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Lattice Defects in Plastic Organic Solids 4. A Comparison of Plastic Flow and Nuclear Magnetic Resonance Studies of Self-Diffusion in Camphene†

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Abstract—A study has been made of nmr line narrowing at high temperatures for pure and impurity-doped camphene in the plastic phase. This phenomenon, which is usually attributed to self-diffusion, was found to be similar in characteristics to that observed in other plastic solids. The activation energies evaluated for the line narrowing process failed however to reflect the variations in this parameter observed for tracer self-diffusion and creep in camphene. Consequently, it is proposed that the line narrowing process in organic solids is not indicative of true self-diffusion.

Organic crystals composed of molecules of globular shape can exist in a highly plastic phase.(1) This phase which is usually cubic in habit is stable immediately below the melting point. At lower temperatures a crystallographic transition occurs to yield a less plastic phase of lower symmetry. In the high temperature phase the molecules are rotationally disordered, a fact which accounts for the characteristically low entropy of fusion (< 5 cal mol^{-1} K^{-1}) of these solids. One technique which has been used successfully to characterize this phase of matter is nmr.(2) This technique reveals that in the low temperature phase the molecules are virtually stationary in the

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crystal lattice; as a consequence the nmr line is " broad ". The onset of molecular rotation at the transition results in a sudden narrowing of the nmr line to a value characteristic of the more freely rotating molecules.

At higher temperatures, but below the melting point, a further gradual decrease occurs to a width similar to that expected for the liquid phase. It has been proposed that this latter narrowing is due to the onset of translational motion (self-diffusion) in the lattice.(3) Similar observations for metals,(4) ionic solids,(5) and rare-gas solids(6) have also been interpreted in this manner. For these other solids the evaluated self-diffusion coefficients and activation energies are in good agreement with values obtained using other techniques.(7,8)

Attempts to make similar comparisons for plastic organic solids have failed. The activation energies for self-diffusion obtained by nmr methods are in general much lower (approximately one-half) than those obtained from radiotracer and creep studies.(9) Only for one substance, adamantane, has reasonable agreement been obtained.(10) This particular study was made using the rotating frame technique(10); two similar studies for other solids have however failed to yield agreement.(11,12) Since, apart from this one study, all the results obtained by nmr methods fail to agree with those from tracer/creep studies the question arises as to whether the high temperature line narrowing for organic solids truly reflects self-diffusion or not.

Recently, it has been found that the addition of small amounts of impurity of similar molecular geometry to the host, to some plastic crystals results in marked changes in self-diffusion parameters as measured by radiotracer and creep methods.(13) These doped systems offer a method of testing the reliability of nmr as a probe for self-diffusion.

All nmr techniques yield similar results for the activation energy of the supposed translational process irrespective of their claimed reliability. For example, for cyclohexane, studies of line narrowing,(3,14) spin lattice relaxation time(14,15) and relaxation time in the local field(11,16) all yield values of the activation energy in the range 8·5–11 kcal mol^{-1} compared to 16.3 kcal mol^{-1} for a radiotracer diffusion study.(17) Since there seems to be little difference between the techniques, we chose the most readily available, line narrowing, for this test. We report the results of the effects of purity and perfection on nmr line narrowing in camphene crystals.

Experimental and Results

The starting material, reagent grade dl camphene, was analyzed by gas liquid chromatography and was found to contain $\sim 15\%$ isomeric tricyclene and $\sim 4\%$ of other impurities which were later identified as other monoterpenes. Attempts to zone refine this material were only partially successful. Some of the minor impurities were segregated to either end of ingot. The tricyclene however remained uniformly distributed through the ingot with some of the minor impurities. The centre portion was removed (Sample A). A better separation was achieved by preparative gas liquid chromatography using a 10% Apiezon L column. By repeated fractionation purer samples (B and C) were obtained. Analytical gas-liquid chromatography showed the purity of the samples to be:

Sample A—15% Tricyclene, $\sim 2\%$ other impurities.
Sample B—1.8% Tricyclene, $< 0.01\%$ other impurities.
Sample C—0.4% Tricyclene, $< 0.001\%$ other impurities.

Portions of these samples were sublimed *in vacuo* into capillary tubes and were grown as single crystals in a Bridgman type oven.(18) Larger samples of the same material were similarly grown into larger crystals for creep and diffusion studies. Experimental details of the tracer-creep study are presented in full elsewhere.(13)

Experiments to assess the segregation of impurities in the crystal samples following growth indicated that the impurities were distributed uniformly throughout the bulk of the solid. Thus the segregation coefficients are approximately unity and the impurities are highly likely to be in solid solution. This latter conclusion was substantiated by melting curves. Microscopic examination showed that the concentration of grain boundaries in all the crystals was extremely low. Dislocation concentrations were $\sim 10^4\ \mathrm{cm}^{-2}$.

Line width studies were carried out using a conventional broad line instrument with a variable temperature probe. The temperature range studied was − 45 °C to + 20 °C (approximate melting point 48–51 °C, transition point − 123 °C). Initially, experiments were carried out with the single crystals. Following this the crystals were quenched below the phase transition and allowed to warm to room temperature. This treatment produced micro-crystalline samples; further measurements were made with these.

The line shapes were gaussian for all three crystals. For the less pure samples a " spike " developed at the peak of the gaussian at high temperatures. This behaviour which has been noted previously,(19) probably results from the presence of the impurity but whether it is a molecular effect or a bulk pre-melting effect due to the presence of the impurity is difficult to assess since the poor definition of the " spike " made it impossible to determine if any increase in intensity occurred with impurity concentration.

In spite of the slight variations in line shape, the line narrowing process was identical for all samples within the experimental error.

The results for all single crystal specimens are depicted in Fig. 1 Those for the polycrystalline specimens were identical with those for the single crystals. Analysis of the temperature dependence of the exponential portion of the line narowing process yielded the activation energies quoted in Table 1.

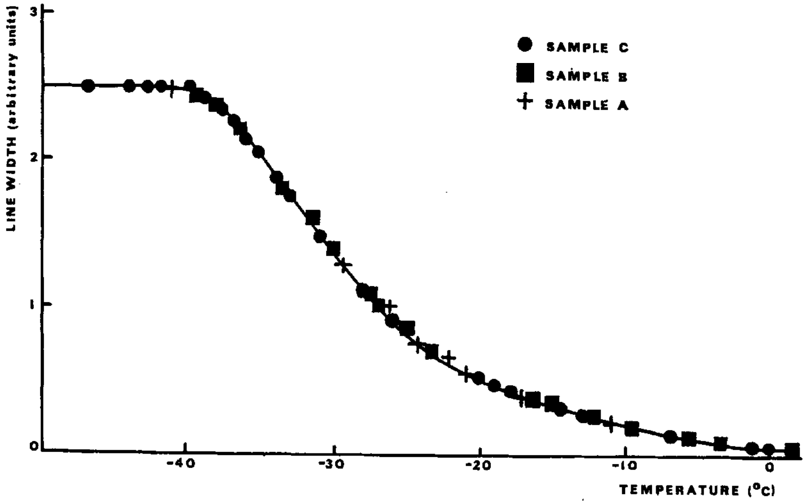

Figure 1. Graph of line width versus temperature for the three single crystal camphene samples.

TABLE 1 Activation Energies for Nuclear Magnetic Resonance Line Narrowing in Camphene (E_n) compared with those for Self-diffusion (E_d)(14) and Creep (E_c)(13)

Sample	E_c kcal/mol^{-1}	E_n kcal/mol^{-1}	E_d kcal/mol^{-1}
A	12.2 ± 0.4	11.9 ± 2	—
B	25.1 ± 1.9	11.9 ± 2	—
C	23.9 ± 1.5	11.9 ± 2	23.4 ± 0.4

Discussion

Experimental studies of self-diffusion by radio-tracer and by creep techniques have shown that the diffusion process can be markedly affected by variations in the purity and perfection of the samples used. In samples of low purity or high imperfection self-diffusion is enhanced; consequently, the values obtained for the activation energy for the process are lower than the true values. Diffusion enhancement due to line imperfections—e.g. dislocations, grain and inter-crystalline boundaries—results when the concentration of these imperfections is high and, more particularly when the bulk self-diffusion coefficient is low compared to that in the boundary. This is the situation which has been shown to exist in organic crystals such as naphthalene(21) ($D < 10^{-11}$ cm^2 s^{-1}). For plastic crystals(9,17) ($D \lesssim 10^{-7}$ cm^2 s^{-1}) this type of enhancement will only be likely where the concentration of boundaries is very high, i.e. in microcrystalline samples. Impurity enhancement can arise from two causes. The impurities can segregate in the lattice to generate dislocations and boundaries(21,22) in which case the enhancement is of the type described above. Alternatively, in those cases in which the impurity enters into solid solution an excess concentration of lattice point defects can be generated. If this concentration is greater than the thermal contribution then lower ($\sim$ 0.5 times) activation energies are observed than in the intrinsic case. This type of behaviour is noted in impure plastic crystals (Table 1) and this is the suggested cause of the variations in self-diffusion activation energy noted for succinonitrile(9) and camphene.(13) Since most of the nmr studies which yield evidence of translational motion have been performed with samples of ill-defined purity and perfection, it seems possible that diffusion enhancement as described above could have occurred. It has been suggested that such sample variations could account for the discrepancies between the results of tracer and nmr experiments,(23) the former having been carried out using single crystals.

The present experiment shows that the process which affects the nmr signal yields an activation energy which is not equivalent to that for self-diffusion even for single crystals of good purity. Furthermore, the process is insensitive to changes in purity and perfection which affect the self-diffusion process. We regard this as convincing evidence that the high temperature line narrowing process and consequently other nmr techniques do not represent true lattice self-diffusion. Since all molecular motions other than translation are well established in plastic solids at these temperatures it is pertinent to speculate on the nature of the process which could cause this effect.

Those other solid systems for which good agreement has been found between high temperature line narrowing and self-diffusion are predominantly monatomic systems. In these, self-diffusion proceeds via a vacancy mechanism which involves single atom jumps. Thus the line width is a measure of the interactions between the moving atom and its neighbours in the lattice and will be directly related to the hopping rate and hence diffusion rate of the atom. In the organic plastic crystals the situation is more complicated. It is fairly well established that the predominant point defect is a relaxed vacancy.(7,17,24) In this defect a number of molecules surrounding the vacancy will have relaxed in to share the vacancy volume and to yield a small disordered region. These relaxed vacancies will be a common feature of the pure and doped crystals. The gross transport of matter via such defects, e.g. as seen in tracer self-diffusion where these motions are integrated over long periods, will be characterized by the energies required to form and move these defects through the lattice. These energies will not be greatly dissimilar to those for a discrete vacancy.(17,23) On the other hand the nmr signal represents the process on a much smaller time scale. In addition to reflecting the long range interactions between molecules as a consequence of the diffusive jump process it will also reflect the shorter range interactions between the mobile molecules within the defect (0.1–1% of the total molecules at the melting point(17)).

Thus it could see a combination of relaxation times characteristic of the defect rather than a unique relaxation time characteristic of the translation process. The energy evaluated would then be a property of the defect rather than its motion. As in the case of monatomic solids, line narrowing would commence when sufficient molecules are undergoing motion fast enough to affect the " rigid lattice " signal. With the former, this will occur when the hopping rate (product of jump probability and vacancy concentration) is large enough; with the latter when the overall motion in the defect is adequate. That it is the nature of the defects rather than their concentration which can cause the effect can perhaps be concluded from the present experiment. If the process were concentration dependent then as we increase the number of defects by doping with impurity we would expect to see differences in the experimental results, e.g. by the onset of narrowing at lower temperatures. This is not the case. It is interesting to note in this context that studies of self-diffusion using anelastic relaxation techniques, a method which also involves measurement on a short time scale, yield activation energies which are lower than those obtained from radiotracer studies. It has been proposed that this difference could arise from the fact that more than one relaxation time is effective in the anelastic effect motions whereas these are averaged out in the longer period of the radiotracer measurements.(24)

We conclude that the current general disagreement between tracer/creep and nmr studies of self-diffusion in plastic crystals is a consequence of the nature of the defect structure of these materials and conversely can be regarded as further evidence for the existence of relaxed vacancies in these solids. The better agreement in the case of adamantane(10) could be the result of the fact that vacancies in this solid are more discrete; a fact associable both with the higher activation energy for line narrowing, the agreement with the tracer/creep studies and the high entropy of fusion of this solid (5 cal mol^{-1} K^{-1}, camphene, 2.3 cal mol^{-1} K^{-1}) which is at the upper extreme of the plastic crystalline range. Further studies to test these speculations are currently in progress.

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