

Effect of molecular solutes on the electron drift velocity in liquid Ar, Kr, and Xe

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Measurements of the electron drift velocity in liquid argon, krypton, and xenon were performed in an electric field up to 100 kVcm^{-1} . At higher field strengths saturation velocities were observed in agreement with other authors. The addition of a small concentration of molecular solutes leads to an increase of the electron drift velocity above the saturation value of the pure liquid. The drift velocity either reaches a higher constant value or passes through a maximum at field strengths greater than 10^4 Vcm^{-1} . This effect was investigated as a function of solute concentration for N_2 , H_2 , methane, ethane, propane, and butane. Inelastic energy losses in collisions of electrons and solute molecules are assumed and by means of the Cohen-Lekner theory the energy dependence of the loss processes is derived.

I. INTRODUCTION

The investigation of electronic conduction in nonpolar liquids is of great fundamental and practical interest. Nonpolar liquids represent relatively simple disordered materials, and the study of the physical properties of excess electrons in these systems may be of considerable importance for the general understanding of the electronic properties of noncrystalline solids.¹ On the other hand, nonpolar liquids are used as insulators in high-voltage devices and the events leading to electric breakdown are certainly determined by the properties of the charge carriers in these liquids.² Recently liquid-filled ionization chambers and counters have been employed in high-energy particle physics, and the detailed understanding of the generation, recombination, attachment, and migration of radiation-induced electrons and positive ions is a necessary presumption for the further development of these detectors (see, e.g., Refs. 3-5).

Electron transport in liquefied rare gases has been studied for over twenty years, and the most powerful method used for obtaining information is the measurement of the drift velocity achieved by a group of excess electrons in an electric field. In low electric fields the drift velocity increases proportionally with the field strength, and electron mobilities much smaller than $1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ were obtained in liquid helium and neon,⁶⁻⁸ while mobilities over $100 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ were measured in liquid argon, krypton, and xenon.⁹⁻¹² The low mobilities were explained by a localized electron model, where, for example, in liquid helium the electron resides in a microscopic bubble of 14 \AA radius.^{13,14} In the liquids showing high electron mobility, the electron state is extended and the magnitude of the mobility is limited by elastic scattering. With increasing field strength the

electron drift velocity increases less than proportionally with the field and eventually saturates. This behavior is due to an increase of the mean electron energy by the electric field.

It has been observed already by Swan,¹⁵ Pruett and Broida,¹² and Spear and LeComber¹⁶ that addition of a small amount of nitrogen, oxygen, or hydrogen influences the electron drift velocity at higher field strengths. No detailed investigation of this effect, however, was carried out.

Here we wish to report measurements of the electron drift velocity as a function of the electric field strength in pure liquid argon, krypton, and xenon and in solutions with nitrogen, hydrogen, methane, ethane, propane, and butane. The experiments are similar to electron swarm experiments in the gas phase.¹⁷

The data are analyzed with the assumption that inelastic energy losses occur in the collisions of electrons and solute molecules, and the energy dependence of the loss process is analyzed.

II. EXPERIMENTAL

The method of drift velocity measurement, the electrical circuit, and the cells have been described in detail elsewhere.¹⁸ Excess electrons were generated by ionizing the liquid with a 5-nsec burst of 15-MeV bremsstrahlung from an electron linear accelerator. After the radiation pulse a homogeneous distribution of positive charge carriers and electrons exists between the plates of the measurement cell. Since the mobility of the positive carriers is much smaller than that of the electrons, their drift towards the respective electrodes is well separated in time scale and can be observed from the decay of the ionization current.

High-quality tank argon, krypton, and xenon (stated purity better than 99.99 vol. %) were purified further by passage through columns of acti-

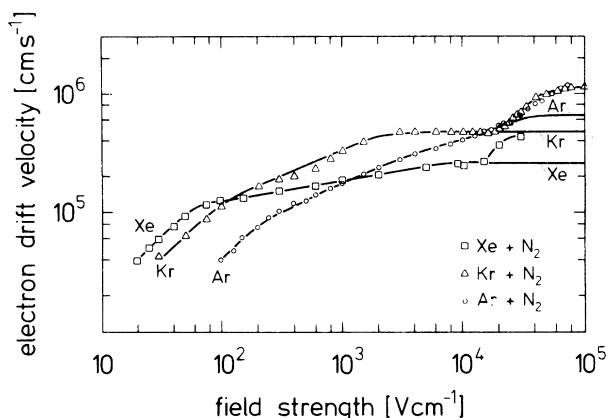


FIG. 1. Electron drift velocity as a function of the electric field strength in pure liquid argon, krypton, and xenon (solid lines) and in solutions of nitrogen in these liquids (symbols). Temperature $T(\text{Ar}) = 87$, $T(\text{Kr}) = 120$, and $T(\text{Xe}) = 165$ °K.

vated copper maintained at 350°C , a molecular sieve, and charcoal maintained at -78°C . The hydrocarbons were purified as described previously.¹⁹ Hydrogen (99.95 vol. %) and nitrogen (99.9995 vol. %) were used without further purification. Solutions of methane, ethane, propane, and butane in the rare-gas liquids were obtained by condensing a known amount of solute into the cell and then filling it up with the rare-gas liquid.

For hydrogen in liquid argon, Henry's constant is known²⁰ and the concentration could be calculated. The concentration of N_2 is not known. The solutions with N_2 were prepared by filling the cell with 10 or 100 Torr of nitrogen, respectively. The argon was then condensed in the cell at a pressure of 800 Torr. The concentrations given in Fig. 1 were obtained by assuming that all the nitrogen went into the solution.

Drift velocity measurements are influenced by

the presence of electron attaching impurities. After purification as described above the lifetime of the electrons due to impurities in a cell with 1-mm electrode separation was >5 μsec . Recombination of electrons and positive charge carriers were negligible, since at low electric field strength an extremely low radiation dose (~ 1 mrad) was delivered per pulse.

III. RESULTS

In order to check the reliability of our method we investigated the electron drift velocity in the pure rare-gas liquids as a function of the applied electric field. The results are in agreement with the data obtained by other authors,^{9,10,12,15,21,22} and Table I gives a comparison of the various values.

Addition of small amounts of nitrogen led to an increase of the drift velocity at higher field strength and to a higher saturation velocity. Figure 1 shows this influence of N_2 on the dependence of the electron drift velocity on the electric field strength. For comparison our data for the pure liquids are included. At lower field strengths the pure liquids and the solutions show the same electron drift velocities, but at some critical field strength where the velocity is already constant in the pure liquid the drift velocity in the solutions starts to increase again until it reaches a higher saturation value. The same effect is observed with hydrogen, and in Fig. 2 v_i/v_p is plotted as a function of the field strength, where v_p is the drift velocity in the pure liquid and v_i is the velocity in the solution. Qualitatively one can state that with hydrogen the effect sets in at a slightly lower field strength than with nitrogen.

An even more dramatic change is observed when the hydrocarbons are added to the rare-gas liquids. Figures 3–5 show the effect of methane, ethane,

TABLE I. Low-field electron mobility and saturation velocity in liquid Ar, Kr, and Xe.

Liquid	T (K)	μ_{el} ($\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$)	v_s (cm sec^{-1})	Reference
Ar	87	400 ± 50	$6.4 \times 10^5 \pm 10\%$	This work
	85	520		22
	85	475	7.5×10^5	9
	87		6×10^5	12
	87		8×10^5	15
Kr	120	1200 ± 150	$4.8 \times 10^5 \pm 10\%$	This work
	117	1800	3.8×10^5	9
	119		3.3×10^5	12
	120.4	1310		10
Xe	165	2000 ± 200	$2.6 \times 10^5 \pm 10\%$	This work
	163	1900	2.9×10^5	9
	167	1100		21

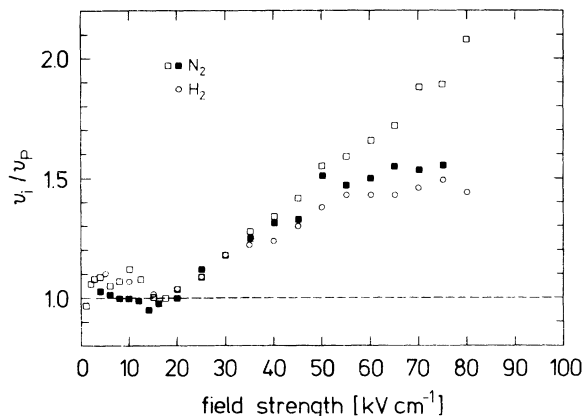


FIG. 2. Ratio of the drift velocity v_i in solutions of nitrogen and hydrogen in liquid argon and pure argon v_p as a function of the field strength. $T(\text{Ar})=87^\circ\text{K}$; approximate concentrations: \square , N_2 : $n \approx 3 \times 10^{20} \text{ cm}^{-3}$; \blacksquare , N_2 : $n \approx 3 \times 10^{19} \text{ cm}^{-3}$; \circ , H_2 : $n = 2.4 \times 10^{19} \text{ cm}^{-3}$.

and propane on the electron drift velocity in argon for several concentrations of the solute. Low solute concentrations have an influence at the higher field strengths only, while in more concentrated solutions [e.g. (Fig. 5), $4.7 \times 10^{20} \text{ cm}^{-3}$ propane] the drift velocity at low field strength is also influenced, indicating an effect on the momentum transfer. In Fig. 6 the influence of methane, ethane, and butane on the field dependence of the electron drift velocity in liquid krypton is shown. Figure 7 gives the influence of butane in liquid xenon. The drift velocity maximum for the low concentrations of ethane in Kr and butane in Xe is very apparent, and is indicated also for the low solute concentrations in the other liquids.

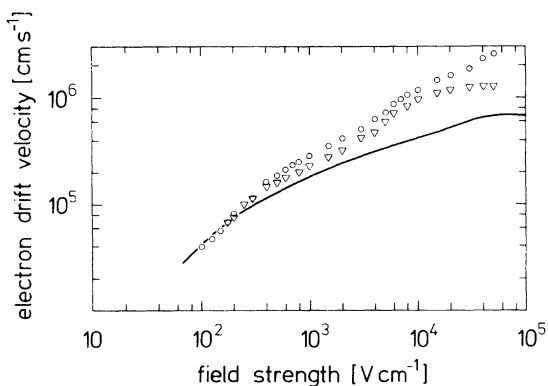


FIG. 3. Influence of methane on the electron drift velocity in liquid argon. ∇ : $2.6 \times 10^{20} \text{ cm}^{-3}$; \circ : $6.5 \times 10^{20} \text{ cm}^{-3}$. $T(\text{Ar})=87^\circ\text{K}$. Solid line: pure argon.

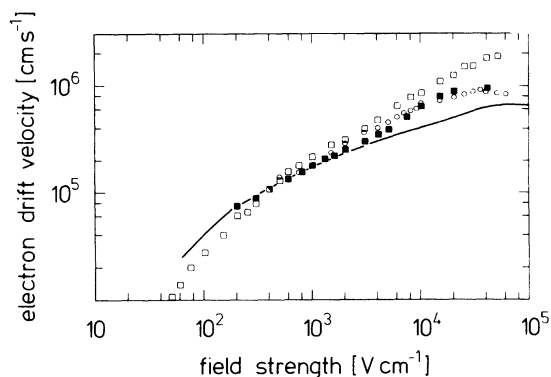


FIG. 4. Influence of ethane on the electron drift velocity in liquid argon. \circ : $5.5 \times 10^{19} \text{ cm}^{-3}$; \blacksquare : $8.7 \times 10^{19} \text{ cm}^{-3}$; \square : $5 \times 10^{20} \text{ cm}^{-3}$. $T(\text{Ar})=87^\circ\text{K}$. Solid line: pure argon.

IV. DISCUSSION

A. General remarks

The nonlinear field dependence of the electron drift velocity in liquid argon, krypton, and xenon is caused by an increase of the mean electron energy due to the applied electric field.^{9,23} At low field strength v_D is proportional to E and the electrons are in thermal equilibrium with the liquid. At higher field strengths electrons pick up more energy between subsequent collisions, leading to a new stationary state with a higher mean energy. The addition of molecular solutes introduces scattering centers for the electrons where they can lose energy by inelastic collisions more efficiently than to the atoms of the liquid. The cross section for this excitation of the solute molecules is energy dependent only for field strengths where the mean electron energy approaches the excitation energy of the molecule.

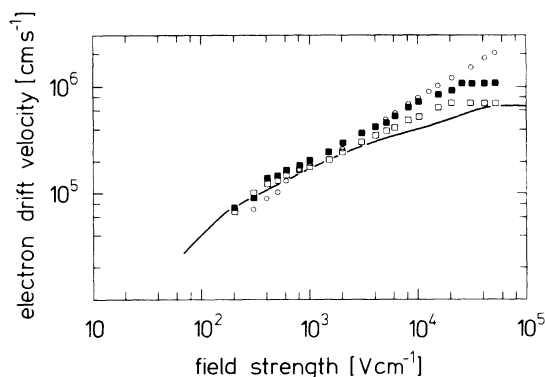


FIG. 5. Influence of propane on the electron drift velocity in liquid argon. \square : $2 \times 10^{19} \text{ cm}^{-3}$; \blacksquare : $7 \times 10^{19} \text{ cm}^{-3}$; \circ : $4.7 \times 10^{20} \text{ cm}^{-3}$; $T(\text{Ar})=87^\circ\text{K}$. Solid line: pure argon.

The drift velocity is then determined by the relative magnitude of the elastic energy loss rate and the inelastic loss rate. If the inelastic loss rate is comparable to or greater than the elastic loss rate the drift velocity will increase above the level in the pure liquid. With increasing field strength the mean electron energy and the elastic loss rate increase. At some field strength the elastic loss rate may become greater than the inelastic loss rate again, and in this case the drift velocity will approach the value of the pure liquid.

B. Simple analysis

We define the field-dependent electron drift mobility as

$$\mu(E) = v_D/E. \quad (1)$$

If the mobility μ_i in the solution at field strength E_i is the same as μ_p in the pure liquid at field strength E_p , then the mean electron energy is the same. The rate of energy loss A suffered by an electron in the solution as we increase the field strength from E_p to E_i is given by

$$A = (v_i E_i - v_p E_p) e_0 \quad (2)$$

(e_0 is the electronic charge) or

$$A = \mu(E_i^2 - E_p^2) e_0, \quad (3)$$

where

$$\mu = \mu_i = \mu_p. \quad (4)$$

The collision of an electron and a solute molecule can lead to an excitation of vibrations and rotations. On the average the electron will transfer energy ΔW , and Eq. (3) becomes

$$\mu(E_i^2 - E_p^2) e_0 = \frac{\Delta W}{\Lambda_{in}/v_{e1}}, \quad (5)$$

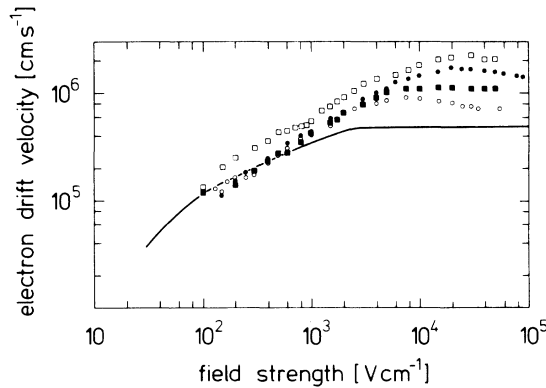


FIG. 6. Influence of methane, ethane, and butane on the electron drift velocity in liquid krypton. Methane: (\square) $\sim 5 \times 10^{20} \text{ cm}^{-3}$; ethane: (\circ) 2.5×10^{19} and (\bullet) $1.2 \times 10^{20} \text{ cm}^{-3}$; butane: (\blacksquare) $4.7 \times 10^{19} \text{ cm}^{-3}$. $T(\text{Kr}) = 120 \text{ K}$. Solid line: pure krypton.

where v_{e1} is the mean electron velocity (given by the mean electron energy ϵ). Since

$$\Lambda_{in} = 1/N\sigma(\epsilon), \quad (6)$$

with N the number density of solute molecules and $\sigma(\epsilon)$ the energy-dependent cross section for the excitation of the molecules, it follows from Eq. (5) that

$$\mu(E_i^2 - E_p^2) e_0 = \Delta W v_{e1} N \sigma(\epsilon). \quad (7)$$

If we know $\epsilon = f(E_p)$ then the rate of energy loss due to the solute, as a function of the mean electron energy ϵ , can be determined.

The mean electron velocity v_{e1} is given by

$$v_{e1} = (2\epsilon/m)^{1/2}, \quad (8)$$

and it follows from Eq. (7) that

$$\Delta W \sigma(\epsilon) = \frac{\mu(E_i^2 - E_p^2) e_0}{N(2\epsilon/m)^{1/2}}, \quad (9)$$

where m is the electron mass.

From Eq. (7) the drift velocity v obtainable with a certain solute concentration follows:

$$v = \mu E_i = \left(\frac{\mu \Delta W \sigma(\epsilon) N (2\epsilon/m)^{1/2}}{e_0} + (\mu E_p)^2 \right)^{1/2}. \quad (10)$$

At high fields μE_p is constant, and for a certain solute concentration N a drift velocity maximum v_{\max} should occur at the electron energy ϵ_m , where $\mu\sigma(\epsilon_m)\epsilon_m^{1/2}$ shows a maximum. The field strength E_{\max} , where v_{\max} is observed, is given by

$$E_{\max} = \left[\frac{\Delta W \sigma(\epsilon_m) N (2\epsilon_m/m)^{1/2}}{e_0 \mu} + E_p^2 \right]^{1/2}. \quad (11)$$

The dependence of v_{\max} and E_{\max} on the solute concentration N approaches $N^{0.5}$ for large N . This dependence was observed for ethane in Kr and butane in Xe.

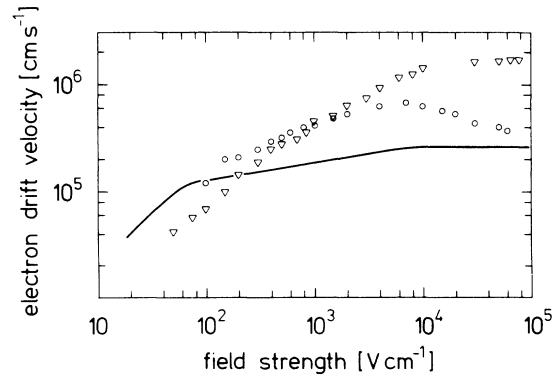


FIG. 7. Influence of butane on the electron drift velocity in liquid xenon. \circ : $1.26 \times 10^{19} \text{ cm}^{-3}$; ∇ : $1.9 \times 10^{20} \text{ cm}^{-3}$. $T(\text{Xe}) = 165 \text{ K}$. Solid line: pure xenon.

C. Cohen-Lekner theory

In order to treat the experimental results with Eq. (9) the dependence of ϵ on E_p has to be known. Cohen and Lekner^{23,24} developed a general theory of hot electrons in gases, liquids and solids. They calculated the change of the velocity distribution function under the influence of an electric field and related this result to the mean electron energy ϵ and the electron drift velocity v_D . Lekner²³ applied this theory to electrons in liquid argon and obtained good agreement between the theoretical dependence of the drift velocity on field strength and the experimental data. Since for these calculations the electron-rare-gas-atom potential has to be known, we used instead the measured dependencies of the drift velocities on the field strength in liquid argon, krypton, and xenon and adjusted the mean free paths for momentum transfer Λ_1 to fit the theoretical dependence. The mean free path for energy transfer Λ_0 was determined by means of the Jortner-Springett-Cohen theory.²⁵ The necessary V_0 values had been measured by Tauchert and Schmidt in our laboratory.²⁶ Table II gives the parameters used in the calculations of the mean electron energy ϵ as a function of the field strength.

D. Evaluation of the data

The experimental data for the drift velocity were analyzed by using Eq. (9) with the dependence ϵ on E calculated as described above. Plots of $\mu = v_D/E$ as a function of E gave curves which at higher field strength split into separate branches with increasing solute concentration (Fig. 8). A horizontal line corresponding to constant μ was drawn and the

TABLE II. Parameters used in the calculations of the mean electron energy with the Cohen-Lekner theory.

F (V cm^{-1})	Λ_1					
	Liquid argon $T=87^\circ\text{K}$		Liquid krypton $T=120^\circ\text{K}$		Liquid xenon $T=165^\circ\text{K}$	
	(\AA)	(eV)	(\AA)	(eV)	(\AA)	(eV)
10	154	0.011	550	0.016	1180	0.021
30	154	0.011	550	0.017	1000	0.022
100	154	0.012	550	0.018	800	0.027
300	154	0.025	540	0.028	460	0.039
1000	154	0.037	500	0.067	240	0.074
3000	120	0.085	300	0.17	135	0.15
10 000	80	0.22	120	0.35	65	0.33
30 000	55	0.54	60	0.91	29	0.65
100 000	38	1.5			14	1.5
V_0 (eV) ^a	-0.21		-0.43		-0.61	
Λ_0 (\AA)	4.3		4.0		3.6	

^a Values determined by Tauchert and Schmidt, Ref. 26.

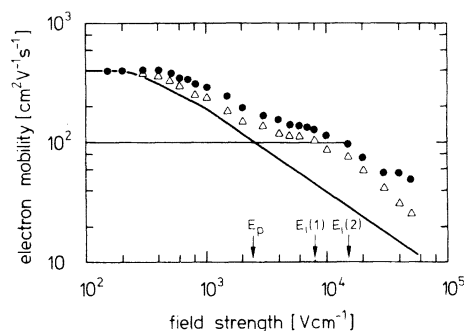


FIG. 8. Electron mobility as a function of electric field strength for pure argon and solutions of methane (data of Fig. 3).

values E_p and E_i read off the graph, enabling use of Eq. (9) to determine $\Delta W\sigma(\epsilon)$ as a function of ϵ . In Fig. 9 this quantity is shown for ethane, propane, and butane as obtained from the data of Figs. 3–7. As the mean electron energy approaches 0.1 eV a steep increase in $\Delta W\sigma(\epsilon)$ occurs with a possible maximum occurring between 0.3 and 0.5 eV.

Ethane is less effective than propane, while butane is best in taking up energy from the electrons. Such behavior is expected, since with increasing chain length the variety of possible vibrations increases and quanta of lower energies can be transferred. Hydrogen is effective at much higher energies.

The data of Fig. 3 for methane in liquid argon are evaluated in Fig. 10. Here we plot $\Delta W\sigma(\epsilon)$ and

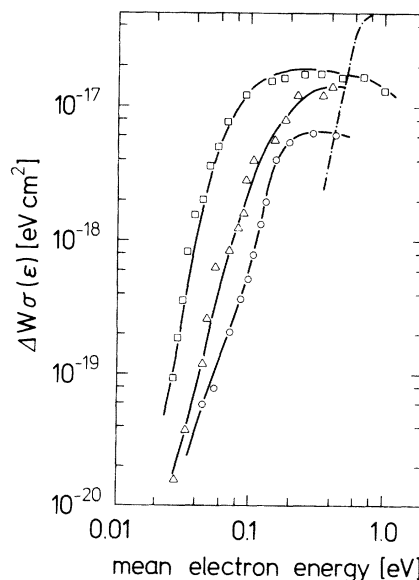


FIG. 9. Product of energy loss quantum ΔW and cross section σ as a function of the mean electron energy ϵ . \circ : ethane; \triangle : propane; \square : butane; $---$: hydrogen.

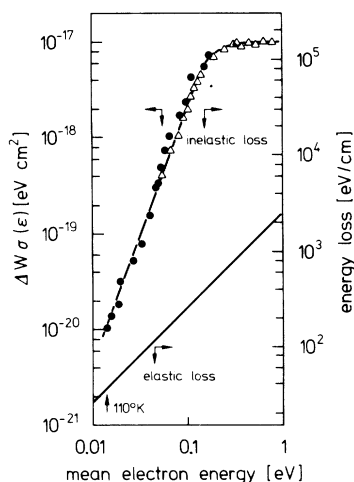


FIG. 10. Energy loss to methane. Left-hand scale: Product of energy loss quantum ΔW and cross section σ as a function of the mean electron energy ϵ . Right-hand scale: $\Delta W\sigma(\epsilon)N$, with N the number density of liquid methane at $T=110^\circ\text{K}$ ($N=1.5\times 10^{22}\text{ cm}^{-3}$).

$\Delta W\sigma(\epsilon)N_M$ as a function of the mean electron energy (N_M is the number density of pure methane), since we want to compare the energy loss per unit length of the electron path with the elastic limit

$$f_{\text{elast}} = \frac{(2m/M)\epsilon}{\Lambda_0} \quad (12)$$

The increase of the energy loss with electron energy is not as steep as in the case of the higher alkanes; Λ_0 , the mean free path for energy transfer, was kept constant, and as is obvious from Fig. 10 inelastic losses are much more important than elastic ones. At $T=110^\circ\text{K}$, the boiling point of liquid methane, the ratio of inelastic to elastic losses is approximately 4. From the onset of the field-strength dependence of the electron mobility in liquid methane we determined a value of 6 for this ratio,²⁷ in reasonable agreement with the present data. It is understandable now why it is that in pure liquid argon the electron drift mobility becomes field dependent above 300 V cm^{-1} even though the low field mobility in both liquids is close to $400\text{ cm}^2\text{ V}^{-1}\text{ sec}^{-1}$; inelastic losses are prevalent in methane, elastic losses in argon.

E. Relation to electric breakdown

In the pure liquefied rare gases the mean electron energy increases rapidly with the applied field strength, and collisional ionization has been observed in liquid xenon.²⁸ The presence of molecular solutes in the rare-gas liquid leads to a decrease of the mean electron energy at a particular field strength due to the inelastic loss mechanism. In pure molecular liquids, such as alkanes, therefore, it should be fairly difficult to increase the mean electron energy in an electric field to values where collisional ionization may take place. Furthermore, since the ionization threshold is probably greater in alkanes than in liquid xenon, higher breakdown fields are expected in molecular liquids. In addition, other phenomena, such as bubble formation or dust particles,²⁹ can also lead to breakdown, so that electronically induced breakdown or electron avalanches may be difficult to achieve.

V. CONCLUSION

At high solute concentrations the low field mobility in the solution is smaller than that in the pure liquid (see Fig. 7 in particular). The mean free path for momentum transfer is decreased due to additional scattering by the solute molecules. Recently this effect has been studied in some detail in mixtures of methane and ethane, and a relation between the solute concentration and the observed mobility was obtained.³⁰ The present data show the same tendency, but are too few for a more refined evaluation.

The modification of the electron drift velocity in liquefied rare gases by small concentration of molecular solutes yields information on inelastic energy losses in electron-molecule collisions. Higher solute concentrations influence the momentum transfer and lead to a decrease of the low field mobility.

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