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ASPECTS OF SELF-DIFFUSION OF SOLVENT IN POLYMER- LOW MOLECULAR WEIGHT SUBSTANCE SYSTEM*

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On the assumption of the independent behaviour of the holes necessary for diffusion it is shown that in the polymer-low molecular weight substance system at $T > T_g^+$ (80-100) where T_g is the glass transition point of the system, the temperature dependence of the self-diffusion coefficient D of the solvent may be described by an equation of the Arrhenius type with the activation energy constant E_D , which was also observed experimentally. It was established that fall in the self-diffusion coefficient with rise in the content of the polymer in the system is due to kinematic restrictions on the movement of small molecules. Rise in E_D with fall in the content of the solvent is due, in the main, to increase in the energy of formation of the hole.

STUDY of the translational movement of small molecules in polymer solutions by the NMR pulse method [1] revealed that the temperature dependence of the self-diffusion coefficient D in the temperature interval 20-120° is usually described by an equation of the Arrhenius type

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right), \quad (1)$$

the value D as a rule falling by several orders and the so-called activation energy of self-diffusion E_D rising with increase in the content of the polymer in the system from 0 to 0.8-0.9 parts by volume.

The aim of this work is to examine the reasons for such patterns.

The forms of dependence noted were observed on measuring D of ethylbenzene in PS solutions of different concentrations (Fig. 1). It will be seen that changes in the volumetric fraction φ_1 of ethylbenzene from 1.0 to 0.12 lead to change in the value D by ~ 4 orders. The dependence of E_D on φ_1 for the ethylbenzene-PS and the corresponding toluene-PS [2] and benzene-PS [3] systems is given in Fig. 2 from which it follows that for $\varphi_1 \sim 0.6-1.0$ the value E_D weakly depends on the content of PS but for $\varphi_1 < 0.6$ sharply rises with increase in the polymer content. Similar relations exist in phthalate-PVC systems [1] used in the work for comparison.

A general review of the process of self-diffusion is presented by Bueche [4] who considers that the molecule may diffuse in the medium in presence of a suffi

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