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A Hydrodynamic Invariant of Polymeric Molecules

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Theories of the hydrodynamic properties of macromolecules in solution are examined, from which the invariant relation $A_0 = k\eta_0(M[\eta]/100)^{1/3}f$ can be obtained between the intrinsic viscosity $[\eta]$, the molecular mass M, and the coefficient of sliding friction of the molecule f. Analysis of the experimental results will indicate the most probable values of the invariant A_0 for various classes of polymers. A list of 314 references is included.

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I. INTRODUCTION

Determination of the molecular mass of a polymer is one of the most important problems in research on macromolecular compounds. Two "absolute" methods—light scattering and sedimentation–diffusion analysis of the polymer in solution—can usually be successfully applied[1]. However, neither method is effective with many polymers commonly used at the present time, which dissolve only in highly specific solvents[2]. The molecular masses of such polymers must therefore be found from certain hydrodynamic characteristics of their molecules, which can be determined experimentally with adequate reliability. Such characteristics are primarily the intrinsic viscosity $[\eta]$ and the coefficient of sliding friction of the molecule f, the latter determined from diffusion in solution.

II. CONCEPT OF THE HYDRODYNAMIC INVARIANT

Both intrinsic viscosity $[\eta]$ and coefficient of friction f are related to the molecular mass M or the contour length of the molecular chain $L = \lambda M/M_0$ (where λ is the projection of a monomer unit in the direction of the chain) by the well known formulae[1,3]

$$[\eta] = \Phi(LA)^{3/2}/M \qquad (1)$$

$$f = kT/D = P\eta_0(LA)^{1/2} \qquad (2)$$

in which D is the coefficient of translational diffusion of the polymer at infinite dilution, η_0 the viscosity of the solvent, A the Kuhn segment length representing the equilibrium rigidity of the polymer chain, M_0 the molecular mass of a monomer unit, k Boltzmann's constant, T is the temperature, and Φ and P are hydrodynamic coefficients depending on L, A, and certain other parameters such as intramolecular hydrodynamic interaction and effects of the excluded volume in non-ideal (non-θ) solvents. Calculation of the functions Φ and P is the main object of theories of the hydrodynamic properties of macromolecules in solution[3]. If the coefficient of friction f is determined experimentally not from diffusion but from sedimentation measurements, formula (2) is replaced by the equivalent expression

$$f = (M/sN_A)(1-\bar{v}\rho) = P\eta_0(LA)^{1/2} \qquad (3)$$

in which s is the sedimentation coefficient at infinite dilution, N_A Avogadro's number, $\bar{v}$ the specific partial volume of the polymer in solution, and ρ the density of the solvent.

Each of the relations (1)–(3) contains, in addition to one quantity that can be measured experimentally ($[\eta]$, D, or s), two molecular characteristics A and L (or $M = LM_0/\lambda$), which determine the equilibrium rigidity and the molecular mass respectively of the polymer chain. In order that the molecular mass can be found from experimental values of intrinsic viscosity or coefficient of friction, it is therefore necessary that both A and the form of function $\Phi(L, A)$ or $P(L, A)$ should be known for the given polymer. Since such data are usually absent for a newly investigated polymer, neither viscometry, measurement of diffusion coefficient, nor rapid sedimentation can usually serve in isolation as an independent method (not involving preliminary calibration) for determining the molecular mass of the polymer. However, use of two independently determined experimental quantities in Eqns.(1)–(3), with simultaneous solution of the appropriate pair of these equations, may yield an expression that does not contain the product LA in explicit form. Thus the two formulae (2) and (3) will give Svedberg's equation, from which are absent not only LA but also the parameters Φ and P and which serves as the chief absolute method for determining molecular mass from combined sedimentation and diffusion data.

Elimination of LA from formulae (1) and (2) yields the relation

$$kP^{-1}(\Phi/100)^{1/3} = \eta_0 D(M[\eta]/100)^{1/3}T \equiv A_0 \qquad (4)$$

while the use of Eqns.(1) and (3) for this purpose gives

$$kP^{-1}(\Phi/100)^{1/3} = R\eta_0(1-\bar{v}\rho)^{-1}M^{-2/3}([\eta]/100)^{1/3}s \equiv A_0 . \qquad (5)$$

The expression on the right-hand side of (4) was first discussed by Vallet[4,5], who measured diffusion coefficients and intrinsic viscosities for polystyrene fractions differing in molecular mass, and showed that the product $(M[\eta])^{1/3}D\eta_0$ was invariant in a series of these fractions. He explained this rule by regarding the polymer molecule as a solid sphere and applying to it the Stokes and Einstein laws to describe the diffusion and viscosity phenomena of polymer solutions. A little later Mandelkern and Flory[6] based the invariance of (5) on a chain molecule regarded as a hydrodynamically impermeable sphere of radius proportional to the mean square distance between the ends of the chain $\langle h^2\rangle^{1/2}$, with both P and Φ considered to be universal constants for all polymers.

At the same time Tsvetkov and Klenin[7], using the Debye–Bueche model of a partly permeable sphere[8], showed that the parameter A_0 (Eqn.4) can in principle be invariant over a

wide range of molecular masses even with appreciable permeability of the molecular coil, i.e. under conditions such that P and Φ do not individually remain constant with variation in molecular mass. They illustrated the invariance of A_0 by measuring D and $[\eta]$ of polystyrene fractions in dichloroethane over the molecular-weight range $(250-1320) \times 10^3$ g mole^{-1} and determining the corresponding value $A_0 = (3.42 \pm 0.06) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. From this they concluded[7] that it was possible and advisable to determine the molecular masses of polymers from viscosimetric data and the measured diffusion coefficient of their solutions by means of formula (4) and the above value of A_0.

In order to demonstrate the possibility of using this method it is necessary to analyse in greater detail the properties of the polymer–solvent system that ensure invariance of the hydrodynamic parameter A_0.

III. THEORY OF THE HYDRODYNAMIC PROPERTIES OF MACROMOLECULES

1. Chain Length and Hydrodynamic Interaction

If a solution is present under θ-conditions and the conformation of a molecular chain can be regarded as a Gaussian coil (i.e. $\langle h^2 \rangle = LA$), expressing P and Φ in formula (4) in terms of the theory of sliding friction and Kirkwood–Riseman viscosity[9] respectively yields for A_0 the expression

$$A_0 = \frac{k}{6\pi}(N_A/100)^{1/3} F(\sigma) \tag{6}$$

$$F(\sigma) = \frac{1+(8/3)\sigma}{\sigma}\left[\frac{\sigma}{1+(2/3)\sigma}\right]^{1/2} \tag{7}$$

in which

$$\sigma = \frac{3}{\sqrt{6\pi}} \cdot \frac{d}{\lambda}\left(\frac{L}{A}\right)^{1/2} \tag{8}$$

is a parameter representing the intramolecular hydrodynamic interaction. It follows from (6)–(8) that A_0 is a function of the relative chain length L/A, the length of a monomer unit λ in the direction of the chain, and its hydrodynamic diameter d (i.e. the diameter of a sphere representing a monomer unit for sliding friction).

For a polymeric homologous series (d/λ constant) the dependence of A_0 on chain length L can be readily ascertained by analysing the expressions (6)–(8). With increase in L/A and hence in the parameter σ the function $F(\sigma)$ tends to the limit $F(\sigma)_\infty = (8/3)(3/2)^{1/3} = 3.053$, while A_0 tends to $A_\infty = 4.1 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$ (or 4.1×10^{-17} J deg^{-1} mole$^{-1/3}$). With very small L/A values and hence $\sigma \ll 3/8$, on the other hand, it follows from (7) that $F(\sigma) \approx \sigma^{-2/3}$ and $A_0 \to \infty$ as $L/A \to 0$, as noted previously[1]. Thus, according to theory[9], at sufficiently low values of L/A the parameter A_0 is by no means invariant but increases with decrease in chain length. Since, however, $d/\lambda \approx 1$, it is readily seen that this increase becomes appreciable only when $L/A < 1$: for example, with $L/A = 0.5$ the value of A_0 exceeds A_∞ by only 10%; throughout the remaining range of values $1 < L/A < \infty$, it follows from (6)–(8) that A_0 is indeed invariant, differing from A_∞ at most by tenths percent.

It must be borne in mind, however, that the hydrodynamic properties of polymer chains in the range $L/A \leq 1$ cannot be discussed in terms of a theory[9] that regards a polymer molecule as a Gaussian chain, which assumes that $L/A \gg 1$.

Hence theories of the hydrodynamic properties of vermiform chains must be used to discuss the dependence of A_0 on chain length throughout the range of possible values of L/A. The best hydrodynamic model of a chain molecule in a θ-solvent may be a vermiform cylinder of contour length L and diameter d, the ends of which are bounded by hemispheres[10,11].

With this model expressions have been obtained for the parameters P and Φ as functions of the relative length L/A and the relative diameter d/A of the chain molecule[10–13]. They can be written as the ratios P_∞/P and Φ/Φ_∞, where $P_\infty = 9/4(\pi/6)^{1/2}\pi = 5.11$ and $\Phi_\infty = 2.87 \times 10^{23}$ mole^{-1} are the asymptotic values of P and Φ as $L/A \to \infty$. In the range $L/A \geq 2.28$ we have[12]

$$\frac{P_\infty}{P} = 1 + \frac{B_2}{B_1}\left(\frac{L}{A}\right)^{-1/2} + \frac{B_3}{B_1}\left(\frac{L}{A}\right)^{-1} + \frac{B_4}{B_1}\left(\frac{L}{A}\right)^{-3/2} + \frac{B_5}{B_1}\left(\frac{L}{A}\right)^{-2} \tag{9}$$

where

$$B_1 = \frac{4}{3}\left(\frac{6}{\pi}\right)^{1/2} = 1.843;$$

$$B_2 = \left[-1-0.01412\left(\frac{d}{A}\right)^2 + 0.00592\left(\frac{d}{A}\right)^4\right]\ln\frac{d}{A} - 1.0561 - 0.1667\frac{d}{A} - 0.19\left(\frac{d}{A}\right)^2 - 0.0224\left(\frac{d}{A}\right)^3 + 0.019\left(\frac{d}{A}\right)^4;$$

$$B_3 = 0.1382 + 0.691\left(\frac{d}{A}\right)^2;$$

$$B_4 = -\left[0.04167\left(\frac{d}{A}\right)^2 + 0.00567\left(\frac{d}{A}\right)^4\right]\ln\frac{d}{A} - 0.3201 + 0.5\frac{d}{A} - 0.585\left(\frac{d}{A}\right)^2 - 0.0094\left(\frac{d}{A}\right)^3 - 0.0421\left(\frac{d}{A}\right)^4;$$

$$B_5 = -0.03 + 0.1209\left(\frac{d}{A}\right)^2 + 0.0259\left(\frac{d}{A}\right)^4.$$

The corresponding expression over the range $L/A \leq 2.28$ is[10]

$$\frac{P_\infty}{P} = \left(\frac{A}{L}\right)^{1/2} B_1^{-1}\left[C_1 \ln\frac{L}{d} + C_2 + C_3\frac{L}{A} + C_4\left(\frac{L}{A}\right)^2 + C_5\left(\frac{L}{A}\right)^3 + C_6\left(\frac{L}{A}\right)^4 + C_7\left(\frac{L}{A}\right)^5 + \ldots\right] \tag{10}$$

in which

$$C_1 = 1 - 0.125\frac{d}{L}\cdot\frac{d}{A} + 0.1406\frac{d}{L}\left(\frac{d}{A}\right)^3;$$

$$C_2 = 0.386 + 0.6863\left(\frac{d}{L}\right) - 0.0625\left(\frac{d}{L}\right)^2 - 0.01042\left(\frac{d}{L}\right)^3 - 0.000651\left(\frac{d}{L}\right)^4 + 0.0005859\left(\frac{d}{L}\right)^5;$$

$$C_3 = 0.1667 - 0.06838\left(\frac{d}{L}\right)^2 + 0.02083\left(\frac{d}{L}\right)^3 - 0.01693\left(\frac{d}{L}\right)^4 - 0.00859\left(\frac{d}{L}\right)^5;$$

$$C_4 = 0.01111 + 0.07517\left(\frac{d}{L}\right)^2 - 0.1799\left(\frac{d}{L}\right)^3 + 0.1055\left(\frac{d}{L}\right)^4 + 0.02461\left(\frac{d}{L}\right)^5;$$

$$C_5 = 0.001058 - 0.00496\left(\frac{d}{L}\right)^2 + 0.001653\left(\frac{d}{L}\right)^3 - 0.07248\left(\frac{d}{L}\right)^4 - 0.03281\left(\frac{d}{L}\right)^5;$$

$$C_6 = 0.0001587 - 0.0007275\left(\frac{d}{L}\right)^2 + 0.0003638\left(\frac{d}{L}\right)^3 - 0.0863\left(\frac{d}{L}\right)^4 + 0.4\left(\frac{d}{L}\right)^5;$$

$$C_7 = 0.00003748 - 0.0001714\left(\frac{d}{L}\right)^2 + 0.0001142\left(\frac{d}{L}\right)^3 + 0.006183\left(\frac{d}{L}\right)^4 - 0.002897\left(\frac{d}{L}\right)^5.$$

The function Φ/Φ_∞ with $LA \leq 2.28$ can be calculated[11] by means of the formula

$$\frac{\Phi}{\Phi_\infty} = \frac{\pi N_A}{24\Phi_\infty}\left(\frac{L}{A}\right)^{3/2} F(p)\cdot f\left(\frac{L}{A}\right) \tag{11}$$

in which $p = L/d$, $\Phi_\infty = 2.87 \times 10^{23}$ mole^{-1}, and

$$F(p) \equiv F\left(\frac{L}{A}, \frac{A}{d}\right) = \frac{16}{15}\left\{\ln p + 2\ln 2 - \right.$$
$$\left. - \frac{25}{12} + \frac{\ln 2}{\ln(p+1)}\left[\frac{8}{75} - 2\ln 2 + \frac{25}{12} - 4.970572\right] + \frac{3.60517}{p^{1/4}} - \frac{15.35634}{p^{1/2}} + \right.$$
$$\left. + \frac{28.0617}{p^{3/4}} - \frac{14.8934}{p} + \frac{3.553442}{p^{5/4}}\right\};$$

$$f(L/A) = 1 - 0.321593\,\frac{L}{A} - 0.0466384\left(\frac{L}{A}\right)^2 + 0.106466\left(\frac{L}{A}\right)^3 -$$
$$- 0.0379817\left(\frac{L}{A}\right)^4 + 0.00399576\left(\frac{L}{A}\right)^5 .$$

Values of Φ in Table 1 of Ref.13 can be used to calculate Φ/Φ_∞ over the range $L/A \geq 2.28$.

Table 1. Values of A_0/A_∞ for various relative lengths L/A and relative diameters d/A of a vermiform chain.

L/A	A/d						
	2000	1000	200	100	100/3	100/6	10
10^6	0.998	0.999	0.999	0.999	0.999	0.999	1.000
10^5	0.995	0.996	0.996	0.997	0.997	0.998	0.999
10^4	0.997	0.998	0.990	0.990	0.991	0.994	0.996
10^3	0.976	0.978	0.978	0.978	0.978	0.983	0.989
500	0.977	0.977	0.975	0.974	0.973	0.978	0.985
200	0.989	0.985	0.976	0.972	0.967	0.971	0.978
100	1.008	1.000	0.982	0.975	0.965	0.965	0.971
70	1.024	1.013	0.989	0.979	0.965	0.962	0.967
50	1.043	1.029	0.997	0.985	0.967	0.960	0.962
20	1.115	1.090	1.033	1.011	0.977	0.956	0.948
10	1.186	1.151	1.070	1.037	0.987	0.953	0.934
7	1.225	1.184	1.090	1.051	0.991	0.951	0.926
5	1.261	1.215	1.108	1.052	0.992	0.948	0.917
2.278	1.339	1.282	1.144	1.084	0.990	0.934	0.897
2.0	1.362	1.300	1.154	1.092	0.995	0.938	0.899
1.0	1.382	1.312	1.149	1.079	0.973	0.910	0.868
0.6	1.380	1.306	1.133	1.060	0.950	0.886	0.844
0.4	1.362	1.286	1.109	1.035	0.923	0.861	0.821
0.2	1.310	1.231	1.051	0.977	0.870	0.813	0.778
0.1	1.242	1.162	0.983	0.912	0.816	0.768	0.758
0.05	1.167	1.088	0.914	0.850	0.768	—	—

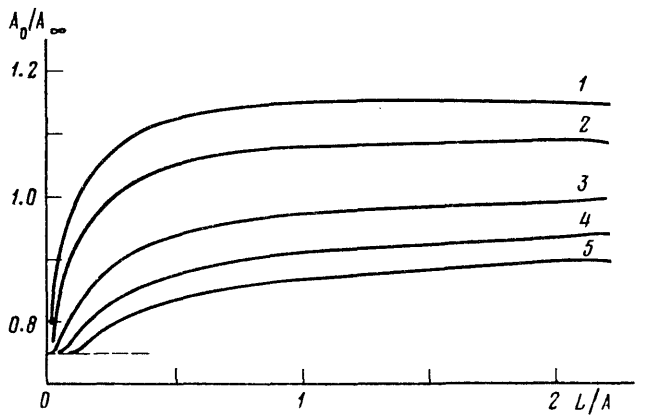


Figure 1. Dependence of A_0/A_∞ on relative length L/A of a vermiform chain in the range of low values $L/A = 0-2$ for different relative chain diameters d/A: *1*) 0.005; *2*) 0.01; *3*) 0.03; *4*) 0.06; *5*) 0.1.

Calculations based on Eqns.(9)–(11) enable the parameter $A_0 = kP^{-1}(\Phi/100)^{1/3}$ to be determined throughout the range of possible values of L/A and A/d. The results thus obtained for $A_0/A_\infty = (P_\infty/P)(\Phi/\Phi_\infty)^{1/3}$ are listed in Table 1 and illustrated by the curves in Figs.1 and 2. The upper limit to A_0 predicted by theory[12,13] is $A_\infty = kP^{-1}(\Phi_\infty/100)^{1/3} = 3.84 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. A finite limiting value of A_0 at low L/A is also predicted by theory[10,11], and is obtained from formulae (10) and (11) by putting $L/A = d/A \to 0$. We then find that $\lim_{L/A \to 0}(A_0/A_\infty)$ and $\lim_{L/A \to 0} A_0$ are respectively 0.75 and 2.88×10^{-10} erg deg^{-1} mole$^{-1/3}$.

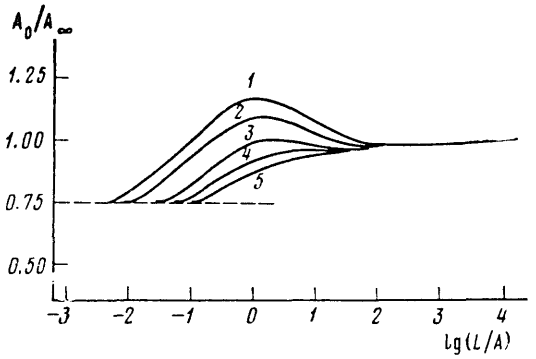


Figure 2. Dependence of A_0/A_∞ on L/A over a wide range for a vermiform chain having the same relative diameters d/A as in Fig.1.

Table 1 together with Figs.1 and 2 shows that according to theory[10,11] the parameter A_0 is invariant and close to A_∞ for all polymers in the range $L/A > 20$, where the molecule has a coiled conformation. With flexible-chain polymers ($d/A > 0.1$) in the range $L/A < 20$ a monotonic decrease in A_0 to its lower limit (i.e. by 25%) must be expected with decrease in chain length. In the case of polymers having moderately rigid chains ($0.1 \geq d/A \geq 0.03$) this decrease begins at lower values of L/A and is most developed in the range $L/A \leq 1$. Finally, the theory predicts for polymers of high equilibrium chain rigidity ($d/A \leq 0.01$) a non-monotonic dependence of A_0 on L/A in the region of short chains: A_0 increases with decrease in L in the range $L/A < 10$, reaches a maximum in the region of $L/A \approx 1$, and then drops abruptly to a lower limit. Thus in the region of short chains ($L/A \leq 10$), where A_0 can be expected to change with L/A, theory[10,11] indicates that a more rigid polymer has a rather higher value of A_0. This last conclusion is consistent with calculations[13] of A_0 for the range $L/A \geq 10$.

2. Excluded-volume Effects

If the conditions of a polymer solution are non-θ, osmotic swelling of the molecular coil may in principle influence not only P and Φ but also A_0, since change in molecular conformation in a thermodynamically "good" solvent is associated with change in intramolecular hydrodynamic interaction.

In the original form of Flory's theory of volume effects it was assumed that, on extension of a molecular coil in a "good" solvent and with increase in its linear dimensions (i.e. $\langle h^2 \rangle^{1/2}$) by a factor α, the coefficient of sliding

friction f also increases by this factor, while the intrinsic viscosity increases by a factor α^3. Hence P and Φ in formulae (1) and (2)—and thus also A_0 in (4)—were regarded as universal constants, remaining unchanged when a θ-solvent was replaced by a "good" solvent.

Later, however, it proved necessary to assume, in order to explain experimental results obtained for solutions of flexible-chain polymers, that linear extension of a molecular coil by a factor α was accompanied by change in f by a factor α_f, and in $[\eta]$ by a factor α_η^3, with both α_f and α_η smaller than α. Therefore the values of P and Φ in a "good" solvent should be less than their limiting values P_∞ and Φ_∞ in a θ-solvent, in conformity with the equations

$$P/P_\infty = \alpha_f/\alpha \; ; \; \Phi/\Phi_\infty = (\alpha_\eta/\alpha)^3 \; . \qquad (12)$$

Theories of volume effects in solutions of flexible-chain polymers and their influence on P and Φ were developed in a series of papers[3]. Although the results of different theories in several cases are by no means in quantitative agreement, they all lead to analogous qualitative conclusions: (i) both P and Φ diminish under the influence of volume effects; and (ii) increase in α produces a greater change in Φ than in P. For example, in an approximate calculation Kurata and Yamakawa obtained[3]

$$\Phi/\Phi_\infty = 1-0.46\,z+\ldots, \quad P/P_\infty = 1-0.22\,z \qquad (13)$$

where z is the excluded-volume parameter. Equation (13) yields the relation

$$A_0/A_\infty = (1-0{,}46\,z)^{3/2}/(1-0{,}22\,z) = 1+0.07\,z \qquad (14)$$

between A_0 in a "good" solvent and A_∞ in a θ-solvent. According to Ref.14 volume effects produce a slight increase in A_0. On the other hand, if results obtained by Fixman[15] ($\Phi/\Phi_\infty = 1-0.2z$) and by Stockmayer and Albrecht[16] ($P/P_\infty = 1-0.03z$) are used, the ratio $A_0/A_\infty = 1-0.04z$ is found, which predicts a slight decrease in A_0 under the influence of volume effects. In view of the above it is evident that, even if volume effects in solutions of flexible-chain polymers do lead to changes in A_0, such changes are so insignificant that they cannot be reliably predicted by existing theories.

Table 2. Theoretical values of Φ_∞ and corresponding values of A_∞ ($P_\infty = 5.11$).

$10^{-23}\Phi_\infty$, mole^{-1}	$10^{10}A_\infty$, erg deg^{-1} mole$^{1/3}$	Ref.	$10^{-23}\Phi_\infty$, mole^{-1}	$10^{10}A_\infty$, erg deg^{-1} mole$^{1/3}$	Ref.
3.62	4.1	[9]	2.68	3.75	[23]
3.37	4.0	[20]	2.76	3.79	[24]
2.87	3.83	[21]	2.19	3.51	[25]
2.84	3.82	[22]	2.51	3.43*	[26]

*$P_\infty = 5.99$.

It has been shown experimentally[17] and confirmed theoretically[18] that the influence of volume effects on molecular conformation is considerably weaker with polymers having molecular chains of enhanced rigidity than with flexible-chain polymers. In practice this means that even in "good" solvents the coefficient α in formula (12) is close to unity, and still more that α_η and α_f are close to α. It can thus be expected that for rigid-chain polymers the parameters P, Φ, and A_0 will be extremely insensitive to volume effects, although Hearst's theory[14] predicts some increase in A_0 with increase in the excluded volume.

3. Numerical Values of the Constants P_∞, Φ_∞, and A_∞

It follows from Eqn.(4) that the value of A_∞ predicted by theory depends on the theoretical values of P_∞ and Φ_∞. Both the latter were first calculated, in terms of the theories of sliding friction and Kirkwood–Riseman viscosity[9], by "pre-averaging" the Oseen hydrodynamic interaction tensor T_{ik} (i.e. by averaging T_{ik} over all chain conformations before using it to calculate f or $[\eta]$). To this approximation the value $P_\infty = 5.11$ was obtained, later refined to 5.2,[19] practically identical with the former value, which is usually employed in modern work.

Calculation of Φ_∞ involves several model concepts and mathematical approximations, depending on the character of which different authors have obtained different results (Table 2, first column). The calculated values show a chronological tendency to decrease, in some measure because in the later calculations the authors attempted to avoid pre-averaging T_{ik}, which always leads to rather lower values of Φ_∞. The lowest value $\Phi_\infty = 2.19 \times 10^{23}$ mole^{-1} was obtained by Hearst and Tagami[25], who differed from all tne other investigators in using as molecular model a vermiform instead of a Gaussian chain.

Values of A_∞ in the second column of Table 2 have been calculated by means of Eqn.(4) from the corresponding value of Φ_∞ and $P_\infty = 5.11$ (apart from the last line, in which it is assumed that $P_\infty = 5.99$).

Values in the last line in Table 2 were obtained by Zimm[26], who made a thorough review of the effect of pre-averaging the hydrodynamic interaction in chain molecules on the calculation of coefficient of friction and intrinsic viscosity. Using the Monte Carlo method and generating in a computer experiment a set of random configurations of the polymer chain, he solved the problem of hydrodynamic interactions in sedimentation and viscosity phenomena for each configuration, and only then averaged the results. The values of Φ_∞, P_∞, and A_∞ thus obtained, extrapolated to a chain having an infinite number of segments, are included in Table 2. The values of Φ_∞ and A_∞ proved to be smaller, but those of P_∞ were larger, than the values usually employed. The value $P_\infty = 5.99$ appears most unusual, but it is noteworthy that at one time Kuhn et al.[27] obtained the still higher value $P_\infty = 7.3$ from experiments with wire models.

The above values of P_∞, Φ_∞, and A_∞ apply to a polymer that is homogeneous with respect to molecular mass. The presence of molecular-mass polydispersity in a specimen may be expected to lead to a decrease in Φ.[28] The parameter A_∞ also depends on polydispersity, and may be either diminished or increased depending on the way in which the experimental quantities D, s, $[\eta]$, and M in Eqns.(4) and (5) have been averaged[29,30]. However, the variations in A_∞ to be expected in moderately polydisperse specimens are small[29], and in many cases can apparently be disregarded.

IV. EXPERIMENTAL RESULTS

1. Values of Φ and P

It follows from Eqns.(1)–(3) that experimental determination of the coefficient Φ or P separately requires the measurement of two or three molecular characteristics. One of these must necessarily be the radius of inertia of the chain molecule, which for a polymer of sufficiently high molecular mass in a θ-solvent is $\langle R\rangle = (LA/6)^{1/2}$. Measurement of this radius, which is based on the asymmetry of light scattering, is a most difficult experimental procedure, always entailing the possibility of considerable errors and

inaccuracies. Incidentally, the method of light scattering permits determination of a second quantity—the molecular mass M—occurring in Eqns.(1) and (3). Finally, the third quantity which must be measured experimentally is either the intrinsic viscosity (for the determination of Φ by means of Eqn.1) or the sedimentation coefficient s (if P is determined from formula 3). When the latter is determined by means of (2), it is necessary to measure the diffusion coefficient D in addition to the radius of inertia, but the molecular mass is not required in this case.

Table 3. Experimental values of the coefficient Φ for polystyrene in a θ-solvent (cyclohexane) at 35 °C.

$10^{-6} M_w$, g mole^{-1}	$10^{-23} \Phi$, mole^{-1}	Ref.
3.2	1.85	31
4.0	1.76	32
0.62—1.6	2.6—2.9	33
0.62—4.4	1.7—2.6 *	33
0.21—1.0	1.8—2.4	34
0.34—2.9	2.4—2.6	35
27—44	1.5—2.0	36
1.2—4.6	2.2—2.8 *	37
8.8—57	2.2—2.4	38, 39
6.5	2.5±0.1	40
0.21—1.0	2.4—1.98 **	34

*In decalin (θ-solvent) at 20.4 °C.
**In cyclohexene ("good" solvent) at 25 °C.

Since viscometry is a considerably more accessible procedure than measurement of sedimentation or diffusion coefficients, the majority of the experimental work has involved the determination of Φ by means of formula (1). In most cases polystyrene having a narrow molecular-mass distribution was used in a θ-solvent. Table 3 gives several typical results of such measurements. The experimental values show a considerable scatter. However, they do indicate that, despite the quite high molecular masses of the test specimens, the values obtained for Φ were usually considerably lower than the theoretically predicted Φ_∞ values (Table 2). An unambiguous dependence of Φ on the nature of the solvent cannot be discerned from existing results[34].

Table 4. Experimental values of the coefficients P for several polymer–solvent systems (under θ-conditions).

Polymer	Solvent	Temp., °C	P	Ref.
Polystyrene	butan-2-one–n-butanol	25	4.7	41
Poly(methyl methacrylate)	1-chlorobutane	35	6.3	42
Polystyrene	cyclohexane	35	5.3	34
Polystyrene	cyclohexane*	25	5.7	34
Poly-α-methylstyrene	cyclohexane	34.5	5.5	43, 44

*Thermodynamically "good" solvent.

Published information on the experimental determination of P is extremely meagre, practically limited to the examples in Table 4. Four of the five experimental values of P exceed the 5.11 predicted by theory, and only one is lower. The difference between values of P for polystyrene in a "good" solvent and in a θ-solvent could be attributed[34] equally to an excluded-volume effect and to scatter due to experimental error. Thus the problem of reliable experimental values of Φ and P remains open, and requires further careful investigation.

Comparison of the experimental results in Tables 3 and 4 with the theoretical values in Table 2 indicates that Zimm's method[26], using the technique of a computer experiment and avoiding pre-averaging of the Ozeen tensor, gives better agreement between theoretical and experimental values of Φ and P than that obtained by other workers. In view of the great scatter and unreliability of available experimental results and also the difficulties of theoretical calculations, however, it seems premature to adopt Zimm's values as the most reliable and the preferred for use.

2. Values of A_0

Discrepancies in the experimental values of Φ and P obtained by different authors are due not only to polydispersity of the specimens (to which reference has often been made) but primarily and in no less degree to errors in the measurements of molecular dimensions $\langle h^2 \rangle$ or $\langle R^2 \rangle$ from the asymmetry of light scattering in solutions of the polymer. As already mentioned, calculation of A_0 from experimental results requires values of molecular mass, intrinsic viscosity, and coefficient of friction, while the procedure involved in determining $\langle R^2 \rangle$ is excluded. Therefore the accuracy and the reliability of the experimental determination of A_0 in principle exceeds considerably those of the determination of Φ and P.

If molecular mass is determined from the scattering of light (in which method asymmetry indicatrixes, though used, play a considerably less important part than in the measurements of $\langle R^2 \rangle$), the calculation of A_0 requires the determination of coefficient of friction in addition to the measurement of intrinsic viscosity. Such determination can be made by rapid sedimentation and A_0 calculated by means of formula (5); or diffusion measurements can be used for this purpose, and A_0 calculated by means of (4). In the latter method the accuracy with which the diffusion coefficient is measured becomes important, since in Eqn.(4) it is raised to a power thrice that of molecular mass and intrinsic viscosity.

If molecular weight is determined by a combination of the diffusion and rapid sedimentation methods, replacing M by M_{sD} in formula (4) or (5) with use of the Svedberg equation yields

$$A_0 = \eta_0 \left(\frac{D}{T}\right)^{2/3} \left(\frac{[\eta] sR}{100(1-\bar{v}\rho)}\right)^{1/3}. \qquad (15)$$

Thus in this case the determination of A_0 involves in effect sedimentation–diffusion and viscosimetric measurements, in which as before the accuracy with which diffusion coefficient is determined is important, since in (15) the power to which this factor is raised is double that of the sedimentation coefficient and the intrinsic viscosity.

A comparative assessment of the suitability of the different methods for determining A_0 must first take into account the experimental difficulties associated with the use of light scattering, which requires that the test solutions be highly purified. This applies especially to those cases in which sparingly soluble polymers are investigated in binary solvents, polyelectrolyte buffer solutions, and other such systems that are difficult to purify.

The sedimentation and diffusion methods do not require such careful purification of the solution, which is a substantial advantage in comparison with the light-scattering method. When aqueous and buffer solvents are

used, however, a complication arises from charge effects when diffusion and sedimentation coefficients are measured in polyelectrolyte systems. Although these effects may be diminished by increasing the ionic strength of the solution and reliably extrapolating to zero polymer concentration[45] using a sensitive interferometric technique[1], their complete elimination is difficult to guarantee. Furthermore, a significant error in the sedimentation method is associated with measurement of the partial specific volume $\bar{v}$, which governs the buoyancy factor $1-\bar{v}\rho$ in Eqns.(5) and (15). This disadvantage is absent in the diffusion method, which does not require measurement of the partial specific volume and enables the coefficient of friction f to be determined most directly.

Table 5. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for fractions of flexible-chain polymers in thermodynamically "good" solvents.

Polymer (M_w/M_n)	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$*	Type of M; methods	Ref.
Rubber, natural	125—515	chloroform	20	3.51±0.20	M_n; S, D, LS, OS	[46]
»	1600	cyclohexane	20	3.26	M_{sD}; S, D,	[47]
Polyacrylonitrile	48—270	dimethylformamide	25	3.52±0.04	M_{sD}; S, D	[48]
», $M_w/M_n=1.69$	105	" (deionised)	25	3.40	M_w; S, LS, OS	[49]
», $M_w/M_n=2.04$	210	»	25	3.01	M_w; S, LS, OS	[49]
cis-Polybuta-1,4-diene (⩽1.1)	50—1100	heptane - hexane (1 : 1)	20	3.15	M_{sD}; S, D	[50, 51]
Poly(vinyl acetate) (1.44)	17—1200	butan-2-one	25	3.04±0.46	M_{sD}; S, D, LS, OS	[52, 53]
Poly-2-vinylnaphthalene	72—1230	benzene	20	3.15±0.09	M_{sD}; S, D	[54]
»	3500	tetrachloromethane	20	3.50	M_{sD}; S, D	[54]
Polyvinyldimethylpropylsilane (1.5 - 2.0)	62—306	cyclohexane	25	3.39±0.24	M_w; S, D, LS	[55]
»	62—306	»	25	(2.56)	M_{sD}; S, D	[55]
Poly-4-vinylpyridine	11.6—847	chloroform	21	2.75±0.24	M_{sD}; S, D	[56]
Polyvinylpyrrolidone	10.6—86	water	20	3.25±0.24	M_{sD}; S, D	[57]
»	13.3—42.1	water	20	3.32±0.10	M_{sD}; S, D	[58]
Poly(vinyl stearate)	62—840	n-octane	18	3.19±0.12	M_{sD}; S, D, LS	[59]
Poly(vinyl chloride)	53, 120	oxolan	25	2.96±0.13	M_w; S, LS	[30]
Poly(vinyl cinnamate)	51—762	butan-2-one	22	3.58±0.10	M_{sD}; S, D	[60]
Polydimethylsiloxane (1.2)	101—550	bromocyclohexane	28	1.90±0.14	M_{sD}; S, D, LS	[61]
»	301—920	toluene	20	3.68±0.21	M_{sD}; S, D, LS	[61]
»	76—2360	tetrachloromethane	24	3.02±0.24	M_w, M_η; D, LS	[62]
Poly-(2,6-dimethyl-1,4-phenylene ether) (M_z/M_w 1.2)	87	toluene	25	2.56	M_w; S, LS, SE	[63]
»	87	tetrachloroethane	25	2.33	M_w; S, LS, SE	[63]
Polyisobutylene (⩾2)	9.7—308	n-heptane	25	3.46±0.25	M_w; D, LS	[64]
»	0.6—35	di-isobutylene	—	3.0	—	[65]
»	31—1420	cyclohexane	20	3.48±0.14	M_n; S, OS	[66]
»	0.6—35	cyclohexane - decalin	—	3.2	—	[65]
», «L-80»	800	ethyl octanoate	22	4.23	M_η; D	[67]
cis-1,4-Polyisoprene (⩽1.1)	50—1000	hexane - propan-2-ol (1 : 1)	21	3.01	M_{sD}; S, D	[51]
Poly-2-methyl-5-vinylpyridine	120—1110	chloroform	21	3.34±0.08	M_{sD}; S, D	[56]
»	100—2590	ethyl acetate	25	3.16±0.20	M_{sD}; S, D	[68]
Polymethylene (2.04 ± 0.34)	4.6—58	1-bromonaphthalene	110	3.41±0.13	$(M_w)_\eta$; S	[69]
Poly-α-methylstyrene (1.00 ± 0.03)	44.4—1675	benzene	30	3.19±0.13	M_w; S, LS, OS	[70]
», (0.95-1.11)	67.6 - 1170	toluene	25	**3.27±0.12	M_w; S, LS	[71]
», "monodisperse"	204—7470	toluene	25	**3.18±0.10	M_w; S, LS	[43]
»	1190—7470	*trans*-decalin	20	**3.35±0.08	M_w; S, LS	[43]
»	204—7470	»	40	**3.22±0.05	M_w; S, LS	[43]
Polynonyloxybenzamidostyrene	37	benzene	21	3.13	M_{sD};S, D	[72]
Polyoxypropylene glycol	0.85—2.64	chloroform	24	3.24±0.25	M_n; D, OS	[73]
Poly(propylene sulphide)	37—208	benzene	21	3.24±0.11	M_{sD};S, D, LS	[74]
Polystyrene	1.18—520	»	—	3.12±0.21	M_{sD};S, D	[75]
», (M_z/M_w ⩽ 1.2)	3600	»	40	**3.17	M_w; S, LS	[32]
»	4.5—85	»	—	2.6	M_w; D, LS	[65]
», "BASF IIID" (M_z/M_w ~1.9)	220	»	25, 30, 35	3.0±0.1	M_{sD};S, D	[76]
»	1000	*trans*-decalin	25	3.19	M_w; D	[77]
Pressure Chemical Co., "lot N14a" (~1.2)	1800	»	25	3.07	—	[78]
», (M_{sD}/M_n 1.06)	420	»	20, 30, 40	3.00±0.09	M_{sD};S, D, OS	[79]
»	250—1320	dichloroethane	—	3.52±0.06	M_w; D, LS	[7]
»	130	3-methylbutan-2-one	20	3.29	—	[5]
»	180—270	butan-2-one	20	2.65—2.85	M_n; D, OS	[4]
»	254—1240	»	20	3.58±0.08	M_η	[80, 6]
»	1000	»	25	3.44	M_w; D	[77]
», (1.44)	114—955	»	20	3.20±0.28	M_w; S, LS, OS	[81]
», "IUPAC 11-26-52" (1.17; M_z/M_w 1.24)	538±75	»	20	3.4±0.1	M_w; S, LS, OS	[82]
»	325—2800	»	25	**3.44±0.18	M_w; S, LS	[41]
»	540	»	20	3.39	M_w; S, D, LS	[83]
», "S102, S111, KL-4" (1.15 ± 0.09)	85—415	»	25	2.81±0.06	M_w; S, LS, OS	[84] [85]
», (~1.06)	51—110	oxolan	30	2.99±0.10	M_w; D_z, LS	
»	51—110	»	30	3.2	M_w; D_z, LS	[86]
»	1000	tetrachloromethane	25	4.23	M_w; D	[77]
»	45—700	»	24	3.42	M_w; D, LS;	[87]
»	130	toluene	20	3.27	—	[5]
»	180	»	20	3.04	—	[4]
»	180	»	20	3.72	—	[88]
»	270	»	20	2.91	—	[4]
»	254—1240	»	20	3.19±0.40	M_η; S	[80, 6]
»	1000	»	25	2.96	M_w; D	[77]
»	510—1920	»	25	3.94±0.12	M_η; D	[89]
»	535	»	25	3.24	M_{sD}; S, D	[90]
», "IUPAC 11-26-52" (1.17; M_z/M_w1.24)	538±75	»	20	3.3±0.2	M_w; S, LS	[82]
»	540	»	20	3.62	M_w; S, D, LS	[83]

Table 5 (cont'd.).

Polymer (M_W/M_η)	10^{-3} M	Solvent	Temp., °C	10^{10} A_2*	Type of M; methods	Ref.
», (≤1.2)	44—2800	»	20	3.35±0.17	M_{sD}; S, D	[91]
», "P-30"	75	»	23.5	2.82	M_w; S, LS	[67]
»	930—21000	»	21	2.1±0.4	M_w; S, LS	[92]
», (3 ± 1)	250—411	»	25	2.83±0.10	M_w; D_Z, LS	[85]
Pressure Chemical Co., "lot NN 4b, 3b, 14a"	110—1800	toluene	25	3.07±0.10	—	[78]
», (M_{SD}/M_n 1.02)	112	»	25	3.12±0.09	M_{sD}; S, D, OS	[79]
», (1.2)	23 400—40 000	»	20	3.14±0.05	M_w; S, D, LS	[93, 94]
», (M_Z/M_W 1.19)	118	»	25	**3.13	M_w; S, LS, SE	[63]
»	180	toluene–butanol (9:1, 8:2, 7:3)	(20)	3.01—2.30	M_n; D, OS	[88]
»	540	toluene–butan-2-one (1:1, 1:3, 3:1)	20	**3.51—3.43	M_W; S, D, LS	[83]
»	540	chloroform	20	**3.50	M_w; S, D, LS	[83]
»	115—2800	»	25	**2.94±0.06	M_w; S, LS	[41]
», (M_Z/M_W ≤1.2)	3600	cyclohexane	45, 55	**2.95; 3.10	M_w; S, LS, SE	[32]
»	130	cyclohexanone	20	3.44	—	[5]
», (1.02–1.14)	199—1064	cyclohexene	25	**3.15±0.10	M_w; S, D, LS	[34]
», "S102, S111, KL-4", (1.15 ± 0.09)	85—415	ethyl acetate	25	2.84±0.05	M_w; S, LS, OS	[84]
»	1000	ethylbenzene	25	2.53	M_w; D	[77]
Polystyrene latex	5870	0.098M NaCl	25	3.04	M_w; S	[95]
Polyepichlorohydrin (≤1.3)	28.9—168.4	oxolan	20	2.65±0.19	M_w; S, LS	[96]
Polyethylene, high density (1.55 ± 0.43)	3.8—245	1-bromonaphthalene	110	3.25±0.33	$(M_w)_\eta$, S	[69]
»	8—250	»	110	3.14	M_w; S, LS	[97]
Poly(ethylene oxide)	—	water	30	2.55	M_w; S, LS	[98]
(M_{SD}/M_n < 1.1)	320	»	25	2.88	M_{sD}; S, D	[99]
Poly(ethylene terephthalate) (M_{SD}/M_n 1.08 ± 0.09)	23—111.6	*m*-cresol	25	3.43±0.38	M_{sD}; S, D, OS	[100]
Polymers with a comb-like macromolecular structure, acrylates, and methacrylates						
Polyacrylamide (2.5)	770—5270	0.5M NaCl	20	2.76±0.26	M_w; S, LS, OS	[101]
», (1.2–1.4)	130—6700	water	20	3.38±0.48	M_w; S, LS	[102]
Poly-*p*-acryloylazoxybenzene	10—199	tetrachloroethane	27	3.29±0.31	M_{sD}; S, D	[103]
Poly(butyl acrylate)	40—940	butan-2-one	25	3.95±0.30	M_{sD}; S, D	[104]
Poly-n-butyl-*p*-acryloylazoxybenzene	26—78	tetrachloroethane	27	3.22±0.16	M_{sD}; S, D	[103]
Poly-(t-butyl crotonate), atactic (1.11–1.26)	60.6, 161	1-chlorobutane	25	3.75±0.02	M_w; D, LS, OS	[105]
»	60.6, 161	»	25	(3.54±0.10)	M_n; D, OS	[105]
Poly(butyl methacrylate)	34—148	butan-2-one	24	2.96±0.12	M_{sD}; S, D	[106]
»	40—8200	chloroform	24	**3.10±0.24	M_w; D, LS	[107]
poly-(*p*-t-butylphenyl methacrylate) (1.3)	42—1125	butan-2-one	25	2.97±0.10	M_w; S, LS	[108]
»	60—3650	chloroform	24	3.13±0.16	M_w; D, LS	[7, 109, 110]
Poly(vinyl laurate)	24—3000	heptane	25	3.31±0.18	M_{sD}; S, D	[111]
Poly(heptafluoromethoxyethylethylene oxide), isotactic (≤1.2)	450—1970	hexafluorobenzene	20	3.46±0.03	M_w; S, LS	[112]
»	833—1970	chloropentafluorobenzene	20	2.25±0.28	M_w; S, LS	[112]
»	573—952	hexafluorobenzene	20	3.46±0.05	M_w; S, LS	[112]
»	»	chloropentafluorobenzene	20	2.39±0.31	M_w; S, LS	[112]
Poly(decyl acrylate) (M_Z/M_W 1.26 ± 0.09)	63—1110	heptane	24	**3.63±0.27	M_{sD}; S, D	[113]
Poly(decyl methacrylate)	42.5—4950	heptane	21	3.37±0.11	M_{sD}; S, D	[114]
Poly-*p*-ethoxycarbonylphenylmethyacrylamide	180—1080	ethyl acetate	20	3.36±0.50	M_w; S, D, LS	[115]
Poly-(*p*-menth-5-yl methacrylate) 1.5)	125—2290	benzene	25	2.90±0.13	M_w; S, LS	[108]
Poly(methyl *p*-methacryloyloxy-benzoate)	180—4000	butyl acetate	24	3.25±0.05	M_{sD}; S, D	[116]
Poly(methyl acrylate)	70—2900	butan-2-one	25	3.26±0.24	M_{sD}; S, D	[104]
Poly(methyl methacrylate) (M_{SD}/M_n 1.16–1.46)	24.6—7440	acetone	20	3.29±0.16	M_{sD}; S, D, OS	[117—119]
»	24.6—7440	»	20	3.25±0.15	M_{sD}; S, D, LS	[120]
»	145—7600	»	20	3.33±0.18	M_w; S, D, LS	[120]
»	200—6550	»	20	**2.98±0.05	M_{sD}; S, D	[42]
»	200—6550	dioxan	25	**3.18±0.10	M_{sD}; S, D	[42]
»	70—4320	chloroform	24	3.19±0.15	M_w; D, LS	[7, 109, 110]
»	79—931	ethyl acetate	20	3.59±0.19	M_{sD}; S, D	[121]
»	64—1168	»	20	3.38±0.13	M_{sD}; S, D	[122]
», (M_Z/M_W 1.7)	23 700	»	23	3.73	M_{sD}; S, D	[76]
», branched	769—2140	»	20	3.76±0.12	M_{sD}; S, D	[122]
», (1.48 ± 0.06)	162, 296	»	20	3.12±0.04	M_w; S, LS, OS	[123]
», branched*** (1.74 ± 0.05; n_W 0.26)	195, 396	»	20	2.75	M_w; S, LS, OS	[123]
», (M_Z/M_W 2.36 ± 0.43; n_W 1.02)	301—620	»	20	2.14	M_w; S, LS, OS	[123]
», (10.1; n_W 7.25)	1340	»	20	(0.89)	M_w; S, LS, OS	[123]
Poly-(2-hydroxyethyl phthalimidomethacrylate)	770—20000	dimethylformamide	20	3.12±0.09	M_{sD}; S, D	[124]
Poly(octadecyl acrylate)	180—3590	heptane	25	3.00±0.10	M_{sD}; S, D	[104]
Poly(octyl acrylate)	120—3100	»	25	3.05±0.23	M_{sD}; S, D	[104]
Poly(octyl methacrylate)	150—2450	»	25	2.97±0.11	M_{sD}; S, D	[106]
Poly-(*p*-n-nonyloxyphenyl *p*-methacryloyl-oxybenzoate)	119—1700	benzene	24	3.28±0.14	M_{sD}; S, D	[125]
Polystyrene, comb-shaped (10)	90—190	»	25	3±1	M_n; S, D	[126]
»	440—1840	»	25	(6±2)	M_{sD}; S, D	[126]
Poly-(2-triphenylmethoxyethyl methacrylate) (M_Z/M_W 1.16 ± 0.07) (≤1.2)	68—5200	»	26	2.85±0.13	M_{sD}; S, D	[127]
	51—2630	toluene	25	3.16±0.11	M_w; S, LS	[128]
Poly(phenyl methacrylate) (M_Z/M_W 1.4 ± 0.2) (1.81 ± 0.16)	23—1100	butyl acetate	24	3.49±0.20	M_{sD}; S, D	[129]
	740—4970	butan-2-one	25	3.08±0.10	M_w; S, LS, OS	[130]
Poly(phenylmethacrylyl nonyloxy-benzoate)	200—2200	tetrachloromethane	25	3.26±0.16	M_{sD}; S, D	[131]
Poly(phenylmethacrylyl hexadecyloxy-benzoate)	1900	benzene	25	3.74	M_{sD}; S, D	[132]
»	1900	oxolan	25	2.80	M_{sD}; S, D	[132]
»	1900	tetrachloromethane	25	2.90	M_{sD}; S, D	[132]
»	146—20000	»	25	3.19±0.28	M_{sD}; S, D	[131]
Poly-(*p*-chlorophenyl methacrylate) (1.54 ± 0.07)	105—5630	benzene	25	3.93±0.09	M_w; S, LS, OS	[133]
Poly(cholesteryl acrylate)	140—780	»	21	3.07±0.24	M_{sD}; S, D	[134]
Poly(hexadecyl acrylate) (M_Z/M_W 1.2–1.4)	47—140000	heptane	25	3.44±0.24	M_{sD}; S, D	[135]
Poly(hexadecyl vinyl ether)	3—30	»	25	3.13±0.10	M_{sD}; S, D	[136]
Poly(hexadecyl methacrylate) (M_Z/M_W 1.22 ± 0.08)	1370—12600	»	25	3.23±0.21	M_{sD}; S, D	[137, 138]
»	220—2540	»	25	3.48±0.14	M_{sD}; S, D	[106]

Table 5 (cont'd.).

Polymer (M_W/M_η)	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$*	Type of M; methods	Ref.
Poly(cylohexyl methacrylate) (1.11 ± 0.07)	170—4190	butan-2-one	25	3.21±0.20	M_w; S, LS, OS	[130]
»	170—1960	cyclohexane	25	3.26±0.17	M_w; S, LS, OS	[130]
Poly-(1*H*, 1*H*, 5*H*-octafluoro-n-pentyl methacrylate) (≤1.15)	2100—35700	»	21	3.36±0.09	M_{sD}; S, D	[139]
Poly-(1*H*, 1*H*, 7*H*-dodecafluoro-n-heptyl methacrylate) (≤1.15)	450—12400	»	21	3.03±0.12	M_{sD}; S, D	[139]
Poly(hexadecyl *p*-methacryloyloxybenzoate)	16—500	tetrachloromethane	25	3.29±0.38	M_{sD}; S, D	[140]
		Copolymers				
Butadiene-acrylonitrile, random 74:26	50—1300	butan-2-one-cyclohexane 36:64	20	2.98	M_{sD}; S, D	[51]
», 60:40	30—800	», 47.5:52.5	22	2.89	M_{sD}; S, D	[51]
», 82:20 (1.1-1.3)	35—291	butan-2-one-propan-2-ol 59:41	20	2.85±0.14	M_{sD}; S, D	[141]
», 46:54 (1.1-1.3)	17—162	butan-2-one-cyclohexane 74:26	21	2.79±0.10	M_{sD}; S, D	[141]
Butyl-hexadecyl methacrylate, random 1:1	220—920	heptane	25	3.22±0.04	M_{sD}; S, D	[106]
Vinyl acetate-vinylcaprolactam (6-10%), random	100—190	acetone	22	2.73±0.20	M_{sD}; S, D	[142]
1,1-Difluoroethylene-tetrafluoroethylene random (M_{SD}/M_η 1.2-1.6)	6—1250	dimethyl sulphoxide	25	4.0±0.20	M_{sD}; S, D	[143]
(M_{SD}/M_η 1.7-4.5)		»	25	(4.6±0.42)	M_{sD}; S, D	[143]
N-Vinylpyrrolidone-crotonic acid, random	34	0.2 M $NaNO_3$ in DMF	20	3.58±0.02	M_{sD}; S, D	[144]
Octyl-hexadecyl methacrylate, random 1:1	130—450	heptane	25	2.94±0.03	M_{sD}; S, D	[106]
Polystyrene-poly(methyl methacrylate) graft 0.9:0.1	600—7600	butyl acetate	25	2.62±0.33	M_{sD}; S, D	[145]
»	600—7600	chloroform	25	2.50±0.52	M_{sD}; S, D	[145]
» 0.87:0.13 (1.2)	775, 1310	butyl acetate	21	3.11±0.10	M_{sD}; S, D	[146]
» 0.875:0.125 (M_Z/M_W 1.08-1.17)	80—697	»	21	3.15±0.09	M_{sD}; S, D	[147]
Styrene-butadiene, random 27:75	40—800	octane	21	3.26	M_{sD}; S, D	[51]
Styrene-*p*-divinyltetrachlorobenzene (branched polystyrene) n(1.15% Cl), random (1.16 ± 0.09, internodal *M* 95 000)	47—1550	cyclohexane	35	3.51±0.12	M_w; S, LS, OS	[148]
Styrene-methacrylic acid		oxolan	—	3.1	—	[149]
Phenylmethacrylyl hexadecyloxybenzoate-hexadecyl methacrylate (6.5-88%)	1590—3460	tetrachloromethane	25	3.30±0.42	M_{sD}; S, D	[150]
», 1:1	700—120000	»	25	3.08±0.03	M_{sD}; S, D	[151]
», 7:3	320—11300	»	25	3.87±0.02	M_{sD}; S, D	[151]

*Values of A_0 in parentheses in Tables 5—10 disregarded in calculation of mean experimental values of A_0.

**These fractions investigated both in a thermodynamically "good" solvent (in this Table) and in a θ-solvent (Table 6).

***Here and subsequently n_W is the number of branchings per molecule.

From the above considerations it may be expected that the combination of light-scattering and sedimentation methods using formula (5) will lead to the greatest errors in the determination of A_0. On the other hand, the combination of diffusion and sedimentation methods involves formula (15), in which the buoyancy factor occurs as the cube root, which diminishes errors in the determination of partial specific volume, while the diffusion coefficient, occurring to the two-thirds power in (15), is measured quite reliably (by an interferometric technique[1]). Therefore the sedimentation—diffusion method for determining A_0 must be the most strongly preferred, at least when organic solvents are used.

Tables 5—10 list experimental values of A_0 for various polymer—solvent systems obtained by different methods in various laboratories. The methods used are indicated in the appropriate column by the abbreviations D for diffusion, S sedimentation, SE sedimentation equilibrium, LS light scattering, and OS osmometry. The type of averaging of molecular mass (M_W, M_n, M_{SD}) used in the calculation of A_0 is also indicated. In all cases viscometry was used in addition to the methods listed.

Table 5 lists numerous results obtained for flexible-chain (mainly vinyl) polymers in good (non-θ) solvents. All measurements were made on fractions of molecular-mass range indicated in the first column. Examination of original sources (from literature references) does not usually reveal any systematic variation in A_0 for individual fractions with their molecular weight. Table 5 gives values of A_0 averaged over all fractions of a given polymer in each paper, while the error indicated is a mean of the deviations from this value for different fractions. On comparing values of A_0 for the 172 different polymer—solvent systems (including ~800 fractions) represented in Table 5, it is impossible to detect any systematic dependence of A_0 on the method used.

The average of all values of A_0 in Table 5 is $(3.2 \pm 0.2) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. This mean scatter of values obtained by different authors in different polymer—solvent systems has the same order of magnitude as the scatter of A_0 values between different fractions of a polymer investigated in the same work, which gives grounds for supposing that differences in the values for different polymers lie within the limits of experimental error.

Table 6. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for flexible-chain polymers in θ-solvents.

Polymer	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0^*$	Type of M; methods	Ref.
Poly(butyl methacrylate)	40—8200	propan-2-ol	21.5	**3.44±0.20	M_n; D, LS	[107]
Poly(decyl acrylate) (M_z/M_w 1.26 ± 0.09)	63—1110	n-butanol	24.5	**3.60±0.28	M_{SD};S, D	[113]
»	63—1110	ethyl acetate	10	**3.10±0.20	M_{SD};S, D	[113]
Polydivinylstyrene	65—710	n-octane	21	3.20±0.10	M_{SD};S, D	[152]
Polyisobutylene	1170	ethyl octanoate	10.8	3.53	M_η; S	[153]
Poly(methyl methacrylate)	200—6550	1-chlorobutane	35.6	**3.09±0.03	M_{SD}; S, D	[42]
	391	tetrachloromethane	15	3.55	M_η; S	[153]
Poly-α-methylstyrene, monodisperse	204—7470	*trans*-decalin	9.5	**3.37±0.07	M_w; S, LS	[43]
»	204—7470	»	»	(3.41)	M_w; S, LS	[154]
» (M_w/M_n 0.95–1.11)	42.5—1170	cyclohexane	39	**3.53±0.13	M_w; S, LS	[71]
» monodisperse	44.4—1675	»	39	3.27±0.08	M_w; S, LS, OS	[155]
» (M_w/M_n 1.03)	49—268	»	38.2	3.23±0.07	M_w; S, LS	[156]
» monodisperse	204—7470	»	34.5	**3.21±0.10	M_w; S, LS	[43]
» ($M_z/M_w \leqslant 1.2$)	120—2900	»	32	3.15±0.10	M_{SD};S, D	[157]
Polystyrene	830—2300	butan-2-one–butan-1-ol 72:26	25	**3.38±0.12	M_w; S, LS	[41]
»	31.5—1500	cyclohexane	35	3.01±0.13	M_w; S, D, LS	[158]
»	530	»	35	**3.10	M_w; S, D, LS	[83]
» ($M_z/M_w \leqslant 1.2$)	3600	»	35	**2.98	M_w; S, LS	[32]
» (M_w/M_n 1.09)	85—3950	»	35	2.79±0.14	M_w; S	[159]
»	27—495	»	35	3.28±0.11	M_w; S, LS	[160]
»	27—495	»	35	(3.19)	M_w; S, LS	[154]
» (M_w/M_n 1.02–1.14)	208—1010	»	35	**3.33±0.08	M_w; S, D, LS	[34]
»	208—1010	»	35	(3.25)	M_w; S, D, LS	[154]
» "S105" (M_w/M_n 1.05)	160	»	35	3.08	M_w; S, LS	[161]
» "Waters prod. No. 25170" (M_w/M_n 1.04)	51	»	15—35	3.03±0.04	M_w; S, LS	[162]
»	1500	»	32—42	2.93±0.07	M_η; S	[162]
» (M_w/M_n 1.03–1.12)	109—422	»	35	3.07±0.09	M_w; S, LS, OS	[156]
» "narrow fractions"	10—2200	»	34.5	3.28±0.03	M_w; S, LS	[163]
» (M_z/M_w 1.19)	118	»	35	**3.82	M_w; S, LS, SF	[63]

*, **As for Table 5.

Table 6 contains results for fractions of flexible-chain polymers analogous to those in Table 5 but obtained for solutions in θ-solvents. The average value over all 26 systems (total number of fractions 137) is $A_0 = (3.2 \pm 0.2) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, the same as that obtained in "good" solvents (Table 5).

Values obtained both in thermodynamically "good" solvents and in θ-solvents are given in Tables 5 and 6 for several of the polymers (denoted by a pair of asterisks **). Comparison shows that for the same fractions the experimental value of A_0 under θ-conditions may be either slightly greater or slightly smaller than A_0 in a "good" solvent. However, these differences are no greater than those in A_0 in different θ-solvents or in different "good" solvents, and lie within the limits of experimental error.

Thus it can be concluded from Tables 5 and 6 that excluded-volume effects have no appreciable influence on the value of A_0.

Experimental information on the influence of molecular-mass polydispersity on A_0 is rather meagre. Several results are given in Table 7, which compares values of A_0 for the initial unfractionated specimens and those obtained from their fractions. The number of polymers is 14, and the total number of fractions 203. Table 7 reveals no unambiguous independence of A_0 on polydispersity, since in about half the cases A_0 is greater for the unfractionated specimen than for the corresponding fractions, whereas for the other half the opposite relation is found. The observed differences lie within the limits of experimental error, and therefore may in general be disregarded. These results are consistent with the theoretical conclusions[29] mentioned above: for moderately polydisperse polymers ($M_w/M_n < 2$) only a slight dependence of A_0 on the width of the molecular-mass distribution can be expected.

Table 8 lists experimental values of A_0 obtained for fractions of polymers whose molecules have a ladder or semi-ladder structure. They cover 31 different polymer–solvent systems with a total of 351 fractions. The mean is

Table 7. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for fractions and unfractionated initial specimens (u.i.s.).

Polymer (degree of substitution)	Fractions and specimens	M	$10^{10}A_0$	Ref.
Poly(vinyl cinnamate)	13 fractions	M_D=51 000—762 000	3.58±0.10	[60]
ditto	u.i.s.	M_{SD}=223 000	3.51	[60]
Poly-2,5-(4′,4″-diphenylene phthalide)-1,3,4-oxadiazole	10 fractions (M_w/M_n 1.14–1.31)	M_w=8500—855 000	3.12±0.35	[164]
ditto	u.i.s. (M_w/M_n 3)	M_w=227 000	2.60	[164]
Polyisobutylene	9 fractions ($M_w/M_n \geqslant 2$)	M_v=9700—308 000	3.46±0.25	[64]
ditto	u.i.s.	M_w=77 500	2.83	[64]
Poly-*m*-phenyleneisophthalamide	8 fractions	M_{SD}=8000—250 000	3.74±0.26	[165]
ditto	u.i.s.	M_{SD}=142 000	3.65	[165]
»	48 fractions (M_z/M_w 1.2–1.4)	M_{SD}=1300—305 000	3.59±0.05	[166]
»	u.i.s. (M_w/M_n 1.8)	M_{SD}=113 000	3.73	[166]
Cellulose nitrate (1.9)	7 fractions	M_{SD}=15 900—78 300	3.23±0.07	[167]
ditto (1.9)	u.i.s.	M_{SD}=65 000	3.54	[167]
» (2.7)	13 fractions	M_{SD}=56 000—983 000	3.23±0.05	[168, 169]
» (2.7)	u.i.s. (M_z/M_w 1.36)	M_{SD}=335 000	3.36	[168, 169]
» (2.31)	27 fractions	M_{SD}=60 000—813 000	3.40±0.05	[170]
» (2.31)	u.i.s. (M_z/M_w 1.4)	M_{SD}=470 000	3.47	[170]
» (2.4)	10 fractions (M_z/M_w 1.19 ± 0.07)	M_{SD}=25 600—282 000	3.61±0.19	[171]
» (2.4)	u.i.s. (M_z/M_w 1.45)	M_{SD}=169 000	3.56	[171]
» (1.2)	8 fractions	M_{SD}=67 000—566 000	3.15±0.19	[171]
» (1.2)	u.i.s.	M_{SD}=261 000	3.20	[171]
» (2.0)	12 fractions	M_{SD}=5500—51 400	3.39±0.13	[172]
» (2.0)	u.i.s.	M_{SD}=23 200	3.57	[172]
Poly-(2-triphenylmethoxyethyl methacrylate)	15 fractions (M_z/M_w 1.16 ± 0.07)	M_{SD}=68 000—5 200 000	2.85±0.13	[127]
ditto	u.i.s. (M_w/M_n 2.9, M_z/M_w 2.3)	M_{SD}=100 000	3.00	[127]
Polychlorophenylsiloxane, ladder	20 fractions	M_{SD}=33 500—4 230 000	3.05±0.17	[173]
ditto	u.i.s.	M_{SD}=454 000	2.90	[173]
Poly(ethylene terephthalate)	6 fractions (M_{SD}/M_n 1.08 ± 0.09)	M_{SD}=25 000—111 000	3.58±0.24	[100]
ditto	u.i.s.	M_{SD}=87 300	2.51	[100]

$A_0 = (3.14 \pm 0.13) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, which coincides within the limits of experimental error with the corresponding experimental value for flexible-chain polymers (Tables 5–7), although ladder polymers are characterised by increased equilibrium rigidity of the molecular chains, which may exceed several times the rigidity of flexible-chain polymers[17]. This difference in rigidity is apparently insufficient, while the molecular masses of polymers in Table 8 are too large, for experiments to be able (in conformity with the predictions of theory, Figs.1 and 2) to detect a difference in the values of A_0 for more rigid polymers (Table 8) and for more flexible polymers (Tables 5–7).

Table 9 contains experimental values of A_0 for derivatives of cellulose and other polysaccharides, obtained for 62 polymer–solvent systems with a total of 428 fractions. They can conveniently be divided into two groups, applying respectively to solutions in organic solvents and to aqueous and buffer systems. If values in organic solvents are averaged, obtained by light-scattering and sedimentation methods, the result is $A_0 = (3.30 \pm 0.23) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, whereas averaging in the first group of values, obtained by sedimentation and diffusion methods, yields $A_0 = (3.32 \pm 0.32) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. These two values are almost identical, and agree within the limits of

Table 8. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for polymers having a ladder or semi-ladder molecular structure.

Polymer	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0$	Type of M; methods	Ref.
		Ladder polymers				
Polydichlorophenylsiloxane	42—540	benzene	24	3.21±0.17	M_{sD}; S, D	[174]
», (M_z/M_w 1.2–1.6)	42—2200	»	21	3.05±0.20	M_{sD}; S, D	[175]
Poly-3-methylbut-1-enylsiloxane	92—600	butyl acetate	24	3.11±0.10	M_{sD}; S, D	[176]
»	3.5—740	»	24	3.04±0.18	M_{sD}; S, D	[177]
Polyphenylisobutylsiloxane 1:1	13—2290	»	24	3.42±0.15	M_{sD}; S, D	[178]
»	13—2290	»	24	3.48	M_{sD}; S, D	[179]
Polyphenylisohexylsiloxane 1:1	6.1—386	»	24	3.26±0.21	M_{sD}; S, D	[178]
Polyphenylsiloxane, TsLFS-3	40—3350	benzene	21	3.30±0.25	M_{sD}; S, D	[179]
ditto	40—3350	»	21	2.71	M_{sD}; S, D	[17]
», TsLFS-1	37—420	»	21	3.22±0.12	M_{sD}; S, D	[180—182]
», TsLFS-2	17—311	»	21	2.73±0.15	M_{sD}; S, D	[180—182]
», (M_z/M_w 1.38 ± 0.16)	25—750	»	22	3.23±0.20	M_w; S, D, LS	[183]
», specimen A	15—430	»	24	3.08±0.16	M_{sD}; S, D	[184]
», specimen B	9—470	»	24	3.25±0.22	M_{sD}; S, D	[184]
»	34.8—181.5	»	20	(1.70±0.16)	M_w; S, LS	[185]
»	47—753	»	24	3.24±0.14	M_{sD}; S, D	[186]
Polychlorophenylsiloxane	49—1590	»	24	3.24±0.10	M_{sD}; S, D	[187]
»	33.5—4230	»	24	3.05±0.17	M_{sD}; S, D	[173]
		Semi-ladder polymers				
Polyarylate*	12.2—26.8	oxolan	20	3.15±0.19	M_w; S, LS	[188]
Polyarylate**	26.3—107.2	tetrachloroethane	20	3.33±0.16	M_w; S, LS	[188]
Polyacenaphthylene, "PAtsN-1"	10—930	benzene	24	3.10±0.16	M_{sD}; S, D	[189]
"PAtsN-2"	14—1140	»	24	3.10±0.13	M_{sD}; S, D	[189]
», "solid phase"	6—230	»	24	3.20±0.10	M_{sD}; S, D	[190]
Poly-*N*-2,4-dimethylphenylmaleimide	38—198	butyl acetate	21	2.90±0.09	M_{sD}; S, D	[191]
Poly-2,5-(4′,4″-diphenylene phthalide)-1,3,4-oxadiazole (M_w/M_n 1.14–1.31)	8.5—855	dimethylacetamide	20	***3.12±0.35	M_w; S, LS	[164]
Poly-*N*-isobutylmaleimide (M_z/M_w 1.08–1.27)	190—3400	butyl acetate	21	2.90±0.09	M_{sD}; S, D	[192]
Polycarbonate****	1.5—87.8	benzene	21	2.93±0.12	M_{sD}; S, D	[193]
Polycarbonate	8.5—266	oxolan	20	3.52±0.26	M_{sD}; S, D	[194]
Polycarbonate from Bisphenol A (M_w/M_n 1.13 ± 0.05)	4.3—466	»	25	3.33±0.08	M_w; S, LS, OS	[195]
Poly-*p*-tolylmaleimide	40—560	dimethylformamide	21	2.98±0.25	M_{sD}; S, D	[196]
Polyphenylisobutylsiloxane, helical ladder	2.8—750	cyclohexane	24	3.12±0.21	M_{sD}; S, D	[197]
Polyphenylene, methylated	5.5—270	toluene	20	2.98±0.14	M_{sD}; S, D, OS	[198]

*Polyarylate based on sebacoyl chloride and 3,3-bis-*p*-hydroxyphenylphthalide.

**Polyarylate based on terephthaloyl chloride and 9,9-bis-*p*-hydroxyphenylfluorene.

***Sedimentation constants s_0 from concentration dependence[164] of s on c recalculated with mean $k_s/[\eta] = 1.7$ by means of the equation $s_0 = s(1 + kc)$.

****Polycarbonate based on 1,1-di-*p*-hydroxyphenylcyclohexane.

Table 9. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for cellulose, amylose, their ethers, esters, and copolymers, and other polysaccharides.

Polymer (degree of substitution)	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0^*$	Type of M; methods	Ref.
		Solutions in organic solvents				
Amylose, unsubstituted, M_z/M_w 1.28	34—2630	dimethyl sulphoxide	25	2.87±0.36	M_w; S, LS	[199]
Cellulose acetate, "narrow" fractions	10.4—194	acetone	20	3.25±0.15	M_{sD}; S, D	[200]
ditto	10.4—194	»	20	(3.60)	M_n, $\upsilon = 0.74$	[6]
», 53.8% acetate groups, M_sD/M_n 1.11 ± 0.14	23—123	»	20	3.70±0.23	M_{sD}; S, D, OS	[201]
», » (2.34)	26—150	»	25	(5.7±0.6)	M_n; S, OS	[202]
Cellulose benzoate (2.3 ± 0.1)	51—660	dioxan	26.6	2.7±0.5	M_{sD}; S, D	[203]
Cellulose diphenylphosphonocarbamate (2.3 ± 0.5)	1—1670	»	26.6	3.1±0.5	M_{sD}; S, D	[203]

Table 9 (cont'd.).

Polymer (degree of substitution)	$10^{-3} \cdot M$	Solvent	Temp., °C	$10^{10} A_0^*$	Type of M; methods	Ref.
Cellulose monophenylacetate (2.6 ± 0.2)	65—5410	benzene	26	3.15±0.30	M_{sD}; S, D	[203]
Cellulose nitrate, 10.5-12.25% N	6.2—613	acetone	20	2.67±0.36	M_{sD}; S, D	[204]
ditto 11.10-13.98% N	13.8—1175	»	20	3.47±0.28	M_{sD}; S, D, SE, OS	[205]
», 13.1-13.8% N	74.5—2490	»	21	3.71±0.22	M_{sD}; S, D	[206]
», (2.88)	13—2490	»	20	4.14±0.31	M_{sD}; S, D	[207]
»	190—344	»	20	3.67±0.15	M_{sD}; S, D	[208]
»	76—1400	»	20	3.75±0.34	M_w; S, LS	[209]
», (1.9)	15.9—78.3	butan-2-one	25	3.23±0.07	M_{sD}; S, D	[167]
», (3), M_{sD}/M_n 1.36 ± 0.11	93—1500	ethyl acetate	20	4.30±0.66	M_{sD}; S, D, OS	[210]
», (2.84), M_z/M_w 1.35 ± 0.14	41.3—573	»	30	3.32±0.19	M_w; S, LS, OS	[211]
», (2.7)	56—983	»	21	3.23±0.05	M_{sD}; S, D	[168, 169]
», (2.31 ± 0.05), M_w/M_n <1.5	60—813	»	25	3.40±0.05	M_{sD}; S, D	[170]
», (2.39 ± 0.03), M_z/M_w 1.19 ± 0.07	25—282	»	25	3.61±0.19	M_{sD}; S, D	[171]
», RS1/8, 11% N	5.5—51.4	»	25	3.39±0.13	M_{sD}; S, D	[172]
», (1.15 ± 0.10)	67—566	DMA-6% LiCl	25	3.15±0.19	M_{sD}; S, D	[171]
Polysaccharides, synthetic, stereoregular						
tribenzyl(1-6)-α-glucan	180, 867	benzene	8	2.66±0.40	M_w; S, LS	[212]
tribenzyl(1-6)-α-mannan	524, 685	»	8	3.52±0.32	M_w; S, LS	[212]
tribenzyl(1-6)-α-galactan, M_w/M_n 2-3	189—922	»	8	3.38±0.40	M_w; S, LS	[212]
Cellulose tributyrate (2.94), M_w/M_{sD} 1.2	74—1700	bromoform	20	3.37±0.20	M_{sD}; S, D	[213]
ditto	74—1700	»	20	(3.40±0.13)	M_w; D, LS	[214]
»	63—1700	butan-2-one	20	3.32±0.13	M_{sD}; S, D	[213]
»	63—170	»	20	(3.40±0.20)	M_w; D, LS	[214]
Cellulose tributyrate-2-methyl-5-vinylpyridine 15-71%, M_z/M_w 1.2-1.4	130—940	»	20	2.36±0.84	M_{sD}; S, D	[215, 216]
Cellulose phenylcarbamate	105—1399	acetone	20	3.59±0.50	M_w; S, LS	[209]
ditto (3), M_w/M_n 1.10 ± 0.05	1.28—2580	1.4-dioxan	20	3.42±0.07	M_{sD}; S, D	[217]
», (2.1 ± 0.1)	14—107	»	23	3.62±0.24	M_{sD}; S, D	[218—220]
», (3), M_w/M_n 2.01	170—1085	cyclohexanone	25	2.31±0.08	M_w; S, LS, OS	[221]
»	170—1085	»	25	(1.48)	M_w; S, LS, OS	[221]
», (2.2)	20—920	ethyl acetate	23	3.35±0.23	M_{sD}; S, D	[222]
», (2.5)	2600	»	2.5—50	2.73±0.30	M_{sD}; S, D	[223]
», (2.67)	152—2600	»	25	3.09±0.21	M_{sD}; S, D	[224]
Ethylcelluose (2.75)	11.45—78.3	acetone	20	3.42±0.05	M_{sD}; S, D	[225]
», unfractionated, M_z/M_w = 1.10-1.19	27.5—67.5	ethyl acetate	20	3.54±0.32	M_{sD}; S, D	[226]
», (2.27)	5—31	»	24	3.73±0.12	M_{sD}; S, D	[227]
		Aqueous and buffer systems				
Amylose from potatoes	160—2290	0.33 M KCl	20	2.79±0.05	M_w; S, LS	[228]
Amylose tricarbanilate, M_w/M_n 1.5	300—2440	pyridine-water 86.71:13.29	25	2.98±0.14	M_w; S, LS	[229]
Hydroxypropylcellulose M_{sD}/M_n 2.1	73	water	25	3.77	M_{sD}; S, D, OS	[230]
»	73	»	25—40	3.87±0.07	M_{sD}; S, D, OS	[231]
Hydroxyethylcellulose	160—570	»	25	4.2±0.3		[232]
ditto (0.88), M_w/M_n 1.65 ± 0.07	190—625	»	25	4.04±0.16	M_n; S, D, LS, OS	[233]
»	190—625	»	25	(4.48±0.07)	M_{sD}; S, D, LS, OS	[233]
»	190—625	»	25	(4.78±0.12)	M_w; S, D, LS, OS	[233]
», Natrasol 250 G	150	»	25	4.06	M_{sD}; S, D	[230]
Dextran	14—38000	0.025 M Na_2HPO_4 + 0.025 M NaH_2PO_4	20	2.86±0.14	M_{sD}; S, D	[234]
», NRRL B-512, hydrolysed, M_w/M_n 1.25 ± 0.11	17.7—2700	water	20	2.73±0.18	M_w; S, LS	[235]
», B-512-Ph and A-179, 5-30% branched units, M_w/M_n 1.4-1.6	11.2—437	0.05 *N* Na_2HPO_4+0.05 *N* NaH_2PO_4	20	3.17±0.14	M_{sD}; S, D, LS (M_n)	[236]
Cellulose dimethylphosphonocarbamate (urethanecellulose) (2.0)	200—2400	0.2 *M* NaCl	22	4.36±0.41	M_{sD}; S, D	[237]
Carboxymethylcellulose (0.69 ± 0.04)	44.7—346	0.1 *M* NaCl	25	4.90±0.25	M_{sD}; S, D	[238]
Lignin, alkali	290—1860	$NaHCO_3$-NaOH buffer	25	3.18±0.54	M_w; S, LS	[239]
Methylcellulose	22.6—302	water	20	3.21±0.16	M_{sD}; S, D	[240]
Levan polysaccharide from *S. salivarius*, $M_w/M_n \leqslant 1.08$	17400—29700	»	25	2.89±0.20	M_w; S, LS	[241]
», partly hydrolysed	9.96—42800	»	25	2.92±0.87	M_w; S, LS	[242]
Schizophyllan, native polysaccharide, M_z/M_w 1.4 ± 0.1	96—5700	»	25	4.24±0.21	M_w; S, LS	[243]
Ficoll-400 synthetic polysaccharide	400	»	25	(1.00)	M_w; S	[230, 244]
Proteoglycan, bovine nasal cartilage	1000—2400	4M guanidine HCl	20	3.24±0.57	M_w; S, LS	[245]
Galactomannan polysaccharide	152—657	0.025 M KH_2PO_4 + 0.025 M Na_2HPO_4	20	(4.8±0.1)	M_{sD}; S, D_A	[246]
Sulphoethylcellulose, Na salt	80—310	0.1 M NaCl	21	3.60±0.29	M_{sD}; S, D	[247]
Chitosan	14.2—160	trifluoroacetic acid	25	3.04±0.31	M_w; S, SE	[248]
Cellulose, M_w/M_n ~2	42.2—747	Cadoxene-water 1:1	25	3.80±0.08	M_{sD}; S, D	[249]
» M_w/M_n 1.9 ± 0.2	10.1—33.7	»	25	2.95±0.13	M_w; S, LS, SE, OS	[250]
», linters, M_z/M_w 1.6 ± 0.5	2—700	»	20	3.73±0.33	M_{sD}; S, D	[251]
»	500 and 560	»	20	3.84	M_{sD}; S, D	[252]
Cellulose-acrylamide 78-94%, M_z/M_w 1.2 ± 0.2	240—4030	»	20	3.55±0.35	M_{sD}; S, D	[252, 216]
Ethylhydroxyethylcellulose (0.56 C_2H_5O, 0.84 C_2H_4O), M_w/M_n 3, M_{sD}/M_n 1.7	92—310	water	20	4.23±0.17	M_{sD}; S, D, LS, OS	[253]

*Values of A_0 in parentheses disregarded in calculation of mean values of A_0.

Table 10. Values of A_0 (erg deg^{-1} mole$^{-1/3}$) for rigid-chain polymers.

Polymer	$10^{-3}M$	Solvent	Temp., °C	$10^{10}A_0^*$	Type of M; methods	Ref.
Rigid-chain polyamides and heterocyclic polymers						
Polyamide-benzimidazole	9.5—60.9	dimethylacetamide	25	3.55±0.15	M_{sD}; S, D	[255]
»	6.6—72	»	25	3.81±0.45	M_w; S, SE	[256]
Polyamide-benzoximidazole	10—24.3	dimethylacetamide-3% LiCl	25	3.55±0.20	M_{sD}; S, D	[76]
Polyamide-hydrazide	5—34	dimethylacetamide	24	3.67±0.33	M_{sD}; S, D	[257]
ditto	3.63—47.7	»	24	(4.19±0.44)	M_w; D, LS	[257, 258]
»	21—34	dimethyl sulphoxide	24	3.80±0.05	M_{sD}; S, D	[257]
»	3.63—47.7	»	24	(4.07±0.27)	M_w; D, LS	[257, 258]
Poly-*p*-benzamide	7—18	96% H_2SO_4	25	3.60±0.07	M_w; D, LS	[259]
ditto, non-mol. soln.	9—80	dimethylacetamide-3% LiCl	25	(4.5±0.5)	M_{sD}; S, D	[259]
»	13.8—52.5	»	25	(3.2±0.1)	M_w; S, SE	[260]
Poly(butyl isocyanate)	3.8—1380	tetrachloromethane	24	4.16±0.45	M_{sD}; S, D	[261]
»	18—211	oxolan	20	(2.00±0.16)	M_{sD}; S, D	[262]
Poly(hexyl isocyanate) $M_z/M_w \leqslant 1.05$	68—7240	hexane	25	3.60±0.10	M_w; S, LS	[263]
Poly(chlorohexyl isocyanate)	12—306	tetrachloromethane	20	3.84±0.16	M_{sD}; S, D	[264]
Polybistri-*t*-butylphosphineplatinum-buta-1,4-dienediyl, $M_w/M_n \sim 1.1$	20.6—141	heptane	25	3.66±0.12	M_w; S, LS	[265]
Tobacco mosaic virus	33 200	0.01 M NaCl	20	3.63	M_{sD}; S, D	[266, 267]
Poly-(γ-benzyl *L*-glutamate)	37—332	dimethylformamide	20	4.15±0.16	M_w; S, D, LS	[268, 269]
ditto	37—332	»	20	4.00±0.13	M_{sD}; S, D	[268, 269]
»	42—364	»	21	3.99±0.55	M_{sD}; S, D	[270, 271]
», M_w/M_n 2.12 ± 0.26	17.6—394	»	25	3.34±0.12	M_w; S, SE, OS	[272, 273]
»	18.5—414	»	25	(3.18±0.12)	M_w; S, LS	[272]
»	34.7—414	»	25	3.27±0.20	M_w; S, SE	[274, 273]
»	36.4—435	»	25	(3.11±0.20)	M_w; S, LS	[274]
»	200—500	»	25	5.20±0.62	M_w; D, LS	[275]
», P. Ch. № G-100	320	»	25	3.98	M_w; S	[276]
»	37—659	»	25	3.68±0.13	M_{sD}; S, D	[76]
Poly-(ε-benzoxycarbonyl-*L*-lysyl-γ-benzyl *L*-glutamate), M_w/M_n 1.18-1.34	77.9—476	dimethylformamide	25	3.69±0.10	M_w; S, LS	[273]
Poly-$N_{(5)}$-3-hydroxypropyl-*L*-glutamine, partial helix	19—140	water	20	3.86±0.14	M_{sD}; S, D	[277]
ditto	53.5—333	»	25	3.13±0.09	M_w; S, LS, SE	[278]
», helix	19—140	methanol	20	4.03±0.26	M_{sD}; S, D	[277]
»	26.9—333	»	25	3.51±0.27	M_w; S, LS, SE	[278]
DNA, native, calf thymus	7700	0.15 M NaCl+0.015 M $C_6H_5O_7Na_3$ (citrate buffer)	20	4.14	M_w; S, LS	[279, 280]
ditto, ultrasonically degraded fragments	300—7400	0.2M NaCl, citrate buffer or 0.0025M Na_2HPO_4 + 0.005M NaH_2PO_4 + 0.001M $EDTANa_2$	20	3.74±0.09	M_w; S, LS	[281, 282]
»	300—7400		20	(4.3±0.5)	M_w; S, LS	[281]
»	300—7400	»	20	(3.78±0.30)	M_w; S, LS	[281, 283]
», mechanically degraded fragments M_w/M_n 1.44-2.32	1950—14100	0.006M Na_2HPO_4 + 0.002M NaH_2PO_4 + 0.001M $EDTANa_2$ + 0.0179M NaCl	20	3.68±0.07	M_{sD}; S, D	[282]
ditto	8900	buffer solution	20	3.70	M_{sD}; S, D	[284]
», *D. pneumoniae*	1250—2860	»	20	3.71±0.09	M_w; S, LS	[285]
»	1800 and 5000	»	20	4.12±0.16	M_w; S, LS	[283]
»	16 000	»	20	3.3	—	[286]
», Herring sperm	570—6200	»	20	3.68±0.12	$(M_{sD})_w$; S, D	[287, 288, 283]
», P. mirabilis	30 600	»	20	3.51	—	[289]
», Salmon sperm	6300	»	20	4.76	M_w; S, LS	[290]
», bacteriophage T7	24 600	»	20	3.55	M_w; S, LS	[291, 292, 282]
»	24 600	»	20	3.35	M_w; S, LS	[292—295, 282]
	25 200	»	20	3.53	M_{sD}; S, D	[296, 284]
»	25 200	(4.2-∞)pM CH_3HgOH + 0.005M Na borate + (0.005-0.5)M Na_2SO_4	20	2.88±0.17	—	[297]
», bacteriophage T4	112 400	0.2 M NaCl	20	3.42	M_{sD}; S, D	[284]
», bacteriophage T3	24 600	buffer solution	20	3.4	M_w; S, LS	[298]
Collagen, native, M_w/M_n 1.11	345	2 M KCNS	20	4.30	M_w; S, LS, OS	[299]
»	137—374	citrate buffer	24.8	4.49±0.14	—	[300]
»	301 1690	0.06 M K acetate buffer	—	4.32±0.39	M_w; S, SE	[301]
Poly-(*L*-lysine HBr)	128	1.0 M NaCl	25	3.59	M_w; S, SE	[302]
», $[Lysine]_n > 0.4$ g dl^{-1}	240	0.5 M Na_2CO_3 + 0.5 M $NaHCO_3$	25	3.33	M_w; S, SE	[302]
», $[Lysine]_n < 0.4$ g dl^{-1}	126	»	25	3.90	M_w; S, SE	[302]
Polymers with semi-rigid aromatic chains						
Polyamide-ester, aromatic	7.8—125	dimethylformamide	25	3.89±0.52	M_w; S, LS	[303]
Poly-4,4′-diphenylphthaleinterephthalamide	29.4—1110	»	25	3.67±0.14	M_w; S, SE	[304]
Poly-4′,4″-diphenylenephthalidepyromellitimide	8.2—51.6	»	25	4.56±0.23	M_w; S, LS	[303]
Polyimide**	20—280	dimethylacetamide	25	3.73±0.40	M_{sD}; S, D	[305]
Polyimide***	20—1400	»	20	2.94±0.27	M_w; S, SE	[306]
Poly-*m*-phenyleneisophthalamide, M_z/M_w 1.2-1.4	4.3—165	»	26	3.40±0.33	M_{sD}; S, D	[76]
ditto	74	DMA-0.25% LiCl	25	3,1	M_w; S, LS	[307]
»	8—250	DMA-3% LiCl	25	3.74±0.26	M_{sD}; S, D	[308]
»,	4,3—306	»	25	3.59±0.05	M_{sD}; S, D	[309]
Polysulphonamide****	25—106	dimethylacetamide	25	3.36±0.08	M_w; S, SE	[310]
Poly(tolyl isocyanate)	32—152	acetone	24	3.93±0.09	M_{sD}; S, D	[311]
Polyphenylquinoxaline	24—370	*N*-methylpyrrolidone	25	3.85±0.06	M_w; S, SE	[312]
»	6—120	tetrachloroethane	21	3.06±0.20	M_{sD}; S, D	[313]
Polyphthaloyl-*trans*-2,5-dimethylpiperazine	13.1—406	*N*-methylpyrrolid-2-one	25	3.94±0.33	M_w; S, LS	[314]
»	13.1—160	dimethylacetamide	25	3.47±0.18	M_w; S, LS	[314]

*Values of A_0 in parentheses disregarded in calculation of mean experimental values of A_0.

**Polyimide based on diaminodiphenylmethylphenylmethane and oxydiphenyl-3,3′,4,4′-tetracarboxylic acid.

error with the value for flexible-chain polymers. This is not unexpected, since the rigidity of the molecular chains of cellulose derivatives, though greater than for flexible-chain polymers, is close to that of the ladder polymers considered above.

A rather different situation is found for the second group of values, obtained in aqueous and buffer solutions of polysaccharides. The mean obtained by light-scattering and sedimentation is $A_0 = (4.02 \pm 0.38) \times 10^{-10}$, but the use of sedimentation and diffusion gives a mean of $A_0 = (3.50 \pm 0.80) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. Both values exceed that obtained in organic solvents, and are characterised by a greater experimental error. This illustrates the difficulties of working with aqueous and buffer solutions, especially when the sedimentation–diffusion method is used together with Eqn.(15).

In Table 10 data have been assembled on rigid-chain polymers, which are divided into three classes. The first comprises rigid-chain aromatic polyamides, polyamides having heterocycles in the chain, and poly(alkyl isocyanates), whose molecules have high equilibrium rigidity characterised by a Kuhn segment length 500–600 Å.[228] Polymer molecules in the second class are no less rigid than those in the first class, but the rigidity is due to the presence of a secondary structure leading to a helical chain conformation[1]. Finally, the third class comprises compounds, mainly also aromatic, arbitrarily termed "semi-rigid". Although the Kuhn segment length for their chains is smaller than for molecules of the first two classes[228], it is sufficient to ensure considerable permeability of the molecular coil in solution, which should increase the parameter A_0. This is confirmed on comparing values in Table 10 for the three classes of polymers.

The total number of polymer–solvent systems covered in Table 10 is 61, and the total number of fractions investigated 412. The mean over all polymers and fractions is $A_0 = (3.7 \pm 0.4) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$. The averaging excluded values for specimens No.7 and 8, solutions of which are not molecularly disperse. As with cellulose derivatives, the error in determination of A_0 is appreciably greater for rigid-chain than for flexible-chain polymers, as a consequence of specific experimental difficulties in working with solutions of the polymers in Table 10. Yet the average value of A_0 exceeds considerably that for flexible-chain polymers, and this difference is real, since it lies outside the experimental error. For all specimens in Table 10 (other than No.9) the parameter A_0 was invariant in the series of fractions investigated. For fractions of poly(butyl isocyanate) (No.9), investigated over a wide range of molecular weights, A_0 increased with decrease in chain length L. This can be regarded as confirmation of the theoretical predictions (Fig.1) for a polymer in which d/A is lower than for other polymers.

V. CONCLUSION

The experimental results surveyed in the previous Sections can be summarised in the statement that, for every polymer–solvent system throughout the range of molecular masses accessible to experiment, the parameter A_0 determined from formulae (4), (5), and (15) is indeed invariant, independent of chain length, solvent, and, for moderately polydisperse specimens, their degree of polydispersity.

For all flexible-chain polymers and synthetic polymers having moderately enhanced chain rigidity the most reliable experimental value is

$$(A_0)_{\text{flex}} = (3.2 \pm 0.2) \cdot 10^{-10} \text{ erg deg}^{-1} \text{ mole}^{-1/3} = (3.2 \pm 0.2) \cdot 10^{-17} \text{ J deg}^{-1} \text{ kmole}^{-1/3} \quad (16)$$

from which we obtain

$$\beta \equiv P^{-1}(\Phi/100)^{1/3} = 2.3 \cdot 10^6 .$$

These experimental values are considerably lower than those predicted by analytical theories—$A_\infty = 3.8 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$ and $\beta = 2.71 \times 10^6$—and agree well with those obtained by Zimm's computer experiment[26]—$A_\infty = 3.13 \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$ and $\beta = 2.33 \times 10^6$ (Table 2).

For polymers of high chain rigidity the mean experimental value

$$(A_0)_{\text{rig}} = (3.7 \pm 0.4) \cdot 10^{-10} \text{ erg deg}^{-1} \text{ mole}^{-1/3} \quad (17)$$

is identical with that of A_∞ predicted by the analytical theories. However, this experimental value cannot be regarded as A_∞, since it has been obtained for short polymer chains, in several cases with $L/A < 10$. It is more logical to adopt as experimental value of A_∞ the quantity $(A_0)_{\text{flex}}$ determined by means of Eqn.(16), since it has been obtained with the maximum chain lengths accessible to experiment. In conformity with this the difference between $(A_0)_{\text{rig}}$ and $(A_0)_{\text{flex}}$—respectively from Eqns.(17) and (16)—must be regarded as a result of increase in the ratio A_0/A_∞ for a rigid-chain polymer ($d/A \ll 1$) in the region of low values of L/A in conformity with the theory of vermiform chains (Table 1 and Figs.1 and 2).

Thus in the practical utilisation of the present results to determine the molecular mass of a polymer from experimental values of $[\eta]$ and f by means of formulae (4) and (5) the value of A_0 determined by means of formula (16) can be recommended for flexible-chain and moderately rigid-chain polymers, and that obtained from (17) for polymers of high chain rigidity. For derivatives of cellulose and other polysaccharides of adequate purity and molecular dispersity of non-electrolyte solutions Table 9 indicates use of the value $A_0 = (3.30 \pm 0.30) \times 10^{-10}$ erg deg^{-1} mole$^{-1/3}$, obtaining which, however, has involved considerable error.

As mentioned at the beginning of this Review, use of the invariant A_0 in determining molecular masses M is especially important for polymers of high chain rigidity, which have low molecular mass and also are soluble only in such specific solvents as concentrated sulphuric acid. The combination of all these properties in effect excludes the possibility of using sedimentation and makes light scattering a relatively ineffective method[2]. The most useful combination under these conditions is that of viscometric and diffusion measurements with the use of formula (4) and the above experimental values of A_0. This method is widely used at the present time.

The fact that the experimental A_∞ corresponds to $\beta = 2.3 \times 10^6$ instead of the 2.7×10^6 predicted by theories of sliding friction and viscosity of macromolecules means that the theoretical values $P_\infty = 5.11$ and $\Phi_\infty = 2.8 \times 10^{23}$ mole^{-1} are incompatible. Thus interpretation of experimental data on diffusion (or sedimentation) and on solution viscosity for the same polymer in terms of a single theory of these

Table 10 (cont'd.).

***Polyimide based on oxydiphenyl-3,3′,4,4′-tetracarboxylic dianhydride and 9,9-di-*p*-aminophenylfluorene.
****Polysulphonamide based on di-*p*-aminophenyl sulphone and terephthalic acid.

processes[12,13] cannot yield identical values of chain rigidity (Kuhn segment length). Theories of transport processes in polymer solutions require elaboration, which in turn should eliminate the above inherent contradiction and provide a theoretical value of A_∞ corresponding to experimental results. By means of Zimm's computer experiment[26] it has proved possible to do this by some decrease in the theoretical value of Φ_∞ and a considerable increase in the theoretical value of P_∞. Whether this is the only possible method should appear from further research.

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