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Modeling of spatial–temporal distribution of the components in the drying sessile droplet of biological fluid

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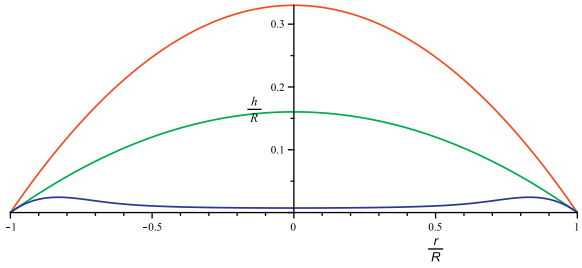
HIGHLIGHTS

- Final shape of the droplet is a doughnut.
- Proteins accumulate near the edge of the dried drop.
- Salts are distributed uniformly across the diameter of the dried drop.

GRAPHICAL ABSTRACT



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ABSTRACT

Using lubrication theory, drying processes of sessile droplets of blood serum (i.e. colloids with the salt admixture) on a solid hydrophilic horizontal substrate are studied. The concentration of the solute is supposed to be high enough to ensure good adhesion and strong anchoring (pinning) of the triple line, thereby a drop is desiccating with constant base. The simulation of spatial distribution of the components in the droplet of biological fluid drying on a substrate is performed using advection–diffusion equation. The proposed model explains the redistribution of components in a sessile drop of biological fluid when it dries. Competition between advection and diffusion leads to large particles (protein) accumulating at the edge of the drop (well-known coffee-ring effect), while solutes (salts) are distributed more uniformly across the diameter of the sample.

1. Introduction

Desiccation of droplets of biological fluids (blood serum, urine, tears, cerebrospinal fluid, etc.) on a horizontal impermeable hydrophilic substrate attracts attention due to various applications including medical tests [1–4], high-throughput drug screening [5], preservation processes [6], etc.

A common feature of biological fluids is the presence of a suspended colloidal particles (proteins) and dissolved salts. In most cases, there are two distinct zones in the dried droplets, i.e. the rim at the edge of the sample and the crystalline region in its center [5–9]. In addition to these large-scale structures, small-scale structures can be formed, which are used, for instance, in medical diagnosis. High reproducibility of the structures allows using them

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to identify proteins [10,11]. Crystal structures depend on the concentration of protein [12,7], on the concentration of salt [8] as well as on the type of salt [13].

To our best knowledge, no models describing spatial component (proteins and salts) redistribution in such complex colloidal drops during desiccation have been developed. At the same time, there are a variety of models to describe the desiccation of drops containing colloidal particles only [14–22].

2. Model of the component redistribution in ternary system

2.1. Principal assumptions

Our model is based on the works [23,16,21].

As a rule, the concentration of suspended colloidal particles in the biological fluids is high enough to ensure strong adhesion, hence there is permanent anchoring (pinning) of the triple line. From this end, we utilize the model of desiccation with constant base [14]. Depinning and stick-and-slip motion (receding of the triple line) [24] are excluded from our consideration.

Following [23], we believe that immediately after a drop being placed on a hydrophilic substrate, the colloidal particles form narrow ring near the droplet edge, providing triple line pinning. The thickness of the ring is much smaller than the height of the drop.

The droplet is supposed to be thin enough to apply lubrication approximation [30]. In our consideration, vertical distribution and sedimentation of colloidal particles is neglected. Nevertheless, sedimentation can be involved in the consideration, e.g. as in [17].

The features of the system are described in [9]. Initially, the system is single-phase; outward flow carries the colloidal particles and dissolved substances to the edge of a drop. The concentration of solute increases sharply near the edge of a drop. At the end of this stage, the volume fraction of the colloidal particles on the edge of the drop reaches critical value, gelation process begins and the second phase (gel) forms at its edge. This phase is gradually moving towards the center of the drop. Although the evaporation of water from the surface of the gel goes on, it does not affect hydrodynamic processes in the liquid part of the droplet, because filtration of liquid in gel is very slow. At the end of the second stage, salt concentration in the central part of the liquid droplet exceeds saturation concentration, rapid crystallization process begins. At the last stage of drying drops, gel losses the water slowly.

Initially, the evaporation process is driven by the colloid convection inside the drop. At the final stage, it is driven by the porous media drying dynamics [33].

In fact, our model treats the drop as a single phase system during the entire time of evaporation. However, one can distinguish an area with a high and constant volume fraction of colloidal particles at the edge of the drop. This area has a very high viscosity and low evaporation from its free surface. High viscosity prevents the significant hydrodynamic flows. In contrast, the solution in the central part of the droplet has a lower volume fraction of the colloidal particles, the viscosity is relatively small, advective flows play an essential role. Between these two areas, there is a narrow transition region, in which the volume fraction of the particles and viscosity increases sharply [18]. In general, the viscosity of the solution may depend not only on the concentration of the colloidal particles, but also on the ionic strength (salt concentration). Due to the lack of experimental data, we take into account the dependence of the viscosity of the solution only on the concentration of colloidal particles as a first approximation. We avoid using the terms 'phase' and 'phase transition', because the phase transition from sol to gel is not instantaneous when the volume fraction of colloidal particles reaches the critical value. Gelation time depends, in particular, on the ionic strength (salt concentration) (see, for example, [25]).

In our consideration, it is assumed that the diffusion coefficients do not depend on concentration.

Calculation of spatial–temporal dynamics of the components in the drying sessile drops of the ternary system (water–albumin–NaCl) were performed using the lubrication approximation and advection–diffusion equations, which allow to describe the formation and motion of the phase front in the evaporating droplets containing the solutes and colloidal particles. Model for the case of two-component system (water–albumin) is described in detail and analyzed in our articles [26,21]; we have published a brief preliminarily description of the improved model to the case of ternary system in [27,28].

Our method of solution is characterized by absence of tracking the position of the front sol-gel explicitly. Although formally the model equations are written for the liquid phase, when the volume fraction of colloidal particles (proteins) approaches the critical value, velocity of the current becomes negligible due to the increase of viscosity by several orders of magnitude (7). A model law for the density of the vapor flux which we have chosen ensures that the evaporation stops when a critical volume fraction of colloidal particles is reached. As a consequence, in the absence of flow and evaporation, the profile of the drop and the concentration of substances stop changing, i.e. edge of the drop freezes, its evolution stops.

2.2. Master equations

Compared with [26,21], a diffusion term has been added in the equation for colloidal particles, moreover, a similar equation has been written for salt.

Written in the dimensionless form set of equations

$$\frac{\partial h}{\partial t} + u\frac{\partial h}{\partial r} = -\frac{h}{r}\frac{\partial}{\partial r}(ru) - \mathrm{E}J, \tag{1}$$

$$\frac{\partial C_\mathrm{p}}{\partial t} + u\frac{\partial C_\mathrm{p}}{\partial r} = \frac{D_\mathrm{p}}{D_\mathrm{s}}\frac{\varepsilon}{\mathrm{Sc}}\frac{1}{rh}\frac{\partial}{\partial r}\left(rh\frac{\partial C_\mathrm{p}}{\partial r}\right) + \mathrm{E}\frac{C_\mathrm{p}J}{h}, \tag{2}$$

$$\frac{\partial C_\mathrm{s}}{\partial t} + u\frac{\partial C_\mathrm{s}}{\partial r} = \frac{\varepsilon}{\mathrm{Sc}}\frac{1}{rh}\frac{\partial}{\partial r}\left(rh\frac{\partial C_\mathrm{s}}{\partial r}\right) + \mathrm{E}\frac{C_\mathrm{s}J}{h}, \tag{3}$$

$$u = \frac{1}{3\mathrm{Ca}}\frac{h^2}{\eta}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right) \tag{4}$$

describes the spatial–temporal dynamics of the drop profile $h(r, t)$ (1), height-averaged concentrations of the suspended colloidal particles (protein) $C_\mathrm{p}(r, t)$ (2) and dissolved salts $C_\mathrm{s}(r, t)$ (3), and the height-averaged horizontal velocity inside the drop $u(r, t)$ (4) [23]. Viscosity $\eta(C_\mathrm{p})$ is a function of concentration of colloidal particles [29].

We assume that the drop on the hydrophilic substrate is axisymmetric, so the equations are written in the cylindrical coordinates. D_p and D_s are the diffusivity of albumin and NaCl, respectively.

- The vertical coordinate, h, and the radial coordinate, r, are scaled by the drop radius R.
- The velocity, u, is scaled by the characteristic viscous velocity.

$$u_c = \frac{\eta_0}{\rho h_0},$$