Translated from *Uspekhi Khimii*, 48, 1309-1335 (1979) U.D.C. 541.64:532.72

The Sedimentation of Polydisperse Polymers

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The most important problems in the sedimentation of one component of two-component mixtures and polydisperse polymers have been discussed. Particular attention has been paid to the application of theory in the treatment of sedimentation data. It has been shown that to calculate the molecular mass distribution (MMD) from sedimentation diagrams of polydisperse polymers, the best theory is that based on the Trautman relationships describing the Johnston-Ogston effect for the case of a binary mixture, the concept of local concentration, and the principle of additivity of the paired interactions of the components of the mixture. Allowance for the diffusion broadening of the curves is made using Fujita's theory by means of model functions. The distribution with respect to the sedimentation coefficients (or the MMD) is calculated by means of a computer from one recording. The bibliography contains 99 references.

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I. INTRODUCTION

One of the chief methods for determining the molecular mass distribution (MMD) of synthetic polymers is by the velocity sedimentation of polymer solutions in the ultracentrifuge[1-4].

The theoretical principles of the method of velocity sedimentation were formulated at an early date[5], various aspects of the application of the method to specific systems have been dealt with in many reviews and monographs[2-15], and the construction of ultracentrifuges is being improved[15-17]. Nevertheless, velocity sedimentation has not found extensive application in research by synthetic chemists. Both theoretical problems in the analysis of polymerisation mechanisms[18] and technical problems in modelling synthesis processes and the selection of reactor design[19,20] require rapid determination of the MMD. The generally adopted extrapolation method[2-6] for finding the MMD is too cumbersome and tedious, however, and the single-concentration and single-recording approximations[3,21-26] have insufficient theoretical foundation. The method of equilibrium sedimentation in an ideal solvent, which has good theoretical basis[2-7,11-15], is not used in practice to determine the MMD of polydisperse polymers. This method is inconvenient chiefly because it is necessary to carry out the ultracentrifuging of the polymer solutions for a long period (several days).

The form of the boundary in the sedimentation of a polydisperse polymer depends not only on the non-uniformity of the specimen but also on a number of other factors: the hydrostatic pressure, diffusion, the concentration dependence of the sedimentation coefficients S, the sector form of the cell, and the cross-term hydrodynamic interactions of the components—the Johnston-Ogston effect (JOE).[3,13,14,27-29] In spite of some progress in the understanding of the nature of these effects, there is no simple and reliable method which makes it possible to take account of all the factors influencing the form of the sedimentation boundary. It is obviously appropriate to raise the question of the influence of a given factor on the form of the sedimentation distributions, their dependence on the properties of the polymer–solvent system, the average molecular masses, the polydispersity, and the type of MMD curve. In particular, neither the hydrodynamic[30-32] nor the thermodynamic[33-35] aspects of the influence of the hydrostatic compression of the solvent on the sedimentation and flotation (negative sedimentation)[36-42] of solutions of polydisperse polymers have been fully studied.

The present review examines the sedimentation of one- and two-component† systems and polydisperse synthetic polymers, except for the special problems of the sedimentation of biological materials[7]. In the examination of the first two problems, only some fundamental questions will be dealt with.

II. SEDIMENTATION OF ONE COMPONENT

Velocity sedimentation gives directly the distribution $g(S_0)$ (S_0 is the sedimentation constant) of a polydisperse polymer. The molecular mass distribution $g(M)$ (M is the molecular mass) is then found from the equations

$$S_0 = K_S M^{\gamma},\ M = (S_0/K_S)^{1/\gamma}; \quad (1)$$

$$g(M) = \gamma S_0 g(S_0)/M, \quad (2)$$

where K_S and γ are constants for a series of polymer homologues in a given solvent. It can be seen that to determine the MMD from Eqns. (1) and (2) it is necessary to find both the sedimentation constants and the absolute molecular masses of the polymer fractions (preferably narrow).

The study of the sedimentation of the fractions is of not only practical but also theoretical interest (for the comparison of the results with conclusions reached from theory)[13,14]. To anticipate slightly, it may be noted that it is only for the sedimentation of one component that a rigorous theoretical approach has been developed[13,14] and

† Here and subsequently, reference is made to hydrodynamic and not thermodynamic components, that is the solvent is regarded not as a component but as the medium.

the molecular parameters of the solute and the solvent used to calculate the time dependence of the radial distribution of the concentration in the cell[13,14,43-49].

Polymers in all solvents, including thermodynamically ideal, are characterised by the following concentration dependence of the sedimentation coefficients:

$$S=S_0/(1+kc), \tag{3}$$

where S is the sedimentation coefficient of the component (fraction), c the concentration, and the coefficient k characterises the hydrodynamic interactions of identical macromolecules (which also depend on the thermodynamic properties of the system). A theoretical interpretation of the parameter k has been given[50,51], and in the study of fractions, extensive experimental material has been accumulated on the relationship between k and the characteristics of the polymer chains[3,36,52-62].

The influence of pressure P on the sedimentation coefficients is taken into account by means of the parameter μ:[2-15,43-49,53,63,64]

$$S^P=S^1/(1+\mu P), \tag{4}$$

or

$$S^P\approx S^1(1-\mu P), \tag{4a}$$

where S^P and S^1 are the sedimentation coefficients at pressures P and 1 atm respectively. It can be seen that Eqn. (4a) is a particular case of the more general equation (4), but before the work of Jones and coworkers[44-48], the theoretical analysis of sedimentation processes was based on Eqn. (4a). Eqns. (4) and (4a) lead to the following equations:

$$S^P=S^1/[1+m(r-1)],\ r=(x/x_0)^2; \tag{5}$$

$$S^P=S^1[1-m(r-1)]; \tag{5a}$$

$$m=\frac{1}{2}\mu\rho_0 x_0^2\omega^2, \tag{6}$$

where x and x_0 are the running coordinate and the coordinate of the meniscus respectively, ρ_0 the density of the solvent, and ω the angular rate of rotation of the rotor of the ultracentrifuge.

With allowance for the concentration dependence of the sedimentation coefficient, the influence of pressure and diffusion, and also the sector form of the cell, the equation for the ultracentrifuge was solved[48] by a numerical method, that is the time dependence of the radial distribution of the concentration and the concentration gradient was calculated. These calculated characteristics show good agreement with the experimentally observed relationships. It is usually necessary, however, to solve the inverse problem—to find the molecular parameters from experimental data. It was found that any analytical expressions describing sedimentation in terms of the coordinate of the boundary and time are approximate. The relative error between the exact (numerical) and approximate (analytical) solutions is 3% for S_0 and 12% for m. The theory[48] does not take account of the reflection of macromolecules from the meniscus[13,14] or the pressure dependence of the diffusion coefficient[49]. Moreover, in the analysis of experimental data, the correction for dispersal should not be forgotten[21,65,66]. In view of the approximate nature of the simple analytical expressions, it has been suggested[48] that the variable coordinate of the meniscus be used in calculations in the treatment of experimental data.

In spite of these unsatisfactory features, the theory[48] marks an important stage in the development of velocity sedimentation and makes it possible to interpret reliably the experimental data on the sedimentation of fractions of synthetic polymers. The most important conclusions from this work are examined below.

1. In agreement with experimental data[30,67], in the sedimentation of one component, there is produced a plateau region in which there is no concentration gradient.

2. The concentration in the range of the plateau (c_a) is given by the expression

$$c_a=c_0[1+m(r-1)]/r, \tag{7}$$

where c_0 is the initial concentration. Thus the simple dilution law $c_a = c_0/r$ is realised only in the limit as $m \to 0$. For $m = 1$, there is not change in concentration with time in the range of the plateau: $c_a(t) = c_0$; a value $m < 1$ corresponds to dilution, and $m > 1$ corresponds to concentration in the sedimentation process.

3. The determination of the position of the boundary from the second moment of the distribution of the displacements[3,13,21,43,53,65,68] is justified only for the limiting case[69] ($m = 0$, $c_a = c_0/r$) of the sedimentation of one component.

4. The following equation is proposed[48] for the determination of S_0 and m

$$\ln r/(2\omega^2 t)=B/2\omega^2 t+E+H\cdot 2\omega^2 t,$$

where t is the time, and B, E, and H are constants which are found by the least squares method. The constant B corresponds to the displacement of the meniscus (by not more than 1.2 mm), and can apparently partly compensate the effects of reflection from the meniscus and the displacement of the actual start of sedimentation. If the constants E and H are calculated, S_0 and m can be determined from the equations:

$$S_0=(1+\alpha)E,\ \alpha=kc_0;$$

$$m=[1/(2\alpha+1)]\cdot\left[\alpha-\frac{(1+\alpha)H}{E^2}\right].$$

5. Fujita's equation[13,14,43] has been widely used in the treatment of experimental data

$$S=\ln r[1-R(r-1)]/2\omega^2 t\ \ R=-\frac{m}{2}+\left(\frac{1-m}{2}\right)\frac{kc_0}{1+kc_0} \tag{8}$$

and is applicable for small values of m.

6. The fact that $\ln x$ or $\ln r$ are linearly dependent on t does not indicate that the effects of compression and dilution are compensated, just as extrapolation to the meniscus does not guarantee that complete allowance has been made for the influence of pressure. As already noted, this is due to the inadequacy of the simple analytical expressions for the actual sedimentation of a polymer fraction, characterised by a definite polydispersity.

7. In a number of cases[21,59,60,70], an increase in the coefficient k with increase in the angular rate of rotation of the centrifuge rotor ω has been detected. This effect is usually related to an increase, with increase in ω, in the average concentration in the region of the plateau, corresponding to the experimental range of change in the coordinate x; this leads to a decrease in S and hence to an increase in k. It is not accidental that with decrease in the molecular mass, the magnitude of this effect decreases.

8. The scatter in the values of m or μ determined by different methods[26] or even by the same method[21] is due both to the approximate nature of the original analytical

expressions and to the fact that these parameters are determined from small changes in the sedimentation coefficients.

III. SEDIMENTATION OF TWO COMPONENTS

The sedimentation of two macromolecular components is accompanied by cross-term hydrodynamic interactions, leading to an increase in c and a decrease in S for the slow component, and to a decrease in c and an increase in S for the fast component. Some experimental data[71] on the Johnston–Ogston effect will be examined.

Table 1. Characteristics of PαMS specimens[71].

Specimen	10^{-6} M	S_0, Svedberg units	k, dl g^{-1}	Solvent
A–S	0.73	13.89	0.489	cyclohexane
A–F	1.52	19.47	0.648	cyclohexane
B	0.46	11.37	1.98	toluene
C	1.38	17.78	4.01	toluene



Figure 1. Sedimentation diagram for a mixture of specimens A–S and A–F PαMS in cyclohexane: $c_0 = 0.316$ g dl^{-1}, 35°, $\omega = 59\,780$ r.p.m.

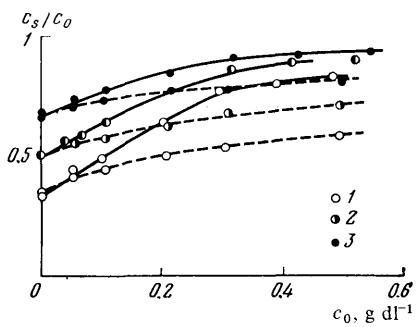


Figure 2. Dependence of the apparent relative concentration of the slow component of PαMS on the total initial concentration. The broken lines correspond to a mixture of specimens A–S and A–F in cyclohexane: *1*) $c_F^0/c_S^0 = 1.848$; *2*) 1.00; *3*) 0.478. The continuous lines give the data for a mixture of specimens B and C in toluene: *1*) $c_F^0/c_S^0 = 1.957$; *2*) 1.00; *3*) 0.498.

Fig. 1 gives the sedimentation diagram of a specimen A of poly-α-methylstyrene (PαMS) in cyclohexane (CH) at 35° (close to the θ-point). This specimen was obtained by anionic polymerisation[72] with the simultaneous use of mono- and bifunctional initiators, and is practically a mixture (1 : 1) of two specimens A–S and A–F (see Table 1). It can be seen that there is a marked difference in the areas under the peaks, although the original concentrations of the components are identical. Similar sedimentation diagrams were obtained for mixtures of specimens B and C. Fig. 2 gives the dependence of the apparent relative concentrations of the slow component of PαMS on the total initial concentration. The Johnston–Ogston effect (the increase in the concentration of the slow component) is clearly observed in both toluene and cyclohexane, but the effect is much greater in the thermodynamically good solvent (toluene) than in the ideal solvent (cyclohexane).

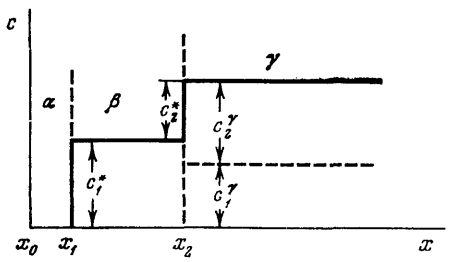


Figure 3. Schematic representation of the dependence of the concentration c on the coordinate x in the cell of the ultracentrifuge in the sedimentation of a two-component mixture.

A theory of the effect has been given[29] on the basis of the ideas of Johnston and Ogston[27]. The sedimentation of a two-component mixture can be considered; the slow component is denoted by the index 1, and the fast component by the index 2; the sedimentation constants of the components are S_{01} and S_{02} respectively, and $S_{02} > S_{01}$. At some moment of time in the cell of the ultracentrifuge, the dependence of the total concentration c on the coordinate x has the form shown in Fig. 3 (if the influence of diffusion is neglected). Here and subsequently it is assumed that the increments in the refractive indices of the components are identical, and that any optical system of the centrifuge can be used to determine this relationship. The α-region corresponds to the pure solvent, the β-region corresponds to the sedimentation of component 1, and in the region of the γ-plateau, movement of both components takes place (Fig. 3). The concentrations c_1^* and c_2^* are recorded directly. The expressions

$$p_i = c_i^* r_i / c_i^0, \quad i = 1, 2, \tag{9}$$

where c_i^0 is the concentration of the component i in the original solution, are compiled. If the correction for pressure is small, and the sedimentation of one component does not influence the sedimentation of the other, then $p_i = 1$. It has been shown experimentally, however, that in all cases $p_1 > 1$, and $p_2 < 1$ [7,14,27–29,71] (see Fig. 2).

The experimentally observed picture of the movement of the components of the mixture is as follows. At the initial moment of time, the slow first component "remains in its position", since for this component the medium containing the fast (high-molecular-weight) second component represents a medium with an increased hydrodynamic resistance, whereas for the second component, the first (low-molecular-weight) component represents a medium with a lowered hydrodynamic resistance. In the region left by the fast component, there is a relative increase in the rate of movement of the slow component; the moving boundary then acts as a kind of "dam", and the concentration of the first component increases, leading to a relative decrease in the concentration of the second component. Thus the physical factor responsible for the JOE is the increase (fast) or decrease (slow) in the rate of movement of one component in the presence of the other.

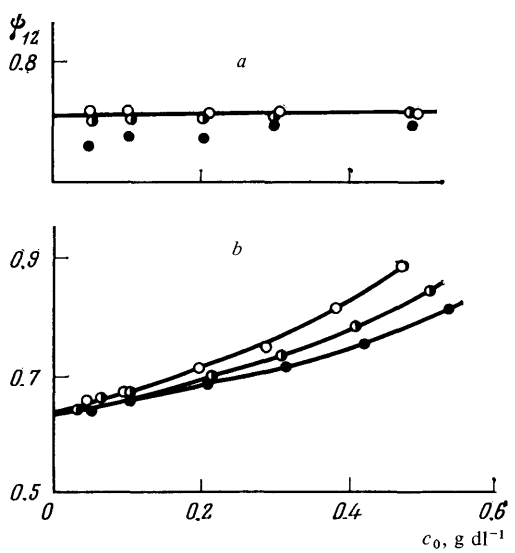


Figure 4. Concentration dependence of ψ_{12}: the symbols are the same as in Fig. 2; solvents: *a*) CH, *b*) toluene; the points of intersection of the curves with the ordinate correspond to the values $S_S^0/S_F^0 = S_{01}/S_{02}$.

In the theory of Trautman and coworkers[29], the changes in the concentrations of the components are taken into account by means of the parameter ψ_{12} (see Fig. 3):

$$c_1^\gamma/c_1^0 = (x_0/x_2)^{2\psi_{12}} = r_2^{-\psi_{12}}, \quad (10)$$

where the index γ refers to the values of the quantities in the region of the γ-plateau. It can be shown that the value of ψ_{12} is determined by the difference in the values of the sedimentation coefficients of the first and second components in the region of the γ-plateau:

$$\psi_{12} = \int_0^t S_1^\gamma \, dt \Big/ \int_0^t S_2^\gamma \, dt. \quad (11)$$

The experimental data[71] indicate that the concentration dependence of the sedimentation coefficients of the components of the mixture satisfies the relationship

$$S_i = S_{0i}/(1 + k_i c_i + k_{ji} c_j), \quad (12)$$

where the coefficient k_{ji} reflects the influence of the jth component on the sedimentation of the ith component. In a θ-solvent (CH for PαMS), $k_{ji} = k_i$, but in a good solvent, only the approximate relationship $k_{ji} \simeq k_i$ holds. Application of Eqn. (12) to the sedimentation of the components in the region of the γ-plateau gives:

$$\psi_{12} = S_{01}/S_{02}. \quad (13)$$

The original concentrations of the components c_1^0 and c_2^0 are related to the parameter ψ_{12} as follows:

$$c_1^0 = c_1^* (r_2 - r_1)/[r_2^{1-\psi_{12}} - 1], \quad (14a)$$

$$c_2^0 = c_1^* r_1 + c_2^* r_2 - c_1^0. \quad (14b)$$

By measuring the areas under the peaks c_i^* (see Fig. 1), it is possible to use Eqns. (14a) and (14b) to determine the parameter ψ_{12}. Fig. 4 gives the concentration dependence of this parameter[71]. For the θ-system PαMS–CH, relationship (13) is fulfilled, whereas in a good solvent (toluene), the value of ψ_{12} increases with increase in concentration.

Undoubtedly, the most important feature is that in the limit, as $c \to 0$, the parameter ψ_{12} does not tend to unity, which would correspond to the widely held view that the JOE decreases with decrease in the concentrations of the components, but becomes equal to the limiting value corresponding to Eqn. (13) in the case of the PS–CH system, or approaches it in the case of the PS–toluene system (PS = polystyrene). This in turn leads to the important conclusion that it is impossible to eliminate the influence of the Johnston–Ogston effect by extrapolating the experimental data to zero concentration.

If the influence of hydrostatic pressure is taken into account from the generalised dilution law (7), the following equations are obtained instead of Eqns. (14a) and (14b):

$$c_1^0 = c_1^* (y_2 - y_1)/[y_2^{1-\psi_{12}} - 1]; \; y_i = r_i/[1 + m(r_i - 1)]; \quad (15a)$$

$$c_2^0 = c_1^* y_1 + c_2^* y_2 - c_1^0. \quad (15b)$$

IV. SEDIMENTATION OF POLYDISPERSE POLYMERS

1. CHARACTERISTICS OF THE EXTRAPOLATION METHOD

The graphical–analytical procedure widely adopted at present[2-4] for determining the distribution curves with respect to sedimentation coefficients (and also the MMD) of polymers is based on the assumption of simple additivity of the movement of the components and the factors operating in the system. It is assumed that the effects of pressure, diffusion, and the concentration dependence of the sedimentation coefficients are independent and additive and can be considered in turn. The apparent distributions $g^*(S, t)$, not corrected for diffusion broadening, are calculated from Eqns. (5), (5a), and (6) and the relationship

$$g^*(S, t) = zrx/[1 + m(r-1)]^2, \quad (16)$$

where the displacement $z \sim dc/dx$. Extrapolation of the $g^*(S, t)$ curves for a number of concentrations to infinite time (that is $1/t \to 0$) eliminates the diffusion factor, after

which the $g(S)$ distributions are extrapolated to zero concentration, which makes it possible to take account of the $S(c)$ relationship. It is assumed that these extrapolations simultaneously eliminate the influence of cross-term interactions; as shown in the previous section, however, the JOE cannot be eliminated by extrapolating the data to zero concentration. It is apparently not accidental that research experience[23] shows that there are considerable complications in carrying out the extrapolations. Moreover, the final distribution loses "fine" details (small or poorly resolved maxima, a "tail"), and are too narrow.

It is possible to distinguish three types of polymer, differing from one another in the width of the distribution curves $g(S)$: 1) highly polydisperse polymers contain high-molecular-weight fractions (a "tail"), which reach the foot of the cell, whereas the low-molecular-weight components do not leave the meniscus; 2) for polymers of medium polydispersity, the boundary occupies almost the entire column of solution, that is the boundary leaves the meniscus, but the "tail" of the distribution does not reach the foot; and 3) the boundary for weakly polydisperse polymers occupies approximately half (or less) of the height of the column of solution in the cell.

This division is of course to some extent arbitrary, since a given specimen in a thermodynamically ideal solvent and in a good solvent, or with a considerable variation in concentration, may correspond to different types of polydispersity with respect to $g(S)$. As will be shown subsequently, however, polymers of the second and third types differ considerably from one another in the relative roles of diffusion and the JOE. The sedimentation of highly polydisperse polymers (the first type) has already been examined[37].

The practical realisation of the extrapolation of distributions sometimes encounters difficulties even in making allowance for diffusion[23,73]. Thus the sedimentation of an industrial specimen of polystyrene (its characteristics will be given below) at $c \leq 0.3$ g dl^{-1} gives $g^*(S, t)$ curves which do not change in the same sense, and the height at the distribution maximum decreases with time. The introduction, with fairly crude assumptions, of corrections for dilution leads to $g^*(S, t)$ distributions for which the ordinates at the maximum increase with increase in t, and it is possible to eliminate the influence of diffusion[73]. The example given illustrates a characteristic unsatisfactory feature of calculations using Eqns. (5), (5a), (6), and (16)—the neglect of sector dilution. For a polymer which is non-uniform with respect to mass, this problem is not so simple, since different components of the mixture are diluted in different ways, both from purely geometric considerations and because they are situated in regions with different local concentrations.

Another unsatisfactory feature of the above widely adopted method of treating sedimentation diagrams is that the treatment is implicitly based on the concept of plateau concentration. In fact, all polymers are characterised by a $S = S(c)$ relationship, so that it is possible to relate a distribution $g^*(S, t)$ to a specific concentration c without additional corrections only if the concentration remains unchanged during sedimentation. The concentration remains practically unchanged in the region of the plateau, whereas along the boundary it increases from zero to the plateau concentration. Thus Eqns. (5), (5a), (6), and (16) are inseparable from the assumption that a decisive role in the sedimentation of a polydisperse polymer is played by the concentration in the region of the plateau. This concept is directly contradicted by the above results of the study of the sedimentation of two-component systems. This leads to the consideration of another fundamental problem.

On the basis of Fujita's equation (8),[13,14] relationships have been obtained[74] for calculating $g^*(S, t)$ with allowance for the $S(t)$ relationship and the change in the concentration along the boundary. Fig. 5 gives the $g^*(S, t)$ curves for a polystyrene specimen PS-1 (data on this specimen are given below) in CH at 34°C, calculated from the published equations[74]. The distributions with respect to sedimentation coefficients change in different senses to such an extent that it is not possible to eliminate diffusion broadening. The error in this case[74] is that for the intermediate range, the simple concentration c is used throughout, with no indication of its constituent components.

2. ROLE OF THE DIFFUSION FACTOR IN THE SEDIMENTATION OF POLYDISPERSE POLYMERS

a) The use of Fujita's theory[75] to estimate the diffusion broadening of the boundary

Allowance for diffusion broadening of the boundary is usually made[2-4] for each concentration with extrapolation of the distributions $g^*(S, t)$ or $G^*(S, t)$ (where $G^*(S, t)$ is the integral curve) to infinite time (that is $1/t = 0$). It is necessary, however, not only to eliminate the diffusion broadening of the distributions but also to determine quantitatively the role of diffusion and to determine the dependence of the diffusion factor on the molecular mass, polydispersity, and nature of the MMD curves of the polymers. This last feature is important in itself, and also in the development of single-point (single-recording) methods for calculating the MMD of polymers.

Fujita's theory[14,75] makes it possible to determine the role of diffusion in the sedimentation of polydisperse polymers[26,66,76]. This theory examines the sedimentation, in an "ideal sedimentation solvent"[14] in a rectangular cell, of a polymer of medium or low polydispersity, which does not contain appreciable quantities of low-molecular-weight fractions, that is $g(S)|_{x=x_0} = g'(S)|_{x=x_0} = 0$, and which does not contain high-molecular-weight fractions, that is a distribution "tail" which rapidly reaches the foot of the cell. Thermodynamically ideal behaviour is included as a necessary condition in the concept of an "ideal sedimentation solvent". Another important condition is the absence of all hydrodynamic interactions or the absence of concentration dependences $S(c)$ and $D(c)$ (D is the diffusion coefficient) and cross-term interactions. In addition, the following approximate relationship is used:

$$x - x_0 = x_0\omega^2 tS.$$

Since the sedimentation is ideal, the parameter K is constant:

$$K = SD = S_0D_0 = \text{const.} \qquad (17)$$

Subsequently, the interpretation of the experimental data will be related chiefly to this parameter. Using familiar relationships[3], it is possible to express K in terms of molecular parameters

$$K_0 = S_0D_0 = \frac{RT(1-\bar{v}\rho_0)}{N_A^2P^2\eta_0^2}\left(\frac{M}{\bar{h}_0^2}\right) = K_0^{\text{theor}}, \qquad (18)$$

where R is the universal gas constant, T the temperature, N_A Avogadro's number, P the frictional constant ($P = 5.1$

was used in the calculations), η_0 the viscosity of the solvent, $\overline{h_0^2}$ the dimensions of the coiled molecule in the ideal solvent, and $\overline{v}$ the partial specific volume of the polymer.

Despite these restrictions, Fujita's theory was the first to deal simultaneously with the sedimentation and diffusion of polymers of medium polydispersity, since Gosting's relationships[77] were derived with the condition that D = const for all components, that is, strictly speaking, for polymers (fractions) with low polydispersity. Analysis of the published expressions[66] for the dispersion of the displacements $\overline{\xi}^2$ from the theories of Fujita and Gosting shows that they are identical, but the former theory has the advantage of being general. Fujita's theory shows that Gosting's relationships are also inapplicable to the sedimentation of polymers of medium polydispersity if the weighted-mean diffusion coefficient is used. After allowance for the effect of self-contraction, the experimental data[66,78,79] on the dependence of $\overline{\xi}^2$ on t show qualitative agreement with theory.

Table 2. Characteristics of the systems studied*.

No.	Polymer	Conditions of synthesis	Solvent for the sedimentation; temperature, °C	Density of solvent ρ_0, g ml^{-1}	$10^9\mu$	$10^{15}K_S$	ν	$10^{-5}\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1	PS	laboratory (high-weight fraction (Ref.80))	CH; 34°	0.7670	1.6	1.5	0.50^{21}	10.8	1.70
2	PS	industrial	CH; 34°	0.7670	1.6	1.5	0.50^{21}	2.25	2.27
3	PVA	laboratory (Ref.81)	BEK; 29°	0.8183	1.5	6.03	0.44^{**82}	13.6	2.01
4	PVA	laboratory (Ref.81)	BEK; 29°	0.8183	1.5	6.03	0.44^{**82}	5.19	1.78
5	PPhIA	polycondensation in solution (Ref.83)	DMF—0.25% LiCl; 25°	0.9474	4.0	2.8	0.39^{84}	3.33	1.48
6	PPhIA	polycondensation in solution (Ref.83)	DMF—0.25% LiCl; 25°	0.9474	4.0	2.8	0.39^{84}	2.04	1.85
7	PPhIA	polycondensation in solution (Ref.83)	DMF—0.25% LiCl; 25°	0.9474	4.0	2.8	0.39^{84}	1.27	2.29
8	PAN	industrial	DMF—THF (1 : 1)	0.9165	1.7	2.0	0.43	2.12	2.15
9	PVC	industrial	THF; 25°	0.8880	0	9.87	0.35^{85}	0.89	2.06

*Abbreviations: PS = polystyrene, PVA = polyvinyl acetate, PPhIA = poly(*m*-phenylene)isophthalamide, PAN = polyacrylonitrile, PVC = polyvinyl chloride, BEK = butyl ethyl ketone, DMF = dimethylformamide, THF = tetrahydrofuran.
**The equation is applicable for a concentration of 0.4 g dl^{-1}.

As noted above, allowance for the diffusion broadening of the boundary for polydisperse polymers is made difficult by the fact that the distributions $g^*(S, t)$ do not change in the same sense (see Fig. 5). By modifying slightly the correction for dilution[73], it is possible to improve considerably the extent to which the $g^*(S, t)$ curves change in the same sense and to carry out the extrapolation to $1/t = 0$ for specimens of PS and polyvinyl acetate (PVA) (see Table 2). For polymers with a low polydispersity—poly(*m*-phenylene)isophthalamide (PPhIA), polyacrylonitrile (PAN), and polyvinyl chloride (PVC)—calculation using Eqn. (5), (6a), (6), and (16) gave distributions $g^*(S, t)$ which changed satisfactorily in the same sence[76].

The asymptotic solution of the equation describing the broadening of the boundary in the sedimentation of a polydisperse substance has the following form[75]:

$$g^*(S, t) = g(S) - \frac{1}{4\tau}\frac{d}{dS}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right] - \ldots; \quad (19)$$

$$G^*(S, t) = G(S) - \frac{1}{4\tau}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right] - \ldots; \quad (20)$$

$$\tau = \omega^2 x_0^2 t/4K. \quad (21)$$

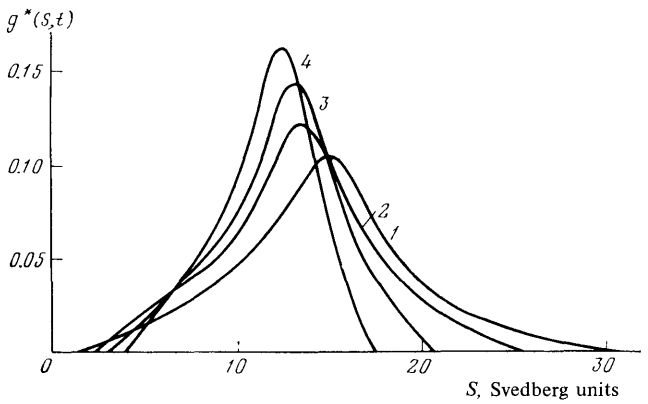


Figure 5. Normalised $g^*(S, t)$ curves for the specimen PS-1 (c = 0.3016 g dl^{-1}, ω = 40 000 r.p.m.), calculated from published equations[74]; time, s: *1*) 887, *2*) 1487, *3*) 2387, *4*) 3287.

In accordance with Eqn. (20), by plotting the sedimentation coefficients S^* against $1/t$ for constant G, it is possible from the magnitude of the intercept to find the values of $S = S^*_{t=\infty}$, and finally to obtain the distribution $G(S)$ corrected with allowance for diffusion.

The time dependence of S^* at constant G^* is given by the equation

$$S^* = a_0 + a_1/\tau + \ldots; \quad (22)$$

$$a_0 = S, \; a_1 = \frac{1}{4}\left[\frac{1}{S^2} - \frac{g'(S)}{Sg(S)}\right]. \quad (22a)$$

The slope of this relationship $Y(S)$ is given by[75]:

$$Y(S) = -\left[\frac{K}{\omega^4 x_0^2 g(S)}\right]\frac{d}{dS}\left[\frac{g(S)}{S}\right]. \quad (23)$$

Since $dG = g(S)dS$,

$$\int_{G^0}^{1} Y(S)\,dS = \Xi = \frac{K}{\omega^4 x_0^2}\left[\frac{g(S^0)}{S^0}\right], \quad (24)$$

where Ξ is the area under the plot of Y against G, and the quantities G^0, $g(S^0)$, and S^0 correspond to the value $Y(S^0) = 0$. Thus K can be calculated from the experimentally determined values of Ξ, $g(S^0)$, and S^0 using Eqn. (24).

If the $g^*(S, t)$ distributions are extrapolated, it is possible to determine K as follows[86]. The slope $W(S)$ of the plot of $g^*(S, t)$ against $1/t$ for constant S, in accordance with Eqn. (19), is given by

$$W(S) = -\frac{K}{\omega^4 x_0^2}\frac{d}{dS}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right]. \quad (25)$$

Integration of this expression with respect to S gives the basic relationship for determining K:

$$\int_{S_A}^{S_B} W(S)\,dS = -\frac{K}{\omega^4 x_0^2}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right]_{S_A}^{S_B}. \quad (26)$$

The limits of integration S_A and S_B correspond to the value $Y(S_{A,B}) = 0$. For a Gaussian function, that is for

$$g(S) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left\{-\frac{(S-S_m)^2}{2\sigma^2}\right\}, \quad (27)$$

the values of $S_{A,B}$ are found from the obvious condition $g^*(S_{A,B}) = g(S_{A,B})$, which leads to the following equation:

$$\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(S-S_m)^2}{2\sigma^2}\right]_{S_A}^{S_B} = \frac{1}{\sigma^*\sqrt{2\pi}}\exp\left[-\frac{(S-S_m)^2}{2(\sigma^*)^2}\right]_{S_A}^{S_B},$$

where $\sigma^* = \sigma + \Delta\sigma$ is the dispersion of the distribution $g^*(S, t)$. If it is assumed that $\Delta\sigma \ll \sigma$, then

$$S_{A,B} = S_m \pm \sigma, \quad (28)$$

$$\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right]_{S_m-\sigma}^{S_m+\sigma} = \frac{2S_m(S_m^2 - 3\sigma^2)}{\sqrt{2\pi e}\,\sigma^2(S_m^2-\sigma^2)^2}. \quad (29)$$

The value of the integral in the left-hand side of Eqn. (26) is determined from experimental data, so that K can be calculated from Eqns. (26) and (29). If the $g^*(S, t)$ curves are symmetrical and similar to a Gaussian distribution function, and if there is no removal of the distributions from the meniscus, it is better to use this method for determining K.[86]

Both methods for determining K have been verified using a large amount of experimental material; thus the calculations for all concentrations of the systems PS–CH and PPhIA–DMF–0.25% LiCl have been duplicated. Since the two methods gave practically identical results, the values of K are subsequently given without an indication of the method of determination. Fig. 6 gives the concentration dependence of the parameter K for the systems studied. The extrapolated values of K and the values calculated from Eqn. (18) are given in Table 3; the relationship $(\bar{h}_0^2/M) = bA/M_0$ was used (b is the length of the monomeric unit, M_0 the molecular mass of the monomeric unit, and A the length of the Kuhn segment). The data in Table 3 show that for the first two θ-systems, the experimentally determined values of K_0 are much greater than the theoretical values K_0^{theor}, calculated from Eqn. (18). For polymers in good solvents, these values are similar; in their comparison it must be borne in mind that K_0^{theor} is in fact the limiting value, since for non-ideal solutions it is necessary in Eqn. (18) to take account of the dimensions $\bar{h}^2$ of the coiled molecules in the good solvent.

From the experimental relationships $D(c)$ [88] and $S(c)$ for PS in CH, it is possible to calculate $K^{calc}(c)$ directly from Eqn. (17) (see Fig. 6*a*). Extrapolation gives for PS-1 the value $K_0^{calc} = 1.8\times10^{-19}$ and for PS-2, $K_0^{calc} = 2.0\times10^{-19}$, that is there is a very large difference between the experimental and calculated values of K_0. In addition, the published illustrations[21] can be used to determine the values of K for various PS specimens: the specimen with $\bar{M}_w = 3.16\times10^5$, $\bar{M}_w/\bar{M}_n = 1.02$, and $c = 0.3180$ has $K = 2.0\times10^{-19}$, and the specimen with $\bar{M}_w = 3.52\times10^5$, $\bar{M}_w/\bar{M}_n = 1.53$, and $c = 0.3253$ has $K = 2.3\times10^{-19}$. For PS-2 at $c = 0.3050$, $K = 17\times10^{-19}$, and for PS-1 at $c = 0.3016$, $K = 41\times10^{-19}$.

These examples show that there is a definite relationship between K and the polydispersity and average molecular mass. Comparison of the values of $\bar{D}_0$, calculated from the values of K_0 and K_0^{theor} (see Table 3) shows that the excess broadening (that is the broadening which is not due to the polydispersity) of the boundary of the solutions of specimens of PS in CH and of PVA in BEK is due chiefly not to diffusion but to other factors.

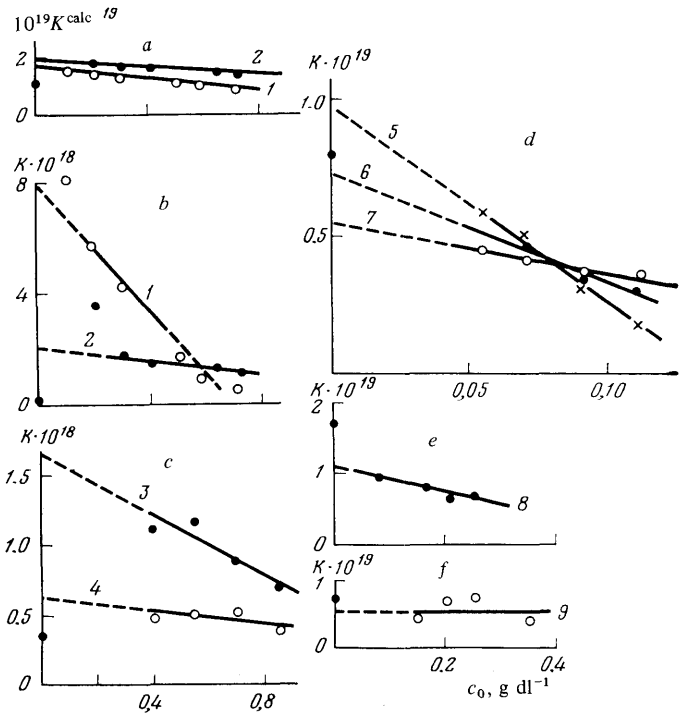


Figure 6. Concentration dependence of the parameter K for the systems: PS–CH, 34° (*a*, *b*); PVA–BEK, 29° (*c*); PPhIA–(DMF–0.25% LiCl), 25° (*d*); PAN–DMF : THF (1 : 1), 25° (*e*); PVC–THF, 25° (*f*). The points on the ordinate correspond to the values of K_0 calculated from Eqn. (18), and the figures give the numbering of the specimens in Tables 2 and 3.

Table 3. Characteristics of the systems studied, related to the determination of the parameter K*.

No.	Polymer	Solvent for the sedimentation; temperature, °C	$10^2\eta_0$, P	M_0	$10^8 b$, cm	$10^8 A$, cm	S_0, Svedberg units	σ_0, Svedberg units	$K_0\cdot10^{19}$	$10^{19}K_0^{theor}$	$10^6\bar{D}$ (from K_0)	$10^6\bar{D}$ (from K_0^{theor})
1	PS	CH; 34°	0.751	105	2.3	20.0[3]	15.7	3.75	80	1.12	5.1	0.071
2	PS	CH; 34°	0.751	105	2.3	20.0[3]	5.65	1.63	20	1.12	3.5	0.198
3	PVA	BEK; 29°	0.710	86	2.3	17.4[3]	11.7	2.83	16.7	3.64	1.43	0.311
4	PVA	BEK; 29°	0.710	86	2.3	17.4[3]	8.20	1.74	6.40	3.64	0.78	0.444
5	PPhIA	DMF—0.25% LiCl; 25°	0.810	242	12.3	34.0[84]	4.26	0.87	0.97	0.82	0.228	0.193
6	PPhIA	DMF—0.25% LiCl; 25°	0.810	242	12.3	34.0[84]	3.43	0.95	0.73	0.82	0.213	0.239
7	PPhIA	DMF—0.25% LiCl; 25°C	0.810	242	12.3	34.0[84]	2.91	0.89	0.55	0.82	0.189	0.282
8	PAN	DMF—THF (1 : 1); 25°	0.633	53	2.3	21.0[87]	3.64	0.90	1.14	1.72	0.313	0.472
9	PVC	THF; 25°	0.471	62.5	2.3	17.9[85]	5.09	0.98	0.55	0.70	0.108	0.137

* Symbols: M_0 is the molecular mass of the monomeric unit; b the length of the monomeric unit; A the length of the statistical segment; and σ_0 the dispersion of the distribution $g(S_0)$.

The values of $\bar{D}_0$ determined from K_0 and K_0^{theor} for PPhIA in DMF–0.25% LiCl do not differ so markedly, but they show the opposite dependence on the average molecular mass (or on $\bar{S}_0$ from Table 3): the value of D_0 decreases with increase in the average molecular mass of the specimen in the first case, and decreases in the second case, so that the excess broadening of the boundary for this system is not due entirely to diffusion.

An important role is apparently played by the hydrodynamic interactions of the components of the mixture (that is the JOE). The cross-term interactions of the flow of the individual components of a polydisperse polymer should lead to a decrease in the rate of sedimentation for the low-molecular-weight fractions and to an increase in this rate for the high-molecular-weight fractions, and this leads to broadening of the $g^*(S, t)$ curves, similar to diffusion broadening. Extrapolation to $1/t = 0$ apparently takes partial or complete account of this broadening, and leads to an increase in the values of K_0 and $\bar{D}_0$ (see Table 3).

b) The use of model functions to take account of the diffusion broadening of distribution curves with respect to sedimentation coefficients in a single recording

In real systems, the correction for diffusion in the sedimentation of polymers with medium and low polydispersity is comparatively small (10–30%), and the second term in the right-hand side of Eqns. (19) and (20) has the character of a correction, and this makes it possible to take it into account by means of model functions[26,66,89]. This can be done most simply on the basis of the Gaussian function (27) by an iteration method[26,66].

The distribution $g(S)$ in the second term in the right-hand side of Eqn. (19) is replaced by the distribution $g^*(S, t)$, and this in turn is replaced by the function (27), with parameters $S_m = \bar{S}^*$ and $\sigma = \sigma^*$,

$$(\sigma^*)^2 = \int_0^\infty (S^* - \bar{S}^*)^2 g^*(S, t)\, dS \Big/ \int_0^\infty g^*(S, t)\, dS. \qquad (30)$$

The following equations are obtained in place of Eqns. (19) and (22):

$$g(S) = g^*(S, t) \Big/ \left\{1 - \frac{1}{4\tau S}\left[\frac{1}{(\sigma^*)^2} - \frac{1}{S^2} - \left(\frac{S - \bar{S}^*}{(\sigma^*)^2} + \frac{1}{S}\right)^2\right]\right\}, \qquad (31)$$

$$S^* = S + \frac{1}{4\tau}\left[\frac{1}{S^2} + \frac{S - \bar{S}^*}{S(\sigma^*)^2}\right]. \qquad (32)$$

The distribution $g(S)$ obtained can be used again to refine the parameters S_m and σ of the Gaussian curve, after which the calculation from Eqns. (31) or (32) is repeated, etc. It should be noted that this procedure involves not the replacement of the real distribution by a model function[23,90–92] but the determination of the law corresponding to the deformation of this distribution (the denominator in Eqn. (31)).

By proceeding analogously, it is possible to obtain expressions[89] for taking account of the diffusion broadening of the boundary by means of the functions of Schulz[93] and Beasley[94]. Fig. 7*b*, for the specimen PPhIA-5, compares the extrapolation distribution $g(S)$ with the distributions calculated from one sedimentation diagram on the basis of the model functions of Gauss, Schulz, and Beasley[89]. The calculation based on the functions of Gauss and Schulz led to good agreement between the calculated and extrapolation curves $g(S)$, since the models coincide fairly closely with the distribution $g^*(S, t)$ (Fig. 7*a*). At the same time, in spite of the fact that the model based on the Beasley function had nothing in common with the distribution $g^*(S, t)$, the $g(S)$ curve calculated on the basis of this function did not differ greatly from the extrapolation distribution.

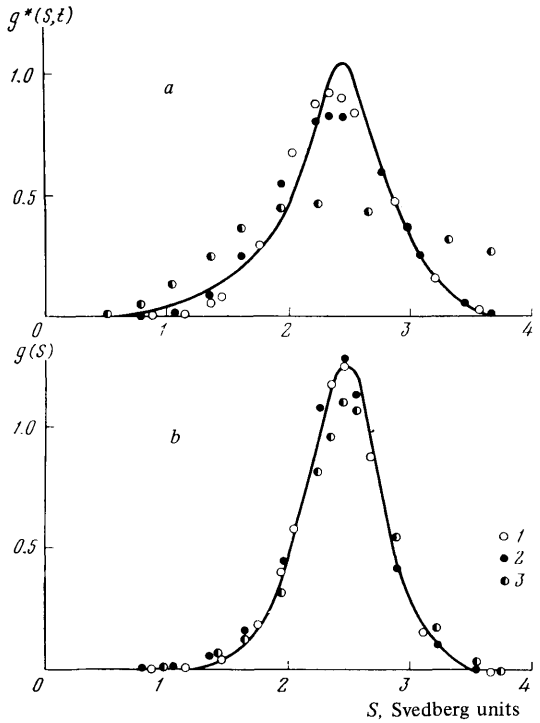


Figure 7. Comparison of the distribution $g^*(S, t)$ for specimen PPhIA-5 ($c = 0.11$ g dl^{-1}) in DMF–0.25% LiCl, $t = 4953$ s (continuous line) with model functions (*a*), and comparison of the extrapolation curve $g(S)$ (continuous line) with the distributions calculated from one recording, based on model functions (*b*): *1*) Gauss; *2*) Schulz; and *3*) Beasley.

Thus when allowance is made for diffusion from a single recording, the slight lack of agreement between the model curve and the real curve $g^*(S, t)$ does not play a significant role, but when the model is completely "separated" from the real distribution $g^*(S, t)$, allowance for diffusion from a single recording leads to distortion of the form of the $g(S)$ curves. Naturally, in real situations, the form of the sedimentation diagrams, the nature of the process by which the polymer is obtained, etc. should influence the type of model function which will make it possible to take account of the diffusion broadening of the distributions $g(S)$.

3. CONCENTRATION DEPENDENCE OF THE SEDIMENTATION COEFFICIENTS OF POLYDISPERSE POLYMERS

For a number of systems (see Table 2), the treatment of the $S(c)$ relationships in the extrapolation of the distributions $G(S)$ to $c = 0$ is carried out in accordance with

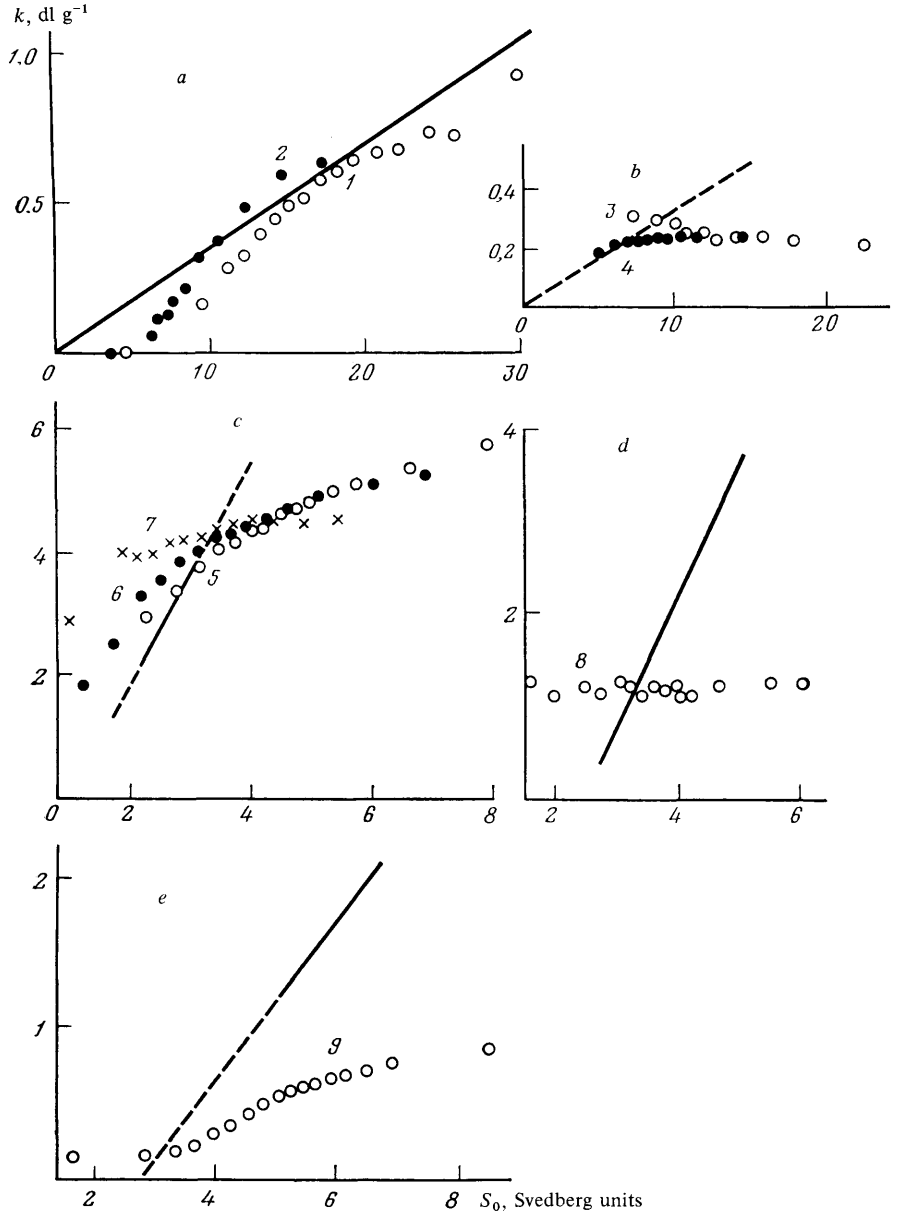


Figure 8. Dependence of k on S_0 for the systems: *a*) PS–CH, 34°; *b*) PVA–BEK, 29°; *c*) PPhIA–(DMF–0.25% LiCl), 25°; *d*) PAN–(DMF : THF = 1 : 1), 25°; *e*) PVC–THF, 25°; the numbers next to the symbols correspond to the numbering of the specimens in Table 2; the continuous and broken lines represent the functions $k(S_0)$ for the fractions.

Eqn. (3). In Fig. 8, the functions $k = k(S_0)$ obtained from these relationships are compared with the same functions for the fractions. The data in Fig. 8 show that polydisperse polymers in good solvents (Figs. 8*c*, 8*d*, and 8*e*) are characterised by a marked weakening of the concentration dependence of the sedimentation coefficients for the high-molecular-weight components, and an intensification of the concentration dependence of the sedimentation coefficients for the low-molecular-weight components. In the system PS–CH (Fig. 8*a*), there is a relatively poor correspondence between the functions for the polydisperse specimens and the fractions.

The following points should be noted regarding the θ-system PVA–BEK (Fig. 8*b*). For this system, a $S(c)$ relationship was not detected[82], but this relationship appeared when a correction was introduced for the pressure μ. The cross-term interactions in the polydisperse polymer compensate one another about the centre of gravity ($\overline{S}$) of the distribution $g(S)$, so that the $\overline{S} = \overline{S}(c)$ relationship (or the analogous functions found from the maxima of the gradient curves) should not be distorted by Johnston–Ogston effects. On the other hand, both theory[50] and experiment[21,54] give a linear dependence of k on S_0 for the case of flexible-chain polymers in a θ-solvent, although

for rigid-chain macromolecules this relationship is apparently more complex[61,62]. In view of these features, the function $k(S_0)$ for the fractions of the system PVA–BEK was estimated from the $\overline{S} = \overline{S}(c)$ relationship for two non-fractionated specimens, and is given by the broken line in Fig. 8*b*. In this system, as in the case of polymers in good solvents, marked differences are observed between the $k(S_0)$ relationships for polydisperse polymers and the analogous functions for homogeneous polymers (fractions).

If it is assumed that diffusion extrapolation does not eliminate completely the broadening of the distributions $g(S)$ due to cross-term interactions, there arises the question of how these interactions influence the concentration dependence of the sedimentation coefficients. The scheme in Fig. 9 can be examined in this connection. The hypothetical distribution with identical relative concentrations of all the components undergoes the usual self-contraction (straight lines *AB* and *CD*) and additional broadening due to cross-term interactions (straight lines *A'B'* and *C'D'*). The concentration dependence $S(c)$ is determined by the difference in the values of S for corresponding points of these straight lines for a given G = const. For the extreme points of the distributions, $A'C' > AC$ and $B'D' < BD$, indicating an increase for low-molecular-weight components, and a decrease for high-molecular-weight components, in the value of the function $\kappa(S_0)$ for polydisperse polymers compared with the same function for the fractions.

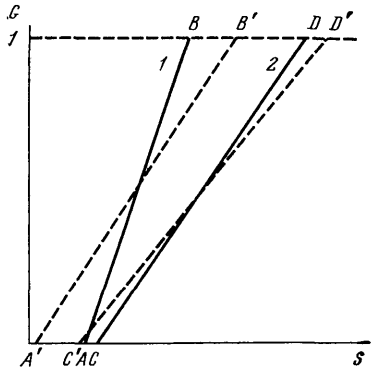


Figure 9. Schematic representation of the influence of effects of the Johnston–Ogston type on the integral distributions $G(S)$; the continuous lines correspond to distributions not perturbed by these effects, and the broken lines represent distributions influenced by these effects. The numbers 1 and 2 correspond to the distributions at concentrations c_1 and c_2 ($c_1 > c_2$).

In the examination of the data in the PS–CH system, it is necessary to take account of the difference by a power of ten between K_0 and K_0^{theor} and K_0^{calc} (see Table 3). It may be assumed that in this system, complete allowance is made for the Johnston–Ogston effects in the extrapolation of $g^*(S, t)$ to $1/t = 0$, so that the functions $k(S_0)$ are similar for the fractions and the polydisperse polymers.

Finally, it should be noted that the interpretation of the concentration dependence of S for polydisperse polymers by means of the scheme in Fig. 9 is inseparable from the concept of local concentration. Thus the concentration dependence of the high-molecular-weight components disappears (the value of k is small), since for these components, the components with higher and lower molecular weights represent a medium with a lower hydrodynamic resistance. Similarly, the accumulation of low-molecular-weight fractions in the sedimentation process may lead to a slight increase in the value of κ.

4. CROSS-TERM HYDRODYNAMIC INTERACTIONS OF THE COMPONENTS IN THE SEDIMENTATION OF POLYDISPERSE POLYMERS

a) Allowance for the JOE of polydisperse polymers

The experimental facts described above leave no doubt that local concentration plays a part in the sedimentation of a polydisperse polymer. Thus in the region of the boundary, the value of the sedimentation coefficient of the ith component will be determined by the concentrations and the interactions of the components with numbers from 1 to i, and in the region of the plateau it will be determined by the concentrations and interactions of all the components. In the general case, it is possible to determine phenomenologically the sedimentation coefficient of the ith component in a solution of q components of a polydisperse polymer as follows[8,95]:

$$S_i = S_{0i} \Big/ \left(1 + k_i c_i + \sum_{j=1}^{q} k_{ij} c_j\right);\ j \neq i;\ i = 1, 2, \ldots, q, \qquad (33)$$

where S_{0i} is the sedimentation constant of the ith component, and the coefficients k_i and k_{ij} were defined earlier. Eqn. (33) represents a generalisation of Eqns. (3) and (12), and is applicable for sufficiently dilute solutions, since in the denominator of the right-hand side the terms with the products (squares) of the concentrations have been discarded. If the concentrations c_i are taken as the concentrations in the region of the plateau, Eqn. (33) gives the values of the sedimentation coefficients in the region of the plateau.

As already noted, for an ideal solvent, $k_{ij} = k_j$, and the following equation is obtained in place of Eqn. (33):

$$S_i = S_{0i} \Big/ \left(1 + \sum_{j=1}^{q} k_j c_j\right), \qquad (34)$$

and for the intermediate region (see Fig. 10):

$$S_i = S_{0i} \Big/ \left(1 + \sum_{j=1}^{i} k_j c_j^*\right). \qquad (35)$$

A slightly different argument may be used. It may be assumed that the solvent for the ith component is the solution of the components from 1 to $i - 1$ (Fig. 10), and the influence of these components on the sedimentation of the ith component reduces to a decrease in the rate of its movement as a result of the viscosity of the medium. Neglecting quadratic terms, the following relationships are obtained for the viscosity η of the solution of the $i - 1$ components:

$$\frac{\eta - \eta_0}{\eta_0 c} \simeq [\eta];\ c = \sum_{j=1}^{i-1} c_j^*;\ [\eta] = \sum_{j=1}^{i-1} [\eta]_j,$$

where $[\eta]_j$ is the characteristic viscosity of the jth component. The obvious relationship $S_1\eta_1 = S_2\eta_2$ (the indices 1

and 2 here correspond to different solvents) and Eqn. (3) give:

$$S_i = S_{0i}\Big/\left[1+\left(\sum_{j=1}^{i-1} c_j^*\right)\left(\sum_{n=1}^{i-1}[\eta]_n\right)\right](1+k_ic_i^*).$$

Rejection of the "cross-terms" $c_j[\eta]_n$, $j \neq n$, gives:

$$S_i = S_{0i}\Big/\left(1+\sum_{j=1}^{i-1} c_j^*[\eta]_j\right)(1+k_ic_i^*). \quad (36)$$

For flexible-chain polymers, $k_j = A[\eta]_j$, where A is a constant for a given polymer–solvent system[3, 61, 62]. Using this relationship, Eqn. (36) can be transformed to

$$S_i = S_{0i}\Big/\left(1+\sum_{j=1}^{i-1} k_jc_j^*/A\right)(1+k_ic_i^*).$$

In the particular case where $A = 1$, Eqn. (36a) becomes Eqn. (35).

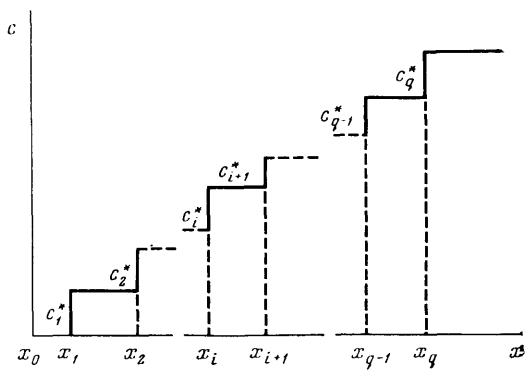


Figure 10. Schematic representation of the dependence of the concentration c on the coordinate x in the centrifuge cell in the sedimentation of a polydisperse polymer consisting of q components.

In the calculation of the true concentrations of the components c_i^0, the idea of additivity of the paired interactions is used, that is it is assumed that for an arbitrary pair of components i and j, by analogy with Eqns. (13), (15a), and (15b), the following relationships are applicable:

$$\psi_{ij} = S_{0i}/S_{0j},\ i = 1, 2, \ldots q; \quad (37)$$

$$c_{ij}^0 = c_i^*(y_j - y_i)/[y_j^{1-\psi_{ij}} - 1],\ i < j; \quad (38a)$$

$$c_{ji}^0 = c_i^*y_i + c_j^*y_j - c_{ij}^0, \quad (38b)$$

where c_{ij}^0 is the concentration of the ith component in the original mixture, calculated from c_i^* with allowance for the interaction with the jth component, neglecting the influence of the other components of the mixture. The sedimentation constants S_{0i} are determined from Eqns. (34), (35), and (36a). Averaging with respect to the interactions with all the components gives finally:

$$c_{i0} = \sum_{j=1}^{q} c_{ij}/(q-1),\ j \neq i. \quad (39)$$

The change to the distribution $g_i(S_{0i})$ is brought about by means of the relationship:

$$g_i(S_{0i}) = c_{i0}x_i/[1 + m(r_i - 1)]. \quad (40)$$

For centrifuges fitted with the usual refractometric optics, the experiment gives the distributions of the displacements $z_i(x_i)$. Since the calculations require the values of the concentrations throughout, it is necessary either to carry out a separate diffusion experiment or to make use of the relationship[48, 65]:

$$R\Delta x\sum_{i=1}^{q} z_iy_i = c_0, \quad (41)$$

where R is the refractometric coefficient, and $\Delta x = x_i - x_{i-1}$. By determining $R\Delta x$, it is possible to find c_i^*:

$$c_i^* = z_iR\Delta x\,. \quad (42)$$

In addition, it is necessary to know the function $k_i = k_i(S_{0i})$, preferably determined in experiments with narrow fractions. In the case of the linear relationship

$$k_i = \pm a + bS_{0i} \quad (43)$$

Eqn. (35) gives:

$$S_{0i} = S_i^*\left(1+\sum_{j=1}^{i-1} k_jc_j^* \pm ac_i^*\right)\Big/(1 - S_i^*bc_i^*). \quad (44)$$

The system of equations (43) and (44) is solved successively, beginning from $i = 1$.

Thus the theory takes account of the following factors influencing the form of the sedimentation curves: the hydrostatic pressure, the concentration dependence of the sedimentation coefficients, the sector form of the cell, and the hydrodynamic interaction of the components (JOE). Only the part played by diffusion is not taken into account. The last section will deal with the characteristic features of the application of this theory to specific systems, and in particular, methods of eliminating the diffusion broadening of the distributions $g(S)$.

b) Determination of the distributions $g(S_0)$

Allowance for the JOE not only gives a new series of equations for calculating $g_i(S_{i0})$ but also makes it possible to take a fresh look at various problems of sedimentation analysis[96]. The disappearance of the high-molecular-weight "tails" of the MMD of a number of PS and PE specimens during sedimentation was first detected by Belyaev[97]. It is obviously incorrect to attribute this fact to dilution or to a decrease in concentration in the region of the plateau[98, 99]. The concept of the JOE provides a comparatively simple explanation of this phenomenon. As a result of cross-term interactions in the sedimentation process, there is an accumulation of the low-molecular-weight components and a relative decrease in the concentration of the high-molecular-weight components. With the passage of time, this leads to a displacement of the maximum towards smaller values of S and to disappearance of the "tail" of the distribution.

In the determination of the MMD of highly polydisperse polymers by the coordinate method[37], an increase in the height of the maximum on the $g(S, t)$ curves of polyethylene (PE) in α-bromonaphthalene at 110°C with increase in the distance between the fixed coordinate and the line corresponding to the start of sedimentation was detected. The displacements (and concentrations) for different fixed coordinates in fact correspond to different stages of the sedimentation process. The farther the coordinate from

the line corresponding to the start of sedimentation, the stronger the manifestation of the cross-term interactions (see Eqn. (38a)) and the higher the maxima on the $g(S, t)$ curves for PE, corresponding to fairly low-molecular-weight components. These results show that the JOE is marked in the sedimentation of strongly polydisperse polymers, and it is for this reason that it is hardly possible to determine correctly the concentration of low-molecular-weight compounds in a polymer without allowance for this effect[41].

Table 4. Characteristics of the distribution $g(S_0)$, calculated from one recording by different methods.

c, g dl^{-1}	$10^{-3}t$, s	Allowance for the JOE		Method (Refs. 26, 66)	
		$\bar{S}_0$, Svedberg units	σ_0 Svedberg units	$\bar{S}_0$, Svedberg units	σ_0 Svedberg units
PS-1 in CH (34°)					
0.7110	3.02	14.1	4.48	15.1	3.93
	3.62	14.4	4.12	15.3	3.46
	4.22	14.6	4.20	15.5	3.29
	5.12	14.7	4.11	15.4	3.18
0.3016	0.887	19.0	7.39	18.7	5.60
	1.487	18.5	6.73	17.3	4.17
	2.387	18.2	6.16	17.7	4.65
	3.287	17.7	5.85	17.2	4.23
0.1142	1.22	16.2	6.41	14.7	4.62
	1.82	17.1	6.59	16.0	5.35
	2.42	16.7	5.95	15.6	4.77
average value*		17.4±0.8	6.3±0.3	16.4±1.0	4.6±0.3
PPhIA-5 in DMF—25% LiCl (25°C)					
0.110	1.92**				
	3.12	2.88	0.838	calculations impossible	
	4.32	3.04	0.875		
	6.24	3.10	0.895		
	7.32	3.03	0.924		
0.090	1.304				
	2.493	2.94	1.051		
	3.693	2.96	1.065	3.78	1.151
	4.893	3.13	1.059	3.94	0.951
	6.093	3.62	1.261	4.07	1.012
0.070	0.974				
	2.17	3.26	1.201	3.46	1.170
	3.37	3.27	1.179	3.45	1.033
	5.17	3.35	1.121	3.53	0.827
	6.37	3.44	1.155	3.56	0.794
0.055	1.056				
	1.953	3.26	1.201	3.46	1.170
	2.853	3.27	1.179	3.45	1.033
	4.053	3.35	1.121	3.53	0.827
	4.953	3.44	1.155	3.56	0.794
average value		3.30±0.18	1.13±0.08	3.70±0.18	0.97±0.14

* For PS-1, the values for $c = 0.711$ and the values for the first recording $c = 0.3016$ were not included in the averaging (for explanation see text); for PPhIA-5, the values for $c = 0.11$ and the values for the second recording ($t = 2.493 \times 10^3$ s) $c = 0.09$ g dl^{-1} were not included.
** The first recordings for all concentrations of PPhIA served only for the determination of the end of the $g(S)$ curve (see text).

Table 4 gives the characteristics of the distributions $g(S_0)$ for specimens of PS-1 in CH at 34°C and of PPhIA-5 in a DMF–0.25% LiCl mixture at 25°C, calculated from a single recording using the theory taking account of the JOE or by a method[26,66] based on the mathematical formalisation of the extrapolation procedures, that is on the empirical values of the diffusion parameter K and the empirical functions (43).[76] In the calculations by the first method, the distributions $g_i^*(S_i)$ are first corrected with allowance for the concentration dependence of the sedimentation coefficients, pressure, the JOE, and dilution, after which (for $c = 0$) a correction is introduced for diffusion from the theoretical value of the parameter K.[76] For polystyrene, the correction for the $S(c)$ dependence was introduced from Eqn. (43) ($a = 0$, $b = 0.036$ dl g^{-1}) for both methods. The algorithms for the calculations were naturally different in these cases, since the original concepts are diametrically opposed (local concentration and plateau concentration). The sedimentation coefficients of PPhIA were corrected for the concentration dependence using different relationships: the first method (with allowance for the JOE) was based on data for fractions: $k_i = 0$ for $S_i \leq 0.75$; $k_i = -1.11 + 1.48\, S_{i0}$ for $S_i > 0.75$ (Svedberg unit); the second method was based on data for non-fractionated specimens $k_i = 2.12\sqrt{S_{0i}}$.

As already noted, the cross-term interactions of the components of a specimen non-uniform with respect to mass lead to the loss of the distribution "tail". Theory[95] provides a somewhat unusual method for reconstructing the end of the $g_i(S_{i0})$ curve. It is assumed that the true end of the distribution is the point obtained for short ultracentrifuging times. To supplement q graphical fractions (with concentrations $c_i^* > 0$), n "correction" components (with concentrations $c_j^* = 0$, $j > q$) are introduced into the computer store. Here it should be noted that the calculations are carried out by computer, and the complexity of the mathematical treatment is no obstacle to the determination of $g_i(S_{i0})$. The calculations using Eqns. (37)–(39) give non-zero concentrations for the "corrected" components.

Fig. 11 gives the distributions $g(S_0)$ for PS-1 in CH, $c = 0.3016$ g dl^{-1}, calculated by the first method with allowance for the JOE (circles). One of the curves was calculated with restoration of the "tail" for the values $q = 26$ and $n = 6$ (empty circles) and differs little from the curve obtained without restoration of the "tail" (filled circles). The calculation by the second method[26,66] gives a distribution which is very much sharper (crosses), and which differs considerably from the distribution determined by the first method. It is possible to point to three reasons for this sharpening. Firstly, the loss of the "tail" in the calculation by the second method[26,66] is irreversible. Secondly, the diffusion contribution to the broadening of the boundary is greatly over-estimated as a consequence of the JOE.[76] Thirdly, when there is appreciable diffusion, there is significant distortion of the $g(S_0)$ curves as a consequence of the difference between the model (Gaussian function) and the real distribution $g^*(S, t)$, whereas when there is little diffusion, these differences are not significant[89].

The generally accepted extrapolation procedures[2-4] lead to the following characteristics of the $g(S_0)$ distributions for the specimens studied: for PS-1, $\bar{S}_0 = 15.7$ and $\sigma_0 = 3.80$ Svedberg unit; for PPhIA-5, $\bar{S}_0 = 3.6$ and $\sigma_0 = 0.98$ Svedberg unit. Comparison of these parameters with the data in Table 4 confirms the familiar fact that extrapolation of the $g(S)$ curves in the case of polymers (PS) of medium polydispersity leads to a loss of the fine details of the distributions (for example, poorly resolved maxima) and the "tail", and to sharpening of the distributions (compare the values of σ_0).

The data obtained by different methods for the polymer PPhIA-5 with a low polydispersity show better agreement with one another (Table 4), but it was not possible, by the second method, to determine $g(S_0)$ for all recordings at $c = 0.11$ g dl^{-1} and for the first recording at $c = 0.09$ g dl^{-1}, whereas the calculations using the theory of Ref. 95 can be carried out for all values of c and t.

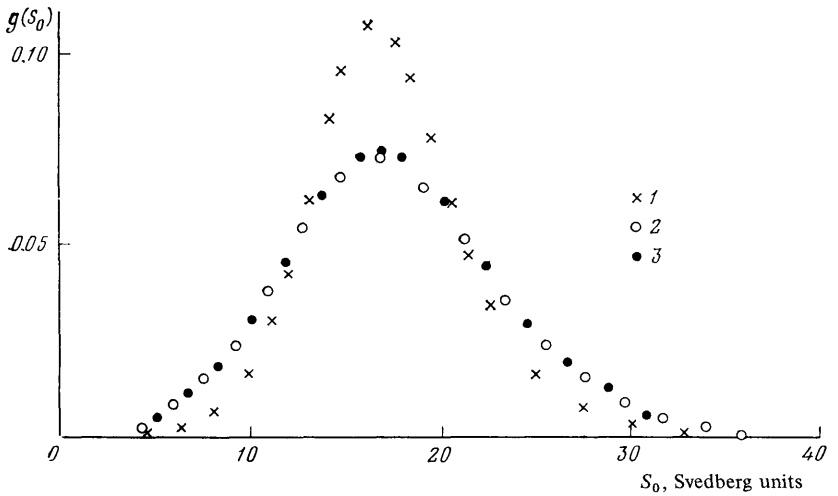


Figure 11. Distributions $g(S_0)$ for PS-1 in CH, 34°, $c = 0.3016$ g dl^{-1}, calculated from one recording for $t = 3287$ s by the published method[26,66] (*1*) and from theory, with allowance for the JOE, with (*2*) and without (*3*) additional components.

The slight decrease in the value of $\bar{S}_0$ in the calculations by the first method is apparently due to two features. Firstly, the theory[95], strictly speaking, refers to ideal systems. The results of the study of the JOE of binary mixtures in a good solvent indicate that the theory of Ref. 29 in this case is confirmed quantitatively only in the limit as $c \to 0$.[71] For PPhIA-5, the calculation algorithm should be based not on Eqn. (35) but on Eqn. (36). Secondly, the first recording was carried out too late, and part of the "tail" was lost. This applies particularly to the data for $c = 0.11$ g dl^{-1}.

A characteristic feature is that the parameters of the distributions $g(S_0)$ calculated by the first method have a much smaller scatter than the analogous values calculated by the second method. All the results obtained using Eqns. (35)–(44) must be regarded as preliminary—they can be improved considerably—whereas it is practically impossible to improve the calculation by the procedure of Refs. 26 and 66. The last approach preserves some of the unsatisfactory features characteristic as a whole of the extrapolation of the distributions, which is based on a number of arbitrary assumptions: simple additivity of the factors operating and the movement of the components, neglect of the cross-term interactions of the components, and the concept of plateau concentration. The approach based on allowance for the JOE and the concept of local concentration appears more correct[95,96].

V. CONCLUSION

Detailed analysis of the experimental data leaves no doubt that the cross-term hydrodynamic interactions of the components—the Johnston—Ogston effect (JOE)—play an important part in the sedimentation of polymers of high and medium polydispersity, and can be observed in the sedimentation of polymers of low polydispersity. Such phenomena as the displacement of the maxima, the loss of the "tail", the increase in the height of the maximum of the distribution $g^*(S, t)$ with increase in the distance between the fixed coordinate and the line corresponding to the start of the sedimentation, the non-diffusion broadening of the $g(S)$ curves, the decrease in the effect of the $S(c)$ dependence for the high-molecular-weight components of a mixture, and the increase in its effect for the low-molecular-weight components, can be explained only on the basis of the JOE and the concept of local concentration.

The distinctive feature of the situation is that no method has been found for making rigorous allowance—via the equations of motion—for the cross-term interactions of the components undergoing sedimentation, even for a binary mixture; the expectation of an exact theory of the sedimentation of many-component systems is therefore illusory. Thus at present the only possible approach is that based on the principle of additivity of the paired interactions[95].

The fact that the problem of the sedimentation of polydisperse polymers is insoluble theoretically, and decades of the preferred application of the extrapolation method, the concept of plateau concentration, unjustified single-recording and single-concentration approximations, and the view that different effects are "compensated" on the one hand have not stimulated serious experimental-methodological studies and on the other have effectively "immunised" research workers against theoretical work. This is the only possible explanation for the fact that very important work[48,75] has remained neglected, although the first of the works cited provides a theoretical basis for the treatment of sedimentation measurements on fractions, and the second makes it possible to carry out a quantitative estimation and allowance for the role of the diffusion factor in the sedimentation of polydisperse polymers[26,66,76,86,89].

The natural failure of the concept of plateau concentration and the development, on a new basis, of the concept of local concentration[95] indicates not only the usefulness but also the necessity of determining $g(S_0)$ from a single concentration, since for polymers of medium polydispersity, the extrapolation of the $g(S)$ distributions to $c = 0$ has no physical foundation. Using Fujita's theory[75], it is possible from a single recording to take account of the diffusion broadening of the $g^*(S, t)$ curves[26,66,89]; thus the required $g(S_0)$ distribution is obtained by computer

calculation from a single sedimentation diagram. Preliminary data[96] indicate that this method of determining $g(S_0)$ is promising.

In conclusion, the calculation procedure should be mentioned: it is not simple, and can only be carried out by computer. Eqns. (8) and (16) are first used to find the distribution $g^*(S, t)$ for which it is possible to introduce a correction for diffusion broadening (see Part III); the choice of the values of K is discussed below.

As already noted, for polymers of high and medium polydispersity, the required distribution $g(S_0)$ (or $g(M)$) is distorted by the loss of the "tail". The first recording must therefore be fixed at different times of ultracentrifuging. The time of ultracentrifuging should not be so short that the introduction of a correction for dispersal by the formal rule has no influence on the values of the sedimentation coefficients.

Using the parameter of the distribution $g(S)$, the diffusion problem is solved for the end of the distribution of the displacements, obtained in the first recording. In this case it is not strictly necessary to determine the entire distribution; it is sufficient to determine only the position of the end of the curve. The overall result gives the value of the sedimentation coefficient for the end of the distribution S_{end}, from which the number of components "lost" is subsequently determined.

Eqns. (41) and (42) are used to calculate c_i^*; the values of the sedimentation constants of the components S'_{i0} are then found in a first approximation from Eqns. (43) and (44), and this makes it possible to take account of the JOE from Eqns. (37), (38a), (38b), and (39). The corrected concentrations of the components c_{i0} can then be used to obtain more accurate values of the sedimentation constants S_{i0} and the functions $g_i(S_{i0}, t)$ from Eqn. (4). Since the concentration effects are eliminated, the diffusion broadening can be taken into account from the theoretical value of the parameter K (see Eqn. (18)). Alternatively, the values of K obtained from diffusion experiments can be used.

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