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I. Ya. Poddubnyi, V. A. Grechanovskii

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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I. Ya. Poddubnyi, V. A. Grechanovskii

ON THE CONCENTRATION DEPENDENCE OF THE SEDIMENTATION CONSTANT IN “IDEAL” SOLVENTS

(Presented by Academician V. A. Kargin on 7 VI 1963)

The study of the dependence of the sedimentation constant S on the concentration C of a polymer in solution occupies an important place in investigations of the molecular-weight distributions of polymers. Of particular interest are data on the dependence $S(C)$ in thermodynamically ideal solvents, since it is precisely in them that the maximum resolving power of the ultracentrifuge is realized. In addition, this question is of independent physical interest.

At present there are two opposing points of view on the nature of the dependence $S(C)$. From Yamakawa’ s theoretical calculations ([1]) it follows that the concentration dependence of the translational friction coefficient in a θ-solvent should be practically absent (at least in the region of concentrations where the third virial coefficient can still be neglected). On the other hand, Gekhtiya ([2]) showed that the concentration dependence of the sedimentation constant (and, consequently, of the friction coefficient of macromolecules) has a rather complex form and is not connected with the thermodynamic properties of the solvent. There is also the assumption that the presence of a concentration dependence in θ-solvents is associated with the formation, during sedimentation, of certain virtual ensembles of macromolecules ([3]). The literature contains limited experimental material confirming both the first ([4,5]) and the second ([6,7]) points of view. Therefore, obtaining additional information, as well as establishing new regularities, is of great interest in solving the problem of the concentration dependence of the translational friction coefficient of macromolecules.

Fig. 1. Extrapolation to infinite dilution of the sedimentation constant of linear

cis-1,4-polybutadiene in a hexane + heptane mixture for fractions of different molecular weight:
a –55 000, –142 000, –262 000, –395 000, –1 080 000.
$\partial(1/S)/\partial C = 0.90$

In the present work, the dependence of the sedimentation constant on the initial concentration was studied for a number of thermodynamically ideal polymer-solvent systems. Only that concentration region was investigated in which the resolving power of the ultracentrifuge was still high.

In Figs. 1, 2, and 3, in the usual coordinates $1/S$–C, data are presented for the following systems:

1) linear cis-1,4-polybutadiene –hexane + heptane mixture (1 : 1) (θ-temperature +5°);
2) branched cis-1,4-polybutadiene –hexane + heptane mixture (1 : 1) (θ-temperature +3°);
3) a copolymer of divinyl with styrene–n-octane (θ-temperature +21°). All data were obtained on a "Phywe" ultracentrifuge. The experiments were carried out at a temperature of 20°; sufficiently homogeneous fractions of the corresponding polymers were used in them; experimental details are described in ([8]). Some deviations from the θ-temperature do not change the character of the dependences presented ([8]).

Analogous results were obtained by us also for cis-1,4-polyisoprene in a mixture of hexane with isopropyl alcohol (θ-temperature +21°). The data presented indicate that in all the systems studied there is a distinct dependence of the sedimentation constant on the solution concentration. This dependence is more pronounced for linear macromolecules than for branched ones, and at the same time is almost the same for the divinylstyrene copolymer and the linear sample of cis-1,4-polybutadiene. Attention is also drawn to the fact that when the molecular weight of the fractions changes by a factor of 15–20, the character of the concentration dependence, i.e., the slope of the straight lines in the graphs, practically does not change; in other words, $\frac{\partial(1/S)}{\partial C}$ does not depend on the molecular weight. According to the generally accepted method, extrapolation of the sedimentation constant to infinite dilution is performed using the equation:

[Figure 2 graph]

Fig. 2. Extrapolation to infinite dilution of the sedimentation constants of branched cis-1,4-polybutadiene in a hexane + heptane mixture for fractions of different molecular weight: a–60,000, –167,000, –174,000, –350,000, –830,000. $\partial(1/S)/\partial C = 0.55$

$$\frac{1}{S} = \frac{1}{S_0}(1 + K_S C); \tag{1}$$

whence we have

$$\frac{\partial(1/S)}{\partial C} = \frac{K_S}{S_0}. \tag{2}$$

For a linear polymer in a θ-solvent:

$$S_0 \sim M^{1/2}. \tag{3}$$

In addition, it is known (^{9}) that for the sedimentation of Gaussian coils:

$$K_S \sim \frac{V}{M} \sim \frac{(\overline{r_0^2})^{3/2}}{M} \sim M^{1/2} \tag{4}$$

(V—volume, M—mass, $\overline{r_0^2}$—mean square radius of inertia of the macromolecule).

[Figure 3 graph]

Fig. 3. Extrapolation to infinite dilution of the sedimentation constants of a divinylstyrene copolymer in *n*-octane for fractions of different molecular weight: *a*—80,000, —186,000, —340,000, —710,000. $\partial(1/S)/\partial C = 0.87$

Thus, in the present case $\frac{\partial(1/S)}{\partial C}$ does not depend on M and is determined only by the sizes and shape of the sedimenting molecules. This result agrees with the experimental data obtained by us and explains the difference in the character of the concentration dependence of linear and branched polymers, since the proportionality coefficients in equations (3) and (4) depend on the degree of branching. In the case of branched macromolecules, violations of the equations may in principle occur.

(3) and (4), leading to a dependence of the slope on molecular weight in plots of $1/S$ versus C; however, this effect is very small.

The fact that the character of the concentration dependence in the thermodynamically ideal polymer-solvent systems studied corresponds to equation (1), with $\partial(1/S)/\partial C$ independent of molecular weight, makes it possible to conclude that in the present case we are dealing with the sedimentation of individual macromolecules that do not form any structural ensembles.

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