Methodology of investigation of binary liquids in the unstable states

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Abstract. This work is devoted to the development of a measurement methodology for a new object in the thermophysics of extreme states – a partially-soluble binary liquid, which is short-term transferred to the region of unstable states above the diffusional spinodal. On an example of PPG-425/water solution having the lower critical solution temperature, the key hypothesis of the study on the general measurability of the properties of unstable solutions has been confirmed. The heating rate was varied from $10^5$ to $10^6$ K/s, and the pressure was varied from units of MPa to 100 MPa. The superheat of the solution with respect to the diffusional spinodal was up to 150 degrees. The conditions for the transition from measurements on pure components to measurements on the solution are formulated. The characteristic thermal patterns of the decay of unstable states depending on pressure and heating rate are revealed. The possibility of using this binary solution as a promising coolant in processes with powerful local heat release is assumed.

1. Introduction
Most fluid technologies are based on mixtures. Scientifically, the phase diagrams of solutions are much more diverse than the phase diagrams of pure substances [1]. In this regard, the study of the properties of solutions composed of components with various degrees of thermodynamic compatibility is relevant. In general, the degree of compatibility depends on both temperature and pressure [2]. The properties of solutions, their thermophysical properties, in particular, are usually studied in thermodynamically stable states. For these states, a complex of experimental methods and techniques has been developed for measuring primary quantities and converting them into the actual values of thermophysical properties. THW-technique should be indicated as an example of a widely used technique for determining the thermal conductivity of solutions [3]. It is accompanied by the requirement for the constancy of the heat release power in the wire probe, which serves as the basis for the correct recalculation of the primary values into the values of thermal conductivity [4].

Methods for studying the properties of solutions in region of not fully stable states, superheated (in the case of lower critical solution temperature, LCST) with respect to the liquid-vapor or liquid-liquid equilibrium line and unstable states, superheated with respect to the diffusional spinodal have not yet received proper development. This circumstance is obviously associated with experimental difficulties [5]. They are due to limitations on the duration of the measurement and also limitations on the volume of the superheated sample. At the same time, such states can and do arise during the intensification of the heat transfer process and miniaturization of the device dimensions, which is a modern trend [6].
2. Problem statement
This work is devoted to the development of an approach to the study of solution properties, which are transferred successively into not quite stable [7] and unstable states. At this stage of the study, the term "properties of solutions" means the lifetime in an unstable state depending on the degree of superheating and the instantaneous heat transfer coefficient with respect to its values for a pure component obtained in comparable conditions or a solution of the given concentration, determined by extrapolating values from the region of stable states. In the course of the research, we proceed from the following hypotheses:

- the hypothesis of the short-term feasibility of solution's unstable states and the measurability of its properties in such states;
- hypothesis about the confinement of the unstable state decay process (spinodal decomposition) with respect to time, sufficient for the unambiguous registration of its signs in real-time;
- the hypothesis of the response signal change in the polarity when the pressure value (in the step-by-step pressure increase course) crosses the critical isobar or its effective value.

The object of study is a solution of water and 425-molecular-weight polypropylene glycol (PPG-425) having LCST in the vicinity of 328 K [8]. The initial state of the solution is at a temperature of $T_{0} \approx 295$ K, that is, in the region of its stable states. The instrument is a method of controlled pulse heating of a wire probe immersed in the investigated medium.

3. Experimental procedure
To solve this problem, the wire probe’s pulse heating method [9, 10] with the function of fine control of the heating parameters during the pulse was used [7, 11]. The choice of the method is due to the possibility of minimizing the product of the volume of the superheated sample and the observation time, $V \cdot t$, detecting the heat-flux density disturbance, associated, for example, with spontaneous boiling-up, against the background of monotonic heating and repeating the selected heating mode in a series of measurements with high precision. The latter circumstance is important for the correct comparison of the signal-response characteristics in the course of a systematic change in the experimental parameter. The parameter of the experiment can be the pressure $p$, the concentration of the solution $c$, and the degree of its superheating $T - T_{sp}$. In experiments, in accordance with the modern version of the method, the change in the average integral probe temperature is monitored during the pulse $T(t)$ of a given power $P(t)$. The primary data are the voltage drop across the probe and the standard resistor $U(t)$ as described elsewhere [7]. On their basis, the reproducibility of the set value $P(t)$ in a series of measurements and, taking into account the standard calibration of platinum resistance thermometers, the evolution of the temperature of the probe $T(t)$ are monitored.

To reduce the influence of approximations inherent in probe methods [3], it is convenient to use the mode of relative measurements. In this case, it is advisable to fix one of the key variables of the method, namely, $P(t) \approx \text{const}$ or $T(T>T_{1}) \approx \text{const}$, where $t_{1}$ is the duration of heating from the initial temperature $T_{0}$ to its specified value. Then the difference in the course of the resulting curves $T(t)$ in the first case or $P(T>T_{1})$ in the second case, due to a change in the experimental parameter, will reflect the difference in the coefficient of heat transfer from the probe to the medium at a selected (generally, arbitrary) timing. Following [12], the necessary condition for the transition from measurements on pure components to measurements on a solution will be the repeatability of the heating function in a series of experiments and the sensitivity of the response signal to a small change in the parameter, see Fig. 1. The latter circumstance makes it appropriate to use also the heating mode in the form of a constant current in the probe circuit, $I(t) \approx \text{const}$. This mode is a natural amplification of differences in signal-response amplitude against the background of small parameter changes. As a result, we can conclude that with a strictly specified heating mode, the results of such measurements serve as functions of not only the characteristics of the process but also, in a relative mode, the sample properties' functions.
Figure 1. Heating curves for water under the constant power mode at subcritical ($p = 19$ MPa) and supercritical (the other curves) pressures.

4. Results
Typical results of experiments on the fast transition from initially-stable to unstable states are presented below, see Fig. 2-5. The object of study is a 30% PPG solution in water. This composition is close to the critical solution concentration, being $c_{LCST} \approx 25\%$. As a result, the region of unstable states is separated from the region of stable states only by a narrow (in temperature) strip of metastable states. To exclude the spontaneous boiling-up effect of a solution superheated with respect to the liquid-vapor equilibrium temperature [5, 9], the experiments were carried out at elevated pressures, from $p/p_c \approx 0.3$ to supercritical values $p > p_c$. The heating rate was varied from $10^5$ K/s (constant power mode) to $10^6$ K/s (constant current mode). The probe was a platinum wire having a diameter of 20 μm and a length of 1 cm. It was connected to a negative feedback loop [7]. This circuit reproduces the specified heating mode, taking into account the change in the properties of the probe material and substance with temperature. The degree of superheating of the solution with respect to the diffusional spinodal was 150 K and higher.

Figure 2. Derivatives of probe temperature with respect to time for the solution along the isobars from 6.6 to 15.1 MPa under the constant current mode. Insert shows the last subcritical isobar at 12.6 MPa and the first supercritical isobar at 13.1 MPa.
A sign of spinodal decomposition [13], as the most probable relaxation process in the considered part of the phase diagram ($T>T_{sp}$), was a disturbance of the signal-response smooth course in the form of $U(t)$ or $T(t)$. The downward deviation of the signal relative to the extrapolation of its undisturbed path corresponds to an increase in the heat flux through the probe surface (for example, in the case of spontaneous boiling-up), and upward deviation corresponds to its decrease (in the case of a supercritical transition). A change in the signal-response polarity during the pressure’s change is a sign of crossing the critical isobar ($p=p_c$). This circumstance underlies the technique for assessing the critical pressure of a solution in unstable states [5, 14], see Fig. 2. For assessing the corresponding value of critical temperature $T_c=T(p=p_c)$, application of the calibration procedure for the probe with respect to the reference substances is required.

**Figure 3.** Heating curves for the solution under the constant power mode (a) and the constant current mode (b); the pressure serves as a parameter.

The time concentration of the effect due to spinodal decomposition [6, 15], turned out to be less than that of the effect due to spontaneous boiling-up, see Fig. 3. This circumstance required the application of the differentiation procedure, see Fig. 4 and 5, as well as procedures for accumulating response signals for a given heating mode. At the initial, so-called diffusion stage of spinodal decomposition, a decrease in the heat flux density is more likely. At the next, convective stage, its intensification is more likely. The scale of the effect systematically decreased with increasing heating rate, see Fig. 3a and 3b, which is evidently explained by a decrease in the thickness of the heated layer that forms the signal-response. For the lowest heating rate in our experiments, the temperature curves have a tendency to level off [16]. In this case, the density of the heat flux in the solution essentially exceeded the corresponding value for pure water, obtained under comparable conditions. For the highest heating rate, the effect was significantly "smeared". Its separation was carried out by comparison with a known homogeneous "reference substance". Water at supercritical pressure was chosen as such a substance. For the comparison, corresponding selection of the parameters of the heating function was performed, see Fig. 3b-5b. In its turn, the comparison of heating function parameters for the solution and pure water, which provides close trajectories of the probe heating, makes it possible to calibrate the intensity of heat transfer by the solution in the appropriate units for water, as the most common heat carrier. In particular, at not too short heating times up to the onset of spinodal decomposition ($t_{sp}>1$ ms), a significant heat transfer enhancement was observed. For the 30% PPG solution discussed above, the enhancement is almost an order of magnitude.
5. Conclusions
Based on the experience of working with "inconvenient" systems, a methodology is proposed that is focused on the study of solutions in thermodynamically unstable states. The essence of the work within the framework of the methodology is demonstrated on the example of PPG-425/water solution superheated with respect to the diffusion spinodal. Taking into account the variety of phase diagrams of partially compatible solutions, the general approach in passing to other systems may undergo particular changes. The discussed objects of study, judging by the unexpectedly large (for definite process parameters) enhancement in heat transfer, can find application in the problems of removing high-density heat fluxes from local areas of the heat-generating surface [17-19], for example, in miniature chemical reactors and microelectronics.

Figure 4. Derivatives of probe temperature with respect to time for the solution (see Figure 3). The arrows show the estimated timing of spinodal decomposition onset for two selected isobars. Here and below, the dotted line (Figure b) shows the corresponding curve for pure water obtained under comparable heating conditions.

Figure 5. The second derivatives of probe temperature with respect to time for the solution (see Figure 3).
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