Experience of superheat of solutions: doubly metastable systems

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Abstract. The phenomenon of attainable superheat of two-component mixtures has been studied experimentally by the method of pulse heating of a wire probe. Special attention was called to the appearance of double metastability in the course of heating. Besides the usual superheating with respect to the liquid–vapor equilibrium temperature, the objects under study turn out to be supersaturated with respect to the carbon dioxide content. Preliminary experiments were carried out in the region of instability located above the diffusion spinodal. The results obtained lead to the choice of the program of further research on doubly metastable and unstable systems with different degrees of component compatibility.

1. Introduction
Preliminary assessment of the efficiency of a working fluid is performed taking into account its primary thermophysical properties, in particular, the coefficient of thermal conductivity, specific heat and critical constants. In a number of engineering tasks, an important factor is the ability of the heat transfer agent to withstand a certain superheat (with respect to the liquid–vapor equilibrium line) without boiling-up. In general, the phenomenon of superheat (or stretch) of a liquid in nature and technology is more the rule than the exception [1–5]. When the power of local heat release in the system is increased and/or its characteristic sizes are decreased, the degree of superheat can reach significant values predicted by the theory of homogeneous nucleation with the work of critical bubble formation written in a thermodynamic approximation [1–4]. In laboratory practice, special set-ups and experimental approaches were developed to penetrate into the highly superheated states [1–11]. In particular, we are developing a method of controlled pulsed heating, which is applicable throughout all region of pressure change in a liquid [12, 13]. A set of the previous results, including those for solutions with a thermally unstable component are presented elsewhere [14–17].

The report focuses on the study of attainable superheat of solutions under high-power pulse heating and the interaction of double metastability (with respect to the liquid–vapor and liquid–liquid equilibrium lines) degree and the conditions of spontaneous boiling-up. The difficulty of the very formulation of the problem is caused by the complexity of interaction of two relaxation mechanisms with their characteristic times and, as a consequence, by increased requirements for the techniques of pulse experiments and monitoring the actual state of the initial sample.

2. Background
The superheated liquid is observed when the parameters of the system (temperature $T$ and/or pressure $p$) cross the liquid–vapor equilibrium line $T_s(p)$. The corresponding trajectories of the liquid
superheating are shown in figure 1. As the introductory remarks to the content of the report, let us note the following. The methodological condition for experimental observation of a highly superheated liquid is the minimization of the product \( V \cdot t \), where \( V \) is the superheated volume, \( t \) is the characteristic time of the experiment [1, 10]. Following the “path of least resistance”, the majority of work on attainable superheat was performed for pure fluids. Indeed, the transition to two-component systems is accompanied by increased requirements for an experimental apparatus and measurement technique [14–16]. Here, we just pay attention to the substantial extension of the region of superheated states for the mixture, which is schematically shown in figure 1. In the general case, such an extension is associated with the phenomenon of limited solubility (up to zero solubility) over a wide temperature range, which is characteristic of components of a different chemical nature. Let us mention, in this connection, a decrease in the solubility of carbon dioxide in most liquids with increasing temperature along the isobar. This circumstance is equivalent to supersaturation of the solution with respect to the equilibrium line \( T_s(p; c = \text{const}) \) of a solution at a given concentration \( c \), see trajectory \( w_3 \) in figure 1.

In the development of the reasoning, figure 2 shows a phase diagram of a water-oligomer system with the lower critical solution temperature (LCST). The main field of the figure is occupied by the region of solution instability located above the diffusion spinodal (and the liquid–vapor equilibrium line as well). This region serves as an analogue of “No men’s land” in experiments with the stretching of a supercooled liquid [5]. At the same time, it is available for experimental study with an appropriate choice of the characteristic times and sizes of the system \( V \cdot t \).

3. Experimental
Experiments on attainable superheat of solutions against a background of double metastability were carried out by the method of pulse heating of a wire probe. This method makes it possible to track the evolution of the mean integral temperature of the probe and determine the liquid boiling-up timing \( t = t^* \) marked by confined in time and reproducible with respect to temperature signal on the heating curve [12–14, 17]. Based on the primary data recorded in the experiment (namely, voltage drops on the probe and the standard resistor in time) and known probe parameters, we calculated the temperature value \( T^* \) corresponding to the spontaneous boiling-up onset [14], as well as the density of heat flux through the probe surface at any time. Explanations of the essence of electronic circuit concept and measurement methodology were given in Refs. [12, 13].
3.1. Materials
The objects of study were solutions of carbon dioxide in hexadecane and triethylene glycol (TEG) as systems with double metastability; the temperature dependence of their solubility is similar, but varies quantitatively. An aqueous solution of polypropylene glycol PPG-425 was chosen as a LCST–type system with a wide range of unstable states. Dissolution of water in PPG was carried out in a closed volume representing a miniature magnetic stirrer. Dissolution of carbon dioxide vapor was carried out through the free surface of the liquid, up to the saturated state for given temperatures and pressures. The completion of the dissolution process was monitored by the level-off of the characteristic response signal related to the concentration of the substance in the solution and the degree of its homogeneity.

3.2. Results and discussion
Let us start with carbon dioxide solutions. The choice of solvents was dictated by the following circumstances. They have nearly equal values of \( T^* (p = 0.1 \text{ MPa}) \), as well as close solubility of carbon dioxide at room temperature. At the same time, the scale of the change in their solubility with temperature varies considerably. For example, in a region from 300 to 400 K, the molar solubility of carbon dioxide in hexadecane decreases by \( \sim 2.7 \) times slower than in triethylene glycol, see figure 3. Let us clarify the effect of this circumstance on the attainable superheat \( T^* (t^*) \) of these solutions at a comparable change in the heating rate. It is known that the systematic dependence \( T^* (t^*) \) is manifested in thermally unstable substances [15, 16]. But the dissolution of CO\(_2\) transfers the \( T^* \) values of these substances to the region of thermal stability. Consequently, the differences in the course of their dependences \( T^* (t^*) \), if they are found, can be associated to the difference in solubility values at elevated temperatures. From figure 3 it follows that by choosing the conditions of CO\(_2\) dissolution, i.e., the \( p^g \) and \( T_0 \) values along a curve of constant composition \( c = \text{const} \), it is possible to change the supersaturation of a solution of a given concentration during its heating up to spontaneous boiling–up timing. The scale of this change, which is given by the \( \Delta p^g \) value, is different for the selected samples.

![Figure 3. The saturation pressure for hexadecane (1) and triethylene glycol (TEG, 2) corresponded the constant mole fraction of carbon dioxide in solution (c = 0.1) versus the initial temperature [18].](image)

![Figure 4. The attainable superheat temperature for TEG (1) and CO\(_2\) solutions in hexadecane (2, 3) and TEG (4-8) against of heating time at different initial conditions (\( p^g / T_0 \)): 1.1 MPa/293 K (2); 3.3/293 (3); 1.1/380 (4); 1.1/341 (5); 2.0/333 (6); 1.1/293 (7); 2.1/293 (8).](image)
In the experiments, the $T^*$ values were measured at $p_g$ values from 1 to 3 MPa and $T_0 = 290, 333, 380,$ and 420 K. The heating time varied from $t^*_{\text{h}} = 20$ to $t^*_{\text{h}} = 670 \mu$s. It turned out that the results for these solutions are qualitatively different, see figure 4. For hexadecane solutions, the total value of the change $\Delta T^* = T^*(t^*_{i}) - T^*(t^*_{0})$ was several degrees. Such a result is typical for the majority of two-component systems, which we studied earlier [14]. A more interesting picture was obtained for triethylene glycol. The $\Delta T^*$ value increased up to 100 K depending on the dissolution conditions ($p_g, T_0$). The main change in $T^*$ occurred in the vicinity of $t^* \sim 100–200 \mu$s and had a step-like character.

Several explanations can be given to this result. We are of the opinion that it is caused by microphase separation in the second solution, which is occurred during its heating (and supersaturating as well). It is well-known that the formation of a critical bubble in a micro-inhomogeneous solution required the lowered (for given $p, T$) activation barrier. (In a recent paper [14], the similar result was found by the example of a solution with upper critical solution temperature.) Consequently, its boiling-up is observed at a lower temperature for comparatively large length of the heating pulse. A violation of the confinement in time of boiling-up signal typical of homogeneous liquids has been observed simultaneously. In addition, this hypothesis is indirectly confirmed by the correlation of $\Delta T^*$ of triethylene glycol solutions with the degree of supersaturation $\Delta p_g$ in the content of carbon dioxide. The analysis of the data in figures 3 and 4 shows a decrease in the $\Delta T^*$ value of solution of a given concentration with reduced $\Delta p_g$. The decrease in $\Delta p_g$ was achieved by increasing the values of $T_0, p_g(T_0)$ along the curve of constant concentration, and also by increasing the pressure at the attainable superheat measurements with respect to the gas saturation pressure, $T^*(p > p_g)$.

The next object of our study was an aqueous solution of polypropylene glycol. In accordance with figure 2, the initial temperature was chosen in the region of stable states of the system. At this stage, the experiments were preliminary in nature and aimed at elucidating the applicability of our method for selecting a reproducible response signal from a system in an unstable state, that is, beyond the diffusion spinodal. The solution of this point will allow us to formulate the general problem of studying solutions in states of double metastability and unstable states. It is important to find a relationship between the characteristic times of the penetrating into an unstable state, spontaneous boiling-up, phase separation by the mechanism of liquid–liquid or spinodal decomposition, and the convection onset. Systems with LCST are of additional interest due to the effect of significant heat release accompanying spinodal decomposition. By the example of a triethylamine/water solution, it has been shown that the heat transfer coefficient of a decomposing system exceeds the corresponding coefficient of a homogeneous system by 2.5 times [19].

The experimental results are shown in figure 5. The parameters of the experiments were as follows: the probe diameter was 20 μm, the probe length 1 cm, the heating was carried out by a rectangular voltage pulse. It turned out that at the selected heating rates, the transition across the diffusion spinodal was not accompanied by any peculiarities up to boiling-up. The heating curves retained a smooth monotonous appearance typical for ordinary superheated liquids. Further, it has been found that water additives substantially reduce the temperature of spontaneous boiling-up of the solution, increase its critical pressure and increase the instantaneous heat transfer coefficient

$$k = P(t)/\pi dl \cdot \Delta T(t).$$

Here $\Delta T(t)$ is the temperature rise at chosen timing $t$; the probe parameters ($d, l$) remain constant in the course of experiment; the value of the power $P$ is selected in accordance with the investigated temperature range. Note that an increase in the $k$ value is accompanied by a decrease in the temperature on the heating curve.

4. Outlook
Experiments with not fully compatible solutions were carried out by the method of pulse heating. The temperature dependence of solubility of the components of selected solutions had the similar character with significant quantitative differences. The experiments were carried out in such a way that heating of the system was accompanied by its transfer to the region of not fully stable (solutions of carbon...
dioxide) or unstable states (aqueous solution, the region of low concentrations). Let us sum up the current stage of the research.

![Figure 5](image)

Figure 5. Characteristic heating curves at constant heating power mode in PPG-425 (above) and water/PPG-425 mixture (5 wt.%, below). The pressure serves as a parameter. The arrows show the timing of spontaneous boiling-up for subcritical pressures. The inserts illustrate identification of this moment (below) and the change in the instantaneous heat transfer coefficient with pressure (above).

What we managed: to develop an approach that is acceptable for studying the behavior of solutions in unconventional phase states; to detect the effect of double metastability on the conditions of spontaneous boiling-up of an initially homogeneous solution; to clarify the principal measurability of the system properties in the phase diagram region beyond the diffusion spinodal.

We failed: to detect the phenomenon of spinodal decomposition in experiments with the third solution and to reveal the inherent perturbations of the instantaneous heat transfer coefficient.

What needs to be done: to clarify the relationship of the characteristic relaxation times of solutions in unconventional phase states under given heating and pressure conditions; to determine the scale of the thermal effects accompanied phase transitions by the liquid–liquid, liquid–vapor mechanism and during the spinodal decomposition. To solve this problem, it is appropriate to apply two modern modes of controlling the pulse heating, namely, the constant heating power mode (in this case, the evolution of the probe temperature serves as an informative parameter) and the “temperature plateau” mode (the heating power necessary for stabilizing the probe at the selected temperature serves as an informative parameter) [17, 20]. Further, based on the results of measurement of the $T^*(p)$ dependence and taking into account the previous experience [14, 17], it is important to estimate the apparent critical parameters of unstable solutions and to clarify the specificity of manifestation of the known phenomena of critical slowing down/speeding up [21] for unstable solutions in the microscale of characteristic times and sizes.

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