

## A SIMPLE AND EXACT CALCULATION METHOD FOR BINARY DIFFUSION COEFFICIENTS FROM THE DATA OF POLARIZATION INTERFEROMETER

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A very simple equation has been derived allowing in the case of a two-component diffusion to determine the binary diffusion coefficient and zero time correction,  $\Delta t_c$ , from the polarization interferometer data. To determine  $D$ , two pairs of the interference fringes are needed;  $D$  is determined from the slope of a straight line representing the time dependence of the difference of squared distances between these pairs. The intercept on the ordinate then gives the correction  $\Delta t_c$ . The calculation is very quick, sufficiently accurate, not requiring the use of a computer; moreover, it allows to check reliably a troublefree performance of the experiment. The possibilities offered by the suggested procedure have been checked on diffusion measurements of biphenyl in benzene, sucrose in water and monodisperse polystyrene in toluene.

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The polarization interferometer suggested by Bryngdahl<sup>1-3</sup> has been widely used in the recent years in measurements of the free diffusion in solutions<sup>4-7</sup>, diffusion in melts,<sup>8</sup> and thermal diffusion<sup>9,10</sup>. The described procedures of evaluation of the experimental data supplied by this apparatus for diffusion in two-component systems are either very time consuming or of low accuracy; the calculations are carried out with a computer by means of an appropriate iterative procedure which optimizes the experimental data<sup>4,7</sup>. Moreover, they do not allow to check reliably if the experimental data are not subject to a systematic error due for instance to the fact that at the beginning of or during the experiment there occur convection disturbances at the boundary between the diffusing solutions (caused, *e.g.*, by temperature oscillations, vibration or evaporation of volatile solvents through leaks in the diffusion cell).

The present paper describes a very simple method of calculation, which allows the diffusion coefficient in a two-component system to be determined with the same accuracy as that obtained when the general procedure suggested earlier<sup>11-13</sup> for polydisperse polymers is employed; moreover, the new method allows a reliable check-up of troublefree performance of the apparatus during the diffusion run.

### THEORETICAL

The polarization interferometer used<sup>1-3,14</sup> compares the optical paths of two parallel beams passing through the diffusion cell at a distance  $b$  ( $b$  being a constant of the apparatus). Assuming

an exact adjustment of the apparatus, the corresponding interference conditions are given by the relationship<sup>3</sup>

$$(\Delta n/\Delta x)_{\Delta x=b} = j\lambda/2bl = a_j \cong dn/dx, \quad (1)$$

where  $\Delta n$  is the difference between the refractive indices in the two planes of the cell through which the interfering beams pass,  $j$  is the ordinal number of the fringe,  $l$  is the thickness of the cell,  $\lambda$  is the wavelength of the light used and  $dn/dx$  is the refractive index gradient at point  $x$  in the cell; in the case of free diffusion in a two-component system it holds

$$dn/dx = [\Delta n_0/2(\pi Dt)^{1/2}] \exp(-x^2/4Dt). \quad (2)$$

Here,  $\Delta n_0$  is the difference between the refractive indices of solutions under investigation at a time  $t = 0$  and  $D$  is the diffusion coefficient. With respect to the bell-shaped gradient curve (2) it is evident from Eq. (1) that for each value  $a_j$  one pair of interference fringes is formed which actually represents the contour line of the gradient curve; its position at time  $t$  indicates the position of a constant value of the refractive index gradient,  $dn/dx = a_j$ . The experimentally accessible quantities are the mutual distances ( $2x_j$ ) between the two fringes of a given ( $j$ -th) pair, which can be obtained from photographs of the interference system taken at appropriate experimental times  $t$ . An exact relationship between the quantities  $(\Delta n/\Delta x)_{\Delta x=b}$  and  $dn/dx$  was derived<sup>2,3</sup> by expanding  $(\Delta n/\Delta x)_{\Delta x=b}$  into a Taylor series

$$\left(\frac{\Delta n}{\Delta x}\right)_{\Delta x=b} = \frac{dn}{dx} \left(1 + \frac{1}{2^2 \cdot 3!} \frac{b^2}{2Dt} \frac{x^2 - 2Dt}{2Dt} + \dots\right). \quad (3)$$

On substitution from Eqs (1) and (2) we obtain after rearrangement

$$\exp\left[\frac{x_j^2}{4D(t + \Delta t)}\right] = \frac{\Delta n_0}{2a_j[\pi D(t + \Delta t)]^{1/2}} \left(1 + \frac{b^2}{48Dt} \frac{x_j^2 - 2Dt}{2Dt}\right). \quad (4)$$

Here, only the first correction term is included from the general relationship (3); this is justified already after a short time after the beginning of the experiment<sup>14</sup>. Furthermore, it is necessary to introduce a zero time correction  $\Delta t$  which corrects the non-ideality of the initial boundary between the diffusing solutions; it is a time necessary for the diffusion to proceed from a hypothetical, ideally sharp boundary until the moment at which the actual measurement is started. On taking logarithms and passing to the experimentally accessible quantities ( $2x_j$ ) we obtain

$$\frac{(2x_j)^2}{16D(t + \Delta t)} = \ln \left\{ \frac{\Delta n_0}{2a_j[\pi D(t + \Delta t)]^{1/2}} \left(1 + \frac{b^2}{48Dt} \frac{(2x_j)^2 - 8Dt}{8Dt}\right) \right\}. \quad (5)$$

For the  $j$ -th and  $(j + k)$ -th interference pair at a given time  $t$  it is possible to calculate the difference  $(2x_j)^2 - (2x_{j+k})^2$  which after rearrangement and introduction of the approximation\*  $\ln(1 + x) \cong x$  becomes

$$(2x_j)^2 - (2x_{j+k})^2 = 16D(t + \Delta t) \left[ \ln \frac{a_{j+k}}{a_j} + \frac{b^2}{48Dt} \frac{(2x_j)^2 - (2x_{j+k})^2}{8Dt} \right]. \quad (6)$$

Eq. (6) can be further simplified: neglecting a term of a lower order of magnitude and using the approximations\*  $1/(1-y) \cong 1+y$  and  $(1+y)(1+z) \cong 1+y+z$ , we obtain

$$(2x_j)^2 - (2x_{j+k})^2 = 16Dt(1 + \Delta t/t + b^2/24Dt) \ln(a_{j+k}/a_j). \quad (7)$$

If the apparatus has not been adjusted with sufficient accuracy<sup>12</sup>, the relation  $a_{j+k}/a_j = (j+k)/j$  does not hold and it is necessary to substitute from the equation<sup>14</sup>

$$a_j^2 = 2(\Delta n_0)^2/e\pi(2x_j)_{\max}^2, \quad (8)$$

where  $e$  is the base of natural logarithms and  $(2x_j)_{\max}^2$  is the maximum value of  $(2x_j)^2 = f(t)$ . The final result reads

$$(2x_j)^2 - (2x_{j+k})^2 = 8D \ln \frac{(2x_j)_{\max}^2}{(2x_{j+k})_{\max}^2} \cdot t + 8D \ln \frac{(2x_j)_{\max}^2}{(2x_{j+k})_{\max}^2} \Delta t_c \quad (9)$$

with the zero time correction<sup>2,14</sup> given by

$$\Delta t_c = \Delta t + b^2/24D. \quad (9a)$$

The diffusion coefficient is determined from the slope of the straight line (9); the intercept on the ordinate gives  $\Delta t_c$ .

## EXPERIMENTAL

Biphenyl was purified by zone melting<sup>14</sup>, sucrose was medical purity grade (Spofa, Prague); monodisperse polystyrene, Waters Associates Standard Polystyrene No 41995, had  $M_w = 98\,200$ ,  $M_n = 96\,200$ , and monodisperse polystyrene, Pressure Chemical Co., had  $M_w = 160\,000$  and  $M_w/M_n < 1.08$  (both according to the producers' data). Benzene and toluene (anal. purity grade, Lachema, Brno) were distilled on a column (150 cm, Berl's saddles). The apparatus, the thermostat, preparation of solutions, measurement procedure and three different diffusion cells employed have been described elsewhere<sup>12,14,15</sup>. All measurements were performed at 25°C against pure solvent.

## RESULTS AND DISCUSSION

To calculate the diffusion coefficient and zero time correction according to Eq. (9), it is necessary to determine the maxima of time dependences of the values of  $(2x_j)^2$  and  $(2x_{j+k})^2$  corresponding to the chosen fringe pairs – here, the pairs are always those having  $j = 2$  and  $k = 1$ . The interferograms were measured with a recording photometer<sup>14</sup> and the maxima  $(2x_j)_{\max}^2$  and  $(2x_{j+k})_{\max}^2$  were determined by a graphical method. An example illustrating the accuracy of determination of these maxima (which is to a major extent decisive for the errors of calculated  $D$ ) is given in Fig. 1. In Fig. 2 the differences  $(2x_j)^2 - (2x_{j+k})^2$  are plotted against time for both poly-

\* The corresponding terms designated schematically  $x$ ,  $y$ ,  $z$  decrease rapidly with time and approach zero; the validity of the approximations given here is determined similarly as in ref.<sup>14</sup>.

styrene samples under investigation. Using the least squares method, we calculated the diffusion coefficient from the slope of the straight lines, and  $\Delta t_c$  from the intercept on the ordinate. The experimental points from the beginning of the experiment (small  $t$ ) for which the difference quotient cannot be replaced with the first two terms of expansion (3) with sufficient accuracy were not included in the calculation of  $D$ ; the corresponding condition is<sup>14</sup>  $t \gg b^2/6 \cdot 18D$ . The values of  $D$  thus obtained, the corresponding zero time corrections  $\Delta t_c$  and the deviations of the measured diffusion coefficients from the respective average values are listed in Table I.

The  $D$  values used for comparison (Table I) were calculated by means of a procedure suggested earlier<sup>14</sup>, based on the equation<sup>2,14</sup>

$$\tau = \ln [(2x_j)_{\max}^2 e/8Dt_0] - \eta/8D + (\eta - 8D) \Delta t_c/8Dt, \quad (10)$$

where  $\tau = \ln(t/t_0)$ ,  $\eta = (2x_j)^2/t$ , and  $t_0$  is the chosen time unit. This equation is also valid for a two-component diffusion and represents a special case of the general relationship<sup>13</sup> derived for polydisperse systems. If corrected times  $t_{\text{cor}} = t + \Delta t_c$  are substituted for the experimental times  $t$ , the last term on the right-hand side is cancelled, and Eq. (10) becomes an equation of a straight line. The values of  $\Delta t_c$  were determined by extrapolation described in ref.<sup>14</sup>. With respect to the accuracy required, however, smoothed experimental data must be used in this extrapolation,  $\Delta t_c$  must be calculated for more than one pair of fringes, and average values of  $\Delta t_c$  must be substituted into Eq. (10). This part of the calculation requires the use of a computer;

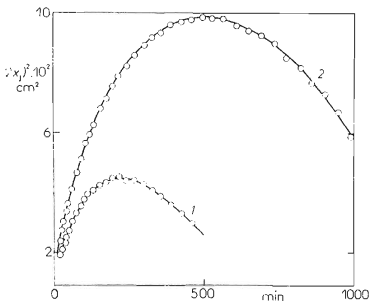


FIG. 1

Time Dependence of Squared Distances Between the Interference Fringes of Two Pairs for the System Polystyrene-Toluene ( $M_w = 160000$ )—Toluene ( $\bar{c}_0 = 0.0446 \text{ g dl}^{-1}$ )

1 Pair 3,  $(2x_3)_{\max}^2 = 4.50 \cdot 10^{-2} \text{ cm}^{-2}$ ,  
2 pair 2,  $(2x_2)_{\max}^2 = 9.83 \cdot 10^{-2} \text{ cm}^{-2}$ .

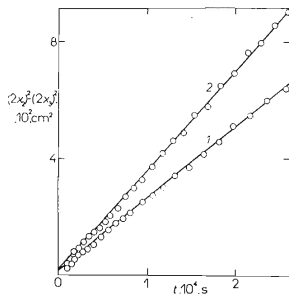


FIG. 2

Determination of the Diffusion Coefficient and Zero-Time Correction  $\Delta t_c$  According to Eq. (9) for the System Polystyrene-Toluene

1  $M_w = 160000$ ,  $\bar{c}_0 = 0.0446 \text{ g dl}^{-1}$ ,  
2  $M_w = 98200$ ,  $\bar{c}_0 = 0.0488 \text{ g dl}^{-1}$ .

TABLE I

Diffusion Coefficients ( $D$ ,  $\text{cm}^2 \text{s}^{-1}$ ) and Zero-Time Corrections ( $\Delta t_c$ , s) in Two-Component Systems

$\bar{c}_0$  is a mean concentration of the solutions measured (in  $\text{g dl}^{-1}$ ),  $\Delta D$  is a relative deviation from the mean value (in %); if not indicated otherwise the measurements were performed in a stainless steel cell.

$\bar{c}_0$	Calculation according to					
	Eq. (9)			Eq. (10)		
	$D \cdot 10^7$	$\Delta D$	$\Delta t_c$	$D \cdot 10^7$	$\Delta D$	$\Delta t_c$
Biphenyl-benzene <sup>a</sup> (Duralumin cell)						
0.0525	155.3	-0.06	52.9	155.6	+0.19	76.0
0.0577	155.8	+0.26	76.6	156.6	+0.84	75.0
0.0514	153.0	-1.54	64.0	155.2	-0.06	70.0
0.0519	155.3	-0.06	66.8	154.9	-0.26	60.0
0.0500	157.7	+1.48	58.0	155.3	0	78.0
average:	155.4		average:	155.3		
Sucrose-water <sup>b</sup> (plexiglass cell)						
0.0501	52.2	-1.32	0	52.1	-0.57	99.8
0.0502	53.9	+1.89	42.1	52.6	+0.38	67.0
0.0273	51.8	-2.08	43.9	52.3	-0.19	87.0
0.0480	53.9	+1.89	11.8	52.4	0	70.0
average:	52.9		average:	52.4		
Biphenyl-benzene <sup>a</sup>						
0.0497	156.4	-0.38	19.8	155.2	-0.45	21.0
0.0504	157.3	+0.19	26.2	156.4	+0.32	19.0
0.0503	157.7	+0.44	26.9	155.9	0	21.0
0.0503	156.7	-0.19	28.6	156.2	+0.19	23.0
average:	157.0		average:	155.9		
Polystyrene ( $M_w = 98\ 200$ )-toluene						
0.0488	5.25	-1.32	872.0	5.41	+0.93	464.0
0.0488	5.39	+1.32	491.0	5.31	-0.93	502.0
average:	5.32		average:	5.36		
Polystyrene ( $M_w = 160\ 000$ )-toluene						
0.0538	3.99	+1.78	19.0	3.95	+1.28	682.0
0.0538	3.89	-0.76	418.0	3.80	-2.56	744.0
0.0446	3.88	-1.02	994.0	3.93	+0.77	648.0
0.0396 <sup>c</sup>	3.94	+0.51	1 491.0	3.94	+1.02	1 360.0
average:	3.92		average:	3.90		

<sup>a</sup> According to ref.<sup>16</sup>  $D = 1.556 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . <sup>b</sup> According to ref.<sup>17</sup>  $D = 5.226 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ . <sup>c</sup> Measured in a duralumin cell.

an NE 803 B machine was used for this purpose. The value of  $D$  is calculated using the least squares method from the slopes of straight lines  $\tau = f(\eta)$ . The time intervals at which the individual exposures were taken were adjusted to fit the latter calculation procedure. They were so chosen as to comprise, if possible, the whole course of the five pairs of the interference fringes ( $j = 1 \dots 5$ );  $\Delta t_c$  was always calculated for pairs 3, 4 and 5 (sometimes also 2). The diffusion coefficient was calculated as an average from pairs 2 to 5 while expecting the best result for pair 2 which contained the largest number of experimental points at higher times.

It follows from a comparison of deviations of the individual experiments from the calculated average values (Table I) that both ways of calculation are virtually equivalent as to the accuracy of the diffusion coefficients. When calculations are made using Eq. (9), the required accuracy can be attained with two pairs of interference fringes; the agreement of the results could be improved still more by a more appropriate choice of the time-table of photographing, so that pairs 2 and 3 should comprise the largest possible amount of experimental points. A comparatively small number of points of pair 3 (fourteen to fifteen) is the cause of somewhat larger deviations observed in some experiments with biphenyl. A larger scatter of values appears in the case of corrections  $\Delta t_c$  calculated according to Eq. (9). Here, the fact comes to the fore that pairs 2 and 3 have higher experimental times (so that  $\Delta t_c$  plays a relatively less important role) compared with pairs 4 and 5 which (along with pair 3) were used in the determination of the  $\Delta t_c$  values needed for substitution in Eq. (10). It can be seen, however, that this fact does in no way affect the accuracy of determination of  $D$ .

A rather more pronounced difference between both calculations can be observed only in the experiments with sucrose measured in a plexiglass cell, which was more sensitive toward perfect thermostating<sup>15</sup>. A graphic representation of data using Eq. (9) confirmed this finding. The scatter of points, particularly at the beginning of the experiment, was larger, and in some cases the straight lines became curved (especially for low experimental times); this is reflected in the  $\Delta t_c$  values determined here and in a larger scatter of the calculated values of  $D$ . In calculations using Eq. (10) this effect appeared in a curving of the dependences  $\tau = f(\eta)$  for low times and in a larger scatter of the  $D$  and  $\Delta t_c$  values calculated for the individual pairs. These effects can serve as an indication of disturbing influences which may arise during measurements.

The sensitivity toward possible (though minute) disturbances in the course of measurements, which can cause convections in the diffusion cell, represents another advantage of the procedure suggested here (along with the simplicity mentioned above). The procedure allows to test the cell easily and with great sensitivity; moreover, any significant deviation from the straight line indicates that some disturbing effects took place during the experiment and that a systematic error may appear in the calculated diffusion coefficients. From this viewpoint the use of a calculation according to Eq. (9) is of more advantage for binary systems; it automatically comprises a check-up of a trouble-free course of the measurements while preserving the accuracy of the calculated diffusion coefficients.

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