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Figure 1

Figure 1: Figure 1

Abstract

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EFFECT OF THE MOLECULAR WEIGHT OF HYDROCARBONS ON THEIR DIFFUSION IN POLYMERS

(Presented by Academician S. S. Medvedev, 13 IV 1965)

The diffusion rate depends on the mass of the molecules of the diffusing substance. For low-molecular systems and dilute polymer solutions, the diffusion coefficient is inversely proportional to the molecular weight of the substance to a power close to 1/2 ([1]). The dependence of the diffusion coefficient on the nature of the substance diffusing in a polymer is more complex: in such systems not only the mass of the molecule but also its structure plays a role ([2–8]). For homologous substances, the diffusion coefficient D is related to the molecular weight M by the equation:

$$D = KM^{-\gamma}, \tag{1}$$

where the constant γ has a value equal to unity ([7]) and even higher ([5,8–12]). Diffusion of molecules of small mass has mainly been studied and, with rare exceptions ([9,11]), over a very narrow interval of molecular weights.

Fig. 1. Concentration distribution curves in equilibrium for PIB—hydrocarbon systems: 1 —cetane (60°); 2 —paraffin (100°); 3 —ceresin (100°). Time 36 min.

The aim of the present work was to determine experimentally the interdiffusion coefficients D_v in polymer—hydrocarbon systems under conditions in which the molecular weight of the latter varies by 1-2 orders of magnitude. Its successful solution will make it possible to approach more rationally the problem of studying diffusion in polymer—polymer systems, since it will permit estimation of

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

the time interval necessary for a measurable depth of interpenetration of macromolecules in an experiment. This, in turn, will make it possible to obtain direct proof of the validity of the diffusion theory of adhesion.

The diffusion of hydrocarbons was investigated: octane, dodecane, cetane, paraffin ($M \sim 325$), ceresin ($M \sim 525$), and two fractions of low-molecular polyethylene ($M \sim 2000$ and $M \sim 5000$) in polyisobutylene (PIB), and the last four substances also in atactic polypropylene (PP) and polyethylene (PE). The diffusion of solvents in PIB was studied over the temperature interval 20-120°, of paraffin 60-100°, and of ceresin and the PE fractions 100-130°. The PIB sample was obtained from the technical product of grade P-85 by fractionation using the fractional precipitation method. According to Flory, the weight-average molecular weight of PIB is $2.5 \cdot 10^5$. The PP sample was obtained by extraction with sulfur ether of an atactic fraction with $M \sim 2 \cdot 10^4$. The molecular weight of PE is $1.8 \cdot 10^4$. To study diffusion, an interferometric micromethod was used ([13,14]). The interdiffusion coefficient was calculated by the Matano—Boltzmann method and, for systems with insignificantly differing

···refractive indices of the components according to Einstein' s equation,

$$D = \frac{x^2}{2t}. \tag{2}$$

The concentration-distribution curves along the diffusion coordinate for several systems are presented in Fig. 1. As the molecular weight of the hydrocarbon increases, the deviation from the Gaussian distribution decreases. This is most noticeable for the PP—hydrocarbons system, not shown in the figure, which is probably associated with the low molecular weight of PP (15). The mutual-diffusion coefficients vary with composition along a curve with a maximum (Fig. 2). The larger the size of the hydrocarbon molecule,

Fig. 2. Dependence of the mutual-diffusion coefficient on the composition of PIB—hydrocarbon systems: 1 —octane; 2 —dodecane; 3 —cetane; 4 —paraffin; 5 —ceresin; 6 —PE fraction ($M \simeq 2000$) at 100°.

Fig. 3. *a* —Dependence of E on the composition of the PIB—hydrocarbon system: 1 —octane; 2 —dodecane; 3 —cetane; 4 —paraffin; 5 —ceresin; 6 —PE fraction ($M \simeq 2000$).
b —Dependence of E on the molecular weight of the diffusing substance at different V_s (1—0.2; 2—0.5; 3—0.8 volume fraction).

Figure 4

Figure 4: Figure 4

the smaller the diffusion coefficient and the weaker its variation with concentration. It may be assumed that, in the mutual diffusion of chemically similar polymers with close molecular weights, the mutual-diffusion coefficient does not depend on the composition of the system, and the distribution curves are described with sufficient accuracy by the Gaussian distribution law.

The activation energy of the diffusion process decreases as the hydrocarbon content in the system increases. Qualitatively, this change is the same for all the systems studied. However, the greatest change is characteristic of substances with low molecular weight (Fig. 3a). In the example of

diffusion of hydrocarbons in PIB, it has been established that the curve E—V_s (where V_s is the volume fraction of hydrocarbons), as $V_s \to 0$, extrapolates to a value close to the activation energy of viscous flow of the polymer ([16]). At a hydrocarbon content greater than 0.4 volume fraction, the activation energy remains practically unchanged. The size of the hydrocarbon molecule affects the magnitude of the activation energy only up to a certain limit (Fig. 3b), corresponding to a paraffin molecule. Consequently, the size of a paraffin molecule approximately corresponds to the size of the kinetic unit participating in the elementary act of diffusion and, possibly, is close to the size of a segment of the macromolecule of the polymers studied.

Fig. 4. Dependence of the mutual-diffusion coefficient on the molecular weight of the hydrocarbon: *a*—for PIB (*I*) and PP (*II*); *b*—for PE (*III*).
1—100°; 2—110°; 3—120°; 4—130° C

The dependence of the mutual-diffusion coefficient on the molecular weight of the hydrocarbon obeys equation (1). The slope coefficient of the straight line depends on the composition of the polymer—hydrocarbon system: the greater the hydrocarbon content in the system, the smaller it is. An increase in the hydrocarbon content lowers the viscosity of the system and, consequently, increases its mobility.

The coefficient γ depends on the nature of the polymer (Fig. 4). For PIB at 100–120°, the coefficient γ is constant and equal to ~ 3. For PP at the same temperatures it is equal to ~ 2. The coefficient γ for PE depends on temperature. At 120° it is equal to ~ 2.5, and at 130° to ~ 1.5. This last circumstance, it seems to us, is connected with an increase in the number of ordered regions (crystallites) in PE as the temperature decreases. With increasing temperature the possibility of crystal formation decreases, the mobility of the chains increases, and the coefficient γ falls. Thus, the dependence of γ on the nature of the polymer (and on temperature for PE) is a consequence of differences in the mobility of macromolecules and their segments. The elementary act of displacement of a molecule of the diffusing substance is associated with cooperative motion of the molecules of the medium. As the size of the hydrocarbon molecule increases, ever larger portions of the macromolecules of the medium are involved in the diffusion process. The rate of displacement of these portions is determined by their mobility. The mobility of molecules depends on their structure. The presence of side substituents, for example CH groups, reduces mobility to a greater extent the more such groups there are in the chain (^{8}). The presence of double side substituents in the PIB molecule makes the displacement of such molecules still more difficult. In addition, symmetrical side substituents make possible a denser packing of PIB molecules as compared with PP molecules. In molten PE, the absence of side substituents and branches makes the chains most mobile. At 130° C the slope coefficient of the straight line $\lg D$— $\lg M$ increases in the sequence:

$$\gamma_{\mathrm{PE}} < \gamma_{\mathrm{PP}} < \gamma_{\mathrm{PIB}}.$$

Extrapolation of the straight lines (Fig. 4) shows that for a hydrocarbon (of the PE type) with molecular weight $2 \cdot 10^4$, the diffusion coefficient at 120° should have a value in PIB of $\sim 6 \cdot 10^{-12}$ cm^2/sec, in PP $\sim 2 \cdot 10^{-10}$, and at 130° in PE $\sim 7 \cdot 10^{-10}$ cm^2/sec. The times corresponding to penetration into the polymers to a depth of 10 μ are, respectively: 8 h, 14 min, 4 min.

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REFERENCES

[1] V. N. Tsvetkov, S. I. Klenin, DAN, 88, 49 (1953). [2] R. M. Barrer et al., J. Polym. Sci., 3, 549 (1948); Trans. Farad. Soc., 51, 126 (1955). [3] G. S. Park, Trans. Farad. Soc., 46, 684 (1950); 47, 1007 (1951). [4] S. Prager, F. A. Long, J. Am. Chem. Soc., 73, 4072 (1951); 75, 1255, 6142 (1953). [5] S. N. Zhurkov, G. Ya. Ryskin, ZhTF, 24, 797 (1954). [6] D. W. McCall, W. P. Slichter, J. Am. Chem. Soc., 80, 1861 (1958). [7] J. Auezbach et al., J. Polym. Sci., 28, 129 (1958). [8] R. M. Vasenin, High-Molecular Compounds, 2, 857 (1960). [9] F. Grün, Experientia, 3, 490 (1947). [10] A. S. Kuzminskii, S. A. Reitlinger, E. V. Shemastina, DAN, 98, 611 (1954). [11] S. E. Bresler, G. M. Zakharov, S. V. Kirillov, High-Molecular Compounds, 3, 1072 (1961). [12] F. Bueche, M. Cashin, P. Debye, J. Chem. Phys., 20, 1956 (1952). [13] A. E. Chalykh, R. M. Vasenin, Scientific Proceedings of the Moscow Technological Institute of Light Industry, collection 30, 200 (1964). [14] A. E. Chalykh, R. M. Vasenin, DAN, 161, 1580 (1965). [15] V. K. Gromov, A. E. Chalykh, R. M. Vasenin, S. S. Voyutskii, High-Molecular Compounds, 7, 795 (1965). [16] A. A. Tager, V. E. Dreval, R. A. Khasina, High-Molecular Compounds, 5, 432 (1963).

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