Analysis of polymer heterogeneity by sedimentation transport: 2. Carboxymethyl cellulose in a water/cadoxene mixture

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Sedimentation velocity data obtained for solutions of monosubstituted carboxymethyl cellulose samples with molecular weights from 1.2×10^5 to 3.8×10^5 in a water/cadoxene mixture were used to determine the heterogeneity parameters. Linear dependence has been established for the x-spectrum standard deviation of the distribution of macromolecules in the ultracentrifugal field, as a function of the sedimentation boundary shift. This result proved the applicability of the novel method for elimination of the diffusion and concentration effects by a more reliable and convenient method than other known methods. The parameter M_z/M_w for different polymer samples was determined to lie between values of 1.8 and 3.5.

(Keywords: polymolecularity; sedimentation analysis; carboxymethyl cellulose)

INTRODUCTION

In the previous paper[1], a novel treatment of sedimentation velocity data was suggested for the reliable elimination of concentration and diffusion effects in a polymer–solvent system with concentration-dependent sedimentation rate. The method is based on the assumption that in such a system the width of the sedimentation boundary increases with time during centrifugation, in linear proportion to the sedimentation boundary shift. In other words, boundary width may be well approximated by a linear function of the distance between the boundary and the rotation axis. In this case the method is applicable, and provides some advantages, in the elimination of diffusion and concentration effects when applied to the determination of polydispersity indices. To examine the validity of the basic assumption above, sedimentation velocity data obtained for carboxymethyl cellulose (CMC) solutions are analysed in this work.

EXPERIMENTAL

Samples of Na-CMC with a degree of substitution of 0.9 ± 0.1 were investigated. Preparation of the samples and solutions has already been described[2,3]. Decadiluted cadoxene (mixture of one part of cadoxene with 10 parts of water by weight) was used as a solvent. Solvent density and viscosity were $1.003\,\mathrm{g\,cm^{-3}}$ and $1.02 \times 10^{-2}\,\mathrm{g\,cm^{-1}\,s^{-1}}$ at 26°C, respectively. The refractive index increment for CMC in this solvent was found[4] to be $(\mathrm{d}n/\mathrm{d}c)_{546} = 0.15\,\mathrm{cm^3\,g^{-1}}$.

Sedimentation velocity experiments were performed with a MOM model 3180 (Hungary) analytical ultracentrifuge equipped with a polarizing interferometric recording system[5] with twinning of the spar pair with $a = 0.020$ cm. A single-sector cell 1.2 cm thick was used. Experiments were performed at 26°C and a rotation frequency of $n = 50\,000\,\mathrm{rev\,min^{-1}}$ with dilute solutions of different concentrations, up to full spreading of the sedimentation boundary (from 70 to 120 min). The weight-average value of the sedimentation coefficient, s, was calculated from the time dependence of the sedimentation curve first moment, and subsequently extrapolated to zero solute concentration. Effective time was measured from when the boundary left the meniscus.

Translational diffusion was investigated with the aid of a polarizing diffusometer[5]. The diffusion coefficient, D, was calculated from the time dependence of the diffusion curve reduced second moment[1], σ^2, using $D = (1/2)\,\partial\sigma^2/\partial t$.

The value of σ^2 was used as a measure of the width of the macromolecule's distribution $(1/c_0)\,(\partial c/\partial x)$ on displacements x (c_0 is the initial solute concentration) in both diffusion and sedimentation experiments. For symmetric curves with a form close to the Gaussian function, σ values were calculated by the height–area method[5]: $Ha/Q = \Phi(a/\sqrt{8}\sigma)$, where H and Q are maximum height and area of the interference curve, respectively, and Φ is the probability integral. For asymmetric curves, σ values were calculated by the method of moments[1].

Molecular weights (M_{sD}) were calculated by means of the Svedberg equation using the limiting sedimentation coefficient, s_0, the infinite dilution value of the weight-average diffusion coefficient, D, and the buoyancy term[2], $(1 - \bar{v}\rho_0) = 0.52$.

RESULTS AND DISCUSSION

Spreading of the sedimentation boundary with time was used for the determination of the polymer sample

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heterogeneity. The reduced value of the second moment for the sedimentation curve is known to increase with time in accordance with equation (1), valid for concentration-independent velocity sedimentation[6]:

$$\sigma^2 = 2Dt + x_m^2 \omega^4 \sigma_s^2 t^2 \qquad (1)$$

where t is the sedimentation time, $\omega = 2\pi n/60$ is the angular rotor rate, x_m is the distance from rotation axis to boundary and σ_s^2 is the reduced second moment of the sedimentation coefficient distribution. The latter is of interest as its relative magnitude σ_s^2/s_0^2 is the absolute measure of the polymer sample heterogeneity in terms of sedimentation coefficients (here s_0 is the s value at $c = 0$).

In accordance with equation (1), the experimental σ^2 value increases with time. *Figure 1* shows such dependences of σ^2 obtained for dilute CMC solutions at various solute concentrations. For all CMC samples, a strong influence of the solute concentration on the dependence $\sigma^2(t)$ can be observed. With increasing c (for sample 1, for example, when $c \geqslant 0.07$ g dl^{-1}) experimental points fall below the straight line (curve 6 in *Figure 1a*) describing the diffusion spreading of the concentration boundary, i.e. $\sigma^2 \leqslant 2Dt$. This means that at these c values, equation (1) is not obeyed, and the experimental sedimentation data cannot be treated according to the Gralén–Eriksson method[7], for example. Moreover, at solute concentrations when $\sigma^2 \leqslant 2Dt$, extrapolation of the data to infinite time does not lead to the elimination of diffusion effects, in contrast to the generally accepted opinion.

To eliminate concentration and diffusion effects, the standard deviation (root square reduced second moment), σ, for a distribution of displacements was extrapolated

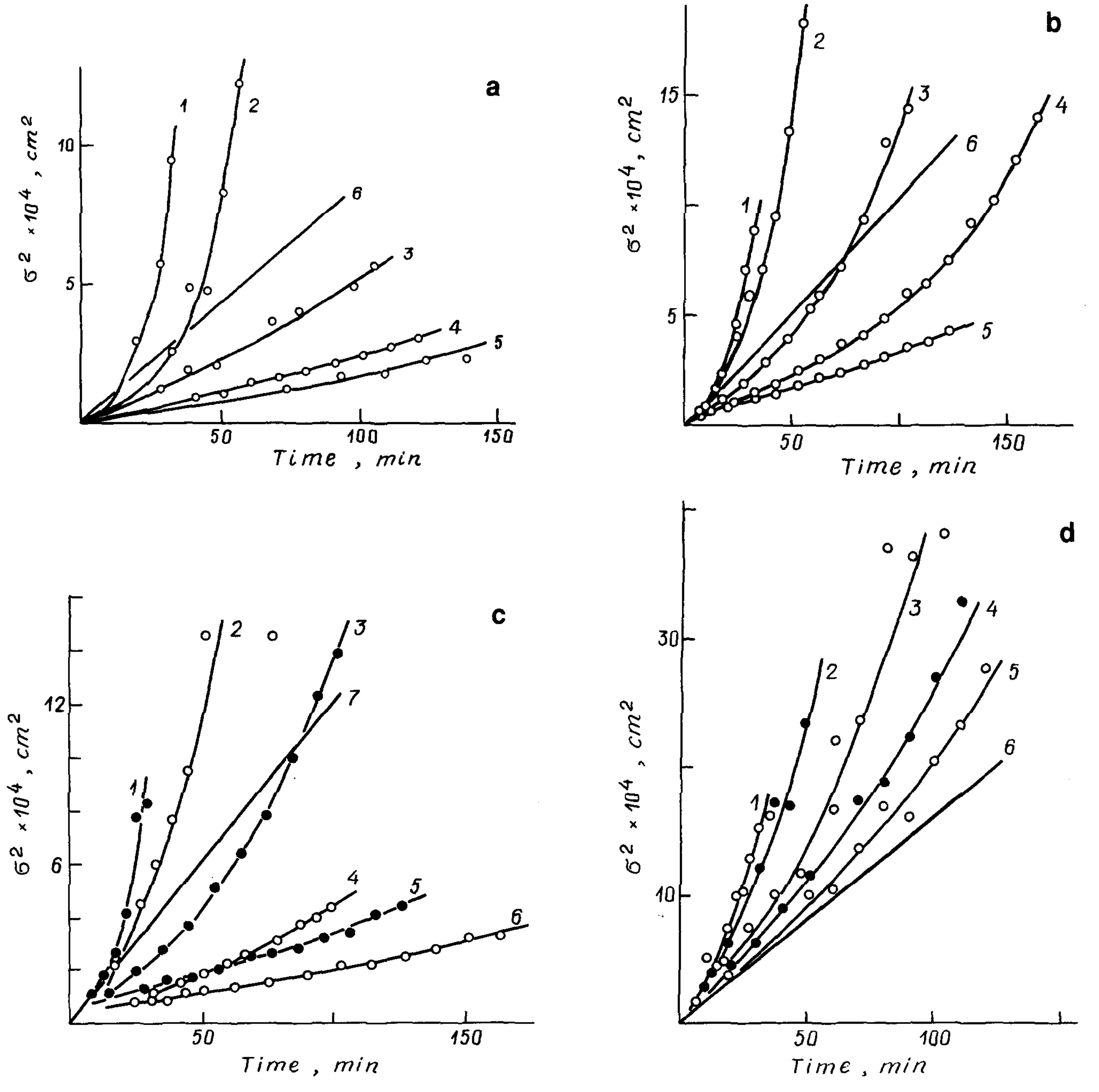

Figure 1 Time dependence of x-spectrum dispersion for the CMC macromolecules dissolved in a mixture of cadoxene and water (1:10) in the ultracentrifuge field at $n = 5 \times 10^4$ rev min^{-1} and various concentrations: (a) sample 1, c = (1) 0.025, (2) 0.050, (3) 0.099, (4) 0.150 and (5) 0.199 g dl^{-1}; (b) sample 2, c = (1) 0.024, (2) 0.050, (3) 0.100, (4) 0.149 and (5) 0.193 g dl^{-1}; (c) sample 4, c = (1) 0.030, (2) 0.060, (3) 0.120, (4) 0.179, (5) 0.240 and (6) 0.295 g dl^{-1}; (d) sample 6, c = (1) 0.02, (2) 0.090, (3) 0.129, (4) 0.175 and (5) 0.215 g dl^{-1}; curves 6 (in a, b and d) and 7 (in c) correspond to diffusion spreading calculated by $\sigma_D^2 = 2Dt$

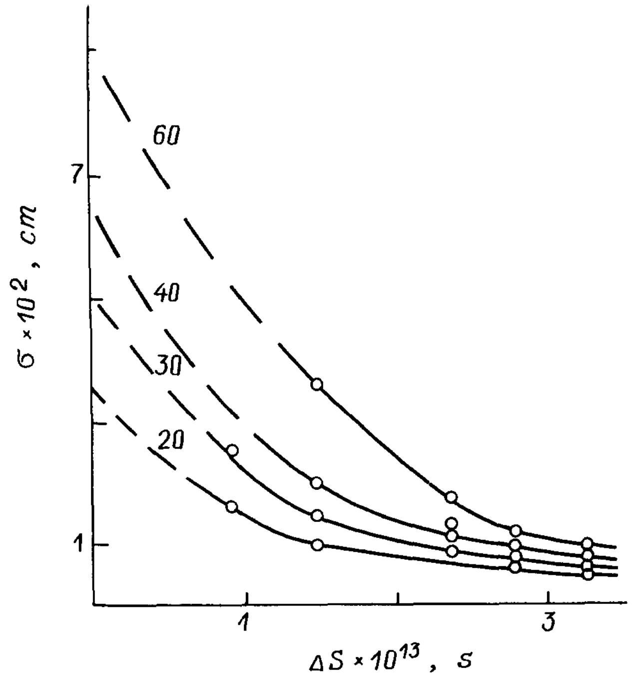

Figure 2 Standard deviation of *x*-spectrum σ *versus* Δs for CMC sample 1; numbers on curves correspond to time moments (in min) from the beginning of experiment

to zero concentration (*Figure 2*) at a few fixed time moments, as proposed in ref. 8, with coordinates σ–Δs ($\Delta s = s_0 - s$, with s the sedimentation coefficient at solute concentration c). It can be seen, however, that for the polymer under investigation the relation between σ and Δs is essentially non-linear over the concentration range studied. This non-linearity obviously leads to a significant error in determination of the ordinate intercept, and hence in the inhomogeneity parameter. Therefore, polydispersity parameters obtained in this way[3] should be considered tentative.

In an attempt to find a more linear approximation, the method proposed in part 1 for the treatment of sedimentation data was used. *Figure 3* shows the dependence of σ on x_m for the same experimental data as in *Figures 1* and *2*. It is clear that the experimental points in *Figure 3* fit more linear dependences than those in *Figure 2*. Each of these dependences could be well approximated by a straight line and characterized by a reliably determined slope, $\partial\sigma/\partial x_m$. A wide collection of experimental data is presented here to illustrate that the linear dependence of σ on x_m is not a rare experimental finding. On the other hand, the existence of the time range with linear $\sigma(x_m)$ dependence is a major requisite for applicability of the method discussed[1].

The slope $\partial\sigma/\partial x_m$ was extrapolated linearly to infinite

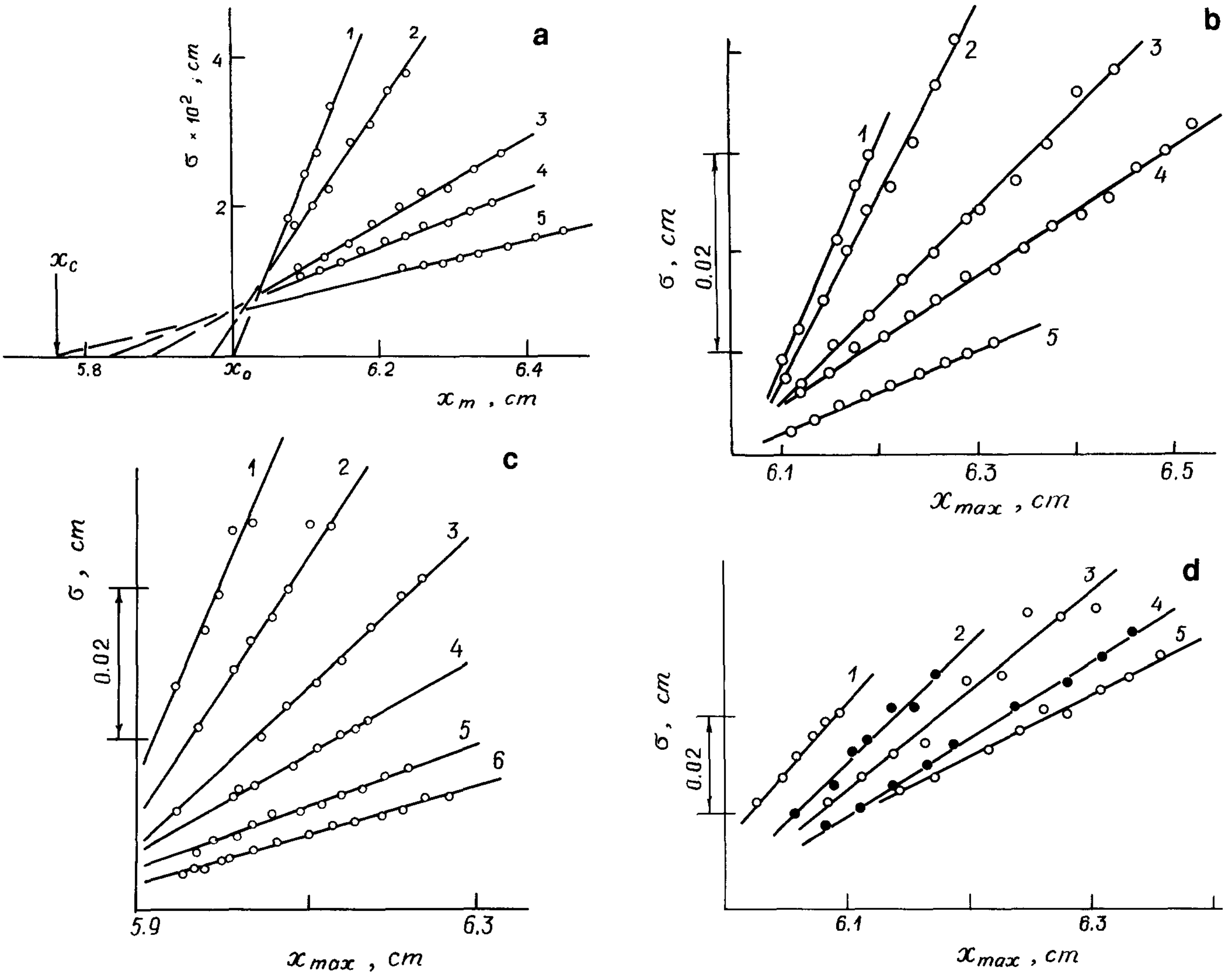

Figure 3 Standard deviation of *x*-spectrum σ for the CMC macromolecules in an ultracentrifugal cell *versus* shift of the sedimentation curve first moment x_m; numbers on curves correspond to those in *Figure 1*

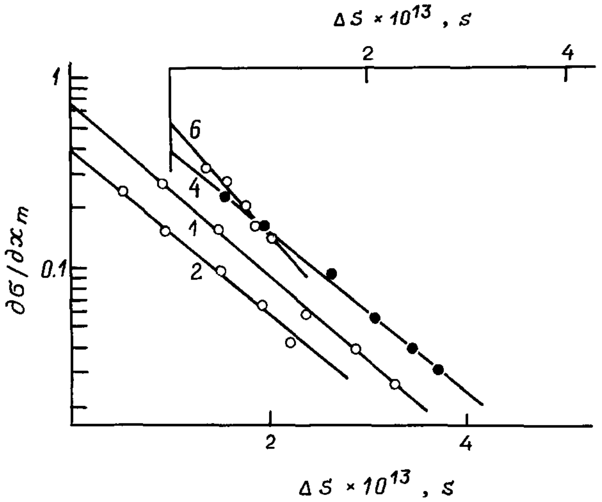

Figure 4 Dependence of $d\sigma/dx_m$ on Δs for CMC samples in a half-logarithmic scale; numbers on curves correspond to the sample numbers in *Table 1*

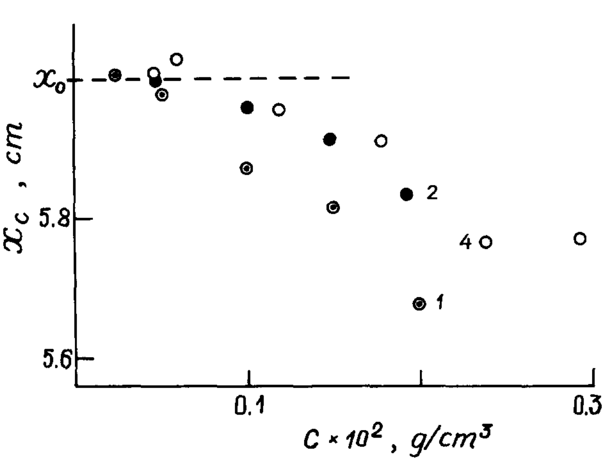

Figure 5 Intercept of dependence $\sigma(x_m)$ with abscissa axis in *Figure 3* as a function of the solute concentration for CMC samples 1 (⊙), 2 (●) and 4 (○)

Table 1 Inhomogeneity characteristics of CMC samples on the sedimentation coefficients σ_s/s_0, molecular weights σ_M/M_w and the values of polymolecularity parameter M_z/M_w

Sample no.	$M_{sD} \times 10^{-3}$	$(\partial\sigma/\partial x_m)_0$	σ_s/s_0	σ_M/M_w	M_z/M_w
1	380	0.66	0.63	1.58	3.50
2	260	0.39	0.37	0.93	1.86
4	230	0.38	0.36	0.90	1.81
6	120	0.50	0.47	1.18	2.39

dilution, as shown in *Figure 4*. The value of $(\partial\sigma/\partial x_m)_0$ unperturbed by concentration effects was obtained as the ordinate intercept and then used in the calculations below.

The standard deviation σ_0 of the displacement distribution, obeying the condition $c=0$, was related to x_m, in linear approximation, by the equation[1]:

$$\sigma_0 = (\partial\sigma/\partial x_m)_0 \, (x_m - x_0) \qquad (2)$$

where x_0 is the value of x_m at $t=0$ coinciding with the meniscus position in this work, where a conventional cell was used. The validity of equation (2) is the second important point in the foundation of the proposed method[1]. Its validity is confirmed by the experimental data in *Figure 3a*, which show that with decreasing solute concentration, the intercept x_c of the abscissa axis with a straight line $\sigma(x_m)$ approaches x_0. A similar regularity was observed for other CMC samples (*Figure 5*). Therefore, x_0 was used as the initial count point, under the condition $c=0$, for all CMC samples, and equation (2) was applied for calculating σ_0.

Note that under the conditions $c=0$, when $\sigma=\sigma_0$, equation (1) is obeyed. Therefore, further calculations of the inhomogeneity parameter were carried out using equation (3) following from equation (1)[1]:

$$\sigma_s^2 = [(\partial\sigma/\partial x_m)_0^2 \, (x_m - x_0)^2 - (2D/\omega^2 s_0) D \log(x_m/x_0)] / [x_m^2 s_0^{-2} \log^2(x_m/x_0)] \qquad (3)$$

Values of σ_s/s_0 were obtained when the average value of the boundary abscissa in experiment was substituted in equation (3) as x_m and the experimental values of ω, s_0, D and $(\partial\sigma/\partial x_m)_0$ were applied. Then, the relative magnitude of MWD dispersion was calculated, assuming that the CMC sample's inhomogeneity on s is due only to inhomogeneity in M, by[9]:

$$\sigma_M^2/M_w^2 = (1-b)^{-2} \sigma_s^2/s_0^2$$

Here b is the coefficient in the equation $s_0 = K_s M_w^{1-b}$, which was found[3] to be equal to $b=0.59$ for this system. The corresponding values of the polydispersity parameter M_z/M_w calculated[8] as $M_z/M_w = (\sigma_M^2/M_w^2) + 1$ are given in *Table 1*.

CONCLUSIONS

The experimental data discussed above show that the system under investigation (monosubstituted CMC in decadiluted aqueous cadoxene) exhibits a linear dependence of the standard deviation for the distribution of the macromolecule displacements during velocity ultracentrifugation on the shift of the sedimentation boundary. This confirms the applicability of a novel method of moments for the characterization of the CMC samples' inhomogeneity. The method utilizes linear approximations and a physically better-founded procedure for the elimination of diffusion spreading than previous methods. Further investigations are required to corroborate the applicability of the relations used above to other polymer systems.

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