On Excess Electron Mobility in Liquid and Glassy 3-Methylpentane

I. Kalinowski, J. G. Rabe, and W. F. Schmidt Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, Berlin

(Z. Naturforsch. 30 a, 568-569 [1975]; received March 3, 1975)

The temperature dependence of the excess electron mobility in liquid 3-methylpentane was measured from 258 K to 371 K. The results are compared with the data obtained by Maruyama and Funabashi in the glassy state between 4.2 K and 77 K.

Electron transport in disordered systems has received much interest during recent years. The motion of excess electrons under the influence of an electric field has been investigated in many systems and the problems of evaluating the transport process have been pointed out recently 1. In liquid hydrocarbons drift velocities v_d of excess electrons were measured as a function of the electric field strength F. At low field strengths $v_d \propto F$ was found and mobilities $\mu = v_d/F$ could be defined (e.g. Ref. 2). The values obtained depend strongly on the structure of the molecules and on the temperature of the liquid. The temperature dependence could be expressed as an Arrhenius plot and activation energies of the order of 10^{-1} eV were determined. In liquids with larger activation energies the electron is assumed to exist in a localized state and transport occurs by jumps.

Of interest is the investigation of electron transport in 3-methylpentane (3MP), a hydrocarbon which forms a glass at lower temperatures. Some experiments on charge carrier transport in the liquid and glassy state have been carried out by Willard et al. 3 and by Kosa-Somogyi et al. 4.

For radiation induced charge carriers Kosa-Somogyi measured rather low mobilities which varied from 10^{-3} to 10^{-5} cm² V⁻¹ s⁻¹ in the temperature interval 295 K to 170 K. These values are characteristic of the motion of ions which were probably formed by reaction of the initially produced electrons and positive charge carriers with impurities. In 3 MP glass between 4.2 K and 77 K excess electron mobilities were measured by Maruyama and Funabashi ⁵. They found a virtually constant mobility of $0.03~\rm cm^2~V^{-1}~s^{-1}$ between 4.2 K and 35 K and a thermally activated mobility from 35 K to 77 K with an activation energy of $E_a\approx 0.01~\rm eV$. At 77 K the mobility was $0.1~\rm cm^2~V^{-1}~s^{-1}$ a value

Reprint requests to Dr. W. F. Schmidt, Hahn-Meitner-Institut, Bereich Strahlenchemie, *D-1000 Berlin 39*, Postfach 39 01 28.

which was also measured in n-hexane (an isomer of 3 MP) at room temperature.

Measurements of the electron mobility in liquid 3 MP, therefore, seemed to be of special interest and here we report the results obtained in the temperature range 371 K to 258 K. The method, the cell and the circuit have been previously described (e.g.²). Purification of the 3 MP was effected by chromatography through columns of activated silica gel, preirradiation under vacuum with ⁶⁰Co-γ-rays and degassing by trap to trap distillation under high vacuum conditions. Sometimes, however, the purity of the samples was not sufficient to enable the direct observation of the drift times and electron attachment had to be taken into account in order to obtain mobility data ⁶.

The results are shown in Figure 1. The activation energy of the electron mobility was estimated as $E_{\rm a}\approx 0.2~{\rm eV}$. The data of Maruyama and Funabashi are shown also for comparison.

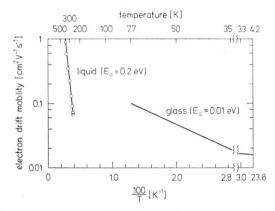


Fig. 1. Temperature dependence of electron mobility in liquid and glassy 3-methylpentane; liquid: this work; glass:

Reference 5.

As can be seen no continuous transition occurs between the electron mobility in the liquid phase and the glassy state. The mobility at 77 K is even greater than in the liquid at 258 K. The activation energies differ by a factor of 20. Maruyama and Funabashi pointed out that in their experiments only a small fraction of the electrons injected into the glass crossed the interelectrode gap and exhibited the measured mobility. The major part is assumed to be trapped in deep traps and their release occurs at times that are much longer than the time of observation in the experiment. Low electron mobilities ($\mu < 1$) in liquid hydrocarbons have been explained by a trapping model whereby the transport is thermally activated and occurs by jumps between traps $^{7, 8}$. The residence time τ_1 in a trap is long compared to the jump time and given



by $\tau_1 = \tau_0 \exp \left\{ E_{\rm a}/k_{\rm B} T \right\}.$

The residence time increases rapidly with decreasing temperature. If we assume that the average trap depth $E_a = 0.2$ is also prevalent in the glass, and τ_0 is of the order of 10^{-13} s to 10^{-15} s as in liquid ethane and propane, respectively ^{7,8}, then at 77 K a residence time of 1 s to 10^{-2} s is estimated. This is much longer than the experimentally observed time of several μ s.

¹ H. Scher, Stochastic Model of Dispersive Transient Photoconductivity in Amorphous Solids, Conf. Amorph. Liqu. Semicond., Berchtesgaden 1973.

W. F. Schmidt, Electron Migration in Liquids and Glasses, a Review, HMI-Report B 156 (1974).

 J. E. Willard, Int. J. Radiat. Phys. Chem. 4, 405 [1972].
 I. Kosa-Somogyi, L. Toth, and J. Balog, Proceedings of the 3rd. Tihany Symposium on Radiation Chemistry, Acad. Sci. Budapest 1972, p. 205. The electrons which are observed in the glassy state represent the fraction which is not captured by the deep traps. They are probably also present in the liquid phase, but their effect on the mobility measurement is completely obscured by the large fraction of electrons which exhibit the thermally activated mobility with $E_{\rm a}=0.2~{\rm eV}$. They might be detected if the mobility measurements were performed with a time-of-flight spectrometer as has been described by Meyer et al. 9 .

⁵ Y. Maruyama and K. Funabashi, J. Chem. Phys. **56**, 2342 [1972].

⁶ I. Kalinowski, J. G. Rabe, and W. F. Schmidt, to be published.

W. F. Schmidt, G. Bakale, and U. Sowada, J. Chem. Phys. 61, 5275 [1974].

⁸ G. Bakale, U. Sowada, and W. F. Schmidt, 1974 Ann. Rep. Conf. Electr. Insul. Dielectr. Phenom., Acad. Sci., Washington, D. C. 1975.

⁹ L. Meyer and F. Reif, Phys. Rev. 110, 279 [1958].