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Solid Phase Studies of the *n*-Eicosane: *n*-Docosane System by Positron Annihilation

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Positron lifetime spectra have been obtained as a function of temperature for various solid mixtures of *n*-eicosane ($C_{20}H_{42}$) and *n*-docosane ($C_{22}H_{46}$). These compounds, when mixed in various proportions, are known[1] to form at least six distinct solid phases. Positron lifetime parameters τ_2 and I_2 have been measured in each of these phases and are found to exhibit both a temperature and a phase dependence. Comparison with crystallographic data reveals that τ_2 variations in the *n*-eicosane : *n*-docosane system depend more strongly on the lattice dimensions *a* and *b* than on the dimension *c*.

INTRODUCTION

It is well established that positron annihilation characteristics in solids can depend on the physical structure of the medium in which annihilation occurs.[2] Thus, the binary system of *n*-eicosane and *n*-docosane provides an interesting case for investigation, since it exhibits at least six distinct solid phases whose structures have been previously reported by Lüth *et al.*[1] Their recent calorimetric and x-ray crystallographic studies have shown that the two terminal solids, γ_1 and γ_2, representing the pure components are triclinic. Samples of intermediate composition may include the high temperature orthorhombic phase β_0 as well as the low temperature orthorhombic phases β, β_1 and β_2. These phases may occur separately or in various combinations, depending on the eicosane–docosane weight ratio and the temperature. Lüth *et al.*[1] have summarized their results in a detailed phase diagram (temperature vs. composition of sample). The present work examines not only the correlation of positron lifetime parameters with that phase diagram but also the relationship between the lifetime of the long-lived component τ_2 and the crystallographic data for the phases of these binary samples.

EXPERIMENTAL

The *n*-eicosane was obtained from Eastman Organic Chemicals and the *n*-docosane from Aldrich Chemical Company. Binary mixtures were prepared by melting weighed amounts of the two components and stirring the mixture thoroughly while liquid. In all twenty-six binary mixtures and the pure components were studied. Each sample was examined by differential scanning calorimetry to aid in identifying the polymorphic forms. Positron lifetime measurements were made over the temperature range from about −22°C to about 40°C, using the apparatus previously described.[3] Each positron lifetime run had a duration of about ten hours. Data were analyzed into two components using the computer program of Tao.[4]

RESULTS

Figure 1 gives the positron lifetime results obtained at 21°C for twenty-eight samples, as a function of the weight per cent *n*-docosane. Shown along the base of the diagram are the various phases expected according to Lüth *et al.*[1] The positron lifetime parameters for certain mixtures did not remain

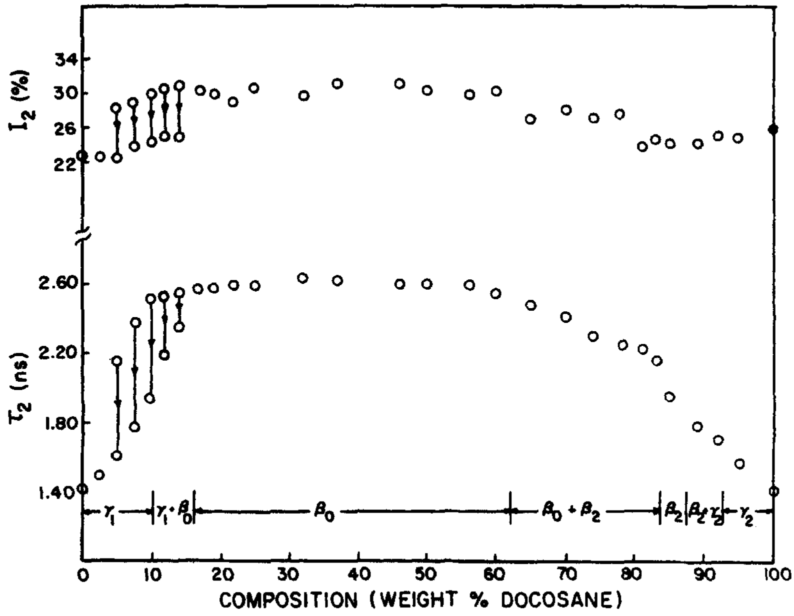

FIGURE 1 Dependence of τ_2 and I_2 on sample composition at 21 C.

constant in time, decreasing gradually over a period of days or weeks. The arrows in Figure 1 connect the initial and final values. This behavior has been discussed elsewhere.[5]

It is seen in Figure 1 that τ_2 has the same value in the pure *n*-eicosane and the pure *n*-docosane samples while mixtures of the two have a larger τ_2 value in every case. This is not surprising since the pure samples are in triclinic phases (γ_1 and γ_2, respectively) while the mixtures are either in pure orthorhombic phases or a combination of orthorhombic and triclinic phases. The τ_2 value for the high temperature orthorhombic phase β_0 is essentially independent of the particular mixture of the samples. Samples in which combinations of two phases occur, e.g., $\gamma_1 + \beta_0$, exhibit τ_2 values which lie between those observed for the pure phases. Values of I_2, the intensity of the τ_2 lifetime component, show a behavior similar to that of τ_2, i.e., I_2 has approximately the same value for all samples in the β_0 phase, is smaller for the γ_1 and γ_2 phases, and has intermediate values for phase combinations.

Figure 2 shows the results obtained at 10°C for all samples. At this temperature τ_2 has its largest value in the low temperature orthorhombic phase β, decreases somewhat for the orthorhombic phases β_1 and β_2, and decreases still further for the triclinic phases γ_1 and γ_2. I_2 values are approximately the same in β, β_1 and β_2 phases and slightly smaller for γ_1 and γ_2 phases.

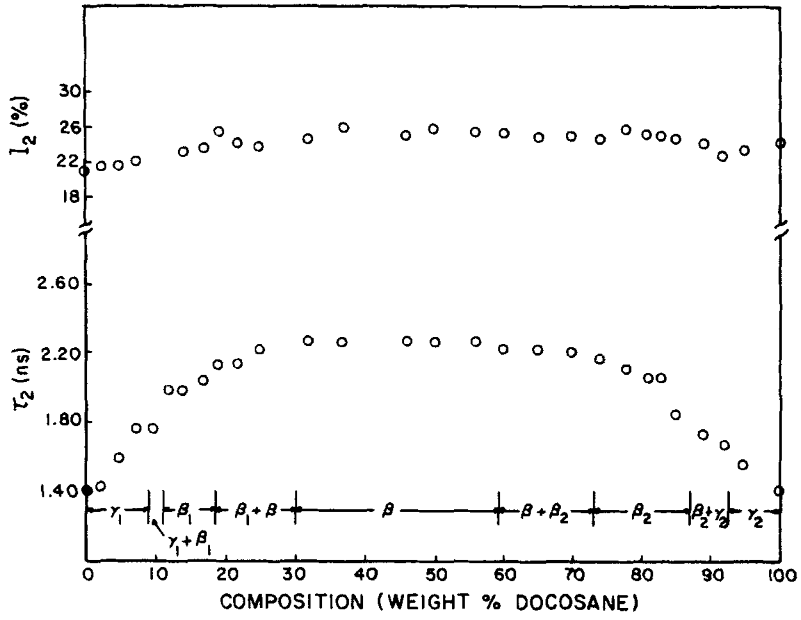

FIGURE 2 Dependence of τ_2 and I_2 on sample composition at 10 C.

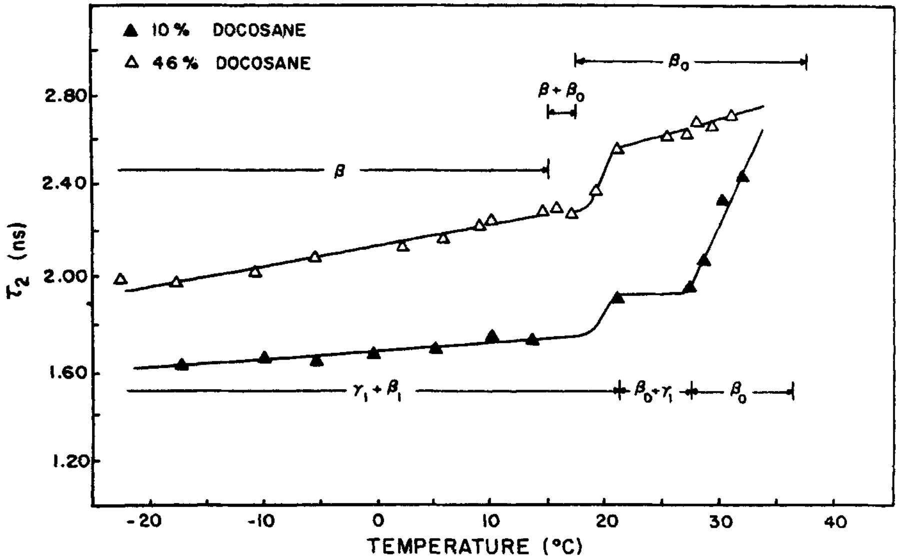

FIGURE 3 Dependence of τ_2 on temperature for samples of 10% *n*-docosane and 46% *n*-docosane.

Figure 3 gives the τ_2 variation with temperature for two of the ten solid samples for which τ_2 vs. temperature data were obtained. The various phases expected on the basis of the phase diagram of Lüth *et al.*[1] are labeled in the appropriate regions. Table I lists the transitions and the transition temperatures read to the nearest degree from that phase diagram. Also shown in the table are the temperatures at which a change was observed in the τ_2 lifetime, indicating a transition. These temperatures are also given to the nearest degree and correspond to the temperature at which a new slope of τ_2 vs. temperature was established. The transition temperatures based on positron lifetimes differ on the average by less than ± 2 degrees from those given in the phase diagram. Possible causes for these differences include the quite different heating rates employed, the large differences in sample sizes, the differences in the purity of the samples, and the fact that the transition temperatures were determined by quite different techniques in the two cases. As seen in Table I two transitions were not detected by the positron technique. Both transitions, however, belong to samples corresponding to regions of the phase diagram for which a small error in sample composition could eliminate these particular transitions.

From the τ_2 vs. temperature data a number of observations can be made.

1) τ_2 values in the triclinic phases of the pure components are indistinguishable at all temperatures investigated.

TABLE I

Comparison of transition temperatures obtained by Lüth *et al.*[1] and the present work

Sample (% *n*-docosane)	Transition[a]	Transition temperature[a] (°C)	Transition temperature based on τ_2 data (°C)
5%	$\gamma_1 \rightarrow \beta_0 + \gamma_1$	29	23
	$\beta_0 + \gamma_1 \rightarrow \beta_0$	32	30
10%	$\gamma_1 + \beta_1 \rightarrow \beta_0 + \gamma_1$	21	21
	$\beta_0 + \gamma_1 \rightarrow \beta_0$	27	27
14%	$\beta_1 \rightarrow \beta_1 + \beta_0$	18	18
	$\beta_1 + \beta_0 \rightarrow \beta_0 + \gamma_1$	21	—
	$\beta_0 + \gamma_1 \rightarrow \beta_0$	23	25
25%	$\beta_1 + \beta \rightarrow \beta + \beta_0$	15	15
	$\beta + \beta_0 \rightarrow \beta_0$	16	19
46%	$\beta \rightarrow \beta + \beta_0$	15	15
	$\beta + \beta_0 \rightarrow \beta_0$	17	21
70%	$\beta + \beta_2 \rightarrow \beta_0 + \beta_2$	17	18
	$\beta_0 + \beta_2 \rightarrow \beta_0$	24	25
85%	$\beta_2 \rightarrow \beta_0 + \beta_2$	22	—
	$\beta_0 + \beta_2 \rightarrow \beta_0 + \gamma_2$	28	26
	$\beta_0 + \gamma_2 \rightarrow \beta_0$	30	31
95%	$\gamma_2 \rightarrow \beta_0 + \gamma_2$	33	34
	$\beta_0 + \gamma_2 \rightarrow \beta_0$	39	39

[a] Lüth *et al.*[1]

2) τ_2 values in the low temperature orthorhombic phases β_1 and β_2 are indistinguishable.

3) The low temperature orthorhombic phase β has τ_2 values some ten percent higher than β_1 or β_2.

4) τ_2 values in phase mixtures of β and β_1 or β and β_2 cannot be distinguished from those in pure β.

5) Phases $\gamma_1, \gamma_2, \beta, \beta_1$, and β_2 all exhibit a slight increase in τ_2 with increase in temperature.

It is obvious that for the regions labeled β_0 in Figure 3 the τ_2 values as well as the τ_2 dependence on temperature are quite different for the two samples shown. This is in disagreement with the 21° data shown in Figure 1, which displays no dependence of τ_2 on sample composition in the β_0 phase. It was found that the τ_2 behavior as a function of temperature in the 25% and the 70% samples is practically identical with that shown in Figure 3 for the 46% sample. Thus it is likely that the β_0 phase assignment is correct in those cases. On the other hand, the samples composed predominantly of one of the compounds (i.e., the 5%, 10%, 14%, 85%, and 95% samples) exhibit considerably smaller τ_2 values as well as much stronger temperature effects (as shown in Figure 3 for the 10% sample), leading one to the conclusion that the β_0 phase assignments are probably incorrect for these samples. Since none of the other phases previously mentioned shows such a strong temperature effect, it is likely that an entirely different phase is involved here. This phase may be a hexagonal phase, since numerous reports[6–8] of such a phase just below the melting point for many pure alkanes have been published. Thus one might expect the hexagonal phase to be more likely for those samples consisting predominantly of one alkane. Lüth *et al.*[1] searched for the hexagonal phase in the *n*-eicosane : *n*-docosane system using x-ray and calorimetric techniques but were unable to establish unambiguously its presence.

The I_2 data as a function of temperature also support the proposal above concerning the hexagonal phase since, for example, I_2 values as well as the I_2 dependence on temperature are considerably different for the 10% and the 46% samples in the region expected to correspond to phase β_0. I_2 data for the other samples are also consistent with this interpretation.

DISCUSSION

Variations in τ_2 and I_2 in the solid binary system of *n*-eicosane and *n*-docosane must be attributed to structural changes in the crystalline lattice since each component has essentially the same positron annihilation characteristics when examined separately. Due to the similarity of these compounds one cannot attribute τ_2 or I_2 variations to chemical structural changes or changes in chemical functional groups.

Upon comparison with the crystallographic data of Lüth *et al.*[1] it appears that τ_2 variations in the *n*-eicosane : *n*-docosane system depend more strongly on the lattice dimensions *a* and *b* than on the dimension *c*. This conclusion is supported by the following:

1) *n*-eicosane and *n*-docosane have essentially the same triclinic structure with the same *a* and *b* dimensions, but different *c* dimensions due to different chain lengths. τ_2 values in each of these compounds are the same.

2) The area of the (*ab*) plane increases about 85% in transforming from the triclinic phase γ_1 to the orthorhombic phase β_0. Although the exact agreement is certainly fortuitous, τ_2 also increases about 85% during this change. Since the triclinic phase γ_1 is based on one layer of molecules while the orthorhombic phase β_0 is based on two layers of molecules, one must use half the *c* parameter of the β_0 phase when making comparisons with the γ_1 phase. This interlayer periodicity increases only by about ten percent in going from γ_1 to β_0.

3) There is virtually no change in dimension c in passing from the low temperature orthorhombic phases (β, β_1, and β_2) to the high temperature orthorhombic phase (β_0), but the area of the (ab) plane increases about 3%. τ_2 increases about 10% at this transition.

4) The c dimension of the orthorhombic phase β_0 increases monotonically with increasing percentage of n-docosane, yet τ_2 remains essentially constant for all compositions of the β_0 phase. (See Figure 1).

On the other hand, I_2 apparently does depend somewhat on dimension c since n-docosane with its larger c value exhibits a larger I_2 value than n-eicosane.

The fact that τ_2 values in the orthorhombic phases β_1 and β_2 are the same is not surprising since Lüth *et al.*[1] found phases β_1, β_2, and β to be indistinguishable on the basis of x-ray powder photographs. However, the fact that β can be distinguished from β_1 and β_2 by the positron technique is unexpected.

In conclusion, positron lifetimes have been shown to be quite sensitive to the multiple phases of the binary system consisting of n-eicosane and n-docosane. Changes in the long lifetime τ_2 have been found to be at least qualitatively related to changes in the area of the (ab) plane of the crystalline lattice. Since τ_2 is the reciprocal of the rate at which triplet positronium is "picked off" by electrons of the lattice, the results of this work agree with the expectation that longer lifetimes will occur when the local electron density is decreased due to lattice expansion.

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