

|                  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Title            | Change of liquid drop shapes on electrification                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Sub Title        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Author           | 渡辺, 彰(Watanabe, Akira)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
| Publisher        | 慶應義塾大学藤原記念工学部                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| Publication year | 1970                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| Jtitle           | Proceedings of the fujihara memorial faculty of engineering keio university Vol.23, No.93 (1970. ) ,p.71- 86                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
| JaLC DOI         |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Abstract         | A liquid drop from a capillary, when it is electrified, can take different forms in association with the amount of electrification. This behavior was studied for 36 kinds of liquids. For the liquids with electrical conductivity above $10^{-12}$ (ohm cm) <sup>-1</sup> , the drops tended to be disintegrated and to become mist with increasing applied voltage. In this case, the disintegration was found to be strongly affected by the surface charge density of drops. For the liquids with conductivity below $10^{-12}$ (ohm cm) <sup>-1</sup> , however, the increase of applied voltage only resulted in the increase of the volume of drops, and no mist formation was observed. The results were interpreted as kind of prebreakdown phenomena accompanying mists between needle and plane electrodes. |
| Notes            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Genre            | Departmental Bulletin Paper                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| URL              | <a href="https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00230093-0071">https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00230093-0071</a>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |

慶應義塾大学学術情報リポジトリ(KOARA)に掲載されているコンテンツの著作権は、それぞれの著作者、学会または出版社/発行者に帰属し、その権利は著作権法によって保護されています。引用にあたっては、著作権法を遵守してご利用ください。

The copyrights of content available on the Keio Associated Repository of Academic resources (KOARA) belong to the respective authors, academic societies, or publishers/issuers, and these rights are protected by the Japanese Copyright Act. When quoting the content, please follow the Japanese copyright act.

# Change of Liquid Drop Shapes on Electrification

(Received June 24, 1970)

Akira WATANABE\*

## Abstract

A liquid drop from a capillary, when it is electrified, can take different forms in association with the amount of electrification. This behavior was studied for 36 kinds of liquids. For the liquids with electrical conductivity above  $10^{-12}$  (ohm cm) $^{-1}$ , the drops tended to be disintegrated and to become mist with increasing applied voltage. In this case, the disintegration was found to be strongly affected by the surface charge density of drops. For the liquids with conductivity below  $10^{-12}$  (ohm cm) $^{-1}$ , however, the increase of applied voltage only resulted in the increase of the volume of drops, and no mist formation was observed. The results were interpreted as kind of prebreakdown phenomena accompanying mists between needle and plane electrodes.

## I. Introduction

It has been known since long that electrostatic forces direct towards the bulk volume of a liquid drop deform or disintegrate it. These phenomena are caused by electrohydrodynamic effects in the dielectric liquid, and analysis of these phenomena are thought to be difficult. Basic researches of the electrical forces arising from the action of electrical field applied to dielectric liquids have been done since ten years.

The present reseaches originally attempted to analyze the mechanism of electrical atomization. But, the author reached a conclusion that the basic mechanism of electrical disintegration of a liquid drop has not been investigated throughly, and the purpose of this research, therefore, changed to experimental studies of change of liquid drop shapes on electrification. A few papers can be found on this subject, but most of the researchers used the impure liquids samples and the results of the experiments cannot be free from interfering factors other than electrostatical forces.

Phenomena of deformation of the liquid drop by electrification and emergence of the liquid from the capillary electrode that produces liquid threads which immediately break into the globules were investigated in this paper.

## II. Experimental Procedure

The essential parts of the apparatus is shown in Fig. 1. *M* is a capillary electrode

---

\*渡 辺 彰 Assistant Professor, Faculty of Engineering, Keio University.

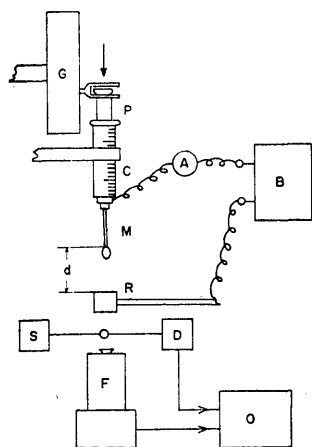


Fig. 1. Schematic illustration of experimental apparatus

photographed by a camera mounted on a low power microscope.

Thirty-six kinds of liquid hydrocarbons (Guaranteed Reagent) were chosen as the samples and the impurities including water were analyzed by gas chromatography.

### III. Results

#### III. 1. Change of the Shapes of Liquid Drop on Electrification.

The shapes of the liquid drops from the capillary under the conditions described are classified into the following two patterns:

A) The volume of the falling drops decreases with increasing the applied voltage, and the misting is produced at definite voltage.

B) The volume of the falling drops increase with the applied voltage, and no mist is produced.

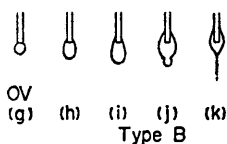
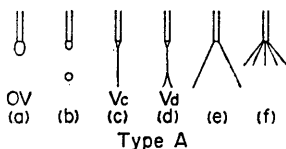


Fig. 2. Various stages of liquid drops

Generally speaking, each of the test liquids are to belong to one of the either A or B of the patterns, and the liquids, therefore, are conventionally nominated in this paper as Group A or Group B according to their behaviors under the classification mentioned above.

The change of the liquid shapes are illustrated in Fig. 2. in which the applied voltage is higher in the right side.

Group A (a) : Applied voltage is zero.

(b) : The volume of the falling liquid

### Change of Liquid Drop Shapes on Electrification

drops decreases with the applied voltage and the numbers of the drops in unit time and the speed of the falling drops are both increased, too.

- (c) : At a critical voltage  $V_c$ , the drops become a fine thread from the edge of the capillary.
- (d) : Further increasing the applied voltage makes the lower part of the liquid stream conically dispersed, and misting begins on the lower end of the cone. Every liquid has its own critical value for this voltage  $V_a$  together  $V_c$  in a definite geometrical arrangement of the electrode.
- (e) and (f) : In most cases, the finite liquid streams are drawn radially and symmetrically from the edge of the capillary. The numbers of the fine threads are counted from two to ten, which increases step-wise with the applied voltage.

Group B (g) to (h) : The volumes of the falling drops increase with the applied voltage, and both of the falling speed and the numbers of the drops decrease with the voltage. Occasionally, some irregular pull out of the small drops and the transient misting are seen at high voltage, but this ceased away even though the electric field was still being applied. The pictures of the drops in various conditions are shown in Fig. 3. In (a) to (d), the drop shapes of benzene (Group B) were photographed with the aid of Schlieren system. The transient drawn out of the small drops are shown in (d). The drops of isoamyl acetate (Group A) are shown in (e) to (h), among which (f) is the occasion of five fine threads and (g) and (h) are the examples of up-side-down arrangement of the electrodes to investigate the influence of gravity. These pictures were taken in the same conditions except the exposure time.

It is clear from the pictures that the fine threads mentioned above are consisted of the fine particles of high velocities.

#### III. 2. Change of the Volume of the Liquid Drops on Electrification.

In Fig. 4, a few examples of change of the volume of the liquid drops are shown; heptane (Group B), isoamyl acetate (Group A) and thiophen an intermediate of the both groups, are compared in parameters of various applied voltages.

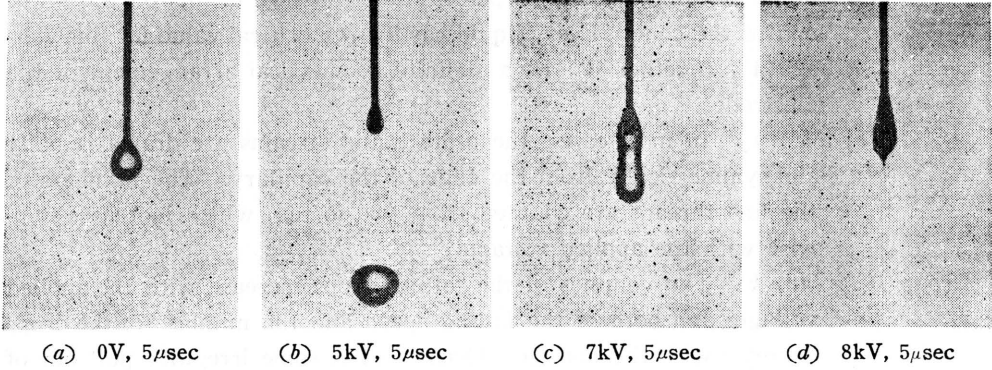
Generally, the relation between the applied voltage  $E$  (kV) and the volumes (in  $10^{-3}$  cc) of the falling drops is expressed by the following experimental formula:

$$V = V_0 + aE^b \quad (1)$$

where  $V_0$ ,  $a$  and  $b$  are the constants related to the kinds of the liquid and geometry of the electrodes ( $a < 0$  for Group A and  $a > 0$  for Group B). The values of  $b$  are near two for most liquids.

Classification of the liquids into the groups,  $V_c$  and  $V_a$ , relative permittivity,

Benzene



Isoamyl acetate

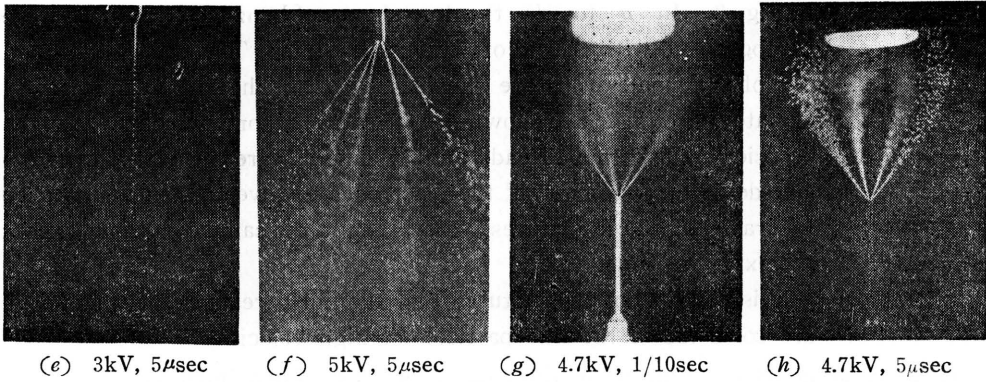
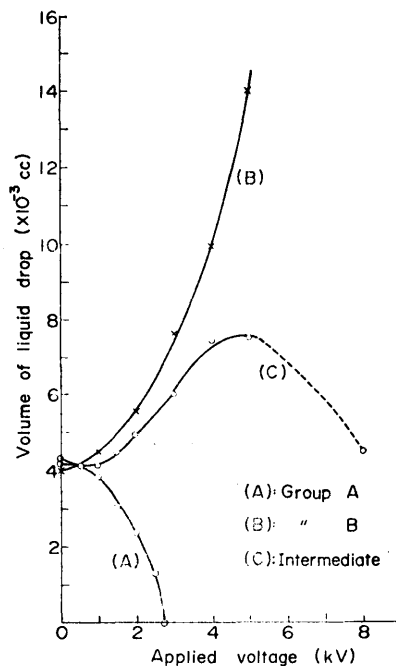


Fig. 3. Photographs of example of shapes

## Change of Liquid Drop Shapes on Electrification



**Fig. 4. Relations between volume of droplet and applied voltage, (A) Isoamyl acetate, (B) Heptane, (C) Thiophene**

and electrical conductivity are shown in Table 1. In Table 2, the values of  $a$  and  $b$  in equation (1) are tabulated. Values of electrical conductivity were measured by means of the leakage current method with the vibrating reed electrometer, as it varies widely with the impurities of the samples.<sup>2)</sup> Change of electrical conductivity with time is seen in Fig. 5, in which a steady value seems to be obtained within the time of this measurement. Group A and B seems to be well characterized by the electrical conductivities listed in Table 1. The electrical conductivities of Group A are larger than  $10^{-12}$  (ohm cm)<sup>-1</sup>, and those of Group B are smaller than this value.

### III. 3. Quantity of Electric Charge for the Applied Voltages below $V_c$ .

It was confirmed by the measurement with Faraday cage that the falling drops drawn out from the electrode have the charge of the same polarity as the capillary electrode itself. The tendency of the charge of the quantity of charge with the applied voltage is shown in Fig. 6 (a). It can be seen that there is a distinct correlation between charge of the liquid drop of Group A and the applied voltage. It is known from the measurement of the charge quantity shown in Fig. 6 (b) that the volume charge density is a linear function of the applied voltage, therefore, the

following expression is obtained for the relation between volume charge density,  $Q_v$  and applied voltage  $E$ :

$$Q_v \approx kE \quad (2)$$

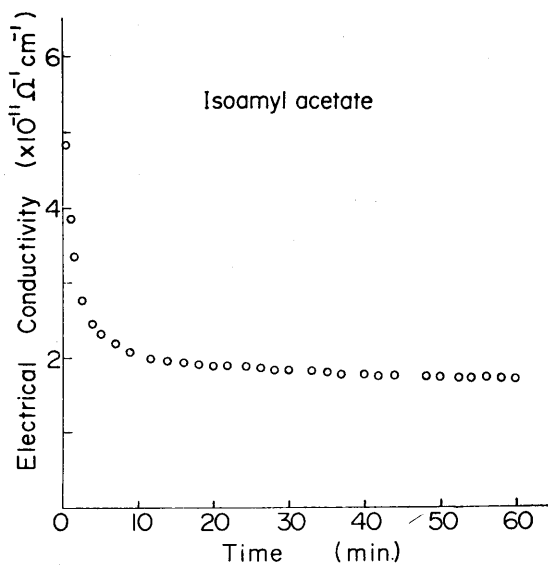
Table 1. Grouping of the samples by experimental data and relating physical constants.

| Liquid               | Group | Relative Permittivity | Dipole moment (debye) | Surface tension $\gamma$ (dyn/cm) | Electrical conductivity $\sigma$ [ $\Omega \cdot \text{cm}$ ] $^{-1}$ ) | $V_1$ (kV) | $V_2$ (kV) |
|----------------------|-------|-----------------------|-----------------------|-----------------------------------|-------------------------------------------------------------------------|------------|------------|
| Hexane               | B     | 1.80                  | 0.08                  | 18.9                              | $6 \times 10^{-18}$                                                     | $\times$   | $\times$   |
| Heptane              | B     | 1.92                  | 0                     | 20.9                              | $2 \times 10^{-17}$                                                     | $\times$   | $\times$   |
| Carbon tetrachloride | B     | 2.24                  | 0                     | 26.8                              | $5 \times 10^{-16}$                                                     | $\times$   | $\times$   |
| Benzene              | B     | 2.28                  | 0                     | 28.9                              | $5 \times 10^{-16}$                                                     | $\times$   | $\times$   |
| Toluene              | B     | 2.38                  | 0.39                  | 28.5                              | $6 \times 10^{-15}$                                                     | $\times$   | $\times$   |
| Methylal             | A     | 2.7                   | —                     | 21.1                              | $3 \times 10^{-11}$                                                     | 4.0        | 7          |
| Thiophene            | B     | 2.76                  | 0.54                  | —                                 | $4 \times 10^{-13}$                                                     | $\times$   | $\times$   |
| Isoamyl ether        | B     | 2.82                  | 1.23                  | —                                 | $2 \times 10^{-14}$                                                     | $\times$   | $\times$   |
| Diethyl carbonate    | A     | 2.82                  | —                     | 26.4                              | $5 \times 10^{-12}$                                                     | 2.5        | 2.6        |
| Propionic acid       | A     | 3.44                  | 0.63                  | 26.7                              | $2 \times 10^{-10}$                                                     | 2.8        | 3.1        |
| Anisol               | A     | 4.33                  | 1.2                   | 36.2                              | $6 \times 10^{-11}$                                                     | 2.9        | 3.4        |
| Isoamyl acetate      | A     | 4.63                  | 1.8                   | 25.8                              | $3 \times 10^{-11}$                                                     | 2.6        | 3.3        |
| Butyl acetate        | A     | 5.01                  | 1.84                  | 25.2                              | $1 \times 10^{-10}$                                                     | 2.7        | 2.9        |
| Bromobenzene         | A     | 5.40                  | 1.73                  | 36.3                              | $2 \times 10^{-12}$                                                     | 3.1        | 3.5        |
| Propyl acetate       | A     | 5.69                  | 1.86                  | 24.3                              | $4 \times 10^{-9}$                                                      | 2.6        | 2.7        |
| Tetrachloroethane    | A     | 8.2                   | 1.85                  | 36.0                              | $3 \times 10^{-10}$                                                     | 2.9        | 3.0        |
| Acetone              | A     | 20.7                  | 2.72                  | 23.3                              | $2 \times 10^{-9}$                                                      | 2.7        | 3.0        |
| Ethanol              | A     | 24.3                  | 1.68                  | 22.3                              | $7 \times 10^{-9}$                                                      | 2.7        | 3.0        |
| Ethylene glycol      | A     | 38.8                  | 3.8                   | —                                 | $3 \times 10^{-7}$                                                      | 4.1        | 4.8        |
| Distilled water      | A     | 80.1                  | 3.37                  | 72.8                              | $1 \times 10^{-8}$                                                      | 5          | 5          |

## Change of Liquid Drop Shapes on Electrification

**Table 2.** Coefficient of empirical formula  
(1) and (2).

| Liquid               | <i>a</i> | <i>b</i> | $\frac{k}{10^{-3} \text{cc} \cdot \text{kV}}$ |
|----------------------|----------|----------|-----------------------------------------------|
| Hexane               | 0.4      | 1.8      | —                                             |
| Heptane              | 0.5      | 1.9      | —                                             |
| Carbon tetrachloride | 0.1      | 2.2      | —                                             |
| Benzene              | 0.4      | 1.8      | —                                             |
| Toluene              | 0.4      | 1.9      | —                                             |
| Methylal             | -0.9     | 1.1      | $6.2 \times 10^{-12}$                         |
| Thiophene            | 0.2      | 1.8      | 1.9 "                                         |
| Isoamyl ether        | 0.2      | 2.0      | 0.3 "                                         |
| Diethyl carbonate    | -0.5     | 2.0      | 5.7 "                                         |
| Propionic acid       | -0.5     | 1.8      | 5.6 "                                         |
| Anisol               | -0.4     | 2.0      | 4.8 "                                         |
| Isoamyl acetate      | -0.6     | 2.0      | 5.3 "                                         |
| Butyl acetate        | -0.6     | 1.9      | 5.7 "                                         |
| Bromobenzene         | -0.3     | 2.0      | 5.7 "                                         |
| Propyl acetate       | -0.7     | 2.0      | 5.1 "                                         |
| Tetrachloroethane    | -0.1     | 2.4      | 5.7 "                                         |
| Acetone              | -0.6     | 1.9      | 5.0 "                                         |
| Ethanol              | -0.5     | 2.2      | 4.8 "                                         |
| Ethylene glycol      | -0.6     | 1.6      | 3.5 "                                         |
| Distilled water      | -1.6     | 1.0      | 2.2 "                                         |



**Fig. 5.** Decrease of electrical conductivity  
with time



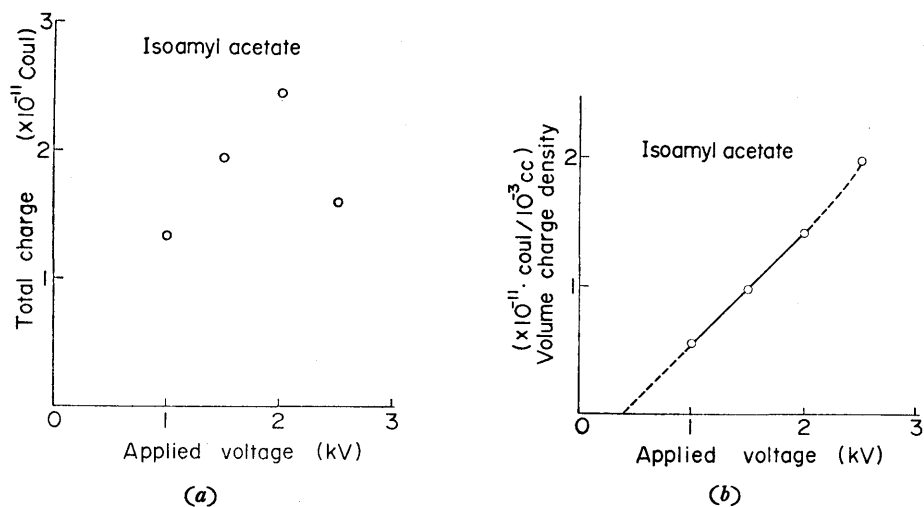


Fig. 6. (a) Charge quantity of droplet (b) Volume charge density of droplet

The values of  $k$  for Group A are shown in Table 2. The reliable values of  $k$  for Group B were unable to obtain owing to the extremely small quantities of the charge and lack of stability of the measurement. No significant change of the values of  $k$ ,  $V_c$  and  $V_d$  for Group A was observed within precision of the measurement for the flow rate of 1 to  $10 \times 10^{-3}$  cc/sec. On the other hand, those of Group B materials are very much dependable on the flow rate; the smaller the flow rate, the larger the charged quantity.

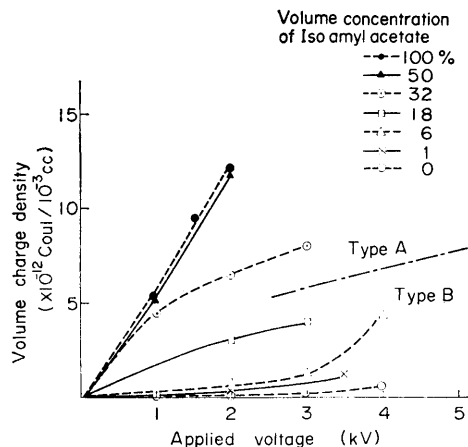


Fig. 7. Influence of additive effect of Type A to B on charge quantity

of isoamyl acetate exceeds 32%. The similar effect was observed for the other mixtures of Group A and B.

Addition of Group A material to Group B makes the increasing of the electrical conductivity of the latter then the mixture takes up the character of the former. This tendency is shown in Fig 7 in which the volume charge density of pentane (Group B) with the applied voltage increases with addition of isoamyl acetate (Group A).

Electrical conductivities,  $V_c$  and  $V_d$  of the mixture are tabulated in Table 3. Electrical conductivity of the mixture becomes greater than  $10^{-12}$  (ohm cm) $^{-1}$  and the mixture becomes possessed the character of the materials of Group A when the concentration

### Change of Liquid Drop Shapes on Electrification

#### III. 4. Quantity of Charge for Applied Voltage Higher than $V_c$ .

In this case the quantity of charge of a particle cannot be measured by Faraday cage, therefore, a.c. field method<sup>3)</sup> was applied for the purpose. Trajectory of a falling particle follows a sine curve by a.c. electric field applied horizontally. Radius and charge of particle were calculated from applied electric field, amplitude of trajectory and wave length measured in the photographic pictures taken a.c. electric field method. Change of charge quantity with radius of the particles of ethyl acetate is seen in Fig. 8. Similar results to Fig. 8 were obtained with other liquids of Group A. A typical surface charge density of the mist is about  $2 \times 10^{-9}$  coul/cm<sup>2</sup>. This value is nearly equal to that of Lenard effect at the rupture of a water drop. Moreover, the electric field on the liquid surface caused by this charge density is about  $3 \times 10^6$  V/cm which happens to be equal to the electric field to cause a corona discharge in the air.

Table 3. Influence of additive effect of Type A to B on electrical conductivity and dispersive characteristics.

| Volume concentration of Isoamyl acetate | Electrical conductivity     | $V_c$ | $V_e$ |
|-----------------------------------------|-----------------------------|-------|-------|
| %                                       | $\Omega^{-1}\text{cm}^{-1}$ | kV    | kV    |
| 100                                     | $6 \times 10^{-10}$         | 2.6   | 3.3   |
| 50                                      | $1 \times 10^{-11}$         | 2.6   | 3.3   |
| 32                                      | $2 \times 10^{-12}$         | 3.6   | 4.4   |
| 18                                      | $6 \times 10^{-13}$         | ×     | ×     |
| 6                                       | $4 \times 10^{-13}$         | ×     | ×     |
| 1                                       | $2 \times 10^{-14}$         | ×     | ×     |
| 0                                       | $2 \times 10^{-14}$         | ×     | ×     |

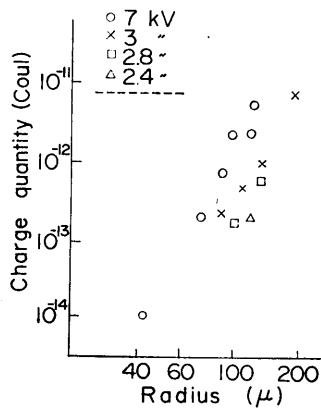


Fig. 8. Charge quantity of individual droplet

### III. 5. Discharge Current

The corona pulse and the discharge current are observed when the materials of Group A are emerged from a capillary with increasing the applied voltage. Relation between applied voltage and discharge current is shown in Fig. 9. Similar discharge characteristic is observed in better stability of current without the liquid. It was found that the fine liquid charged particles are emitted from the electrode below the corona onset voltage which is higher than  $V_a$ . The spray is made unstable and the larger particles become contained by corona discharge onset. Corona discharge for the liquids of Group B was not observed at voltages below 12kV.

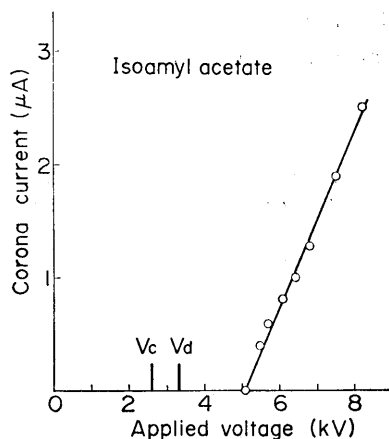


Fig. 9. Corona discharge characteristics

### IV. Discussions

The liquid samples used in this research were not pure dielectric materials, as they produce the steady current by applying the d.c. voltage. The reasons why the organic liquids are electrically conductive are attributed to (a) trace ionic impurities, and (b) an effect that the charge is injected into the liquid from the electrode surface<sup>4)</sup>. Dissociation of the ionic trace impurities in the organic liquids is stronger in the liquids of higher relative permittivity than in the lowers. This is explained as the results that the recombination power of positive and negative ions in the liquids is inversely proportional to the relative permittivity. As the results, the experimental values of d.c. electrical conductivity are higher for the samples of higher relative permittivity, as seen in Table 1. With these liquid, the electrical current decreases with time under a definite electric field, it reaches to an equilibrium state after a long time (Fig. 5). This is considered to be caused by that the concentrations of the ions which contribute to electrical conductivity get lowered with time on account of formation of ionic layer near the electrode owing to moving of the mobile ions in the liquid by the effect of electric field. The appearance of discharging

### Change of Liquid Drop Shapes on Electrification

current for a long time after removing the power source, also proves above explanations. Both the dipoles and the ions should be considered in order to analyze the electrical forces in the liquid drop under the electric field. Therefore, it is not easy to measure the influence by relative permittivity and dipolemoment, as the almost ions in the liquid form the space charges.

For discussing the phenomena, a simple model is considered in which a liquid drop is attached at the lowest end of the electrode positively charged. The positive charges in the liquid drop are repelled to the far end of the drop from the electrode and the negative charges are consumed at the electrode, if the other transfer of charge is not occurred to and from outside.

Consequently, adherent force by surface tension of the liquid drop, which is attached to the capillary electrode, is in a balance with a resultant force of sum of gravitational and electrical force as expressed in the following equation:

$$c r \gamma = \rho V g + \sum q E \quad (3)$$

where  $c$  is a constant,  $r$  is diameter of a capillary electrode,  $\gamma$  is surface tension,  $\rho$  is density of a liquid,  $V$  is the volume of a liquid drop,  $g$  is gravitational constant,  $\sum q$  is excess positive charge in a liquid drop, and  $E$  is electrical field strength in which the liquid drop is placed. In equation (3), if the right side of the equation becomes larger than the left, the component of downward force worked on a liquid drop becomes larger, and the drop falls. In the absence of electric field the volume,  $V_0$  in an equilibrium is expressed in the following equation:

$$c r \gamma = \rho V_0 g \quad (4)$$

Supposing electric field  $E$  is proportional to the applied voltage, equation (2) becomes,

$$\sum q = k' E \quad (5)$$

where  $k'$  is a constant.

Therefore,

$$V_0 - V = k'' E^2 \quad (6)$$

( $k''$  is a constant) is reached, the tendency of change of the volume of Group A which is expressed in equation (1) can be explained from expression (6). For performance of this phenomenon, the charge inside the liquid drop has to neutralize quickly with an counter charge on the electrode, when the drop grows at the lowest end of the capillary electrode. Mechanism of the injection and the dissipation annihilation of the ions have not yet well understood. However, it is considered, if the relaxation time  $\tau = \epsilon / \sigma$  ( $\epsilon$  is absolute permittivity,  $\sigma$  is electrical conductivity) of charge is effective on dissipation of the ions, that it seems to be proceeded in a short time with a some larger value of  $\sigma$ , as the change of  $\epsilon$  is rather small compared with  $\sigma$ .

On the contrary, with a liquid of low electrical conductivity, influence of relative

permittivity is effective, because of time required for dissipation is long and low density of dissociated ions. In this case, an dielectrophoretic force occurs by polarization which pulls up the liquid drop. Excess pressure caused by dielectrophoretic force<sup>5)</sup> is proportional to the square of the strength of electric field. This relation is expressed in an equation (7), which describes the volume change. (in Group B)

$$V_0 + V = k''' E^2 \quad (7)$$

The liquids can be classified to Group A and B by the difference of the two kinds of forces already stated. This classification, however, depends on the flow rate, decreasing the flow rate Group B changed to Group A. But the residual ions in the liquids of lower electrical conductivity tends to separate electrically in an inhomogeneous electric field.<sup>6)</sup> The tendency, that a liquid having the nature of Group A in the initial period changed to Group B later, has been often observed.

It could happen that a part of the liquid surface is broken to pull out a fine thread of the liquid while misting, which breaks into small globules.

In general, it is considered that several kinds of forces work on the liquid surfaces; (1) cohesion due to surface tension, (2) static pressure due to liquid column on the liquid surface, (3) excess vapor pressure owing to curvature of the liquid surface, and (4) electric force on the liquid surface. Forces (2) and (3) can be neglected in this experiment, therefore, force (1) should be larger than (4) for the stable conditions.

The vertical component  $P$  of the force caused by electrostatical effects is expressed in an equation,

$$P = \frac{E_0^2}{8\pi} \left( \frac{\epsilon_r - 1}{\epsilon_r} - \frac{\rho}{\epsilon_r^2} \frac{d\epsilon_r}{d\rho} \right) \quad (8)$$

where  $E_0$  is the strength of electric field applied to the liquid surface,  $\epsilon_r$  is relative permittivity of the liquid, and  $\rho$  is density of the liquid. Equation (8) becomes (9) by simplification,

$$P = \frac{E_0^2}{8\pi} f(\epsilon_r, \rho) = C \cdot f(\epsilon_r, \rho) E_0^2 \quad (9)$$

The value for  $C \cdot f(\epsilon_r, \rho)$  have been calculated by Henriquez<sup>8)</sup> giving 0.11 for toluene. 16.7 for acetone...

As the value of  $P$  becomes larger with proportional to square of the electric field, the pressure caused by electrical force becomes stronger than the surface tension of the liquid to break the balance with increased applied voltage. A relation was shown by Glasstone<sup>9)</sup> which indicates the strength of tensile force  $\tau$  of a liquid thread of radius  $r$  drawn out of the surface of the liquid having surface tension of  $\gamma$ .

$$\tau = \frac{2\gamma}{r} \quad (10)$$

### Change of Liquid Drop Shapes on Electrification

Hence, a fine liquid column or thread is drawn out of the liquid surface when the force balance in a condition to satisfy the equations (9) and (10). Electric field  $E_d$  on the surface of the liquid drop of radius  $r_d$  having charge  $q$  becomes  $E_d = q/r_d^2$  if the radius of a particle of the mist has the same radius as a fine liquid column drawn out. Therefore, an equilibrium in the following relation is derived

$$\left(\frac{q}{r_d^2}\right)^2 \frac{f(\epsilon_r, \rho)}{8\pi} = \frac{2\gamma}{r_d} \quad (11)$$

According to equation (11), the minimum charge of a particle of radius 100 microns,  $\gamma = 20$  dyne/cm and  $f(\epsilon_r, \rho) = 20$ , is approximately  $2 \times 10^{-12}$  coul. Experimental values of the charge of a particle of radius 100 microns are in a similar range to this value (Fig. 8), and this agreement seems to support the explanation of the misting mechanism mentioned above.

A relation exists between the number of the liquid threads and the applied voltage. This is illustrated in Fig. 10.

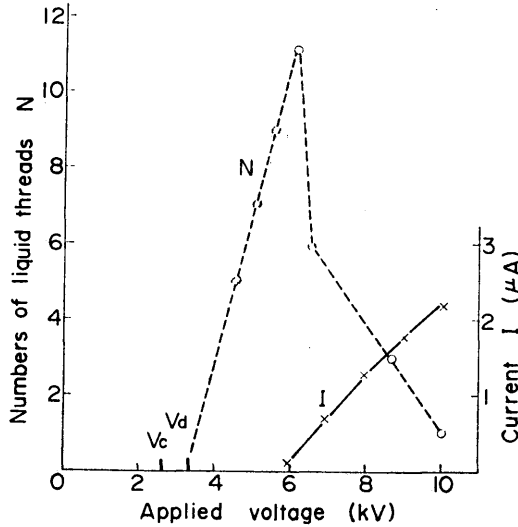


Fig. 10. Relations between numbers of liquid threads and applied voltage

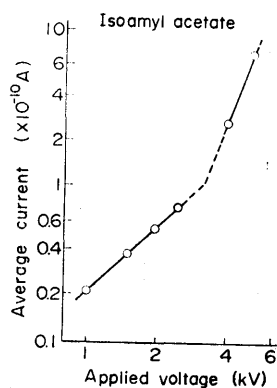
Mostly, the straight line connecting the points of applied voltage versus the number of thread relation falls to  $V_d$  by the extrapolation at  $N=0$ . For the increased value of  $N$  in the range of 6 to 10, corona discharge occurs, then the particle of the mist increases and irregularity of the liquid thread appears. The stable mist of the fine liquid drop can be produced only by the applied voltage between  $V_d$  and the starting voltage of corona discharge. The ionized zone produced at the lowest end of the capillary electrode by the corona discharge influenced to the space charge and it gives disturbance to the misting. Little change is seen for the misting from the negative capillary electrode compared with positive capillary below  $V_d$ . Upper than

$V_d$ ,  $N$  varies frequently with time even with the fixed voltage, and coarse drops are emitted in the unstable misting. Charge density is, by the first approximation, proportional to the applied voltage to the capillary electrode with constant flow, and a particle seems to accumulate the charge until the force caused by the charge density overcome the surface tension. At a higher voltage, a large amount of charge stored at the lowest end of the capillary is released by the increasing of total surface of the fine liquid drops.

But, at very high voltages, releasing of the charge cannot over take the supply of the charge at an unstable point on the surface of the liquid drop, the second and the third unstable points are required to expell the excess charge. This results the increase of the number of the liquid threads. The liquid threads have the same polarity of charge, and therefore, the repulsive forces among them make the liquid threads apart one another.

The liquids of Group *B* cannot attain enough charge density even at the higher voltage and no instability is seen. Furthermore, as seen in Fig. 3, following the fallen drop the small liquid drop or film is remained around the edge portion of the capillary electrode. Presumably, the local field strength near the edge portion is reduced with the liquid film. It may be considered, by this reason, that no corona discharge from the capillary was observed with the voltage up to 10 kV.

From the measured values of charge quantity of disintegrated drops by the method described in III.3 and III.4, the mean current carried from the needle electrode by the liquids was calculated for each applied voltages. Results are shown in Fig. 11, where the abscissa represent the logarithm of the average current and the coordinate represent the logarithm of the applied voltage respectively. The curve connected the points is approximately shown by two straight lines which turn off at a certain point. As shown in Fig. 11, this point appears about 3 kV of the applied voltage near the critical value  $V_d$ .



**Fig. 11.** Average current carried by liquid drops

From this result it may be considered that the mechanisms of electrification of the liquid drop when the applied voltage is higher than  $V_d$  is different from the lower one. For example, there is a tendency that the lower end of the liquid drop deforms and produces a sharp tip where the disintegration is occurred. The accumulation of the surface charges produces the local discharge from this point, therefore, the charge transfer from the liquid surface gives the excess charges on the surface of the drop.

Radial spraying of the liquid threads was not affected by the existence of the micro-scratches on the edge of the capillary. A set of experiments under the following conditions were done to examine this effect:

## Change of Liquid Drop Shapes on Electrification

(1) Several new capillary electrodes were replaced successively, but the schemes of spraying were quite reproducible. (2) Even for replacing the capillary electrode to a needle electrode (cotton sewing needle) so as to make the liquid sample to be supplied over the surface of the needle, the scheme was analogous as in the former case. (3) Up-wards spraying is not affected the scheme of spraying near the electrode. (4) Variation of the electrode spacing ( $d$  in Fig. 1) is scarcely affected to the scheme.

The inversion of the polarity of the electrode and variation of the electrode spacing are not affected to the values of  $V_c$ ,  $V_a$  and  $k$ . Furthermore, when the glass cylinder containing the sample liquid is replaced by the metal one, the measured values of  $V_c$ ,  $V_a$  and  $k$  were quite as same as in the former case. But a metal capillary with a spheric end diminishes the disintegration effect. As mentioned above, it may be considered that the local electric field on the lower end of the capillary is mainly influenced to the phenomena of the electrical disintegration.

## V. Conclusion

A liquid drop from a capillary, when it is electrified, can take different forms in association with the amount of their electrification. The forms were classified into two groups. For the liquid with electrical conductivity above  $10^{-12}(\text{ohm cm})^{-1}$ , the drops tended to be disintegrated above the critical applied voltage  $V_a$ . For the liquid with conductivity below  $10^{-12}(\text{ohm cm})^{-1}$ , however, the increase of applied voltage only resulted in the increase of the volume of drops and no mist formation was observed. The role of the electrical conductivity is to supply the adequate surface charge to the rupture of the liquid surface.

The phenomenon of electrostatic disintegration of the liquid drop is classified into three patterns by the corresponding applied voltage.

(a) Charging region below  $V_a$ , (b) Prebreakdown region accompanying the mist between  $V_a$  and the corona break down voltage, and (c) Corona discharge region.

Both of the local field strength and the electrical conductivity mainly affected to the disintegration phenomena, but no effect was observed with variation of chemical composition of the liquid samples.

The author wishes to express his deepest thanks to Prof. M. Mashima for his valuable suggestions on this research project.



Akira WATANABE

References

1. H. Schott: *J. Appl. Phys.*, **36** (1965) 3399, etc.
2. A. Sharbaugh: *Progress in Dielectrics*, (Heywood Co. Ltd., London, 1962), **4** p. 201.
3. K. Kawasaki; *Researches of the Electrotechnical Laboratory*. No. 690.
4. G. B. Brière: *Brit. J. Appl. Phys.*, **15** (1964) 413.
5. S. S. Hakim: *Proc. Phys. Soc.*, **80** (1962) 190.
6. H. A. Pohl; *J. Electro-chem. Soc.*, **107** (1960) 386.
7. V. Drozin: *J. Colloid. Sci.*, **10** (1955) 138.
8. P. C. Henriquez: *Rec. Trav. Chim.*, **54** (1935) 574.
9. S. Glasstone: *Textbook of Physical Chemistry* (D. Van Nostrand 1940), p. 471.