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FLOWING-BOUNDARY DIFFUSION CELL AND THE DETERMINATION OF ZERO-TIME CORRECTION IN FREE DIFFUSION MEASUREMENTS IN VERY DILUTE POLYMER SOLUTIONS WITH A POLARIZATION INTERFEROMETER

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One of the decisive conditions of a successful measurement of free diffusion in solutions is an appropriate cell, which allows to form, at the beginning of the experiment, as perfect a boundary as possible between the solutions under investigation, thus approaching as much as possible the initial conditions $c = c_2^0$ for $x \leqq 0$ and $c = c_1^0$ for $x > 0$ at $t = 0$. As a number of authors have shown[1-4], best results are obtained with cells in which the boundary is formed by a slow outflow of the solution and the solvent through a narrow horizontal slit. In this way, the initial rough boundary is sharpened in the plane of the slit; the time $t = 0$ is given by the closing of the outflow. The sharpening can also be accomplished[5-8] by inserting a fine capillary from above into the centre of the measuring space; the solvent is then sucked through the capillary at a constant rate, and the capillary is slowly removed when the sharpening is completed. The latter method, however, is less suitable from the hydrodynamic point of view[7]; it is also hardly possible to avoid certain disturbances while removing the capillary.

The cells described above, although for the present being the best available, do not yield an ideally sharp boundary, so that the initial conditions cannot be perfectly met. The arising error is eliminated by introducing the so-called zero-time correction Δt (defined as the time necessary for the diffusion to proceed from a hypothetical, ideally sharp boundary until the moment at which the measurement begins); this value ought to be added to the measured time t. The calculation of the diffusion coefficient in which experimental times are used yields time-dependent quantities D' which with increasing t approach the correct value; the correction Δt is obtained together with

the diffusion coefficient for example by extrapolation to infinite time according to a relationship suggested by Longsworth[2]

$$D' = D(1 + \Delta t/t) . \qquad (1)$$

It can also be seen from the definition of the zero-time correction that the experimentally established Δt values must be inversely proportional to the diffusion coefficient, because the construction of the cell used roughly defines the hydrodynamic conditions[7] of the boundary formation. Fujita[9] derived theoretically a general relationship between Δt and D; using a simplifying assumption that the concentration change across the boundary at $t = 0$ can be approximated by a straight line, he obtained

$$\Delta t = (\varepsilon + \lambda)^2/24D ; \qquad (2)$$

here, $(\varepsilon + \lambda)$ gives (in Fujita's notation) the thickness of the boundary formed.

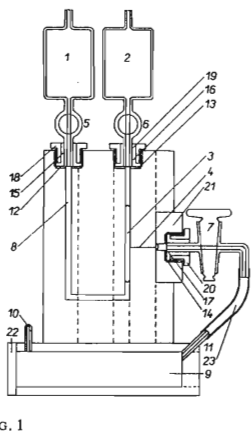

FIG. 1

Sectional View of Cell *II*

1 Solution tank (35 ml), *2* solvent tank (volume 35 ml), *3* measuring space, *4* outflow slit, *5*, *6*, *7* stoppering cocks, *8* connecting channel, *9* waste solution tank (64 ml), *10* connecting tube, *11* tank feeding, *12*, *13*, *14* silicone rubber sealing, *15*, *16*, *17* flanges, *18*, *19*, *20* nuts, *21* cylindrical insert with a collecting channel, *22* lid, *23* silicone tube.

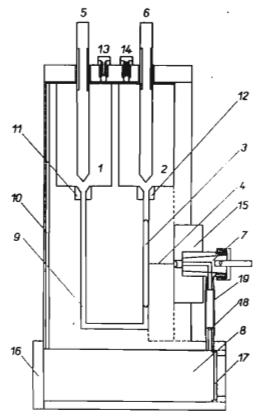

FIG. 2

Sectional View of Cell *III*

1 Solution tank (61 ml), *2* solvent tank (61 ml), *3* measuring space, *4* outflow slit, *5*, *6* stoppering needle valves, *7* stopcock with a teflon core, *8* waste solution tank (105 ml), *9*, *10* connecting channels, *11*, *12* teflon saddles, *13*, *14* feeding holes stoppered with screws with teflon packing, *15* cylindrical insert with a collecting channel, *16* lid, *17* glass window, *18* feeding tube, *19* teflon tube.

The optical investigation of the diffusion process in very dilute solutions requires optical systems of maximum sensitivity; the sensitivity of the method can also be increased by extending the optical path in the cell[10,11]. However, under these conditions the requirements on the quality of the initial boundary also increase, together with the demands on the complexity of the cell design; this is due to the low gravitational stability of the boundary between two solutions which differ but slightly as to their density, so that mechanical vibrations and/or temperature gradients and oscillations in the cell can lead in a pronounced way to convection disturbances.

When measuring diffusion[12–14] of polydisperse polymers, we used a cell type[15] with an outflow slit and needle-valve closure, similar to that suggested by Varoqui and coworkers[16]. (The design is designated here as cell *I*). At the start of the experiment some disturbances of the boundary were observed in this cell due to the closing of the outflow with the needle-valve. The present paper describes two new cells in which most of the disadvantages have been removed; the needle-valve used for closing the outflow has been replaced by a cock, and the measuring space has been narrowed in accordance with the theoretical analysis of the effect of convections[4].

EXPERIMENTAL

Biphenyl was the same as in paper[14], sucrose was pharmacopoeial purity grade (Spofa, Prague); the monodisperse polystyrene used (Pressure Chemical Co.) had $M_w = 160\,000$ and $M_w/M_n \simeq \simeq 1{\cdot}08$. Benzene and toluene (both analytical purity grade, Lachema, Brno) were redistilled on a column (150 cm, Berl saddles).

The apparatus, thermostat, preparation of solutions, measuring procedure, calculation of the diffusion coefficient and the determination of Δt have been described earlier[13,14]. All experiments were made at 25°C; the short-time temperature fluctuations in the cell during the measurements did not exceed[14] 10^{-4}°C.

The sectional view of a cell made of organic glass for aqueous solutions (cell *II*) is in Fig. 1. The brass flanges *15*, *16*, *17* were glued to the glass tanks *1*, *2* and the outflow cock *7* with epoxide resin. The whole cell consists of parts indicated in the Figure by broken lines, glued together with chloroform. The outflow slit *4* is 0·07 mm wide and was obtained by setting two parts together. The measuring space *3* is 45 mm high and 3 mm wide; its length in the direction of the optical path of the beam is $49{\cdot}35_5$ mm. It is covered with plane-parallel glass windows, ground with an accuracy of one interference fringe in 5 cm. The windows are fixed to the fronts of the cell with flanges and sealed with a 0·1 mm thick teflon sheet, slightly coated with an appropriate lubricant, which also seals the bearing surface of the insert *21*.

The cell was filled by all-glass syringes. The rate of outflow through the slit is controlled with the cock *7*, and the sharpening is followed visually; the time $t = 0$ is given by the closing of the cock *7* on reaching a satisfactory boundary.

During the formation of the boundary, the laminary character of the flow is well visible at the beginning — the interference fringes follow the shape of streamlines, and the existence of a laminar layer along the cell walls in which the relative flow rate is virtually zero can also be clearly seen. The sharpening therefore continued until the laminary film disappeared, and the boundary did not visually change any more during further outflow; the sharpening times for polymers in all the three cells were ranging from 60 to 90 min at an outflow rate 0·25—0·5 ml/min, and from 10 to 15 min for low-molecular-weight compounds (at a rate of 1·5—2 ml/min).

The sectional view of the cell for organic solvents (cell *III*) is in Fig. 2. The stainless cell consists of parts indicated in the Figure by broken lines, cemented together with Monomet 308 (Loctite Corp., USA). The outflow slit is 0·07 mm wide; the measuring space is 50 mm high, its width being 3 mm and length in the direction of the optical path being $48{\cdot}89_0$ mm. For sealing of the glass windows (whose set-up is the same as described above) and the ring packing *15*

and for the lubrication of the cock 7, a lubricant for non-polar solvents was used. The outflow tank is provided with a window 17 which allows to follow directly the outflow. The filling and sharpening are the same as described above.

RESULTS AND DISCUSSION

The results of testing of the individual cell types are summarized in Table I. In the second column, the initial concentration differences are given; all experiments were measured against pure solvent. The third column gives values of Δt_c which are obtained with the wave-front shearing interferometer when the zero-time correction is determined using a procedure described earlier[14]. This quantity is given by[17]

$$\Delta t_c = \Delta t + b^2/24D , \tag{3}$$

where b is the distance between the two interfering beams in the diffusion cell. The expression $b^2/24D$ originates from the second term of the series expansion[17] of the difference quotient $(\Delta n/\Delta x)_{\Delta x = b}$. The resulting equation of a straight line for the calculation of the diffusion coefficient (if we substitute the corrected experimental times $t_{cor} = t + \Delta t_c$) is

$$\tau = \ln [(\Delta n_0)^2/4\pi D a_j^2 t_0] - \eta/8D . \tag{4}$$

Here, $\tau = \ln (t_{cor}/t_0)$ (t_0 is the chosen time unit), $\eta = (2x)^2/t_{cor}$, ($2x$) being the distance between the inteference fringes of a given pair of these fringes, formed at points where the refractive index gradient is equal to $a_j = j\lambda/2bl$; l is the light path in the cell, j is a natural number and λ is the wave length of the light employed. Bryngdahl[4] has shown that for an ideal boundary one pair of interfer-

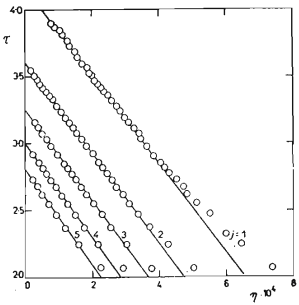

FIG. 3

Dependence $\tau = f(\eta)$ of Five Fringe Pairs

Cell *I*, $\Delta c^0 = 0{\cdot}1029$ g/dl; orders of interference fringes (j) are given for the individual lines; the lowest points of the individual straight lines correspond to $t = 60$ s.

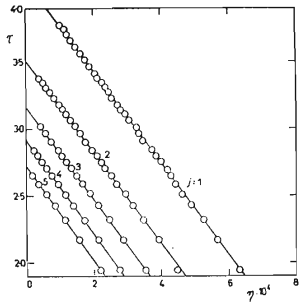

FIG. 4

Dependence $\tau = f(\eta)$ of Five Fringe Pairs

Cell *III*, $\Delta c^0 = 0{\cdot}1006$ g/dl, $\Delta t_c = 21$ s; orders of interference fringes (j) are given for the individual lines.

ence fringes is formed, separated by a distance b. It follows from comparison of Eqs (*2*) and (*3*) that in the case of this interferometer a contribution of optical origin proportional to b^2 is added to the width of the boundary at the beginning of the experiment. With respect to the fact that the correction Δt_c thus defined appears only in the case of this apparatus, the fourth column of Table I gives the values Δt calculated according to (*3*), which are common for the other optical arrangements. (The quantity b is 0·7585 mm for the apparatus used in this work[14]). Since the compounds

TABLE I

Zero-Time Corrections and Diffusion Coefficients of Biphenyl in Benzene, Sucrose in Water and Polystyrene in Toluene in the Individual Cells

Compound	Δc^0 g/dl	Δt_c s	Δt s	$D \cdot 10^7$ cm^2/s	$D\,\Delta t \cdot 10^4$ cm^2
		Cell *I*			
Biphenyl	0·1029	70	55	155·2	8·5
	0·1038	60	45	154·9	7·0
	0·1001	78	63	155·3	9·8
	0·1051	76	61	155·6	9·5
	0·0502	68	53	156·2	8·3
				mean	*8·6*
Polystyrene	0·0793	1 360	752	3·94	3·0
		Cell *II*			
Sucrose	0·1001	83	37	52·4	1·9
	0·1001	99	53	52·1	2·8
	0·1005	67	21	52·6	1·1
	0·0960	70	24	52·4	1·3
	0·0546	87	41	52·3	2·1
				mean	*1·8*
		Cell *III*			
Biphenyl	0·0995	21	6	155·2	0·95
	0·1007	19	4	156·4	0·61
	0·1006	21	6	155·9	1·01
	0·1006	23	8	156·2	1·26
				mean	*0·96*
Polystyrene	0·0859	682	75	3·95	0·30
	0·0892	648	41	3·93	0·16
				mean	*0·23*

under investigation are monodisperse, the diffusion coefficients D listed in the last but one column have been calculated[12,13] only from the slope of the straight lines (*4*). The last column contains products $D\,\Delta t$, which can be accepted (Eq. (*2*)) as a criterion of the hydrodynamic efficiency of the cell, *i.e.* of the boundary quality, and used to compare all three cell types.

The hydrostatic head conception of the outflow was chosen on purpose in order to eliminate all additional equipment which always complicates the manipulation, can be a source of leakage or vibrations and also impairs the possibility of an appropriate thermostating of the cell. The same reasons led to the design of the cell as a single compact unit.

With cell *I*, disturbances in the boundary appeared when the outflow was closed with the needle-valve: when the teflon valve tip bears on the saddle, a minute volume of the solution is squeezed back into the measuring space through the slit, which impairs abruptly the quality of the boundary. This is probably the cause of the comparatively high Δt values observed for this cell. It is true that this fact impairs only the construction of the generalized gradient curve[13,17]; however, the consequences of this disturbance can easily be seen from the graphical representation of Eq. (*4*) in Fig. 3. Whilst for higher fringe pairs the points fit well the straight lines, the disturbance still appears in the curvature of pair *1* in the region of low t. Thus, the disturbance has the longest effect in the bottom part of the gradient curve. If the compounds under investigation are monodisperse, it is sufficient to neglect the region of curvature. In the case of a polydisperse polymer, however, the dependences $\tau = f(\eta)$ cease to be linear[12]; the polydispersity of the sample has as its consequence the same curvature of this dependence so that the imperfection of the initial boundary causes an apparent

TABLE II

Comparison of Different Cell Designs

Measured system	Cell type	Δc^0 g/dl	$D\,\Delta t \cdot 10^4$ cm^2	Ref.
Biphenyl–benzene	*III*	*cf.* Table I	0·96	[a]
Polystyrene–toluene	*III*	*cf.* Table I	0·23	[a]
Biphenyl–benzene	sharpening with capillary	comparable	6·2	8
Polyisobutylene–octane	sharpening with capillary	comparable	3·3	8
Poly(dimethylsiloxane)–toluene	sharpening with capillary	comparable	7·9	8
Sucrose–water	one outflow slit	comparable	1·7[b]	20
2-Aminoethanol–water	one outflow slit	comparable	4·3[b]	20
Calcium chloride–water	one outflow slit	10 × higher[c]	1·2	21
Urea–water	two outflow slits	10 × higher[c]	1·4	22
Sucrose–water	two outflow slits	10 × higher[c]	1·1	23
Ethanol–benzene	two outflow slits	10 × higher[c]	6·4	23
Sucrose–water	two outflow slits	10 × higher[c]	0·0–2·0[d]	24

[a] This work; [b] The published values of zero-time corrections were recalculated according to (*3*) on the assumption $b = 0{\cdot}75$ mm; [c] Approximately; [d] Depending on the outflow rate through both slits.

increase in polydispersity. Therefore, when constructing the generalized gradient curve, it was necessary to use only experimental points corresponding to higher t's, where this disturbance does not play a significant role; this, however, extended the region to be determined approximatively[13]. This fact was also the main cause for developing the two new cells. A plexiglass cell, much simpler to produce, and developed for diffusion measurements in aqueous solutions fully removed the disadvantages mentioned above; however, it was much more delicate from the point of view of perfect thermostating. The cause ought probably to be seen in a combination of three different construction materials having different thermal properties.

Indeed, the lowest values $D\,\Delta t$ were found in a stainless cell *III* (Table I). An improvement in comparison with cell *I* is also corroborated by Fig. 4, representing the dependence $\tau = f(\eta)$ found in cell *III* under the same experimental conditions as in Fig. 3. All points, including those corresponding to the shortest experimental times $t = 60$ s, lie on straight lines. It is also of interest to learn, from comparison of the products $D\,\Delta t$, that for the polymer solutions the boundaries in both cell *I* and cell *III* are roughly three to four times better than for solutions of low-molecular-weight compounds; a considerable difference in the viscosities of the solution and the solvent are likely to play their part here[8].

It is of interest to consider the meaning of Δt (or in our case Δt_c) and its effect upon the evaluation of experimental data for polymers having a very wide molecular weight distribution. It follows from the dependence of Δt on the diffusion coefficient that a certain Δt_M corresponds to the polymer fraction with the molecular weight M. As a distribution of diffusion coefficients can be assigned to molecular weight distribution of the polymer by means of the relation $D = K \,.\, M^{-\alpha}$, it follows that we should actually consider a corresponding "distribution of zero-time corrections". When calculating Δt we therefore obtain only a certain average value which, however, is not defined unambiguously. Consequently, the experimental values of Δt (in our case Δt_c) have to be made as small as possible, and only those points are to be used in the subsequent calculations which correspond to sufficiently long times in comparison with the zero-time correction. Ignoring this fact can lead to diffusion coefficients by 10 and more per cent higher. If cell *III* is used for the measurements, the requirement that neither the uncertainty in Δt_c due to the polydispersity of the sample nor the effect of the approximation[14] $(\Delta n/\Delta x)_{\Delta x = b} \cong \mathrm{d}n/\mathrm{d}x$ should be of any importance, can be expressed by a semiempirical condition $t \geqq 2b^2/6{\cdot}18D$. In this way we also eliminate the effect of optical aberrations of the second and third order[18,19]. It should be borne in mind that it is not advisable to underestimate the problems involved in the determination of Δt while measuring the diffusion of polymers.

It is rather difficult to compare the three cell types described above with other published designs. The authors often mention the Δt values only in passing; also the dependence of Δt on the diffusion coefficient is sometimes ignored. Moreover, Δt obtained by extrapolation from long experimental times are often subject to a comparatively large error. It is also impossible to predict if, and in which way, the very low initial differences in concentration employed in our measurements (Table I) would influence the formation of boundary in different cells. (The Δc^0 values employed by most authors vary within the region 0·4—1 g/dl). However, the product $D\,\Delta t$ can be used as a rough measure.

Table II offers a comparison of cell *III* with results reported by other authors who tried to determine Δt in more detail. The cell *III* is of a simpler design and is more easily handled than cells with one outflow slit listed in Table II; nevertheless, the $D\,\Delta t$ values found give evidence in its favour. The Table also includes cells in which two outflow slits were used, situated opposite each other on both sides of the measuring space. The data do not suggest any considerable improvement in the quality of the boundary obtained; on the other hand, this modification always brings along an even more complex design and more difficult manipulation. There is one exception[24], where the Δt values have been found to depend considerably on the rate of outflow through the slits,

and under certain conditions Δt was virtually zero. However, this conclusion need not be true in the case of two solutions whose densities differ by a factor ten times lower. (In the region of outflow rates used here the Δt values have not been found to change significantly). Moreover, the determination of the optimum rate necessitates several complete diffusion runs which in themselves are very time-consuming.

The cell described in the present work seems to be an adequate compromise from the viewpoint of simplicity of the design and ease of manipulation while at the same time keeping the high quality of the boundary formed; it also meets satisfactorily the strict conditions presented by the diffusion measurements of polydisperse polymers in very dilute solutions.

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