INVESTIGATION OF THE BUTYL RUBBER – TOLUENE
SYSTEM BY THE PARAMAGNETIC PROBE METHOD

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The use of free radicals as a paramagnetic probe (PMP) yields information on the microdynamics and structure of liquids and polymers [1-3]. The PMP method can also be used to investigate concentrated solutions of polymers, since in a study of such solutions by classical methods, definite difficulties arise. In this work, solutions of butyl rubber in toluene in a broad range of concentrations were investigated by the PMP method at various temperatures. The main attention was paid to resolving the question of homogeneity of the system and the possibilities of the method in the investigation of such systems.

EXPERIMENTAL METHOD

Butyl rubber, mol. wt. 210,000, unsaturation 1.4 mole %, without stabilizer, and analytical grade toluene were used. The stable radical 2,2,6,6-tetramethylpiperidine-1-oxyl [4] was used as the probe. The butyl rubber was dissolved at \( \sim 20^\circ \). The equilibrium state was considered reached if the ESR spectrum of the radical in polymer solution was unchanged for 24 h. Depending on the concentration of the solvent, the time of reaching the equilibrium state was from 3 to 7 days. The radical was introduced into butyl rubber by

![Fig. 1](image1)

**Fig. 1.** Dependence of \( \log \nu \) on \( 1/T \) for the rotation of a radical in butyl rubber (1), in solutions containing 90, 60, 55, 50, 40, and 25% butyl rubber (curves 2-7, respectively), and in toluene (8).

![Fig. 2](image2)

**Fig. 2.** Dependence of exchange broadening \( \delta H_e \) on the radical concentration at \( \nu = 5 \cdot 10^8 \) sec\(^{-1} \): 1) pure toluene (a), butyl rubber (b), 60% solution (c), 50% solution (point I, see Fig. 1) (d); 2) 50% solution (point II, see Fig. 1); 3) 50% solution (point III, see Fig. 1).

TABLE 1. Activation Energies (E) and Preexponential Factors (v0) of the Rotation Frequencies of the Radical in Toluene Solutions of Butyl Rubber

<table>
<thead>
<tr>
<th>Butyl rubber concentration (%)</th>
<th>Temperature interval, °K</th>
<th>E 0.5 kcal/mol</th>
<th>ν0, 10^15, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>150–200</td>
<td>3,1</td>
<td>0,06</td>
</tr>
<tr>
<td>25</td>
<td>170–210</td>
<td>4,0</td>
<td>0,4</td>
</tr>
<tr>
<td>60</td>
<td>250–290</td>
<td>6,7</td>
<td>0,9</td>
</tr>
<tr>
<td>90</td>
<td>290–320</td>
<td>8,8</td>
<td>9,7</td>
</tr>
<tr>
<td>100</td>
<td>330–370</td>
<td>10,1</td>
<td>14,0</td>
</tr>
</tbody>
</table>

Diffusion from the vapors, and into the solutions by dissolution in the toluene–polymer system. The concentration of the radical in an investigation of its rotational diffusion was ≈10¹⁷ spins/cm³. The ESR spectra were recorded on the EPR-2 spectrometer of the Institute of Chemical Physics. The accuracy of thermostatic control was ±1°C. The time of correlation of rotatory diffusion of the radical was considered analogously to [2].

DISCUSSION OF RESULTS

The temperature dependences of the rotation frequency of the radical (ν = 1/τ) in the coordinates of the Arrhenius equation are cited in Fig. 1. For toluene and pure butyl rubber, as well as for solutions containing 25, 60, and 90% of the polymer, a linear dependence log ν = f(1/T) is fulfilled. For these systems the activation energy of rotation of the radical increases with increasing content of the polymer (Table 1).

For solutions containing 55, 50, and 40% of the polymer, a complex dependence of the rotation frequency of the radical on the temperature is observed (see Fig. 1). This dependence can be divided into three portions, which are characterized by an approximately linear dependence of log ν on 1/T.

On the first portion the rotation frequency decreases with decreasing temperature; in this case the Arrhenius equation is fulfilled. On the second portion an increase in ν is observed, while on the third the rotation frequency again drops with decreasing temperature. The curves are entirely reproduced both when the temperature is raised and when it is lowered in the interval 77–300°C. The absence of temperature hysteresis is evidence that the equilibrium state of the system is reached during the heating of the sample (3–6 min).

From the observable peculiarities of the temperature dependences of the rotation frequencies of the radical probe it follows that a drop in the mutual solubility in the butyl rubber–toluene system, containing 40, 50, and 55% of the polymer, begins at 225, 227, and 235°C, respectively. Since the equilibrium state is reached in a short time segment, the process of drop of the mutual solubility is evidently accompanied not by macro-, but by micro-stratification of the system. In this case, portions with an increased content of the polymer are formed in the system, as well as portions with a high solvent concentration. On account of the better solubility of the radical in toluene, it is concentrated chiefly in the portions with an increased content of the solvent, in which the local viscosity is lower than in the homogeneous solution. This explains the increase in ν on the second portion of curves 4–6 (see Fig. 1).

The decrease in the rotation frequency of the radical on the third portion of the curve is due to the fact that at all temperatures the increase in the rotation frequency associated with the microdistribution is compensated for by a decrease in ν, caused by a decrease in the temperature.

To verify the assumption of a change in the microstructure of the system, we determined the local radical concentrations at temperatures corresponding to the points I, II, and III of curve 5. In [5], it was shown that in the case of a uniform distribution of radicals, the rate constants of spin exchange (K_C) at constant τ_C for different systems (both liquids and polymers) have the same value. If the distribution of radicals is nonuniform, i.e., the local concentrations exceed the average value, then at the same τ_C the value of K_C should be larger than in the case of a uniform distribution of the radical. The ratio of K_C in the case of nonuniform and uniform distribution of the radical is equal to the ratio of the local concentrations to the average.

The rate constants of spin exchange are determined according to the exchange broadening of the lines of the ESR spectrum from the function δH_e = K_e C, where δH_e = δH_e0 – δH_0 is the exchange broadening; C is the average concentration of the radical. The dependences of exchange broadening on the radical concentration for toluene, pure butyl rubber, and solutions containing 50 to 60% of the polymer are cited in Fig. 2. The exchange broadening was investigated at the same value ν = 5 · 10⁵ sec⁻¹. Constancy of ν was achieved by selection of the corresponding temperatures, which were 163°C for toluene, 328°C for butyl rubber, and 280°C for a 60% solution of butyl rubber in toluene. For systems containing 50% rubber, the selected value of ν corresponds to three temperatures: 232°C (point I), 220°C (point II), and 188°C (point III) (see Fig. 1). Moreover, in the pure solvents and polymer, in a 60% solution of butyl rubber in toluene and a 50% solution