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Impurity Size Effect on Self-Diffusion in Plastic Crystals of *d*-Camphor

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Mutual translational diffusion of *d*-camphor host molecules and molecules of three different types of nitroxide radicals is considered. It is shown that when an impurity has a similar size and shape to the molecules of the host crystals, quenching of self-diffusion of the host molecules around the impurity occurs.

INTRODUCTION

Recent investigations of nuclear dynamic polarization[1] and paramagnetic probe diffusion in cyclohexane[2] have indicated that strong quenching of molecular self-diffusion can take place around a radical impurity in the plastic phase. It was proposed in Ref. 2, that this results from small differences in the packing between the cyclohexane and nitroxide radicals, and occurs when the radicals are in substitutional solid solution. It is important to know how the quenching of self-diffusion is associated with the ratio of impurity to matrix molecule sizes. Nitroxide radicals are convenient for such a study since radicals of various sizes are easily introduced into the matrix.

In this note mutual translational diffusion of *d*-camphor host molecules and molecules of three different types of nitroxide radicals is considered. The scientific point this note raises has to do with the mutual translational diffusion coefficient $D = \frac{1}{2}(Dr + Ds)$, where Dr is the inherent radical translational diffusion coefficient, Ds is the translational diffusion coefficient of the host molecules. The mutual translational diffusion coefficient was found with the

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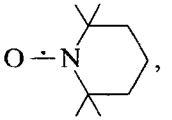
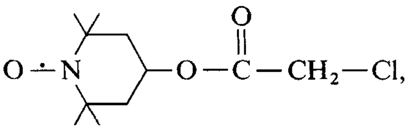
help of the theory of electron–nuclear spin transitions under molecular mobility conditions.[2] The new point the theory gives is the determination of *D* from the temperature dependence of the intensity of forbidden electron–nuclear spin transition arising from magnetic superhyperfine interactions of the unpaired electron with the nuclei (protons) of the matrix. The intensity of the forbidden electron–nuclear spin transition is primarily determined by mutual translational diffusion of radical and adjacent host molecules (at any distance away from the radical up to 4–5 lattice constants, as it follows from our estimations). So, *D* does have to mirror self-diffusion of host molecules at any distance up to 30–40 Å from the radical. Thereby a possibility is given for studying the tanslational diffusion of matrix molecules nearby nitroxide radicals based on measuring the intensity of the forbidden spin transition. In this note this possibility was used for studying the influence of nitroxide radicals on molecular self-diffusion in plastic crystals of *d*-camphor. Measurement was made of forbidden EPR transitions intensities at X-band microwave frequencies $\omega_e \pm \omega_n$ (where ω_e and ω_n are Larmor frequencies for electron and proton spins, accordingly). The inherent translational diffusion of radicals *Dr* in the matrix can be investigated (as it has been done in cyclohexane[4]) by measuring the temperature dependence of the intensity of the forbidden electron–electron spin transition in half d.c. field and spin exchange frequency, which are sensitive to inherent translational radical mobility.

EXPERIMENTAL

D-camphor of quality "pure for analysis" was used. Plastic crystal samples were prepared by slow evaporation of ethanol solutions of twice distilled *d*-camphor and the radicals:



(1)



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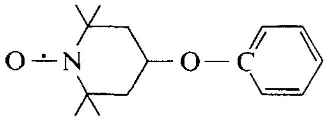

(3)

at room temperature. Following crystallization the samples were evacuated to a pressure of $\approx 10^{-4}$ mm Hg. The spectra were recorded with a "Siberia" EPR-3 spectrometer operating at X-band microwave frequency ($\approx$9.5 GHz) with 20-kHz d.c. magnetic field modulation and maximum microwave field amplitude $\approx$0.85 Oe.

RESULTS AND DISCUSSION

All samples gave well resolved hyperfine structure (HFS) triplets due to the ^{14}N nucleus of the nitroxide radical (radical concentration $C \approx 8.10^{16}$ cm^{-3}).

Samples with radicals (1) which are likely to become incorporated substitutionally had inhomogeneously broadened EPR lines and demonstrated discrete line saturation by means of double electron-electron resonance with spin-packet width $\lesssim 2$ MHz.[3] Forbidden lines intensities for samples with radicals (1) were within $\approx 2.0 \pm 1\,\%$ of the allowed HFS lines intensities over the temperature range $-25°\text{C}$–$+40°\text{C}$ (Figure 1).

Comparison of these data with computer BESM-6 calculations of forbidden transitions intensities (Figure 2) shows that the mutual translational diffusion coefficient over the temperature range covered can be expressed as $D = D_0 \exp(-Ea/RT)$ with $D_0 = 1.6 \cdot 10^{-8}$ cm^2 sec^{-1} and $Ea = 8 \pm 2$ K

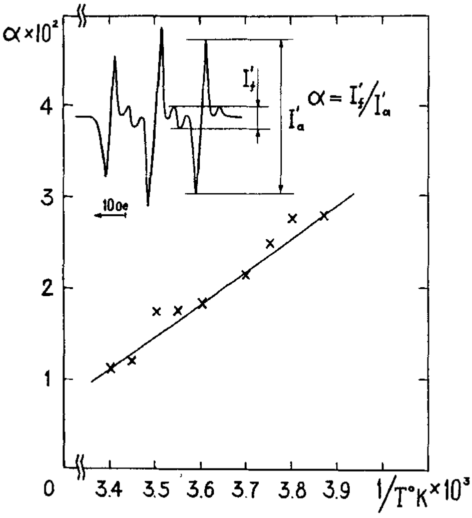

FIGURE 1 Experimental temperature dependence of relative intensity of forbidden EPR transition α of radical (1) in *d*-camphor is shown. The measurements were carried out employing an observing microwave power of ≈ 10 mW. The upper EPR spectrum of radical (1) in *d*-camphor was recorded employing an observing microwave power of ≈ 250 mW at $-25°$C.

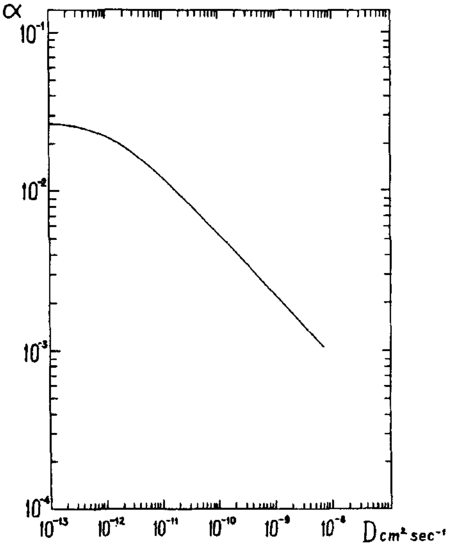

FIGURE 2 Theoretical values of α of radical (1) in *d*-camphor as a function of mutual translational diffusion coefficient D of the host molecules and radical (1) are shown.

Cal. mol^{-1}. Thus, as in cyclohexane the mutual translational diffusion coefficient of radicals (1) and host molecules of *d*-camphor is three orders of magnitude lower than the expected values for self-diffusion coefficients in plastic crystals ($\approx 10^{-9}$ cm^2 sec^{-1}).[5] As D is directly connected with translational diffusion of the adjacent host molecules it can be said with confidence that molecular self-diffusion near the radical is quenched.

For samples with radicals (2) the intensities of forbidden line-satellites were at spectrometer noise level and formed $\lesssim 0.2\%$ of the intensities of allowed HFS lines. Calculations show that such small intensities of forbidden transitions correspond to mutual translational diffusion coefficient $\gtrsim 10^{-10}$ cm^2 sec^{-1}.

Furthermore, the intensities and shapes of the allowed HFS triplet lines correspond to a radical (2) rotation frequency $\approx 2.7 \cdot 10^{10}$ sec^{-1}. In our opinion, during crystallization radicals (2) become trapped in extended defects in the crystal (dislocation centres, inter-microcrystalline cracks, etc.), where their rotational and translational diffusion is less closely connected with diffusion of the matrix molecules in the bulk. In these defects mutual diffusion is sufficiently rapid to decrease the intensity of forbidden transition.

Samples with radicals (3) demonstrated allowed triplet spectra corresponding to radical rotational correlation times $\approx 10^{-9}$ sec. For these samples we could not observe forbidden lines. The shape of the asymmetrical radical (3) is quite different from that of the *d*-camphor molecule. Thus, radicals (3) can be incorporated only in very large defects e.g. grain boundaries. It is reasonable to conclude that the rotational correlation time of radical (3) and the translational correlation time of surrounding camphor molecules will be of the same order ($\approx 10^{-9}$ sec). Then the translational diffusion coefficient of the surrounding plastic crystal molecules near radical (3) is $\approx 10^{-6}$ cm^2 sec^{-1} as expected for grain boundary diffusion.

We conclude that when the impurity size is appreciably different from the host molecule, the impurity molecules become incorporated in defects and do not strongly affect self-diffusion.

On the other hand, when an impurity has a similar size and shape to the molecules of the host crystal substitutional solid solution occurs. This leads to quenching of the molecular self-diffusion around the impurity.

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