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Fast and Convenient Implementation of the Taylor Dispersion Method

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A highly labor-efficient implementation of the Taylor dispersion method for measuring mutual diffusion coefficients in binary liquid systems is described. The experimental setup has been fully automated; it is possible to measure the diffusion coefficients over the whole concentration range in a single experiment using standard HPLC equipment. Software has been developed for processing the data; diffusion coefficients can be calculated from the measured concentration against time curve in various ways (e.g. from the first and second moments and by fitting procedures) within a few seconds. Experiments on the methanol + water system (25 and 35 °C) and the ethanol + water system (25 and 40 °C) have an accuracy of 0.5−1.5%.

1. Introduction

Liquid diffusion plays an important role in chemical engineering, and the design of process equipment requires a knowledge of mutual diffusion coefficients. The purpose of this work is to develop an apparatus for measuring diffusion coefficients in liquid systems over a wide range of temperature and pressure in a fast, accurate, and labor-efficient way. The instrument developed here should not need any repeated calibration, and the calculation of the diffusion coefficient from the measured variables is simple and easy to computerize.

Experimental techniques used widely for measuring diffusion coefficients are the diaphragm cell technique, interferometric methods, and the Taylor dispersion method (*1−5*). Interferometric methods permit the most accurate measurements near room temperature, but it is not (yet) possible to employ these instruments over a wide range of temperature and pressure. The disadvantages of the diaphragm cell are the necessity for calibration of the cell with a system of known diffusivity. Another disadvantage is the long measuring time. The Taylor dispersion technique provides a good alternative. The method is fast, the setup consists of standard HPLC components, and the measurements can be readily automated (*6*). Therefore, we have chosen the Taylor dispersion method.

The Taylor dispersion method is based on the following principle (*7, 8*): a slow, laminar flow of a liquid mixture is pumped through a long capillary and a narrow pulse of a mixture of a slightly different composition is injected into this capillary. Due to the combined effects of convective flow and molecular diffusion, the pulse ultimately assumes a Gaussian distribution, whose temporal variance is dependent on both the average flow velocity and the molecular diffusivity.

At the end of the diffusion capillary the concentration is measured as a function of time; the diffusion coefficient is calculated from the first and second temporal moments or by fitting the dispersion equation to the experimental curve.

2. Theory

When a pulse of a different concentration is injected into a fluid flowing slowly through a long capillary, it spreads out due to the laminar velocity profile in the tube and the molecular diffusion. The concentration at the end of the diffusion tube is given by

$$\bar{c}(t) = \frac{V_i c_i}{2\pi R^2} \frac{1}{\sqrt{(\pi k t)}} \exp\left(\frac{-L^2\left(1 - \frac{t}{\tau}\right)^2}{4kt}\right) \tag{1}$$

In this expression $V_i c_i$ is the number of moles of component i in the injected pulse in excess of those present in the same volume of the carrier stream (solvent), $\bar{c}(t)$ is the radially-averaged concentration of component i at time t relative to the background concentration, R is the internal radius of the diffusion tube, L is the diffusion tube length, and $\tau = L/\bar{u}$ is the mean residence time with $\bar{u}$ the linear velocity averaged over the cross section. The dispersion coefficient k is found to be (*9*)

$$k = \frac{R^2 L^2}{48\tau^2 D_{12}} + D_{12} \tag{2}$$

where D_{12} is the binary molecular diffusion coefficient. Equation 2 simplifies to (*7, 8*)

$$k = R^2 L^2 / 48\tau^2 D_{12} \tag{3}$$

for liquid-phase diffusion.

The assumptions made in the derivation of eq 1 impose some constraints on the experimental conditions:

Axial (molecular) diffusion can be neglected when $\bar{u} > \alpha_1(D_{12}/R)$. α_1 is a constant: its value ranges from 6.9 (*7, 8*) to 700 (*14*) (*7, 8, 10−17*).

Radial concentration differences are assumed to be small when $\bar{u} < \alpha_2(LD_{12}/R^2)$. α_2 ranges from 4 to 0.1 (*6, 7, 10−15, 18−24*).

If $\alpha_2 = 0.048$ (*25*), the perturbations due to temperature/pressure reduction occurring in a short length between the capillary and the detector are negligible.

The development of secondary flow due to the coiling of the capillary can be neglected when $\mathrm{De}_2\mathrm{Sc} \leq 20$ and $R_c/R \geq 100$, in which the Dean number is $\mathrm{De} = (2R\varrho\bar{u}/\eta)(R/R_c)^{1/2}$, the Schmidt number $\mathrm{Sc} = \eta/\varrho D_{12}$, η the solvent viscosity, ϱ the solvent density, and R_c the radius of the tubing coil (*14−15, 20−21, 24, 27−33*).

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Other restrictions on the experimental conditions and corrections on the ideal average residence time and variance are well described by Alizadeh (*14*) and Baldauf (*26*).

When the concentration is measured, the relation between the detector signal $s(t)$ and the concentration against time curve (eq 1) is assumed to be

$$s(t) = \alpha\bar{c}(t) + a + bt + \epsilon(t) \qquad (4)$$

in which α is the detector sensitivity, a and b compensate for the detector drift (which is assumed to be linear in time), and $\epsilon(t)$ is noise. The signal is sampled with a sample interval of Δt_i: $y_i = s(t_i)$. The sample interval Δt_i must be chosen such that it provides a minimum of N data points within the solute peak ($N = 200$ (*24*)).

Diffusion coefficients can be calculated from the measured concentration against time curves in two different ways: calculation from the first and second moments; fitting of the theoretical eq 4 to the experimental curve.

Calculation from the First and Second Moments. For the calculation of the first and second moments the discrete signal without the drift is required: $y_i = y_i^* - (a + bt_i)$. For the calculation of a and b, regions of this signal are visually marked in our software as baseline, i.e. the concentration is negligibly small. Through these regions of the signal the drift is fitted and subtracted from the signal.

The first moment $\bar{t}$ and the second moment σ^2 are defined as follows:

$$\bar{t} = \frac{\sum_{i=0}^{N} t_i y_i \Delta t_i}{\sum_{i=0}^{N} y_i \Delta t_i} \qquad \sigma^2 = \frac{\sum_{i=0}^{N} (t_i - \bar{t})^2 y_i \Delta t_i}{\sum_{i=0}^{N} y_i \Delta t_i} \qquad (5)$$

The mean residence time can be calculated for either a closed or an open system: For a closed system (no diffusion through the cross-section at both ends of the tube, finite tube) $\tau \equiv \bar{t}$. For this system Taylor derived the explicit relation (*7, 8*)

$$D_{12} = R^2\bar{t}/24\sigma^2 \qquad (6)$$

For an open system (infinite tube) the expression can be derived

$$\tau = \bar{t} - (R^2/24D_{12}) \qquad (7)$$

which results in an implicit relation for the diffusion coefficient (eq 3 combined with Van der Laan (*25*)):

$$D_{12} = \frac{R^2}{48\sigma^2}\left\{\bar{t} - \frac{R^2}{24D_{12}} + \left[\left(\bar{t} - \frac{R^2}{24D_{12}}\right)^2 + 8\sigma^2\right]^{1/2}\right\} \qquad (8)$$

Other relations are derived by Alizadeh (*14*) and Matthews (*34, 35*).

Fitting of the Theoretical Equation 4 to the Experimental Curve. This can be done in several different ways:

1. The drift parameters a and b are calculated as indicated above. The term $V_i c_i \alpha$ is calculated by integration of the signal. D_{12} is fitted, τ is calculated using eq 7 during the iterative process (one-parameter fit).
2. a, b, and $V_i c_i \alpha$ are calculated as in 1. D_{12} and τ are fitted (two-parameter fit).
3. a, b, and $V_i c_i \alpha$, and D_{12} are fitted; τ is calculated during the fitting process using eq 7 (four-parameter fit).
4. a, b, and $V_i c_i \alpha$, D_{12}, and τ are fitted (*4, 36*) (five-parameter fit).

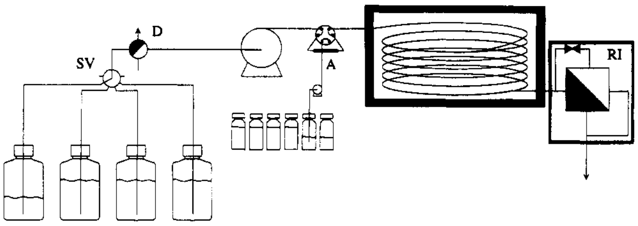

Figure 1. Experimental setup: SV, selection valve; D, degasser; A, autosampler; RI, refractive index detector.

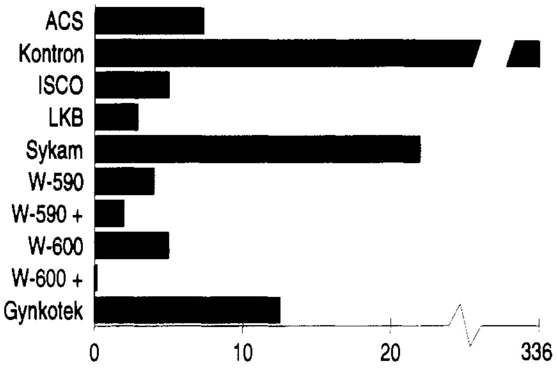

Figure 2. Pulsations of the pump (pulsations in 10^{-5} bar, back pressure 2 bar): ACS, ACS 351 isocratic HPLC pump; ISCO, ISCO LC-5000 syringe pump; Kontron, Kontron HPLC; LKB, LKB 2150 HPLC pump; Sykam, Sykam S-1000 HPLC pump; W-590, Waters 590 programmable solvent delivery module; W-590 +, W-590 + pulsation dampeners; W-600, Waters 600/625 MS PowerLine multisolvent delivery system; W-600 +, W-600 + pulsation dampeners; Gynkotek, Gynkotek HPLC pump Model 300.

Other fitting procedures are possible (e.g. three-parameter fits).

Calculation methods were compared by processing a concentration against time curve calculated by means of eq 1 with a superposition of randomly generated noise or superposition of an experimentally measured baseline.

Calculation of moments is extremely simple and fast. The Van der Laan method (eq 8) yields the best fit to the shape of the experimental curve (vizualization), the lowest sum of squares $\sum_{i=1}^{N}(y_i - \alpha\bar{c}(t_i))^2$, and minimal deviations in D_{12} and τ. Fitting is more accurate though. The one- and two-parameter fits are, of course, faster than the four- and five-parameter fits, and they yield consistent diffusion coefficients and are therefore preferred.

3. Equipment and Experimental Procedure

The apparatus used is shown schematically in Figure 1. The pump must deliver a constant laminar flow. Several pumps of different types were tested. The amplitude and frequency of the fluctuations in the pressure were measured at various back pressures (Figure 2). We selected an HPLC pump (type LKB 2150) combining a low pulsation and constant flow with the capability of continuous operation. Implementation of computer control in our software was relatively easy. The selection valve allows the solvents to be changed during one experiment. To prevent bubbles from disturbing the flow, an in-line degasser (Separations DG1300) was installed. Moreover, the solvent flask was purged once with helium for 10−15 min. The pump was connected to an autosampler (Spark Marathon) with a fixed volume sample loop (20 μL); the sample tray can hold 96 vials. Zero dead volume fittings were used to connect the diffusion tube with the autosampler and the detector. For installation of the capillary tube in a water bath of circular cross section (d = 0.50 m), which could be kept at the desired temperature within ±0.025 °C with a Lauda CSG 2.0 kW thermostat, it was necessary to coil the tube horizontally (d = 0.40 m). To measure the diffusion coefficient in liquid systems with a wide range of viscosities (and diffusion coefficients), stainless steel tubes (i.d. 1.041 mm) of various lengths (10, 15, 25, 50 m) were installed. The differential refractometer (Shodex SE 61) measured the difference in refractive index between the sample stream and the reference liquid (solvent). The analogue output signal of the refractometer was converted by a Multilab system which consists of an A/D–D/A conversion system developed at Eindhoven University of Technology (sample interval 0.98 s yielding 3000–4000 data points per peak). The Multilab was used to interface between detector and PC and between selection valve and PC. The pump and autosampler were controlled directly by a personal computer.

Software has been developed for data acquisition and controlling the equipment (called Linus) which makes it possible to measure diffusion coefficients in 16 different solvents in a single experiment. All aspects of the experiment except the preparation of the solvents and sample solutions have been automated. An optional manual control was included. To process the data, a module was added to an MS Windows signal processing software package that provides extensive visualization and data-manipulating capabilities. This module provides various methods for the calculation of the diffusion coefficient from the first and second moments (eq 5), using the equations of Taylor (eq 6, Van der Laan correction eq 7 optional), Van der Laan (eq 8), Alizadeh (*14*), and Matthews (*34, 35*) and by means of fitting procedures, based on the least-squares approximation between the experimental data points and the points calculated according to eqs 1 and 3. The method of Levenberg and Marquardt (*37*) is used for two-parameter fitting and the Golden section search algorithm (*38*) for the one-parameter fitting. Initial guesses for the diffusion coefficient are obtained by means of the equation of Matthews (*34, 35*). The amount in the injected pulse, $V_i c_i$, is calculated by equalizing the integral of the measured concentration against time curve to the integral of eq 1, assuming the detector response to be linear with the concentration. Visual confirmation of the calculated values of τ and D_{12} is possible by overlaying the experimental peak with the fitted peak.

In a typical diffusion experiment the solutions are prepared by mass and mixing and degassed by sparging with helium. Injection solutions are made by volumetrical mixing of the degassed solvents. The flow velocity is set in accordance with the conditions of section 2. In Linus a new program is created (or an already existing method is edited), and after an emulation, the program is run.

Preparation of the solvents and injection solutions (sufficient for three experiments) takes one day's work, and creating the new program takes a few minutes. The data gathered in a week's run can be processed within a few hours. Calculation of the diffusion coefficient from one concentration against time curve takes only a few seconds.

4. Experimental Results and Discussion

Diffusion coefficients were measured for methanol + water and ethanol + water. Deionized water filtered through a Milli-Q water purification system (Millipore, resistivity 18 MΩ·cm) was used. Analytical grade methanol (purity ≥ 99.8%, water < 0.05%) and ethanol (purity ≥ 99.8%, water < 0.2%) were obtained from Merck and used without further purification.

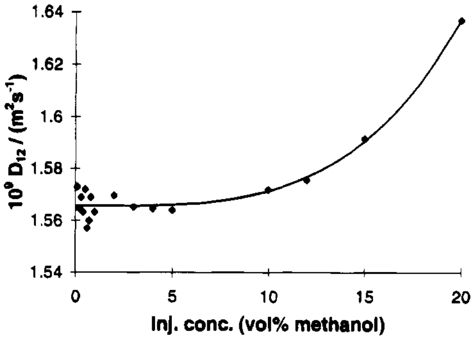

Figure 3. Influence of the concentration of the injected sample (methanol in water, 25 °C): ◆, D_{12}; —, fit (powerlog).

Experiments were performed to show that the detector response was linear with concentration and to test the influence of the concentration of the injected sample on the measurement of the diffusion coefficient. Samples of increasing methanol concentration were injected into pure water, and the peak area and the diffusion coefficient were calculated. Between injection and detection of a sample, subsequent samples were injected for enhanced time efficiency. Simultaneous dispersion of two or more δ-pulses in the tube did not disturb the diffusion process provided the time between two subsequent injections was large enough to prevent overlapping of the solute peaks. Degassing of the injection solutions after preparation appeared to be unnecessary.

The diffusion coefficient as a function of the methanol concentration of the sample injected into pure water is shown in Figure 3. Below a concentration difference of 5 vol % no influence was observed. A minimum difference of 0.5 vol % was necessary to obtain an accurate concentration against time curve (as a result of detector noise). Measurements at other solvent compositions confirmed this result. Experiments for the system ethanol + water also showed a linear detector response and an independence of the concentration difference up to 4 vol %.

To examine whether short time pulsations produced by the pump influence dispersion, experiments were carried out using a "pulsation-free" ISCO syringe pump (500 cm^3) as well as our LKB pump; solvents were pure water and a water + methanol mixture (83 vol % methanol). The noise in the concentration against time curves of the ISCO experiments appeared to decrease a little and was of a slightly different shape. The calculated diffusion coefficient and the inaccuracy in the results were not significantly different. Therefore, we preferred the LKB pump.

To investigate the influence of the mean residence time (and the flow velocity), experiments were carried out at various flow velocities in the 15 m tube as well as in the 25 m tube for both the methanol + water and the ethanol + water system. The results as shown in Figure 4 demonstrate the validity of the conditions of section 2.

Finally, the binary diffusion coefficients of the methanol + water system and the ethanol + water system at various temperatures were measured as a function of composition. After the eluents were switched, the system was flushed for 30 min at a high flow rate (1.5 cm^3·min^{-1}) and for 6 h at the flow rate of the diffusion experiment (e.g. 0.15 cm^3·min^{-1}) to attain a stable, linear baseline.

Results are listed in Tables 1 and 2; each value is the average of the calculated diffusion coefficients of several injections (various sample concentrations in the range 0.5–5 vol %). The values at mole fraction 0 are extrapolated (sample concentration 0%). The confidence limits ("inaccuracy") of the data (calculated according to the

Student's *t* distribution, probability level 95%, two-tail test (*39*)) increase close to the maximum in the refractive index−concentration curve of the system, as expected.

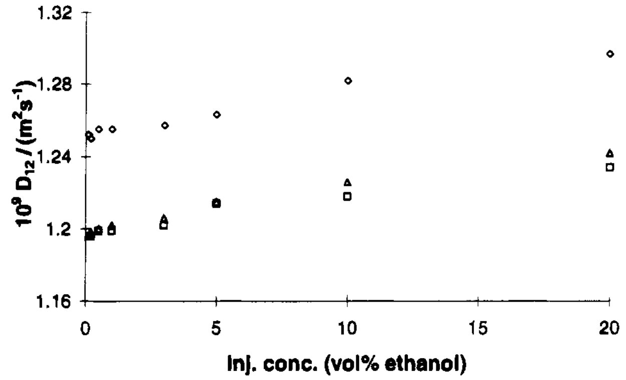

Figure 4. Influence of the flow and the injection concentration (ethanol in water, 25 °C): □, 0.1 cm³·min⁻¹; △, 0.2 cm³·min⁻¹; ◇, 0.4 cm³·min⁻¹.

Table 1. Mutual Diffusion Coefficients for Methanol (1) + Water (2) at 25 and 35 °C

	25 °C				
x_1	$10^9D_{12}/(m^2·s^{-1})$	inacc, %	$10^9D_{12}/(m^2.s^{-1})$	inacc, %	35 °C $10^9D_{12}/(m^2·s^{-1})$
0	1.560	0.49	1.560	0.49	1.94
0.048	1.350	1.88			
0.058			1.330	0.77	1.66
0.100	1.210	0.70			
0.123			1.170	1.67	1.45
0.160	1.070	0.92			
0.194			1.030	1.40	1.29
0.236	0.989	1.35			
0.272			0.956	1.82	1.21
0.307	0.940	3.91			
0.366			0.948	2.85	1.22
0.400	0.957	3.63			
0.458			0.978	2.88	1.25
0.510	1.030	3.88			
0.568			1.119	3.15	1.41
0.640	1.200	1.80			
0.691			1.266	0.30	1.71
0.801	1.630	4.91			
0.835			1.845	7.56	2.12
0.996	2.130	2.34	2.145	4.33	2.61

Table 2. Mutual Diffusion Coefficients for Ethanol (1) + Water (2) at 25 and 40 °C

	25 °C		40 °C	
x_1	$10^9 D_{12}/(m^2·s^{-1})$	inacc, %	$10^9D_{12}/(m^2·s^{-1})$	inacc, %
0	1.200	0.5	1.745	0.3
0.09			1.020	4.7
0.10	0.695	1.1		
0.20	0.393	2.8	0.642	4.7
0.23			0.595	2.9
0.24	0.374	1.6		
0.27			0.573	6.3
0.28	0.367	0.9		
0.36			0.629	4.1
0.37	0.392	2.8		
0.42	0.444	5.9	0.677	7.0
0.48			0.821	2.4
0.49	0.504	5.0		
0.56	0.692	58.4		
0.73			1.318	5.3
0.74	0.834	5.3		
0.94	1.100	3.0		

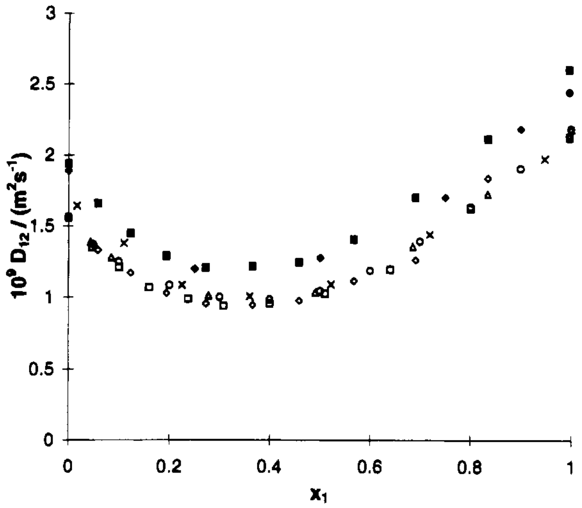

Figure 5. Diffusion coefficient of methanol (1) + water (2). 25 °C: □, expt 1; ◇, expt 2; ×, ref 5 (dual bellows diaphragm cell, 3%); ○, ref 41 (diaphragm cell); △, ref 42 (diaphragm cell). 35 °C: ■, expt; ◆, ref 40 (Taylor dispersion, 1%). The points at mole fractions 0 and 1 are extrapolated values.

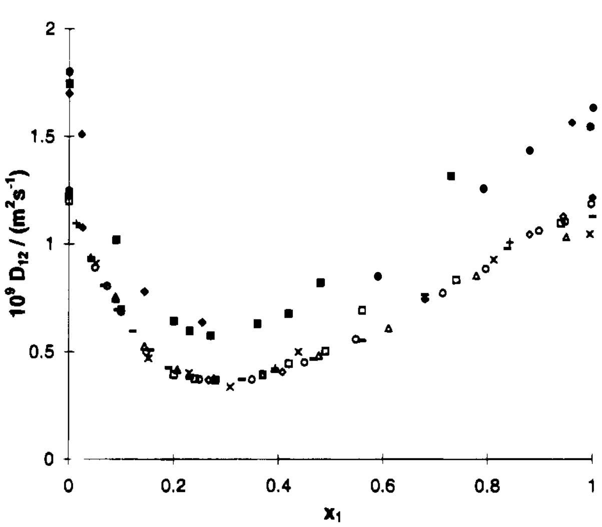

Figure 6. Diffusion coefficient of ethanol (1) + water (2). 25 °C: □, expt; △, ref 5 (dual bellows diaphragm cell, 3%); ×, ref 24 (Taylor dispersion, 2.5%); ○, ref 43 (Taylor dispersion, 2%); ◇, ref 44 (diaphragm cell, 2.6%); −, ref 45 (diaphragm cell, 1%); +, ref 46 (diaphragm cell, 2%). 40 °C: ■, expt; ●, ref 24 (Taylor dispersion, 2.5%); ◆, ref 44 (diaphragm cell, 2.6%). The points at mole fractions 0 and 1 are extrapolated values.

Comparison with literature values in Figures 5 and 6 shows a good agreement. The high deviation in the points of Pratt at mole fraction 0.44 and ours at mole fraction 0.56 for the ethanol + water system is believed to be caused by using the refractive index detector close to the maximum in the refractive index−concentration curve. For the methanol + water system fewer literature values are available. The higher experimental values of Kircher (*5*) are believed to be caused by the method used (dual bellows diaphragm cell). As Woolf (*41*, *42*) did not mention the accuracy of the measurements, it is not possible to decide whether the deviation is significant. Taylor dispersion data at 25 °C were not available. At 35 °C and high mole fractions the diffusion coefficients of Lee and Li (*40*) are lower than the diffusion coefficients obtained in our measurements, with a deviation of 5−8%.

5. Conclusions

The Taylor dispersion method for measuring diffusion coefficients is an accurate technique. In this paper we have shown that the technique can be fast as well if the experimental setup is extensively automated.

Various calculation methods have been discussed. A simple one-parameter fit or even the Van der Laan equation newly presented in this paper yield sufficiently accurate results.

In easily determinable systems diffusion coefficients can be measured with an inaccuracy of ±0.5−1.5%, e.g. our measurements on methanol and ethanol in pure water. Concentration differences in methanol + water and ethanol + water mixtures with a composition close to the maximum in the refractive index−concentration curve are more difficult to measure; in this case the inaccuracy in the obtained diffusion coefficients is less than ±4−5%.

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