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A New Interferometric Method for the Determination of Diffusion Coefficients of Very Dilute Solutions

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A new simple and rapid interferometric method is described for studying diffusion and other phenomena giving rise to a refractive index gradient in a solution. The method utilizes birefringence interferences and is found to possess a high degree of precision which probably cannot be attained by methods where the optical power of resolution sets a serious limit to the amount of accuracy attainable. In addition the method is particularly valuable in the study of cases where the refractive index gradient has a low value. By virtue of this fact, measurements can be extended to very low concentration differences. The possibility of arranging differential diffusion experiments with very low concentration gradients also provides a convenient means of studying the concentration dependance of the diffusion coefficient. The new method should further offer a possibility of verifying the Fuoss and Onsager theory for the diffusion coefficients of very dilute electrolytic solutions.

The observation of diffusion processes includes delicate and troublesome measuring problems because of the difficulty in arranging the experiments and the great demands made upon the optical methods. The methods used most for the determination of diffusion coefficients are: the "scale"- and schlieren methods of Lamm with a series of modifications and the Gouy interference method. To enhance the precision of the diffusion measurements the resolution of the optical method must be increased and the influence of the concentration dependance decreased. In order to diminish the influence of the concentration dependance of the diffusion coefficient, it is necessary to work with a small concentration difference, implying that the relative accuracy of the concentration measurement must be correspondingly increased. Under these conditions all the methods mentioned are subject to the fundamental difficulty of the limitation of the optical resolution. This is primarily based on a wave uncertainty principle, analogous to that of Heisenberg to which Wolter, among others, has called attention.[1] A method using birefringence interferences, which contains no resolution-limiting stops, has been introduced in this field by Ingelstam [2a,2b]. As will be described below, there were indi-

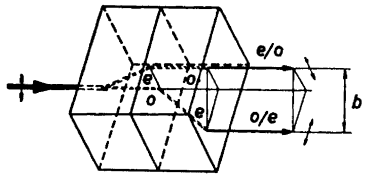

Fig. 1. The Savart plate. The splitting up of an entering ray into an extraordinary-ordinary and an ordinary-extraordinary ray is shown. The arrows at the rays indicate polarization directions.

cations *a priori* that this method would be capable of giving a greater accuracy than earlier ones, and would be especially convenient for very low concentrations. The experiments described in the following sections seem to confirm these expectations.

I. THE OPTICAL METHOD

A plane wave front is distorted in passing through a diffusion cell (of rectangular cross section with plane parallel glass windows) in accordance with the variation of the concentration within the solution. A wave front, defined as the locus of the same optical paths traversed by an originally plane wave front, gives a representation of the optical paths Z. In the diffusion process examined here, Z varies with one space coordinate x (the diffusion direction), and with time t. The relation between Z and the refractive index n and the cell thickness a is as follows:

$$Z(x,t) = n(x,t)a = [k_0 + k_1c(x,t) + k_2c^2(x,t) + \ldots]a \approx [k_0 + k_1c(x,t)]\ a, \quad (1)$$

the last form presupposing that the linear relation between the concentration and the refractive index holds (with is a good approximation in most cases).

By means of a shearing interferometer [3] the derivative of such a concentration curve can be conveniently measured. The wave front is to be split up, in the x-direction, into two parts separated from each other a small distance Δx. This shearing is easily realizable using a birefringent double crystal plate in parallel light. The Savart plate, (Fig. 1), with the incident light plane polarized in such a direction that the oscillation plane bisects the two principle planes of the crystal plate, divides the wave front into two equally strong, perpendicularly polarized, and coherent wave fronts which are at the same time sheared. In Fig. 1 it is also seen how the shear, $\Delta x = b$, results from the fact that the extraordinary rays are oblique in both parts of the Savart plate. The double plate makes the oscillations of the two wave fronts perpendicular, and by means of an analyzer introduced at 45° in relation to the principal planes of the crystal plates, the two wave fronts are enabled to interfere. As will be described below, the interference pattern consists of a set of horizontal fringe pairs. The number of fringe pairs corresponds to the total Z-increment Z_0, in the notation of eqn. (1) $Z_0 = Z(+\infty, t) - Z(-\infty, t)$, *i.e.*, the cell thickness times the total refractive increment of the solution. There is a difference of the optical thickness Z of one wave length between two fringes.

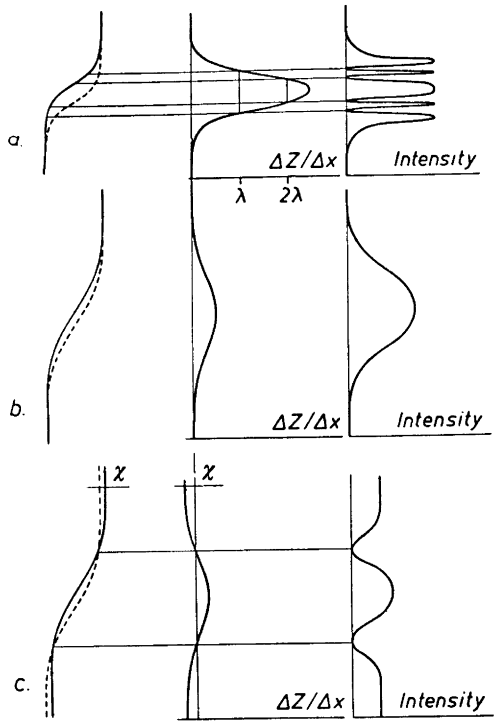

Fig. 2. The optical path as a function of x governed by the concentration gradient is shown (left). The optical path difference between the two separated wave fronts is seen in the middle and the light intensity of the interference pattern at the right. *a* represents an earlier time than *b* when the derivative curve has diminished so that no fringe pair remains. By tilting the Savart plate a constant path difference, χ, between the two wave fronts is introduced and a fringe pair has arisen as shown in *c*.

To the left in Fig. 2, the two laterally displaced wave fronts are shown. The path difference, ΔZ, between two rays emerging from the double crystal plate at the same spot, but originating from different parts, at the distance b, of the entering wave front (Fig. 2) is measured interferometrically. The resulting wave fronts interfere destructively or constructively when the path difference $\Delta Z = m\,\lambda/2$ (m = whole number). If the axes of the two polarizers, P_1 and P_2 in Fig. 3, are perpendicular to each other, the light is extinguished when $m = 0, 2, 4$, etc., and dark fringes are obtained at the corresponding x-coordinates. Similarly for polarizers whose axes are parallel dark fringes arise when $m = 1, 3, 5$, etc. The situation with crossed polarizers is represented in Fig. 2. As shown in Fig. 2a, the fringe pairs correspond to path differences of 0, λ, 2λ, etc., and the possibility of constructing $\Delta Z/\Delta X$ as function of x from the positions of the fringe pairs is clear. When the derivative curve is so low that $\Delta Z < \lambda/2$, which means that no fringes are obtained (Fig. 2b), the Savart plate can be tilted a slight amount and, on account of this, the wave fronts

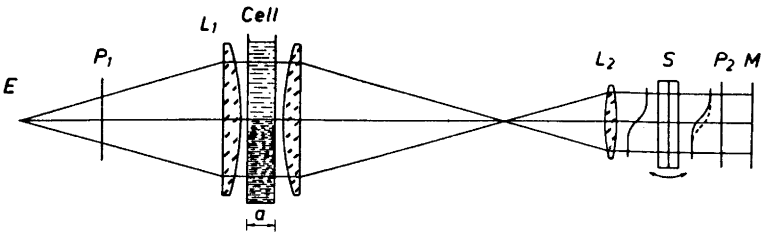

Fig. 3. Optical arrangement. For notation see text.

are displaced a desired path difference χ and a fringe pair has arisen according to Fig. 2c. Thus this method makes it possible to work with concentration differences corresponding to an optical path difference as small as about one wave length.

The interference pattern produced is related to the Gaussian curve, which represents the ideal concentration gradient. An evaluation method used by Lamm in the schlieren method is modified here and the diffusion coefficient is deduced from the rate at which the fringe pattern changes.

II. APPARATUS

1. *The lens system.* The lens system is shown schematically in Fig. 3. E is a horizontal slit illuminated by monochromatic light. It is located in the focal plane of the first lens in the system L_1. The system L_1 is composed of two equal lenses, each having a focal length of 1 m, and corrected for both chromatic and spherical aberrations. By means of the lens L_2, $f = 12$ cm, an image of the cell plane is obtained in the object plane M. The strict collimation necessary in the wavefronts traversing the crystal plate is accomplished by the displacement of L_2. During the experiments the cell is placed between the lenses L_1 where the light is parallel. The numerical value of the optical magnification, G, is 0.120.

2. *The Savart plate.* The crystal plate, which is traversed by strictly parallel light, introduces a displacement between of the wavefronts in the x-direction equal to b. If the Savart plate is adjusted so as to be perpendicular to the optical axis, so that no phase shift is introduced between the two wavefronts, b is determined by the equation,

$$b = e\sqrt{2}\ \frac{n_e^2 - n_0^2}{n_e^2 + n_0^2} \tag{2}$$

where e is the thickness of each part of the double plate and n_e and n_o are the principal refractive indices. The quartz plate, which is used in the experiments with very dilute solutions, has $e = 10$ mm and $b = 84.2\ \mu$. If the magnification is G, the real distance at the object is not b but b_1 which is equal to b/G.

3. *The cell.* The diffusion cell used was a flowing-junction cell, having a stainless steel body, kindly lent to us by Dr. H. Svensson, who designed and

used it in his earlier developmental work.[4] In this type of cell the initially sharp boundary is formed by allowing solution and solvent to flow together into a narrow horizontal exit slit in the side wall of the diffusion channel, the horizontal cross section of which is 3×50 mm^2 and the height of which is 70 mm. The cell windows are 10 mm thick and the flatness before clamping is about one wave length.

4. *The monochromator.* The horizontal entrance slit is illuminated by a 100 W mercury lamp with a filter that transmits only the green Hg-line (5 461 Å).

5. *The camera.* In the experiments with liquid gradients, where a quick registration of the beginning of the run is desired (an exposure every tenth second), a Robot camera which automatically feeds the film is used. Together with this a Leitz bellow adjustment apparatus and an Elmar objective ($f = 5$ cm) is used.

6. *Photography.* For all photographic recordings Ilford HPS film is used with Ilford Microphen fine grain developer. HPS film is used to attain a minimum time of exposure (about 2 sec).

7. *Control of temperature.* Unfortunately, no thermostat is available during the experiments, but they are carried out in a room with a remarkably constant temperature, held within $\pm$ 1 degree with an electric radiator for 10 h before the experiment. The cell part of the arrangement is shielded with an aluminium box to give radiation equilibrium. A thermometer placed close to the cell shows, in general, a variation in temperature of less than $\pm$ 0.05° during an experiment. Care was taken not to warm up the thermostat by touching or by radiation from the body.

8. *Support.* All the optical components are mounted on a 3 m steel beam resting on sheets of sponge rubber on concrete tubes which stand on the floor. In this way vibrations communicated to the optical system through the floor are effectively damped out.

III. CALCULATION

At small concentration differences, the skewness of the gradient arising from the concentration dependance of the coefficient disappears and Fick's second law is presumed to be valid. The derivative of the optical path gradient can be written

$$\frac{\partial Z(x,t)}{\partial x} = \frac{Z_0}{2} \cdot \frac{1}{\sqrt{\pi Dt}} \cdot e^{-(x/\sqrt{4Dt})^2} \qquad (3)$$

The correction between the path difference $\Delta Z/b_1 = \Delta Z/\Delta x$ that is measured, and the path derivative desired, eqn. (3), can easily be calculated [2a, 2b]. In the neighbourhood of the inflexion points the magnitude of the corrections is extremely small, and for a birefringence displacement, b_1, less than 3 σ, where $\sigma = \sqrt{2Dt}$ is half the distance between the inflexion points of the Gaussian curve, the correction is practically negligible over the whole curve.

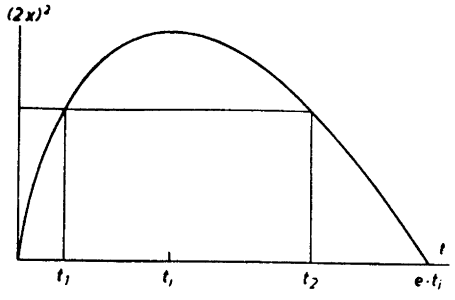

Fig. 4. The square of the distance between the fringes as function of time. The diffusion coefficient is obtained from pairs at certain distances and their corresponding times, as

$$D = \frac{(2x)^2(1/t_1 - 1/t_2)}{8 \ln t_2/t_1}$$

The difference ratio measured can be expanded in a series and the derivatives substituted by polynomists in x/σ as follows:

$$\frac{\Delta Z(x)}{b_1} = \frac{Z(x + \frac{1}{2}b_1) - Z(x - \frac{1}{2}b_1)}{b_1}$$

$$= Z'(x)\left\{1 + \frac{1}{3!}\left(\frac{b_1}{2}\right)^2 \frac{Z^{III}(x)}{Z'(x)} + \frac{1}{5!}\left(\frac{b_1}{2}\right)^4 \frac{Z^{V}(x)}{Z'(x)} + \cdots\right\} \quad (4)$$

$$= Z'(x)\left\{1 + \frac{1}{2^2 \cdot 3!}\left(\frac{b_1}{\sigma}\right)^2 (x^2 - \sigma^2) + \frac{1}{2^4 \cdot 5!}\left(\frac{b_1}{\sigma}\right)^4 (x^4 - 6x^2\sigma^2 + 3\sigma^4) + \cdots\right\}$$

From this it appears that when b_1/σ is small the corrections for obtaining the gradient are conveniently small.

The curve constructed from the interference pattern (the fringe pairs represent symmetrical points with a fixed value of $\Delta Z/\Delta x$) can easily be corrected and the derivative determined.

An accurate evaluation method, due to Lamm [5], having the advantages of using only the region not far from the inflexion points of the Gaussian curve, is modified for this method. From the set of fringes, a distance $2x$ between corresponding fringes in the interference pattern is measured. Following a definite fringe pair with time, we may plot $(2x)^2$ *vs.* t (Fig. 4). The diffusion coefficient is then obtained from a value of $(2x)^2$ and its co-ordinate times t_1 and t_2 by the equation

$$D = \frac{(2x)^2 (1/t_1 - 1/t_2)}{8 \ln t_2/t_1} \quad (5)$$

The equation of the curve in Fig. 4 is

$$(2x)^2 = 8Dt \left(1 + \ln \frac{t_i}{t}\right) \quad (6)$$

where t_i represents the time corresponding to maximum distance between the fringes. When $t = t_i$

$$(2x_i)^2 = 8Dt_i \quad (7)$$

and $2x_i = 2\sigma$, which is the distance between the inflexion points of the Gaussian curve.

At higher concentration differences a group of such curves is obtained and the information about the diffusion process is very copious.

IV. ZERO-TIME CORRECTION

Since the infinitely sharp initial boundary, required for rigorous application of the equations, cannot be obtained experimentally, the observed time, t, after a certain time zero point in the formation of a boundary must be corrected by a small constant increment Δt, in order to arrive at the zero point where the boundary would have been infinitely sharp.

Method 1. In experiments with concentration differences giving many fringes, a *rough* estimate of the diffusion coefficient and the zero-time correction can be made. By combining the maximum points in Fig. 9 a straight line, $(2x)^2 = 8Dt$, is obtained. The slope of the line is $8D$ and from the intersection with the abscissa axis the zero-time correction is determined.

Method 2. A more accurate method exploiting only the variation of one fringe pair is obtained by the following.

A diffusion coefficient D' is computed by using the measured time in eqn. (5). The true diffusion coefficient D is related to D' by the expression

$$D = \frac{(2x)^2 \left(\frac{1}{t_1 + \Delta t} - \frac{1}{t_2 + \Delta t}\right)}{8 \ln \frac{t_2 + \Delta t}{t_1 + \Delta t}}$$

$$\approx \frac{(2x)^2 \left(\frac{1}{t_1} - \frac{1}{t_2}\right)}{8 \ln \frac{t_2}{t_1}} \cdot \frac{1}{\left(1 + \Delta t \frac{t_1 + t_2}{t_1 t_2}\right)\left(1 - \Delta t \frac{\frac{1}{t_1} - \frac{1}{t_2}}{\ln \frac{t_2}{t_1}}\right)}$$

$$\approx \frac{D'}{1 + \Delta t \cdot \vartheta} \qquad (8)$$

$$\text{where} \quad \vartheta = \frac{t_1 + t_2}{t_1 t_2} - \frac{\frac{1}{t_1} - \frac{1}{t_2}}{\ln \frac{t_2}{t_1}}$$

and D and Δt are readily obtained from a plot of D' *vs.* ϑ (Fig 10). This method is not applicable at very short experimental times, *i.e.*, when $(\Delta t)^2$ no longer can be neglected in comparison with $t_1 \cdot \Delta t$.

Method 3. An iteration method has been adopted for obtaining higher accuracy and an estimation of the precision of the calculation. Fig. 11 shows how D varies with $(2x)^2$ for different values of the parameter Δt. In this way a Δt giving the most constant D can be determined.

V. EXPERIMENTAL TEST

Work with the present apparatus has been confined to solutions of glycine and sucrose. In the experiments with glycine a small downward drift of the diffusion coefficients was observed. Reaction products between glycine and iron were found which is equivalent to an absorption process. In the experiments, discussed here, sucrose of analytical purity has been used. Accurate measurements of the diffusion of this material have recently been performed elsewhere [6-8].

The solvent and solution are put in the thermostat, and after about 10 h when thermal equilibrium is obtained, the stopcocks of the reservoirs, which are provided with handles for operation from outside the aluminium box, are opened. After another half an hour, when the gradient is very sharp and temperature equilibrium is obtained, the stopcocks are closed and the outflow stopped so that diffusion may take place. About 50 exposures are taken during the diffusion process, more frequently at the beginning.

For obtaining the highest precision measurement of the films, a photometer is used. The distance, $2x$, between corresponding centres of the density minima are measured with an accuracy of 1 μ. In one of the experiments, (II), a comparator reading to 1 μ has been used.

From the data taken in these experiments it is evident that, in general, no advantage is gained from photometric measurements. Photometry is advisable in working with concentration differences corresponding to an optical path difference of about one wave length. At the very end of the diffusion process, when the derivative curve is low (Fig. 2 b and c), the asymmetry and blurring of the fringes are troublesome when the distance between coordinate fringes is small (representing points at the very top of the derivative curve). As a rule, in these cases, one has no interest in following the fringes so long that the asymmetry and broadness of the fringes will be troublesome. The higher the concentration difference, the sharper the fringes, since this depends on the slope of the gradient curve (*cf.* Fig. 2). For determination of the fringe pair positions at smaller concentration differences (with a small broadening of the density minima in the film) an increase of the exposure time will give sharper fringes ("Minimumstrahlkennzeichnung", Wolter [1]).

A procedure, "Äquidensitenverfahren", designed by Krug and Lau [9] has been tried for obtaining greater measuring accuracy at wide interference strips. It must be stressed that this procedure has only an advantage for wide fringes, which appear here when working with concentration differences corresponding to an optical thickness of about one wave length.

For density curves, running more or less steep, points with the same density (these curves are called Äquidensiten) can be connected by a photographic procedure [9]. Practically this can be done by making a positive on hard film from the original negative. When it is nearly developed, the film is illuminated by uniform light, which has most influence on the positions not illuminated before. So by the Sabattiereffect a plate is obtained in which a positive and a negative are in precise covering and the Äquidensiten arise where the negative and positive have about the same density.

Here, however, one is looking for the minima in the negatives, but then the method fails because of the impossibility of computing the density values corresponding to the Äquidensiten, neither does it give a comprehension of the amount of asymmetry. Thus it is impossible to find the minimum point by producing Äquidensiten at different density values and extrapolating to the minimum.

The difference between the refractive index of water and a solution of 1 g sucrose in 100 cm^3 water gives a retardation of 132 (air) wave lengths for the cell used (around 50 mm thick). From this it is evident, that as low a concentration as about 0.01 %, corresponding to an optical path difference of 1.32 wave lengths, can be used.

A series of exposures taken during a diffusion run is shown in Fig. 5. The position of the fringes is very accurately determined by constructing the medians in the photograms (Fig. 6).

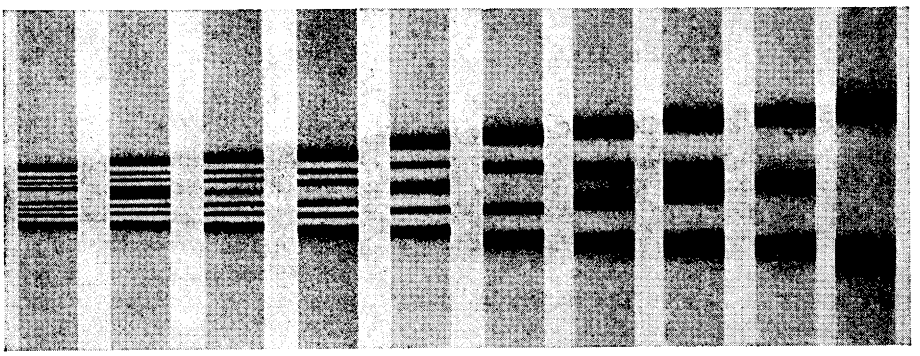

Fig. 5. Exposures taken during a diffusion experiment (Expt. IV).

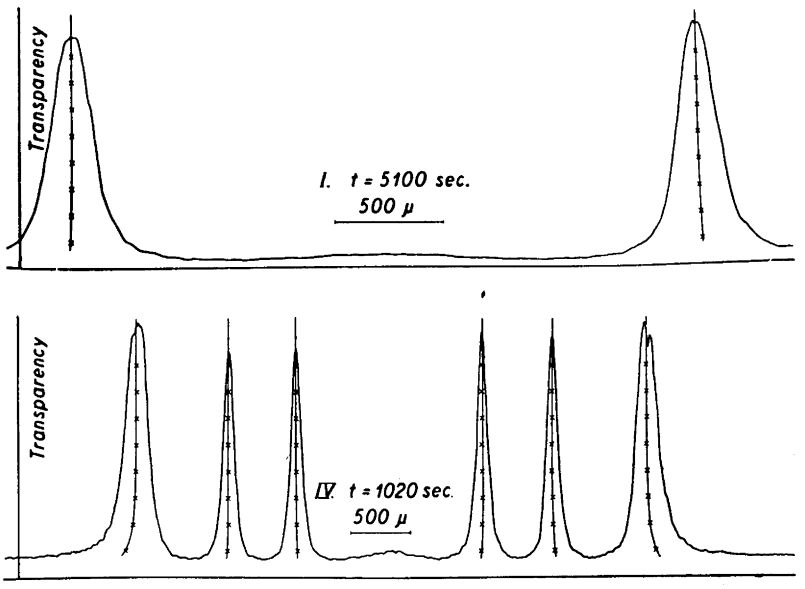

Fig. 6. Photograms showing how the exact positions of the fringes are found by constructing the medians of the curves. Observe how precisely the position can be measured with such low a concentration difference as in expt. I.

Four experiments with different concentrations were performed (Table 1). Every run has been calculated in detail.

Table 1.

Run	Sucrose conc. above/under the boundary %	Thermostat temp. °C	Fringe pairs at the beginning (in air wavelengths)	χ Å
I 31.1.57	0/0.0112	21.33±0.07	1.48	470
II 30.1.57	0/0.0500	20.76±0.20	6.60	1 890
III 4.2.57	0/0.1018	23.62±0.05	13.48	3 680
IV 5.2.57	0.7249/0.8253	23.84±0.06	13.25	2 430

Eqn. (6) has been adapted to the experimental points of run I in Fig. 7. Good agreement over the whole curve, except for very low time values, is clear from the diagram. Despite the fact that the method gives high values at the very beginning of the process, all distances were found to be smaller than the theoretical ones. This indicates that a high zero-time correction is obtained, owing to the difficulties of producing sharp boundaries at such a low concentration. The results obtained using the iteration method on run I (concentration corresponding to an optical path difference of 1.48 wave lengths) are shown in Fig. 8. The dotted part of the curves, represents disturbances at the beginning, which are found to die out very quickly. With the parameter $\Delta t = 205$ sec, the curve runs well horizontally and the corresponding value of the diffusion coefficient is determined very accurately.

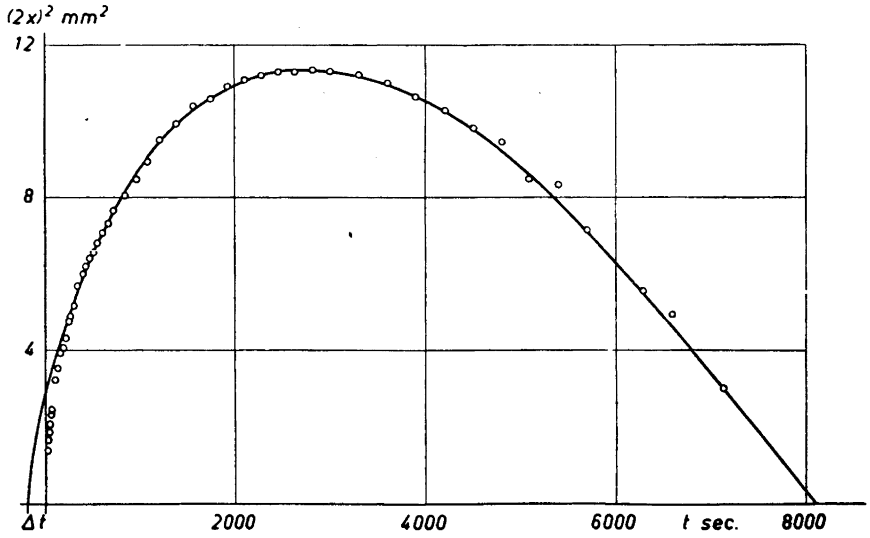

Fig. 7. $(2x)^2$ as function of time for expt. I. Eqn. (6) has been adapted to the experimental points.

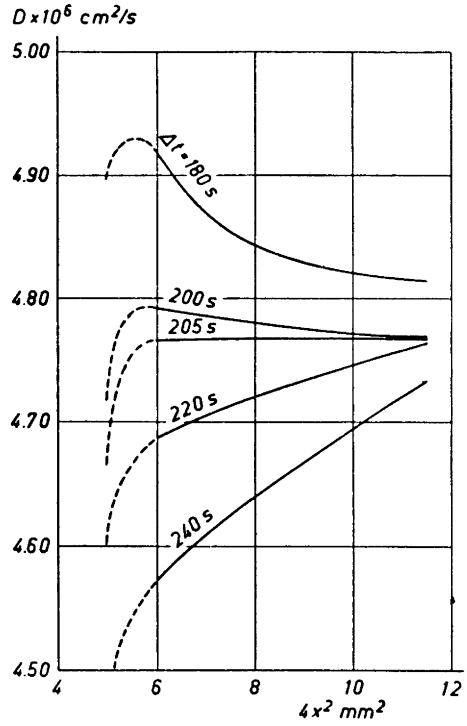

Fig. 8. D as a function of $(2x)^2$. The dotted part represents disturbances. *Cf.* Fig. 7.

In order to illustrate the simplicity, rapidity, accuracy and amount of information given by this method, the above mentioned ways of finding the zero-time correction are applied to run III (Figs. 9, 10 and 11). In Figs. 10 and 11 the curves refer to the next outermost fringe pair. From a comparison with the values calculated from the curves corresponding to the other fringe pairs a good agreement, within 0.02 %, is obtained. In Fig. 11 the influence of the correction between the difference and the derivative appears. The dotted parts represent the uncorrected values. It must be observed that this curve at the beginning corresponds to points far from the inflexion points of the Gaussian curve. Nevertheless, the influence of the correction is dying out very fast and can be ignored in all practical measurements. In order to compare the diffusion coefficients obtained with the values given in Refs.[6–8], corrections were applied to 25.0 °C using Stoke-Einstein's relation. These data are given in Table 2, where values extrapolated from the measurements in Ref.[7] are also found.

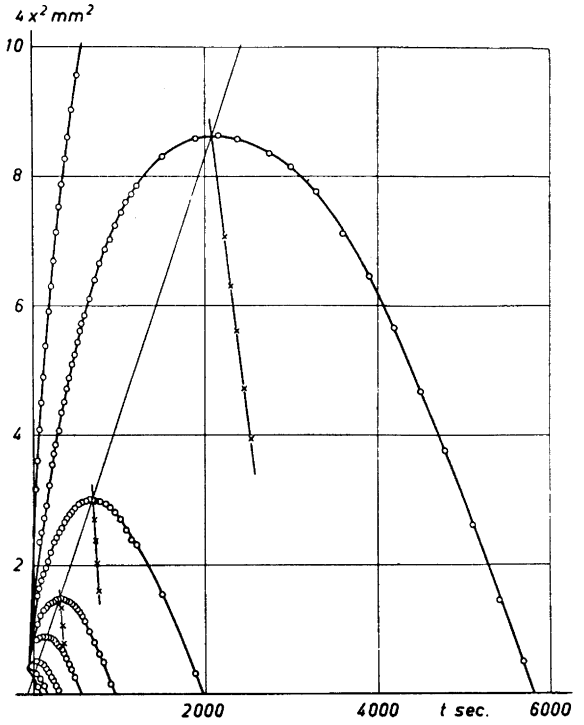

Fig. 9. $(2x)^2$ as a function of time for expt. III. The maximum points of the curves are easily found by constructing the medians, and the line combining the maximum points gives a rough estimate of the diffusion coefficient and the zero-time correction.

Table 2.

Run	c %	Δc %	Δt sec.	$D_{25} \times 10^6$ cm²/s	$D_{25} \times 10^6$ cm²/s extracted from Ref.[7]
I	0.0056	0.0112	205	5.229±0.011	5.228
II	0.0250	0.0500	54	5.193±0.042	5.224
III	0.0509	0.1018	47	5.235±0.008	5.222
IV	0.7751	0.1004	55	5.193±0.011	5.170

In Fig. 12 it is clearly seen how the results obtained by this method agree with the values extracted from the equation of the concentration dependance of the diffusion coefficient stated in Ref.[7]. From this diagram it is evident that a *very* small concentration difference can be used. The exactness of the measurements is also indicated. Experiment II with poor temperature control has given too low a value.

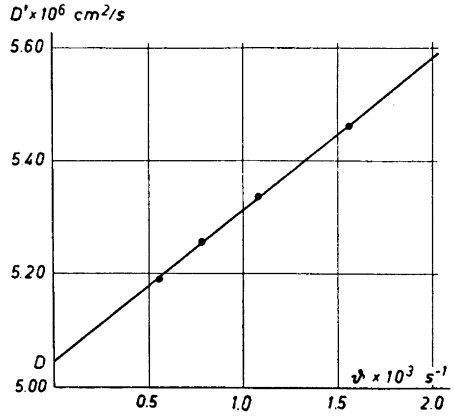

Fig. 10. The calculated diffusion coefficient D' as a function of the factor ϑ (see IV, 2). D is obtained from the intersection with the ordinate axis. The slope of the line is $\Delta t D$.

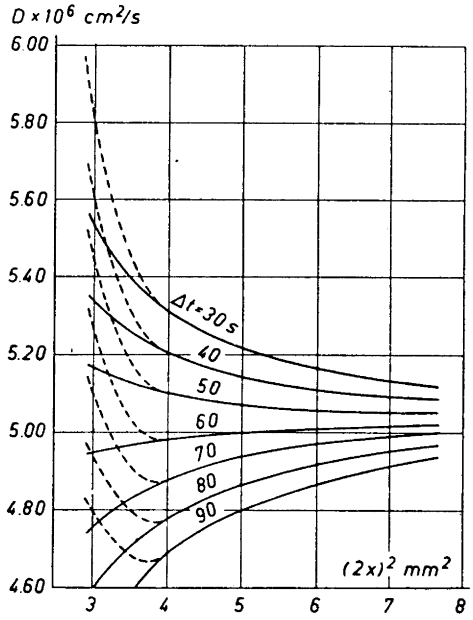

Fig. 11. D as a function of $(2x)^2$ obtained from the next outermost fringe pair. The dotted parts represent values obtained without regard to the correction between difference and derivative. Observe in this curve, that in the part representing points far from the inflexion points (for $(2x)^2 < 5$ mm^2), the corrections are obtainable and die out fast.

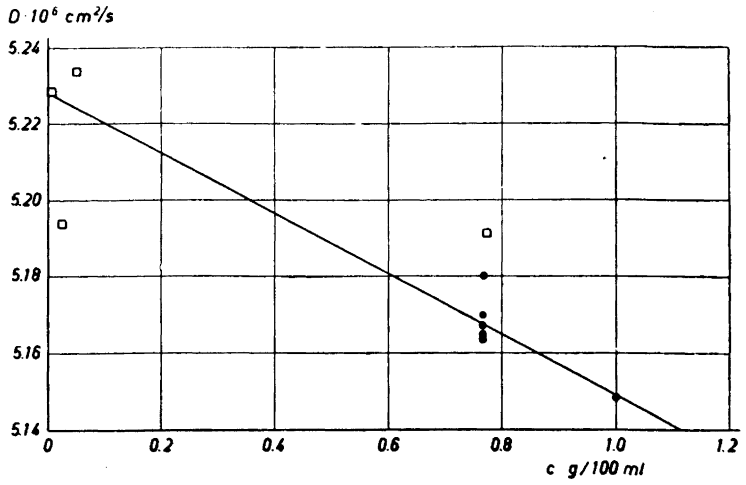

Fig. 12. Determination of diffusion coefficients for sucrose. Filled circles, Refs. [6-8], having been determined with the Gouy interference method. The line drawn is obtained from Akeley and Gosting [7]. Empty squares, results from the investigations presented in this paper.

VI. DISCUSSION

The determined diffusion coefficients deviate from the values in Refs.[6-8] by less than 0.5 %, which is very small compared with the accuracy in the referenced values quoted above. It should be stressed that the results do not really give the method full justice, since these experiments were carried out without careful thermostating and that large temperature corrections (the uncertainty in the absolute value of temperature is about 0.1 °) have been applied.

It is difficult to give a quantitative estimate of the effect of the sources of error on the accuracy and precision of the measurements. In the method described the following factors have an influence on the calculated diffusion coefficient:

a. insufficient control of temperature (about 0.2 %),

b. overlapped thermal gradient (a temp. gradient of 0.1 ° corresponds to an optical path difference of about 5 000 Å, this effect dies out in a few minutes),

c. the concentration dependance of the diffusion coefficient (about 0.05 % in these experiments),

d. correction between difference and derivative (has an exceedingly small influence in these calculations, where only points not far from the inflexion points of the Gaussian curve have been used),

e. determination of the distance between the fringes; the measurements are performed with an accuracy of 1 μ at the beginning and about 3 μ

at the end (consistent with the sharpness of the fringes), see Fig. 4. Here also a possible error in the magnification factor has an influence,

f. calculation (the last two sources introduce an error of about 0.05 %),
g. error of focusing,
h. non-parallel light through the cell,
i. lens effect of the cell (can be compensated by displacement of L_2),
j. a wedge shaped diffusion column (has an extremely small influence in this method).

The maximum error in the estimates (except II with bad temperature constancy) is about 0.2 % (with regard to the uncertainty in the absolute temperature about 0.5 %) which in its greater part arises from the variation of temperature. With accurate temperature control, it would easily be possible with the present method to determine the diffusion coefficient within 0.1 %.

The cell used gives an extremely great zero-time correction compared with other measurements with flowing-juction diffusion cells. Longsworth [10], for example, stated 4—6 sec. Thus, in general, the determination of the zero-time correction will not give rise to such a marked problem. It should be emphasized that the zero-time correction does not appreciably increase with the dilution and so the values found here show good agreement with those obtained by Svensson [11] with the same cell at higher concentration difference.

Contrary to expectation the method is not extremely sensitive to minor imperfections in the optical system, nor to contaminations in the cell. However, good quality optical equipment is essential in order that the advantages of the method be fully utilized. The importance of proper focusing is naturally also more prominent in working with a method giving such a precision in the measurements as the above mentioned, than in less sensitive methods. We owe a good deal to Svensson for his prethought of developing the theory of second and third order aberrations in the interferometric measurement of concentration gradients. The adjustment of our optical system was carried out in conformity with his prescriptions.

Svensson has shown [12, 13] that the aberration corresponding to the Wiener skewness of the gradient curve disappears if the camera is focused on a plane 1/3 of the cell thickness from the front wall. The photographic enlargement factor is determined experimentally by placing an object in the plane of the middle of the cell, although this is not optically conjugate to the plate. If the light through the cell is converging, it gives rise to an aberration, which may be corrected for by determining the optical magnification factor of the cell from the slightly defocused plane through the middle of the cell [12].

A result of Svensson's calculations [14] is that the third order aberrations depend on the entrance angle, and that there is a certain entrance angle (the light source should be situated below the optical axis) that is more favourable than any other angle. The third order aberrations are found to decrease very rapidly with time. The critical time of diffusion (when all aberrations have decreased to 1/50 of a light wave) in these measurements with low concentration differences is surprisingly small, about a few seconds.

There seems to be little justification in stating a diffusion coefficient within a few tenths of a per cent, using a total concentration difference corresponding to an optical path difference of about 100 wave-lengths, bearing in mind that the coefficient varies to the extent of several per cent in the concentration region examined. The present method on the contrary works with very low concentration differences and thus the concentration dependance of the diffusion coefficient is correspondingly smaller. This is one of the great advantages of this method. Other advantages are that only part of the Gaussian curve near the inflexion points is used and that an image of the whole diffusion column is obtained.

Another striking feature of the new method is that it enables diffusion experiments to be carried out in a very short time — 20 min or even less (observing inner fringe pairs or very dilute solutions). No doubt, this is to be ascribed to the greatly enhanced power of resolution, which makes the method equally well suited to measurements on medium and very low refractive index gradients.

The present method has by no means an unlimited power of resolution — this would rule out the wave uncertainty relation completely. But a great enhancement results from choosing the conditions of the experiment and the method of registration in a suitable way. The described method possesses the same degree of high precision which is achieved by Wolter [1] who modified the schlieren method by changing the slit to a 180° phase plate. "Minimumstrahlkennzeichnung" and all advantages attaching thereto (as *e.g.*, unlimited high beam sharpness and enhancement of the measuring precision making photometry superfluous) are exploited by birefringence interferometry in polarized light. *The Savart plate has some advantages compared to the phase plate:* it is simpler to realize in practical measurements and gives more information (many fringe pairs) about the process.

The fact that the extrapolated values obtained by Akeley and Gosting [7] show a fair agreement with the results of the exceedingly accurate experiments reported in this paper is probably a mere coincidence.

The conductance method of Harned and French [15], which implied a considerable improvement in accuracy at concentrations ten times lower than optical methods existing at that time, was applicable to cases where the original concentration differences was of an order of magnitude not less than 0.0025 molal in KCl. Our method enables measurements to be carried out with a concentration difference of 0.0015 molal in KCl. The precision of our measurements would be of the order of $\pm$ 0.1 % while the accuracy reported by Harned and French is approximately $\pm$ 0.9 % which was later reduced to about $\pm$ 0.1 % with concentrations down to 0.00125 molal [16].

As pointed out by Svensson [12], it is desirable to carry out experiments with very low concentration gradient when studying polydisperisity, in order that the influence of the concentration dependance of the diffusion coefficient can be disregarded and the effect of polydispersity studied separately.

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