



Self-stabilization of droplet clusters levitating over heated salt water

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ABSTRACT

When the water surface is heated locally, a self-ordered regular cluster of levitating droplets is formed above it. A condensational growth of water droplets leads to coalescence of the cluster with water layer. At the same time, the intended use of water droplets as biochemical microreactors is possible only when the cluster is stable. A method of self-stabilization of a droplet cluster levitating over the locally heated water surface is proposed for the first time. The physical analysis of the problem shows that the desired result can be reached by dissolving a small amount of sodium chloride in a layer of water. This is explained by simultaneous action of two processes with opposite effects on evaporation. On the one hand, when water evaporates, a thin layer of increased salt concentration that prevents evaporation is formed at its surface. On the contrary, diffusion of salt in water decreases the surface concentration of salt. Different combinations of water heating intensity and average salt concentration are expected to result in the stable size of nearly identical levitating droplets, when there is a balance between the droplet evaporation and the condensation of vapor from the ascending vapor-air flow. The predicted phenomenon has been observed experimentally. In a series of laboratory experiments, a range of parameters has been obtained for which self-stabilization of the droplet cluster takes place. The theoretical analysis of necessary conditions for spontaneous stabilization of a droplet cluster uses a steady-state solution for temperature and salt concentration in the water layer. The localization of a small cluster makes it sufficient to derive a solution to the one-dimensional problem. The obtained analytical solution to this problem takes into account the temperature dependence of the salt diffusion coefficient. The resulting threshold values of salt concentration agree well with the experimental data.

1. Introduction

It is known that various organic reactions are accelerated when reagents are present in microdroplets or in thin films. The reaction rate increases by orders of magnitude with decreasing droplet size. The rate constant is usually inversely proportional to the square root of the droplet volume. This phenomenon has long attracted the attention of researchers, but remains understudied, despite its great practical importance [1,2]. Laboratory research requires the generation of steadily levitating small water droplets of a given constant size (with a diameter of about 20–200 μm). The droplet clusters we study usually consist of water droplets of this size. It should be also noted that fine water droplets suspended in the air may contain microorganisms, and the transfer of such droplets in the atmosphere is one of the mechanisms for the spread of plant pathogens, as well as animal and human diseases

[3,4]. Therefore, the study of biochemical processes in small droplets is of important practical value.

It is known that small droplets are always suspended in humid air above heated water. These droplets condense from water vapor and are usually positioned randomly over the water surface [5]. In paper [6], it was first discovered that, with local heating of water, droplets are self-arranged and form a flat ordered cluster, which levitates over the hot spot of the water surface. The peculiarities of the formation and structure of a droplet cluster have attracted the attention of many researchers. In particular, we can mention the works [7–11], which consider various possible mechanisms of cluster formation, as well as the use of droplet clusters to solve some applied problems.

Unfortunately, the droplet cluster is not stable and exists for a short time (no more than a few minutes): as a result of the condensational growth of droplets, the cluster coalesces with the water layer. A method for cluster stabilization using the external infrared radiation, which

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Nomenclature			
a	droplet radius	κ	thermal diffusivity
\tilde{a}	normalized droplet radius	μ	molar mass
A, B	coefficients in Eq. (10)	$\bar{\mu}, \tilde{\mu}$	relative molar masses
c	concentration of salt in water	ξ	relative mole fraction
D	diffusivity	ρ	density
d	thickness of water layer or sital substrate	φ	relative humidity
H	distance	<i>Subscripts and superscripts</i>	
\dot{m}	mass rate of evaporation	air	air
p	pressure	av	average
\bar{p}	relative pressure	diff	diffusion
R	gas constant	e	external
r	radial coordinate	eq	equilibrium
S	parameter of evaporation	gas	gas
T	temperature	heat	thermal
t	current time	max	maximum
\tilde{t}	normalized time	mix	mixture
u	velocity	salt	salt
x	coordinate measured from the lower surface of substrate	sat	saturation
z	coordinate measured from the bottom of water layer	sub	substrate
\bar{z}	relative coordinate	surf	surface
<i>Greek symbols</i>		w	water
γ	coefficient in Eq. (11)	0	reference value
		*	critical value

heats the droplets and increases their evaporation has been developed by the authors [12,13]. Such a stabilization of droplet clusters for a long time, when the droplet size remains unchanged for tens of minutes, makes them suitable for chemical and biochemical studies in droplet micro-reactors [11,14]. We should say about the disadvantage of this method. Unfortunately, the technical characteristics of compact sources of the near-infrared radiation do not ensure their reliable long-term operation and the droplets are additionally heated, which may be undesirable in experiments with living microorganisms. The use of modulation of the heating power to prevent the condensational growth of droplets made it possible to reduce the droplet growth rate by about half [15], but this turned out to be insufficient for the long-time stabilization of clusters. The foregoing motivated the development of a fundamentally different method for suppressing the growth of cluster droplets using self-regulation of the evaporation rate of the water layer. The use of an alternative technology for generating an initial cluster, where the droplets are supplied by an external source made it possible, in particular, to work with a layer of water in which a non-evaporating substance is dissolved. In the present study, we consider sodium chloride (NaCl hereafter called simply "salt") as such a substance.

The objective of the present paper is to investigate the potential of using salt water for stabilizing the droplet cluster without any external action, such as infrared irradiation of the cluster. A physical analysis of the effects associated with the addition of salt to the water layer is presented in the next section of the article. Theoretical estimates have shown that, in a certain range of parameters, a spontaneous stabilization of the droplet size is expected even at a low average concentration of salt.

2. Physical analysis of the problem

Understanding the process of the gradual formation of steady-state parameters of a layer of water salt dissolved in it requires a comparison of the characteristic time of salt diffusion with the thermal relaxation time. This can be done using the following relations:

$$t_{\text{heat}} = d^2 / \kappa_w \quad t_{\text{diff}} = d^2 / D \quad (1)$$

where d is the thickness of water layer, κ_w is the thermal diffusivity of water (a small concentration of salt is neglected) and D is the diffusivity of salt in water. In the temperature range of $40^\circ\text{C} < T < 80^\circ\text{C}$, κ_w increases slightly from $1.5 \times 10^{-7} \frac{\text{m}^2}{\text{s}}$ to $1.7 \times 10^{-7} \frac{\text{m}^2}{\text{s}}$, whereas D increases with temperature from about $2.1 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$ to $4.4 \times 10^{-9} \frac{\text{m}^2}{\text{s}}$ [16–18]. For $d = 0.4 \text{ mm}$, we obtain the values $t_{\text{heat}} \approx 1 \text{ s}$ and $36 \text{ s} < t_{\text{diff}} < 76 \text{ s}$. This means that the temperature profile in the water layer under the cluster can be established in 1 s, and it takes about 1 min to establish the salt concentration profile.

Obviously, at the beginning of water evaporation, the salt concentration increases in a thin surface layer. As a result, the surface salt concentration, c_{surf} , becomes greater than its average value, c_{av} , in the water layer. At the same time, rather slow diffusion does not have time to counteract this local increase in salt concentration. Therefore, in the case of low-salinity water, the cluster droplets first grow until the evaporation rate decreases considerably. This growth of water droplets slows down because, according to Raoult's law, the rate of evaporation decreases as the surface concentration of salt increases. After a time exceeding t_{diff} , one should expect a decrease in the size of water droplets in the cluster to a certain equilibrium value. At the same time, a steady-state profile of salt concentration over the thickness of the water layer is achieved.

3. Experimental study

3.1. Experimental procedure

The schematic of the experiment is shown in Fig. 1a. A 0.4 mm thick sital substrate (3) is glued to the metal bottom of the cuvette. The cryothermostat CC 805 (Huber, Germany) with the coolant temperature of $8 \pm 1^\circ\text{C}$ allows stabilizing the temperature of water layer. The water layer is heated by a laser beam (5) (MRL-III-660D-1W, manufacturer – CNI, China) aimed at the lower blackened surface of the substrate. The radial temperature profile of the water layer surface (Fig. 1b) was recorded with a CG640 thermal imager (COX, Korea).

Throughout the experiment, the bottom of the cuvette (4) was cooled

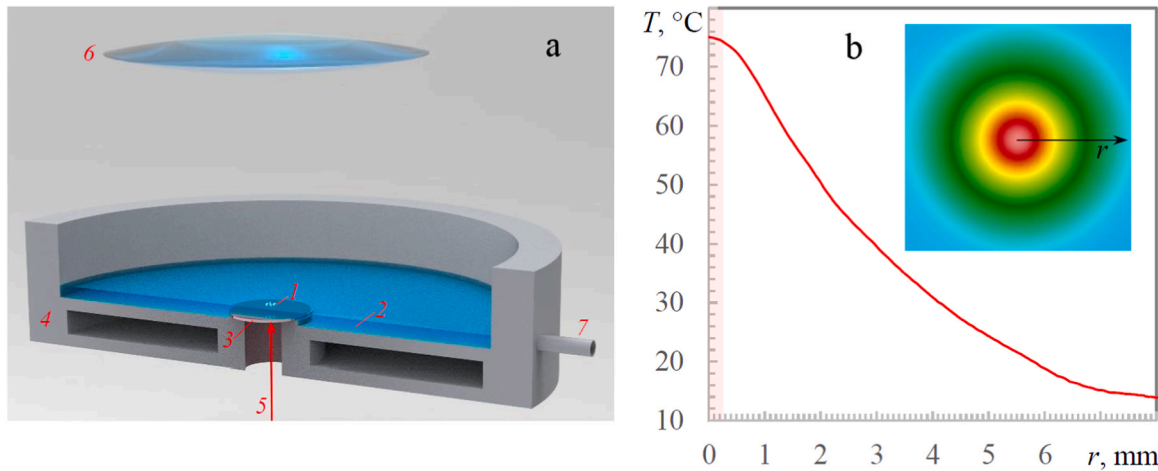


Fig. 1. (a) Schematic of experimental setup: 1 – the droplet cluster, 2 – the layer of water of thickness d with small concentrations of a surfactant and salt, 3 – the sital substrate of thickness d_{sub} , 4 – the cuvette with a sealed channel connected to the external circuit of a cryothermostat, 5 – the laser beam, 6 – microscope and thermal imager lens, 7 – water feeder for maintenance of the layer thickness; (b) Typical temperature profile at the water surface (the pink stripe marks the cluster localization).

by pumping a coolant. As a result, the temperature of water (2) away from the heated central zone was low, which led to condensation of water vapor from the humid air. Considering that the processes proceeded in a hermetically sealed working volume, this condensation was practically sufficient to compensate water evaporation in the central zone.

Video recording of the cluster image was carried out using an AXIO Zoom.V16 stereomicroscope (Zeiss, Germany) equipped with a camera Andor iXon Ultra 888 (Oxford Instruments plc, UK) (6). The thickness of the water layer (2) is equal to 0.4 mm. It was controlled by a laser confocal sensor IFC2451 (Micro-Epsilon, USA) (7) and maintained with an accuracy of $\pm 2 \mu\text{m}$. The experiments were carried out with salt solutions (impurity content of NaCl was less than 0.1%) in distilled water. Analytical scales with an accuracy of 0.1 mg were used to weigh the salt, making it possible to obtain solutions with a mass concentration of salt differing from the set value by only a hundredth of a percent. The mass concentration of salt in water was varied from one experiment to another. The solution always contained a surfactant (sodium lauryl sulfate) with a concentration of 0.02 g/l, which is necessary to suppress the thermocapillary flow in the water layer. The water surface temperature under the cluster was monitored with a CTL-CF1-C3 pyrometric sensor (Micro-Epsilon, USA) (6). The spectral range of the sensor sensitivity was from 8 to 14 μm , and the resulting error is equal to $\mp 1 ^\circ\text{C}$.

A small cluster with the number of droplets from 10 to 20 (1) was “printed” from distilled water by injection of microdroplets with a piezoelectric dispenser (MicroFab Technologies, Inc., USA). The nozzle of the dispenser generated a chain of very close-sized separately flying droplets. With the right choice of parameters (nozzle position, velocity and size of the droplets, etc.) these droplets are captured by the vapor-air flow over a locally heated area of the water layer and form a cluster. Intensive heating of the water layer eliminates the penetration of spontaneously condensed microdroplets into the cluster, so the cluster contains only droplets with a given initial concentration of the dissolved substance. In our case, the cluster was printed from ultrapure water produced by the Sartorius Arium Mini Plus Water Purification System (Germany). The use of small clusters is explained by the fact that such clusters are located near the maximum temperature of the surface of the water layer (Fig. 1b), which provides almost the same external conditions for all droplets in the cluster. The designation T_{surf} is hereafter used for the constant temperature under the cluster.

After that, a pause of about 300 s was maintained, which was necessary to stabilize the droplet size, and the cluster image was

recorded. Then, the laser heating power was increased by 20 mW. The equilibrium droplet radius, a_{eq} , was measured for several values of the laser heating power. A special computer code analyzes all the droplets in each frame and measures the diameter of each droplet. After that, the average diameter of the droplets in the cluster is calculated. It was more convenient for us to work with the average radius of the droplets. Each a_{eq} value was then averaged over 50 consecutive frames of all droplets in the cluster. The experiments were carried out for pure water and also at the following values of the average mass concentration of salt in the water layer: $c_{\text{av}} = 0.1\%$, 0.2% , 0.3% , and 0.4% , but the first two of these values appeared to be insufficient to obtain the self-stabilized cluster of levitating water droplets in a wide temperature range.

3.2. Experimental results

Let us consider typical results of the laboratory experiments in which the formation of stable/equilibrium droplet clusters was observed. At the $T_{\text{surf}} = 60 \pm 0.5 ^\circ\text{C}$ and two values of the salt concentration of $c_{\text{av}} = 0.3\%$ and 0.4% , small clusters of 11 and 13 droplets are formed, respectively. Photographs of these clusters at different points in time are shown in Fig. 2. The regular arrangement of the cluster droplets, the distance between which is approximately the same and they are all in the same plane has been studied and received a physical explanation in the works [13,14,19,20].

The change in the radius of water droplets over time is clearer in Fig. 3a. The radii of all droplets of each of the two clusters were measured at different points in time, and all results of the measurements are shown in this figure. That is why the number of points is so large and there is a small scatter of radii of different droplets of the same cluster. Obviously, the experimental results presented in Fig. 3a confirm the above theoretical predictions concerning non-monotonic changes in time of the radius of levitating water droplets and the transition of this radius to an equilibrium value.

As one might expect, the dependences $a(t)$ at different values of c_{av} are similar to each other, but at a higher salt concentration in the water layer, the cluster droplets are smaller and their initial growth stops earlier, after which the droplet radius decreases to the equilibrium value a_{eq} . It is interesting that the results for two values of salt concentration practically coincide with each other (except for the regime close to equilibrium) when the physical coordinates (t, a) are replaced by the conventional coordinates $(\tilde{t}, \tilde{a}) = (c_{\text{av}} t, \sqrt{c_{\text{av}}} a)$ (see Fig. 3b), which might be expected according to the usual criteria for diffusion-like processes when we are dealing with the ratio of t/d^2 (as in the expressions for the

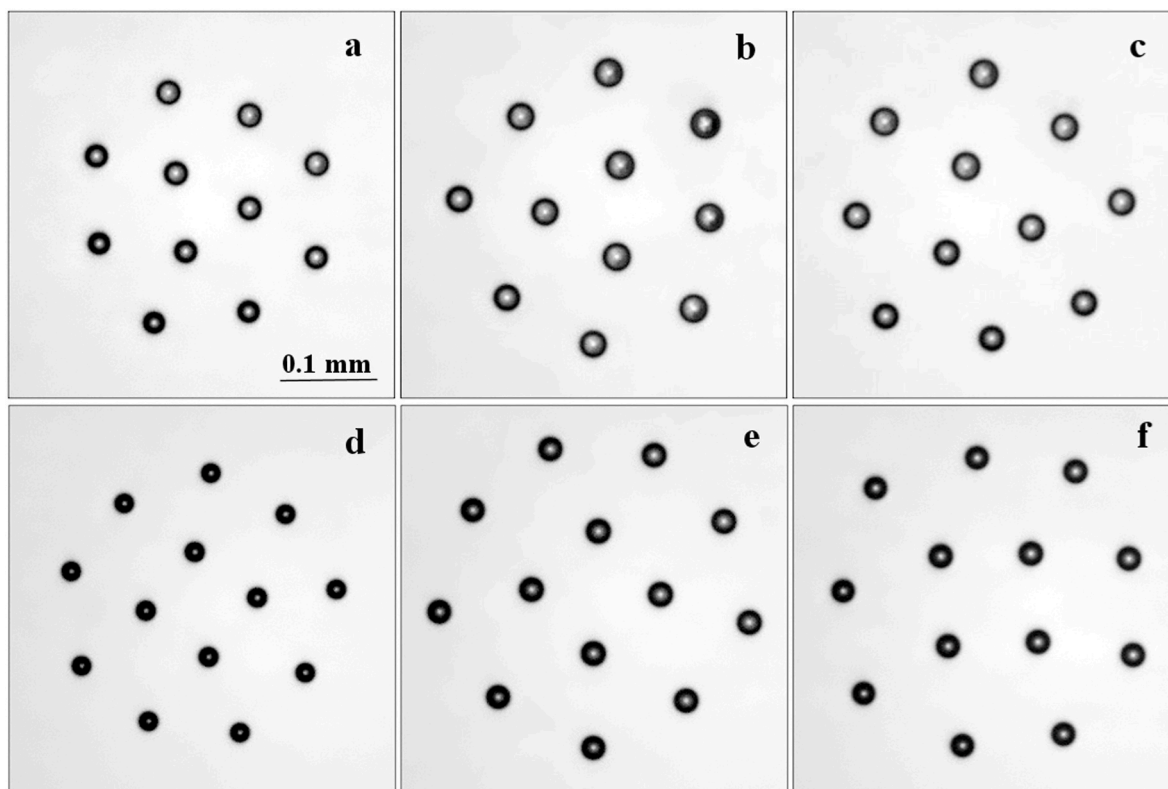


Fig. 2. Images of small clusters of water droplets at $c_{av} = 0.3\%$ (a, b, c) and 0.4% (d, e, f): a, d – $t = 0$; b, e – $t = 90$ s; c, f – $t = 290$ s. Experiments at $T_{surf} = 60\text{ }^\circ\text{C}$.

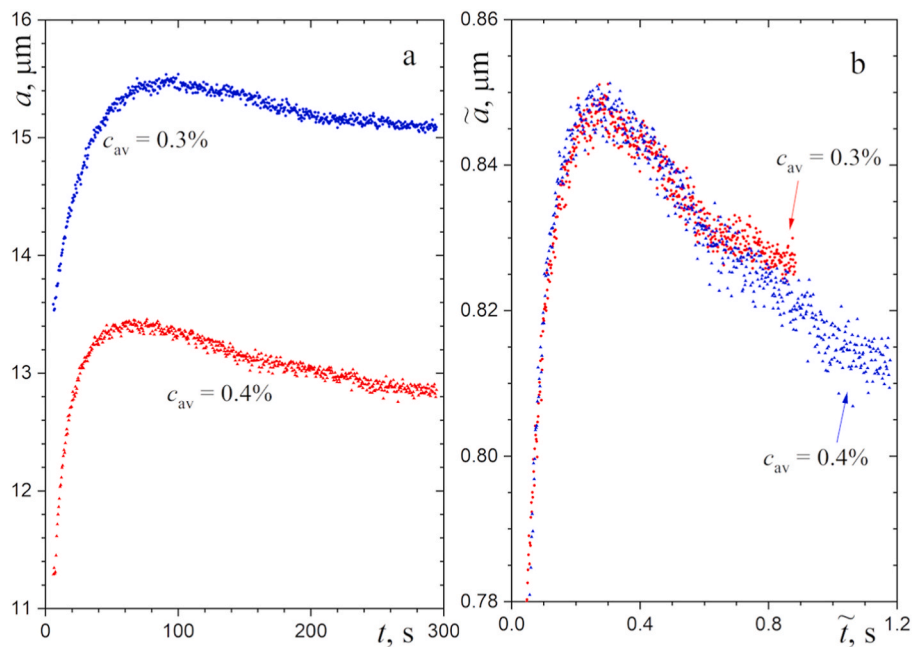


Fig. 3. Time variation of radius of water droplets in two clusters: a – in the physical coordinates, b – in the conventional coordinates. Experiments at $T_{surf} = 60\text{ }^\circ\text{C}$.

conductive and diffusion Fourier numbers).

It turns out that an increase in water temperature is favorable for the self-stabilization of the cluster. As shown in Fig. 4a, at $T_{surf} > 74\text{ }^\circ\text{C}$ this effect is observed even at $c_{av} = 0.2\%$. For any values of c_{av} , the equilibrium radius of droplets a_{eq} increases almost linearly with increasing the water temperature. The experimentally determined domain of self-stabilization of droplet clusters levitating over a layer of salt water is shown in Fig. 4b. Strictly speaking, the boundary of this domain is not a

straight line, which is the result of interpolation over a limited number of experimental points. Perhaps, the calculated boundary (dashed line in Fig. 4b) is more realistic one (the details of the approximate calculations are discussed in Section 4.2 of the paper). In all cases, this diagram seems to be physically correct and convenient for choosing parameters at which droplet clusters are stabilized.

It should be noted that the self-stabilized equilibrium droplet clusters, formed over a layer of salt water for about 5 min, did not undergo

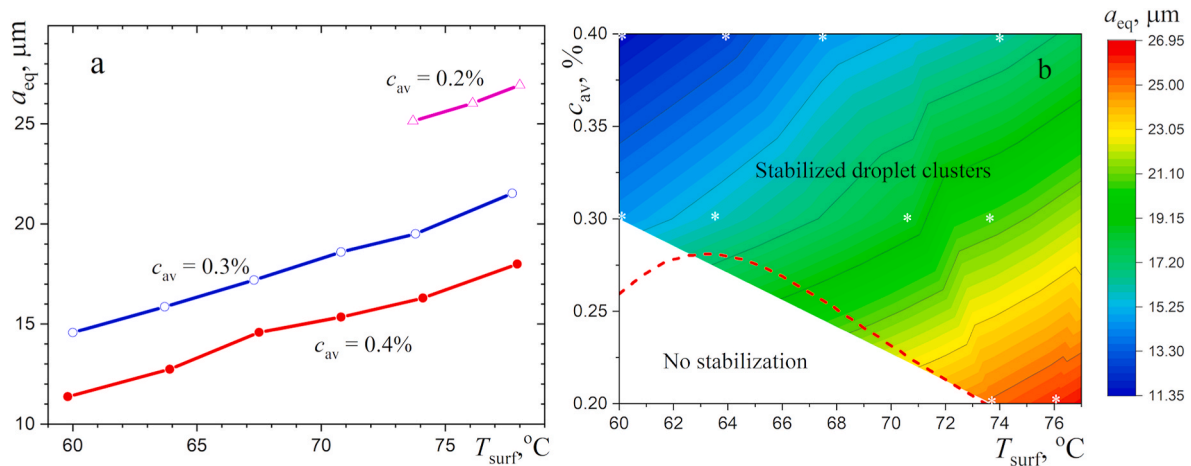


Fig. 4. Equilibrium water droplets in stabilized droplet clusters: a – dependences of droplet radius on water surface temperature; b – domain of self-stabilized droplet clusters, white stars are some of the points from Fig. 4a, the dashed line is an approximate calculation of the domain boundary.

any changes for at least another half an hour, which is quite sufficient for conducting biochemical experiments in the individual droplets. This experimental result looks especially spectacular compared to clusters over a layer of pure water or slightly salted water, when the droplets grow rapidly and then almost instantly coalesce with the layer of water. Measurements of the droplet radius of such clusters at the water surface temperature $T_{\text{surf}} = 60$ °C are presented in Fig. 5. The droplet growth rate decreases considerably with increasing salt concentration in the water layer even at salt concentration $c_{\text{av}} \leq 0.2$ %, which leads to an increase in the cluster life time from 64 s to 140 s.

4. Computational results

4.1. A description of the general approach

This section does not consider a general theoretical model that could claim to obtain a necessary and sufficient condition for spontaneous stabilization of a droplet cluster levitating over a thin layer of salt water. The experimental results obtained allow us to limit ourselves to determine the conditions under which such spontaneous stabilization of the cluster is physically impossible.

Obviously, cluster stabilization cannot occur at very low salt concentration, when the droplet cluster evolution is the same as over a layer of pure (unsalted) water. Therefore, it is a matter of theoretical determination of some threshold salt concentration, at which spontaneous

stabilization of the cluster becomes possible. A stable droplet cluster can exist only over a layer of water with a steady salt distribution when the salt concentration on the water surface is maximum. It is this constant surface salt concentration that provides the necessary reduction of water evaporation, which prevents excessive intensive condensation of water vapor on the surface of water droplets and an increase in the droplet size of the cluster.

In Section 2 it was shown that the steady-state temperature field in the water layer is reached much faster than the steady-state distribution of the dissolved salt. Since the small concentration of salt does not affect the thermophysical properties of water, the calculation of the temperature field can be done independently. For this purpose, it is sufficient to solve the axisymmetric heat conduction problem, i.e., the boundary value problem for the equation with appropriate boundary conditions. Of course, the computational domain must include a broad layer of water, the sittal substrate, and the boundary conditions should take into account the laser heating of the substrate and cooling of the metal cuvette. The thermal diffusivity coefficient is different for water and sittal and its value for water depends on the temperature. Such a problem was solved in Ref. [21] using the known finite-difference numerical method [22]. The details of the algorithm are not of interest to this work. Let us note only that our calculation took into account the peculiarities of the design of the modified experimental setup.

$$\frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(\kappa r \frac{\partial T}{\partial r} \right) = 0 \quad (2)$$

A typical temperature field in the central part of the water layer is shown in Fig. 6. This temperature field seems to be rather complex, but the steady-state profile of water temperature under the cluster (along the vertical axis of the computational region) is obviously linear:

$$T(z) = T_{\text{max}} - (T_{\text{max}} - T_{\text{surf}})z/d, \quad 0 < z < d, \quad (3)$$

where z is the coordinate measured from the lower boundary of the water layer.

Strictly speaking, the axisymmetric field of salt concentration in a water layer is described by a transient diffusion equation in which salt transport in two orthogonal directions is taken into account. However, for a very thin layer of water, which thickness is an order of magnitude smaller than the layer radius, the problem degenerates and we can limit ourselves to the solution of 1D problem for a conventional plane-parallel layer of water under the droplet cluster. Additional simplification is connected with insignificant change of water layer thickness due to evaporation. The resulting diffusion equation for the current mass concentration of salt, $c(t, z)$, and the initial and boundary conditions can be written as follows:

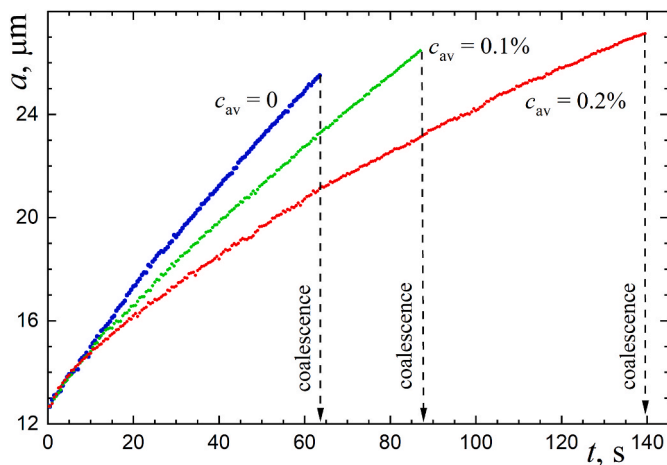


Fig. 5. Time variation of radius of droplets levitating over pure water ($c_{\text{av}} = 0$) and slightly salted water at $T_{\text{surf}} = 60$ °C.

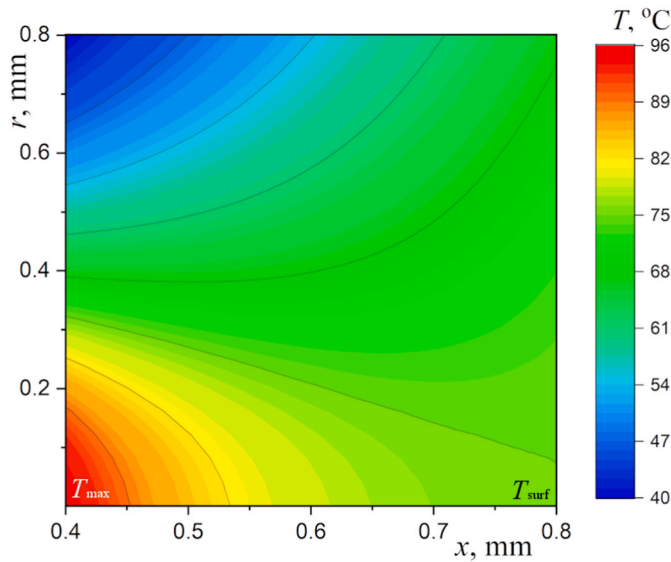


Fig. 6. Typical temperature field in the central part of the water layer (the open water surface is on the right; the substrate is on the left); The axial coordinate $x = z + d_{\text{sub}}$ is measured from the bottom of the sittal substrate.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left(D(z) \frac{\partial c}{\partial z} \right) - \frac{u_{\text{surf}}}{d}, \quad t > 0, \quad 0 < z < d \quad (4a)$$

$$t = 0, \quad c = c_{\text{av}}, \quad (4b)$$

$$z = 0, \quad \frac{\partial c}{\partial z} = 0, \quad (4c)$$

$$z = d, \quad D \frac{\partial c}{\partial z} = u_{\text{surf}}, \quad (4d)$$

where $u_{\text{surf}} = \dot{m}/\rho_w$, $\dot{m}(T_{\text{surf}}, c_{\text{surf}})$ is the mass rate of water evaporation per unit area measured in $\text{kg}/(\text{m}^2\text{s})$, and ρ_w is the density of water. The coordinate dependence of D is related with its dependence on temperature:

$$D(T) = D_0(T - 273) / (T_0 - 273), \quad (5)$$

where T is measured in Kelvin, $T_0 = 333 \text{ K}$, and $D_0 = 3.3 \times 10^{-9} \text{ m}^2/\text{s}$. Eq. (5) is a linear approximation of the experimental data [16–18].

A complete model of evaporation should include consideration of a thin Knudsen layer at the water surface [23]. However, in the present paper we limit ourselves by the diffusion approach taking into account the Stefan flow [24]:

$$\dot{m} = \frac{D_{\text{gas}}(T_{\text{surf}})p}{H_c R_{\text{mix}} T_{\text{surf}}} \ln \frac{1 - \varphi_e \bar{p}_{\text{sat}} \bar{\mu}_w}{1 - \xi_w \bar{p}_{\text{sat}} \bar{\mu}_w}, \quad (6)$$

where D_{gas} is the diffusion coefficient of water vapor in air, p is the atmospheric pressure, $\bar{p}_{\text{sat}} = p_{\text{sat}}(T_{\text{surf}})/p$, $p_{\text{sat}}(T_{\text{surf}})$ is the saturation pressure of water vapor at temperature T_{surf} , $\bar{\mu}_w = \mu_w/\mu_{\text{mix}}$, μ_w and $\mu_{\text{mix}} \approx \mu_{\text{air}}$ are molar masses of water vapor and the mixture of air with the vapor, $R_{\text{mix}} \approx R_{\text{air}} = R/\mu_{\text{air}}$ (R is the universal gas constant), H_c is the distance from the water surface at which the relative humidity of air is equal to φ_e , and ξ_w is the local mole fraction of water in salt solution, which can be expressed through the mass concentration of salt at the surface of the water layer:

$$\xi_w = \frac{1}{1 + \tilde{\mu}_w c_{\text{surf}} / (1 - c_{\text{surf}})}, \quad (7)$$

where $\tilde{\mu}_w = \mu_w/\mu_{\text{salt}}$, μ_{salt} is the molar mass of NaCl. Note that the coefficient ξ_w in Eq. (6) corresponds to Raoult's law $p_{\text{sat}}(T_{\text{surf}}, c_{\text{surf}}) =$

$\xi_w p_{\text{sat}}(T_{\text{surf}}, 0)$. We use an approximate value of H_c obtained from a comparison of the diffusion approach of the present work with the exact kinetic model of evaporation [25]. The relative humidity of air in the laboratory was taken equal to $\varphi_e = 45 \%$.

The following approximation was used for the diffusion coefficient of water vapor [26]:

$$D_{\text{gas}}(T) = -2.775 \times 10^{-6} + 4.479 \times 10^{-8} T + 1.656 \times 10^{-10} T^2 \quad (8)$$

where D_{gas} is measured in m^2/s . Eq. (8) is applicable in the temperature range of $280 \text{ K} < T < 360 \text{ K}$. According to Ref. [27] the saturation pressure (in Pa) in the range of $256 \text{ K} < T < 373 \text{ K}$ can be approximated as:

$$p_{\text{sat}} = 10^{9.6543 - 1435.264/(T - 64.848)} \quad (9)$$

In both Eqs. (8) and (9), the temperature is measured in Kelvin. The error of these approximations is no more than 3%.

4.2. Analytical solution to the steady-state diffusion problem

It is obvious in Fig. 4a that there is no considerable effect of a small increase of the surface concentration of salt in the initial period of $t < 30 \text{ s}$. This can be seen from the almost linear growth of the water droplets over time. On the other hand, there is a subsequent variation in the radius of the levitating droplets up to the equilibrium value a_{eq} . Under such conditions, the transient diffusion problem (4a-d) is of no interest and it makes sense to focus on the steady-state solution which can be obtained analytically. The steady-state problem for the profile of the salt concentration can be written as follows:

$$\frac{d}{d\bar{z}} \left(D(\bar{z}) \frac{dc}{d\bar{z}} \right) = S, \quad (10a)$$

$$\left(\frac{dc}{d\bar{z}} \right)_{\bar{z}=0} = 0, \quad D(1) \left(\frac{dc}{d\bar{z}} \right)_{\bar{z}=1} = S, \quad (10b)$$

$$\int_0^1 c(\bar{z}) d\bar{z} = c_{\text{av}}, \quad (10c)$$

where $\bar{z} = z/d$, $S = u_{\text{surf},0} d$, and the value of $u_{\text{surf},0}$ corresponds to the steady-state regime. It should be noted that the dimension of the parameter S is the same as that of the diffusion coefficient and it can be considered as a characteristic of the diffusion transfer of water vapor from the surface of evaporating water. The value of S should not be too large, as this makes it difficult (and even may make it impossible) to form a steady-state salt concentration profile with a maximum on the surface of the water layer.

Eqs. (3) and (5) give the following linear variation of the salt diffusion coefficient across the water layer:

$$D = A - B\bar{z}, \quad A = D_0 \frac{T_{\text{max}} - 273}{T_0 - 273}, \quad B = D_0 \frac{T_{\text{max}} - T_{\text{surf}}}{T_0 - 273} \quad (11)$$

where temperatures are measured in Kelvin. Substitution of Eq. (11) into Eq. (10a) and subsequent integration with conditions (10b,c) leads to the following analytical solution for the salt concentration profile:

$$c(\bar{z}) = c_{\text{av}} + \frac{S}{B} \left\{ \frac{1}{2} - \bar{z} + \gamma \left[(\gamma - 1) \ln \frac{\gamma}{\gamma - 1} + \ln \frac{\gamma}{\gamma - \bar{z}} - 1 \right] \right\}, \quad \gamma = \frac{A}{B} \\ = \frac{T_{\text{max}} - 273}{T_{\text{max}} - T_{\text{surf}}} \quad (12)$$

Note that, assuming a constant salt diffusion coefficient in the water layer, the analytical solution of the problem is much simpler:

$$c(\bar{z}) = c_{\text{av}} + \frac{S}{2D} \left(\bar{z}^2 - \frac{1}{3} \right), \quad (13)$$

Unfortunately, at a typical temperature difference along the water layer thickness $T_{\max} - T_{\text{surf}} = 20^\circ\text{C}$ the value of D at the water surface (at $\bar{z} = 1$) turns out to be twice as large as at $\bar{z} = 0$, and therefore a more complicated formula (12) has to be used.

According to Eq. (12), the salt concentration at the bottom of the water layer and at the surface of the layer when the stationary regime is reached is determined as follows:

$$c(0) = c_{\text{av}} - \frac{S}{B} \left\{ \gamma \left[I - (\gamma - I) \ln \frac{\gamma}{\gamma - I} \right] - \frac{I}{2} \right\}, \quad (14a)$$

$$c_{\text{surf}} = c(I) = c_{\text{av}} + \frac{S}{B} \left\{ \gamma \left[\gamma \ln \frac{\gamma}{\gamma - I} - I \right] - \frac{I}{2} \right\}. \quad (14b)$$

To calculate the concentration profile, it is necessary to know the parameter S , which is determined by the value of the equilibrium salt concentration on the water surface c_{surf} . This can be done by solving the following transcendental equation:

$$\frac{\dot{m}(T_{\text{surf}}, c_{\text{surf}})d}{\rho_w} = -\frac{2B(c_{\text{surf}} - c_{\text{av}})}{I + 2\gamma(I + \gamma \ln(I - I/\gamma))} \quad (15)$$

in the left and right parts of which are different expressions for S . In the left part of Eq. (15) is the definition of S , and the formula in the right part of this equation was derived from Eq. (14b).

The resulting steady-state salt concentration profiles $c(\bar{z})$, calculated using Eq. (12), are shown in Fig. 7. It can be seen that these profiles are not very sensitive to the surface temperature of the water layer and are similar to the parabolic profile described by Eq. (13). However, there is no need in the parabolic approximation.

It is important that the above analytical solution for the steady-state profile of the salt concentration cannot be obtained when Eq. (14a) gives a negative value of $c(0)$. This leads to the following critical condition for the self-stabilization of the droplet cluster:

$$c_{\text{av}} > c_{\text{av}}^*(T_{\text{surf}}) = \frac{S}{B} \left\{ \gamma \left[I - (\gamma - I) \ln \frac{\gamma}{\gamma - I} \right] - \frac{I}{2} \right\} \quad (16)$$

This theoretical estimate shows that the stabilization of a droplet cluster over a layer of salt water is possible only at a not too low salt concentration.

When calculating the boundary of the stabilization area (see Fig. 4b), the dependence of water evaporation rate on temperature and salt concentration at the surface of the water layer was taken into account. However, the used approximate model of evaporation is not very accurate. This is the main source of an error in the calculated dependence of $c_{\text{av}}^*(T_{\text{surf}})$.

5. Conclusions

The laboratory experiments confirmed that the suggested method of self-stabilization of a levitating droplet cluster is really effective when the mass concentration of sodium chloride in water is greater than about 0.2%. It was shown that the size of nearly identical droplets in the equilibrium cluster decreases inversely proportional to the average concentration of salt in water. The theoretical estimate of the minimum required salt concentration in the water layer agrees well with the experimental findings.

The new method of self-stabilization of droplet clusters opens up promising possibilities for studying chemical and biochemical processes in small droplets, which can be used as natural micro-reactors. The results obtained can also be interesting for studies of processes in the surface layer of the ocean and in the analysis of the remote sensing results.

Declaration of competing interest

The authors declare that they have no known competing financial

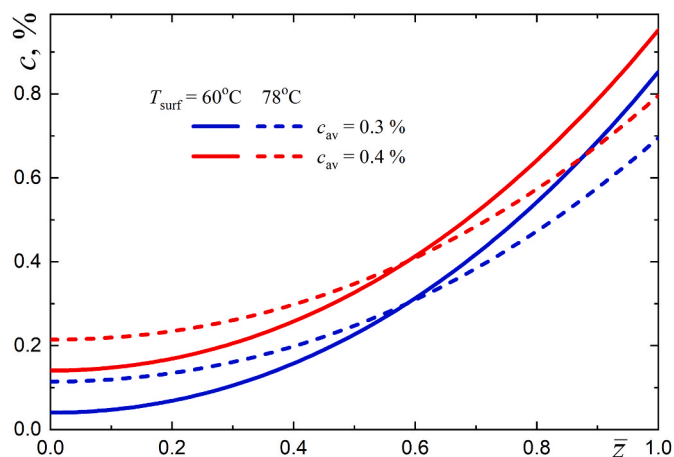


Fig. 7. Steady-state profiles of salt concentration in the water layer under the equilibrium cluster of levitating water droplets.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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