The Impact Ionization and Electrical Breakdown Strength for Atomic and Molecular Liquids

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ABSTRACT

The ionization electron avalanche development determines electrical breakdown strength of high electron mobility liquids Ar, Kr and Xe. The dc. and laser-induced breakdown strengths of these liquids are lower than low-density gas extrapolation values. This difference is the consequence of the absence of inelastic electron energy losses in liquids, In low electron mobility molecular liquids the electrical breakdown for a long pulse duration occurs via the 'bubble' mechanism, but with the shortening voltage pulse duration and gap length, the ionization avalanche mechanism would become more preferable. The interpretation is given on this basis of electric strength measurements for high-density supercritical vapors.

INTRODUCTION

DURING the last years prebreakdown investigations in liquids were basically concentrated with the 'bubble' mechanism [1,2]. Under this model, breakdown occurs through gas-phase formation. Nevertheless, some experimental data demonstrate the possibility of breakdown initiation by electron avalanche. In pure liquid argon, krypton and xenon, the electrons have high mobility [3] and can be heated by an external electric field F up to the energy of several eV [4], It was shown by measurements of the electric strength of liquid Ar in uniform field that the breakdown field F_{br} is independent of external hydrostatic pressure [5]. Impact electron multiplication was also observed in liquid Xe [6]. The values of ionization coefficients known for gas cannot be used for dense media. The theory of the ionization avalanche development based on these experimental data is given below. This theory permits calculation of ionization coefficient and breakdown voltage for planar geometry. The theory can be applied to breakdown from electrical pulses and to high frequency (laser-induced) breakdown.

Molecular liquids, such as saturated hydrocarbons, are low-mobility liquids for thermal electrons. Moreover they cannot be purified easily. The electric breakdown of plane gaps occurs in these liquids via the 'bubble' mechanism under voltage pulses > 1 μs [7]. Under such conditions, the field strength is high enough for gas bubble formation and subsequent breakdown. The magnitude of this field increases with the hydrostatic pressure [8] and with reduced electric pulse duration [7]. However in the limit of very short pulses, there is no time for bubble development and the ionization avalanche mechanism becomes preferable. It is very important to estimate this upper limit of electric strength of liquid hydrocarbons. The theory developed below is based on analysis of the measurement data of electric strength for high-density supercritical gaseous n-hexane [9]. The theory accounts for the large electron energy losses due to molecular vibra-

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tion excitation. The ionization coefficient and breakdown voltage expression are obtained. The calculated results for n-hexane and short voltage pulses ($\tau < 1$ μs) are in good agreement with experimental data.

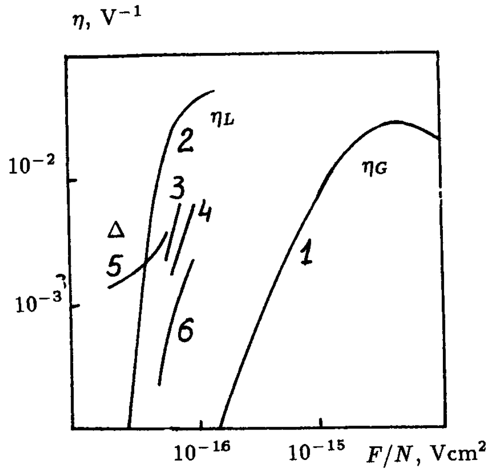

Figure 1.

Ionization coefficient in Ar *vs.* F/N. Calculated curves. 1: $\eta(F/N)$ in rare gas, 2: $\eta(F/N)$ in high-density gas and liquid. Experimental data, Δ: 3 and 4: dc breakdown voltage measurements in liquid [5,13,14]. 5, 6: laser-induced breakdown measurements in high-density gaseous Ar (Rb-laser) [16], and liquid Ar (CO$_2$-laser) [15].

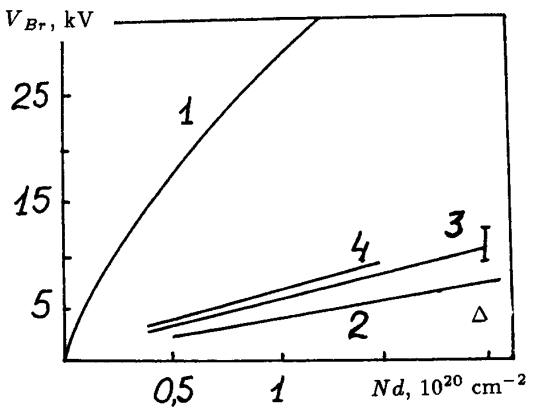

Figure 2.

Breakdown voltage in argon *vs.* Nd. Calculated curves. 1: extrapolation of the low-density gas data Equation (5), 2: calculation for liquid Equation (6). Experimental data. Δ: [5], 3: [13], 4: [14].

HIGH MOBILITY ATOMIC LIQUIDS

THE electron drift velocity in liquid Ar, Kr and Xe is very high and electrons may obtain energy enough for the impact ionization. Some experimental results indicate the important role of impact ionization and electronic processes in the development of breakdown in these liquids. Since the experimental breakdown voltage of LAr is independent on pressure the 'bubble' mechanism cannot be responsible for the breakdown. Impact ionization avalanches have been observed in LXe, and we may construct the theory of prebreakdown events for liquids in the same way as for gases. But we shall take into account the important density effects [10]. These density effects influence essentially the Townsend ionization coefficient values for LXe and the breakdown voltage of LAr is smaller than the high-density extrapolation of GAr data,

In a strong external field the electron concentration increases exponentially away from the cathode, $n_e \propto \exp(\alpha x)$. The Townsend ionization coefficient $\alpha(F,N)$ depends on the field strength F and the matter density N, and governs the rate of electron avalanche development. The reduced ionization coefficient $\eta(F/N) = \alpha(F,N)/F$ is a function of F/N only for a low-density gas: $\eta = \eta_G(F/N)$. The measurements of $\eta(F/N)$ in liquid Xe had demonstrated the radical difference from the universal relation $\eta = \eta_G(F/N)$.

In gas electrons obtain energy under the influence of external field and lose it due to elastic and inelastic collisions with atoms. Inelastic processes are the atomic ionization and the atomic excitations. The last do not lead to ionization events, but reduce a number of fast electrons. Inelastic energy losses prevent electron heating to the energies above the ionization potential. In gases the inelastic energy losses strongly affect the Townsend coefficient α

$$\alpha = \frac{eF\nu_i(F)}{\delta\nu\epsilon + E\nu_B(F)} \qquad (1)$$

Here $\nu_i(F)$, $\nu_B(F)$ and ν are, respectively the mean frequencies of ionization, excitation and elastic collisions; $\delta = 2m/M$ is twice the electron-atom mass ratio, *i.e.* the energy fraction lost by elastic electron-atom collision; E is the energy threshold for inelastic collisions; • is the mean electron energy. For prebreakdown conditions we have $\delta\nu\epsilon \ll E\nu_B$. For calculation of frequencies $\nu_i(F), \nu_B(F)$ it is necessary to take into account the strong influence of inelastic collisions on the electron distribution function over the energies. In this paper we reproduce the result of analytical calculation on the basis of a simple model, in which an atom is a three-level system (that is, ground state, excited state with energy E and conduction band bottom I, the ionization potential of gas atoms). The processes of elastic collisions, excitation and ionization are characterized by the collision cross sections $q \simeq 10^{-15}$ cm^2 (elastic), and $q_E \simeq q_i 7 \times 10^{-17}$ cm^2 [11]. For ionization coefficient $\eta = \alpha/F$ it is

$$\begin{aligned} \eta_G &= \frac{eq_i}{Iq_E}\frac{E}{I-E}\left[\frac{F}{F_E}\right]^{\frac{2}{3}} \exp\left[-\frac{F_E}{F}(\frac{I-E}{E})^{3/2}\right] \\ F_E &= \frac{NE(qq_E)^{0.5}}{e} \end{aligned} \qquad (2)$$

The parameter of this model is the effective threshold energy of excitation E. It may be chosen by comparison results from (2) with experimental data. This procedure results in $I - E = 3.6$ eV for Ar, $I = 15.6$ eV.

The atomic energy level system changes considerably with matter density. As the density N increases, the ionization potential $I(N)$ decreases. That is the result of the shift of the conduction band bottom and is caused by an interaction between charges and atoms. Polarization interaction considerably contributes to ionization potential lowering ΔI. So in a medium with large polarizability β this effect has the value $\Delta I \simeq 10\beta e^2 N^{4/3}$ [6]. Thus at the triple point of Xe the ionization potential in liquid decreases to 9.2 from 12.2 eV [12]. The ionization potential lowering significantly depletes the number of excited states of atoms in the liquid. For example, the experiment [12] indicates the existence in Xe of a single weakly bound exciton-type level with the excitation energy 8.6 eV. While in a gas the first excitation level E is quite remote from the conduction band bottom, $I - E = 3.5$ eV, in liquid this value amounts to 0.6 eV only. Since the ionization potential lowering in liquid $\Delta I(N)$ is greater then the bond energies of excited levels, these levels do not exist and excitation energy losses are completely absent, $\delta\nu\epsilon \gg E\nu_E$. In this limiting case $\eta(F/N)$ is expressed in terms of elastic energy losses and electron drift velocity W

$$\begin{aligned} \eta_L &\simeq \frac{2.8e}{IW}\left[\frac{I\delta}{m}\right]^{0.5}\left[\frac{F_{e1}}{F}\right]^{1.75} \exp\left[-(\frac{F_{e1}}{F})^2\right] \\ F_{e1} &= 0.87e^{-1}\delta^{0.5}qIN \end{aligned} \qquad (3)$$

The values of $\eta_L(F/N)$ calculated according to this expression are presented in Figure 1, curve 2. So the disappearance of inelastic energy losses results in a significant increase in $\eta(F/N)$.

If electric breakdown is governed by the electron avalanche development, breakdown takes place when the product of the gap length d and the Townsend ionization coefficient $\alpha(F, N)$ attains a certain value. For the plane-plane electrodes the applied voltage is $V = Fd$, and the breakdown criterion can be written in the form

$$V_{br}\eta\left[\frac{V_{br}}{Nd}\right] \simeq 20 \qquad (4)$$

For a gas $\eta(F/N)$ depends on the F/N ratio only. The criterion (4) leads to the Paschen scaling law $V_{br} = V_{br}(Nd)$. Using expressions (2) and (3) for $\eta_G(F/N)$ and $\eta_L(F/N)$ and the breakdown criterion (4) we can obtain the expression for breakdown voltage as universal functions of Nd as for rarefied gases (where inelastic energy losses prevail) and also for high-density media (where inelastic losses are absent)

$$\begin{aligned} V_{br}^G &\simeq \frac{F_E}{N}\left[\frac{I-E}{E}\right]^{3/2}\frac{Nd}{\ln(2.4\times10^{-19}Nd)} \\ &\simeq \frac{0.9\times10^{-15}Nd}{\ln(2.4\times10^{-19}Nd)} \end{aligned} \qquad (5)$$

$$V_{br}^L \simeq \frac{F_e1}{N}\frac{Nd}{\ln^{0.5}(2.2\times10^{-18}Nd)} \simeq \frac{10^{-16}Nd}{\ln^{0.5}(2.2\times10^{-18}Nd)} \qquad (6)$$

where Nd is expressed in cm^2, V_{br}^b and V_{br}^L in V. The extrapolation of the low-density gas values V_{br}^G to high densities (or to large Nd) in accordance with Equation (5) overestimates V_{br} in comparison with the experimental data, Figure 2, curve 1. On the contrary the results of calculations Equation (6) (Figure 2, curve 2) are in agreement with the experimental data. We can also use the criterion (4) to construct the $\eta(F/N)$ values from experimental $V_{br}(Nd)$. These recalculated $\eta_L(F/N)$ for liquid Ar are demonstrated in Figure 1 for density $N = 2\times10^{22}$ cm^{-3} and $d = 100$ μm [5], 20 to 80 μm [13], 20 to 70 μm [14].

Irradiation of liquids by laser pulse may initiate breakdown in the bulk of the liquid. Laser-induced breakdown occurs as soon as laser beam intensity exceeds the threshold value S_{br}. The S_{br} value (or high-frequency electric field strength $F = 19$ $(S)^{0.5}$) depends upon pulse length τ (F is expressed in V/cm, S in Wt/cm^2). The criterion of laser-induced breakdown is $\nu_i(S_{br})\tau \simeq 20$.

For high density gases or for liquids the electron-atom collision frequencies ν are large compared with electric field frequency ω and we can use our theory of breakdown in static fields. Thus we can recalculate the experimental data for $S_{br}(\tau)$ for liquid Ar [15] and for high pressure gaseous Ar [16] in terms of $\eta(F/N)$ values as $\eta(F/N) \simeq \nu_i(S_{br})/(WF_{br})$.

These results are shown in Figure 1 with those for static fields. The experimental points are drawn on curve 2.

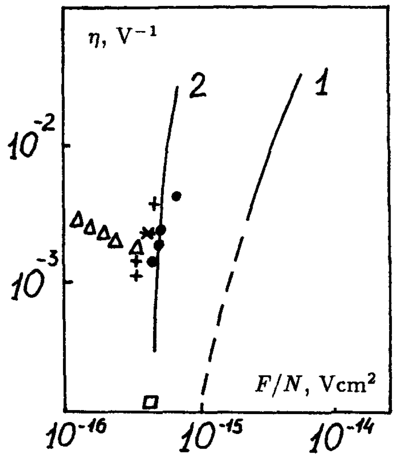

Figure 3.

Ionization coefficient in n-hexane vs. F/N. Calculated curves. 1: for low-density gas Equation (2), solid part of the curve is the domain of low-pressure experiments [17]; 2: for high-density medium Equation (8) Experimental data. ●: supercritical gas, 10 μs pulse [9], Δ: liquid, 10 μs pulse [9], $*$: liquid, 0.5 μs pulse [21]; □: liquid, 0.2 μs pulse [22]; +: liquid, 1.2 μs pulse [8].

MOLECULAR LIQUIDS.

The breakdown strength of hydrocarbon gases at low pressures [17] increases regularly with density in accordance with the Townsend mechanism. In external fields, electrons acquire sufficient energy to ionize molecules. On the other hand, electrons lose energy by excitation of molecular vibrations and molecular electronic states (threshold energies $E_v \simeq 0.2$ eV and $E \simeq 8$ eV. The latter process plays a significant role in rarefied gases under prebreakdown conditions. The theory gives for the ionization coefficient $\eta(F/N)$ for molecular gases the same expression (2) as for atomic ones. The difference consists in cross section values. For n-hexane the elastic cross section is $q = 8\times10^{-15}$ cm^2, the cross section for ionization and excitation of electronic states is $q_i \approx q_E \approx 3\times10^{-15}$ cm^2, and ionization potential $I = 10$ eV. Experimental data for the quantities q_i, q_E are not available. It is possible however to chose q_i and q_E values to fit expression (2) to the empirical formula $\eta = A\exp(-B/F)$. Here A and B are constants determined from the experimental data [17], Figure 3 curve 1. Using (2) and the criterion (4) one can construct the $V_{br}(Nd)$ expression:

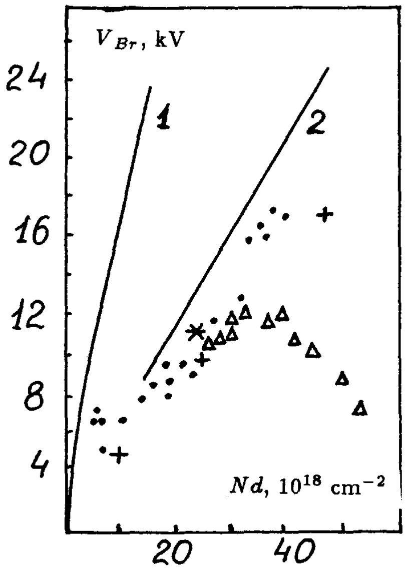

Figure 4.

Breakdown voltage in n-hexane vs. Nd. Calculated curves. 1: extrapolation of the low-density gas data [17] Equation (7), 2: calculation for high-density medium Equation (9). Experimental data. ●: supercritical gas, 10 μs pulse [9], Δ: liquid, 10 μs pulse [9], +: liquid, 1.2 μs pulse [8], $*$: liquid, 0.5 μs pulse [21].

$$\begin{aligned} V_{br}^{G}(Nd) &\simeq \frac{F_E}{N}\left[\frac{I-E}{E}\right]^{3/2}\frac{Nd}{\ln(7\times10^{-18}Nd)} \\ &\simeq \frac{6.3\times10^{-15}Nd}{\ln(7\times10^{-18}Nd)} \end{aligned} \tag{7}$$

where Nd is expressed in cm^2, V_{br}^{G} in V. According to this formula the breakdown voltage of n-hexane (density of liquid $N = 4.6\times10^{21}$ cm^{-3} and gap $d = 100$ μm) is 50 kV. It must be compared with the typical value of 10 kV for liquid [9], Figure 4. An extrapolation of the Paschen curve into the high-density region leads to the values of V_{br} which exceed the experimental data. The departures from Paschen's curve are observed at gas pressures $\gtrsim 300$ kPa. For a supercritical gaseous hexane ($N = 3.5\times10^{21}$ cm^{-3}) the experimental V_{br} values [9] are appreciably lower than the extrapolated low-pressure results, Figure 4.

The impact ionization mechanism is realized in condensed inert gases, provided that electrons have a high mobility. In liquid hydrocarbons with density 4.6x10^{21} cm^{-3} thermal electrons are localized by density fluctuations and have a low mobility [18]. However, in strong fields $F \geqslant 1$ MV/cm, the electrons are in quasi-free states with high gas-kinetic mobility, as a result of field delocalization [19], and electron heating enables them to ionize molecules. Moreover, as the density increases, the ionization potential decreases due to the strong polarizing interaction between ions and the medium. In n-hexane, $\beta = 1.2\times10^{-23}$ cm^3 and at $N = 4.6\times10^{21}$ cm^{-3}, $\Delta I = 2$ eV. It results in a vanishing of excited states of molecules, and in the reduction of the electron energy loss by excitation of electronic states. Therefore one can neglect them in comparison with the energy losses by excitation of molecular vibration. The expression for the ionization coefficient for high density media takes the form

$$\begin{aligned} \eta_{Liq} &\simeq \frac{3e}{I}\left[\frac{F_v}{F}\right]^2 \exp\left[-(\frac{F_v}{F})^2\right] \\ F_v &\simeq \frac{N}{e}(E_v I q q_v)^{0.5} \end{aligned} \tag{8}$$

The characteristic field strength F_v is defined by vibration excitation cross section $q_v \simeq 10^{-16}$ cm^2. This value for n-hexane can been estimated from drift data [20]. The results of calculations by expression (8) are presented on Figure 3, curve 2. Using the criterion (4) one can recalculate the experimental $V_{br}(Nd)$ data to the $\eta(F/N)$ values. The result of this operation for data [9] is presented in Figure 3 also. The calculated values agree well with the measurement data for supercritical high-density gas. As to the experimental points [9] for liquid, they deviate from the calculated curve. Apparently, the breakdown in liquid proceeds through the bubble mechanism.

Using the criterion (4) one can obtain expression for $V_{br}(Nd)$ from expression for $\eta_L(F/N)$

$$V_{br}^L \simeq \frac{F_v}{N}\frac{Nd}{\ln^{0.5}(10^{-16}Nd)} \simeq \frac{1.3\times10^{-15}Nd}{\ln^{0.5}(10^{-17}Nd)} \tag{9}$$

The results of Equation (9) are given on Figure 4, curve 2. We see that the breakdown voltage for liquid [9] is lower. These experimental data have been obtained for 10 μs voltage pulse duration. As to the experimental data for liquid n-hexane breakdown voltage for short pulse duration (< 1 μs [8, 21, 22]), they are in agreement with the high-density calculated curves at Figures 3, and 4. Apparently, the obtained expression (9) is the upper limit for breakdown voltage induced by impact electron avalanche development in the liquid. The corresponding breakdown strength is $F_{br} \simeq 0.34F_v \simeq 2.2$ MV/cm for liquid n-hexane, density $N \simeq 4.6\times10^{21}$ cm^{-3}.

CONCLUSION

We believe that high-mobility liquid breakdown is governed by the electron ionization mechanism. We demonstrate the satisfactory correspondence of our calculations of ionization kinetics and breakdown voltage to experimental data. The lowering of the electric strength of these liquids is the consequence of the decrease in inelastic electron energy losses. It is possible to increase this electric strength by introducing molecular impurities into the liquids.

The electron ionization breakdown mechanism has a characteristic development time of the order of several ns. The gas bubbles formation time is $\geqslant 1$ μs. Thus the electric strength of liquid hydrocarbons increases with decreasing pulse duration. The ionization avalanche mechanism defines the upper limit of the electric strength of these liquids under very short voltage pulses.

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This paper is based on a presentation given at the 10th International Conference on Conduction and Breakdown in Dielectric Liquids, Grenoble, France, September 1990.

Manuscript was received on 7 December 1990, in revised form 9 April 1991.