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Abstract

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Investigation of Diffusion in the Polyisobutylene–Solvents System by an Interference Micromethod

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The diffusion behavior of a binary system, of which the polymer–solvent system is a special case, can be described by several diffusion coefficients. Their physical meaning and magnitude depend on the choice of the section through which the fluxes of the components are measured ([1]). Usually these coefficients reflect the process of interpenetration of the components and are called binary coefficients or interdiffusion coefficients. One of the most widespread coefficients, and one that is easily measured from experimental data, is the interdiffusion coefficient D_v, defined from the flux through a volume-fixed section ([1]).

A feature of diffusion in the polymer–solvent system is the enormous difference in the mass, and consequently in the mobility, of the components. If the section is fixed in such a way that the flux of polymer through it is equal to zero, then the diffusion coefficient of the solvent with respect to the diffusion medium can be determined. The solvent diffusion coefficient measured under such conditions is called the one-sided coefficient D. It is related to the interdiffusion coefficient by the equation ([2]):

$$D = \frac{D_v}{1 - \varphi_s}, \tag{1}$$

where φ_s is the volume fraction of the solvent.

The displacement of molecules during diffusion is caused by their thermal motion. In the absence of a gradient of chemical potential, the motion of molecules has no directed character. In this case the rate of displacement of molecules is determined by the self-diffusion coefficient D^*. It depends on the composition of the system and can be determined by the tracer-atom method.

It may be assumed that the one-sided diffusion coefficient of the solvent, characterizing, like the self-diffusion coefficient, the individual mobility of the component, should be close in magnitude to the latter at all compositions of the system. To this end we investigated diffusion in the polyisobutylene–solvents system, in particular polyisobutylene–cetane, the self-diffusion in which had been studied by the tracer-atom method ([3]).

The object of the study was polyisobutylene with a viscosity-average molecular weight of 2.01×10^6, close to that used in work (3). To study diffusion we used the interference micromethod described in a number of papers (4-7). By the described methods of processing interferograms (4) and by the measured refractive indices, curves of the concentration distribution along the diffusion coordinate were determined at three temperatures and at different times (Fig. 1). The distribution curves are sharply asymmetric and differ considerably from Gaussian curves. This is explained by the dependence of the interdiffusion coefficient on concentration. The interdiffusion coefficients were calculated by the Matano-Boltzmann method (5) and compared with the self-diffusion coefficients of cetane (3) in Fig. 2a. The interdiffusion coefficient changes as the

increase in the concentration of the solvent by a curve with a maximum, and the self-diffusion coefficient by a monotonically increasing curve. The one-sided diffusion coefficients of cetane, calculated from equation (1), as well as the self-diffusion coefficient, increase as the solvent content increases. Within the limits of measurement error these diffusion coefficients coincide in magnitude. In Fig. 2b, for comparison, the curves $\lg D - \varphi_s$ are shown by dashed lines and $\lg D^* - \varphi_s$ by solid lines at 24 and 48°.

Satisfactory agreement between the one-sided and self-diffusion coefficients cannot be considered accidental. According to the statistical theory developed for regular solutions, the interdiffusion coefficient can be represented as the product of two factors, one of which takes into account the deviation from ideality, and the other the individual mobility of the molecules of the component

[Fig. 1 and Fig. 2]

Fig. 1

Fig. 2

Fig. 1. Concentration distribution curves along the diffusion coordinate for the polyisobutylene—cetane system. 24°. 1 –90 min, 2 –120 min, 3 –154 min

Fig. 2. Dependence of the logarithm of the self-diffusion coefficients of cetane (4, 5, 6) and of the interdiffusion coefficients (1, 2, 3) of the polyisobutylene —cetane system on composition. 1, 4 –24°; 2, 5 –40°; 3, 6 –48°. Below: dependence of the logarithm of the one-sided diffusion coefficients and of the self-diffusion coefficients (solid lines) of cetane on the composition of the system. 1 –24°, 2 –48°

$$D_v = D^* \frac{d \ln a_s}{d \ln C_s}, \tag{2}$$

where a_s is the activity of the solvent, C_s is the concentration of the solvent in g/cm^3.

To calculate D^* from equation (2), it is necessary to find the value of the thermodynamic factor. According to the Flory—Huggins theory, the activity of the solvent is equal to:

$$\ln a_s = \ln \varphi_s + \left(1 - \frac{1}{x}\right)(1 - \varphi_s) + \frac{B\bar{v}_s}{RT}(1 - \varphi_s)^2, \tag{3}$$

where $B = [(\Delta E_s/\bar{v}_s)^{1/2} - (\Delta E_p/\bar{v}_p)^{1/2}]^2$, $\bar{v}_i$ is the partial molar volume, x is the number of segments in the polymer chain, and $\Delta E_i/\bar{v}_i$ is the cohesive energy density.

After differentiating equation (3) and carrying out the corresponding transformations, we obtain the expression:

$$\frac{d\ln a_s}{d\ln \varphi_s} = (1 - \varphi_s) + \varphi_s\left[\frac{1}{x} - \frac{2B\bar{v}_s}{RT}(1 - \varphi_s)\right]. \tag{4}$$

Since the product of the solvent concentration (g/cm^3) and the partial specific volume (volume fraction of solvent) is $C_s\bar{v}_s = \varphi_s$, then $d\ln a_s/d\ln C_s \simeq d\ln a_s/d\ln \varphi_s$. Substituting expression (4) into equation (2), we obtain

$$D_v = D^*\left\{(1 - \varphi_s) + \varphi_s\left[\frac{1}{x} - \frac{2B\bar{v}_s}{RT}(1 - \varphi_s)\right]\right\}. \tag{5}$$

Since $x \gg 1$, and the cohesive energies of the solvent and polymer are close, then

$$D_v = D^*(1 - \varphi_s). \tag{6}$$

Comparing equations (1) and (6), we come to the conclusion that for athermal systems the coefficients of self-diffusion and one-way diffusion should coincide with one another. In Fig. 3 the dependence on composition is presented for the self-diffusion coefficient (solid line), calculated from formula (2) and the data of paper (8), and for the one-way diffusion coefficient of isooctane (points) for the polyisobutylene—isooctane system. The thermodynamic properties of the polyisobutylene—cetane system, unfortunately, have not been investigated; therefore the athermality of the system can only be assumed by drawing an analogy with the thermodynamic properties of solutions of polyisobutylene—cetane with solutions of other hydrocarbons of the saturated series that have already been investigated (8, 9). In the same figure, for comparison, dependences on composition are given for the self-diffusion coefficients calculated from equation (2) and experimental data taken from paper (8) (solid curve), from equation (5) (dashed curve), and for the one-way coefficient (points) for the polyisobutylene—cyclohexane system.

Fig. 3. Dependence of the logarithm of the one-way diffusion coefficients (2, 3) and self-diffusion coefficients (1, 4, 5), calculated from equation (2), on the composition of the systems: 1, 2 –isooctane; 3, 4, 5 –cyclohexane.

Thus, on the basis of comparison and theoretical calculations, one may conclude that it is possible to estimate the individual mobility of the low-molecular component in a polymer–solvent system indirectly, by measuring diffusion by an optical method.

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