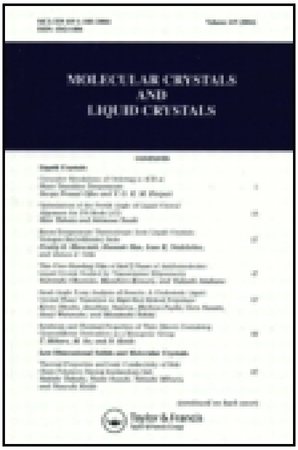

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Phase Transitions in Chlorobenzene-Cis-Decalin Mixtures: A Nuclear Magnetic Resonance, Thermal Analysis and Phase Diagram Study

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Phase Transitions in Chlorobenzene-Cis-Decalin Mixtures: A Nuclear Magnetic Resonance, Thermal Analysis and Phase Diagram Study

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Using nuclear magnetic resonance and differential scanning calorimetry we have been able to observe the molecular rotation properties of chlorobenzene-cis-decalin mixtures in their glassy, amorphous and crystalline phases. The results indicate: that in "rapidly" cooled samples the behavior of the host dominates the properties of the mixtures; that reorientation of the guest molecule is less restricted in the amorphous phase than in the glassy phase; that when the material crystallizes from the amorphous phase on warming, reorientation again becomes severely restricted. The temperatures at which these phenomena occur agree with the phase diagram that has been determined for these materials. Similar experiments on *t*-butyl chloride-cis-decalin mixtures support the above conclusions. These conclusions are in agreement with the previous dielectric studies.

INTRODUCTION

Recent studies of the dielectric behavior of polar molecules in glassy phases of non-polar molecular hosts, derived from rapidly cooled sam-

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ples, have indicated two different dielectric relaxation regions.[1-3] In addition, a recent study[1] of chlorobenzene (CB) in cis-decalin (CD) indicated a variety of phases; a very low temperature phase called the glassy phase, where molecular reorientation is restricted but to not as great an extent as in crystalline material; an intermediate temperature phase called amorphous, where molecular reorientation and diffusion is present although the material is not crystalline; and on further warming, a transition to the crystalline phase. The purpose of this study is to use the techniques of nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) to investigate these phases supplementing information from the dielectric studies. NMR, by virtue of the motional narrowing of the proton resonance line width, is a sensitive indicator of molecular motion.[4] DSC allows us to observe the thermal properties of the materials as a function of temperature. Dielectric studies are incapable of providing information about the neat non-polar host. The addition of the polar guest molecule provides a probe for studying the properties of the glassy or amorphous host. NMR suffers no such restriction. The phase diagram of CB with CD has been constructed to determine the eutectic melting temperature.

EXPERIMENTAL

Magnetic resonance studies were performed at 26 MHz using instrumentation previously described.[5] Averaged line widths are precise to within 5%. In order to study the behavior or the guest polar molecule *exclusively*, CB or *t*-butyl chloride, we used deuterated CD supplied by Aldrich Chemical Company at 99.5% deuteration. The CB and *t*-butyl chloride were also supplied by Aldrich and used as received. Samples of 25 mole % CB were placed in a thinwalled glass container in a cylindrical dewar pipe connected to a source of cold nitrogen gas. Sample volumes were approximately 0.2 ml (0.04 ml chlorobenzene).

The gas temperature was controlled by an RFL thermocouple temperature controller which controlled a preheater on the nitrogen gas to within 0.5 K. The sample temperature was measured with a copper-constantan thermocouple with ice bath reference and a digital microvolt-meter. The thermocouple was downstream from the sample and, at the coldest temperatures, may be in error, too warm, by as much as 5 K. The lowest temperatures achievable with this system were of the order of 110 K.

Thermal analysis measurements were made using a Dupont 990

Thermal Analyser in DSC mode. Crimped teflon coated aluminum pans were used and the sample mass was approximately two milligrams for the rapidly quenched specimens and eight milligrams for the phase diagram studies. In DSC mode, extended cooling thermograms are difficult to obtain, and most of the information on the glass, amorphous and crystalline transformations were obtained on warming. Two cooling procedures were used. One procedure was to allow the sample to "free" cool as quickly as possible. This permitted cooling rates of 30–40 K/min. The other technique was to quench the sample in a liquid nitrogen bath and then transfer to a precooled DSC. These "quenched" samples have cooling rates of approximately 50 K/sec. We estimate the sensitivity of the thermal analyser to be of order of 50 mJ for a first order transition with the sample volumes used.

RESULTS AND DISCUSSION

A. Chlorobenzene-cis-decalin phase diagram

The phase diagam was determined using protonated CD and CB. The samples were slow cooled at 5 K/min and invariably exhibited no "abrupt" exotherms on cooling. Warming rates were 1 K/min and slower where necessary to separate the eutectic melting from the liquidus line. No attempt was made to determine solid solubility. We see from Figure 1 that the system forms a simple eutectic mixture with composition 53 mole % CB and eutectic temperature 210 (1) K. The liquidus temperature was determined using the peak value prior to the end of melting. We estimate this value to be correct to ±2 K.

B. Neat cis-decalin

The proton nmr line width, full width at half intensity, of cis-decalin as a function of temperature is plotted in Figure 2. If the material is slow cooled (1 K/min) it supercools to 190 K, some 40 K below the normal freezing point of 230 K. (From an NMR point of view, this is simply the end of the motional narrowing, not necessarily crystallization.) A line width of 14.5 gauss is then constant to the lowest temperature of 114 K. On warming, the line width is reasonably constant up to the normal melting point. However, if the sample is rapidly cooled (30–35 K/min) through the normal freezing point, the line width behavior on warming is completely different and is also illustrated in Figure 2. From the lowest temperature, the line width DECREASES in a monotonic fashion reaching a minimum of 5 gauss near 155 K. There is then

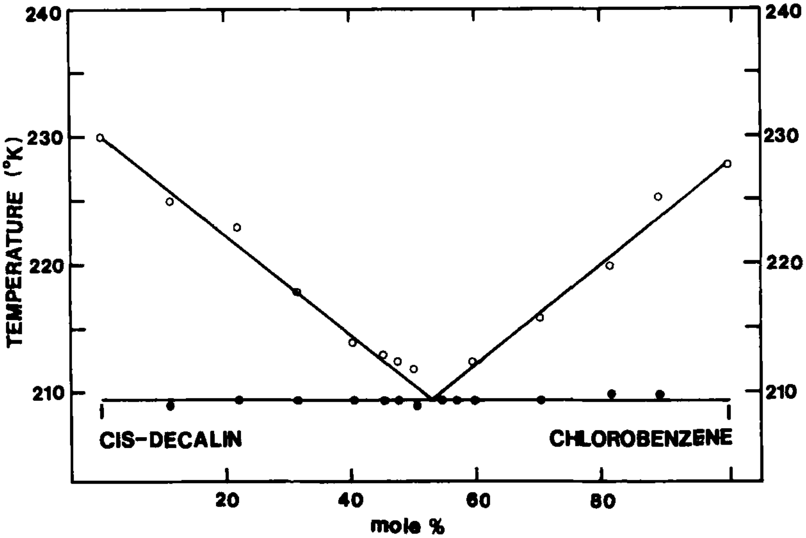

FIGURE 1 Phase diagram of chlorobenzene-cis-decalin. ●—eutectic melting; ○—liquidus termination (see text).

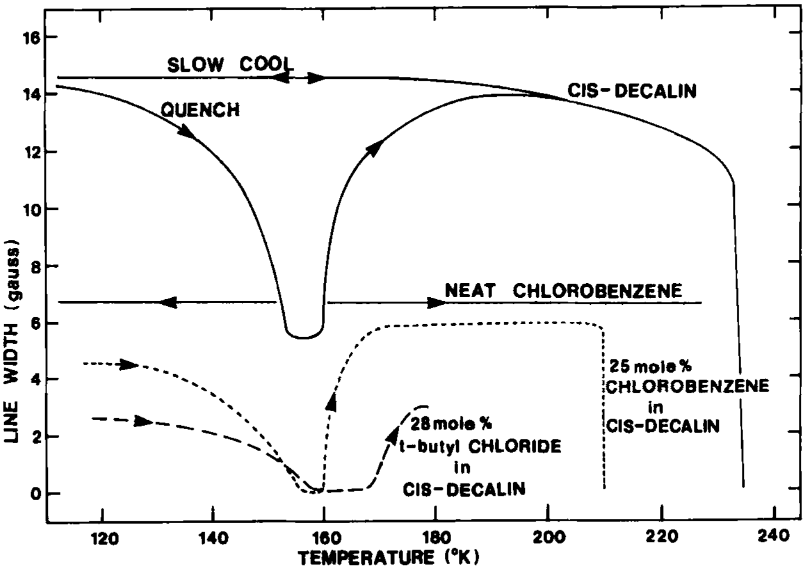

FIGURE 2 NMR line width vs. temperature. Curves are "smoothed" data.

an abrupt rise in the line width near 160 K and it returns to the "normal" value of 14.5 gauss. If the warming process is interrupted after crystallization and the sample returned to 115 K, subsequent warming shows no evidence of this line width reduction. Temperature cycling below the crystallization temperature shows a completely reversible line width variation.

The thermal analysis of rapidly cooled neat CD (22 K/min) show no exothermic freezing. On warming there is a tendency for the baseline to rise (exothermic) starting near 135 K and continuing to 212 K. The baseline then returns to normal till the melting point is reached at 230 K, where the sample gives rise to an exceedingly sharp endotherm. On "quenched" samples (50 K/sec) this behavior, shown in Figure 3, is reproduced with the exception that a sharp exotherm on warming ap-

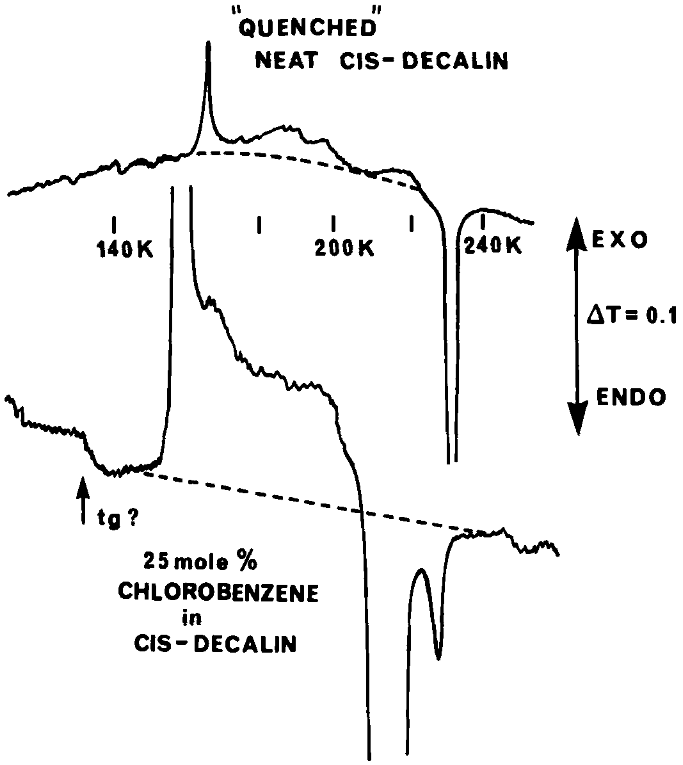

FIGURE 3 Thermograms for "quenched" neat cis-decalin and 25 mole % chlorobenzene in cis-decalin. Warming runs only. Dashed curve is baseline estimate in region of interest.

pears at 163 K. We see no indication of a glass transition as described by Johari.[6] These results will be summarized after the next section on 25 mole % CB in CD.

C. Neat chlorobenzene and 25 mole % chlorobenzene in cis-decalin

The NMR line width behavior of neat CB was independent of thermal history and is shown in the lower part of Figure 2. Slow cooling and quenching both yield a low temperature line width of 6.7 gauss, with a supercooling of some 10 K below the normal freezing point of 227 K. On warming, the line width was constant at this value up to the normal melting point.

The line width behavior of 25 mole % CB in CD-d_{18} is also illustrated in Figure 2. Quenched samples (30–35 K/min) show a proton line width of approximately 4.5 gauss, somewhat smaller than the neat material. On warming the line width DECREASES to zero (motionally narrowed to the homogeniety of the magnetic field) at a temperature of 155 K. Near 160 K there is an abrupt rise to a value near 5.5 gauss, close to the value appropriate to the neat material. On further warming, the line width remains constant with the first evidence of motional narrowing at 212 K, close to the eutectic temperature of 210 K.

The thermal behavior of 26 mole % CB in protonated CD, shown in Figure 3, is a good deal more dramatic than neat CD, and apparently independent of thermal procedure, rapid cooling and quenched samples yielding the same results. On warming at 5 K/min, we see evidence of an endothermic offset in the baseline at 136 K, which is presumably the glass transition described by previous authors.[6,7] There is an abrupt and large exotherm on further warming at 158 K where most of the material apparently crystallizes but with continuous exothermic offset up to about 205 K. At the eutectic temperature of 210 K there is a large endotherm and a liquidus "tail" which terminates at 228 K.

These data on neat and doped CD are in good agreement with the previous dielectric experiments of Mansingh *et al.*[1] They indicate that in rapidly cooled CD, a glassy phase is formed at the lowest temperatures which restricts the motion of both guest and host molecules. This restriction is not quite so great as in the crystalline phase since the CB proton line width in this phase is less than its line width in the crystallized mixture. On warming there is a gradual transition to an amorphous phase (150 K) where the molecular motion persists for about 10 K°. In this phase CB is not only reorienting but diffusing as well. Temperature recycling below 160 K provides a completely reversible change in the line width. On further warming there is a transformation to the crystalline phase (above 160 K) where once again, motional processes are restricted. The observation that the proton NMR line width of the guest molecule in CD-d_{18} "tracks" the behavior of the neat material suggests that it is the host material that determines the behavior of the mixture. Such a conclusion is not possible from dielectric studies alone because CD is non-polar.

It has also been possible to observe the deuteron NMR in the doped CD-d_{18}. Whenever the molecule is not undergoing rapid reorientation, there will be a time average quadrupole coupling from the C–D bond which will severely broaden the resonance. However, rapid reorientation will average this quadrupole coupling to zero. In a temperature scan we only observe a deuterium resonance, motionally narrowed, in the liquid phase and that narrow temperature range 150–160 K, which we assign to the existence of the amorphous phase material, prior to crystallization.

D. 28 mole % *t*-butyl chloride in DC-d_{18}

In order to investigate the possibility that nearly spherical molecules may have an "easier" time reorienting in glassy and amorphous phases in contrast to planar molecules,[8] we have investigated the NMR line width behavior of *t*-butyl chloride (2-chloro-2-methyl propane) in CD-d_{18}. The proton line width of the neat material has been investigated previously. At the temperatures of interest, it consists of a constant line width of 4 gauss, constant up to 220 K where the molecule reorients and diffuses. Since the line width reduction in chlorobenzene, between the glassy and crystallized mixture, is approximately that for *t*-butyl chloride it is not possible to evaluate the proposition that nearly spherical molecules have an easier time executing molecular rotation in the glassy phase. But it does raise the question as to why the line width in the crystallized mixtures is measurably smaller than in the crystallized *neat* material. Some dimunition in the line width is expected due to the fact that the molecular neighbors are now lacking in protons with their large magnetic moment. But these neighbors would only be seen by the molecules of the surface of the grains in the eutectic mixture. But it is possible that in these eutectic mixtures, formed on warming, that we have an extremely fine grain eutectic so that the argument would be that most guests see hosts as nearest neighbors. This proposition is still under consideration.

SUMMARY

Our magnetic resonance and thermal analysis experiments support the argument that the behavior of the CD host dominates the behavior of guest polar molecules in rapidly cooled mixtures. At the lowest temperature (110 K) CD forms a glassy phase unaccompanied by any heat of crystallization. On warming this glassy phase transforms near 150 K to an amorphous phase where considerable motion of both host and guest molecules occurs. Above 160 K the material crystallizes and reorientation is once again severely restricted up to the eutectic melting of 210 K. There appears to be no time dependence to these transformations and, as long as one stays below the crystallization temperature, the glassy-amorphous transition is reversible.

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