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Self-sufficiency of velocity sedimentation for the determination of molecular characteristics of linear polymers[*]

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General possibilities of velocity sedimentation in the hydrodynamic study of macromolecules are discussed. It is shown that, using the mass-spectrometric effect of the ultracentrifuge together with the calculation of molecular weights by means of a recently introduced sedimentation parameter β_s, allows complete analysis of all the macromolecular parameters of polymers by velocity sedimentation only, without additional procedures. The sedimentation parameter is given by $\beta_s = N_a[S]k_s^{1/3}M^{-2/3}$, where $[S] = S_0\eta_0/(1-\bar{v}\rho_0)$ is the intrinsic sedimentation constant, k_s is Gralen's concentration coefficient, M is the molecular weight and N_a is Avogadro's number. In this way molecular weight distributions etc. can be obtained. The validity of the suggested approach is demonstrated on a cellulose nitrate (CN) sample with a substitution degree of 2.7, in acetone. The sample is characterized by the polydispersity index $M_w/M_n = 1.66$ in the molecular weight range $20 \leqslant M \times 10^3 \leqslant 620$. By means of velocity ultracentrifugation, values of the equilibrium rigidity of CN (Kuhn's segment length), $A = (360 \pm 13) \times 10^{-8}$ cm, and of hydrodynamic diameter, $d = (4.8 \pm 0.4) \times 10^{-8}$ cm, are obtained. All data obtained are in good agreement with published data for real fractions of CN in acetone.

(Keywords: velocity sedimentation; sedimentation parameter; molecular weight)

INTRODUCTION

The analysis of dilute solutions by means of velocity sedimentation gives the opportunity to determine two hydrodynamic characteristics which depend differently on the size, shape and molecular weight of the sedimenting particles. The first value is the sedimentation coefficient[1] extrapolated to zero concentration:

$$S_0 = \frac{(1-\bar{v}\rho_0)}{N_a}\frac{M}{f_0} \qquad (1)$$

where $(1-\bar{v}\rho_0)$ is the buoyancy factor characteristic for the given polymer–solvent system, N_a is Avogadro's number, M is the molecular weight of the sedimenting particles and f_0, the transitional friction coefficient of the macromolecules, is given by:

$$f_0 = P_0\eta_0(\overline{h^2})^{1/2} \qquad (2)$$

with η_0 the solvent viscosity, $P_0 = \lim P(L \to \infty)$ the Flory dimensionless hydrodynamic parameter and $(\overline{h^2})^{1/2}$ the mean-square distance between chain ends. In the general case[2] $P = P(L/A;\ d/A;\ \alpha)$, L being the contour length of a chain, d its effective diameter, A Kuhn's statistical segment length and α Flory's swelling parameter. The limiting value of P_0 also depends on the way in which the hydrodynamic interactions in the polymer chain are calculated[2-4]. The value $P_0 = 5.11$, obtained on the basis of a preliminary averaging of the hydrodynamic interaction tensor, is usually employed.

The second characteristic obtained from the velocity sedimentation experiment is Gralen's coefficient k_s, determined from[2,5]

$$S^{-1} = S_0^{-1}[1 + (k_s + \bar{v})c + \ldots] \qquad (2a)$$

where $\bar{v}$ is the polymer specific partial volume.

There is a set of theories describing the concentration dependence of S for hard spheres[6-9] as well as for different models of real macromolecules[2,10-16]. In the latter theories a dependence on the thermodynamic quality of the solvent must be considered. In θ conditions all the theories converge to the expression

$$k_s = \Lambda \frac{N_a}{M} V_h$$

where V_h is the hydrodynamic volume of the macromolecule and Λ is a dimensionless coefficient that depends on the models and mathematical approaches used in these theories.

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[*] This paper is dedicated to V. N. Tsvetkov, member of the Russian Academy of Sciences, on the occasion of his 85th birthday

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Expressing V_h through $(\overline{h^2})$, using the concept of a hydrodynamically equivalent sphere, gives

$$V_h = (4\pi/3)(P/6\pi)^3(\overline{h^2})^{3/2}$$
$$= 2^{-8}\pi^2(3\pi/2)^{1/2}(\overline{h^2})^{3/2}$$

and

$$k_s = B\frac{(\overline{h^2})^{3/2}}{M}$$
$$B = 2^{-8}\pi^2(3\pi/2)^{1/2}N_a\Lambda \qquad (3)$$

where B is a parameter that depends, in the general case, on hydrodynamic interactions in the sedimenting system and on the thermodynamic quality of the solvent; $B = B(L/A, d/A, \alpha)$. In addition, in principle, a dependence on the angular speed of the rotor is not excluded.

Analysis of k_s is usually carried out following Newman and Eirich[17], when a dimensionless parameter $\gamma \equiv k_s/[\eta]$ ($[\eta]$ being the intrinsic viscosity) is calculated. For flexible-chain molecules in thermodynamically good solvents $\gamma = 1.7$ (refs 17 and 18) but, when volume effects are absent, as a rule $\gamma < 1$ (refs 19 and 20). The value of γ is used as a measure of the asymmetry of sedimenting particles[19,21] or as an extent of interpenetration of macromolecules[22].

From the Flory equation for intrinsic viscosity

$$[\eta] = \Phi(\overline{h^2})^{3/2}/M \qquad (4)$$

and equation (3) the expression $\gamma = B/\Phi$ follows, if the character of averaging $(\overline{h^2})$ and M is the same in both formulae.

Much more informative, however, is a direct comparison of S_0 and k_s obtained from the same series of sedimentation experiments. Wales and van Holde[18] first pointed out this fact, suggesting the following formula for the determination of M when S_0 and k_s are measured

$$M_{ks} = 9.19 \times 10^{24}[S]^{3/2}k_s^{1/2} \qquad (5)$$
$$[S] = S_0\eta_0/(1 - \bar{v}\rho_0)$$

In that paper[18] Flory's formula (4) was used to obtain the expression (5). However, it is evident from the correlation of equations (1)–(3) that there is no need for use of the intrinsic viscosity to get the expression (5).

As a consequence of an analogy with the hydrodynamic invariant[23–26]

$$\beta \equiv A_0/k \equiv N_a[S][\eta]^{1/3}M^{-2/3}$$

one can introduce[27,28] a sedimentation parameter

$$\beta_s = B^{1/3}P^{-1} = N_a[S]k_s^{1/3}M^{-2/3}$$

and use it in a similar way to β to yield a generalization of expression (5):

$$M_{ks} = (N_a/\beta_s)^{3/2}[S]^{3/2}k_s^{1/2} \qquad (6)$$

The analysis of extensive experimental data[29–32] permitted us to establish the true invariance of this parameter with respect to the contour length of the macromolecule (i.e. M) and the structure of the repeating chain unit. The values are $\beta_s = (1.25 \pm 0.14) \times 10^{-7}$ mol$^{1/3}$ for flexible-chain polymers in thermodynamically good solvents and $\beta_s = (1.00 \pm 0.08) \times 10^{-7}$ mol$^{1/3}$ for rigid-chain and flexible-chain polymers under θ conditions. It may be noted that similar small but systematic divergences are observed for β or A_0 (ref. 26). For cellulose, its derivatives and some polysaccharides, the mean value $\beta_s = (1.00 \pm 0.18) \times 10^7$ mol$^{1/3}$ was obtained.

Hence when two values, S_0 and k_s, are determined in one series of experiments, it is possible to calculate a hydrodynamic average molecular weight M_{ks} by using equation (6).

Furthermore, the distribution of polymer sedimentation coefficients that is obtained by the usual method and corresponds to finite solution concentrations can be extrapolated to infinite dilution by using the well-known 'graphic fractionation' approach[33,34]. The extrapolated straight lines corresponding to 'graphic fractions' are used to determine the S_0 and k_s values for these 'fractions' and to calculate their M_{ks}. In other words, the distributions with respect to sedimentation constants may be transformed into those for molecular weights. The known values of S_0 and M_{ks} of 'graphic fractions' are used to determine the parameters of equations of the Kuhn–Mark–Houwink type. When the appropriate hydrodynamic theories are applied to a set of 'graphic fractions', in a series of polymer homologues, one can determine the length of the Kuhn segment A and the effective hydrodynamic chain diameter d.

Hence, a series of experiments using exclusively the velocity sedimentation of solutions of several concentrations of an unfractionated polymer sample turns out to be sufficient for a complete analysis of the hydrodynamic and conformational properties of the macromolecules.

EXPERIMENTAL

We will illustrate the feasibility of this approach using as an example the sedimentation investigations of a high molecular weight sample of cellulose nitrate (CN) in acetone. This choice is based on three factors. First, the high values of S_0 in this system ensure general reliability of the data. Second, highly substituted CNs in acetone are fairly well investigated. Therefore, the results of the suggested analysis can be compared with published data and thus enable us to estimate the correctness of our evaluations. Third, there is much current interest in cellulose derivatives because of the great practical value of such polymers.

Sedimentation experiments were carried out in an analytical MOM 3170 ultracentrifuge with a one-sector or two-sector cell with an aluminium insert of $h = 30$ mm in length. The rotor speed was $n = 40\,000$ rev min^{-1}. The sedimentation boundary was observed by means of a Philpot–Swensson optical system. The average experimental time was 40–60 min. The temperature was kept constant to within ± 0.1°C during each experiment. The average temperature of the whole series was (18.6 ± 0.8)°C. Variations in temperature in different experiments were taken into account in the usual way by assuming the constancy of the characteristic sedimentation coefficient.

Previous investigations of this sample have shown its homogeneity with respect to the degrees of substitution of fractions[35]. The average degree of substitution for fractions is 2.70 ± 0.14, which is in agreement with the value 2.65 ± 0.06 obtained for an unfractionated sample. For the sample investigated here the following characteristics were obtained in acetone at 18°C: $S_0 = 16.1$ Svedberg units, $k_s = 353$ cm^3 g^{-1}, coefficient of translational diffusion $D_0 = 2.15 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$, $[\eta] = 840\,\mathrm{cm^3\,g^{-1}}$, $M_{sd} = 312000$, $(1-\bar{v}\rho_0) = 0.58$, $\eta_0 = 0.331 \times 10^{-2}$ Poise. The values of the hydrodynamic invariants

$$A_0 = (R[D]^2[S][\eta])^{1/3}$$

and

$$\beta_s = N_a(R^{-2}[D]^2[S]k_s)^{1/3}$$

where R is the universal gas constant and $[D] = D_0\eta_0/T$, were also obtained. They are $A_0 = 3.37 \times 10^{-10}$ erg $\mathrm{deg^{-1}\,mol^{-1/3}}$ and $\beta_s = 0.85 \times 10^7\,\mathrm{mol^{1/3}}$ and are close to those obtained for other cellulose derivatives[31,36].

The use of a thick rotor and cells with $h = 30$ mm made it possible to study sedimentation in the range of low concentrations at values of the refractive index increment of $dn/dc = 0.10\,\mathrm{cm^3\,g^{-1}}$ (ref. 37). In a reliable range ($c_{max}/c_{min} > 3$) for all investigated concentrations the condition $c[\eta] < 1$ was fulfilled.

RESULTS AND DISCUSSION

Integral distributions of sedimentation coefficients depending on time, $G(S, t)$, were calculated from differential distributions $dn/dx(x)$ taking into account sectorial dilution for concentrations of 3.0, 4.6, 6.3, 8.1 and $9.8 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$. Diffusion effects were eliminated by the extrapolation of $G(S, t)$ to $t^{-1} = 0$.

Figure 1 shows the dependences $S^{-1}(c)$ corresponding to the procedure of 'graphic fractionation'. The values of S_0 and k_s of 'graphic fractions' were determined from the dependences of S^{-1} on c in *Figure 1*, and these values were used to calculate molecular weights M_{ks} (*Table 1*). The calculations of S_0 and k_s were carried out by the least-squares method, the mean-square errors were calculated from linear correlation coefficients r_i[38]. The mean-square errors of M_{ks} were calculated from ΔS_0 and Δk_s.

The curve in *Figure 2* describes the molecular weight distribution $G(M_{ks})$ obtained from the sedimentation of an unfractionated sample of CN in acetone. Molecular weights of different types of averaging (the 'q-averages'[34] and the parameters characterizing the width of the distribution are as follows:

$$M_n = 146\,000, \quad M_w = 245\,000, \quad M_z = 340\,000,$$
$$M_w/M_n = 1.66, \quad M_z/M_w = 1.39$$

The fulfilment of the condition $2 - M_n/M_w = M_z/M_w$ is characteristic of Shulz's distribution which is a special form of Γ distribution[34].

On the basis of the results given in *Table 1*, it is possible to plot the dependences k_s–S_0 and S_0–M for 'graphic fractions' on a double logarithmic scale (*Figure 3*). These dependences are known to be described by the equations of the Kuhn–Mark–Houwink type

$$S_0 = K'M^{1-b} \tag{7}$$

$$k_s = K''S_0^{æ} \tag{8}$$

K', K'', $1-b$ and æ being constants for a given system.

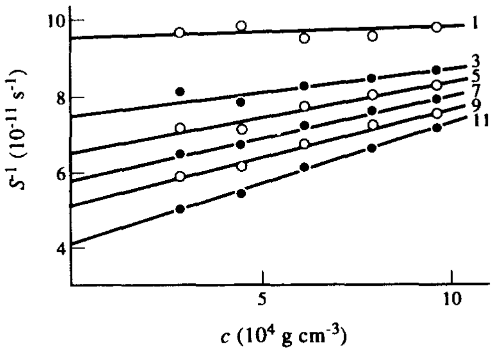

Figure 1 Extrapolation of distributions of the sedimentation coefficients of CN solutions in acetone to $c = 0$; $G(S_0) = 0$ (1), 0.2 (3), 0.4 (5), 0.6 (7), 0.8 (9), 1.0 (11)

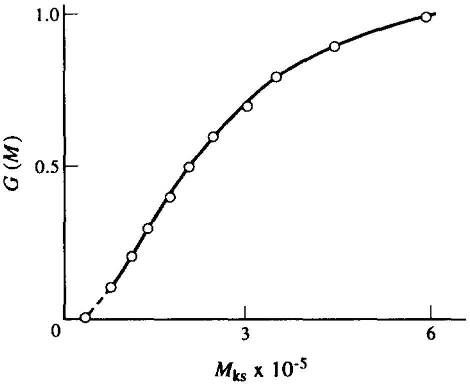

Figure 2 Molecular weight distribution of an unfractionated sample of highly substituted CN

Table 1 Values of S_0, k_s and M_{ks} of 'graphic fractions' of CN in acetone

$G(S)$	S_0 (Svedberg units)	ΔS_0 (Svedberg units)	k_s ($\mathrm{cm^3\,g^{-1}}$)	Δk_s ($\mathrm{cm^3\,g^{-1}}$)	$M_{ks} \times 10^{-3}$	$\Delta M/M$
0	9.6	0.2	12	40	20	–
0.1	11.2	0.3	77	35	63	0.25
0.2	12.1	0.3	130	40	93	0.17
0.3	13.1	0.6	190	60	125	0.18
0.4	14.4	0.6	280	65	177	0.13
0.5	15.2	0.6	320	60	204	0.11
0.6	16.1	0.7	370	60	242	0.10
0.7	17.5	0.7	470	60	308	0.09
0.8	18.9	0.7	570	60	377	0.08
0.9	20.2	0.7	670	60	456	0.07
1.0	23.3	0.5	820	35	621	0.04

Moreover, as shown previously[29]

$$æ = (3b - 1)/(1 - b) \qquad (9)$$

In our case, dependences (7) and (8) exhibit a definite tendency towards a change in a slope on passing into the range of low M even if a first 'graphic fraction' is disregarded. The character of this change corresponds to the case of draining macromolecules in the absence of volume effects[36,39,40]. This character of Kuhn–Mark–Houwink dependences (scaling dependences) is manifested particularly clearly when the $[\eta]$–M dependences are compared[36], but was also observed in an investigation carried out in a wide M range of real polymer fractions with very rigid chains and when S_0–M dependences were compared (see, for example, ref 30). It should be noted that this shape of dependences of friction characteristics on M is probably one of the few convincing criteria (if not the only rigorous criterion in the framework of hydrodynamic investigations) for the draining of molecules, i.e. the criterion for their assignment to the class of rigid-chain polymers.

In this case the slope of the S_0–M dependence decreases on passing to the range of relatively low M. This agrees with an increase in slope of the k_s–S_0 dependence according to equation (8) on passing to the range of low S_0. In the latter case the change in slope, in principle, is more pronounced. The data shown in *Figure 3* may be tentatively divided into two ranges: $S_0 > S^*$ and $S_0 < S^*$ where $S^* \approx 13$ Svedberg units. Now it is possible to calculate the coefficients in equations (7) and (8) from the results listed in *Table 1*. It is known that in the analysis of the contour of sedimentation diagrams the regions with great errors are those close to the so-called 'tails' of distributions. Hence, in the analysis, statistical weight $\xi = 0.2$ was ascribed to the limiting 'graphic fractions', whereas for other 'graphic' and all real fractions ξ was assumed to be unity. The calculations of coefficients were carried out by the least-squares method. The results of this processing are given in *Table 2* along with the results of the processing of literature data on the investigation of CN in acetone[41–48] (*Figure 4*). In this case the average value of $\bar{v} = (0.54 \pm 0.03)\,\mathrm{cm^3\,g^{-1}}$ obtained according to data in refs 41–48 was taken for the specific partial volume. *Table 2* requires the following extrapolations.

The concentration coefficients of sedimentation k_s for real fractions have been determined only in ref. 41 (see also ref. 37) at $S > S^*$. Satisfactory agreement is observed between the æ values obtained for real and 'graphic'

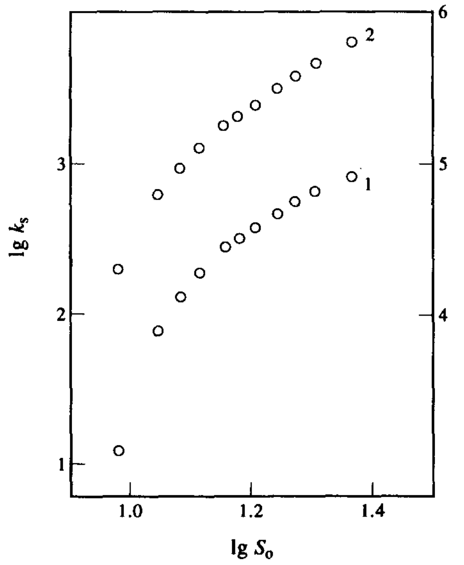

Figure 3 Logarithmic dependences k_s–S_0 (1) and S_0–M (2) for 'graphic fractions' of CN in acetone

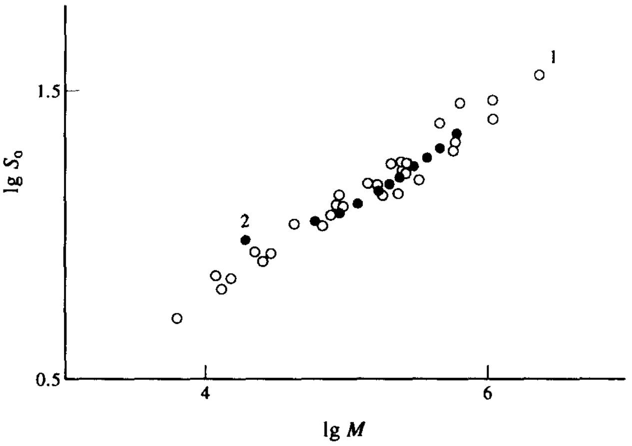

Figure 4 Logarithmic dependence S_0–M for solutions of CN in acetone according to data in refs 42–48 (1) and for 'graphic fractions' (2)

Table 2 Coefficients of the Kunh–Mark–Houwink type equations for highly substituted CN in acetone

Correlating characteristics	b_i[a]	$\pm\Delta b_i$	$\lg K_i$	$\pm\Delta \lg K_i$	n[b]	r_i	Ref.
	$S_0 > S^*$						
k_s–S_0	2.3	0.4	−0.3	0.5	11	0.8764	37, 41
k_s–S_0	2.5	0.1	−0.43	0.1	7	0.9964	Present paper
S_0–M	0.22	0.10	0	0.6	12	0.5298	37, 41
S_0–M	0.36	0.03	−0.69	0.20	20	0.9276	42–48
S_0–M	0.364	0.007	−0.75	0.04	7	0.9992	Present paper
	$S_0 < S^*$						
k_s–S_0	7.7	0.5	−6.2	1.1	4	0.9601	Present paper
S_0–M	0.18	0.03	+0.20	0.10	4	0.9792	Present paper
S_0–M	0.32	0.02	−0.50	0.10	14	0.9807	42–48

[a] $b_i \equiv æ_i$, or $b_i \equiv 1 - b$

[b] n = the number of points from which the parameters of dependences (7) and (8) were determined

Table 3 Evaluation of equilibrium rigidity and hydrodynamic chain diameter of highly substituted CN in acetone

Fraction	Slope $\times 10^{15}$	Intercept $\times 10^{13}$	$(A \pm \Delta A)$ $\times 10^8$ (cm)	$(d \pm \Delta d)$ $\times 10^8$ (cm)	n	r	Ref.
Real	2.1 ± 0.2	6.5 ± 1.0	410 ± 60	3.5 ± 1.4	27	0.9485	42–48
'Graphic'	2.19 ± 0.04	5.4 ± 0.2	360 ± 13	4.8 ± 0.4	10	0.9985	Present paper

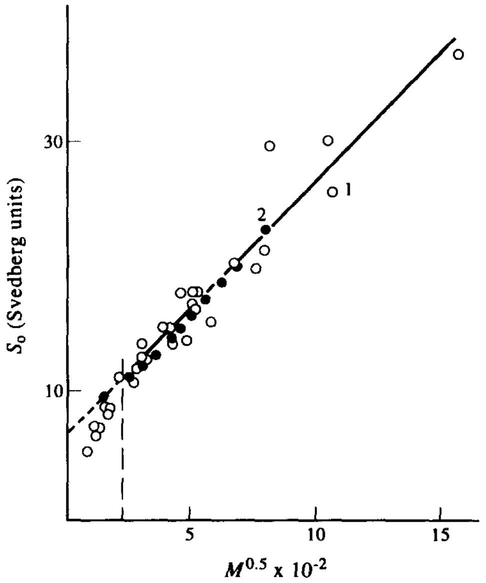

Figure 5 Dependence of S_0 on $M^{1/2}$ for solutions of CN in acetone according to data in refs 42–48 (1) and for 'graphic fractions' (2)

fractions. However, when S_0 and M_{sd} values reported in ref. 41 are compared, their weak correlation is quite apparent ($r = 0.5298$). Moreover, analysis of the results in ref. 41 shows that exponents æ and $1-b$ do not agree with one another as they should in accordance with equation (9). In our opinion, the uncertainty of the results reported in ref. 41 is not due to errors in the sedimentation data of this work. In further interpretation based on the comparison of S_0 and M_{sd}, the data of ref. 41 were excluded.

The comparison between S_0 and M values obtained in other papers for real fractions 42–48 and 'graphic fractions' investigated in the present paper shows satisfactory agreement between the coefficients of the corresponding scaling equations at $S > S^*$. At relatively low S values, the data on k_s for real fractions are absent. The comparison of scaling exponents for the S_0–M dependence in the two tentative ranges of $S(M)$ reveals a weaker tendency towards the change in slope for real than for 'graphic' fractions (*Figure 4*). This may be caused by various factors. First, as already mentioned, by a large error in the determination of the characteristics of distribution 'tails', in particular those of the first 'graphic fraction'. Furthermore, real CN fractions investigated by different authors could have different degrees of substitution. This M range requires further investigation.

However, the fact that cellulose derivatives belong to the class of rigid-chain polymers has already been established by Flory and co-workers[49,50] and generalized by others[36,51]. Therefore, it is possible to calculate the conformational characteristics of CN on the basis of modern theories of translational friction of persistent chains in the absence of volume effects[36,39]. The results of these theories in the range $L/A \geqslant 2.3$ are described by the equation

$$S_0 = \frac{1-\bar{v}\rho_0}{\eta_0}\,\frac{1}{P_0 N_a}\left\{\left(\frac{M_L}{A}\right)^{1/2} M^{1/2} + \frac{P_0 M_L}{3\pi}[\ln(A/d) - \varphi(0)]\right\} \qquad (10)$$

where $M_L = M_0/\lambda$ is the mass of unit length of CN and $\varphi(0) = 1.056$ (ref. 39). For cellulose and its derivatives we have $\lambda = 5.15 \times 10^{-8}$ cm and, for CN with a means degree of substitution $y = 2.7 \pm 0.2$, the average molecular weight of the repeating unit is $M_0 = 284 \pm 9$.

The plot corresponding to equation (10) is shown in *Figure 5*. The broken line describes the region of $L/A = 2.3$. The data for fractions with molecular weights that correspond to the range of $L/A < 2.3$ ($M < 50\,000$) were not taken into account in the calculations. The plots for real and 'graphic' fractions were processed separately. The results given in *Table 3* show that the values of both A and d obtained for the two systems of data are in satisfactory agreement.

SUMMARY

This work illustrates the self-sufficiency of velocity ultracentrifugation (as a practically absolute method) for the hydrodynamic investigation of at least fast-sedimenting macromolecules. It is shown that the ability of a centrifuge to operate as a mass spectrometer combined with the application of the sedimentation parameter β_s for the calculation of molecular weights makes it possible to analyse the hydrodynamic and molecular properties of the polymer without using additional methods and without preliminary fractionation (only the knowledge of $1-\bar{v}\rho_0$ and η_0 is required). In this case the following parameters may be obtained: molecular weight distribution, molecular weights of different averaging types, the constants of the Kuhn–Mark–Houwink type equations for the coefficients S_0 and k_s, the length of Kuhn's segment, and the effective hydrodynamic diameter of the molecular chain.

The hydrodynamic and molecular characteristics of CN in acetone determined by the suggested method are in agreement with literature data based on the analysis of real fractions.

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