NON-ISOTHERMAL DESORPTION OF DROPLETS OF COMPLEX COMPOSITIONS

by

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This paper presents the process of non-stationary evaporation of aqueous solutions of $LiBr\text{-}H_2O$, $CaCl_2\text{-}H_2O$, $NaCl\text{-}H_2O$ *droplets on a horizontal heating surface. The following typical stages of heat and mass transfer depending on wall temperature have been considered: evaporation below boiling temperature and nucleate boiling. The significant decrease in desorption intensity with a rise of initial mass concentration of salt has been observed. Formation of a surface crystallization front at evaporation of a droplet has been detected. We have developed the experimental method for direct measurements of the mass of evaporating droplet.*

Key words: *droplets non-stationary evaporation, aqueous salt solutions, desorption, heating surface*

Introduction

The efficiency of absorption thermotransformers is determined by the processes of absorption and desorption. The theory of non-isothermal absorption is presented in monograph [1]. Formally, the analytical solutions obtained in [1] can be used for description of non-isothermal desorption of aqueous salt solutions with consideration of inversion of heat and mass fluxes. However, this is true only for the limited range of problems and simple boundary conditions of heat and mass transfer processes at the interface. The processes of non-stationary evaporation of aqueous salt solutions of droplet on a horizontal heating surface can be hardly described by the available theory of isothermal and non-isothermal sorption, and they need preliminary experimental investigation in a wide range of operation parameters. Theoretical tasks, adequate to the complex physical pattern of non-isothermal desorption, can be formulated on the basis of experimental data.

Evaporation of sessile droplets of single-components liquids and water droplets containing an additive was studied in [2-13]. The following typical stages of heat and mass transfer can be distinguished on the horizontal heating surface depending on its temperature T_w: evaporation below boiling temperature T_b at fixed pressure ($T_w < T_b$); nucleate boiling at ($T_w \geq T_b$); transitional (nucleate-film) boiling up to Leidenfrost temperature T_l, crisis evaporation at ($T_w \geq T_l$); with complete separation of liquid from the heating surface by a thin layer of vapor. The theory of heat

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transfer crisis (evaporation in the spheroidal state), based on the hydrodynamic approach to explanation of boiling crisis is presented in [2, 14]. It is characteristic that all these processes are finished by complete transformation of the liquid phase into the vapor one. However, for liquids of the more complex compositions these regularities can gave the different character, and they were studied in [15-25]. For instance, for aqueous salt solutions the phase equilibrium at the "liquid-vapor" interface is also determined by concentration of dissolved substances together with the pressure and temperature [15, 16, 18, 21, 25]. In these solutions in contrast to the single-component liquids the third phase (solid state) can be formed in the process of desorption. To distinguish the physical pattern of heat and mass transfer processes in such systems, we have carried out experimental studies on nonstationary evaporation of droplets of water solutions of NaCl, $CaCl_2$, and LiBr with different initial mass concentration (C_0) of aqueous salt solutions in a wide temperature range T_w under the atmospheric pressure of the ambient medium.

Experimental method

To register the current parameters of non-isothermal desorption of the metered volumes of aqueous salt solutions (droplets) on the horizontal heating surface (see fig. 1), we have developed the experimental method for direct measurements of the weight of evaporating droplet. The working section was mounted on a laboratory balance. Video and thermal image recording allowed us to determine the qualitative and quantitative characteristics of the process of non-isothermal desorption of droplets for heat transfer law T_w = const.

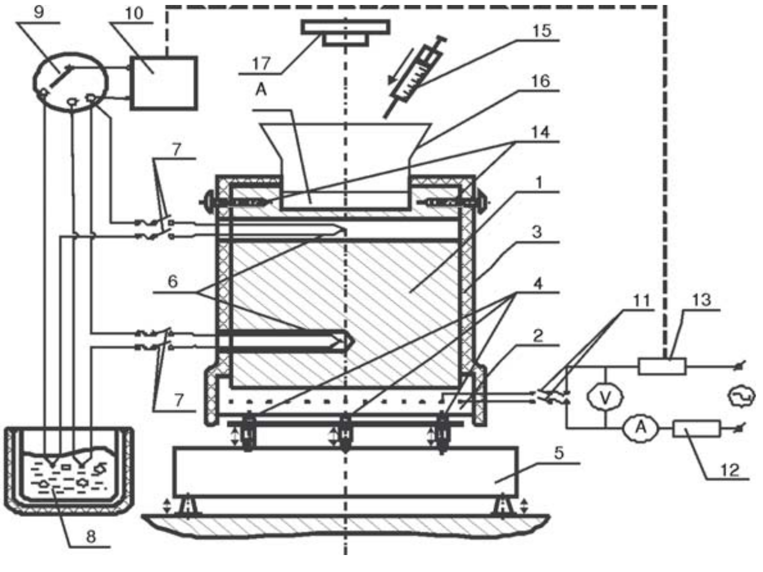


Figure 1. Principle scheme of set-up for the work with batches of single-component liquids and mixtures of complex composition:
A – working heating surface, 1 – titanium cylinder, 2 – electric heater, 3 – multilayer screen thermal insulation, 4 – adjustable supports, 5 – analytical balance, 6 – thermocouples, 7 – flexible detachable element of thermocouple, 8 – Dewar vessel with ice, 9 – thermocouple switch, 10 – millivoltmeter, 11– flexible detachable element of electric wiring, 12 – laboratory thermotransformer, 13 – temperature regulator, V and A – voltmeter and ammeter, 14 – puller ear, 15 – metering device, 16 – protecting screen, 17 – video, and shooting cameras, thermal imager

The use of titanium as the working material allowed experiments with corrosive water solutions of NaCl, $CaCl_2$ and LiBr at heating surface temperatures $T_w \leq 400$ °C. The values of solution concentrations C_0 were determined by the standard densimeters, and their metered volumes V_o were put on the heating surface by microdispensers. To verify the method of measurements of mass m, special experiments were carried out. In these experiments we have obtained data, which proved an insignificant effect of thin flexible contact connections of thermocouples and electric wiring on accuracy of weighting. Due to application of multilayer screen thermal insulation of the working section the effect of the loss of heat fluxes on weighting accuracy in our experiments was also insignificant. It was also found out that the weight of dry residue of salts after experiments corresponded to their content in initial batches of solutions within the weighting error. The thermal field of droplet surface was measured by the thermal imager. The measurement of liquid surface temperature causes some methodical difficulties [3, 6] and requires additional grounding (examination). In our experiments reliability of measurements of interface (liquid-air) temperature was achieved due to the accurate choice of infrared camera radiation coefficient. With this purpose before the experiment we have performed some testing: simultaneous measurement of liquid surface temperature by the infrared camera and thermocouple located on the liquid surface (these measurements were carried out under the stationary conditions, when the temperature gradient in liquid near the surface was relatively low). The temperature range of liquid surface varied from 20 °C to 90 °C. Emissivity was changed with accuracy of 0.01 °C. The difference between the temperature values measured by the thermocouple and thermal imager did not exceed 1.5 ºC. Therefore, the measurement error of the infrared camera was within 2%.

Results and discussion

The following regularities of non-isothermal desorption of aqueous salt solutions were determined. Within temperature range ($T_w < T_b$); the significant decrease in desorption intensity was observed with a rise of C_0 (see fig. 2). This regularity is determined by a decrease in pressure of saturated vapors of water above the interfacial surface of solution (liquid-gas) with a rise of salt concentration.

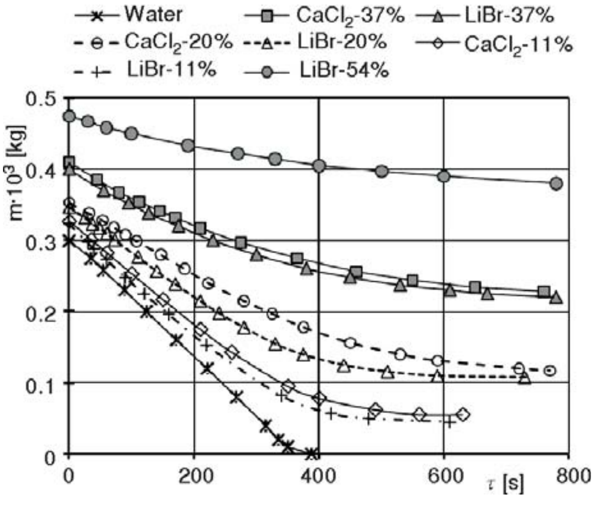


Figure 2. Comparative dependences for evaporation of droplets of distilled water and non-isothermal desorption of aqueous salt solutions with different C_0 (V_o = 300 μl; T_w = 80 °C)

A relative decrease in temperature of droplet surface from the center to the periphery can be seen in thermograms (see fig. 3). The video frames (see fig. 4, 5, and 6) indicate indirectly the more active character of evaporation at the droplet periphery, where the first salt crystals or crystalline hydrates are extracted. At this, the motion of surface front of crystallization is always directed from the periphery to the center. This seeming mismatch is caused by the fact that solution thickness at droplet edges is minimal and, hence, the local heat flux from the heating surface to the droplet at this point is higher than in its center. This leads to more intensive evaporation and surface cooling of solution as well as to its oversaturation and solid phase extraction. Weighting has shown that after forming the solid surface film of crystals or crystalline hydrates the process of desorption continues, albeit extremely slowly. Water diffuses or penetrates through the crystal film and then evaporates. The surface film of crystalline hydrates of water solution of $CaCl_2$ is transparent (see fig. 5). The film of LiBr solution is opaque (see fig. 6). At evaporation of water solutions of NaCl the film was not observed (see fig. 4).

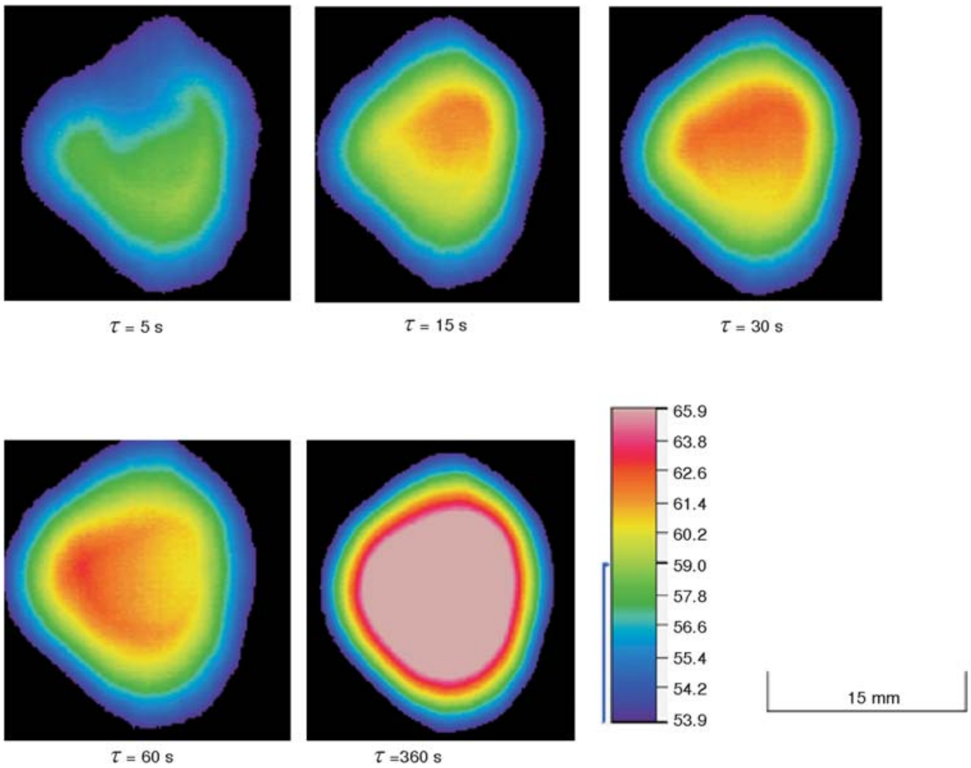


Figure 3. Thermographic images of the process of non-isothermal desorption of the droplet of water solution of LiBr (T_w = 80 °C, V_0 = 300 μl, C_0 = 22%)

Non-isothermal desorption of droplets at $T_w < T_b$ finishes by formation of salt residue for NaCl or crystalline hydrates for $CaCl_2$ and LiBr. Let's note the specific character of LiBr salt residue formation (see fig. 6): with time it spreads as a thin layer over the heating surface, the initial area of the droplet is increased many times. This phenomenon being promising for intensification of heat and mass transfer processes on microstructured heat-exchanging surfaces requires following investigation.

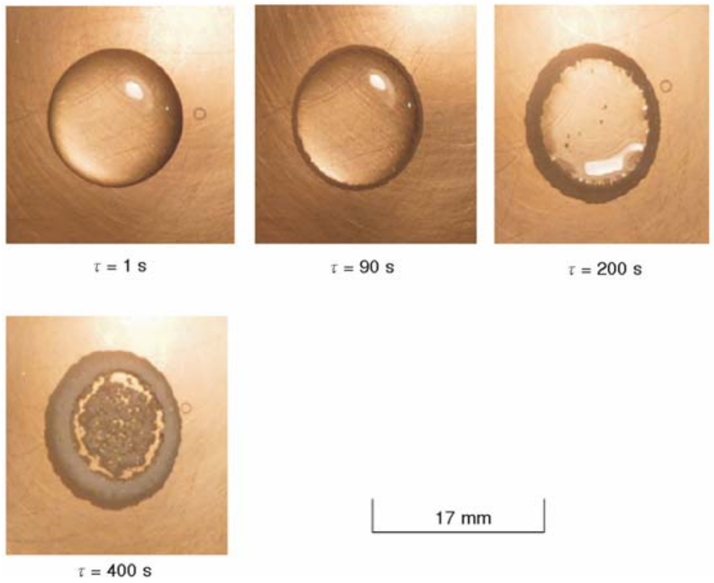

τ = 1 s τ = 90 s τ = 200 s τ = 400 s

Figure 4. Development of the process of non-isothermal desorption of the droplet of water solution of NaCl (T_w = 80 °C, V_0 = 300 μl, C_0 = 20%)

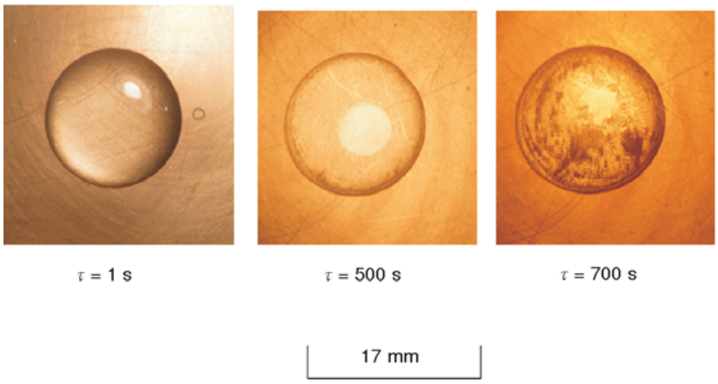
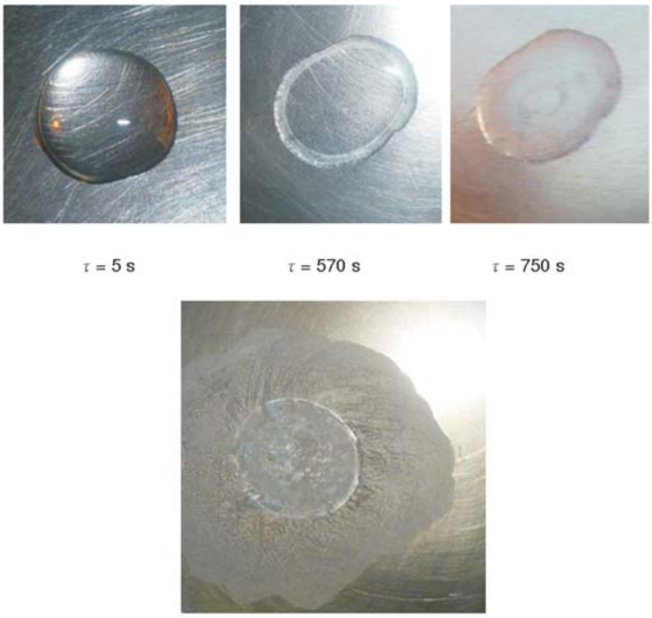

τ = 1 s τ = 500 s τ = 700 s

Figure 5. Development of the process of non-isothermal desorption of the droplet of water solution of $CaCl_2$ (T_w = 80 °C, V_0 = 300 μl, C_0 = 20%)

With a rise of concentration C_0 a relative increase in T_b is determined. The process of heat and mass transfer (see fig. 7) at evaporation of a droplet of distilled water on the heating surface at $T_w > T_b$ includes four successive stages. (1) At the first stage convective-conducting heating of a droplet from initial temperature to T_b occurs. (2) Intensive nucleate boiling leads to intensification of evaporation; the large vapor bubbles is formed; the total area of droplet contact is increased many times and the droplet surface temperature is reduced significantly. (3) A brief reduction of evaporation intensity occurs. (4) The long fourth stage of boiling with a continuous decrease in the size of contact spot completes evaporation of liquid. The similar pattern of the droplet mass change is observed for aqueous salt solutions. However, with an increase in current mass concentration of salt in the droplet the process of its boiling can stop completely because according to the conditions of thermodynamic equilibrium for maintaining of boiling the higher values of T_w are required. This progressing temperature drift towards the higher values of T_b is the main feature of evaporation of aqueous salt solutions.



τ = 5 s τ = 570 s τ = 750 s

τ = 6600 s

Figure 6. Development of the process of non-isothermal desorption of the droplet of water solution of LiBr (T_w = 80 °C, V_0 = 300 μl, C_0 = 20%)

The behavior of evaporating solution droplets separated at $T_w \geq T_l$ from the heating surface by a thin steam film is special. In contrast to the single-component liquids the physical-chemical nature of aqueous salt solutions (particularly, the degree of salt solubility) generates new physical phenomena, and degeneration of classical heat transfer crisis (evaporation of liquid in the spheroidal state) plays the main role among them [26]. We have observed the following characteristic situation. With evaporation of a spheroid of water NaCl solution, formation of visible salt crystals was observed in its bottom part, directed to the heating surface. Then, the droplet contacted the heating surface, what was accompanied by extraction of these crystals from the solution. Finally, alternation of these cycles of salt clots formation and contact with the heating surface led to formation of dry salt residue on the heating surface.

For the case of high solubility of LiBr in water, we observed the effect of intra-volume vapor explosion with single-stage droplet breakdown into many tiny droplets. We guess that the main factor provoking development of inner thermodynamic instability in the droplet volume is significant local overheating of solution in the bottom part of a spheroid. We should note that phenomena of thermal explosion were registered previously by Baidakov in the "liquid-liquid" systems [27]. Perhaps, this event is typical for a wide range of physical phenomena. In our case the mechanism of overheating can be explained by the following. An increase in salt concentration in a spheroid leads to a decrease in the thickness of the vapor film, protecting a spheroid from the contact with the heating surface. This increases the heat flux to the droplet. The diffusion process occurs much slower than the heat is transferred, so the salt concentration gradient increases significantly in the bottom part of the droplet and evaporation rate decreases, that result in to the growth of overheat of the bottom and generates thermodynamic instability in this area. The instability of the bottom part can lead to instantaneous collapse of the droplet.

Solubility of $CaCl_2$ salt in water is intermediate between NaCl and LiBr; therefore, evaporation of spheroids of water solutions of this salt was something intermediate between desorption of droplets of above solutions.

Therefore, the theoretical models for the single-component liquids can not be used in full for the description of the physical pattern of droplet evaporation of complex liquids. This is especially typical for water solutions of LiBr. Investigation of the physical pattern of non-isothermal desorption of droplets and thin films of complex composition has the interdisciplinary character.

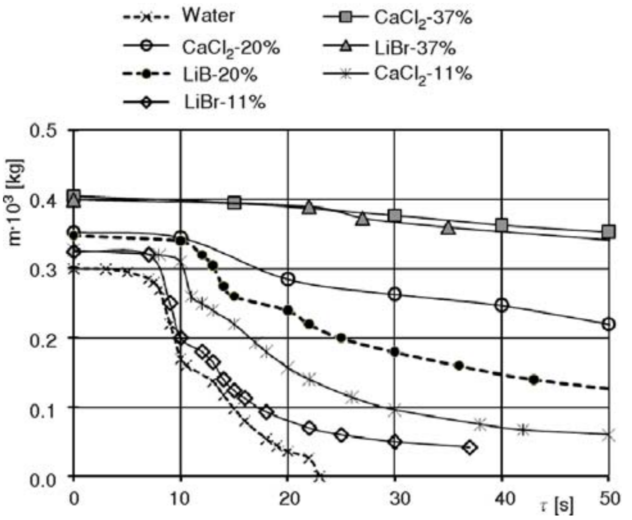


Figure 7. Comparative dependences for evaporation of droplets of distilled water and non-isothermal desorption of aqueous salt solutions with different C_0(T_w = 130 ºC , V_o = 300 μl)

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Nomenclature

C_0 – initial mass concentration of aqueous salt solutions, [%]
m – droplet mass, [kg]
T_b – temperature of liquid boiling beginning, [°C]
T_l – Leidenfrost temperature, [ºC]
T_w – the wall temperature, [ºC]
V_o – the initial batch volume, [ml]

Greek symbol

τ – the current time of evaporation of droplet, [s]

Subscripts

0 – initial value ($\tau = 0$)
w – wall

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