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ARTICLE

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The concentration dependence of sedimentation for polysaccharides

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Abstract The relationship between the sedimentation coefficient s_0 and its concentration coefficient k_S obtained in experiments on velocity sedimentation for polysaccharides is discussed. The values of s_0, k_S and an independently determined molecular weight reported by different authors for different polysaccharides are considered. It was established that the scaling relation. $k_S \sim s_0^{\nu}$ unambiguously relates to the scaling relation $s_0 \sim M^b$. The values of the sedimentation parameter β_S introduced on the basis of Svedberg's equation for s_0 and on the basis of the expression $k_S = B \langle h^2 \rangle^{3/2} M^{-1}$ are discussed and the generalized Wales-van Holde-Rowe equation $M_{KS} = (N_A/\beta_S)^{3/2} [s]^{3/2} k_S^{1/2}$ is used for evaluation of the molecular weights of polysaccharides. The adequacy of this evaluation is illustrated by taking as an example the determination of the unit length weight of an extra-rigid polysaccharide chain and of the equilibrium rigidity of rigid-chain, semi-rigid-chain and flexible-chain polysaccharides. The pair of experimental values s_0 and k_S obtained in a single series of experiments give the same information as may be obtained from the other pairs of hydrodynamic values such as $[\eta]$ and s_0 or $[\eta]$ and D_0, where $[\eta]$ is the intrinsic viscosity and D_0 is the translational diffusion coefficient.

Introduction

Polysaccharides are an important class of biopolymers which contribute to the characteristics of existing forms of life as we know them. They are also an increasingly important source of chemical raw materials. The polysaccharides are a group of macromolecules showing a variety of possible architectures. Among the polysaccharides one can find flexible and rigid molecules; linear and branched; uncharged and charged; homo- and hetero-molecules. The conformational states of polysaccharides are the result of:

1. the particular features of their primary structure; i) the type of pyranose ring bonding, ii) variations in the arrangement of OH groups, iii) the presence of different substituents of OH groups;
2. the formation of multistrand helical structures with maximum attainable chain rigidity.

Therefore to study the polysaccharides is equivalent in essence to studying the general problems of polymer and biopolymer science. In the present article we demonstrate the potential of the study of the concentration dependence of velocity sedimentation for the investigation of linear polysaccharides. Some useful information about the sedimentation analysis of polysaccharides may be obtained from the reviews of Pavlov (1989, 1995); Harding (1992, 1995) and Lavrenko et al. (1992).

Viscometry, isothermal translational diffusion, and velocity sedimentation are the most widespread methods of molecular hydrodynamics used in the study of the molecular characteristics of polymers including polysaccharides (Svedberg and Pedersen 1940; Tanford 1961; Tsvetkov et al. 1970; Cantor and Schimmel 1980). These methods are used for the determination of intrinsic viscosity $[\eta]$, the translational diffusion coefficient D_0 and the sedimentation coefficient s_0 – parameters which are characteristic for an individual macromolecule. The consideration of any of these values *without* comparison with molecular weight M provides only limited and qualitative information about the macromolecule. Quantitative information can be obtained by the consideration of any pair of these values. In sedimentation-diffusion analysis the s_0–D_0 pair is used in the well-known Svedberg equation (Svedberg and Pedersen 1940) obtained on the assumption that the frictional coefficients f of the macromolecule are the same in the sedi-

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mentation (f_S) and diffusional (f_D) transport modes ($f_S = f_D$):

$$M_{SD} = (RT/(1-\bar{v}\rho_0))\,(s_0/D_0) \qquad (1)$$

Here $(1-\bar{v}\rho_0)$ is the buoyancy factor of the polymer-solvent system. This is one of only a few absolute methods for the determination of the molecular weight of polymers.

Two other pairs $[\eta]$–s_0 and $[\eta]$–D_0 require not only the assumption that the chain size during M measurement is constant but also the use of an assumed hydrodynamic invariant (Mandelkern and Flory 1952; Tsvetkov and Klenin 1953)

$$A_0/k \equiv \beta = N_A\,[s][\eta]^{1/3} M^{-2/3} = [D]\,k^{-1}\,(M\,[\eta])^{1/3} \qquad (2)$$

where $[s] \equiv s_0\eta_0/(1-\bar{v}\rho_0)$; $[D] \equiv \eta_0 D_0 T^{-1}$, η_0 is the solvent viscosity, and k is the Boltzmann constant. β is known popularly as the in "Scheraga and Mandelkern" (1993) parameter.

Analysis shows (Tsvetkov et al. 1984) that in the first approximation the parameter A_0 is invariant with respect to M, the Kuhn segment length A (or persistence length a), and the thermodynamic quality of the solvent.

The use of $[\eta]$, s_0, D_0 requires that the experimentally determined values be extrapolated to zero concentration of polymer c. In this case we have (Yamakawa 1971)

$$\begin{aligned} \eta &= \eta_0(1 + [\eta]\,c + k_{1\eta}c^2 + \ldots) \\ D &= D_0(1 + (2A_2M - (k_S + \bar{v}))\,c + \ldots) \qquad (3) \\ s^{-1} &= s_0^{-1}\,(1 + (k_S + \bar{v})\,c + \ldots) \end{aligned}$$

where η and η_0 are the dynamic viscosity of solution and solvent, A_2 is the second thermodynamic virial coefficient; $k_{1\eta}$; k_S are the concentration coefficients and $\bar{v}$ is the specific partial volume of the polymer. All the concentration coefficients of Eq. (3) contain molecular information. The most useful is the viscosity first concentration coefficient $[\eta]$, the so called intrinsic viscosity.

In this paper we consider the concentration sedimentation coefficient k_S in relation to the sedimentation coefficient.

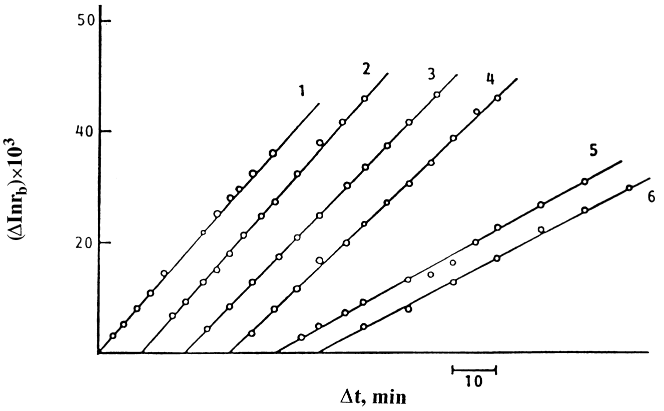

Fig. 1 Sedimentation coefficients for pullulan samples in water. 1–4-sample with $M_{SD} = 644\times10^3$ at the concentrations (g/cm^{-3}) $\times10^4$: (*1*) 4.7; (*2*) 6.6; (*3*) 11.5; (*4*) 14.8, and for sample with $M_{SD} = 87\times10^3$ at the concentrations: (*5*) 9.6; (*6*) 19.6

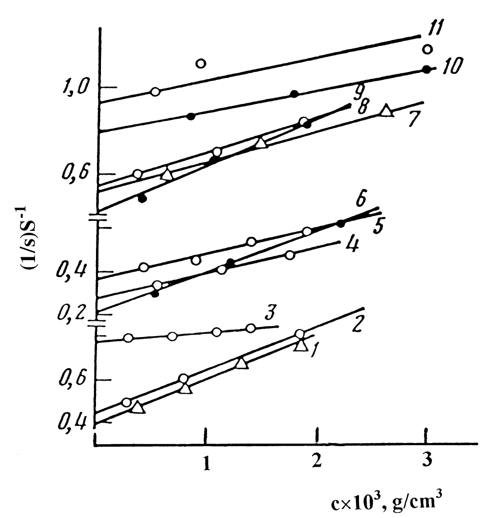

Fig. 2 Concentration dependencies of sedimentation coefficients of chitosan fractions in buffered solvent 0.33 M CH_3COOH + 0.3 M NaCl at 25 °C for the fractions with following $M_{SD}\times10^{-3}$: (*1*) 135; (*2*) 172; (*3*) 35; (*4*) 68; (*5*) 80; (*6*) 137; (*7*) 75; (*8*) 78; (*9*) 104; (*10*) 24; (*11*) 13

Earlier treatments

Figure 1 shows typical dependencies used for the definition of the sedimentation coefficient:

$$s = \Delta \ln r_b/\omega^2 \Delta t \qquad (4)$$

where r_b is the position of the sedimentation boundary at time t (s) and ω is the angular velocity (rad × s^{-1}). Figure 2 shows extrapolation plots corresponding to Eq. (2). The values of s should be reduced to the same temperature (Tanford 1961; Tsvetkov et al. 1970).

At $s < 3$ svedbergs, reliable results can be obtained by using sedimentation cells with an artificial boundary. For obtaining reliable values of s_0 and particularly of k_S, the concentration range investigated should be broad. The upper concentration limit is determined by the "dilute solution" condition that can be described in the following form: $c < [\eta]^{-1}$ (this is the so-called Debye criterion, see for instance (Tsvetkov et al. 1970); the lower concentration limit is determined by the sensitivity of the optical system used for recording the sedimentation boundary. Refractometric methods for recording the data are used most often in the investigation of polymers (including polysaccharides). The most sensitive among these is the method of polarizing interferometry (Tsvetkov et al. 1970; Tsvetkov 1989).

In some cases in the determination of the value of $s_0 = \lim_{(c\to0)} s$ it is necessary to take into account the effects of radial dilution and hydrostatic pressure.

The value of k_S is usually related to the value of $[\eta]$ and the result is considered as an analogue of the Huggins parameter by the ratio $k_S/[\eta]$ (Newman and Eirich 1950). Subsequently this parameter ($k_S/[\eta]$) has been used for excluding concentration effects for other fractions of the system under investigation. For flexible-chain molecules in thermodynamically good solvents $k_S/[\eta] \cong 1.7$ (Wales and van Holde 1954), when volume effects are absent; for rigid-chain molecules as a rule $k_S/[\eta] < 1$ (Creeth and Knight 1965; Skazka and Jamtschikov 1973; Lavrenko et al. 1977). The value of $k_S/[\eta]$ can be used as a measure of the asymmetry of sedimenting particles (Creeth and Knight 1965; Harding and Rowe 1982; Harding 1995) or as an extent of degree of draining of a macromolecular coil (Skazka and Jamtschikov 1973).

As was first shown by Wales and van Holde (1954), the comparison of s_0 and k_S also makes it possible to estimate the molecular weight of polymer chains by the following relation:

$$M = 4.85\pi N_A [s]^{3/2} k_S{}^{1/2} \tag{5}$$

A re-examination of this problem from an original theoretical standpoint was carried out by Rowe (1977). The definitive result for the sedimentation of solvated molecules is given in the following equations:

$$M = N_A (6\pi)^{3/2} [s]^{3/2} \{(3\bar{v}/4\pi)[(k_S/2\bar{v}) - (v_S/\bar{v})]\}^{1/2} \tag{6}$$

where v_S, following Rowe, is the specific volume occupied by the sedimenting component (solute + entrained solvent + bound solvent). Rowe gave the following approximation for the ratio $v_S/\bar{v}$:

$$v_S/\bar{v} = k'[\eta]/k_S = k'(k_S/[\eta])^{-1} \tag{7}$$

where k' is the Huggins parameter. For most polymer systems (and for polysaccharides also) the second term in brackets (Eq. (6)) is negligible in comparison with the first one, so Eq. (6) can be rearranged as:

$$M \cong 9\pi N_A [s]^{3/2} k_S^{1/2} \tag{8}$$

(Equations (5) and (8) differ only by numerical coefficients and for some comparative purposes (scaling relation, for instance) can give the same results.)

Equation (8) has been applied to the determination of the molecular weight of cellulose nitrate (Pavlov and Frenkel 1983), myosin filaments (Persechini and Rowe 1984) and soluble chitin derivatives (Pavlov and Selunin 1986).

The Wales-van Holde-Rowe equation (5 and 8) is presented in the general form (Pavlov and Frenkel 1986, 1988, 1995) with the introduction of the sedimentation parameter β_S:

$$\beta_S = N_A [s] k_S^{1/3} M^{-2/3} \tag{9}$$

A comparison of Eqs. (2) and (9) shows the analogy existing between the hydrodynamic invariant β (or A_0) and the sedimentation parameter β_S. Obviously this analogy reduces to the analogy between $[\eta]$ and k_S values. At the same time these equations expose the fundamental difference existing between them. This difference consists of the following. The value β is obtained from M and from two experimental values s_0 and $[\eta]$ which in turn are obtained in different kinds of experiments, where the macromolecule carries out different kinds of movement: translational (s_0) and rotational ($[\eta]$). The sedimentation parameter β_S is obtained from M and two experimental values s_0 and k_S obtained in a single series of experiments where the macromolecule is under exactly the same conditions. The reason for introducing the sedimentation parameter was the extension of experimental data available in the literature to linear uncharged polymers, both synthetic and natural. The present work considers the literature data on molecular hydrodynamics of the solutions of some linear polysaccharides. A direct comparison of the values of s_0 and k_S obtained in a single series of experiments can provide additional information about macromolecules because these values depend differently on molecular weight and the size of the macromolecule:

$$[s] = M N_A^{-1} P_0^{-1} \langle h^2 \rangle^{-1/2} \tag{10}$$

$$k_S = B \langle h^2 \rangle^{3/2} M^{-1} \tag{11}$$

where P_0 is the Flory dimensionless parameter, $P_0 = \lim_{M \to \infty} P = 5.11$ (value obtained with pre-averaging of Oseen's tensor of hydrodynamic interaction), B is a dimensionless parameter, and $\langle h^2 \rangle$ is the mean-square end-to-end distance of the polymeric chain.

Scaling relation between s_0 and k_S

The comparison of s_0 and k_S makes it possible to determine the exponent in the equation $s_0 = KM^b$. It has been shown (Pavlov and Frenkel 1982) that

$$k_S = \gamma_S M^{v1} \tag{13}$$

where $v_1 = (2-3b)/b$ and γ_S is the parameter which in the first approximation is independent of s_0. Alternative scaling relationships $k_S \sim s_0^v$ can also be mentioned (Lavrenko 1987). It was found for a straight cylinder model that (Peterson 1962)

$$[s]k_S = (2\pi 3^{1/2} N_A)^{-2/3} (A_2 M)^{2/3} \tag{14}$$

where A_2 is the second virial coefficient. In the case, for example, of a straight cylinder (Tanford 1961) we have

$$A_2 = L\bar{v}/Md \tag{15}$$

where $\bar{v}$ is the partial volume of the particle, L is the length, and d is its diameter; we obtain

$$[s]k_S \sim M^{4/3};\ k_S \sim s_0^{v2} \tag{16}$$

where $v_2 = (4-3b)/3b$. On the other hand, for the case of random-coil macromolecules under θ-conditions it has been established by Imai (1970) that

$$k_S \sim L/s_0;\ k_S \sim s_0^{v3} \tag{17}$$

where $v_3 = (1-b)/b$ and L is the contour length of the macromolecular chain.

A similar result can be obtained from the theories of Freed (1983), Muthukumar and de Mense (1983) and Eq. (8)

$$k_S \sim \langle h^2 \rangle^{3/2} M^{-1} = \langle h^2 \rangle / (M/\langle h^2 \rangle^{1/2}) \sim L/s_0 \tag{18}$$

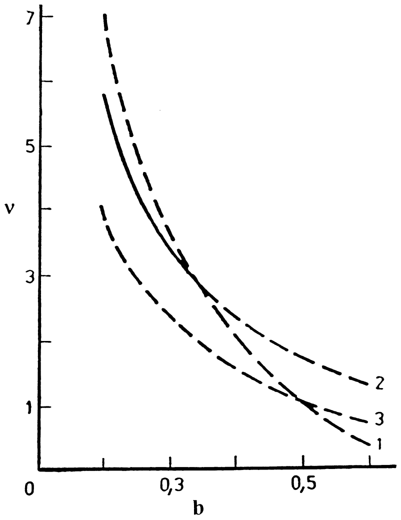

Fig. 3 Relationship between the coefficients v and b: $1–v_1 = (2–3b)/b$; $2–v_2 = (4–3b)/3b$; $3–v_3 = (1–b)/b$

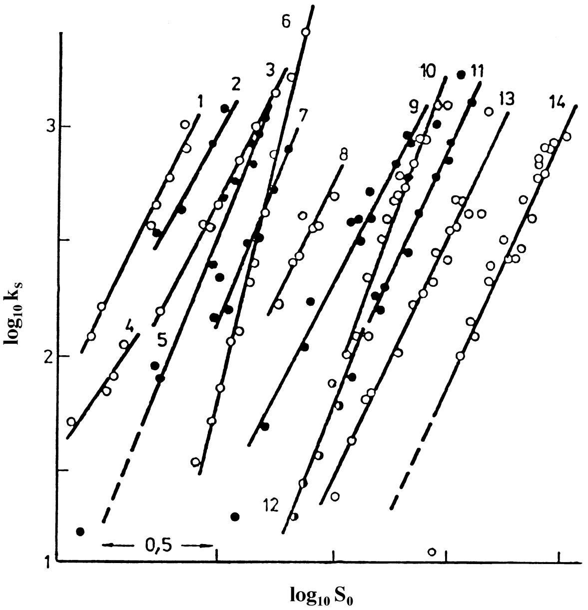

Fig. 4 Dependence of sedimentation characteristics k_S and s_0 in double logarithmic scale for systems: (*1*) 8, (*2*) 6, (*3*) 2, (*4*) 4, (*5*) 7, (*6*) 55, (*7*) 38, (*8*) 30, (*9*) 1, (*10*) 37, (*11*) 26, (*12*) 33, (*13*) 18, 20, (*14*) 36. Numbers of systems correspond to these listed in Table 1

Figure 3 shows the dependence of v on b. The values of v_1 and v_2 are also close to each other in the range of $b < 0.3$ (rigid-chain macromolecules). At $b = 0.5$ (random-coil macromolecules under θ-conditions) were have $v_1 = v_3$. Hence, the dependence $v_1 = f(b)$ is of a very general nature.

For β-(1,4) linked glucans and their derivatives (Fig. 4 and Table 1) we usually have $1.9 < v < 2.7$. For polysaccharides exhibiting the secondary helical structural and represented by chains with an equilibrium rigidity $A > 2000 \times 10^{-8}$ cm, namely the xanthan and Schizophyllum communes, v is 3.7 and 4.3 respectively.

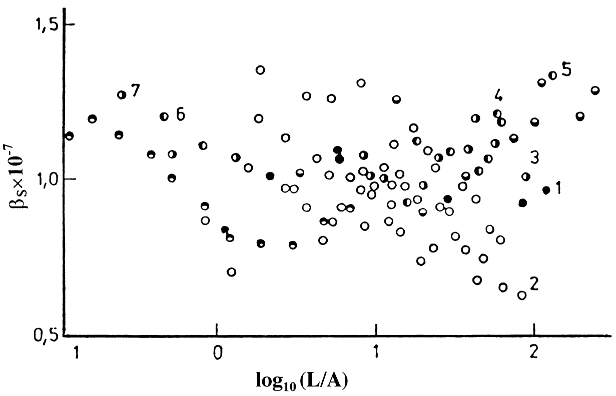

Fig. 5 Dependence of sedimentation parameters β_S on logarithm of reduced contour length of the macromolecule L/A for systems: (*1*) 7, (*2*) 32, 33, 36, 37, (*3*) 26, (*4*) 30, (*5*) 45, (*6*) 54, (*7*) 55. Numbers of systems correspond to those listed in Table 1

Branched polysaccharides represent the other limiting case: for them we have $b > 0.5$ and, correspondingly $v < 1$. In some cases (levan) the $k_S \sim s_0$ correlation is weak ($r = 0.5$), which may be related, in particular, to the fact that the assumption of homologous polymers for the investigated set of branched polysaccharides is not valid.

Sedimentation parameters for polysaccharides

By using the values of M determined by one of the absolute methods (sedimentation-diffusion analysis, sedimentation equilibrium or light scattering) and the values of $(1–v\rho_0)$ and η_0 it is possible to calculate the sedimentation parameters β_S for the system listed in Table 1, on the basis of the values of s_0 and k_S. When the hydrodynamic invariant A_0 (or β) was known, the β_S parameter was estimated from the equation

$$\beta_S = \beta (100)^{1/3} (k_S/[\eta])^{1/3} = A_0 (100)^{1/3} (k_S/[\eta])^{1/3} k^{-1} \quad (19)$$

The contribution from experimental errors in k_S, M, s_0, and $(1–\bar{v}\rho_0)$ to the total error in β_S are different and depend on M. The value of k_S is determined with considerable error but since it is contained in β_S in the form of $k_S^{1/3}$, its contribution is reduced to the same level as that of M and s_0. In the range of the greatest errors in k_S and s_0 (range of small s_0 values, see e.g. (Pavlov and Selunin 1986)), the relative error in the determination of a single value of β_S is about 20%. The analysis carried out by Pavlov and Frenkel (1986, 1988, 1995) has shown that the experimental values of β_S for flexible-chain polymers under θ-conditions and for rigid-chain polymers remain virtually unchanged throughout the range of L/A and d/A values. Therefore, it is possible to use Eq. (9) directly for the determination of molecular weights. It can be seen in Fig. 5 that the values of β_S for cellulose and its derivatives are more scattered as compared to those for synthetic linear homopolymers (Pavlov and Frenkel 1986). The situation is similar to that of a hydrodynamic invariant A_0 for cellulose derivatives [Tsvetkov et al. 1984; Tsvetkov 1989]. The scatter of β_S values probably derives from errors in molecular weight determination and with some contribution also from the sedimentation measurement.

The average β_S values for different groups of rigid polysaccharides (cellulose, its derivatives in aqueous solutions and in organic solvents, and other rigid linear polysaccharides) are close to each other. It may be assumed that to a first approximation the value of β_S depends neither on the nature of the in substituents glucopyranose unit nor on M. A total average value of $\beta_S = (1.0 \pm 0.16) \times 10^7$ mol$^{-1/3}$ may be used as the reference value for rigid polysaccharides.

Table 2 shows a comparison of the values of the hydrodynamic parameter β and the sedimentation parameter β_S for different kinds of macromolecules. The averaged experimental values have been determined to within approximately 6–10%. It follows from Eqs. (2) and (9) that β and β_S are related to the parameters Φ_0, P_0 and B by the following relations (these relations are the definitions of β and β_S):

$$\beta \equiv \Phi_0^{1/3} \times P_0^{-1} \text{ and } \beta_S \equiv B^{1/3} \times P_0^{-1} \qquad (20)$$

where Φ_0 is the Flory parameter in the equation $[\eta] = \Phi_0 \langle h^2 \rangle^{3/2} \times M^{-1}$ (Flory 1953) and P_0 and B are the parameters of Eqs. (10) and (11). It is possible to evaluate experimental values of Φ_0 and B from averaged values of β and β_S utilizing the value $P_0 = 5.11$. These estimations are also given in Table 2.

By using the average experimental value of β_S it is possible to evaluate the molecular weights of samples (fractions) from the generalized Wales-van Holde-Rowe equation

$$M_{KS} = (N_A/\beta_S)^{3/2} [s]^{3/2} k_S^{1/2} \qquad (21)$$

The adequacy of these estimates will now be shown for different kinds of polysaccharides. We consider the following type of linear polysaccharide chains: extra rigid, rigid, semi-rigid (semi-flexible) and flexible. The estimate of some conformational, molecular parameters of polysaccharides will be obtained using either:

1. independently evaluated molecular weights (s_0 and M_W or M_{SD}) or only
2. data from velocity sedimentation (s_0, k_S and β_S).

Extra rigid-chain polymers

Up to the present time, the highest equilibrium rigidity observed has been for polysaccharides from the *Schizophyllum commune* whose macromolecules are three-strand helices. The molecular and hydrodynamic characteristics of *Schizophyllum commune* have been presented by Yanaki et al. (1980).

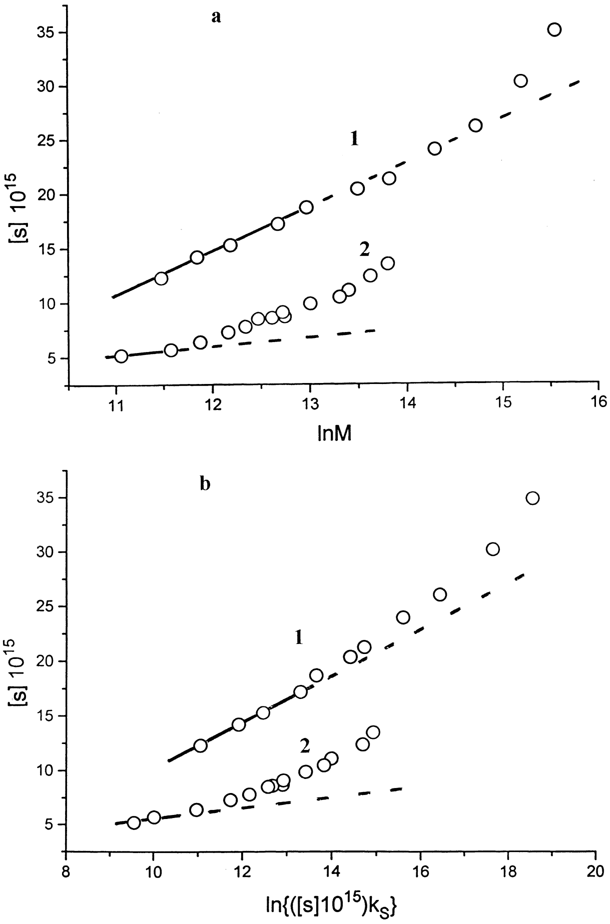

Fig. 6 **a** Dependencies of [s] on lnM for Schizophyllum in water (1) (Yanaki et al. 1980) and for cellulose nitrate in ethyl acetate (2) (Pavlov et al. 1982); **b** Dependencies of [s] on ln([s]^{3}k$_S$) for the same systems

The hydrodynamic properties of extra rigid-chain polymers in the range of small contour lengths L (L/A < 2.3; L ≫ d; d is the hydrodynamic chain diameter) can be described using a model of a weakly bending rod or a cylinder. In accord with theory (Broersma 1960; Yamakawa and Fujii 1974) for this model we have:

$$[s] = (M_L/3\pi N_A)[\ln M - \ln(M_L d) + 0.3863] \qquad (22)$$

The initial slope of the corresponding plot of [s] vs lnM allows the evaluation of the weight per unit length of the macromolecules $M_L = M/L = M_0/\lambda$, where M_0 is the molecular weight of the repeat unit, and λ is the projection of the unit in the chain direction. The data obtained by Yanaki et al. (1980) are presented in Fig. 6. If M_W is used one obtains an estimate for M_L of $(2.3 \pm 0.16) \times 10^{10}$ cm^{-1}, $d = 28 \times 10^{-8}$ cm ($r = 0.9950$) and the use of sedimentation data alone (s_0 and k_S) gives $M_L = (2.47 \pm 0.03) \times 10^{10}$ cm^{-1}, $d = 39 \times 10^{-8}$ cm ($r = 0.9998$). The corresponding slopes were calculated for the first four points.

It should be mentioned that the knowledge of the precise value of β_S is *not* necessary for the estimation of M_L based on s_0 and k_S with the assumption of its constancy being sufficient. A similar plot is presented using data obtained for the more flexible but also rigid-chain polymer, cellulose nitrate (Pavlov et al. 1982). In this case the plot

Table 1 Sedimentation parameters of some polysaccharides

N	Polymer	x[a]	Solvent	t^0C	v	r[b]	M[c]	$\beta_S\ 10^{-7}$	NN[d]	References[e]
1	Cellulose	–	Cuam[f]	20	1.8 ± 0.11	0.975	sD	–	16	Gralen (1944)
2	Cellulose	–	Cadoxen[f]	–	2.01 ± 0.04	0.999	sD	1.37 ± 0.09	7	Brown (1965)
3	Cellulose	–	–″–	–	–	–	W	1.08 ± 0.08	6	Brown (1965)
4	Cellulose		–″–	25	1.6 ± 0.24	0.979	W	1.05 ± 0.06	4	Henley (1962)
5	Cellulose	–	–″–	–	–	–	sD	1.53 ± 0.01	2	Klenin (1975)
6	Cellulose	–	FeTaNa[f] 0.27M	–	2.0 ± 0.22	0.988	sD	–	4	Claesson (1959)
7	Cellulose	–	FeTaNa 0.10M	25	2.3 ±0.17	0.986	sD	0.94 ± 0.09	7	Pavlov (1988)
8	Cellulose	–	FeTaNa 0.30M	21	2.1 ± 0.13	0.990	sD	–	7	Pavlov (1990)
9	Methylcellulose	1.66	H_2O	20	–	–	sD	0.8 ± 0.15	3	Uda (1961)
10	Methylcellulose	1.68	H_2O	25	1.87 ±0.16	–	sD	1.12 ±0.08	6	Pavlov (1995)
11	Hydroxyethylcellulose	–	H_2O	25	2.04 ±0.06	0.999	sD	1.6 ±0.12	4	Brown (1961)
12	Hydroxypropylcellulose	–	H_2O	25	–	–	sD	1.7	1	Nysrtom (1978)
13	Acetohydroxypropylcellulose		DMAA[g]	26	2.60 ±0.22	0.989	sD	0.98	5	Shtennikova (1992)
14	Ethylhydroxyethylcellulose	–	H_2O	20	–	–	W	0.8 ± 0.12	4	Manley (1956)
15	Na/sulphoethylcellulose	0.39	0.1 M NaCl	21	2.9 ± 0.69	0.947	sD	0.88 ± 0.08	4	Skazka (1977)
16	Carboxymethylcellulose	0.9	Cadoxen: H_2O/1:10	26	2.2	–	sD	1.06 ± 0.07	7	Lavrenko (1991)
17	Celluloseurethane	2.0	0.2M NaCl	22	2.5 ±0.15	0.994	sD	1.31 ± 0.09	5	Zacharova (1970)
18	Celluloseacetate	–	Acetone	20	3.1 ± 0.22	0.995	sD	0.91 ± 0.02	4	Singer (1947)
19	Celluloseacetate	2.34	Acetone	25	2.0 ±0.14	0.995	n	1.4 ± 0.13	4	Golubev (1967)
20	Celluloseacetate	2.46	Acetone	25	2.3±0.12	0.993	W	0.75 ±0.04	7	Ishida (1982)
21	Celluloseacetate	2.92	DMAA	25	1.9 ±0.12	0.994	W	1.0 ±0.2	5	Ishida (1982)
22	Cellulosemonophenylacetate	2.6	Benzene	26	1.4 ±0.13	0.973	sD	0.9 ±0.2	8	Korneeva (1979)
23	Cyanethylcellulose	2.6	Acetone	26	3.0 ±0.27	0.980	sD	0.88 ±0.04	7	Tsvetkov (1984)
24	Cellulosebenzoate	2.2	1,4-dioxane	26.6	–	–	sD	1.2 ±0.3	3	Korneeva (1979)
25	Celluloseacetobenzoate		1,4-dioxane	25	2.0 ±0.11	0.983	sD	1.2 ±0.11	14	Bushin (1990)
26	Cellulosebutyrate	2.94	Methylethylketone	20	2.23 ±0.07	0.996	sD	1.06 ±0.07	10	Lubina (1973)
27	Cellulosecarbanilate	3.0	Cyclohexanone	25	1.6 ± 0.21	0.982	W	0.52 ±0.01	4	Shanbhag (1968)
28	Cellulosecarbanilate	3.0	1,4-dioxane	20	1.7 ±0.14	0.985	sD	1.0 ±0.18	7	Sutter (1978)
29	Cellulosecarbanilate	2.7	Ethylacetate	25	2.3	-	sD	0.80 ±0.11	6	Andreeva (1977)
30	Cellulosephenylcarbanilate	2.1	Ethylacetate	–	1.9 ±0.37	0.931	sD	1.11 ±0.07	6	Andreeva (1975)
31	Cellulosediphenylphosphonocarbamate	2.6	1,4-dioxane	26.6	3.0 ±0.49	0.962	sD	0.9 ±0.2	5	Korneeva (1979)
32	Cellulosenitrate	1.1	DMAA+ LiCl	25	2.5 ±0.45	0.955	sD	1.10 ±0.05	5	Bushin (1983)
33	Cellulosenitrate	2.0	Ethylacetate	26	2.5 ±0.10	0.994	sD	1.16 ±0.14	9	Pogodina (1984)
34	Cellulosenitrate	2.0	Ethylacetate	25	1.88	–	sD	0.80 ±0.06	5	Pogodina (1982)
35	Cellulosenitrate	2.4	Ethylacetate	25	2.4 ±0.14	0.984	sD	1.06 ±0.09	11	Bushin (1983)
36	Cellulosenitrate	2.5	Ethylacetate	–	2.2 ±0.13	0.972	sD	0.80 ±0.11	20	Pogodina (1987)
37	Cellulosenitrate	2.7	Ethylacetate	21	2.8 ±0.14	0.985	sD	0.94 ±0.04	14	Pavlov (1982)
38	Cellulosenitrate	2.8	Ethylacetate	30	2.5 ±0.20	0.990	W	1.15 ±0.13	5	Hunt (1956)
39	Cellulosenitrate	2.46	Acetone	20	2.6 ±0.14	0.986	sD	1.18 ±0.18	12	Jullander (1945)
40	Cellulosenitrate	2.96	Acetone	20	2.3 ±0.40	0.870	sD	0.8 ±0.22	12	Gralen (1944)

Table 1 (continued)

N	Polymer	x[a]	Solvent	t^0C	v	r[b]	M[c]	β_S 10^{-7}	NN[d]	References[e]
41	Celluloseacetate-methylol	3.0	DMFA[h]	25	2.44 ± 0.08	–	sD	0.99 ± 0.09	33	Lavrenko (1992)
42	Chitosane	0.8	Buffer[i]	21	2.3 ± 0.65	0.935	sD	1.05 ± 0.10	18	Pavlov (1986a)
43	Carboxymethylchitin	1.8	Buffer[j]	25			sD	1.20 ± 0.11	8	Korneeva (1996)
44	Chitinnitrate	1.75	DMFA	26	2.3 ± 0.15	0.935	sD	1.06 ± 0.19	17	Pavlov (1986b)
45	Amylose	–	DMSO[k]	25	1.61 ± 0.04	0.997	W	1.14 ± 0.13	11	Fujii (1973)
46	Amyloseacetate	–	Methylacetate	25	–	–	sD	0.9 ± 0.3	3	Dombrow (1947)
47	Amylosecarbanilate	3	1,4-dioxane	20	2.06 ± 0.08	0.996	sD	0.8 ± 0.2	8	Sutter (1978)
48	Mannan	–	H_2O	25	2.0 ± 0.6		sD	1.06 ± 0.12	7	Pavlov (1992)
49	Pullulan	–	H_2O	25			W	1.23 ± 0.03	6	Kawahara (1984)
50	Pullulan	–	H_2O	25	1.7 ± 0.14		sD	1.20 ± 0.02	4	Pavlov (1994)
51	Dextran	–	H_2O	25	–	–	W	0.84	1	Wan (1976)
52	Dextran	–	H_2O	20	–	–	n	1.12 ± 0.11	5	Senty (1955)
53	Dextran	–	H_2O	20	1.29 ± 0.05	0.994	W	0.96 ± 0.05	10	Senty (1955)
54	Xanthan	–	0.1M NaCl	25	3.7 ± 0.14	0.993	W	1.1 ± 0.13	12	Sato (1984)
55	Schizophyllum	–	H_2O	25	4.3 ± 0.16	0.994	W	0.97 ± 0.13	11	Yanaki (1980)
56	Polyglucoseamine	–	H_2O	25	2.0	–	sD	1.1 ± 0.2	6	Pavlov (1993)
57	Mucus glycoprotein	–	6MGCl	20	1.23 ± 0.17	0.972	W	0.95 ± 0.09	5	Sheehan (1989)
58	Blood-mycoPC 376	–	–	25	–	–	–	1.32	1	Creeth (1965)
59	Levan	–	H_2O	25	0.29 ± 0.15	0.543	W	(2.7–0.5)	16	Stivala (1981)
60	Proteoglucan	–	4M Cdn HCl	20	0.76 ± 0.08	0.954	W	(2.4–0.9)	10	Kitchen (1978)
61	Ficol	–	H_2O	26	0.87	–	sD	(1.5–0.75)	7	Lavrenko (1986)

[a] Degree of substitution of OH-groups in polysaccharide derivatives;
[b] Linear correlation coefficient in the log k_s on log s_0 dependences;
[c] Method of molecular weight determination;
[d] Number of investigated fractions;
[e] First authors given only;
[f] Complex solvents of cellulose with different cations;
[g] N,N-Dimethylacetamide
[h] N,N-Dimethylformamide
[i] 0.33M CH_3COOH + 0.3M NaCl
[j] $0.05(Na_2HPO_4 \times 12\,H_2O + KH_2PO_4) + 0.15$ M NaCl
[k] Dimethylsulfoxide

Table 2 Averaged values of the hydrodynamic invariant β, the sedimentation parameter β_S, and corresponding Φ and B parameters

Polymer-solvent	$\beta \times 10^{-7}$ $mol^{-1/3(a)}$	$\Phi \times 10^{-23}$ mol^{-1}	$\beta_S \times 10^{-7}$ $mol^{-1/3}$	$B \times 10^{-23}$ mol^{-1}
Flexible-chain polymers in θ thermodynamically good solvents	1.08 (2.32×10^6)	1.67	1.25	2.61
Flexible-chain polymers in θ-conditions	1.08 (2.32×10^6)	1.67	1.0	1.33
Rigid-chain polymers	1.28 (2.75×10^6)	2.77	1.0	1.33
Cellulose and its derivatives	1.13 (2.43×10^6)	1.91	1.0	1.33
Globular proteins	1.03 (2.21×10^6)	1.44	1.17	2.14

[a] There are in brackets β values obtained from $[\eta]$ values expressed in 100 cm^3/g, these are common values in polymer science

has only illustrative meaning, and the straight line is plotted in accordance with the value $M_L = 5.5 \times 10^9$ cm^{-1} obtained from $M_0 = 284 \pm 9$ and $\lambda = 5.15 \times 10^{-8}$ cm.

The more flexible a polymer, the lower the molecular weight range that has to be investigated for the purpose of the determination of M_L.

Rigid-chain polymers

Evaluation of persistence lengths or Kuhn segment lengths in the case of chains without excluded volume effects (rigid-chain or flexible-chain in θ-conditions) can be obtained from the theories of Hearst-Stockmayer (1962) or Yamakawa-Fujii (1974).

In cases when L/A > 2.3 the following relation is fulfilled;

$$[s]N_AP_0=(M_L/A)^{1/2}M^{1/2}+(P_0M_L/3\pi)[\ln(A/d)-\varphi(0)] \tag{23}$$

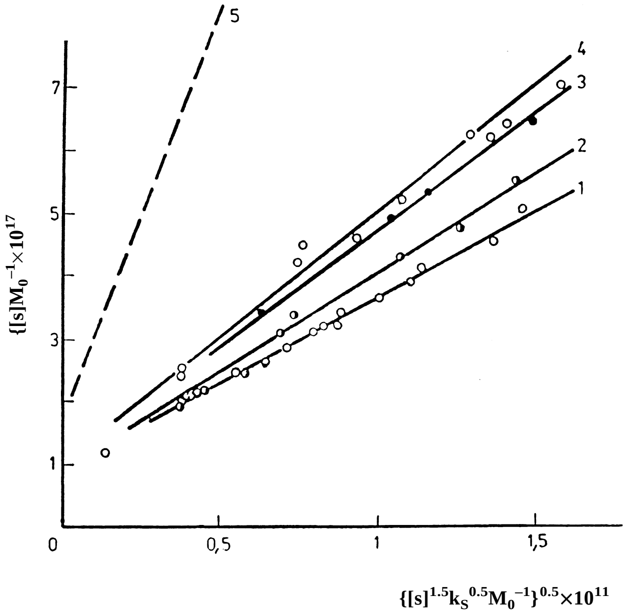

Fig. 7 Plots describing Eq. (7) for cellulose nitrates in ethyl acetate (*1*)-degree of substitution x = 2.7 [37], (*2*)-x = 2.5 [36], and in DMAA + LiCl (*3*)-x = 1.1 [32]; for cellulose (*4*) in FeTaNa-complex [7]; for polystrene and poly-α-methylstyrene (*5*) in cyclohexane (θ-conditions) (Lechner and Steinmeier 1989). Numbers of systems correspond to those listed in Table 1

where $P_0 = 5.11$ is Flory's hydrodynamic parameter, $\varphi(0) = 1.43$ (Hearst and Stockmayer 1962); $\varphi(0) = 1.056$ (Yamakawa and Fujii 1974). An example of the application of these theories is given in Fig. 7 for cellulose and cellulose nitrate (Pavlov 1988). There are grounds to suppose that volume effects for cellulose and its derivatives may be neglected (Flory 1966; Tsvetkov 1989). The dependence of s_0 on M can be re-written by applying Eq. (21) in following form;

$$\begin{aligned}[s]/M_0 = {} & (N_A^{1/4}P_0\beta_S^{3/4})^{-1}(\lambda A)^{-1/2}\{[s]^{3/2}k_S^{1/2}M_0^{-1}\}^{1/2}\\ & +(3\pi N_A\lambda)^{-1}[\ln A/d-\varphi(0)]\end{aligned} \tag{24}$$

where M_0 is the molecular weight of the repeat chain unit, $\lambda = 5.15\times10^{-8}$ cm for cellulose and its derivatives and $\beta_S = 1.0\times10^{7}$ mol$^{1/3}$. Figure 7 shows the dependences corresponding to Eq. (24) for cellulose nitrates with different degrees of substitution (straight lines 1–3) and for cellulose in FeNaTe (straight line 4). For comparison (straight line 5) the dependence obtained for polystyrene and poly-α-methylstyrene in cyclohexane (θ-conditions) is given. The Kuhn segment lengths A are calculated from the slope of straight lines plotted by the least-squares method, and the values of the hydrodynamic diameter d are estimated from the intercepts with the ordinate. Table 3 lists the value of A_{KS} and d_{KS} are well as those obtained by diffusion-sedimentation analysis (A_{DS}, d_{DS}) and the analysis of viscometric data (A_η) (Pavlov et al. 1982). A comparison of the results shows that the values of chain rigidity obtained by different methods are close to each other. The values of A_{KS} indicate the tendency for increasing equilibrium chain rigidity with increasing degree of cellulose nitration (Schulz and Pensel 1968; Lechner and Schulz 1973).

Table 3 Values of the statistical Kuhn segment length A and hydrodynamic diameter d for cellulose and its nitrate

Polymer	Solvent	A_{KS} 10^8 cm	d_{KS} 10^8 cm	A_{SD}	d_{SD}	A_η[b]	References[c]
Cellulose-nitrate (CN), x[a] = 2.8	Ethyl-acetate	360	13	530	6	350	Hunt (1956)
CN, x = 2.7	Ethyl-acetate	390	9	430	11	350	Pavlov (1982)
CN, x = 2.5	Ethyl-acetate	300	9	380	17	250	Pogodina (1987)
CN, x = 2.4	Ethyl-acetate	335	8	260	9	275	Bushin (1983)
CN, x = 2.0	Ethyl-acetate	180	14	130	12	140	Pogodina (1984)
CN, x = 1.1	DMAA+ LiCl	230	3	150	12	110	Bushin (1983)
Cellulose	FeTaNa-complex	190	4	170	6	110	Pavlov (1988)
Poly styrene[d]	θ-condition	27	–	27	–	–	Lechner (1989)

[a] Degree of substitution;

[b] Obtained by utilising Bushin's plot (see, for instance, Tsvetkov 1989);

[c] First authors given only;

[d] Given for comparison

Flexible-chain polysaccharides

For flexible polymers (polysaccharides such as linear dextran and pullulan, with 1,6 linkage in the main chain) the high value of b_f ($s_0 \sim M^{1-b_f}$; $b_f > 0.5$) can be related to volume effects. In this case the plot of Cowie-Bywater (1969) may be applicable for relatively low molecular weights (this plot is valid for the case of low excluded volume effects):

$$M^{1/2}/(N_A[s]) = K_{\theta f} + 0.2\,P_0TM^{1/2}$$
$$= P_0[A/M_L)^{1/2} + 0.2\,TM^{1/2}] \qquad (25)$$

where T is the parameter of thermodynamic polymer-solvent interaction.

For the interpretation of data over the entire range of M and volume effects the Gray-Bloomfield-Hearst theory (1967) must be used in which the molecular weight dependence of the sedimentation coefficient for a wormlike necklace is considered, taking into account the influence of excluded volume effects on the chain dimensions:

$$[s]P_0N_A = [3/(1-\varepsilon)(3-\varepsilon)]\,M_L^{(1-\varepsilon)/2}\,A^{-(1-\varepsilon)/2}\,M^{(1-\varepsilon)/2} +$$
$$+ (M_LP_0/3\pi)[\ln(A/d)-(1/3)(A/d)^{-1}-\varphi(\varepsilon)] \qquad (26)$$

where ε is the parameter characterizing volume effects and $\varphi(\varepsilon)$ is the function which way be calculated according to the Gray-Bloomfield-Hearst theory (1967) ($\varphi(0) = 1.431$). In a thermodynamically good solvent $\langle h^2\rangle \sim M^{1+\varepsilon}$, $\langle h^2\rangle$ is the mean-square end-to-end distance of a chain and ε is a dimensionless parameter which is a measure of the excluded volume effect. According to Ptitsyn and Eizner (1959) we have $\varepsilon = (2b_\eta - 1)/3 = (2|b_D| - 1) = (1 - 2b_S)$ where b_η, b_D and b_S are the corresponding scaling indexes of the Mark-Houwink-Kuhn-Sakurada relations.

Figure 8a shows the dependence of s_0 on $M^{(1-\varepsilon)/2}$. The parameter ε was previously (Pavlov et al. 1994) calculated from the relation $\varepsilon = 1 - 2b_S$. Therefore, $\varepsilon = 0.112$ and $A = (23.1 \pm 1.5) \times 10^{-8}$ cm, $d = (8 \pm 6) \times 10^{-8}$ cm ($r = 0.9889$). Figure 8b shows the same dependence using only sedimentation data (s_0 and k_S). Hence, by using the mean experimental value $\beta_S = 1.25 \times 10^7$ mol$^{-1/3}$ obtained for flexible polymers in thermodynamically good solvents (Pavlov and Frenkel 1995) one obtains $A = (23.0 \pm 1.3) \times 10^{-8}$ cm and $d = (2.6 \pm 1.3) \times 10^{-8}$ cm ($r = 0.9980$).

Semi-flexible (semi-rigid) chain polysaccharides

Complications arise in the interpretation of the hydrodynamic data obtained in the investigation of semi-rigid (semi-flexible) chain polymers (polysaccharides). In this case it is impossible to make the simple choice between the intra-chain excluded volume effect of the intra-chain draining effect. The deviation of the parameters b_η, b_D and b_S from 0.5 ($\Delta b_\eta = b_\eta - 0.5$; $\Delta b_D = |b_D| - 0.5$; $\Delta b_S = 0.5 - b_S$) arises partially from the draining effect and partially from the excluded volume effect. At present there is neither a theory nor a well-grounded approximation (it is one of the unsolved problems in polymer science following the Fujita (1988) definition), which gives the possibility of dividing the deviations Δb into two parts, for instance, $\Delta b_\eta = \Delta b_{v\eta} + \Delta b_{\alpha\eta}$, where $\Delta b_{v\eta}$ is the deviation due to the intra-chain excluded volume effect and $\Delta b_{d\eta}$ is that due to the intra-chain draining effect. Obviously this is related to the problem of adequate determination of the ε-parameter, which may be defined by:

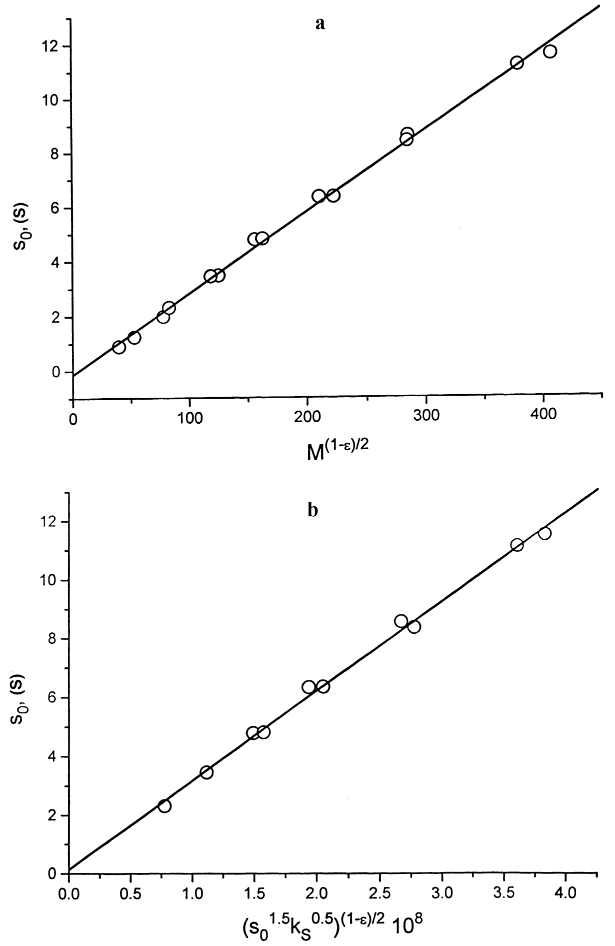

Fig. 8 **a** Dependence of s_0 on $M^{(l-\varepsilon)/2}$ for pullulan in water (Kawahara et al. 1984; Pavlov et al. 1994), **b** Dependence of s_0 on $(s_0^{1.5}k_S^{0.5})^{(l-\varepsilon)/2}$ for the same system

$$\varepsilon = (2b_\eta - 1)/3 = (2/3)\Delta b_\eta \qquad (27)$$

Evidently, in the case where the intra-chain excluded volume effect and the intra-chain draining effect are comparable an adequate evaluation of the ε parameter is possible by the following relation:

$$\varepsilon = (2/3)\Delta b_{v\eta} = 2\Delta b_{vD} = 2\Delta b_{vS} \qquad (28)$$

The value of the hydrodynamic diameter of the chain d may be a reasonable criterion in making the choice of ε (or Δb_v). Unfortunately, in many cases the d-values are determined from the hydrodynamic plots with low accuracy. As one example of the application of a similar approach we consider the results obtained for mannan fractions (Pavlov et al. 1992). The ε parameter was changed in the possible range for this case ($0.16 \geq \varepsilon \geq 0$) and the hydrodynamic data were interpreted with the application of the Gray-Bloom-

Table 4 Values of the equilibrium rigidity parameter A and the hydrodynamic diameter d of β-(1,3)-β-(1,4) linked-poly-mannopyranosil-D-mannose molecules in water

Excluded volume parameter ε	s_0, D_0			s_0, k_S		
	$A \pm \Delta A$ 10^{-8} cm	$d \pm \Delta d$ 10^{-8} cm	r	$A \pm \Delta A$ 10^{-8} cm	$d \pm \Delta d$ 10^{-8} cm	r
0	73 ± 6.3	4.8 ± 1.5	0.9898	79 ± 16	3.6 ± 2.4	0.9752
0.08	59 ± 7.3	6.7 ± 2.9	0.9895	64 ± 14	5 ± 3.6	0.9734
0.16	44 ± 4.7	10.4 ± 4.0	0.9890	50 ± 13	7 ± 6	0.9714

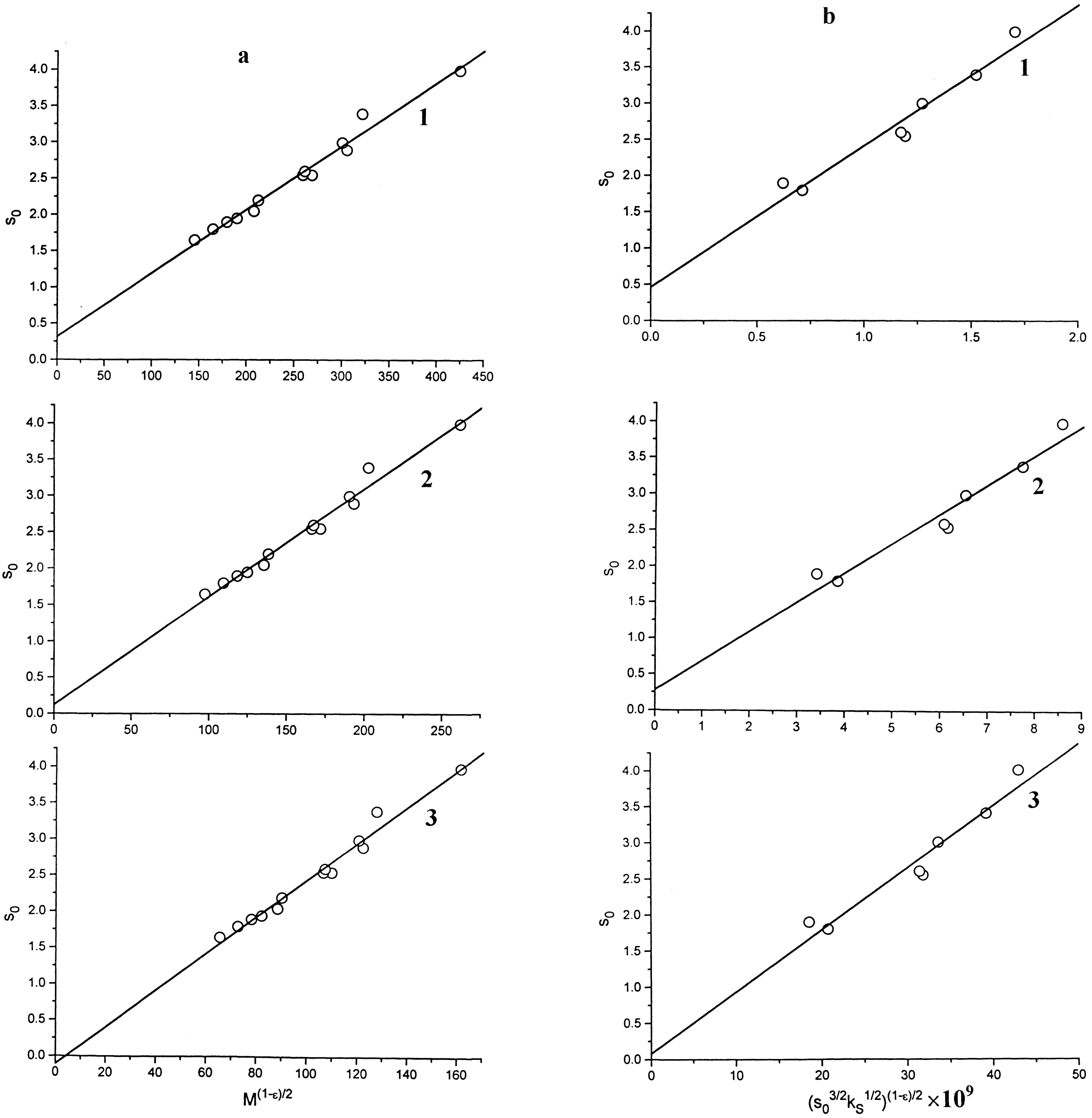

Fig. 9 **a** Dependences s_0 on $M^{(1-\varepsilon)/2}$ for mannan in water (Pavlov et al. 1992) for different values of ε-parameter: $\varepsilon = 0$ (*1*); $\varepsilon = 0.08$ (*2*) and $\varepsilon = 0.16$ (*3*); **b** Dependences s_0 on $(s_0^{1.5}k_S^{0.5})^{(1-\varepsilon)/2}$ for the same system and the same values of ε-parameter

field-Hearst theory (1967). The results are given in Table 4 and in Fig. 9.

The estimations obtained show in both cases (s_0, D_0 or s_0, k_S) satisfactory agreement between the A and d values when taking into account the inaccuracy of their determination. The nature of the variation in both A and d with ε is also reasonable. Nevertheless, the value of the linear correlation coefficient $r = 0.975$ does not suggest a reliable determination, especially of d values.

Further possibilities

The further possibilities in this direction are related to the mass-spectrometric effect of the ultracentrifuge. The combination of the "inherent fractionation" ability of the ultracentrifuge (Kinell and Ranby 1950; Frenkel 1965) and the concept of the sedimentation parameter makes it possible to obtain the following: molecular weight distribution, molecular weights of different averaging types, the constants of the Mark-Houwink-Kuhn-Sakurada 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 distribution of sedimentation coefficients that is obtained by the usual method and corresponds to finite solution concentrations can be extrapolated to infinite dilution by using the "inherent" or "graphic fractionation" approach. 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} values. Thus the distributions with respect to sedimentation constants may be transformed into those for molecular weights. The values obtained for s_0 and M_{KS} of these "graphic fractions" can be used to determine the parameters of the scaling equations. When appropriate hydrodynamic theories are applied to a set of these "graphic fractions" (as a series of polymer homologues), one can obtain the persistence length and the effective hydrodynamic chain diameter. Hence, it possible to analyse the hydrodynamic and molecular properties of the polymer without using additional methods and without preliminary fractionation (only knowledge of $(1-\bar{v}\rho_0)$ and η_0 is required). This transformation is more easy from the integral form of the sedimentation boundary. The use of multi-cell rotors can't, of course, accelerate this procedure. As a good illustration, the hydrodynamic and molecular characteristics of cellulose nitrate in acetone (Pavlov et al. 1995) and methylcellulose in water (Pavlov et al. 1995) determined by this method are in agreement with literature data based on the analysis of real fractions.

Conclusions

The investigation of the concentration dependence of s over a wide range of c values makes it possible to estimate s_0 and k_S reliably. The use of the $k_S = \gamma_S s_0^{\nu}$ scaling relationship enables us to exclude concentration effects and to determine the exponent in the equation $s_0 = KM^b$. Moreover, by using the average experimental value of β_S for linear polymer homologues, it is possible to evaluate the molecular weights of fractions (samples) and relevant conformational parameters of macromolecules. Thus, the comparison of two experimental values obtained in one series of experiments (s_0 and k_S), where the molecules are under the same conditions, is an additional method for obtaining information on certain equilibrium properties of linear macromolecules whether they be synthetic polymers or biopolymers. This concept may therefore be successfully applied to linear polysaccharides.

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