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Rapid Crystallization of Natural Sugars in Bee's Honey under the Influence of Nanosecond Microdischarges

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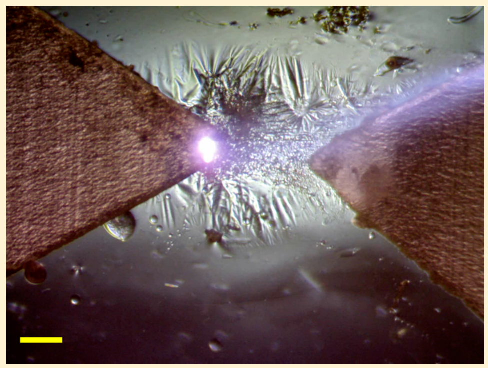
ABSTRACT: Electrical nanosecond microdischarges are produced in bee's honey as an oversaturated solution of sugars for the first time. It is shown that a periodic sequence of microdischarges causes rapid crystallization of sugars.



Pulsed electrical discharges in liquids have been studied for many years already. This area has accumulated a vast amount of factual material: a lot of dissertations, review papers,[1−3] and books[4,5] have been published. Multiple technologies have been developed using discharge in liquids, such as purification[6] and sterilization[7] of liquids, change of color,[8] destruction of living tissues in medicine,[9] and so forth. Discharges have been studied both in low-viscosity liquids, such as water[10−12] and liquefied noble gases,[12] and high-viscosity liquids, such as oil[13] and glycerin.[14] Discharge gaps may have dimensions from a few microns[15,16] or millimeters[17] to one meter.[13]

In this paper electrical nanosecond microdischarges in liquid bee's honey are studied for the first time. Bee's honey is a highly viscous yellow-brown liquid. The physical properties of honey depend on the place of its gathering and storage conditions. According to the literature[18−21] liquid honey may have the following physical properties: moisture content 20−25%, pH 3.1−4.5, and electrical conductivity 0.1−1.1 mS/cm. The viscosity of honey is highly dependent on the temperature; according to ref 19 it can take the value ranging from 10−30 Pa·s at room temperature.

Most importantly, honey is an oversaturated solution of natural sugars in water. The liquid state of an oversaturated solution is known to be unstable. Any small physical disturbance can cause its crystallization. The aim of this work is the experimental verification of the assumption that nanosecond electrical microdischarges within liquid honey can act as disturbances causing rapid crystallization of sugars. The authors are not in the know about any other scientific work dealing with the investigation of electrical discharges in any oversaturated solutions. We are aware of just a single article,[22] in which cavitation in oversaturated aqueous solutions of $(NH_4)_2SO_4$ and $KMnO_4$ under the influence of microsecond laser was studied. In this study the formation of a crystal nucleus was observed.

It should be pointed out that laser cavitation in a liquid and electrical breakdown of a liquid are similar physical processes:[4] in both cases a vapor−gas plasma cavity appears in the liquid, which then collapses. The electrical conductivity of honey is much lower than the electrical conductivity of oversaturated aqueous solutions of salts. Therefore, it is easier to study discharge assisted crystallization of liquid in honey rather than in any conductive aqueous solution of salts, as in ref .

Natural liquid bee's honey produced by a Russian company Medovaya Dolina LLC[23] was used for the experiment. The time of gathering was May 2014. The main honey plants were willow, tatarian maple, coltsfoot, dandelion, white and yellow acacia, and sainfoin. It should be noted that during passive (undisturbed) storage honey remained in a liquid state without any significant saccharification during a one year period.

It is well-known that bees collect honey from flower nectar, which consists of a mixture of glucose, fructose, saccharose, and so forth. If the honey is good, it becomes sugared within a few months; i.e., many thin crystals appear in the liquid fraction in the form of whiskers. These are natural sugars.

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Producers of bad quality cheap honey add industrial sugar to the bee food. Industrial sugar is made usually from the sugar beet in Russia. Its crystals look like sticks, squares, or triangles. Such crystals could be seen in bad honey before and after its processing with the discharges. Arrows show these crystals in the figures. We have found that honey under our investigations contains crystals of industrial sugar.

Simple discharge cells similar to the cells described in refs 24−26 are prepared for the experiment. It is made in the following way: Standard microscope slides with dimensions of 1″ × 3″ and a thickness of 1 mm are taken. First, the slides and two coverslips with the dimensions of 0.94″ × 0.94″ and thickness of 0.15 mm are glued together with the help of a double-sided adhesive tape. Then, two electrodes cut out with good accuracy from household aluminum foil with thickness of 14 μm with the help of household scissors are attached using a double-sided adhesive tape. The electrodes are in the shape of a wedge. Thus, the tips of the electrodes are spaced from the surface of the slide to a thickness of 0.15 mm.

As soon as the electrodes are installed into the electrode gap, a drop of honey 1−2 mm in diameter is introduced, so that the tips of the electrodes are inside the drop to a depth of 0.15 mm. The discharge cell scheme is shown in Figure 1.

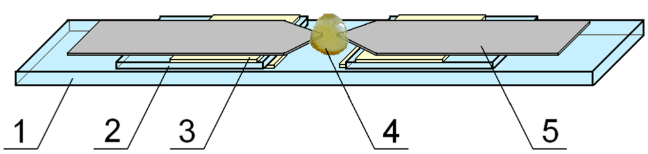

Figure 1. Discharge cell scheme: 1 is slide; 2 is coverslip; 3 is double-sided adhesive tape; 4 is drop of honey; 5 is foil electrode.

For detailed visualization of the channel of microdischarges, an optical microscope Levenhuk D50L NG, equipped with a digital video camera DEM200, is used. The maximum increase of the optical system of the microscope is 640×, and with the additional Barlow lens 1280×. The resulting images have a high resolution (1600 × 1200 pixels). Monitoring of the processes inside the drop was conducted with the help of the hanging drop method.[27] For this the prepared discharge cell is placed on the microscope stage so that the drop is turned down. The crystallization process is recorded in video mode with a frame rate of 7 fps.

A high-voltage impulse generator is connected to the electrodes. As a generator, the household transformer type electric lighter Iskorka-6 providing a sequence of high-voltage nanosecond pulses is used. Pulses follow at a frequency of 20 Hz. When connecting the load to the generator output in the form of a spark gap, circuit discharge current pulses occur. A typical oscillogram of the current pulse in the discharge circuit for a spark gap is shown in Figure 2a. It is the whole current which is equal to the sum of the displacement current and the conductivity current. It has a typical view for the currents of short-pulse discharges: exponentially damped sinusoidal oscillations.[28−30] Such a view corresponds to the displacement current. In the beginning of the signal one can see that sinusoidal oscillations are distorted by the conductive current.

For understanding the correct discharge phenomena, the displacement component must be extracted from the whole current. The procedure of obtaining the conductive current is based on subtraction of the displacement current oscillogram from the whole current oscillogram:

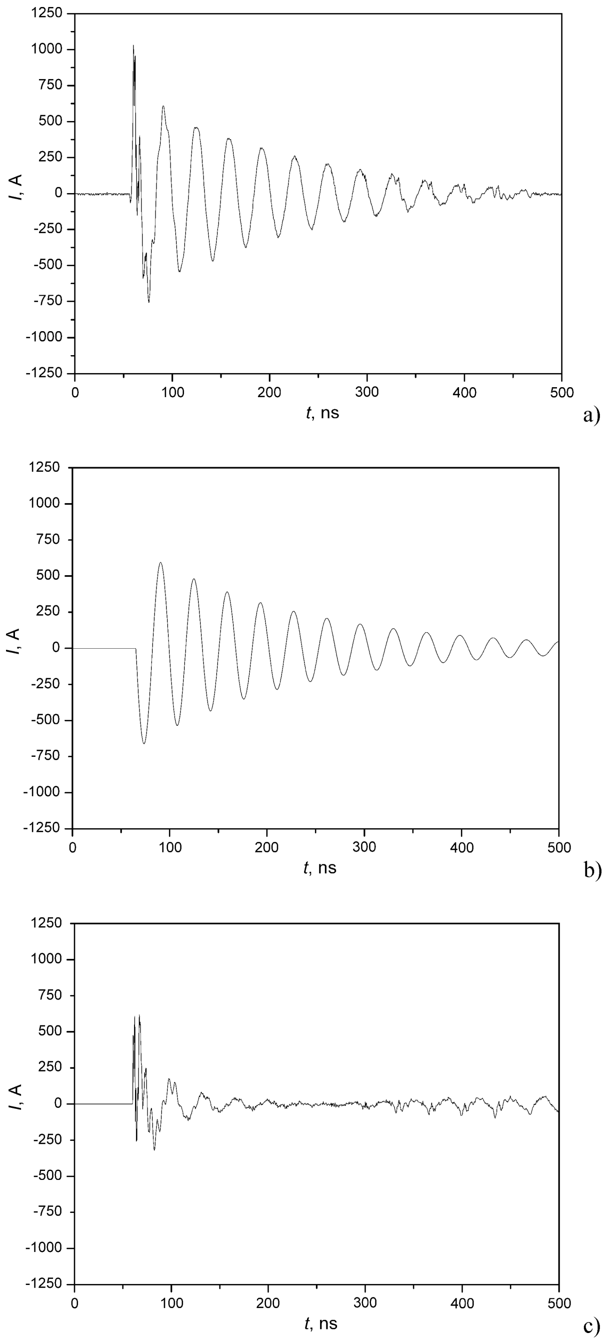

Figure 2. Typical oscillograms of the currents: (a) the recorded whole current; (b) the calculated displacement current; (c) the obtained conductivity current.

$$i_{cond} = i_{whole} - i_{disp} \tag{1}$$

The displacement current oscillogram could be presented in the form of known function

$$i_{disp}(t) = a\ \exp[-h(t - t_0)]\sin\left(\frac{t - t_0}{T} + \pi\right)\theta(t - t_0) \tag{2}$$

where a is the amplitude of the oscillations, h is the decrement, T is the period, t_0 is the moment of the signal beginning on the oscillogram, and θ is the step Heaviside function. Parameters a, h, T, and t_0 were determined from the part of the whole current oscillogram, which is not distorted by the displacement current.

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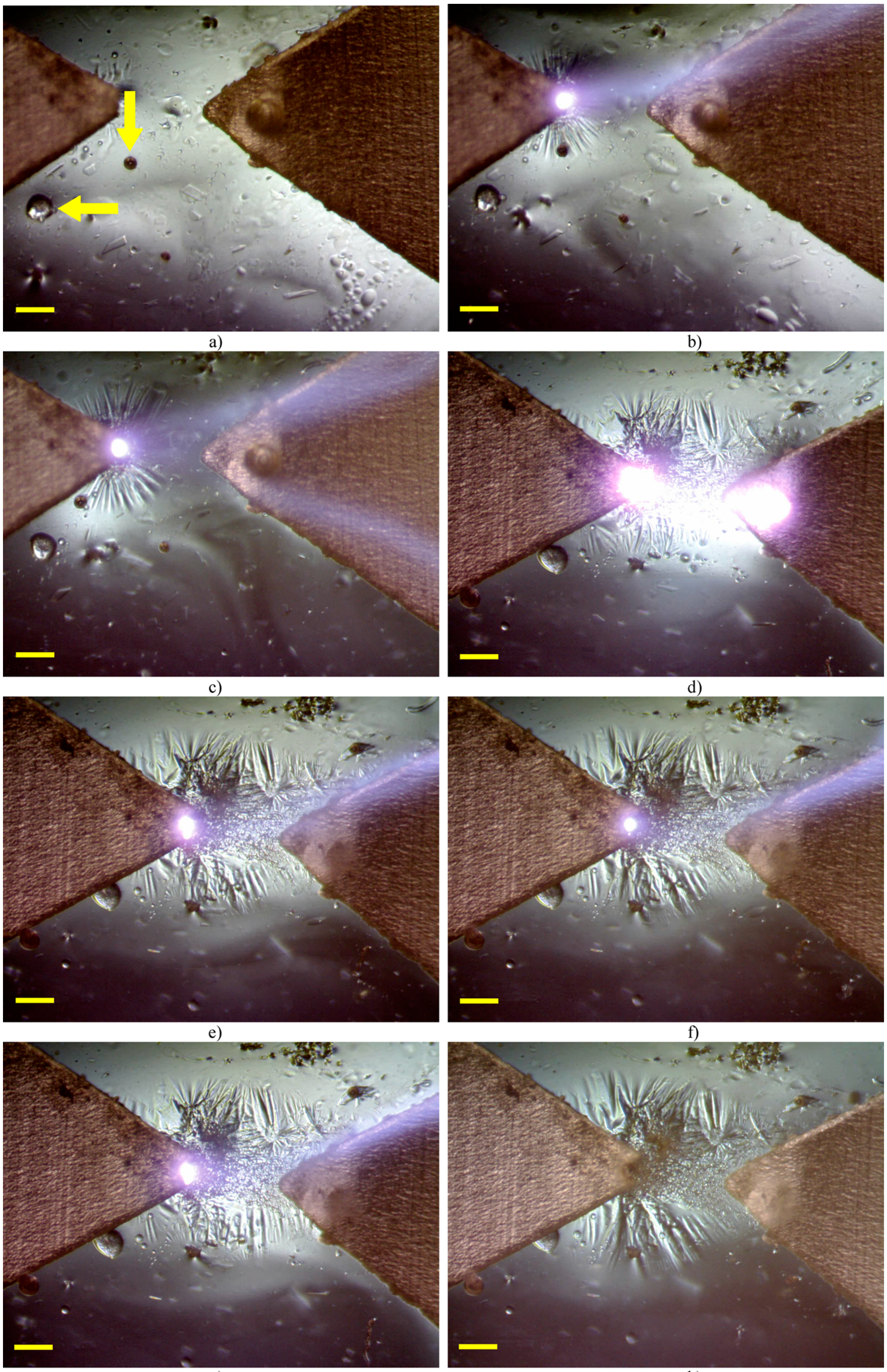

a) b) c) d) e) f) g) h)

Figure 3. Video footage of the process of crystallization of sugars in honey, all bars are 100 μm in the bottom left corner: (a) 3.1 s, birth of crystalline whiskers by the left the tip of the electrode can be seen, a large ball on the left is a bubble ~50 μm in diameter (horizontal arrow), a dark sphere by the left electrode ~30 μm in diameter is a particle of honey plant pollen (vertical arrow). (b) 6.1 s, growth of crystalline whiskers. (c) 17.0 s, further growth of crystalline whiskers. (d) 32.5 s, circuiting of interelectrode gap with crystal channel. (e) 34.1 s, growth of whiskers on the walls of the crystal channel. (f) 42.0 s, further growth of whiskers on the walls of the crystal channel. (g) 45.6 s, further growth of whiskers on the walls of the crystal channel. (h) 50.2 s, final state of the crystal channel.

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For example, the damping was determined from the amplitude ratio of two sequential maximums f_1 and f_2

$$h = \frac{1}{T}\ln\frac{f_1}{f_2} \quad (3)$$

The values of these parameters are

$$a = 650\,\mathrm{A} \qquad h = 0.62 \times 10^7\ \mathrm{s}^{-1} \qquad T = 34\,\mathrm{ns} \qquad t_0 = 76\,\mathrm{ns} \quad (4)$$

After substitution of (4) parameters into (2), we obtain the specific function that describes the displacement current. Its current oscillogram is presented in Figure 2b. After subtraction of (1), we will have the conductive current (Figure 2c). Let us note that the similar method of the conductive current calculation based on determining of the displacement current parameters (period and decrement) and its subtraction from the total current is described in the recent paper.[31] It can be concluded from this oscillogram that within a pulse the polarity of the electrodes and the direction of the current change have a period of about 34 ns and with their own period of the oscillating circuit of the generator output circuit is with the load.

The experiments were performed in the air at atmospheric pressure and a temperature of 21 °C. A few videos of the interaction of electrical nanosecond microdischarges with honey with the duration of about 1 min were made. Figure 3 shows some video footage when the electrode gap was ∼180 μm.

At first, a bit later, after the generator is activated, natural sugar crystal mustaches dissolved in honey appear by the side of one of the electrodes (in our case it is the left). They grow, and by the time of ∼30 s fill the entire interelectrode gap, forming a solid channel. Subsequently, the length of the whiskers increases, as does the thickness of the channel wall. In the process of microdischarges we observed floating of the liquid fraction of honey with velocities less than 100 μm/s.

It is interesting to trace the motion of air bubbles and particles of pollen which happen to be near the interelectrode gap. An air bubble is attracted to one of the electrodes and sticks on it. A pollen particle adheres to the growing crystal whiskers and moves together with the front of crystal growth.

Thus, in this paper for the first time electrical nanosecond microdischarges are produced in bee's honey as an oversaturated solution of sugars, and it is shown that a periodic sequence of microdischarges causes rapid crystallization of sugars.

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Notes

The authors declare no competing financial interest.

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