

# Driving forces of the solute self-organization in an evaporating liquid microdroplet

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## Abstract

A method is proposed for preparing solid phases of desired morphologies from microscopic droplets on solid substrates with a GMS 417 Arrayer, which is commonly used for biochip production. The initial droplet of an aqueous solution is about 100 pl (about 100  $\mu\text{m}$  in diameter), and the evaporation time is about 0.5 s. Such small solution volumes are first considered from the viewpoint of the solute self-organization. Aqueous solutions of inorganic molecular and ionic substances, organic dyes, and latex colloid particles in the evaporating droplets are experimentally studied. Various substrates and solute concentrations are used. The morphology of the solid phase formed on the substrate after water evaporation is analyzed with the use of computer simulation of dynamics of the latex particles within the evaporating microdroplet. Elucidating the self-organization mechanisms will facilitate producing of the desired morphology of the solid phase, which can find an application in nanotechnology.

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## 1. Introduction

Evaporating droplet on a planar substrate is an example of a dissipative structure in an open system [1]. In a droplet decreasing in volume, the solute self-organization occurs. This droplet is a microreactor, where physicochemical processes of sedimentation and crystallization take place. The morphology of the solid phase depends on the experimental conditions.

Self-organization processes in a droplet are initiated by the liquid–gas interface movement as a result of solvent evaporation. The contact line (triple air–liquid–substrate interface) also moves without pinning effect [2–4]. The interface dynamics plays the most important part in the formation of the solid phase.

An intense solvent evaporation results in supersaturation of the solution in the final step of the droplet evaporation. This supersaturation increases as the initial size of the droplet decreases, the initial solute concentration being the same. This makes it possible to obtain nonequilibrium forms of the solid phase. Therefore, reducing the initial droplet volume is an important technological problem.

Previously [5–7], we proposed a method for preparing a solid phase of a special morphology from a microdroplet on a solid substrate with a GMS 417 Arrayer (Genetic MicroSystem), which is commonly used for biochip production. The device makes it possible to obtain matrices of dimensionally uniform droplets. Each matrix is a set of more than a 100 identical microdroplets. Operating with a standard set of droplets facilitates the statistical image processing with the use of computer methods and improves the reliability of the physical interpretation.

Let us consider a liquid droplet on a planar surface surrounded by air under normal conditions. The Bond number [8] gives the conditions in which gravity has a negligible effect on the processes in the droplet:

$$B = \frac{gh^2(\rho_l - \rho_v)}{\sigma} \ll 1, \quad (1)$$

where  $g$  is the acceleration of gravity,  $h$  the droplet height,  $\rho_l$  and  $\rho_v$  the densities of the liquid in the droplet and the vapor in the ambient air, respectively, and  $\sigma$  is the surface tension. If  $h = 10 \mu\text{m}$ ,  $B$  for the water droplet under normal conditions is about  $10^{-5}$ , so that (1) is surely true and gravity can be neglected. It is easy to see that, in this case, the

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equilibrium shape of the droplet on the substrate is a spherical segment.

Hence, the main driving forces of the process are the evaporation intensity governing the velocity of the droplet interface and the change in the surface energy of the droplet followed by the work of the capillary force moving the solute within the droplet. Adsorption of the solute to the substrate, liquid viscosity, diffusion and thermodiffusion coefficients are also important factors governing the final distribution of the solid phase on the substrate.

The main goal of this paper is to study experimentally the crystallization of various solutes. Latex colloid is the simplest type of a solute for the experiments and computer simulation. The interface energy, the particle adsorption to the substrate, and the interaction of the particles in solution are the most important factors of self-organization studied in these experiments.

Simple ionic (alkali, NaOH) and molecular (thiourea,  $\text{CS}(\text{NH}_2)_2$ ) crystals are the solutes that make it possible to study the dissociation and the ionic strength as factors of the self-organization process in a microdroplet.

A cyanine dye combines the properties of ionic and molecular crystals. This substance exhibits polymorphism, that is, the ability to form solid phases with different crystal lattices depending on the environmental conditions and crystallization rate. It is known that the most stable polymorph formed in crystallization of these dyes from aqueous solutions corresponds to the structure of so called J-aggregates [9–11]. They can also form less favorable H-aggregates or, under special conditions, an amorphous phase lacking any long-range order, so called A-aggregates [12]. Cyanine dye nanocrystals formed in solutions can be the elements of self-assembly of a solid phase with certain morphology during drying of a microdroplet.

## 2. Experimental

### 2.1. Reagents

We used 3,3'-di( $\gamma$ -sulfopropyl)-4,4',5,5'-dibenzo-9-ethylthiacyanine dye. According to  $^1\text{H}$  NMR data, the amount of the counter-ions in the dye sample used (Fig. 1) is characterized by  $n=0.6\text{--}0.65$  and  $m=0.35\text{--}0.4$ . The formula weight is approximately 768.

Glass was used as a substrate material. Adsorbed matter was removed from its surface with a 96.6%  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$  solution. Polystyrene-coated substrates ( $M_w = 280,000$ , Aldrich) were also used in the experiments to study the droplets with limiting wetting angles corresponding to hydrophobic coating. The substrates were additionally cleaned by washing in an ultrasonic bath with distilled water.

Latex particles of  $1\ \mu\text{m}$  in diameter with narrow size distribution were produced by the hydrophase polymerization of hydrophobic styrene monomers.

### 2.2. Instruments and procedures

To spot the droplets onto the substrate, we used Pin-and-Ring technology implemented in the GMS 417 Arrayer. The solution

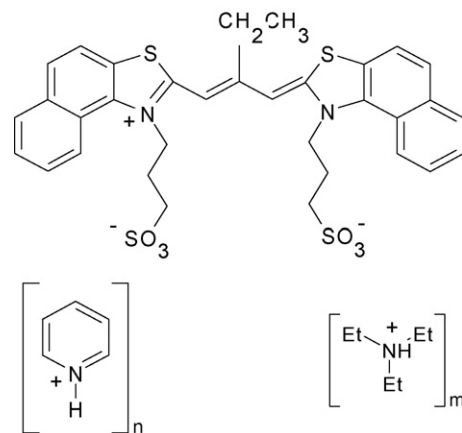


Fig. 1. The structure of 3,3'-di( $\gamma$ -sulfopropyl)-4,4',5,5'-dibenzo-9-ethylthiacyanine and its counter-ions.

to be spotted is taken in the ring, where it is held by the surface tension. To place the droplet onto the substrate, the ring is fixed in the desired position above the substrate, and the pin is lifted above the liquid film in the ring (Fig. 2).

In spotting the droplet, the pin penetrates through the meniscus of the film until touching the substrate. When the pin returns to its starting position, a droplet of solution of approximately 100 pl remains on the substrate. The droplet diameter is governed by the pin diameter ( $125\ \mu\text{m}$ ) and the wettability of the substrate by the solution. Thus, the droplet on a hydrophobic surface is smaller than on a hydrophilic one.

The droplet evaporation time can be estimated using Maxwell diffusion model, which was originally formulated for a spherical droplet and corrected by us to account for the shape of a droplet on a planar substrate [5–7,13,14]:

$$t = \frac{\rho_L R^2 (2 - 3 \cos \theta + \cos^3 \theta)}{4D\rho_R(1 - c) \sin^2 \theta}, \quad (2)$$

where  $\rho_L$  and  $\rho_R$  are the densities of the solvent (here, water) in the liquid droplet and in the saturated vapor at the ambient temperature,  $D$  the diffusion coefficient of the vapor molecules in the air,  $c$  the relative air humidity (for aqueous solutions), and  $\theta$  is the limiting angle for wetting the substrate by the solution. The evaporation time of a water droplet of 100 pl is 0.5 s. Such small droplets are first studied by experiments from the viewpoint of the solute self-organization [15,16].

To study the morphology of the solid phase on the substrate, an Olympus CX41 microscope was used.

### 2.3. Measurement of wetting angles

The limiting wetting angles of droplets on silicon and glass substrates were found from the microphotographs (Fig. 3) obtained using a web camera with a microscope objective. The limiting wetting angle was approximately  $27^\circ$  for glass and about  $77^\circ$  for silicon. The volume of the droplets in study reached  $10\ \mu\text{l}$ . In the computer simulation (see below), we believed that the limiting wetting angles for a 100-pl droplet produced by a GMS 417 Arrayer are the same for the corresponding substrates.

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