CORRELATION BETWEEN VISCOSITY AND POSITRONIUM LIFE-TIMES FOR SIMPLE MOLECULAR LIQUIDS

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ABSTRACT

The life-times of positrons in n-octane and n-hexadecane are measured at different temperatures. The viscosities and densities are shown to be correlated with the life-times on the basis of the free volume model. Similar data for n-alkanes and chemical isomers are interpreted in terms of this model.

INTRODUCTION

IT is well known that the life-time spectra of positrons annihilating in molecular materials exhibit a delayed component, τ_2, which has been attributed mainly to *ortho*-positronium atoms decaying by the pick-off process. A free volume model for the formation and decay of *ortho*-Ps atoms in molecular materials has been reported earlier[1,2] to explain the experimentally observed correlation between the value (τ_2) and the intensity (I_2) of the delayed component. The concept of free volume is important in this context, because the formation of Ps atoms, even if energetically possible, will contribute to the delayed component, only if the Ps atoms are stable in the medium for a time longer than $1 \cdot 5 \times 10^{-10}$ secs. The relative stability of the Ps atom of near thermal energy, diffusing through the medium is enhanced if the material has a number of regions of low electron density, called sites or cavities, where the Ps atom preferentially stays.[3] Thus the free volume and its distribution into sites govern the pick-off rate of *ortho*-Ps atoms and the intensity of the delayed component in a given molecular material.

In a volume V of the material, let V_{exc}, the excluded volume, be the volume actually occupied by the molecules. Let the free volume V_f, given by $(V - V_{exc})$, be distributed into sites having volumes ranging from v' to v'',

such that for any v_i in this range, the number of sites is n_i (v_i). Since the decay probability, λ_2, and the probability of Ps formation, $4/3\ I_2$, are statistical quantities, the volume distribution of sites may be averaged so as to get $n = \sum\limits_{v'}^{v''} n_i\ (v_i)$, where n is the number of sites each of average volume $v = V_f/n$. Thus the actual distribution of sites in a material is replaced by one in which n sites, each of average volume v, are distributed uniformly through the volume of the material. The Ps atom interacting with the excluded volume associated with the site or cavity results in the pick-off process. Since the excluded volume per cavity is related to the molecular volume vm, τ_2 depends upon v and v_m.

It has been shown empirically that for molecularly simple liquids like n-alkanes, the viscosity, η, is related to v_f/v_m where v_f is the free volume per molecule. The self-diffusive motion of the molecules in such a simple liquid may be compared with that of a Ps atom through the free volume distributed into sites, and interacting with the excluded volume. It is, therefore, interesting to look for a correlation between viscosity and the life-times τ_2, in simple liquids like n-alkanes. In this paper the measurements of τ_2 at various temperatures in n-octane and n-hexadecane, two members of the n-alkane series, are reported. The observed correlation between the variation of τ_2 and viscosity with temperature is discussed on the basis of the free volume model.

Experimental Set-Up

The liquids were degassed in order to eliminate the effect of dissolved oxygen on τ_2. The liquid in a pure form was frozen in a glass tube and was pumped to high vacuum. It was then allowed to melt in vacuum and frozen again and the gases liberated in the process were pumped out. This procedure was repeated several times until no gases evolved. The degassed liquid was transferred in vacuum to the glass chamber containing the sealed positron source, Na^{22}, and a thermocouple for measuring temperatures. This glass chamber sealed under vacuum was sandwiched between two scintillation detectors, and the life-time spectra were obtained by the standard technique of slow-fast coincidence using a multichannel analyser as reported earlier.[1] The process of degassing is necessary[4] as the occluded gases, especially oxygen, may give quite erroneous results for τ_2 and its variation with temperature. For example, it was observed that for degassed n-octane at 25° C, τ_2 was 3·6 n. secs, while that for the sample exposed to air was 2·4 n. secs. Similarly, degassing changes the value of τ_2 from 2·6

n. secs. (before degassing) to 3·2 n. secs. (for degassed sample) for *n*-hexadecane.

RESULTS

The measurements of the delayed component, τ_2, at different temperatures from $- 20°$ C. to $+ 55°$ C. in *n*-octane are given in Table I and Fig. 1. This liquid begins to boil at about 65° C. in vacuum. Several spectra were taken to reduce the statistical errors in τ_2 and I_2. The values of fluidity, $1/\eta$, shown in Table I, are obtained by interpolation from the data on viscosity of *n*-octane at different temperatures available in literature.[5] It is seen that both τ_2 and the fluidity, $1/\eta$, increase with increasing temperature. For degassed *n*-hexadecane, τ_2 was measured at various temperatures from 25° C. to near its boiling point in vacuum ($\sim 180°$ C.). These results along with the values of fluidity listed in Table II and Fig. 1 show that both τ_2 and fluidity increase with increasing temperature. The values of $1/\eta$ were obtained by interpolation from the values given by Doolittle.[6]

TABLE I

n-*Octane*

Temperature (°C.)	τ_2 (n.sec.)	Fluidity, $1/\eta$ (poise)$^{-1}$
−20	$3 \cdot 1 \pm 0 \cdot 1$	116·3
25	$3 \cdot 6 \pm 0 \cdot 1$	196·1
35	$3 \cdot 8 \pm 0 \cdot 1$	217·4
45	$3 \cdot 9 \pm 0 \cdot 1$	243·9
55	$4 \cdot 1 \pm 0 \cdot 1$	270·3

The intensity (I_2) for both *n*-octane and *n*-hexadecane was found to be constant within experimental errors, at all the temperatures. This is consistent with the observation of Wilson *et al.*[7] that I_2 remains essentially constant for liquids, when their free volume is varied by external pressure. The observed intensity $I_2 = (30 \pm 2)\%$ for both these liquids agrees fairly well with the values reported in literature.[4]

The measurements of τ_2 were made with the liquid sample in an eva-
cuated and sealed glass tube. The liquid was therefore under low pressure
of its saturated vapour. The compressibility of n-octane at room tempera-
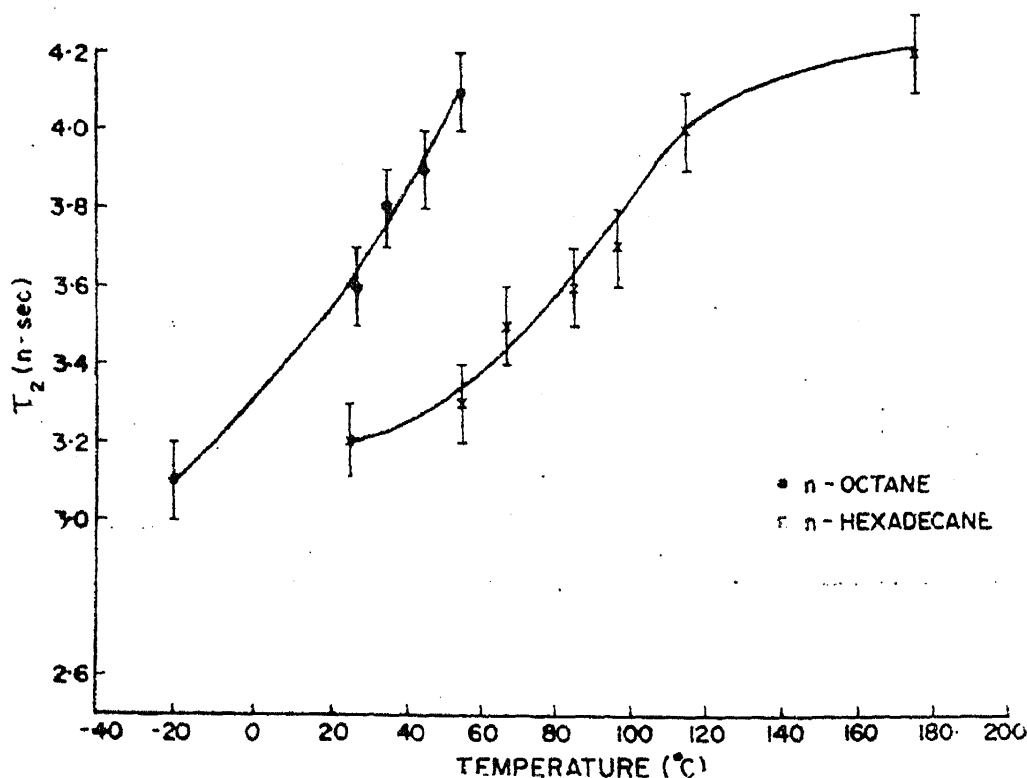ture is $\sim 10^{-4}$ per atmosphere while its coefficient of thermal expansion is

Fig. 1. Plot of observed τ_2 *versus* temperature for n-octane ( ), and n-hexadecane (X).

$\sim 10^{-3}$ per °C. Hence the increase in the free volume of the liquid sample
due to reduction of pressure from one atmosphere to that of saturated
vapour is very small, being equivalent to the increase in free volume pro-
duced by heating the liquid through less than 1° C. Thus the changes in
the free volume of the liquid due to evacuation and due to the variation in
the saturated vapour pressure at different temperatures can be neglected
in comparison to those produced by thermal expansion.

Discussion

In the free volume model reported earlier[1,2] the pick-off rate λ_2 was
related to v by

$$\lambda_2 = \lambda_1 \exp. - \left(\frac{v - v_1}{v_0 - v}\right)$$

where v_1 and v_0 are respectively the lower and upper limits of v. If the
three photon events from *ortho*-Ps atoms are neglected in a condensed

medium where there is a considerable quenching of the *ortho*-Ps atoms, *i.e.*, if λ_3 is neglected in comparison to λ_2, we can write

$$\tau_2 = \tau_1 \exp. \left(\frac{v - v_1}{v_0 - v} \right) \tag{1}$$

where

$$\tau_1 = \frac{1}{\lambda_1} \text{ is a constant} = 0 \cdot 7 \text{ n. secs.}$$

TABLE II

n-Hexadecane

Temperature (° C.)	τ_2 (n.sec.)	Fludity, $1/\eta$ (poise)$^{-1}$
25	$3 \cdot 2 \pm 0 \cdot 1$	$31 \cdot 2$
55	$3 \cdot 3 \pm 0 \cdot 1$	$55 \cdot 6$
65	$3 \cdot 5 \pm 0 \cdot 1$	$64 \cdot 5$
85	$3 \cdot 6 \pm 0 \cdot 1$	$87 \cdot 7$
95	$3 \cdot 7 \pm 0 \cdot 1$	$100 \cdot 0$
115	$4 \cdot 0 \pm 0 \cdot 1$	$128 \cdot 2$
175	$4 \cdot 2 \pm 0 \cdot 1$	$238 \cdot 1$

Setting

$$\frac{v_1}{v_0} = b, \text{ equation (1) can be weitten as}$$

$$\frac{v}{v_1} = \frac{1}{b} \left[\frac{b + \ln \frac{\tau_2}{\tau_1}}{1 + \ln \frac{\tau_2}{\tau_1}} \right]. \tag{2}$$

The value of b was fixed at $0 \cdot 01$ to get the parametric fit of the correlation curves for the experimentally obtained data of I_2 and τ_2.

A3a

In the condensed medium the cavities are surrounded by the molecules, of molecular volume v_m, of the medium. The life-time, τ_2, therefore depends upon the extent to which the Ps wave function is contained in the free volume of the cavity as compared to its overlap with the electrons of the surrounding molecules. The latter depends upon the molecular volume v_m, and the number of molecules enclosing the site, or the co-ordination number. τ_2 thus depends upon v, v_m and the number of molecules forming the cavity. Equation (2) shows that τ_2 is determined by v/v_1. Hence v_1 can be replaced by some monotonic function of v_m, say $f(v_m)$. Since τ_1 is a constant for all condensed molecular systems, $v_1 \, \alpha f(v_m)$. We assume that $v_1 = K_1 v_m$ where K_1 is a constant, which includes the mean electron density due to the molecule and the co-ordination number.

Equation (2) can then be expressed as

$$\frac{v}{v_m} = \frac{K_1}{b}\left[\frac{b + ln\,\frac{\tau_2}{\tau_1}}{1 + ln\,\frac{\tau_2}{\tau_1}}\right].$$

(3)

Since τ_2 depends upon v/v_m, it is interesting to compare the positron annihilation data with those transport properties of the liquids that depend upon the ratio of the free volume to the molecular volume, for example, viscosity. The suggestion, that the viscosity of molecularly simple, un-associated liquids depends primarily on free volume and that the changes in the viscosities of liquids as a function of temperature could be accounted for in terms of changes in free volume, was made by Doolittle.[6] He measured the viscosities of n-alkanes as a function of temperature and suggested for pure unassociated liquids an empirical relation[8] of the type $\eta = A \exp.$ (B v_m/v_f), to describe the linear variation of $ln\ \eta$ with temperature, where η is the viscosity, v_m the molecular volume and v_f the free volume per molecule. A is a constant and B a parameter which is constant for a given n-alkane. He has also tabulated the values of B as a function of molecular weight over the homologous series of n-alkanes.[9] Cohen and Turnbull[10] have developed these considerations theoretically. They consider the molecule in a liquid to be caged most of the time by its immediate neighbours, with an intermolecular potential of the Lennard-Jones type which is essentially constant within a central region of the cage. The diffusive motion in liquids is then effected by the redistribution of the excess volume. The free

volume model of Cohen and Turnbull provides justification for the empirical equation of Doolittle which can be written as

$$ln\ \eta = ln\ A + B\ \frac{v_m}{v_f}.$$

We now assume that the average site volume 'v' in simple liquids is proportional to v_f, the average free volume per molecule, i.e., $v_f = K_2 v$, where K_2 is a constant. Hence

$$ln\ \eta = ln\ A + \frac{B}{K_2}\left(\frac{v_m}{v}\right).$$

Substituting for v_m/v from equation (3),

$$ln\ \eta = ln\ A + \frac{b}{K_1 K_2}\left[B\ \frac{1 + ln\ \frac{\tau_2}{\tau_1}}{b + ln\ \frac{\tau_2}{\tau_1}}\right]$$

$$= ln\ A + \frac{b}{K_1 K_2}\left[B\ \frac{v_0}{v}\right]. \tag{4}$$

n-OCTANE AND *n*-HEXADECANE

Figures 2 and 3 show respectively the plots of *ln* η *versus* B v_0/v for *n*-octane and *n*-hexadecane. The values of v_0/v were calculated at each temperature from the observed values of τ_2 using equation (2). The values B were taken from the data of Doolittle,[9] while the values of η at different temperatures were obtained by interpolation from his data as stated earlier. The linear plots obtained are consistent with equation (4). It may be noted that a rise in temperature increases the free volume per molecule while v_m remains essentially constant for an unassociated liquid. According to the free volume model, the thermal expansion of a simple liquid reduces the annihilation probability, and hence τ_2 increases, as can be seen from Fig. 1 and Tables I and II.

A correlation of life-times with the density, ρ, is also worth noting for these liquids. If M is the gram-molecular weight, and v_f the free volume per molecule,

$$v_f = \frac{M}{\rho N_0} - v_m$$

where N_0 is the Avogadro's number. Since $v_f = K_2 v$

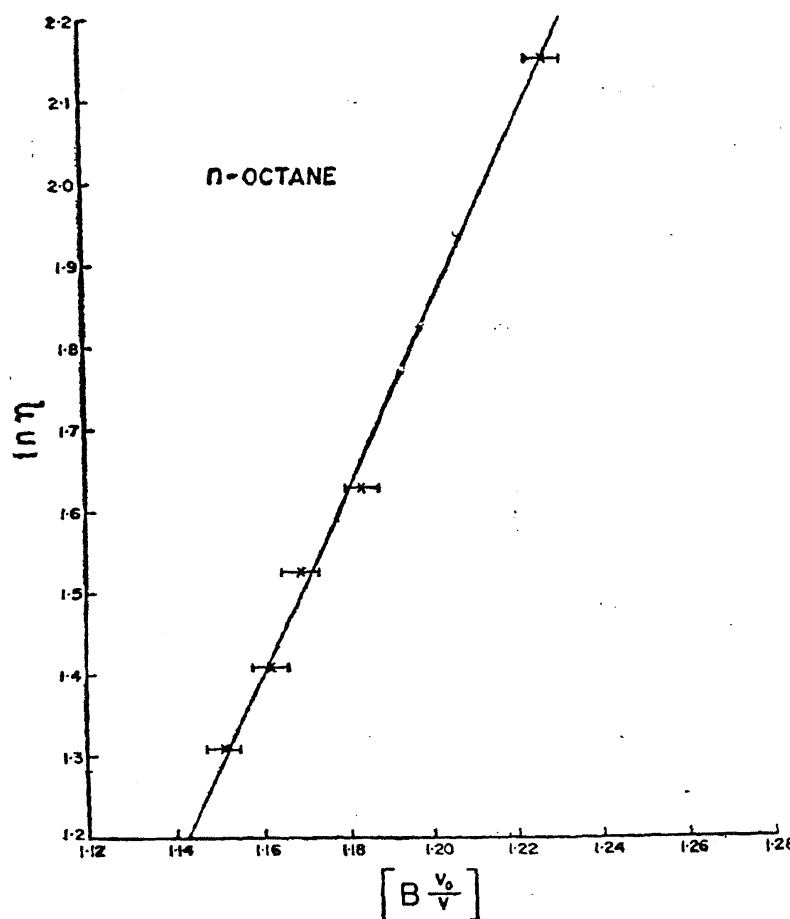$$\frac{v}{v_m} = \frac{M}{K_2 N_0 v_m} \left(\frac{1}{\rho}\right) - \frac{1}{K_2}.$$

FIG. 2. Plot of $\ln \eta$ versus $B\, v_0/v$ for n-octane (η in millipoise).

Using equation (3) for v/v_m, $1/\rho$ can be written as

$$\frac{1}{\rho} = \frac{K_1 K_2 N_0 v_m}{bM} \left[\frac{b + \ln\frac{\tau_2}{\tau_1}}{1 + \ln\frac{\tau_2}{\tau_1}}\right] + \frac{N_0 v_m}{M}$$

$$= \frac{K_1 K_2 N_0 v_m}{bM} \left[\frac{v}{v_0}\right] + \frac{N_0 v_m}{M}.\qquad(5)$$

Figure 4 shows the plots of $1/\rho$ versus v/v_0 for n-octane and n-hexadecane. The values of ρ for both these liquids at different temperatures were obtained by interpolating the data given by Doolittle,[6] and v/v_0 was calcula-

ted from the observed values of τ_2. The plots of $1/\rho$ *versus* v/v_0 are linear since all other quantities in equation (5) are constants for a given simple liquid.
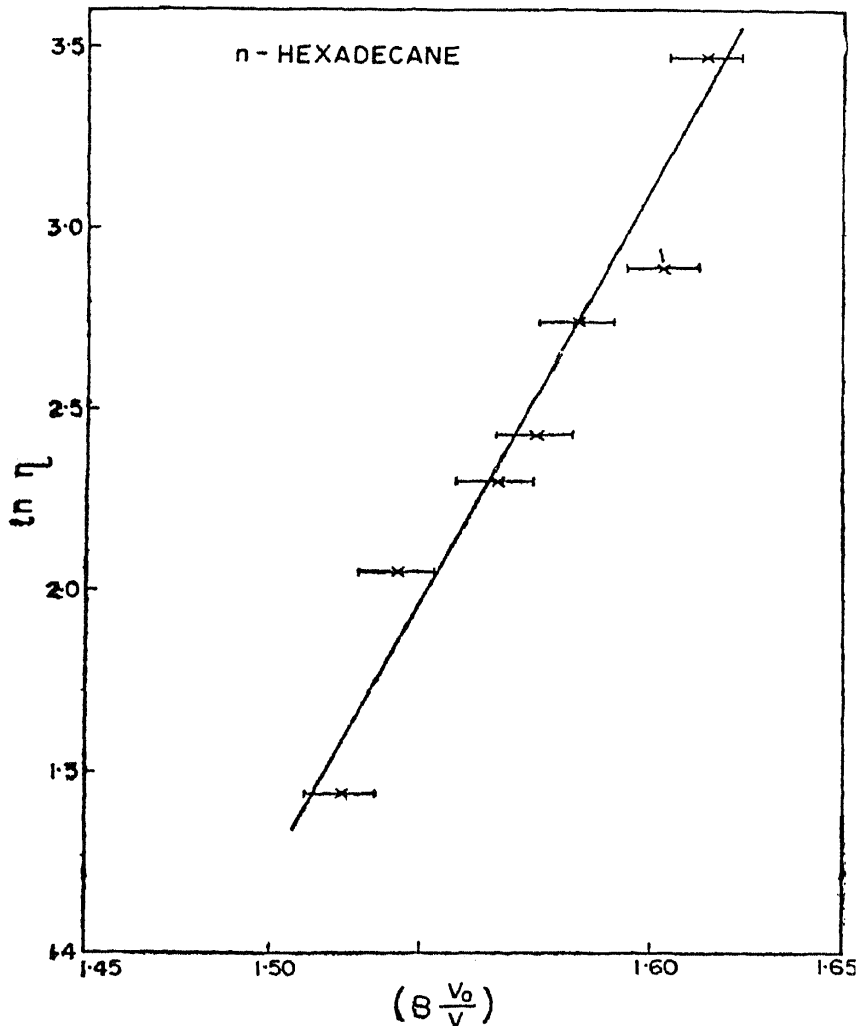

FIG. 3. Plot of *ln η* *versus* B v_0/v for *n*-hexadecane (η in millipoise).

n-ALKANE SERIES

Gray *et al.*[4] have observed that τ_2 decreases systematically along the homologous series of *n*-alkanes from *n*-butane to *n*-octadecane at room temperature. It is known that both viscosity and density which for pure unassociated liquids depend upon the free volume molecule, per increase along this series. Figure 5 shows a plot of *ln η* *versus* B v_0/v [*see* equation (4)], for *n*-alkanes from *n*-pentane to *n*-hexadecane at room temperature. The data for τ_2 is taken from Gray *et al.*[4] and the values of B tabulated by Doolittle[9] are used to compute B v_0/v. The plot shows a monotonic increase as implied in equation (4). The deviations from linearity for higher members of the series may be due to the over-simplification in the two assumptions made. A monotonic dependence of v_1 on v_m and of v_f on v was simplified into a relation of proportionality. Also the constant K_1 in the relation $v_1 = K_1 v_m$,

involving the mean electron density of the molecule and the co-ordination number, may be different for different alkanes. The deviations could also be due to correlated motions of long chain molecules, an additional factor decreasing fluidity.
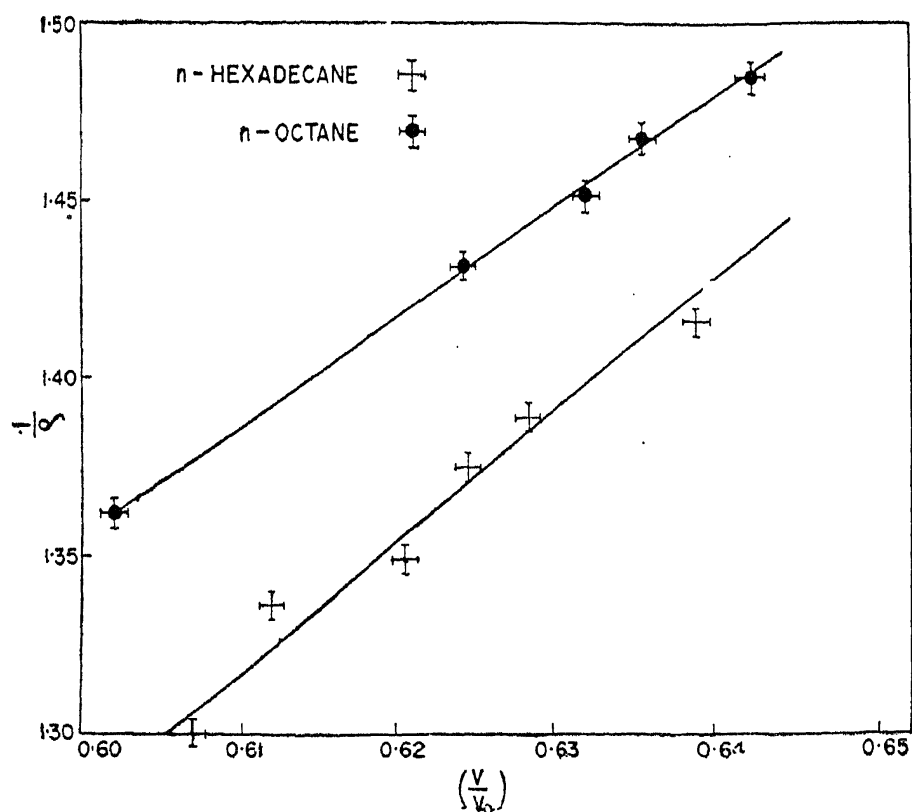

FIG. 4. Plot of $1/\rho$ versus v/v_0 for n-octane and for n-hexadecane.
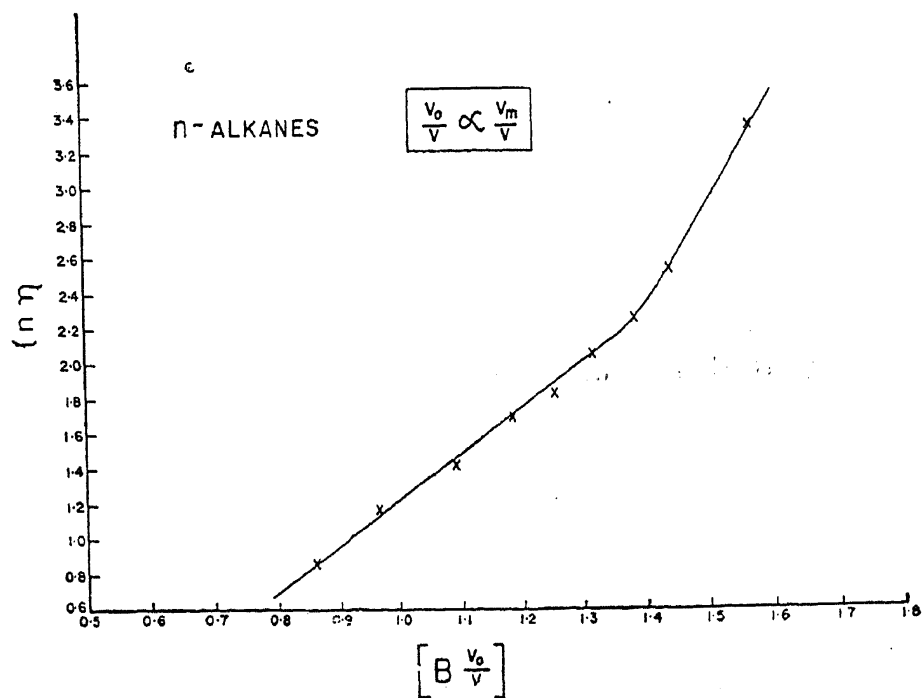

FIG. 5. Plot of $\ln \eta$ versus $B v_0/v$ for the series of n-alkanes at room temperature.

A correlation of life-times with the density for the series of n-alkanes is also interesting. For the homologous series, the molecular volume v_m may be assumed to be proportional to the molecular weight M, *i.e.*, $v_m = K_3 M$.

Equation (5) can then be written as

$$\frac{1}{\rho} = \frac{K_1 K_2 K_3 N_0}{b} \left[\frac{v}{v_0} \right] + K_3 N_0. \tag{6}$$

Figure 6 shows a plot of $1/\rho$ *versus* v/v_0 for the n-alkanes, from n-pentane to n-hexadecane, showing a linear relation between the two quantities. The correlation of *ortho*-positronium life-times with density in simple liquids becomes meaningful when interpreted on the basis of free volume.
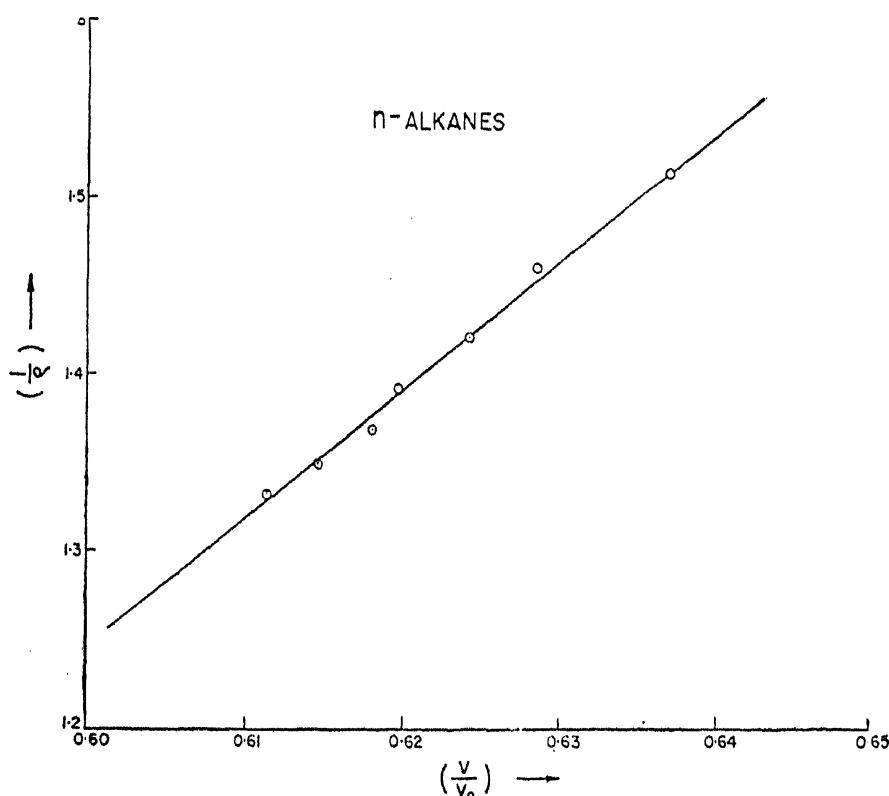

FIG. 6. Plot of $1/\rho$ *versus* v/v_0 for the series of n-alkanes at room temperature.

CHEMICAL ISOMERS

The life-time data of Gray *et al.* on chemical isomers[4] is interesting from the point of view of the free volume model. It is seen from Table III that in each isomeric system, the compound having a side branch in its molecular structure has a lower density and exhibits a larger τ_2 as compared to that for a straight chain molecule. The presence of a side branch increases the average intermolecular separation. Assuming that the molecular volumes (v_m) are essentially the same within each isomeric system, the

increases in free volume per molecule should be accompanied by an increase in τ_2, according to the free volume model.

TABLE III

Chemical isomeric systems

Compound	Structural formula	τ_2 (n. sec.)	$\frac{M/\rho}{N_0 \times 10^{24}}$ (cm.^{3})	Van der Waal's constant b (litres/mole)	v/v_0
Pentane ..	$CH_3 (CH_2)_3 CH_3$	$4 \cdot 12 \pm 0 \cdot 11$	$191 \cdot 4$	$0 \cdot 146$	$0 \cdot 643$
2-Methylbutane ..	$(CH_3)_2 CH CH_2 CH_3$	$4 \cdot 45 \pm 0 \cdot 07$	$193 \cdot 3$	$0 \cdot 1417$	$0 \cdot 653$
2, 2-Dimethylpropane	$(CH_3)_3 C CH_3$	$5 \cdot 03 \pm 0 \cdot 07$	$195 \cdot 3$	..	$0 \cdot 667$
Primary n-butyl alochol	$CH_3 (CH_2)_3 OH$	$3 \cdot 35 \pm 0 \cdot 04$	$151 \cdot 9$	$0 \cdot 1182$	$0 \cdot 614$
Iso-butyl alcohol ..	$(CH_3)_2 CH CH_2OH$	$3 \cdot 36 \pm 0 \cdot 1$	$153 \cdot 9$	$0 \cdot 1143$	$0 \cdot 615$
Tert-butyl alcohol ..	$(CH_3)_3 COH$	$4 \cdot 02 \pm 0 \cdot 08$	$158 \cdot 1$	..	$0 \cdot 640$
n-Propyl alcohol ..	$CH_3 (CH_2)_2 OH$	$3 \cdot 51 \pm 0 \cdot 16$	$124 \cdot 2$	$0 \cdot 1019$	$0 \cdot 621$
Iso-propyl alcohol ..	$(CH_3)_2 CHOH$	$3 \cdot 76 \pm 0 \cdot 03$	$127 \cdot 2$	$0 \cdot 098$	$0 \cdot 631$

It is, therefore, seen that v_f/v_m which determines the self-diffusion of the molecules in a simple unassociated liquid and hence its viscosity, η, is, according to the free volume model, analogous to v/v_m which determines the diffusion and annihilation of *ortho*-Ps atoms in the medium and hence τ_2. The dependence of τ_2 on v/v_m given by equation (3) seems to be of the right type. The data of τ_2 at different temperatures of n-octane and n-hexadecane, as well as that of Gray *et al.*, for n-alkanes and chemical isomers lend support to the free volume model for the formation and quenching of *ortho*-Ps atoms in molecular materials. In the case of associated liquids, like glycerol, where the changes in viscosity cannot be explained on the basis of changes in free volume alone, such a correlation between viscosity and life-time is not seen to hold, as indicated by our preliminary measurements in glycerol.

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