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ELECTRON DRIFT MOBILITIES IN LIQUID LONG CHAIN HYDROCARBONS

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INTRODUCTION

Major efforts have been made to study the transport properties of charge carriers in polyethylene (PE). However, the results obtained to date are contradictory and the reported mobility values for electrons in PE range over several orders of magnitude.¹⁻⁵ Most of these data were obtained from time-of-flight measurements in which a break point in the current - time curve was taken as the transit time t_d . In all these experiments there was insufficient variation of the applied voltage (V) and the sample thickness (d) to verify the relation for the mobility (μ).

$$\mu = \frac{d^2}{t_d V} \quad (1)$$

Recently, Scher and Montroll pointed out that in amorphous solids the concept of mobility breaks down and that it should be replaced by a random walk process characterized by a hopping time distribution.⁶

In recent years, a solid body of information on the mobility of electrons in liquid hydrocarbons has been gathered⁷ and the influence of the molecular structure has been established. With respect to the motion of electrons in PE, it was thought that measurements on straight

chain hydrocarbons (n-alkanes) might also yield information on the electron mobility in PE. While data have been reported for n-alkanes up to C_{10} it seemed to be interesting to extend these measurements to longer molecules. For the same reasons, measurements on molten PE should yield comparable information, since contributions of the crystalline regions would be absent.

In this paper we report electron mobilities in n-dodecane, $CH_3-(CH_2)_{10}-CH_3$ (M.P. = $-9.6^\circ C$), and n-eicosane, $CH_3-(CH_2)_{18}-CH_3$ (M.P. = $36.8^\circ C$), as a function of the temperature. Electronic transient currents were also observed in molten PE. The data with respect to the PE are preliminary and indicative of our way of approaching the problem.

EXPERIMENTAL

Excess charge carriers were generated in a parallel plate measurement cell filled with liquid by irradiating it with a short burst of high energy X-rays from a 15 MeV linear accelerator. After the pulse, a homogeneous distribution of positive ions and electrons exists. Motion of the charge carriers under the influence of an electric field and neutralization at the electrodes leads to a decay of the ionization current with time. Since the electrons move much faster than the positive ions, the current decay consists of two linear parts from which the corresponding transit times can be determined. If electron attaching impurities are present, modification of this linear decay occurs and the determination of the electron mobility under these conditions has been described previously.⁸ The current as a function of time is given by

$$i(t) = i(0) \exp(-t/\tau_a) \left(1 - \frac{\mu V}{d^2} t\right) \quad (2)$$

where τ_a is the life time with respect to attachment. The experiment consists of measuring $i(t)$ as a function of V and d and fitting it to Eq. (2) with τ_a and μ as parameters.

Cells and electronic circuits have been described previously.⁹ Liquid samples of n-dodecane and eicosane were prepared from chemically pure liquids. n-Dodecane was passed through a column of activated silica gel and then introduced into an evacuated bottle connected to the measurement cell. After degassing the liquid, the cell was filled and sealed off. Eicosane was stirred at $60^\circ C$ with concentrated sulfuric acid for several days. The acid

was replaced several times until no coloration persisted. The material was washed with distilled water and dried by passage through a column of activated silica gel. After storage in contact with a sodium mirror for several days, the cell was filled. Sometimes it was necessary to purify the samples further by preirradiation with ^{60}Co - γ -rays. Some preliminary experiments were carried out with molten PE. A granulate of high density PE free of additives was outgassed and melted in the measurement cell. The crystalline melting point of this PE was $\sim 130^\circ C$. Temperature of the molten PE was maintained constant.

RESULTS

A typical decay curve of the ionization current in n-dodecane after the application of a 5 nsec pulse of high energy X-rays is shown in Figure 1. The shape of the decay curve is non-linear although there may be an indication of a kink approximately 27 μsec after the pulse. A similar oscilloscope trace for eicosane is shown in Figure 2.

FIGURE 1 Decay of the electronic component of the ionization current after a short burst of x-rays was applied to ionize the liquid; n-dodecane, $T = 23^\circ C$, $V = 5000$ V, $d = 0.06$ cm.

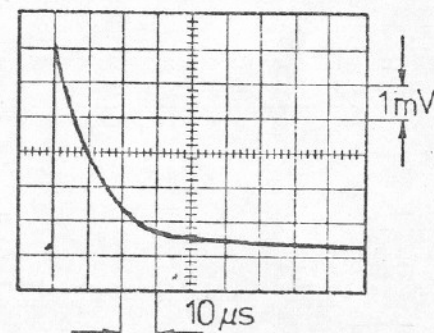
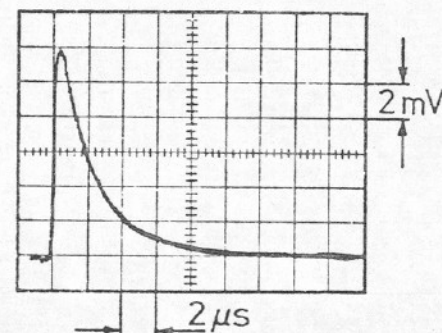


FIGURE 2 Decay of the electronic component of the ionization current in eicosane; $T = 80^\circ C$, $V = 4500$ V, $d = 0.055$ cm.



The critical influence of very small traces of impurities on the conduction process is demonstrated by Figures 3 and 4. These traces were obtained with n-dodecane at $T = 23^\circ\text{C}$ and a field strength of 83.3 kV/cm. In Figure 3, the decay is shown for the sample purified as described above. After preirradiation of the filled cell with approximately 10^5 rad of ^{60}Co - γ -radiation and subsequent degassing, the trace shown in Figure 4 was obtained. The decay time was increased by more than a factor of 10. An example for the ionic component of the current signal is shown in Figure 5. No detailed evaluation of this data was made. The mobility is in the range 10^{-3} to 10^{-4} $\text{cm}^2/\text{V}\cdot\text{sec}$. In molten PE at 170°C , a short lived transient was observed which was attributed to electrons. The decay time of approximately 2 μsec did not change with applied voltage. From this life time and the yield of electrons, taken as 0.1 per 100 eV of absorbed radiation energy, a mobility of the order of 0.1 $\text{cm}^2/\text{V}\cdot\text{sec}$ was estimated. A much longer decay of the current was observed in the same material at 220°C after it had been purified by extraction with organic solvents. An estimated mobility was a factor of 20 smaller.

FIGURE 3 Decay of the electronic component of the ionization current in n-dodecane before preirradiation; 83.3 kV/cm, $T = 23^\circ\text{C}$.

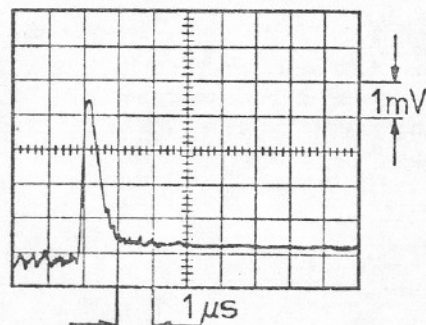


FIGURE 4 Decay of the electronic component of the ionization current in n-dodecane after preirradiation; 83.3 kV/cm, $T = 23^\circ\text{C}$.

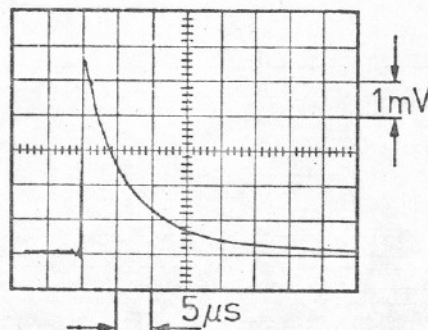
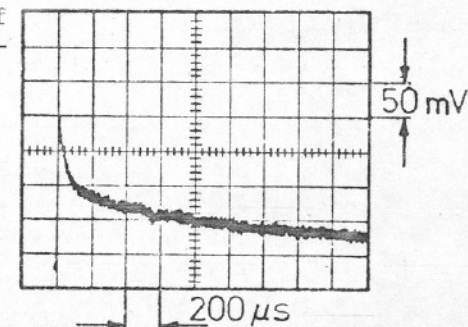


FIGURE 5 Ionic component of the ionization current in n-dodecane; 83.3 kV/cm, $T = 23^\circ\text{C}$.



DISCUSSION

Measurements of the electron mobility in liquid n-alkanes have been carried out extensively by several groups during recent years.⁷ In the temperature range studied, the mobilities reported are ≤ 1 $\text{cm}^2/\text{V}\cdot\text{sec}$; they are thermally activated, with activation energies increasing from 0.1 eV to somewhat over 0.2 eV for increasing hydrocarbon chain length. The absolute values of the mobilities at room temperature seem to level off at 0.04 $\text{cm}^2/\text{V}\cdot\text{sec}$ for $C_n > C_6$ (cf. Table 1). A similar trend is observed if the temperature necessary to give a mobility of 0.1 $\text{cm}^2/\text{V}\cdot\text{sec}$ is plotted as a function of the chain length (number of carbon atoms). Figure 6 shows the results. There is comparatively little influence of the chain length on this temperature for $n > 7$. This might indicate that the mode

TABLE 1 Electron mobility at room temperature ($T = 23 \pm 2^\circ\text{C}$) in n-alkanes and activation energies.¹¹

Liquid	$\text{cm}^2/\text{V}\cdot\text{sec}$	E_a (eV)
n-butane	0.34	0.13
n-pentane	0.15	0.2
n-hexane	0.09	0.19
n-heptane	0.046	0.17
n-octane	0.040	0.18
n-nonane	0.047	0.19
n-decane	0.038	0.22
n-dodecane	0.030	0.22

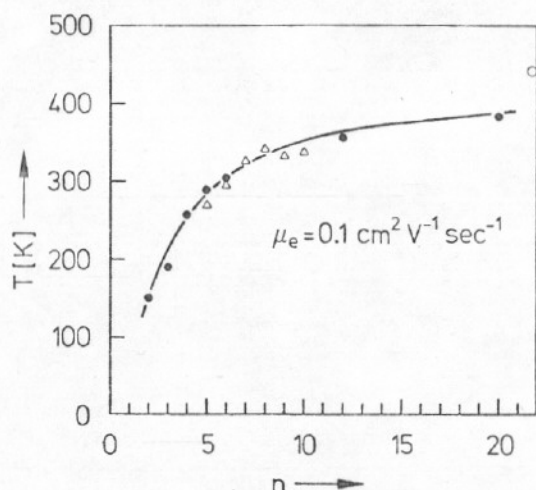


FIGURE 6 Dependence of the temperature required to obtain an electron mobility of $0.1 \text{ cm}^2/\text{V}\cdot\text{sec}$ on the length of the hydrocarbon molecule (n number of carbon atoms); data from different sources (e.g. ref. 11), $n = 12$ and $n = 20$ this work; o is the point for PE estimated in this work, $n \approx 10^4$.

of electron transport is similar in the long chain hydrocarbons.

There are essentially two models which have been proposed for electron motion in low mobility materials in which the mobility is thermally activated: (a) trap controlled band motion where the electrons are moving in a conduction band for a time τ_f and are immobilized temporarily in traps for a time τ_t ; and (b) hopping motion where electrons are thought to be localized in traps separated by potential barriers and transport occurs by jumps from one trap to another. In both models, the activation energy for the mobility is identified with the depth of the trap and the dwell time in the trap depends on the temperature as

$$\tau_t = \tau_0 \exp(E_a/kT) \quad (3)$$

τ_0 is a time related to the vibrational frequencies of the molecules and it is of the order of 10^{-13}s . Since there will be a distribution of trap depths, there will be a distribution of τ_t . In the mobility measurements we are averaging over all these times.

However, if deep traps are present in the material, loss of electrons for the electronic component of the conduction current occurs. The drift mobility is measured only if the drift time t_d is small compared to the life time with respect to trapping by deep traps τ_a , i.e. $t_d \ll \tau_a$. In pure alkanes, no deep traps are present and a mobility is well defined. The influence of electron attaching impurities can in some cases be taken into account. In comparing these results with the conditions in PE, several differences must be noted. First, at temperatures above the crystalline melting point, PE is still very viscous and exhibits properties of a glass rather than of a liquid. Second, PE cannot be prepared with the same degree of purity as that of the liquid hydrocarbons. A certain degree of unsaturation and oxidation is always present and the corresponding molecular groups (as for instance terminal vinyl groups) may provide deep trapping sites for electrons. After their generation by a short pulse of X-rays, the electrons mainly encounter shallow traps characteristic of the $-\text{CH}_2-$ skeleton of the polymer. The mobility is comparable to that of long chain hydrocarbons. With increasing time, however, they encounter deep trapping sites where they have a much longer dwell time. The mean drift velocity of the charge packet slows down, leading to a time-dependent mobility. If the life-time with respect to deep trapping is smaller than the drift time, no electrons reach the counter electrode and the current decays to zero leaving behind an immobilized space charge. For the case in which these two times are comparable, a kink in the current - time curve is observed. It is obvious that the type of decay curve observed is a function of the sample thickness and of the concentration of deep traps.

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