

SELF DIFFUSION IN SOLUTIONS OF POLYVINYL CHLORIDE AND POLYSTYRENE WITH PHTHALATES*

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The self diffusion of phthalate molecules and macromolecules has been investigated in PVC and PS solutions with low polymer contents, using a pulse NMR method. The coincidence appearing in regard to activation energies of self diffusion of the macromolecules and phthalate molecules is explained on the basis of the Frenkel theory. It is proposed that the dissolved macromolecules play the role of traps for rapidly diffusing solvent molecules. It is shown that the translational mobility of phthalate molecules in the temperature region examined is mainly determined by activated jumps. The space network in PVC gels does not influence the mobility of phthalates.

THE state and the properties of polymer-solvent systems are largely determined by the translational mobility of the molecules of both components, which has been the subject of a number of investigations [1, 2].

On a previous occasion we attempted examination of the self diffusion of molecules of phthalic acid esters in a PVC matrix with high PVC concentrations [3].

In this instance an NMR pulse method was used to investigate the self diffusion of molecules of a number of phthalates, as well as that of macromolecules, in solutions of PVC and PS with a low polymer content.

Measurements of self diffusion coefficients were carried out with the aid of an NMR spectrometer [4], using pulse gradients of a magnetic field. The temperature interval was 100-200° for PS and PVC and 20-120° for the phthalates. The solutions investigated were of PVC in dibutylphthalate (DBP) and di-octylphthalate (DOP), polymer content 0-51 mole %, and of PS in dimethylphthalate (DMP) and DBP, polymer content 0-37 mole %. The PS (commercial grade emulsion) had $M_n=95,000$. The characteristics of the other starting materials and the experimental procedure have been described [3]. The method of sample preparation was as follows. A mixture of starting materials of the required concentration was kept at a temperature of 120-160° for 0.5-1 hr, while stirring constantly, until a homogeneous solution was obtained. Solutions in the hot state were transferred into ampoules for the NMR experiments, and were sealed up.

Figure 1 shows the temperature dependences of self diffusion coefficients of phthalate molecules D_1 and macromolecules D_2 for some solutions that were investigated. It can be seen that in any system the D_1 and D_2 values differ by

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