VOLUME 26, NUMBER 7

conceived hypothesis that the existence of supports in the plasma volume was responsible for most of the perpendicular loss. Numerical calculations show that the present observed decay times are $\frac{1}{2}$ to $\frac{1}{4}$ of the expected classical decay time; thus, anomalous loss may exist. The most likely cause of any additional loss seems to be a combination of the existence of magnetic field errors and fluctuations. Although our parameter range is still small, indications are that a small increase of the electron temperature does not change the decay times when the large magnetic field errors are absent. These preliminary results are quite encouraging; but, in order to decide whether an anomalous loss mechanism is still present in this levitated version of the spherator, a wider range of plasma parameters must be investigated.

*Work performed under the auspices of the U.S. Atomic Energy Commission, Contract No. AT(30-1)-1238. Use was made of computer facilities supported in part by National Science Foundation Grant No. NSF-GP579.

¹T. Ohkawa, M. Yoshikawa, and T. H. Jensen, Phys. Rev. Lett. <u>24</u>, 95 (1970).

²R. Freeman, M. Okabayashi, H. Pacher, G. Pacher, and S. Yoshikawa, Phys. Rev. Lett. <u>23</u>, 756 (1969).

³H. Forsen, D. Kerst. D. Lencioni, D. Meade, F. Mills, A. Molvik, J. Schmidt, J. Sprott, and K. Symon, in *Plasma Physics and Controlled Nuclear Fusion Research* (International Atomic Energy Agency, Vienna, Austria, 1969), Vol. I, p. 313.

⁴S. Yoshikawa, M. Barrault, W. Harries, D. Meade, R. Palladino, and S. von Goeler, in *Plasma Physics and Controlled Nuclear Fusion Research* (International Atomic Energy Agency, Vienna, Austria, 1969), Vol. I, p. 403.

⁵S. Yoshikawa, R. Freeman, and M. Okabayashi, Plasma Physics Laboratory Report No. MATT-706, 1969 (unpublished).

⁶R. Freeman, M. Okabayashi, G. Pacher, and S. Yoshikawa, Bull. Amer. Phys. Soc. 1<u>4</u>, 1032 (1969).

⁷G. Pacher, H. Pacher, M. Okabayashi, R. Freeman, and S. Yoshikawa, Bull. Amer. Phys. Soc. <u>14</u>, 1032 (1969).

⁸J. L. Johnson and S. von Goeler, Phys. Fluids <u>12</u>, 255 (1969).

Mechanism of Excess Electron Transport in Liquid Hydrocarbons

R. M. Minday, L. D. Schmidt, and H. T. Davis Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455 (Received 11 January 1971)

Stable excess electrons have been recently observed in liquid hydrocarbons after suitable purification, but the mobilities indicated the existence of short-lived electron traps in the liquids. We have measured electron mobilities in mixtures of n-hexane and neopentane and find that the mobility is given accurately by an expression of the form

 $\mu = \mu_n \exp(-x_h E/kT),$

where x_h is the mole fraction of hexane. It is concluded that the trap cannot be a negative-ion state of a single molecule, but is instead a collective trap involving several fluid molecules.

It has been observed that after suitable purification, stable excess electrons can be produced in the rare-gas liquids^{1,2} and in many nonpolar hydrocarbon liquids.³⁴ Lekner⁵ has shown that a kinetic theory proposed by Cohen and Lekner⁶ (based on the single-scattering approximation and the Boltzmann equation) provides a quantitative explanation of electron mobilities in the rare-gas liquids. In the low-field limit, the theory yields the following expression for the mobility:

$$\mu = \frac{2}{3} (2/\pi m kT)^{1/2} [e/n4\pi a^2 S(0)], \qquad (1)$$

where *a* is the electron-atom scattering length and S(0) is the long-wavelength limit of the structure factor $[S(0) = nkT\kappa_T$, where κ_T is the isothermal compressibility]. The charge carriers in the hydrocarbons, while undoubtedly electronic, generally exhibited much lower mobilities than predicted by Eq. (1) and exhibited large variations between different hydrocarbons. (At 300° K electrons in *n*-hexane and neopentane have mobilities of 0.07 and 70 cm²/V sec, respectively.) Possible explanations³ for this behavior are (1) an increased effective cross section arising from incoherent scattering in polyatomic fluids, (2) a short-lived negative-ion state, and (3) weak trapping by collective interactions in the fluids.

Recent theoretical studies^{3,7} show that, although incoherent scattering could possibly lead to mobilities on the order of one twentieth of that predicted by Eq. (1), this effect alone cannot account for the electron mobilities in hydrocarbon liquids. Thus, the possibilities of short-lived ion states and collective trapping must be considered.

We report here experiments which lead to the conclusion that of these possibilities only collective trapping is consistent with the data. We have measured mobilities of photoinjection excess electrons in mixtures of highly purified *n*-hexane and neopentane as a function of composition and temperature using an electronic double-shutter method.³ The electron mobility in this mixture has been found to be described accurate-ly by the formula

$$\mu_m = \mu_n \exp(-x_h E_0/RT), \qquad (2)$$

where x_h denotes the mole fraction of hexane, E_0 is a constant equal to 3.5 ± 0.4 kcal/mole, and μ_n is the mobility in pure neopentane.

If a free electron drifts through a liquid with a mobility μ_f and may be trapped by s independent mechanisms with trapping frequencies ν_1, \dots, ν_s and trapping lifetimes τ_1, \dots, τ_s , then the effective electron mobility is given³ by the expression

$$\mu = \mu_f / (1 + \sum_{i=1}^{s} \nu_i \tau_i)$$
(3)

if the distance the electron drifts in the trapped state is small compared to its drift distance in the untrapped state.

If the electron is trapped by single-molecule attachment, the trapping frequency should be given by an expression of the form

$$\nu_i = n_i \int \sigma_i (\epsilon/2m)^{1/2} f(\epsilon) d\epsilon, \qquad (4)$$

where n_i is the density of the molecules providing the *i*th trap, σ_i is the attachment cross section, *m* is the electron mass, and $f(\epsilon)$ is the distribution function of the electron energy ϵ . The density of a hexane-neopentane mixture is almost constant, and therefore if each species contributes one trapping mechanism, the product $\nu_i^m \tau_i^m$ for the mixture may be approximated by

$$\nu_i^m \tau_i^m \approx x_i \nu_i^0 \tau_i^0, \tag{5}$$

where x_i is the mole fraction of the *i*th component of the mixture and $\nu_i^0 \tau_i^0$ is the value of $\nu_i^m \tau_i^m$ corresponding to pure liquid *i*, $x_i = 1$. Using this assumption, Eq. (3) may be written in

the form

$$\mu_{m} = \mu_{m}^{f} / (1 + x_{n} \nu_{n}^{0} \tau_{n}^{0} + x_{h} \nu_{h}^{0} \tau_{h}^{0}), \qquad (6)$$

where x_n and x_h are the mole fractions of neopentane and hexane, respectively.

Equation (6) cannot account for the composition or temperature dependence observed for electrons in hexane-neopentane mixtures. The only quantities in Eq. (6) which may be expected to vary strongly with temperature are $\nu_n^0 \tau_n^0$ since the free-electron mobility μ_m^{f} should vary only as a low power of T.^{6,7} Moreover, from data on pure hexane and pure nopentane,³ it is clear that $\nu_h \tau_h \gg \nu_n \tau_n$ and $\nu_h \tau_h \gg 1$, so that for x_h not too small Eq. (6) becomes

$$\mu_{m} \approx \frac{\mu_{m}^{f}}{x_{h} \nu_{h}^{0} \tau_{h}^{0}} = \frac{\mu_{m}^{f}}{\mu_{h}^{f}} \frac{\mu_{h}}{x_{h}}.$$
 (7)

Since the ratio of free-electron mobilities varies slowly with temperature and composition, Eq. (7) implies that the electron mobility in the mixture has the same activation energy as the electron mobility in pure hexane and that the mobility varies as the inverse first power of the mole fraction of hexane. This is in contradiction with the empirical observations summarized by Eq. (2), wherein it is seen that the activation energy increases linearly with an increasing mole fraction of hexane.

To test Eq. (6) further, let us note that on the basis of our model $\mu_i^0 = \mu_i^f / (1 + \nu_i \tau_i)$, i = h, n, where μ_i^0 is the electron mobility in pure liquid *i*, and μ_i^f is the free-electron mobility in pure liquid *i*. Equation (6) may then be rearranged to the form

$$\mu_{m} = \frac{\mu_{m}^{f}}{\mu_{n}^{f}} \left(\frac{x_{n}}{\mu_{n}} + \frac{x_{h}}{\mu_{h}} \frac{\mu_{h}^{f}}{\mu_{n}^{f}} \right)^{-1} .$$
(8)

For dilute solutions of hexane, say, $x_h = 0.1$, it is reasonable to assume that $\mu_m^{\ f}/\mu_n^{\ f} = 1$. Moreover, on the basis of the Cohen-Lekner theory and its extension to polyatomic systems, it seems unlikely that $\mu_h^{\ f}/\mu_n^{\ f}$ would be smaller than 0.1 or larger than 10. The corresponding range of μ_m predicted is $7 \ge \mu_m \ge 0.07 \text{ cm}^2/\text{V}$ sec. The observed mobility for $x_h = 0.1$ is $35 \text{ cm}^2/\text{V}$ sec, 5 to 500 times larger than that predicted.

We therefore conclude that the composition and temperature dependence predicted by single-electron-single-molecule attachment disagrees with observations.

Collective trapping has been observed in liquid helium⁸ where the electron is localized by forming a bubble, and in polar systems such as water

and ammonia⁸ where the electron is localized primarily by the electron-dipolar medium interaction characterized by the Landau potential of the form $V(\mathbf{r}) = -(D_{obt}^{-1} - D_s^{-1})e^2/r$. The quantities D_{opt} and D_s represent the high-frequency and static dielectric constants, respectively. In the liquid hydrocarbons studied here, neither bubble formation nor polaron trapping by the Landau potential seems possible. Bubble formation requires that the energy V_0 of the bottom of the conduction band of the liquid lie above the vacuum. Using the pseudopotential theory of Springett, Jortner, and Cohen,⁹ we estimate that, relative to the vacuum, $V_0 \approx -1.8$ eV for both hexane and neopentane, a result ruling out bubble formation. Since the quantity $D_{opt}^{-1} - D_s^{-1}$ is very small (less than 10⁻²) for saturated hydrocarbons compared to its value of about 0.5 for water and ammonia, polaron trapping by the Landau potential may also be ruled out for the hydrocarbons studied here. Thus, we anticipate that an understanding of the trapping mechanism in hydrocarbons will require a much more detailed picture of the microscopic interaction between the electron and the molecules immediately surrounding it than has been used in the treatment of helium and polar fluids. A recent paper by Coleman, Kestner, and Jortner¹⁰ is a step in this direction

but at present is insufficiently developed to be of use here.

We are grateful to the National Science Foundation for partial financial support of the research reported here.

¹H. Schnyders, S. A. Rice, and L. Meyer, Phys. Rev. 150, 127 (1966).

²L. S. Miller, S. Howe, and W. E. Spear, Phys. Rev. <u>166</u>, 871 (1968).

³R. M. Minday, L. D. Schmidt, and H. T. Davis, J. Chem. Phys. <u>50</u>, 1473 (1969), and to be published.

⁴W. F. Schmidt and A. O. Allen, J. Chem. Phys. <u>50</u>, 5037 (1969), and <u>52</u>, 4788 (1970).

⁵J. Lekner, Phys. Rev. <u>158</u>, 130 (1967).

⁶M. H. Cohen and J. Lekner, Phys. Rev. <u>158</u>, 305 (1967).

⁷H. T. Davis, L. D. Schmidt, and R. M. Minday, Phys. Rev. A (to be published).

⁸For a review of trapped electrons, see J. Jortner and S. A. Rice, in Solvated Electron; A Symposium Sponsored by the Division of Physical Chemistry at the 150th Meeting of the American Chemical Society, Atlantic City, September 1965, edited by R. F. Gould (American Chemical Society, Washington, D. C., 1965).

⁹B. E. Springett, J. Jortner, and M. H. Cohen, J. Chem. Phys. 48, 2720 (1968).

¹⁰D. A. Copeland, N. R. Kestner, and J. Jortner, J. Chem. Phys. 53, 1189 (1970).

Propagation of "Cool" Pulses in Liquid He II

M. Pomerantz

IBM Watson Research Center, Yorktown Heights, New York 10598 (Received 31 December 1970)

We applied pulses of heat to liquid He and found that below the λ transition pulses of lower-than-ambient temperature propagate in the He II. This "cool" pulse is attributed to the temperature change that accompanies a compressive first-sound pulse. The temperature pulse is negative because the thermal expansion of He II is negative near the λ transition.

We have observed a phenomenon in liquid He II in which an input pulse of heat produces the transmission of a pulse of lower-than-ambient temperature. We shall refer to this as a pulse of "cool" that is transmitted through the liquid He.

The experimental arrangement was simply a heater separated by liquid He from a fast and sensitive bolometer. The heater was made of Constantan in the form of a line about 0.1 mm wide and 2 mm long evaporated onto a quartz plate. The bolometer was the kind used in heat pulse experiments¹: a superconducting alloy of 95% In and 5% Sn in the form of a 5-mm×0.1mm line evaporated onto a Si plate. It had a sensitivity >100 Ω /°K and a response time \leq 10 nsec. The two substrate plates were mounted vertically with the heater and detector lines parallel to each other, about 1 cm apart. The assembly was immersed in liquid He and the temperature was varied by pumping on the He. At temperatures below 3.4°K the detector was superconducting; but in order that it be sensitive to temperature