Effect of Isothermal Compression of Polymer on its Diffusion Properties

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The results of the interphase diffusion in the system hydroxyethylcellulose film—water as a function of solid polymer compression are discussed. The experimental technique is briefly described and the possible swelling mechanism is proposed. The pressure dependence of the diffusion coefficient is divided into two regions: the one of elastic and the other of permanent polymer chain deformation. The change to permanent deformation is controlled by deformation time or by values of the external pressure.

Much attention has been paid in the literature to the elucidation of the transport processes in the system solid polymer substance—solvent. The theories of diffusion based on the assumption of the existence of free volume [1, 2], or on the knowledge of the volume density of cohesive energy [3] are of the historic significance. Theories based on the assumption of free volume are of great importance at the present time as well [4—8]. Alternative explanations of the diffusion processes are provided by the theories based on the existence of the activated state. For the dependence of the diffusion coefficient D on the activation energy E in the case of diffusion into a system of the polymer chains [9] the following equation is valid

$$D = \frac{1}{2}\lambda^2 \rho f^v \frac{1}{(f-1)!}\left[\frac{E(f)}{RT}\right]^{f-1} e^{f-1} \qquad (1)$$

where λ is a jump distance, f a number of degrees of freedom, v thermal vibration frequency of a molecule, and ρ a parameter of the cooperative segment motion. Activation energy E depends on the number of degrees of freedom. It can be more precisely specified as [10]

$$E = P_i \Delta V + E_b + fRT \qquad (2)$$

The first term is a product of the internal pressure P_i and the volume ΔV occupied by the system of the polymer chains and a penetrating molecule. ΔV value can be expressed using a length of the polymer segment s, diameter of the penetrating particle d_p, free volume per length unit of the polymer chain Φ, and an average diameter of the macromolecule $\bar{d}_c$ by the equation

$$\Delta V = \frac{1}{2}(d_p - \Phi^{1/2}/2)^2 [s^2/(d_p - \Phi^{1/2}/2)^2 - 1]^{1/2}\bar{d}_c N \qquad (3)$$

where N is a number of the polymer segments.

The term E_b represents a contribution to the activation energy due to chain rotation. It can be expressed by the equation

$$E_b = \frac{2s}{\lambda}\Psi \qquad (4)$$

where λ is the length of a chain along its axis, Ψ is the corresponding rotation potential that can be described as

$$\Psi = 9\Psi_0\lambda^2 s^{-2}[s^2/(d_p - \Phi^{1/2}/2)^2 - 1]^{-1} \qquad (5)$$

The last term fRT represents a contribution of the thermal energy. f is a number of the degrees of freedom of the polymer segment which is proportional to the chain length s according to the formula

$$f = 2sZ/\lambda \qquad (6)$$

Z is a proportionality factor that is usually equal to unity [10]. After substitution of the terms from the aforementioned relationships to eqn (2), we obtain for the total activation energy the following formula

$$E = \frac{1}{2}(d_p - \Phi^{1/2}/2)^2[(f\lambda/2Z)^2(d_p - \Phi^{1/2}/2)^2 - 1]^{1/2}\bar{d}_c NP_i + 36\Psi_0 Zf^{-1}[(f\lambda/2Z)^2(d_p - \Phi^{1/2}/2)^2 - 1]^{-1} + fRT \qquad (7)$$

This relationship implies that activation energy of diffusion is a function of the geometrical sizes of a segment as well as of the penetrating particle, of the number of degrees of freedom of the polymer segment, of pressure and temperature in the system. *Ueberreiter* and *Asmussen* [11] have derived from the swelling kinetics a formula for the temperature dependence of the thickness of the swollen layer δ

$$\delta = \delta_0 \exp(-A_\delta/T) \qquad (8)$$

Physical meaning of the empirical constant A_δ in the product RA_δ (R – gas constant) has been clarified [12] as isothermal activation work performed by a system at the passage of the macromolecular coils from the swollen layer into the solution. Using certain simplification [12] it can be presented by the relationship

$$RA_\delta \approx (P_i + P)(V_D^c - V_d^c) \qquad (9)$$

V_D^c is critical volume of 1 mol of the polymer segments at the diffusion that controls the rate of dissolution, V_d^c is critical volume of 1 mol of segments at their passage into the solvent, P is equilibrium pressure. The quantity RA_δ that is greatly affected by the sum of an equilibrium and an internal pressure, causes increase of the rate of dissolution of the polymer segments u according to the equation [12]

$$\dot{u} = u_0\, e^{-(\Delta G_d - RA_\delta)} \qquad (10)$$

where u_0 is a preexponential factor, ΔG_d is a change in the activation energy of diffusion due to dissolution. The rate u is related to the diffusion coefficient D by the relationship

$$u = D/\delta \qquad (11)$$

After substitution of eqns (11) and (9) into the formula (10) one can express dependence of the diffusion coefficient on the equilibrium and internal pressure as follows

$$D = \delta u_0 \exp\{-[\Delta G_d - (P_i + P)(V_D^c - V_d^c)]\} \qquad (12)$$

Presented paper deals with the investigation of the effect of isothermal compression of hydroxyethylcellulose on the interphase diffusion of the solvent into a polymer sample.

EXPERIMENTAL

Films of hydroxyethylcellulose (Natrosol 250 MR, $M_r = 660\,000$) of thickness 0.25 mm have been used. Distilled water has been used as a solvent.

At the measurement of the interphase diffusion, polymer film has been placed between two planparallel glass plates (Fig. 1), so that the film thickness could have been considered as constant. After fixing of the sample, the polymer and the solvent have been separately tempered. After the temperation a cell with the polymer sample has been inserted into the tempering unit with a solvent, and the countdown has been started at the moment of the contact of a sample with the solvent. Motion of the boundary of the swollen layer (optical interphase) has been observed using an optical
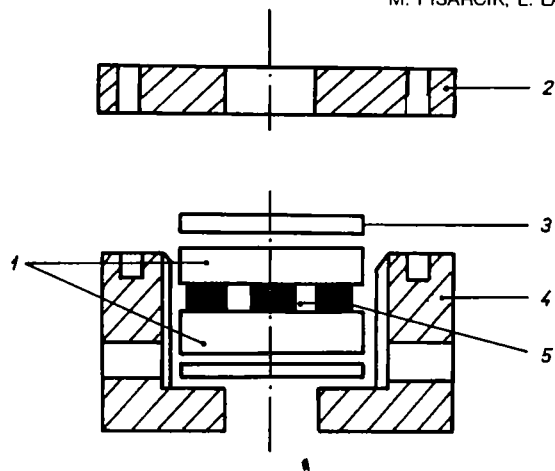

Fig. 1. Cell for the measurement of the rate of motion of the optical interphase. 1. Glass plates, 2. compression site, 3. seal, 4. cell basement, 5. sample.

microscope. The polymer films have been compressed in a press with an external pressure of 0—2×10^7 Pa during the time intervals of 10 s— 30 min. Time of the transfer of the sample from a press to a measuring cell could be neglected in comparison with the duration of tempering and measurement. All measurements have been carried out at 25 °C.

RESULTS AND DISCUSSION

From the point of view of the experimental arrangement in this case we deal with a one-dimensional diffusion of the solvent into a polymer sample along the x axis (Fig. 2). The structure of the swollen layer is known from the literature [13]. Considering a film thickness to be negligible in comparison with its length, we deal with a case of a one-dimensional diffusion that can be described
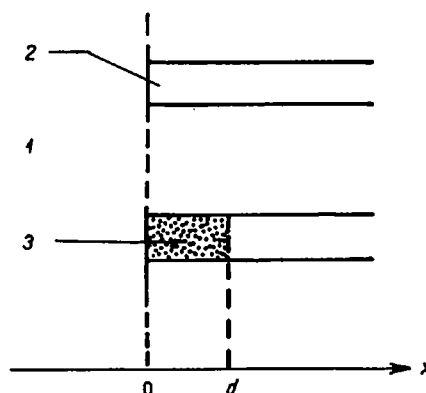

Fig. 2. Experimental arrangement of the measurement of the rate of motion of the optical interphase. 1. Solvent, 2. polymer at time point $t = 0$, 3. polymer at time point $t \neq 0$, optical interphase. d – position of the optical interphase.

by the diffusion equation with the following boundary and initial conditions

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x}\right] \qquad (13)$$

$$
\begin{array}{llll}
t = 0 & c = 0 & x > 0 \\
 & c = c_0 & x = 0 \\
t \neq 0 & c = c_0 & x = 0
\end{array}
$$

where c is concentration, D diffusion coefficient.

Assuming independence of the diffusion coefficient on the concentration, eqn (13) can be solved using Laplace's transformation [14]. After the inverse transformation, the concentration function has a shape of a complementary error function

$$c(x,t) = c_0\, \mathrm{erfc}\left[\frac{x}{(2Dt)^{1/2}}\right] \qquad (14)$$

where c_0 is concentration of the penetrant molecules, $\mathrm{erfc}(y)$ is a complementary error function defined as

$$\mathrm{erfc}(y) = 1 - 2\pi^{-1/2}\int_0^y e^{-x^2}\mathrm{d}x$$

Due to large values of the argument y, the function $\mathrm{erfc}(y)$ might be approximately presented in the form of a series

$$\mathrm{erfc}(y) \approx \frac{e^{-y^2}}{2y}\left[1 - \frac{1}{2y^2} + \frac{1\times 3}{(2y^2)^2} - \frac{1\times 3\times 5}{(2y^2)^3} + ...\right] \qquad (15)$$

Taking into consideration the first two terms of relation (15) in the brackets, the function $c(x,t)$ can be presented as

$$c = c_0\pi^{-1/2}\frac{e^{-y^2}}{2y}\left[1 - \frac{1}{2y^2}\right] \qquad (16)$$

where $y = x(2Dt)^{-1/2}$. Having in mind that the optical interphase represents a front of the penetrant progress (i.e. concentration of the penetrant molecules at the boundary approximately equals zero), magnitude of c in eqn (16) can be considered as close to zero. From this equality it follows for y

$$y^2 = \frac{1}{2} \qquad (17)$$

After the corresponding substitution, a time dependence of the variation of the thickness of the swollen layer δ can be obtained

$$\delta = x(c = 0) = (2Dt)^{1/2} \text{ or } \delta^2 = 2Dt \qquad (18)$$

Eqn (18) is valid with the precision of approximation (16). For the values of the thickness of the swollen layer of the mm order, swelling time is of 10^2 s order, and the values of the diffusion coefficient are of 10^{-6} cm^2 s^{-1} order (characteristically obtained from the experimental measurements), the

magnitude of the argument y is ca. 5. For this value contribution of the higher terms in the formula (15) compared to that of the first two terms in the square brackets is approximately 1 %. This is the impreciseness that is obtained due to the assumption of correctness of eqn (18) at the above-mentioned conditions. The constant D in eqn (18) represents a mean apparent coefficient of mutual diffusion, since the motion of the optical interphase that is registered with a microscope is on the basis of Kirkendall's effect composed of the reversely oriented motions of the molecules of the solvent and of the polymer. Kirkendall's phenomenon for the binary system of the components A and B can be described by the relationship for the diffusion coefficient of the whole system

$$D = D_{A,B}(1 - \gamma_{A,B}) + D_{B,A}\gamma_{A,B} \qquad (19)$$

where $D_{A,B}$, $D_{B,A}$ are coefficients of partial diffusion of the component A into component B and vice versa, $\gamma_{A,B}$ is a mole fraction of component A in component B. From this relationship it follows that experimentally observed total diffusion coefficient depends on the partial diffusion coefficients of the components, as well as on the mole ratio of the components in the system. Mean apparent coefficient of mutual diffusion D (further on just diffusion coefficient) is calculated by a linear regression from the slope of the time dependence of the variation of the thickness of the swollen layer δ (eqn (18)).

From Fig. 3 it follows that at the brief compression of a polymer sample (curves for the times 10 s and 1 min) due to the chain relaxation, no dissipation of free volume takes place. Its dispersion character is retained. After disloading of the sample and its subsequent insertion into the solvent, chain expansion occurs as well as increased motion of the solvent molecules (i.e. motion of the optical interphase) into the polymer due to the Kirkendall's effect. This fact causes the increase of the diffusion coefficient magnitude with the growing external pressure. The region of the elastic deformation of the polymer chains might be in mechanics compared with a spring, while the expansion work RA_δ from eqn (9) corresponds to the potential energy of the spring $1/2\,kz^2$ (z is an immediate amplitude) that is changing into the kinetic form represented in the case of a polymer system by a rate of the advance of the phase boundary (relationship (11)). According to eqn (12) diffusion coefficient of the system compressed polymer film—penetrant exponentially grows with the external compression pressure P that is valid for the region of the elastic deformation of the chains. By means of correlation of the linear parts of the curves corresponding to 10 s and 1 min
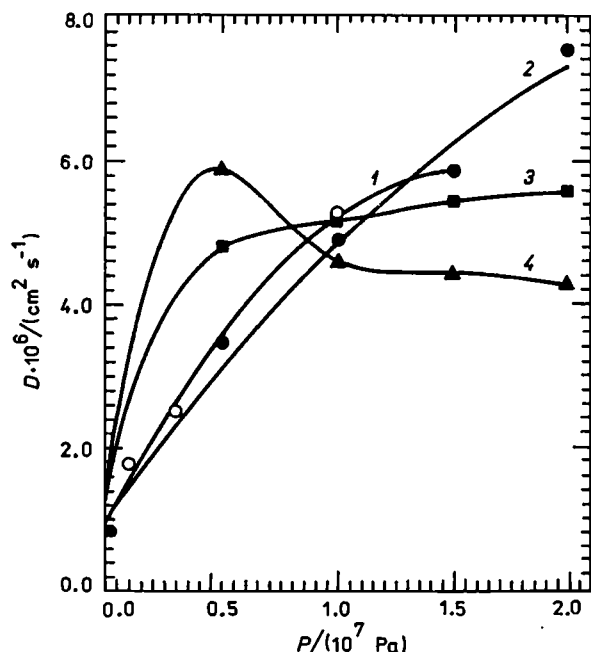
Fig. 3. Dependence of the mean coefficient of mutual diffusion in the system hydroxyethylcellulose film—distilled water at 25 °C on the pressure of film compression and on time of action: *1.* 10 s, *2.* 1 min, *3.* 15 min, *4.* 30 min.
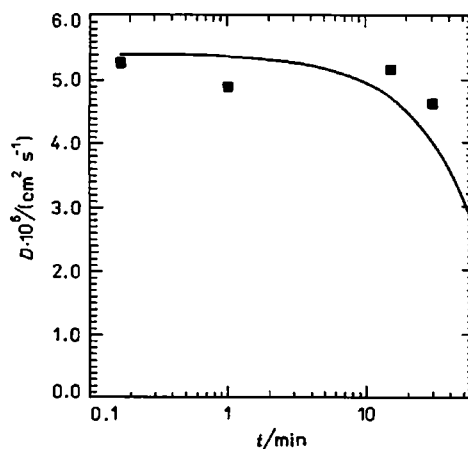

Fig. 4. Dependence of the mean coefficient of mutual diffusion in the system hydroxyethylcellulose film—distilled water on the compression time at a constant pressure of 10^7 Pa and 25 °C.

(Fig. 3) in the region of small pressure values P with the expression (*12*) and using a linear regression procedure it is possible to define a magnitude of the internal pressure P_i that equals 2.7 × 10^6 Pa for compression during 10 s and 4 × 10^6 Pa for compression during 1 min. Taking into account that the values of the internal pressure are proportional to the accumulated energy of the deformed chains, they amount up to 80 % of the value of the applied external pressure P in the region where D is linearly dependent on P. This implies that the polymer chains are apparently to the great extent able to accumulate externally supplied energy and to relax back to the initial state in the region of the elastic deformations.

Different situation occurs at the long-run action of the external pressure. In such a case the conditions are created in the polymer for arising of an internal flow of material and of an anisotropic flow of the free volume associated with a change of its spatial distribution. The curves for the times of 15 min and 30 min in Fig. 3 could be divided in the region of low pressures into an area of elastic deformation (growth of D with increasing external pressure), the mechanism of which has been al-

ready explained, and in the region of higher pressures into an area of irreversible compression of the solid sample that results in the decrease of D with increasing external pressure.

Similarly, it can be seen from Fig. 4 that illustrates the dependence of the diffusion coefficient on the time of sample compression (in the interval 10 s—120 min) at the constant pressure, that at longer compression times an irreversible deformation of the sample occurs that causes lowering of the D value.

REFERENCES

1. Bueche, F., *J. Chem. Phys. 21,* 1850 (1953).
2. Slater, J. C., *Introduction to Chemical Physics.* McGraw-Hill, New York, 1939.
3. Meares, P., *J. Am. Chem. Soc. 76,* 3415 (1954).
4. Vrentas, J. S., *J. Colloid Interface Sci. 130,* 293 (1991).
5. Vrentas, J. S., Duda, J. L., and Ling, H. C., *J. Membr. Sci. 40,* 101 (1989).
6. Lustig, S. R. and Peppas, N. A., *J. Appl. Polym. Sci. 33,* 533 (1987).
7. Vrentas, J. S., Duda, J. L., and Hou, A. C., *J. Polym. Sci., Polym. Phys. Ed. 23,* 2469 (1985).
8. Ito, T. and Seta, J., *Sen'i Gahkaishi 42,* 15 (1986).
9. Barrer, R. M., *Trans. Faraday Soc. 39,* 237 (1943).
10. Brandt, W. W., *J. Phys. Chem. 63,* 1080 (1959).
11. Ueberreiter, K. and Asmussen, F., *J. Polym. Sci. 57,* 187 (1962).
12. Lapčík, Ľ. and Valko, L., *Chem. Zvesti 20,* 489 (1966).
13. Ueberreiter, K., *Diffusion in Polymers.* (Crank, J. and Park, G. S., Editors.) Academic Press, London, 1968.
14. Crank, J., *The Mathematics of Diffusion.* Clarendon Press, Oxford, 1956.