 26°C in (1) cadoxen and (2) cadoxen–water (1+10)

The rather high value of α exceeding 0.5 reflects a drainability of the CMC macromolecules. The assumption of free draining is in agreement with the negative coefficient of temperature dependence of viscosity observed for CMC in cadoxen. For CMC ($M=260\,000$) $\Delta \ln[\eta])/\Delta T$ amounted to $-0.007\,\mathrm{deg}^{-1}$.

Thus, for assessing the molecular dimensions of CMC in cadoxen and cadoxen–water, the theory of the 'worm-like chain'[14,15] seems to be adequate, as it implies a free draining of the macromolecules. According to this theory, the 'characteristic value' of the sedimentation constant:

$$[S]=S_0\eta_0/(1-\bar{v}\rho) \qquad (9)$$

can be expressed by a linear function of the square root of extended chain length $L^{1/2}$ or $M^{1/2}$ according to:

$$[S]=(M_L^{1/2}/N_A P_\infty)A^{-1/2}M^{1/2} + (M_L/3\pi N_A)[\ln(A/\alpha)-1.056] \qquad (10)$$

where $P_\infty=5.11$, N_A is Avogadro's number and M_L is the mass per unit length of the chain.

For Na-CMC with $DS=0.9$, M_L amounts to $454\,\mathrm{nm}^{-1}$. The slope of the dependence of $[S]$ on $M^{1/2}$ may be used for obtaining the Kuhn statistical segment length A and the hydrodynamic chain diameter d. If the concept of the invariance of the parameter A_0 (ref. 13) is applied, simple transformations of equations (5) and (10) lead to the conclusion that equation (10) is equivalent to the dependence of the value $(M^2/[\eta])^{1/3}$ on $M^{1/2}$ corresponding to the equation[13]:

$$(M^2/[\eta])^{1/3}=M_L^{1/2}\phi_0^{-1/3}\mathrm{A}^{-1/2}\mathrm{M}^{1/2} + \mathrm{kM_L}(3\pi 100^{1/3}A_0)^{-1}[\ln(A/\alpha)-1.056] \qquad (11)$$

with $\phi_0=2.87\times10^{23}\,\mathrm{mol}^{-1}$, $A_0=3.36\times10^{-10}\,\mathrm{erg\,deg}^{-1}\,\mathrm{mol}^{-1/3}$ and k = Boltzmann's constant.

The linearity of this dependence is demonstrated in *Figures 4* and *5*, showing plots of our experimental data obtained by sedimentation and viscosity measurements of CMC in cadoxen–water (1 + 10). From the intercepts and the slopes of these plots, we calculated the hydrodynamic chain diameters d and the Kuhn segment lengths listed in *Table 4*. The values of d are compatible with the chemical structure of the polymer chain. The equilibrium rigidity of the CMC molecules in the solvent is characterized by a Kuhn segment length of $A=17\pm2\,\mathrm{nm}$ in cadoxen–water (1 + 10). This value is somewhat higher than that in cadoxen, $A=13\pm2\,\mathrm{nm}$ (*Table 4*).

Table 3 Values of the coefficients in Mark–Kuhn equations for CMC at 26°C in different solvents

Coefficient	Cadoxen	Cadoxen–water (1 + 10)
α	0.84 ± 0.09	0.86 ± 0.07
γ	0.42 ± 0.04	0.40 ± 0.02
$K_\eta \times 10^3$	10^a	12
$K_s \times 10^{15}$	0.89^b	3.5

[a] If $[\eta]$ is given in $\mathrm{cm^3\,g^{-1}}$
[b] If s is given in s

It seems reasonable to compare these data with those of unsubstituted cellulose on the one hand and those of highly substituted cellulose derivatives on the other, as shown in *Table 4*. The Kuhn segment length of 13 nm found here for CMC of $DS \sim 0.9$ in cadoxen is about the same as that of unsubstituted cellulose in the same

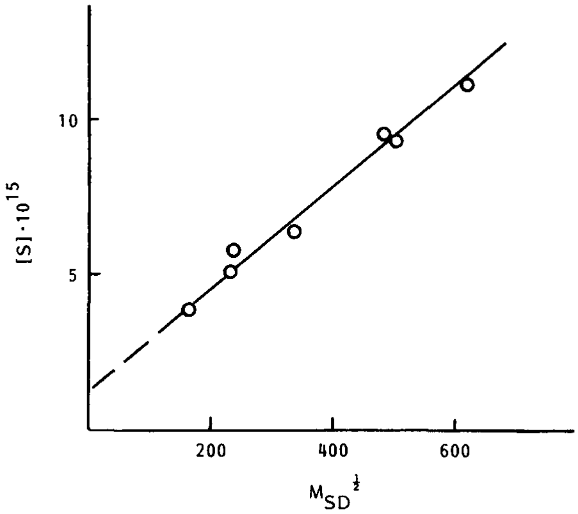

Figure 4 Dependence of $[S]$ on $M^{1/2}$ for CMC in cadoxen–water (1 + 10) at 26°C

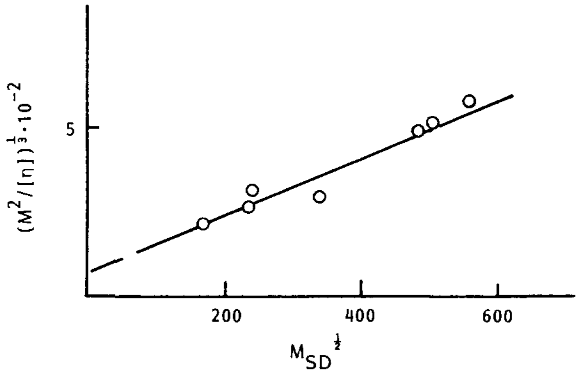

Figure 5 Dependence of $(M^2/[\eta])^{1/3}$ on $M^{1/2}$ for CMC in cadoxen–water (1 + 10) at 26°C

Table 4 Conformation characteristics of some cellulose esters in solutions

System	A (nm)	d (nm)	L/A	σ	Ref.
Carboxymethylcellulose ($DS=0.9$) in cadoxen	13 ± 2	0.6 ± 0.2	5–65	3.3	16
Carboxymethylcellulose ($DS=0.9$) in cadoxen–water (1 + 10)	17 ± 2	1.0 ± 0.5	4–49	3.7	this work
Cellulose in cadoxen	11–14	0.1 – 1	3–200	2.7–3.4	17–19
Nitrocellulose ($DS=2.3$) in ethylacetate	20.0	1.0	6–79	4.1	20
Cyanoethylcellulose ($DS=2.6$) in acetone	35.0	1.4	1.2–16	5.4	11
Cellulose carbanilate ($DS=2.67$) in ethyl acetate	30.0	1.1	5.4–93	5.0	21

solvent. Obviously, within the range of molar mass investigated here, the molecular conformation of both cellulose and CMC ($DS \sim 0.9$) complies with the model of a draining Gaussian coil with a sufficiently large number of statistical segments L/A in the equivalent chain (*Table 4*). On the other hand, the equilibrium rigidity of CMC molecules ($DS \sim 0.9$) is definitely lower than that of highly substituted cellulose derivatives. This difference is caused by the still comparatively low DS as well as by the rather low degree of bulkiness of the carboxymethyl group.

The dilution of a CMC solution in cadoxen with water leads to an increase in $[\eta]$ equivalent to an increase in rigidity of the CMC macromolecule. This becomes clearly visible already in the range of dilution where charge effects are still sufficiently suppressed, and thus may be caused by restoring intermolecular H bonds previously broken during dissolution in cadoxen. Similar phenomena have been reported in cadoxen–water solutions for other polysaccharides, too[22].

The experimental values of the Kuhn segment length A obtained here can be compared with theoretical ones calculated on the assumption of a completely free rotation around the covalent links of the main chain. A parameter of intermolecular rotation hindrance σ can be defined according to:

$$\sigma = (A/A_{\mathrm{fr}})^{1/2} \tag{11}$$

where A_{fr} is the value of A for a completely free rotation within the polymer chain, amounting for cellulose to 1.21 nm[23]. As can be seen from *Table 4* the σ values of CMC as well as of other cellulose derivatives are rather high, significantly exceeding a value of 3, which is considered as an upper limit for flexible macromolecules even in the presence of bulky side-groups. The σ values of CMC are also higher than those of aromatic polyamides and other rigid-chain polymers based on aromatic monomers for which σ values of 1.1–1.5 have been reported[9]. Considering all these results, it may be assumed that with CMC as well as with other cellulose derivatives additional intra- and intermolecular interaction, especially the formation of H-bonds, are effective in enhancing the equilibrium rigidity of the macromolecules.

CONCLUSIONS

From the results presented here on diffusion, sedimentation and viscosity of CMC samples ($DS \sim 0.9$) differing widely in molar mass, and from the data obtained in our previous publications[5,16], it can be concluded that the cellulose solvent 'cadoxen' is an adequate medium for investigating the molecular properties, especially the molecular conformation of this polymer. Suppression of charge effects and a molecular state of dispersion of the polymer are secured even after dilution of the conventional cadoxen solvent with water to a composition of $1+10$ by volume. In calculating molar mass data of CMC in cadoxen, however, complex formation between polymer and solvent by participation of cellulosic OH groups in the solvation of Cd^{2+} has to be taken into account. Nevertheless, dialysis of the solution before the measurements is not a necessary prerequisite for valid results, if a suitable cadoxen concentration has been chosen. The data obtained on molecular parameters of CMC in cadoxen and in cadoxen–water systems (up to a dilution of $1+10$) can be interpreted on the basis of a freely drained Gaussian coil, using the model of the 'worm-like' chain. The hydrodynamic chain diameter thus calculated was found to be compatible with the chemical structure of the macromolecule. The Kuhn segment length of $A = 13 \pm 2$ nm for CMC in cadoxen is rather close to that of unsubstituted cellulose ($A = 10$ nm) in the same solvent, indicating that CMC of $DS \sim 0.9$ is really a suitable soluble model compound for cellulose in discussing solution properties. On addition of water to the cadoxen–CMC systems within the dilution range where charge effects are still suppressed, an increase of the equilibrium rigidity occurs, obviously due to a restoration of intramolecular H bonds along the chain, which had been previously broken during dissolution. The hindrance factor σ obtained by comparing A found experimentally with that calculated on the assumption of free intramolecular rotation is higher for both cellulose and CMC in cadoxen than for many synthetic polymers including aromatic polyamides. This high rigidity of cellulose chains even in the undiluted cadoxen solvent is assumed to be caused by a partial persistence of intramolecular H bonds on dissolution in the cadoxen solvent. On enhancing the DS of the sample, this effect can be expected to become less pronounced, but, on the other hand, the increase in the number of side-groups might result in some chain stiffening. Which of these effects is the predominant one still remains open and will be a topic of our future work on CMC solutions.

REFERENCES

1 Gelman, R. A. *J. Appl. Polym. Sci.* 1982, **27**, 2957

2 Takahashi, S.-I., Fujimoto, T., Miyamoto, T. and Inagaki, H. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 987

3 Dautzenberg, H., Dautzenberg, H. and Linow, K.-J. *Faserforsch. Textiltech./Z. Polymerforsch.* 1978, **29**, 538, 593

4 Yamamoto, T., Mori, Y., Ookubo, N., Hayakawa, R. and Wada, Y. *Colloid Polym. Sci.* 1982, **260**, 20

5 Okatova, O. V., Lavrenko, P. N., Tsvetkov, V. N., Dautzenberg, H. and Philipp, B. *Acta Polym.* 1988, **40**, 297

6 Jayme, G. and Neuschäffer, K. *Naturwissenschaften* 1957, **44**, 62

7 Brown, W., Henley, D. and Öhman, J. *Makromol. Chem.* 1963, **62**, 164

8 Lavrenko, P. N. and Raglis, V. V. *Pribori Tekhnika Eksperimenta* 1986, No. 2, 213; 1986, No. 5, 5

9 Tsvetkov, V. N. 'Rigid-Chain Polymer Molecules', Nauka, Leningrad, 1986 (in Russian)

10 Lavrenko, P. N., Okatova, O. V. and Khokhlov, K. S. *Pribori Tekhnika Eksperimenta* 1977, No. 5, 208

11 Tsvetkov, V. N., Lavrenko, P. N., Andreeva, L. N., Mashoshin, A. I., Okatova, O. V., Mikriukova, O. I. and Kutsenko, L. I. *Eur. Polym. J.* 1984, **20**, 823

12 Vink, H. *Arkiv Kemi* 1957, **11**, 29

13 Tsvetkov, V. N., Lavrenko, P. N. and Bushin, S. V. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 3447

14 Hearst, J. and Stockmayer, W. H. *Chem. Phys.* 1962, **37**, 1425

15 Yamakawa, H. and Fujii, M. *Macromolecules* 1973, **63**, 407

16 Lavrenko, P. N., Okatova, O. V., Filipoova, T. V., Shtennikova, I. N., Tsvetkov, V. N., Dautzenberg, H. and Philipp, B. *Acta Polym.* 1986, **37**(11/12), 663

17 Henley, D. *Arkiv Kemi* 1962, **18**, 327

18 Brown, W. and Wikström, R. *Eur. Polym. J.* 1965, **1**, 1

19 Lyubina, S. Ya., Klenin, S. I., Strelina, I. A., Troitskaya, A. V., Khripunov, A. K. and Urinov, E. U. *Vysokomol. Soedin. (A)* 1977, **19**, 244

20 Pogodina, N. V., Lavrenko, P. N., Pozivilko, K. S., Melnikov, A. B., Kolovoba, T. A., Marchenko, G. N. and Tsvetkov, V. N. *Vysokomol. Soedin. (A)* 1982, **24**, 332

21 Andreeva, L. N., Urinov, E., Lavrenko, P. N., Linow, K.-J., Dautzenberg, H. and Philipp, B. *Faserforsch. Textiltech./Z. Polymerforsch.* 1977, **28**, 117

22 Sato, T., Norisuye, T. and Fujita, H. *Polym. J.* 1985, **17**, 729

23 Holtzer, A. M., Benoit, H. and Doty, P. *J. Phys. Chem.* 1954, **58**, 624