

Study of interfacial diffusion in the system solid poly(vinyl acetate)—solvent by the Matano—Boltzmann method

Numerical processing of experimental data

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A convenient approximation of the concentration profile in the system polymer (PVAc)—solvent (ethyl acetate, acetone, methanol) ascertained by the method of wedge interferometer has been found. The values of mutual diffusion coefficients have been calculated for particular compositions of the system by the Matano—Boltzmann method.

Было найдено подходящее приближение для концентрационного профиля системы полимер (ПВАц)—растворитель (этилацетат, ацетон, метанол) определенного при помощи клинового интерферометра. Методом Матан—Больцмана были рассчитаны значения коэффициентов взаимной диффузии при отдельных составах системы.

The study of the polymer—solvent interaction is of considerable importance from the view-point of the investigation of molecular structure and character of intermolecular forces. The intensity of the polymer (2)—solvent (1) interaction to a substantial degree affects the rate of diffusion processes and consequently the apparent interfacial mass transport through the so-called swollen surface layer (SSL) as well. The curves of the concentration profile of solvent in SSL obtained by the method of wedge interferometry were used for the calculation of mutual diffusion coefficients in the system on the basis of numerical approximation of the concentration profile by the Matano—Boltzmann method. This calculation was carried out with a computer. The method of approximation contributes to a more general solution of the problem of concentration profile in the polymer—solvent interface, as we pointed out in our preceding papers [1, 2].

Interpretation of interferograms

The interferometric method enables us to determine the shape of concentration field in SSL by two experimental procedures, *i.e.* the method of constant optical width and the method of constant width of wedge.

The benefit of the first procedure consists in the fact that it makes possible to obtain arbitrary number of points for construction of the curve of concentration distribution

$$c_2 = f(x) \quad (1)$$

where x is the coordinate of position and c_2 is the molar fraction of polymer. The drawback is the intricacy, need of microcomparator for biaxial measurement and thus a possible occurrence of subjective as well as objective errors [3].

The technique of constant width of wedge was also applied in this study and its principle is represented in Fig. 1. A straight line coalescing with parallel sections in

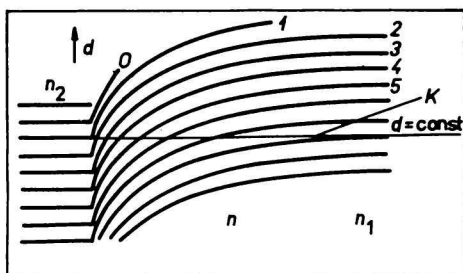


Fig. 1. Interpretation of an interferogram obtained by the technique of constant wedge width.

n_1 — index of refraction of pure solvent ;
 n_2 — index of refraction of polymer ;
 $0, 1, 2, \dots, K$ — numbers of lines ; d — width of wedge.

pure polymer and solvent is drawn through the diffusion field obtained. The interference fringes arise if the following equation is fulfilled

$$N = \frac{2d(n_1 - n_2)}{\lambda} \quad (2)$$

where N , λ , d , n_1 , and n_2 are an integer, wavelength, width of wedge, refractive index of pure solvent, and refractive index of polymer, respectively.

This condition need not be always fulfilled. The coalescence of parallel reference lines in polymer with interference lines in solvent is caused by perfect optical isotropy of particular regions of the swollen surface layer.

If $K - 1$ is the number of lines which intersect the reference line $d = \text{const}$, then the following equation is valid for the refractive index in the i -th point of intersection

$$n_i = n_2 + i \frac{n_1 - n_2}{K} \quad (3)$$

By measuring the position of the points of intersection in relative scale (with respect to magnification) and using eqn (3), the curve $n = f(x)$ may be constructed. The accuracy of the nc transformation depends on the number of lines intersecting the reference line (number of lines = $f(n_2 - n_1)$) and the distance between semi-transparent glass plates.

The wedge microinterferometer may be used only if the refractive index of solvent n_1 is different from the refractive index of polymer n_2 . In this case, two spots with different concentrations have different indices of refraction. The change in refractive index is proportional to concentration change in a not too wide concentration interval.

*Calculation of diffusion coefficient by the
Matano—Boltzmann method*

The mutual diffusion in a system polymer—solvent with one-dimensional experimental arrangement and nonstationary flow may be described by the second Fourier—Fick law (system with concentration dependent diffusion coefficient) in the form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial c}{\partial x} \quad (4)$$

where c is concentration of the polymer expressed arbitrarily. The solution for the following initial and boundary conditions

$$c = c_0 \quad x > 0 \quad t = 0$$

$$c = 0 \quad x < 0 \quad t = 0$$

$$c = c_0 \quad x \rightarrow \infty \quad t > 0$$

ensues from the Boltzmann solution [4] of partial differential eqn (4) and its mathematical application put forward by *Matano* [5]. Provided the mixing of both components is not accompanied by a volume change, the equation allowing to calculate the diffusion coefficient may be written in the form

$$D = -\frac{1}{2t} \frac{dx}{dc_2} \int_0^{c_2} x \, dc_2 \quad (5)$$

The values of the derivative dx/dc_2 and the above integral are to be obtained from numerical or graphical processing of experimental data which is, however, tedious and little accurate. An alternative method of numerical processing which substantially facilitates this processing is put forward in the present paper.

Numerical processing of experimental data

In the plane of experimental data, we have n points $[x_1 : y_1], [x_2 : y_2], [x_n : y_n]$ where $[x_1, x_2, \dots, x_n]$ are the measured values of the independent variable and $[y_1, y_2, \dots, y_n]$ are the obtained values of the dependent variable. We assume that a functional relationship $y = f(x)$ is valid between the variables x and y where $f(x)$

are the used functions of the known type. Provided no measuring errors with which the values of y_i are laden occur, the function $y = f(x)$ would precisely comprehend all experimental points so that it would hold $y_i = f(x_i)$ for $i = 1, 2, \dots, n$ and all points would be situated on the line expressed by $y = f(x)$. In reality, however, it holds

$$y = f(x) + \text{error} \quad (6)$$

which means that the points $x_i : y_i$ are spread along this line. In general, the function $f(x)$ contains p ($p \leq n$) unknown parameters — constants — which we denote b_1, b_2, \dots, b_p . Hence, we may write

$$y_i = f(x_i : b_1, b_2, \dots, b_p) + e_i \quad (7)$$

$$i = 1, 2, \dots, n$$

where e_i are the errors of measurements regarded as random quantities. Eqn (7) is called the control equation of measurement.

If a curve expressed in terms of the equation $y_i = f(x_i : b_1, b_2, \dots, b_p)$ should be drawn through the points $[x_1 : y_1], [x_2 : y_2], \dots, [x_n : y_n]$, we must statistically estimate the unknown parameters b_1, b_2, \dots, b_p which occur in that equation. Simultaneously, we require that it should be, as much as possible, contiguous with the experimental points $x_i : y_i$. The estimated parameters b_1, b_2, \dots, b_p will be denoted by $b_1^*, b_2^*, \dots, b_p^*$. The kind of estimate depends on the criterion used for "the contiguity of curve with points" In the method of least squares, the sum of squared differences $y_i - f(x_i : b_1, b_2, \dots, b_p)$ is chosen as a criterion of "contiguity" and the estimates $b_1^*, b_2^*, \dots, b_p^*$ are determined as the values which make this sum minimum. Hence, if we determine

$$S = \sum_i^n [y_i - f(x_i : b_1, b_2, \dots, b_p)]^2 \quad (8)$$

the "estimates" $b_1^*, b_2^*, \dots, b_p^*$ will be found from the condition

$$S = \min., \text{ resp. } 0 = S(x_i : b_1^*, b_2^*, \dots, b_p^*) \quad (9)$$

Eqn (9) expresses the principle of the method of least squares. Provided eqn (9) has been used, we may say that a curve has been drawn through the points $[x_1 : y_1], [x_2 : y_2], \dots, [x_n : y_n]$ by the method of least squares.

In this paper, we used the function

$$y = 1 - \frac{1}{1 + ax^b} \quad (10)$$

which describes the distribution of concentration along the axis x

$$Y_i = \ln \frac{y_i}{1 - y_i} \quad (11)$$

and

$$X_i = \ln x_i \quad (12)$$

Thus, it may be written

$$A = \ln a ; \quad B = b \quad (13)$$

Application of the method of least squares leads to minimization of the function

$$S(A, B) = \sum_i (Y_i - A - BX_i)^2 \quad (14)$$

i.e. to fulfillment of the conditions

$$\frac{\partial S}{\partial A} = 0 = \sum_i (A + BX_i - Y_i) \quad (15)$$

$$\frac{\partial S}{\partial B} = 0 = \sum_i (AX_i + BX_i^2 - BX_i Y_i) \quad (16)$$

In order to verify the calculated function, we tested the results by the following statistical data:

1. Mean square deviation

$$y^2 = \left[\frac{1}{n} \sum_i (y_i - f(x_i))^2 \right]^{1/2} \quad (17)$$

2. Standard deviation

$$\Delta y_s = \left[\frac{\sum_i (y_i - f(x_i))^2}{n - p} \right]^{1/2} \quad (18)$$

3. Probable deviation

$$\Delta y_p = 0.6745 \Delta y_s \quad (19)$$

4. Correlation coefficient

$$r = \frac{\sigma_{y, f(x)}^2}{(\sigma_y^2 - \sigma_{f(x)}^2)^{1/2}} \quad (20)$$

where $\sigma_{y, f(x)}^2$ is selection covariance

$$\sigma_{y, f(x)}^2 = \frac{1}{n - 1} \left[\sum_i y_i f(x_i) - \frac{1}{n} \sum_i y_i \sum_i f(x_i) \right] \quad (21)$$

σ_y^2 is selection variance y_i

$$\sigma_y^2 = \frac{1}{n - 1} \left[\sum_i y_i^2 - \frac{1}{n} \sum_i y_i \sum_i y_i \right] \quad (22)$$

and $\sigma_{f(x_i)}^2$ is selection variance $f(x_i)$

$$\sigma_{f(x_i)}^2 = \frac{1}{n-1} \left[\sum_i (f(x_i))^2 - \frac{1}{n} \sum_i f(x_i) \sum_i f(x_i) \right] \quad (23)$$

Experimental

A microinterferometer based on light interference in a thin wedge layer formed by two semi-transparent walls [6, 7] was used for measurements. This method is very suited for the investigation of diffusion because it makes possible to shorten the time of experiments several times and reduces the exigencies of thermostating owing to the diffusion taking place in relatively viscous medium. The diagram of this instrument is in Fig. 2.

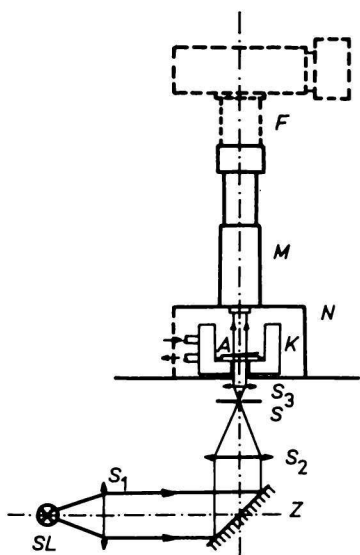


Fig. 2. Diagram of the interferometer used.
 SL — sodium-vapour lamp; S_1 — S_3 — lenses;
 Z — mirror; S — slit; K — temperature-controlled vessel; N — base of microscope;
 M — microscope; F — camera; A — holder of glass plates with sample.

The diffusion process involving the dissolution of the commercial polydisperse polymer, i.e. poly(vinyl acetate) (PVAc) with intrinsic viscosity $[\eta]_{20^\circ\text{C}} = 0.5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ was studied. A film was prepared from this polymer by pouring its solution in tetrahydrofuran on the mercury level in a Petri dish. This film was dried *in vacuo* for 24 h at 25°C and subsequently held in a desiccator. Anal. grade acetone (AC), ethyl acetate (EAc), and methanol (MO) were applied as solvents.

Samples of rectangular cross-section having the area of $(10 \times 2) \times 10^{-6} \text{ m}^2$ and the width of 8×10^{-5} — $6 \times 10^{-4} \text{ m}$ were used. They were put in a temperature-controlled holder of the volume $(23 \times 20 \times 3.5) \times 10^{-9} \text{ m}^3$ between two semi-transparent glass plates with the transpance of about 10%. A sample was so pressed by means of torsion springs that the density of lines and thus the internal pressure was equal for each measurement. The time was always measured from the moment when the thermostatted solution was injected. The

temperature was held constant accurate to $\pm 0.1^\circ\text{C}$. In each measurement, 3—5 shots were taken at convenient time intervals. ORWO 21 DIN sheet film 0.06×0.09 m was used and the exposure was 20 s. The processing of photographic record was carried out by standard procedure under constant conditions.

Results and discussion

In this study, the problem of approximation of the concentration profile of swollen surface layer was solved in order to facilitate the calculation of mutual diffusion coefficient in a system polymer—solvent by the Matano—Boltzmann method. Several authors [3, 8—11] numerically solved eqn (5) by using appropriate transformations. The topic of these papers was diffusion in solutions where the small concentration interval considerably simplifies the studied problem.

In this study, a procedure was elaborated which considerably facilitates numerical evaluation of the integrals and derivatives in eqn (5) in the range of volume fractions 0.0—1.0. This procedure is based on the processing of the proposed two-parameter empirical function (10). The obtained values of mutual diffusion coefficient are represented in Figs. 3—7 as functions of the concentration of particular systems in the temperature interval 20—50°C. As known, the diffusion curve most frequently exhibits a maximum in the region of higher polymer

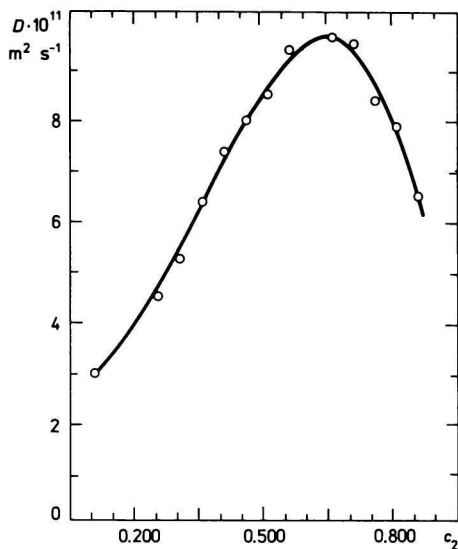


Fig. 3. Variation of mutual diffusion coefficient with concentration in the system PVAc—EAc (30°C, time of measurement 780 s).
 c_2 — volume fraction of polymer.

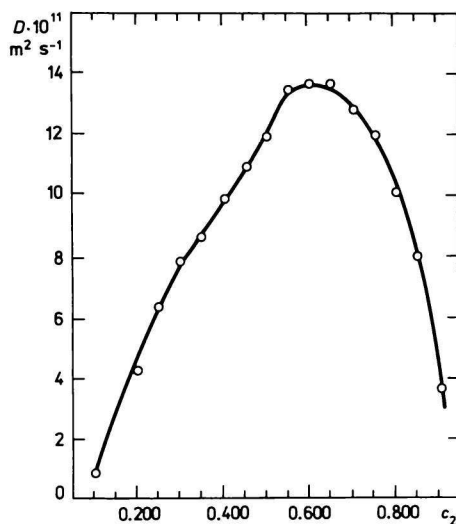


Fig. 4. Variation of mutual diffusion coefficient with concentration in the system PVAc—AC (20°C, time of measurement 1200 s).
 c_2 — volume fraction of polymer.

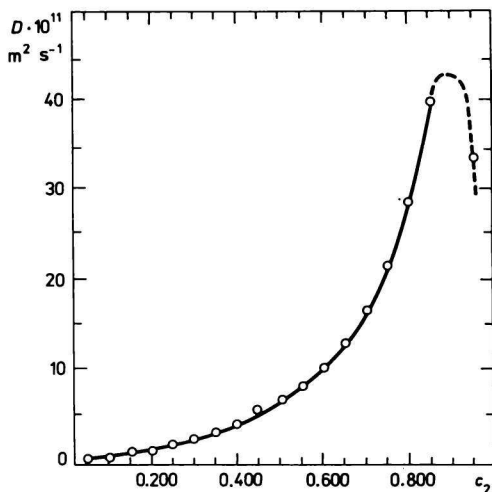


Fig. 5. Variation of mutual diffusion coefficient with concentration in the system PVAc—MO (15°C, time of measurement 1200 s).
 c_2 — volume fraction of polymer.

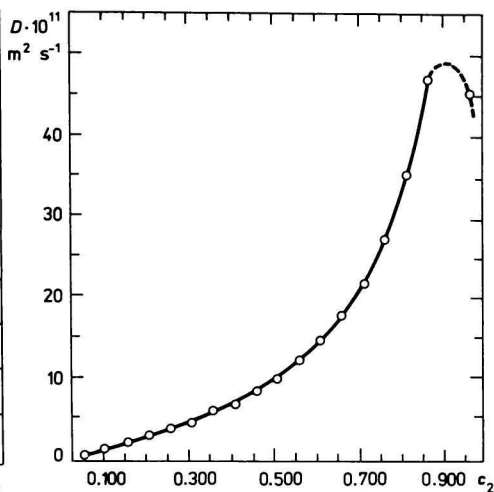


Fig. 6. Variation of mutual diffusion coefficient with concentration in the system PVAc—MO (45°C, time of measurement 960 s).
 c_2 — volume fraction of polymer.

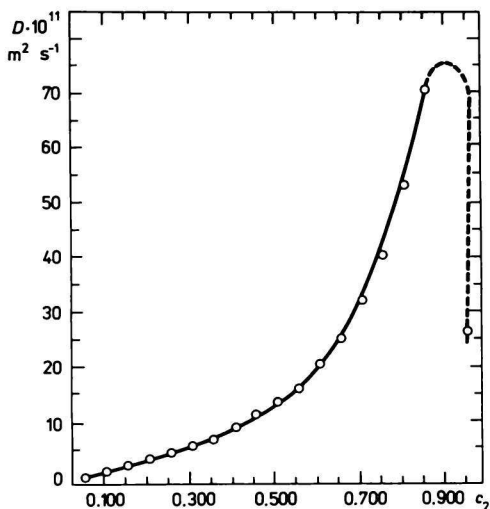


Fig. 7. Variation of mutual diffusion coefficient with concentration in the system PVAc—MO (50°C, time of measurement 1020 s).
 c_2 — volume fraction of polymer.

concentrations. The experimental results show that, in case of the systems PVAc—EAc and PVAc—AC, this maximum appears in the range of volume composition 0.55—0.65. For the system PVAc—MO, this maximum is shifted towards the region of higher concentrations.

Function (10) was statistically tested. It was found that the correlation coefficient was in the interval 0.95—1.00 of the mean square deviation. The standard deviations were approximately 7×10^{-2} and the probable deviations were about 5×10^{-3} . It was obvious from the results of statistical analysis that the approximation used covers the experimental values with satisfactory accuracy. The course of this function is sufficiently variable according to the constants a , b and simultaneously both limiting conditions are fulfilled, *i.e.*

$$\lim_{x \rightarrow 0} \left(1 - \frac{1}{1 + ax^b} \right) = 0$$

$$\lim_{x \rightarrow \infty} \left(1 - \frac{1}{1 + ax^b} \right) = 1$$

which is in agreement with the conditions of validity of the Fick laws as well as with the experimental conditions. By introducing another constant $c' > 1$, function (10) assumes the form

$$y = c' - \frac{c'}{1 + ax^b} \quad (24)$$

Thus, it is possible to omit the second limiting condition and still more approach the values of mutual diffusion coefficient which are consistent with those obtained by tedious graphical procedure.

The numerical testing of particular concentration regions was so carried out by means of a CDS computer that experimental curve was per parts approximated by the quadratic function

$$D = E + FC_2 + GC_2^2 \quad (25)$$

where the constants E , F , G were obtained by the method of least squares for segments involving five experimental points. The coordinates of the dependence of mutual diffusion coefficient were calculated from the known values of constants E , F , G for the nearest experimental point.

On the basis of the testing results obtained by the "SYMP" program, we may state that the calculation of the constants a , b of function (10) is most suited for the concentration interval including volume fractions of polymer 0.25—0.85 while it is laden with the greatest errors in the concentration intervals 0.0—0.25 and 0.85—1.00.

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