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Direct observation and characterization of the generation of organic solvent droplets with and without triglyceride oil by electrospraying

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ABSTRACT

The primary aim of this study was to investigate the generation characteristics of organic solvent droplets with and without triglyceride oil by electrospraying using single-nozzle and nozzle-array devices. The liquids used were ethanol (10 to 99.5%), ethanol (99.5%) solutions containing a triacylglyceride oil, ethyl acetate, hexane, and heptane. The droplet generation behaviors from an electrode nozzle were observed using high-speed video cameras. Unstable micro-dripping mode was observed when using ethanol (<50%), hexane, and heptane. In contrast, the stable electrospraying by cone-jet mode was achieved when using ethanol (>66.7%) and ethyl acetate. The jet diameter values mostly ranged between 10 and 20 μm, which is similar to the estimated ones. High-speed photographic observation at a frame rate of 10^6 s^{-1} demonstrated the generation of ethanol droplets at very high frequencies of $3.0x10^5$ to $5.0x10^5$ s^{-1} by breaking up the jet. The ethanol jet diameter increased with increasing the flow rate (1 to 10 mL/h). The nozzle number per device did not affect the jet diameter when the flow rate per nozzle is the same. The stable cone-jet mode was also achieved when using ethanol solution containing 0.1% triacylglyceride oil. Triacylglyceride oil droplets with diameters of about 2 μm were collected after evaporating ethanol from the droplets generated by electrospraying.

Keywords: Electrospraying; Organic solvent; Triglyceride oil; Droplet generation; Direct observation; Nozzle array

1. Introduction

Electrospraying (electrohydrodynamic spraying) is a method of liquid atomization induced by electrical force [1]. With electrospraying, liquid surface tension is balanced by electrical force at each point on the liquid surface. When electrical force and gravity force that act on a drop overcome the surface tension, the meniscus of the liquid caused the jet formation. The cone-jet leads to fission and subsequently disrupts into fine droplets due to the instability of the jet. From the energy viewpoint, liquid forms a jet when the kinetic energy of the liquid is greater than the surface energy required for creating the surface of the jet [2]. Thus, variations in normal electric stress at the apex of the meniscus, the energy gain per unit area of the liquid, and the tangential electric stress at the meniscus lateral are evaluated in the forms of electrospraying modes. When the tangential electric stress is intense enough, a cone-jet is formed [3].

Electrospray systems have the following advantages over mechanical atomizers. The droplet size can be smaller than 1 μm. The size distribution of the droplets can be nearly monodisperse [4]. The charge and size of the droplet can be easily controlled (including deflection or focusing) to some extent by adjusting the flow rate and voltage applied to the nozzle [5].

Electrospraying can be widely applied to both industrial processes and scientific instrumentations. Interest in industrial or laboratory applications has recently prompted the search for effective techniques that enable control of the processes in which droplets are involved. Electrospraying techniques are aimed at developing new drug-delivery systems, medicine production, and ingredient dosage in the cosmetic and food industries. In particular, electrospraying has recently been adapted for many applications (e.g., medical powder production [6], fine metal powder production [7], film coating [8],

electrostatic painting [9], and fuel injection [10]).

Electrospraying is often performed in typical modes. Among these modes, many studies have focused on the cone-jet mode, in which the liquid meniscus appears to have a Taylor cone [11-15]. The size distribution of the droplets produced in cone-jet mode depends on the jet diameter and the type of jet instabilities (e.g., varicose instability and kink instability) [16]. The jet diameter is a strong function of the axial distance, which may be due to solvent evaporation. Therefore, it is important to make comparisons at a fixed point below which there is negligible change in jet diameter [17]. Xie et al. [18] also developed a hypothesis explaining the characterization of particles obtained by electrospraying under various operating conditions (e.g., polymer solution flow rate, polymer concentration, and type of chemical solvent). Electrospraying are also generally performed using polar liquids (e.g., water, ethanol, glycerol, and polyethylene glycols). Ethanol has been used for understanding fundamental properties of electrospraying and as a carrier fluid for producing micro/nanoparticles [19-21]. Martin et al. [19] reported how liquid flow rate and nozzle and flat plate voltages influence the cone-jet domain for electrospraying using pure ethanol.

Droplets generated by electrospraying have potential food applications as forms of micro/nano-particles and micro/nano-dispersions. However, few electrospraying researches using food-grade materials have been conducted [22,23]. Therefore, the present work attempts to employ the electrospraying technology to generate the fine droplet consisting of organic substances. Here, we investigate the production process focusing on the type of organic solvents, the effects of device and operating conditions, high-speed camera observation of droplet generation. We also investigated the generation of droplets consisting of an organic solvent and a triacylglyceride oil as well

as the formation of triacylglyceride oil droplets by solvent evaporation from the droplets.

2. Materials and methods

2.1. Experimental setup

2.1.1. Electrode nozzle devices

Stainless-steel 24×24-mm devices with different numbers (1, 4, or 12) of electrode nozzles were designed and fabricated for this study (Fig. 1). Initially, each circular through-hole with a diameter of 600 μm on a polished metal plate was fabricated by microdrilling. Subsequently, each electrode nozzle with an inner diameter of 230 μm and a length of 13 mm was connected to the through-hole by solder bonding.

2.1.2. Electrospraying module and peripherals

Fig. 2 is a simplified schematic diagram of the experimental setup for electrospraying using electrode nozzle devices. It consists of a holder equipped with the device, a metal ring with a diameter of 100 mm as the extractor electrode, a syringe pump (Model-11, Harvard Apparatus, USA) for feeding an organic liquid, a high voltage DC power supply (KHV-U5003, Kyoshin Electric Co., Ltd., Japan) for applying an electric field to the liquid, a high-speed video camera with a maximum frame rate of 2.5×10^5 s^{-1} (Fastcam SA1.1, Photron Ltd., Japan) or 10^6 s^{-1} (HyperVision HPV-1, Shimadzu Co., Japan), and a metal halide light source (LS-M210, Sumita Optical Glass, Inc., Japan).

2.2. Chemicals and solution preparation

The organic solvents used in this study are ethanol (purity 99.5%, Nacalai Tesque, Inc., Japan), *n*-hexane (Wako Pure Chemical Industries Ltd.), *n*-heptane (Wako Pure Chemical Industries Ltd.), and ethyl acetate (Wako Pure Chemical Industries Ltd.). Ethanol solutions with a concentration of 10 to 99.5% were prepared by mixing 99.5% ethanol with deionized and filtered water (Milli-Q water). Refined soybean oil (Wako Pure Chemical Industries Ltd.) as a model long-chain triglyceride, and medium-chain triglyceride (MCT) oil (MCT-7, Taiyo Kagaku Co. Ltd., Japan) were also dissolved in 99.5% ethanol at a concentration of 0.1% and a room temperature of 25 ^{o}C.

2.3. Experimental procedure

Prior to the electrospraying experiments, an electric nozzle device was fixed in the holder, and the tip of each electrode nozzle was positioned at 10 mm over the ring grounding electrode. Each liquid was contained a 10-mL glass syringe and was introduced into the module using a syringe pump at a liquid flow rate (Q_L) of 1 to 10 mL/h for the single nozzle device, 6 mL/h for the 4-nozzle device, and 18 mL/h for the 12-nozzle device. Next, the liquid was injected from the nozzle tip under positive DC voltage (V_{DC}) (3.7 to 14 kV) in order to generate organic solvent droplets. At that moment, the nozzle tip was positively electrified, while the ring was grounded. All experiments were conducted at 25 ^{o}C. Electrospraying characteristics were microscopically observed using a high-speed video camera at 9000 to 15000 fps for Fastcam SA1.1 or 10^6 fps for HyperVision HPV-1.

Image-analysis software (WinRoof version 5.6, Mitani Co., Japan) was used to measure the diameters of the droplets on the images captured during experiments. The mean diameter of the droplets generated under each condition was determined using the

measured data of 30 droplets.

2.4. Determination of viscosity, electrical conductivity, and surface tension

A Sine-wave vibroviscometer (SV-10, A&D Co., Ltd., Japan) was used to determine the absolute viscosities of the liquids (defined as the ratio of liquid viscosity to liquid density). The electrical conductivities of the liquids were measured using a conductivity electrode (Model 9382-10D, Horiba Ltd., Japan). The surface tensions of the liquids were determined using a fully automatic surface tensiometer (CBUP-Z, Kyowa Interface Science Co., Ltd, Japan) that adopts the Wilhelmy Plate method. The contact angles of the liquids to a stainless-steel plate were determined using a fully automatic interfacial tensiometer (PD-W, Kyowa Interface Science Co., Ltd, Japan). Measurements of liquid viscosity, electrical conductivity, surface tension, and contact angle were repeated at least three times at 25 ^{o}C; their mean values are presented in Table 1.

3. Results and discussion

3.1. Effect of organic solvent type

3.1.1. Electrospraying characteristics

Electrospraying experiments were first conducted using four different organic solvents. Fig. 3 depicts microscopic snapshots of electrospraying from a single nozzle. The Q_L applied here was 1 mL/h for ethanol, hexane, and heptane, and 6 mL/h for ethyl acetate. Ethanol (99.5%) ejected from the nozzle tip formed a stable cone and jet (cone-jet mode) at a V_{DC} of 3.7 kV (Fig. 3a). Due to electrostatic force, this jet broke up into droplets (see Sect. 3.2). The use of ethyl acetate also resulted in the formation of

163 the cone-jet mode at a V_{DC} of 3.7 kV (Fig. 3b). It should be noted that ethyl acetate
164 rapidly evaporated from the nozzle tip at a Q_L of 1.5 mL/h, as the viscosity of ethyl
165 acetate is about one-third of that of ethanol. The boiling point of ethyl acetate (77.2 ^oC)
166 is similar to that of ethanol (78.4 ^oC). By contrast, heptane and hexane ejected from the
167 nozzle irregularly formed large droplets with diameters of >100 μm nearby the cone tip
168 (microdripping mode) at a Q_L of 6.5 kV for hexane and 5.8 kV for heptane (Fig. 3c and
169 d). The difference in these electrospraying characteristics could be explained using the
170 properties of the organic solvents (Table 1). There was unpronounced difference in the
171 surface tension of the organic solvents. The viscosity values of hexane and heptane were
172 similar to that of ethyl acetate, while remarkable solvent evaporation was not observed
173 for hexane and heptane ejected from the nozzle tip. These results indicate that their
174 surface tension and viscosity are not dominant factors affecting the electrospraying
175 modes in this case. The solvent conductivity was appreciably influenced by solvent type.
176 The conductivities of ethanol and ethyl acetate were at least two orders of magnitude
177 greater than those of hexane and heptane. Earlier studies reported that liquid
178 conductivity plays a critical role in electrospraying characteristics, and that a stable
179 cone-jet mode can be obtained using liquids with a conductivity of 10^{-7} to 10^{-2} S/m
180 [12,16,21]. It is currently assumed that liquids can be electrosprayed in cone-jet mode at
181 conductivities of 10^{-4} to 10^{-8} S/m [5]. The conductivities of ethanol and ethyl acetate are
182 thus considered to be appropriate for stable electrospraying in cone-jet mode.
183
184 *3.1.2. Estimating jet diameter*
185 To achieve stable electrostatic atomization, the electrical relaxation time ($t_e = \beta\varepsilon_0 /$
186 K_L) must be much smaller than the hydrodynamic time ($t_h = l_j d_j^2 / Q_L$) [24]:

$$\frac{\beta\varepsilon_0}{K_L} \ll \frac{l_j d_j^{\,2}}{Q_L} \quad , \qquad (1)$$

where β is the relative permittivity, ε_0 is the permittivity of free space (8.854 x 10^{-12} F/m), K_L is the electrical conductivity, and l_j and d_j are the jet length and diameter. Hence, the dimensionless viscous parameter (δ_m) is defined by Ganan-Calvo et al. [25] as

$$\delta_m = \sqrt[3]{\frac{\rho_L \varepsilon_0 \gamma^2}{K_L \eta_L^{\,3}}} \quad , \qquad (2)$$

where ρ_L is liquid density, γ is surface tension, and η_L is viscosity of liquid. For $\delta_m \gg 1$, the jet diameter (d_j) in stable cone-jet mode can be estimated by [25]:

$$d_j \approx \sqrt[6]{\frac{\rho_L \varepsilon_0 Q_L^{\,3}}{\gamma K_L}} \qquad (3).$$

Substituting the physical values of ethyl acetate in Eq. 2 indicates that δ_m for the ethyl acetate is $\gg 1$ and therefore, d_j is 15 μm at a Q_L of 6.0 mL/h. Conversely, for $\delta_m \ll 1$, d_j is given by [25]:

$$d_j \approx \sqrt[3]{\frac{(\beta-1)^{1/2} Q_L \varepsilon_0}{K_L}} \quad , \qquad (4).$$

Substituting the values of 99.5% ethanol in Eq. 4 yields a d_j of 8 μm at a Q_L of 1.5 mL/h. Based on these results, the measured jet diameters of ethyl acetate and ethanol are similar to the estimated values.

3.1.3. High-speed camera analysis of droplet generation by cone-jet mode

A high-speed camera with a maximum frame rate of 10^6 s^{-1} was used to investigate

droplet generation of 99.5% ethanol using the single-nozzle device. During electrospraying, the liquid formed a conical meniscus at the nozzle tip, and the jet ejected from the nozzle broke up into uniformly sized droplets. High-speed photographic observation (Fig. 4) indicated that fine droplets were generated at remarkably high frequencies of 3.0 x 10^5 to 5.0 x 10^5 s^{-1} under the Q_L of 1.0 mL/h and the V_{DC} of 3.7 kV. In stable electrospraying, the Rayleigh law is defined as [26]

$$\frac{d_d}{2d_j} = 1.89 \quad , \qquad (5)$$

where d_d is the droplet diameter. The d_d calculated using Eq. 5 was 14 μm, which is similar to the d_d measured from the experiment.

3.2. Effect of ethanol concentration and flow rate

Ethanol concentration affects many physical properties of a liquid (e.g., viscosity, density, surface tension, and conductivity); therefore, it is expected to have a great influence on electrospraying characteristics. Single-phase ethanol with a concentration of 10 to 99.5 wt% was made to flow through a single electrode nozzle, 4 electrode nozzles, and 12 electrode nozzles (Fig. 1). The flow rates of all nozzles were the same; 1.5 mL/h for the single nozzle, 6 mL/h for the 4-nozzle array, 18 mL/h for the 12-nozzle array. The V_{DC} values were 4.2 kV for the single nozzle, 9.0 to 11.0 kV for the 4-nozzles, and 12.5 to 14.0 kV for the 12-nozzles. Figure 5a shows the influence of ethanol concentration on the droplet/jet diameter obtained by electrospraying. The influence of ethanol concentration on the surface tension, conductivity, and viscosity of ethanol are also presented in Fig. 5b, c. The processed liquids exhibited microdripping at concentrations of 50% or less (Fig. 5a), which be mainly due to higher surface tension

(Fig. 5b). This may have prevented electrospraying in the stable cone-jet mode at the flow rates and voltages applied here. Electrostatic atomization in cone-jet mode is difficult with liquids containing a high proportion of water [14,27,28] unless specified conditions (e.g., flow rate, surrounding atmosphere, and conductivity) are met [28,29]. The use of ethanol solutions with a concentration of 67% or higher exhibited electrospraying in the cone-jet mode with a narrower jet diameter ranging between 10 and 20 μm (Fig. 5a), indicating that the diameter of ethanol droplets generated in this cone-jet mode decreased slowly with increased the ethanol concentration. The stable cone-jet mode was achieved at surface tensions of 22 to 27 mN/m, conductivities of 1.6×10^{-7} to 8.3×10^{-7} S/m, and viscosities of 0.8 to 1.8 mPa s. It should be noted that the viscosity values of ethanol for the microdripping mode were similar to those for the cone-jet mode (Fig. 5b). The results in Fig. 5a also demonstrated that the resultant jet (and droplet) diameter was hardly affected by the nozzle number at an ethanol concentration of 67% or higher.

Jayasinghe et al. [30] suggested that the flow rate has to be minimized to obtain the finest droplets. However, no stable cone can be formed at flow rates being too low. The values of β, ε_0, and K_L in Eq. 4 do not change for ethanol, and the jet diameter of ethanol increases monotonically with increased flow rates. Among the various parameters, flow rate is the simplest and most effective variable for controlling jet diameter. Therefore, to analyze the influence of 99.5% ethanol flow rate, the applied voltage was kept constant throughout the investigation at 4.4 kV by using the single-nozzle device. Ethanol that ejected from the nozzle tip formed the cone-jet mode at all the flow rates (1 to 10 mL/h). The cone depth, defined as distance from the nozzle tip to the apex of the cone, increased gradually from 150 to 670 μm as the flow rate

253 increased (Fig. 6a). The ethanol flow rate also affected the jet diameter which ranged
254 between 9.0 and 16.1 μm (Fig. 6b). The jet diameter increased slowly with increasing
255 the flow rate in its range of 2 to 10 mL/h, whereas the slope of the jet diameter became
256 higher at the low flow rates of < 2 mL/h.
257
258 *3.3. Electrospraying characteristics of ethanol solution containing triacylglyceride oil*
259 *3.3.1. Effects of oil type and flow rate*
260 Electrospraying an ethanol solution containing MCT (0.1%) or soybean oil (0.1%)
261 formed a stable cone-jet using the single nozzle at a Q_L of 1 mL/h and a V_{DC} of 4.0 kV
262 (Fig. 6). The effect of the flow rate of the ethanol solutions on the cone depth and jet
263 diameter is also shown in Fig. 6. The values of the liquid properties are listed in Table 1.
264 The shape and the wettability of the nozzle material can pronouncedly influence the
265 shape of the cone formed, the stability of the jet, and the electrospraying mode [30,31].
266 The contact angle is an indicator of the wettability of a liquid to the nozzle surface. The
267 wettability of the liquids became poor with increased contact angle on the stainless-steel
268 plate. The static contact angle of 99.5 wt% ethanol to the stainless-steel plate was $<10^o$,
269 indicating that the nozzle surface is easily wetted by ethanol during electrospraying. The
270 static contact angle of MCT on the stainless-steel plate was 20^o, and that of soybean oil
271 was 15^o. The formed cone and jet of the ethanol solution containing soybean oil were
272 somewhat larger (Fig. 6), which may be attributed to its higher wettability to the nozzle
273 surface.
274 At the Q_L of 1 mL/h, the jet diameter was 13 μm for MCT and 18 μm for soybean
275 oil. The jet diameters of the ethanol solutions increased with increasing the Q_L in ranges
276 of >2 mL/h or more for MCT and >1 mL/h for soybean oil. The slope of the lines in Fig.

277 6b became greater between 1 and 2 mL/h for MCT and 0.5 and 1 mL/h for soybean oil.
278 The jet diameters estimated by Eq. 4 that increased with increasing Q_L agreed with the
279 measured results.
280
281 *3.3.2. Optical microscopy of triglyceride oil droplets*
282 Under adequate electrospray condition, droplet relics were collected by swiftly
283 moving a glass slide below the ring ground electrode or over the ring ground electrode.
284 This collection procedure was repeated at least twice. Soon after deposition, the
285 collected droplet relics were analyzed using optical electron microscopy (Leica DMIRM,
286 Leica Microsystems Wetzlar GmbH, Germany). The jet was confirmed to break up into
287 droplets above the ground electrode (Fig. 7a and c). With increasing the distance
288 between the nozzle tip and the glass slide, ethanol evaporated more from droplets, and
289 the size of the collected droplets decreased. The average diameters of the resultant
290 triglyceride oil droplets were about 2 μm, which is reasonable considering the oil
291 concentration in ethanol solution.
292
293 **4. Conclusions**
294 The results have demonstrated that successful electrospraying in cone-jet mode can
295 be achieved when using organic solvents (especially ethanol) with liquid conductivities
296 of $>10^{-8}$ S/m and applying appropriate V_{DC}. The electrospraying behaviors were affected
297 by ethanol concentration as well. High-speed photographic observation demonstrated
298 that the jet formed by electrospraying broke down into fine 99.5% ethanol droplets at a
299 maximum generation frequencies of $5x10^5$ s^{-1}. The jet diameter was affected by the type
300 and composition of organic solvents and increased with increasing Q_L. The jet diameter

obtained from experimentation was similar to the estimated jet diameter. The successful cone-jet mode was achieved using the 4-nozzle and 12-nozzle devices when the Q_L per nozzle was the same. This finding is useful for improving low droplet productivity in electrospraying. Fine triglyceride oils with diameters of about 2 μm were also obtained by electrospraying of ethanol solution containing triglyceride oils and subsequent solvent evaporation from the generated droplets. This combined process could be applicable for forming a thin edible oil layer in foods and pharmaceuticals.

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389

390

391 Table 1 Surface tension, conductivity, and viscosity of organic solvent solutions with
392 and without triacylglyceride oil used for electrospraying.

393

Solution type	Surface tension (mN/m)	Conductivity (S/m)	Viscosity (mPa s)
Ethanol	22.2	1.6×10^{-5}	0.83
Ethanol (0.1% MCT)	22.0	1.7×10^{-5}	0.78
Ethanol (0.1% soybean oil)	22.2	9.0×10^{-6}	0.82
Ethyl acetate	23.4	$<1 \times 10^{-7}$	0.45
Hexane	18.3	$<1 \times 10^{-13}$	0.32
Heptane	19.7	$<1 \times 10^{-9}$	0.41

394

395

Figure captions

Fig. 1 Schematic illustrations of stainless-steel devices with different numbers (1, 4, and 12) of electrode nozzle. (a) Single-nozzle device. (b) 4-nozzle device. (c) 12-nozzle device.

Fig. 2 Schematic representation of the setup for electrospraying.

Fig. 3 Typical electrospraying behaviors of different organic solvents: (a) ethanol, (b) ethyl acetate, (c) hexane, and (d) heptane. Each liquid was ejected using a single nozzle. Scale bars are 100 μm.

Fig. 4 Typical image of stable cone-jet mode and generation of 99.5% ethanol droplets. This image was taken at a frame rate of 10^6 s^{-1}.

Fig. 5 Variations in jet and droplet diameters (a), surface tension and viscosity (b), and conductivity (c) as a function of ethanol concentration.

Fig. 6 Variations in cone depth (a) and jet diameter (b) as a function of flow rate. The images in (c and d) are examples of electrospraying of ethanol solutions each containing a triglyceride oil. The cone depth and jet diameter are defined in (c).

Fig. 7 Optical micrographs of ethanol droplets containing 0.1% MCT (a and b) or 0.1% soybean oil (c and d) collected on a glass slide. The distance in (a and c) was 0.5 cm

below the ring electrode, and that in (b and d) was 2 cm over the ring electrode. Scale bars are 10 μm.

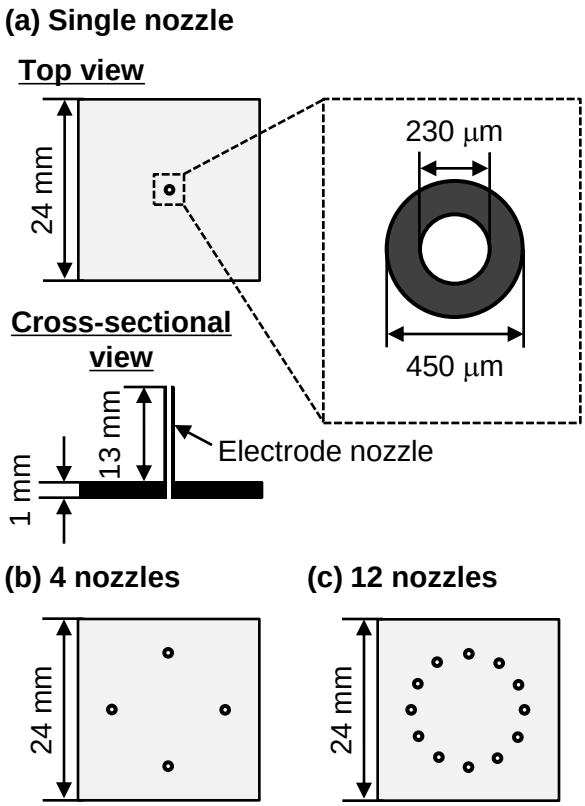

Fig. 1

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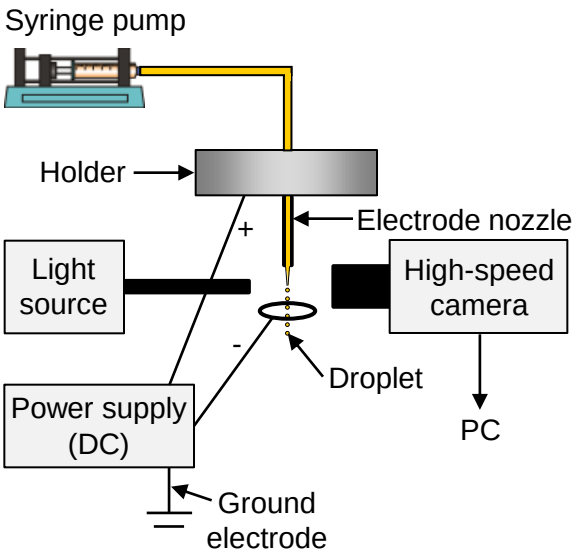

Fig. 2

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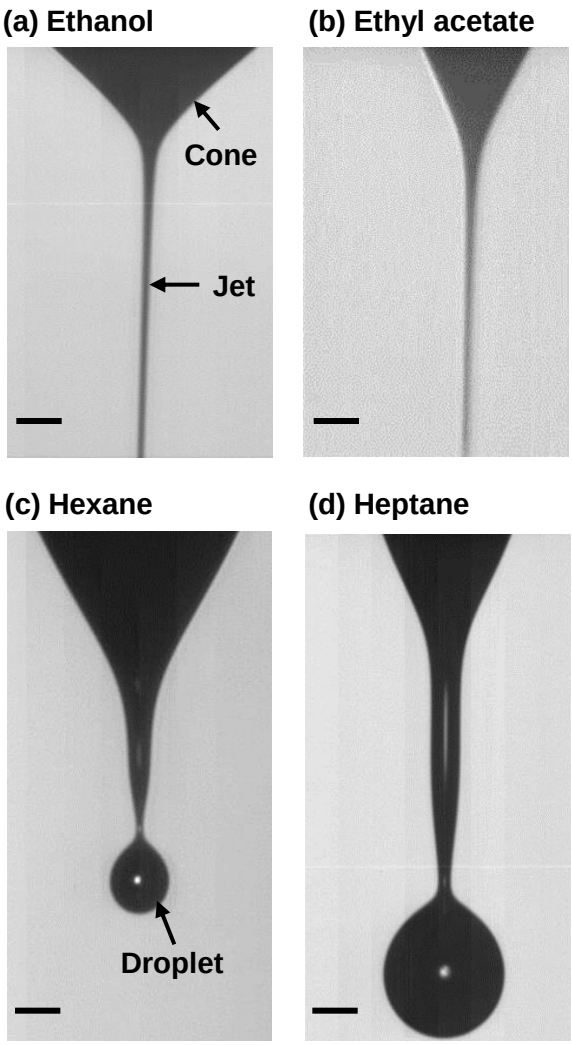

Fig. 3

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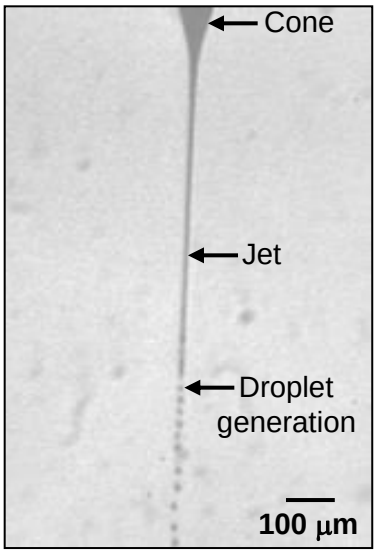

Fig. 4

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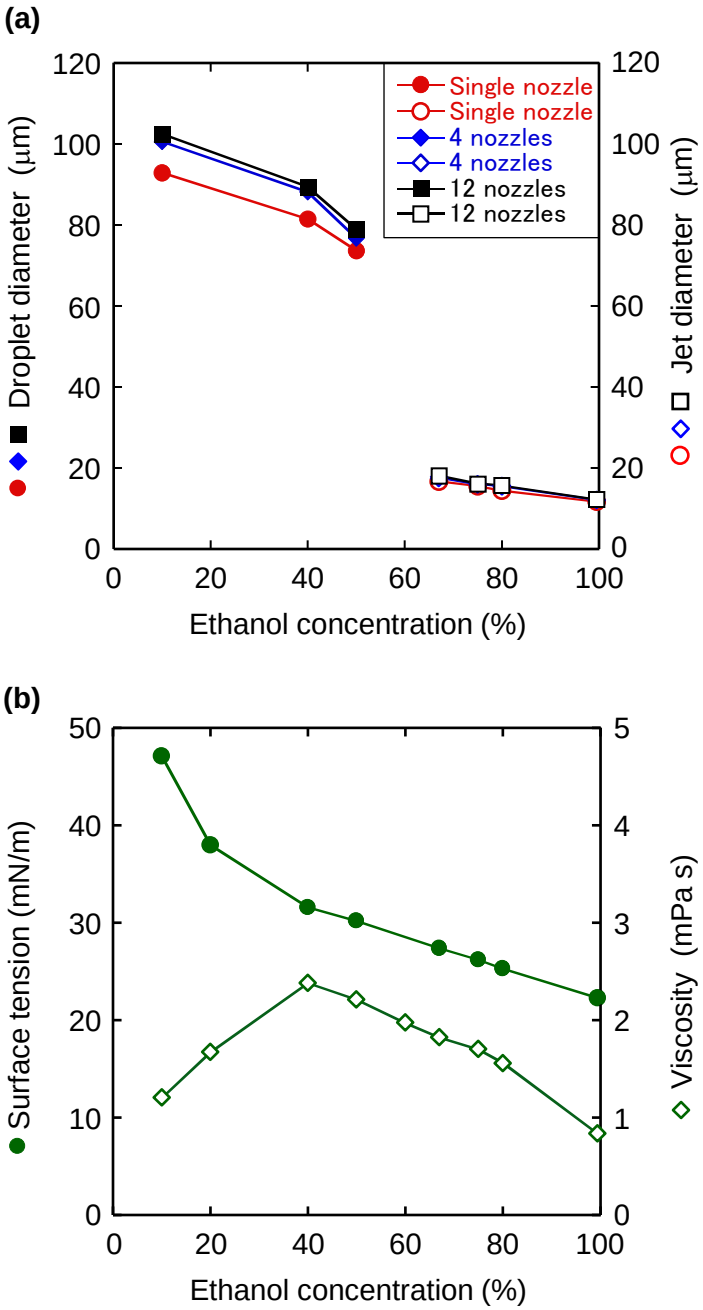

Fig. 5

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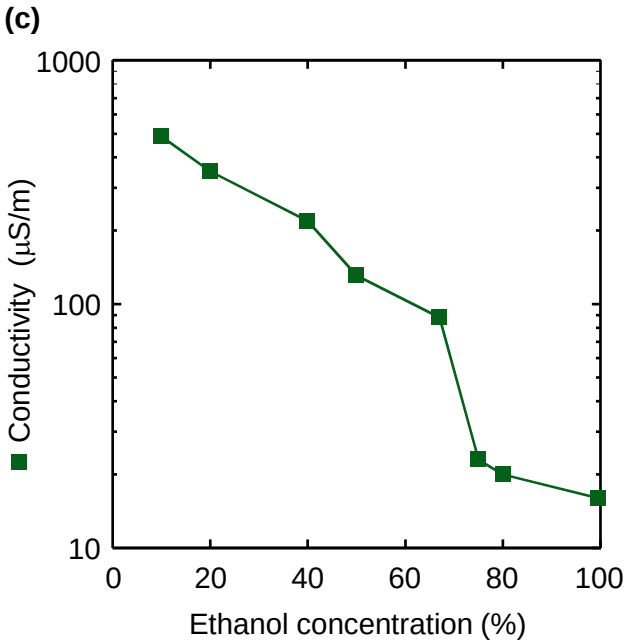

Fig. 5 (Cont.)

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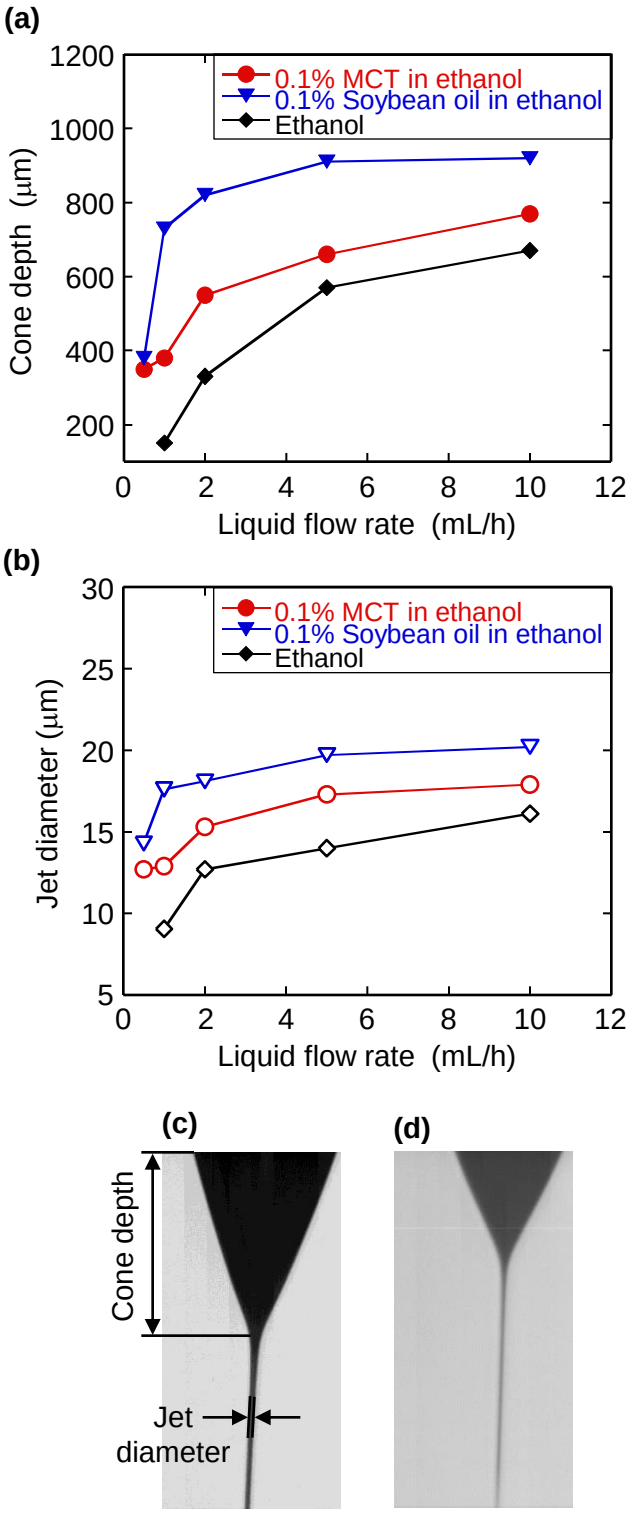

Fig. 6

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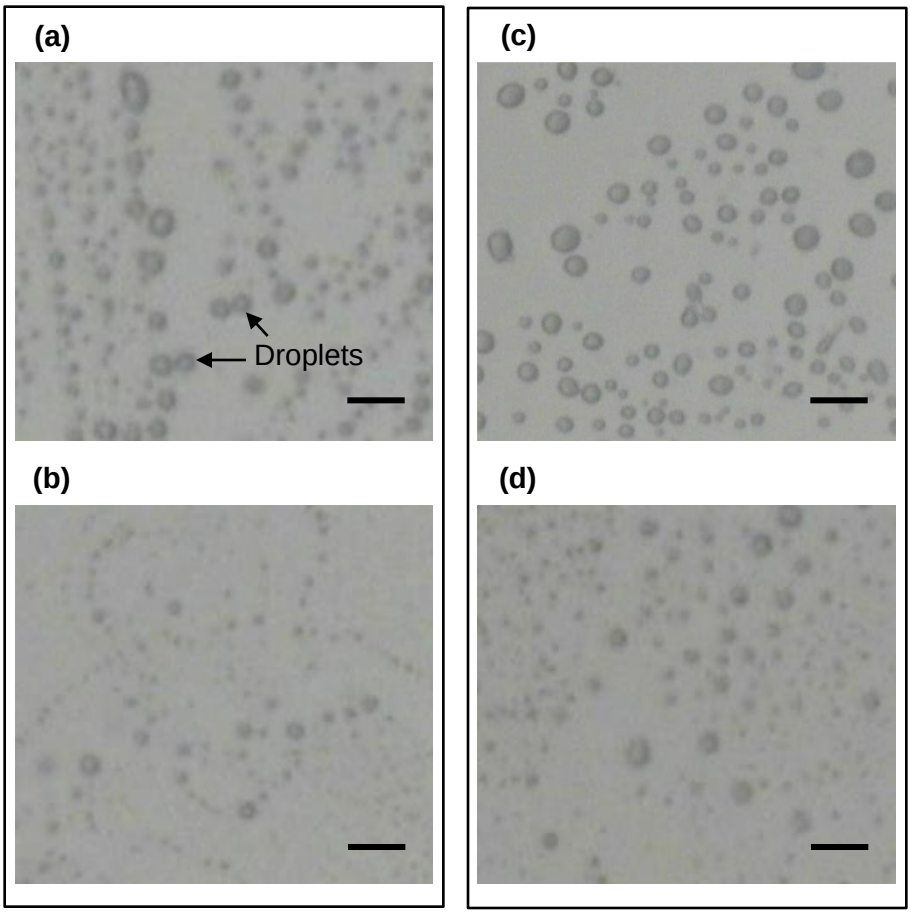

Fig. 7

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