A SIMPLE AND EXACT METHOD FOR CALCULATING DIFFUSION COEFFICIENTS FROM THE DATA OF POLARIZATION INTERFEROMETER. EXTENSION TO THE CASE OF POLYMERS WITH NARROW DISTRIBUTION OF MOLECULAR WEIGHT

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The simple equation derived previously for calculating the diffusion coefficient and the zero-time correction from the data of the polarization interferometer is shown to be valid not only in the case of binary systems but also for the diffusion of polymer solutes with moderately broad molecular weight distribution and results in a diffusion coefficient, which is an average value of a well-defined type. In addition, it is shown experimentally that the equation is applicable with sufficient accuracy also to the evaluation of diffusion coefficients of polymers having a polydispersity index as high as $M_w/M_n = 2$.

A simple and precise method for calculating diffusion coefficients from the data of a polarization interferometer has been proposed previously[1] and it has been shown experimentally that the straight line equation derived for a binary system is applicable also for "monodisperse" standard polymers. It should be pointed out that in general the polarization interferometer gives average values of the diffusion coefficient that range approximately from the number average to the weight average. Thus, for moderately broad fractions, the numerical values obtained may deviate considerably from the *z*-average values obtained from the Doppler-shifted light scattering technique. In order to make the calculation[1] unambiguously applicable also to free diffusion measurements on moderately polydisperse polymer solutes[2] it was felt desirable to determine what type of average diffusion coefficient[3] one obtains.

In the present paper it is shown that the previously derived linear relation[1] holds also in the case of moderately polydisperse solutes giving a well-defined average value of the diffusion coefficient. As a check the theoretical results have been tested experimentally and found applicable for a polymer having $M_w/M_n \cong 2$.

THEORETICAL

The polarization interferometer employed[4,5] compares the optical paths of two beams that pass through the diffusion cell separated by a small distance b which is an instrumental constant. Assuming a proper adjustment of the optical system, the interference conditions are given by

$$(\Delta n/\Delta x)\Delta_{x=b} = j\lambda/2bl = a_j \cong \mathrm{d}n/\mathrm{d}x\,, \tag{1}$$

where Δn is the refractive index difference at the points in the cell where the two interfering beams pass, j is a number of the interference fringe, l is the cell thickness, λ is the wave length of the light and dn/dx is the gradient of refractive index at the point x in the cell. In a free diffusion process the exact relationship between the difference quotient and the derivative in Eq. (*1*) is given by [5,6]

$$\left(\frac{\Delta n}{\Delta x}\right)_{\Delta x=b} = \frac{\mathrm{d}n}{\mathrm{d}x}\left(1 + \frac{1}{2^2\,.\,3!}\,\frac{b^2}{2Dt}\,\frac{x^2 - 2Dt}{2Dt} + \ldots\right) \tag{2}$$

as can be derived from the known equation for the refractive index gradient

$$\mathrm{d}n/\mathrm{d}x = \left[\Delta n_0/2(\pi Dt)^{1/2}\right]\exp\left(-x^2/4Dt\right), \tag{3}$$

where t is time, Δn_0 is the initial ($t = 0$) refractive index difference and D is the binary diffusion coefficient. In view of the bell-shaped form of the gradient (*3*) it is clear that the conditions (*1*) lead to the formation of pairs of interference fringes, the j-th pair corresponding to a given value of a_j. Thus, each pair represents points on the contour line of the gradient curve; the fringes of a given pair first move apart, then approach each other and finally disappear in the middle. The experimentally measured quantity is the distance between the fringes of a given pair, $(2x_j)$, as a function of time.

In a previous paper[1] the following relationship was derived from Eqs (*1*)–(*3*)

$$(2x_j)^2 - (2x_{j+k})^2 = 16Dt(1 + \Delta t_c/t)\ln\left(a_{j+k}/a_j\right), \tag{4}$$

where $\Delta t_c = \Delta t + b^2/24D$; Δt is the zero-time correction resulting from the imperfect shape of the initial boundary and the term $b^2/24D$ stems from the second term of the expansion in Eq. (*2*). It can also be shown[1] that when the optical system is not properly adjusted (so that $a_{j+k}/a_j \neq (j + k)/j$), a_j is given by

$$a_j^2 = 2(\Delta n_0)^2/\mathrm{e}\pi(2x_j)^2_{\max}\,, \tag{5}$$

where e is the base of natural logarithms and $(2x_j)^2_{\max}$ is the maximum ordinate of the function $(2x_j)^2 = \mathrm{f}(t)$. The equation obtained by inserting a_j and a_{j+k} from Eq. (*5*) reads

$$(2x_j)^2 - (2x_{j+k})^2 = 8DA_{j,j+k}t + 8DA_{j,j+k}\Delta t_c\,, \tag{6}$$

where $A_{j,j+k} = \ln\left[(2x_j)^2_{\max}/(2x_{j+k})^2_{\max}\right]$; the diffusion coefficient is obtained from the slope of the straight line (*6*) and Δt_c follows from the intercept.

Consider now the diffusion of a polydisperse polymer characterized by the weight distribution of diffusion coefficients, $g(D)$, defined in such a way that the product $g(D)\,\mathrm{d}D$ gives the weight fraction of the polymer with diffusion coefficients from the interval $(D, D + \mathrm{d}D)$. Moments about zero of the distribution $g(D)$ are defined by

$$\mu'_r = \int_0^\infty D^r g(D)\,\mathrm{d}D\,. \tag{7}$$

Previously we derived a general equation[3]

$$\frac{\mathrm{d}n}{\mathrm{d}x} = \frac{\Delta n_0}{2(\pi D_1 t)^{1/2}}\left[\mathrm{e}^{-\vartheta^2/D_2} + \left(\frac{\vartheta^4}{2}\,\frac{D_2 - D_3}{D_2^2 D_3} - \frac{\vartheta^6}{6}\,\frac{D_2^2 - D_3 D_4}{D_2^3 D_3 D_4} + \ldots\right)\right], \tag{8}$$

where the average diffusion coefficients, defined on the basis of the moments μ'_r as $D_1 = (\mu'_{-1/2})^{-2}$, $D_2 = \mu'_{-1/2}/\mu'_{-3/2}$, $D_3 = \mu'_{-3/2}/\mu'_{-5/2}$, are experimentally accessible[3] and $\vartheta^2 = x^2/4t$. Rearranging one obtains

$$a_j \cong \left(\frac{\mathrm{d}n}{\mathrm{d}x}\right)_j = \Phi_j\left[1 + \frac{z_j}{\exp\left(-\vartheta_j^2/D_2\right)}\right], \tag{9}$$

where the alternating series in (*8*) has been denoted by z_j and

$$\Phi_j = \frac{\Delta n_0}{2(\pi D_1 t)^{1/2}}\exp\left(-\vartheta_j^2/D_2\right). \tag{10}$$

Now, limiting the treatment to adjacent fringe pairs ($k = 1$), one can write

$$\frac{a_j}{a_{j+1}} = \frac{\Phi_j}{\Phi_{j+1}}\left[\frac{1 + \dfrac{z_j}{\exp\left(-\vartheta_j^2/D_2\right)}}{1 + \dfrac{z_{j+1}}{\exp\left(-\vartheta_{j+1}^2/D_2\right)}}\right]. \tag{11}$$

Taking logarithms, inserting from Eq. (*10*), rearranging and using the approximations $(1 + x)/(1 + y) \approx 1 + x - y$ and $\ln(1 + z) \approx z$, valid for small x, y, z, one gets

$$\ln\frac{a_j}{a_{j+1}} = \frac{(2x_{j+1})^2 - (2x_j)^2}{16 D_2 t} + \frac{z_j}{\exp\left(-\vartheta_j^2/D_2\right)} - \frac{z_{j+1}}{\exp\left(-\vartheta_{j+1}^2/D_2\right)}. \tag{12}$$

For $k = 1$, this is clearly equivalent to Eq. (*4*) with $\Delta t_c = 0$, provided the difference of the last two terms in Eq. (*12*) can be neglected. In the following, this difference is denoted $\Delta(j, j+1)$; it thus follows that in the region of ϑ where $\Delta(j, j+1)$ can be neglected, the calculation according to Eq. (*4*) is valid and yields the average diffusion coefficient $D_2 = \mu'_{-1/2}/\mu'_{-3/2}$.

In the previous derivation[1] of Eq. (*6*) the first term of the expansion (*2*) has been included and resulted in a correction term in the definition of Δt_c. It can be shown by a relatively simple algebra that in the range of ϑ where $a_j \doteq \Phi_j$ (with D_1 and D_2 – see Eq. (*10*)) the relation (*2*) remains valid. Thus, under the condition $a_j = \Phi_j$ the derivation of Eq. (*4*) in the previous paper[1] remains unchanged including the value of Δt, and it need not be repeated here.

However, to proceed from Eq. (*4*) to Eq. (*6*) it is necessary to show whether and in what range of ϑ is it justified to set $A_{j,j+1} = \ln (a_{j+1}/a_j)^2$ also for polydisperse samples. Eq. (*10*) can be rewritten in the form

$$(2x_j)^2 = 16D_2 t \ln \left[\frac{\Delta n_0}{2a_j(\pi D_1 t)^{1/2}} \right] \quad (13)$$

which again describes the time dependence of the distance between fringes under the assumption $a_j \doteq \Phi_j$. From the condition for the maximum of this function one obtains

$$(2x_j)^2_{\max} = \frac{D_2}{D_1} \frac{2\Delta n_0^2}{a_j^2 \pi e} . \quad (14)$$

It is immediately apparent that $a_{j+1}^2/a_j^2 = (2x_j)^2_{\max}/(2x_{j+1})^2_{\max}$, so that Eq. (*6*) originally derived for binary diffusion remains valid also for the diffusion of polydisperse polymers with a moderately broad distribution of molecular weight, where one can neglect $\Delta(j, j+1)$ and make use of the approximation $a_j = \Phi_j$ at least within a certain range of ϑ; in this range the plot of experimental data according to Eq. (*6*) is linear.

EXPERIMENTAL

Standard polystyrene NBS 706 (NBS Certificate) was characterized by $M_n = 136\,500$, $M_\eta = 216\,000$, $M_w = 257\,800$ (light scattering), $M_w = 288\,100$ (sedimentation equilibrium). Toluene (reagent grade, Lachema Brno) was distilled on a column (1 500 mm, Berl's saddles). The instrument, thermostat, preparation of solutions, measuring procedure and the stainless steel diffusion cell have been described elsewhere[7-9]. Measurements were performed at 25°C against pure solvent; mean concentrations, $\bar{c}_0$, were always lower than $4{\cdot}5 \cdot 10^{-4}$ g cm^{-3} so that the concentration dependence of diffusion coefficients could be neglected[2].

TABLE I

Diffusion coefficients of polystyrene NBS 706 in toluene at 25°C. Symbols: D_1, D_2, D_3 are average diffusion coefficients, Δt_c — zero-time correction, $(2x_j)$-distance between the fringes of a given pair, j-number of fringes

j	General procedure[3]				Equation (*6*)		
	$D_2 \,.\, 10^{11}$ $m^2\,s^{-1}$	Δt_c s	$D_1 \,.\, 10^{11}$ $m^2\,s^{-1}$	$D_3 \,.\, 10^{11}$ $m^2\,s^{-1}$	$(2x_j)^2_{max} \,.\, 10^6$ m^2	$D_2 \,.\, 10^{11}$ $m^2\,s^{-1}$	Δt_c s
				Experiment A			
2	$2{\cdot}98_7$	1 553	—	—	10·640	$2{\cdot}95_1$	2 096
3	$2{\cdot}95_0$	1 454	—	—	4·642	$2{\cdot}86_7$	1 899
4	$2{\cdot}94_2$	1 315	—	—	2·573		
Mean	$2{\cdot}95_9$	1 384	$3{\cdot}36_8$	$2{\cdot}82_5$	—	$2{\cdot}90_9$	1 997
				Experiment B			
2	$2{\cdot}99_2$	1 387	—	—	9·552	$2{\cdot}97_1$	2 193
3	$2{\cdot}95_4$	1 908	—	—	4·124	$2{\cdot}82_2$	1 632
4	$2{\cdot}97_2$	1 091	—	—	2·222		
Mean	$2{\cdot}97_3$	1 462	$3{\cdot}40_0$	$2{\cdot}88_6$	—	$2{\cdot}89_6$	1 912

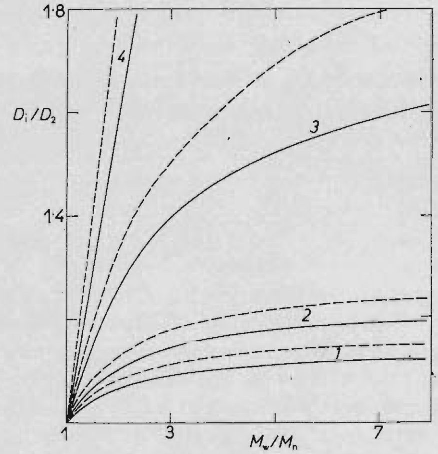

FIG. 1

Quotients D_i/D_2 plotted against M_w/M_n for polymer obeying the Schulz–Zimm distribution function. *1* D_n/D_2; *2* D_1/D_2; *3* D_w/D_2 *4* D_z/D_2; ——— $\alpha = 0{\cdot}5$; ----- $\alpha = 0{\cdot}556$

RESULTS AND DISCUSSION

The necessity to define the type of average of the resulting diffusion coefficient even for polymer samples having a very narrow distribution is immediately apparent from Fig. 1, where the quotients D_1/D_2, D_n/D_2, D_w/D_2 and D_z/D_2 ($D_n = (\mu'_{-1})^{-1}$; $D_w = \mu'_1$; $D_z = \mu'_2/\mu'_1$) are plotted against the ratio M_w/M_n for two values of the exponent α in the equation $D = KM^{-\alpha}$ ($\alpha = 0{\cdot}5$, Θ-solvent; $\alpha = 0{\cdot}556$, a thermodynamically good solvent), assuming that the polymer obeys the Schulz–Zimm distribution function. It should be noted here that it always holds[3] $D_1 \geq D_2 \geq D_3 \geq \ldots$; from the picture it follows $D_2 \leqq D_n \leqq D_1$ and these three averages are quite close to each other. In addition, Fig. 1 also illustrates that the sensitivity of average diffusion coefficients to sample polydispersity increases somewhat with the thermodynamic quality of the solvent.

In the previous paper the use of Eq. (*6*) in the case of the binary diffusion of low-molecular weight solutes was described in detail together with the diffusion of narrow polystyrene standards ($M_w/M_n < 1{\cdot}02$ and $1{\cdot}08$, respectively) in toluene, which according to Fig. 1 should have $D_1/D_2 \sim D_n/D_2 \sim 1{\cdot}01$; all plots according to Eq. (*6*) were in these cases linear in the whole range[9] $t \gg \Delta t_c$. From the present results it follows that the measured values of the diffusion coefficient did correspond to the D_2 – average.

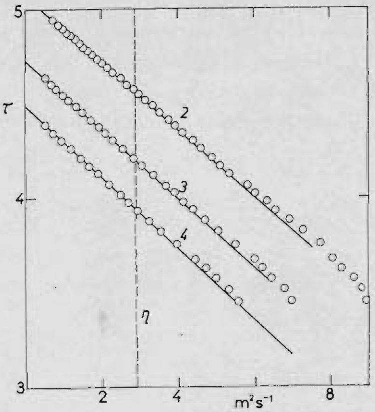

FIG. 2

Plots of $\eta_j = f(\tau)$ for three pairs of fringes in experiment A. η_c determined[3] from the condition of 1% error in Eq. (*15*); numbers are values of *j*. The value on axis *x*: $\eta_j \cdot 10^{10}$

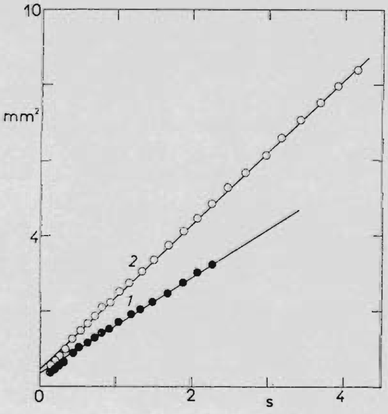

FIG. 3

Time dependence of $(2x_j)^2 - (2x_{j+1})^2$ for three fringe pairs in experiment A ● $j = 3$ ○ $j = 2$. Axis *y*: $(2x_j)^2 - (2x_{j+1})^2$; *x*: $t \cdot 10^{-4}$

In order to verify the range of validity of Eq. (*6*), *i.e.*, the possibility of neglecting $\Delta(j, j + 1)$ and the assumption $a_j = \Phi_j$, the free diffusion of polystyrene NBS 706 which has $M_w/M_n \sim 2$ was measured. Results of two independent maesurements A and B are collected in Table I which summarizes also the values of D_1, D_2, D_3 and Δt_c as obtained by the previously described general procedure[3] valid for polydisperse systems. This method is also based on Eq. (*9*) and, assuming $a_j \cong \Phi_j$ leads to the limiting straight line

$$\ln(t/t_0) = \tau = \ln\left[(\Delta n_0)^2/4\pi a_j^2 t_0 D_1\right] - \eta_j/8D_2\,, \qquad (15)$$

where t_0 is the time unit employed and $\eta_j = 16\vartheta_j^2$. The curvature of the plot τ *vs* η is given by the term $z_j/\exp(-\vartheta_j^2/D_2)$ in relation (*9*), and Eq. (*15*) is valid in that range of ϑ_j where this quotient can be neglected in comparison with unity. A graph of the dependence of η_c/D_2 *vs.* D_1/D_2 (η_c is the maximum admissible value of η, which corresponds to accuracy of 1 or 2% when using the straight-line dependence according to Eq. (*15*)) can be found in[3]. The averages D_2 and D_1 are obtained[3] from the slope and intercept of the linear dependence $\eta_j = f(\tau)$, D_3 can be determined from a deviation graph also described in[3]. As an example, Fig. 2 gives these dependences for three pairs of fringes from experiment A; the range of validity of Eq. (*15*) for a 1% error is indicated and the limiting straight line is drawn; the curvature of the plot is clearly seen.

The same experimental data evaluated according to Eq. (*6*) are plotted in Fig. 3; it is seen that after a short time (comparable with the correction term Δt_c, so that the uncertainty in its determination can be neglected[9]) both plots become linear. A comparison of Figs 2 and 3 also shows qualitatively the compensation of the

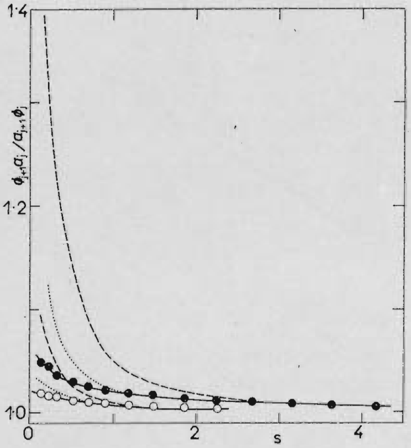

FIG. 4

Calculation of the correction term in Eq. (*11*) for three pairs of fringes in experiment A. The series for z_j truncated after: ——— 7 terms, ······ 5 terms, ----- 3 terms, ● ... $j = 2$, ○ ... $j = 3$. The values of time are in $t \,.\, 10^{-4}$

effect of polydispersity as indicated in Eq. (*12*). These conclusions have been verified by model calculations: from the data of experiment A the quantity

$$[1 + z_j/\exp(-\vartheta_j^2/D_2)]/[1 + z_{j+1}/\exp(-\vartheta_{j+1}^2/D_2]$$

which enters into Eq. (*11*) has been calculated; for small values of ϑ they lead to $\Delta(j, j + 1)$. As the alternating series that defines z_j converges slowly for higher ϑ, it was truncated after the third, the fifth and the seventh term, respectively (the data of experiment A were used, *i.e.*, $D_2/D_3 = 1{\cdot}05$, and for the higher averages it was assumed that $D_2/D_3 = D_3/D_4 = \ldots$). The results are plotted in Fig. 4; the deviations rapidly drop below 2 and 1 percent, respectively. The extent of compensation of the effect of polydispersity is illustrated by some numerical values: at $t = 6\,240$ s (10th exposure) the respective values of $z_j/\exp(-\vartheta_j^2/D_2)$ are 0·0523, 0·0238 and 0·0112 for $j = 2$, 3 and 4, respectively, so that the compensation amounts to some 50 percent. At the same time, these numbers illustrate that the approximation $a_j \sim \Phi_j$ is also valid with sufficient accuracy, since the correction for the replacement of the difference quotient by the derivative is a quantity of second order. With regard to Eq. (*14*) it is sufficient to note here that the ϑ-values for which $(2x_j)^2$ are maximum fall for $j = 2$ to 5 into the region where Eq. (*15*) is fulfilled, so that the assumption $a_j \sim \Phi_j$ is valid.

Comparing from this point of view the resulting values of the average D_2 as determined from both experiments A and B according to Eq. (*6*) (last three columns in Table I) and, on the other hand, by means of the general procedure[3], it is clear that within the limits of experimental error (about 2 percent) the results are equivalent even for a polymer with $M_w/M_n \cong 2$ (*i.e.* $D_1/D_2 = 1{\cdot}14$), but Eq. (*6*) yields somewhat higher values of Δt_c. This difference is not surprising if one considers that in the rather complex general method[3] the values of Δt_c are arrived at in a quite complicated manner. Summarizing, one can state that Eq. (*6*) with all its advantages previously mentioned[1] can be applied with confidence also for evaluating data of free diffusion of common moderately broad polymer fractions. In this case the method yields the average D_2, and the linearity of the plot is in itself a sufficient warranty of the applicability of the method.

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