

# Analysis of polymer heterogeneity by sedimentation transport: 3. Hydroxypropyl cellulose derivatives in organic solvents\*†

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The sedimentation velocity of hydroxypropyl cellulose acetate and cyanoethylhydroxypropyl cellulose molecules has been investigated in dilute solution in organic solvents. For these polymers, a linear dependence of the standard deviation of the displacement spectrum of macromolecules in an ultracentrifuge field on the sedimentation boundary shift was observed. The method of moments with linear approximations was used to exclude the concentration and diffusion effects and to determine the inhomogeneity parameter of the samples,  $M_z/M_w$ . They range from 1.4 to 7. The inhomogeneity of fractions and the initial unfractionated samples is compared. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

Determination of the parameters of the molecular-weight distribution (*MWD*) for samples of cellulose derivatives is complicated by the fact that their molecular-weight inhomogeneity is usually accompanied by inhomogeneity in the degree of substitution and in the regularity of the substituting-group distribution along the chain (structural heterogeneity). Therefore, it is not surprising that significant differences (exceeding the experimental error) exist between the heterogeneity parameters of the same sample determined by different methods, such as sedimentation analysis, gel permeation chromatography (g.p.c.), viscometry and flow birefringence<sup>1</sup>. These differences are due to the fact that the data from each of these methods reflect different aspects of heterogeneity: heterogeneity in translational, chromatographic, or rotational mobility, etc., to which they are sensitive, moreover, to different extents. The advantage of analytical ultracentrifugation is the very high homogeneity of the dispersing medium and the constancy of the separating force. The application of this complicated, but the only absolute, method seems desirable, in particular to polymers with a new and complicated architecture of the macromolecules<sup>2</sup>, to which the polymers discussed here belong.

The spectrum of displacements (*x* spectrum) of the macromolecules observed in the centrifugal field is determined by the various sedimentation velocities of the different macromolecules and, hence, reflects the inhomogeneity of the sample. However, the statistical

processing of this spectrum is complicated by the effects of intermolecular interactions (concentration effects) and those of the diffusion mobility of the macromolecules on the shape of the sedimenting boundary between the solvent and the solution.

The shape of the boundary here means the normalized distribution of concentration gradient of the macromolecules:

$$f_w(x) = (1/c_0) \partial c / \partial x$$

with respect to displacements *x* counted from the axis of rotation of the rotor ( $c_0$  is the initial solute concentration). The boundary width will be described by the dispersion  $\sigma^2$  of the distribution  $f_w(x)$ , which is the second central moment of this distribution:

$$\overline{\sigma^2} = (m_2/m_0) - (m_1/m_0)^2$$

where

$$m_i = \int_0^\infty x^i f_w(x) dx$$

We mean by boundary position the average value of *x* coinciding with the first moment of the *x* spectrum,  $x_m = m_1/m_0$ .

In data processing the separation and exclusion of concentration and diffusion effects can be performed with the aid of a recently proposed method<sup>3</sup>. This method is based on the experimental fact that, in the process of concentration-dependent sedimentation, the boundary width increases proportionally to its shift in the radial direction. This relationship, i.e. a linear increase in standard deviation  $\sigma = (\overline{\sigma^2})^{1/2}$  with increasing  $x_m$ , has already been observed for carboxymethyl cellulose (CMC)<sup>4</sup>.

\* Dedicated to Professor Burkart Philipp on the occasion of his 70th birthday

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**Table 1** Sedimentation characteristics of the HOPC ether-solvent systems at 26 °C

Polymer	$DS^a$	Solvent <sup>b</sup>	$(1 - \bar{v}\rho_0)$	$(dn/dc)_{546}$	$B$	$\kappa$	$(1 - b)$	Ref.
HOPCA	2.25	DMA	0.229	0.042	10	2.9	0.44	6
CEHOPC	2.4	EA	0.290	0.082	2.0	2.2	0.40	This work
		THF	0.310 <sup>c</sup>	0.065				This work
		AC	0.365	0.094				This work

<sup>a</sup> Degree of substitution

<sup>b</sup> DMA = *N,N*-dimethylacetamide; EA = ethyl acetate; THF = tetrahydrofuran; AC = acetone

<sup>c</sup> Calculated by using the value of  $\bar{v}^{25} = 0.783 \text{ ml g}^{-1}$  (ref. 7)

**Table 2** Hydrodynamic properties and heterogeneity parameters for HOPCA and CEHOPC fractions

Fraction no.	$M_{SD} \times 10^{-3}$	$s_0 \times 10^{13}$ (s)	$k_s$ (ml g <sup>-1</sup> )	$D \times 10^7$ (cm <sup>2</sup> s <sup>-1</sup> )	$\left(\frac{\partial \sigma}{\partial x_m}\right)_0$	$\frac{\sigma_2}{s_0}$	$\frac{M_z}{M_w}$
HOPCA in <i>N,N</i> -dimethylacetamide							
1	202	2.7	150	1.45	1.0	0.96	7 ± 2
2	152	2.3	112	1.65	0.8	0.76	4 ± 1
4	99	2.1	95	2.3	0.65	0.60	3 ± 1
CEHOPC in ethyl acetate							
1	580	9.1 <sup>a</sup>	460 <sup>a</sup>	1.25 <sup>a</sup>	0.35 <sup>a</sup>	0.33	1.7
4	290	7.6	190	1.3	0.28	0.26	1.4
8 <sup>b</sup>	190	6.6	120	2.3	0.44	0.40	2.0
10	150	6.0	100	2.9	0.14	0.04	≤ 1.01

<sup>a</sup> Obtained in tetrahydrofuran

<sup>b</sup> Unfractionated sample

To determine the heterogeneity parameters, sedimentation data obtained for hydroxypropyl cellulose acetate (HOPCA) and cyanoethylhydroxypropyl cellulose (CEHOPC) are analysed in detail in this work.

### EXPERIMENTAL

The preparation of the HOPCA and CEHOPC samples, their fractionation and the experimental details have already been described<sup>5,6</sup>. The values of the refractive-index increment  $(dn/dc)_{546}$ , the buoyancy term  $(1 - \bar{v}\rho_0)$  (where  $\bar{v}$  is the partial specific volume of the solute and  $\rho_0$  is the solvent density) and the average value of the degree of substitution for the cellulose ethers are listed in *Table 1*.

Sedimentation experiments were performed with a MOM model 3180 (Hungary) analytical ultracentrifuge as in the previous paper<sup>4</sup>. Velocity ultracentrifugation was carried out up to full (visually controlled) spreading of the concentration boundary between the solvent and the solution. The weight-average value of the sedimentation coefficient,  $s$ , was obtained from the rate of boundary motion in the usual way<sup>4</sup>. It was extrapolated to vanishing solute concentration  $c$  in accordance with the equation:

$$1/s = (1/s_0)(1 + k_s c)$$

where

$$s_0 = \lim_{c \rightarrow 0} s$$

The concentration parameter  $k_s$  was related to  $s_0$  by the expression  $k_s = B(s_0 \times 10^{13})^\kappa$ . The values of  $B$  and  $\kappa$  are listed in *Table 1*. Diffusion coefficient  $D$  and molecular

weight  $M$  calculated by means of the Svedberg equation were taken from the previous papers<sup>5,6</sup> and are given in *Table 2*. The molecular-weight dependence of  $s_0$  was described by  $s_0 = K_s M^{1-b}$ .

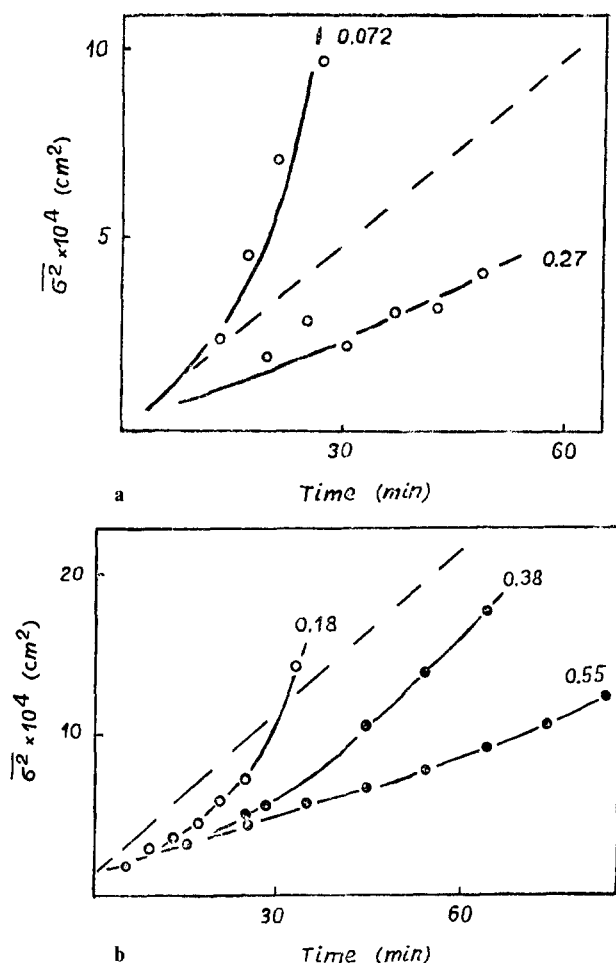
### RESULTS AND DISCUSSION

Spreading of the sedimentation boundary in the process of the radially directed motion of the macromolecules was described by the change with time in the dispersion  $\bar{\sigma}^2$  (*Figure 1*) of the  $x$  spectrum  $f_w(x)$  which (at  $c \rightarrow 0$ ) is satisfied by the equation<sup>8</sup>:

$$\bar{\sigma}^2 = 2Dt + x_m^2 \omega^4 \sigma_s^2 t^2 \quad (1)$$

where  $t$  is the sedimentation time,  $\omega = 2\pi n/60$  is the angular rotor rate,  $x_m$  is the distance from the rotation axis to the boundary,  $n$  is the frequency of rotor rotation, and  $\sigma_s^2$  is the dispersion of the  $s$  spectrum (distribution of the macromolecules with respect to sedimentation coefficients). This dispersion is of interest as its relative magnitude  $\bar{\sigma}_s^2/s_w^2$  is the absolute measure of the sample heterogeneity in terms of sedimentation coefficients.

The position of experimental points in *Figure 1* shows that for both polymers the change in  $\sigma^2$  with time  $t$  is not linear, and the rate of change is profoundly affected by solute concentration. Only at limitingly low  $c$  values do the experimental points rise above the broken curve corresponding to boundary spreading due only to the diffusion phenomenon. The situation is particularly complicated for HOPCA (*Figure 1b*) where further dilution of the solution is unacceptable because of the very low refractive-index increment value ( $0.042 \text{ ml g}^{-1}$ ).



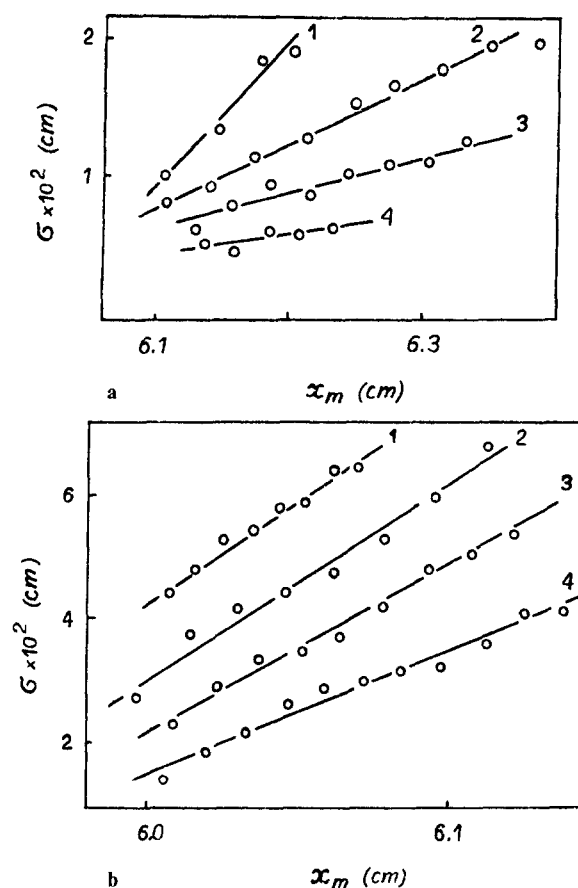
**Figure 1** Dispersion of the sedimentation boundary  $\sigma^2$  versus time for CEHOPC (fraction 4) in ethyl acetate (a) and for HOPCA (fraction 2) in DMA (b). Numbers at the curves denote solute concentration ( $\text{g dl}^{-1}$ ). Broken curves represent diffusion spreading by  $\sigma^2 = 2Dt$

Hence, the problem of determining polydispersity from sedimentation data leads to that of finding a reliable method for data extrapolation to zero concentration, i.e. to the conditions of negligible intermolecular interactions.

One of these methods is the extrapolation of standard deviation  $\sigma$  of the  $x$  spectrum  $f_w(x)$  to zero value of  $\Delta s \equiv s_0 - s$ . This dependence was found to be linear at very low concentrations<sup>9</sup>. However, for HOPCA in *N,N*-dimethylacetamide (DMA) (from the small  $dn/dc$  value) this  $c$  range is almost inaccessible. The range of the  $\Delta s$  argument available for experiment is commensurate with the extrapolation range. This leads to a significant error in determination of the ordinate intercept,  $\sigma_0 = \lim_{c \rightarrow 0} \sigma$ . As a result, the parameters of polydispersity evaluated in ref. 6 should be regarded as approximate and, most probably, too low (if one bears in mind the character of the  $\sigma(\Delta s)$  dependence).

As was mentioned above, the sedimentation data obtained for CMC were presentable in a more linear form with coordinates  $\sigma$  and  $x_m$ . Let us analyse in the same way the spreading rate of the sedimentation boundary in HOPCA and CEHOPC solutions.

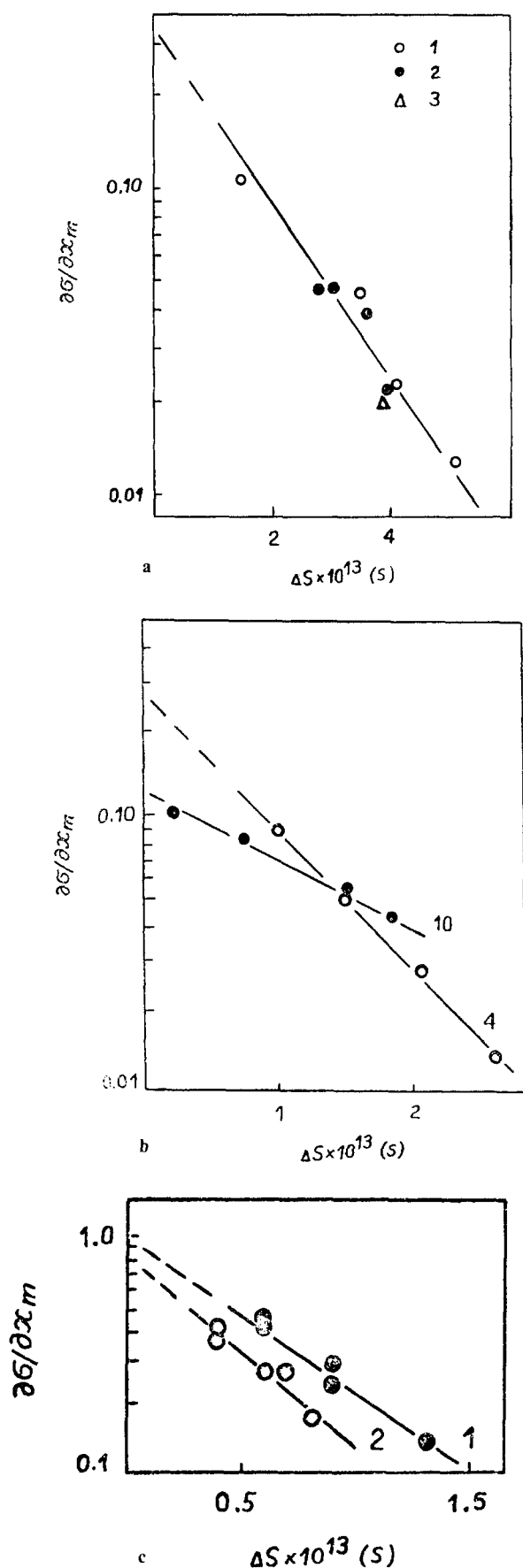
Figure 2 shows the experimental data obtained for samples with different molecular weight and inhomogeneity. The standard deviation  $\sigma$  of the  $x$  spectrum (proportional to the halfwidth of the sedimentation curve) is plotted here against the boundary abscissa  $x_m$ .



**Figure 2** Standard deviation  $\sigma$  of the sedimentation curve versus the boundary abscissa  $x_m$  in solutions of HOPCA and CEHOPC fractions. (a) Fraction 1 of CEHOPC in THF at (1)  $c = 0.065$ , (2) 0.118, (3) 0.199 and (4) 0.285  $\text{g dl}^{-1}$ . (b) Fraction 4 of HOPCA in DMA at (1)  $c = 0.31$ , (2) 0.36, (3) 0.49 and (4) 0.64  $\text{g dl}^{-1}$

Similar dependences (of linear type) were also observed: for CEHOPC fraction No. 1 in ethyl acetate (EA) (at concentration  $c$  from 0.116 to 0.186  $\text{g dl}^{-1}$ ) and in acetone ( $c = 0.118 \text{ g dl}^{-1}$ ); for CEHOPC fraction No. 4 in EA ( $c$  from 0.072 to 0.27  $\text{g dl}^{-1}$ ); for CEHOPC fraction No. 8 in EA ( $c$  from 0.060 to 0.309  $\text{g dl}^{-1}$ ); for CEHOPC fraction No. 10 in EA ( $c$  from 0.068 to 0.304  $\text{g dl}^{-1}$ ); for HOPCA fraction No. 1 in DMA ( $c$  from 0.16 to 0.65  $\text{g dl}^{-1}$ ); and for HOPCA fraction No. 2 in DMA ( $c$  from 0.18 to 0.55  $\text{g dl}^{-1}$ ). Analysis of these data leads to the following conclusions.

- (i) Through the scatter due to experimental error, no systematic curvature of the  $\sigma(x_m)$  dependence is observed with any concavity upwards or downwards. This conclusion is valid for the solutions of one sample in one solvent but at different concentrations (curves in Figure 2), for one sample in different solvents, and for different samples with widely differing molecular weights. This fact implies that the approximation of all experimental dependences by a linear function is valid. Hence, for the polymers under investigation over the available concentration range, the width of the sedimentation boundary increases proportionally to the boundary shift. This statement is not trivial because it contradicts equation (1).
- (ii) Relative spreading of the boundary (slope of the dependence of  $\sigma$  on  $x_m$ ) increases with decreasing



**Figure 3** Relative spreading of the sedimentation boundary  $\partial\sigma/\partial x_m$  versus concentration parameter  $\Delta s \equiv (s - s_0)$  in a system of semi-logarithmic coordinates: (a) fraction 1 of CEHOPC in THF (1), in EA (2) and in acetone (3); (b) fractions 4 and 10 of CEHOPC in EA; (c) fractions 1 and 2 of HOPCA in DMA

solute concentration, in qualitative agreement with the physical nature of the effect of boundary self-sharpening<sup>10</sup> in the solution of a homogeneous polymer and a similar Johnston-Ogston effect<sup>11</sup> in the solution of a polydisperse sample.

*Exclusion of concentration effects*

According to the conclusions made above, the data of a single experiment were converted sufficiently reliably into a certain slope  $\partial\sigma/\partial x_m$ . This value was extrapolated linearly to infinite dilution as shown in Figure 3. The intercept with the ordinate is the value of  $(\partial\sigma/\partial x_m)_0$  corresponding to zero solute concentration (Table 2). Hence, we can evaluate the dispersion of the sedimentation boundary  $(\sigma^2)_0$  under hypothetical conditions of the absence of concentration effects. Then, equation (1) can be used to exclude reliably the diffusion effects.

Another experimental result should also be noted preliminarily. Points 1, 2 and 3 in Figure 3a represent sedimentation data obtained for one CEHOPC fraction in different solvents. The solvent properties are different and, therefore, the rates of sedimentation and diffusion in these solvents are also different. Nevertheless, it is apparent that the points fit a single straight line. This means that the relative value of the  $x$  spectrum standard deviation does not depend on the solvent nature and is determined by the sample heterogeneity.

*Exclusion of diffusion effects*

The  $(\sigma^2)_0$  value corresponding to zero concentration was calculated by<sup>3</sup>:

$$(\sigma^2)_0 = (\partial\sigma/\partial x_m)_0^2 (x_m - x_0)_0^2 \quad (2)$$

where  $x_0$  is equal to  $x_m$  at the initial time  $t = 0$  and coincides with the meniscus position in experiments with a conventional cell. Further calculation of heterogeneity parameters was carried out by using equation (3) following from equation (1)<sup>3</sup>:

$$\sigma_s^2 = \frac{(\sigma^2)_0 - 2(\omega^2 s_0)^{-1} D \ln(x_m/x_0)}{x_m^2 s_0^{-2} \ln^2(x_m/x_0)} \quad (3)$$

Substitution for  $x_m$  in equation (3) of the mean value of the boundary abscissa in the experiment, the experimental values of  $\omega$ ,  $s_0$  and  $D$ , and the  $(\sigma^2)_0$  value determined above provides the  $\sigma_s$  values. We assume below that polymolecularity is the only reason for sample heterogeneity, i.e. that the difference in the sedimentation coefficients  $s_0$  of the macromolecules is due only to the difference in their molecular weight. Hence, the relative dispersion of  $MWD$  was evaluated by<sup>12</sup>:

$$\overline{\sigma_M^2}/M_w^2 = (1 - b)^{-2} \overline{\sigma_s^2}/s^2$$

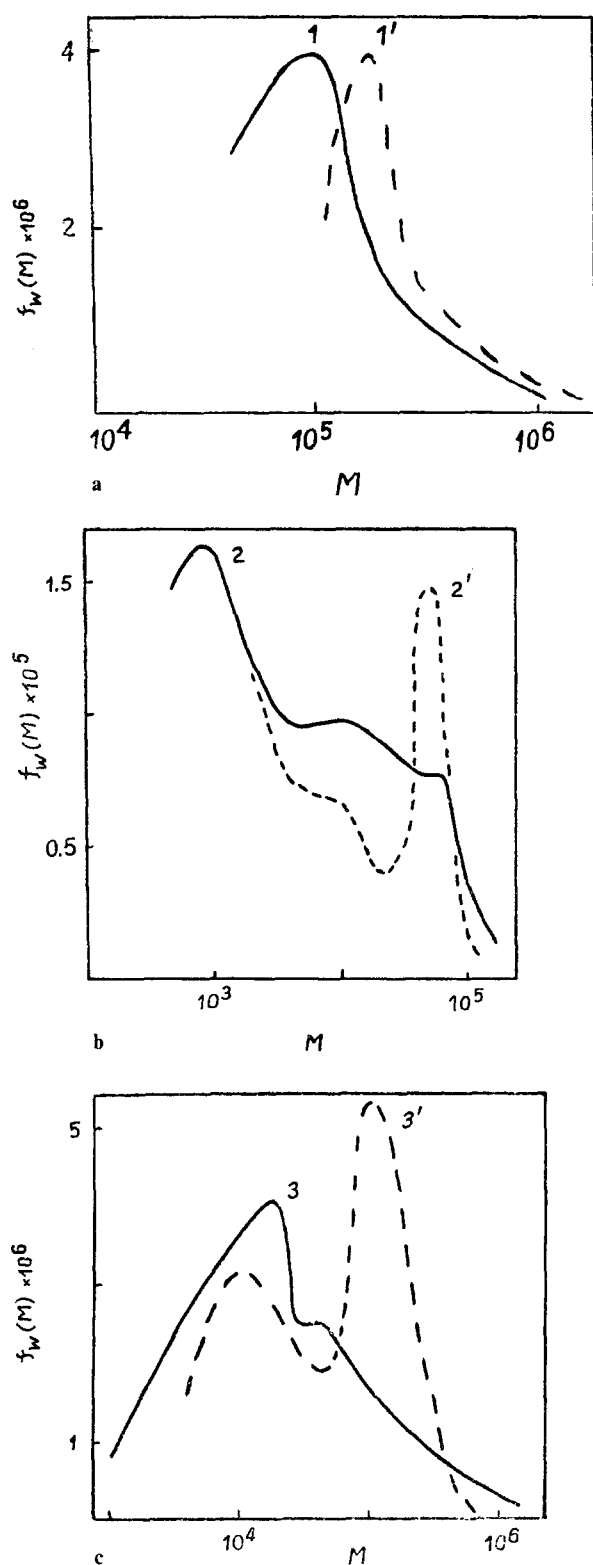
with  $(1 - b)$  from Table 1. The corresponding values of the polymolecularity parameter  $M_z/M_w$  were evaluated by<sup>12</sup>:

$$M_z/M_w = (\overline{\sigma_M^2}/M_w^2) + 1$$

and are listed in Table 2.

*MWD of initial samples*

The data of fractional precipitation were used to plot the  $MWD$  curves for the initial HOPCA and CEHOPC



**Figure 4** MWD curves for sample II of CEHOPC (curve 1 in (a)) and samples I and II of HOPCA (curves 2 and 3 in (b) and (c)) according to fractionation data. Broken curves 1', 2' and 3' are the same distributions calculated by the Schulz method (without taking into account the overlap of the fraction MWD curves). MWD parameters are listed in Table 3

samples taking into account the heterogeneity of fractions obtained above. For three of these samples, the MWD curves shown in Figure 4 were obtained by two methods: (1) by the well known Schulz method<sup>13</sup> without taking into account the overlapping of fraction MWD curves (broken curves in Figure 4); and (2) by summing up the curves of fraction MWD normalized to the weight

**Table 3** Heterogeneity parameters for initial HOPCA and CEHOPC samples according to fractionation data

Polymer	Sample no.	$M_w \times 10^{-3}$	$M_w/M_n$	$M_z/M_w$
HOPCA	I	56	2.9	1.5
	II	160	3.9	$\geq 10$
CEHOPC	II	420	3.3	1.9

part of the fraction (solid curves). One can see that the neglect of fraction overlap considerably distorts the shape of the MWD curve for the initial unfractionated sample, markedly decreasing its width. The MWD parameters for initial samples are given in Table 3.

## CONCLUSIONS

The results of sedimentation analysis of both HOPCA and CEHOPC samples and fractions show that the motion of the macromolecules of these cellulose ethers in a centrifugal field is profoundly affected by concentration effects. It is an experimentally observed fact that the width of the sedimentation boundary in solutions of these polymers increases proportionally to boundary shift in the radial direction.

This relationship has not yet been adequately explained theoretically. In fact, equation (1) shows that the increase in  $\sigma$  with increasing  $x_m$  during sedimentation should slow down, i.e. the dependence of  $\sigma$  on  $x_m$  should be a curve with upward convexity. Hence, the above fact should be ascribed to effects that have not been taken into account in the derivation of equation (1): the concentration dependence of sedimentation boundary spreading due to diffusion and polymer heterogeneity. However, even in the absence of a complete understanding of the reasons for the observed effect, the easily established linear proportionality  $\sigma \propto x_m$  made it possible to apply the method of moments with linear approximations, which has been proposed in paper 1<sup>3</sup>, to a reliable characterization of inhomogeneity of the HOPCA and CEHOPC samples.

The values of polydispersity parameters  $M_z/M_w$  obtained for HOPCA and CEHOPC samples (Table 3) are relatively high if they are compared with those usually obtained for cellulose derivatives. It follows from Table 2 that sample inhomogeneity can be markedly decreased by its fractionation. However, the fractions obtained are also relatively heterogeneous. It is possible that such high  $M_z/M_w$  values reflect the accumulation of heterogeneities of other kinds, namely, compositional and structural heterogeneities, in the processes of two-step cellulose substitution (hydroxypropylation and acetylation or cyanoethylation). Hence, for the HOPCA and CEHOPC samples, relative dispersion of the  $s$  spectrum  $\sigma_s^2/s_w^2$  is the only inhomogeneity parameter that can be reliably determined with the aid of velocity ultracentrifugation. A subsequent transition to the parameters of polymolecularity ( $M_z/M_w$ ,  $M_w/M_n$ , etc.) or to the procedure of MWD plotting for the sample involves the neglect of other kinds of heterogeneity, which should be sufficiently well argued.

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