# To the possibility of experimental estimation of the diffusion spinodal position of binary mixture with LCST via pulsed heating method

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## Abstract

In this paper, we present new data on non-stationary heating of a platinum wire probe, immersed in a binary partially-miscible liquid. A pressure value and a mass fraction of the a polymer in the mixture were the experimental parameters. The characteristic heating time was from 5 to 15 ms. The object of the research was the water/polypropylene glycol-425 (PPG-425) mixture having lower critical solution temperature (LCST). The position of the diffusion spinodal was estimated based on the obtained data on the liquid-liquid binodal in the framework of the Flory-Huggins approximation. An experimental technique to estimate the position of the spinodal of two-component mixtures with LCST on the scale of the mixture component ratio was developed. It was shown that the method of isobaric pulse heating can be used for this purpose. This representation is based on the threshold change in the heat transfer pattern when crossing the phase coexistence curve and the diffusion spinodal.

## 1. Introduction

Polymer solutions are widely used in engineering, medicine, and agriculture. They are also closely related to the processes occurring in living organisms. The study of their physico-chemical properties is of crucial importance. However, phase diagrams (PD) of solutions are much more diverse than PD of pure substances, so the area of study is often limited by the phase coexistence boundary on the $T$–$c$ diagram [1].

An analysis of the Gibbs energy makes it possible to rigorously determine the binodal and spinodal equations for partially-miscible mixtures. The binodal determines the absolute stability limit of a single-phase system, beyond which the system becomes metastable. Concentration fluctuations exceeding the critical size lead to the decay of the metastable system. The critical size of nuclei decreases with increasing degree of penetration into the metastable region. Further growth of nuclei is caused by the diffusion of components from a nonequilibrium solution. The system becomes two-phase with a clear interface. The spinodal is the boundary of the instability of mixture, beyond which it becomes labile. In this case, the appearance of new phases is due to fluctuations of any size. It is not the linear size of

the fluctuations that grows, but the deviation of the concentration from the equilibrium value. The decomposition is accompanied by the formation of two equilibrium liquid phases. The junction point at the PD where the binodal and the spinodal meet is called the critical solution temperature. There are upper (UCST) and lower (LCST) critical solution temperatures [1–3].

Nowadays, methods of experimental determination of phase coexistence curve positions are being actively developed. Among these are visual analysis, light scattering [4], and short-term heating of a platinum wire probe immersed in an investigated liquid [5, 6]. Theoretical models have been developed that can be used to estimate the position of the binodal and the spinodal of two-component systems based on their physico-chemical properties. The theories of regular solution [7] and Flory-Huggins [8, 9] have received the most recognition. However, there are practically no experimental methods capable of determining the diffusion spinodal position of not too viscous systems with sufficient accuracy. Research in this area of PD is accompanied by significant difficulties. Indeed, in the region bounded by the binodal and spinodal, the multicomponent system is not in a fully stable state. Thus, the

characteristic time of the experiment should be comparable with the characteristic time of phase relaxation of the nonequilibrium solution.

In this paper, an aqueous solution of polypropylene glycol-425 (PPG-425) having an LCST at approximately 50 °C and a PPG-425 content of 27 wt.% was chosen as the object of the study. The components of the mixture are non-toxic, easily available and can be used in relatively large volumes. The mixture is isopycnic, i.e. the components of the mixture have almost the same density, which eliminates the influence of the Archimedes force on the process of phase separation.

The aim of this work was to calculate the position of the diffusion spinodal of a water/PPG-425 mixture in the framework of the Flory-Huggins approximation and to develop an experimental technique for estimating the position of the spinodal of two-component mixtures with LCST based on the method of controlled pulsed heating of a wire probe – a resistance thermometer. This method has a number of characteristic advantages: the ability to control and change the heating parameters on a microsecond temporal scale, access to the primary experimental data obtained in the course of heating, and a wide range of temperatures and pressures (up to 800 °C and 100 MPa) available for the research [10].

## 2. Spinodal calculation

Earlier, the calculation of the spinodal of water/PPG-425 mixture based on the regular solution approximation was carried out in the work [11]. Here, we will focus on the Flory-Huggins theory as the most commonly used for this purpose. According to the theory, the change in the chemical potential of the solvent during the formation of a linear polymer solution is determined by the equation:

$$\Delta\mu_1 = RT[\ln(1-\varphi_2) + (1+1/x)\varphi_2 + \chi\varphi_2^2], \qquad (1)$$

where $\varphi_2$ – the volume fraction of polymer in solution; $x$ – the degree of polymerization; $\chi$ – the interchange energy normalized by $RT$.

$$\chi = \alpha + \beta/T, \alpha, \beta = const. \qquad (2)$$

As a result of the phase separation, solutions diluted (I) and concentrated (II) with respect to the polymer are formed. Then,

$$\Delta\mu_1(I) = RT[\ln(1-\varphi_2') + (1+1/x)\varphi_2' + \chi\varphi_2'^2], \qquad (3)$$

$$\Delta\mu_1(II) = RT[\ln(1-\varphi_2'') + (1+1/x)\varphi_2'' + \chi\varphi_2''^2]. \qquad (4)$$

Single and double apostrophes denote the concentration of the component in the dilute and the concentrated solution, respectively. Changes in the chemical potentials of the polymer in coexisting phases are equal:

$$\Delta\mu_2(I) = RT[\ln\varphi_2' - (x-1)\varphi_1' + \chi\varphi_1'^2], \qquad (5)$$

$$\Delta\mu_2(II) = RT[\ln\varphi_2'' - (x-1)\varphi_1'' + \chi\varphi_1''^2]. \qquad (6)$$

The phase coexistence curve corresponds to the system of equations:

$$\Delta\mu_1(I) = \Delta\mu_1(II), \qquad (7)$$

$$\Delta\mu_2(I) = \Delta\mu_2(II). \qquad 0$$

Substituting equations (3) and (4) into equation (7) and performing transformations, one can obtain the following expression for χ:

$$\chi = \frac{ln\dfrac{1-\varphi_2'}{1-\varphi_2''} + (1-1/x)(\varphi_2' - \varphi_2'')}{\varphi_2''^2 - \varphi_2'^2}. \qquad (9)$$

The equation for the spinodal is defined as:

$$\frac{\partial\Delta\mu_1}{\partial\varphi_2} = 0. \qquad (10)$$

The critical point satisfies the condition:

$$\frac{\partial^2\Delta\mu_1}{\partial^2\varphi_2} = 0. \qquad (11)$$

After performing the differentiation operation and transforming the resulting expressions, one can obtain the following equations:

$$\varphi_2^2 + \frac{1}{2\chi}\Big(1 - 2\chi - \frac{1}{x}\Big)\varphi_2 + \frac{1}{2x\chi} = 0, \qquad (12)$$

$$\chi_c = \frac{1}{2(1-\varphi_{2,c})^2}, \qquad (13)$$

$$\varphi_{2,c} = \frac{1}{1+x^{1/2}} \Rightarrow x = \Big(\frac{1}{\varphi_{2,c}} - 1\Big)^2. \qquad (14)$$

Knowing the parameters of the CST and the concentration of the polymer in the solution $\varphi_2'$ and $\varphi_2''$ (2 points on the binodal) at a given temperature, one can calculate the values of α, β and $x$. By substituting the obtained values into equation (12), one can estimate the position of the diffusion spinodal (Figure 1). The data on the estimation of the solution binodal obtained by visual observation (the cloud point method) were used in the calculations [11].

## 3. Pulsed heating method

Experimental setup for pulsed heating of a wire probe – resistance thermometer comprises an analog microcircuit based on a PID controller [12]. The device is controlled by a specially developed software through ADC/DAC signal converters. The excess pressure was created and maintained by means of a WIKA CPP1200-X hydraulic press with a maximum allowable pressure of 120 MPa.

The measurements of pressure value were carried out via a WIKA CPG1500 pressure gauge with a measurement limit of 100 MPa and accuracy class of 0.025. A simplified scheme of the experimental setup is shown in Figure 2.

The measuring cell containing the substance under study and the probe has flexible walls for pressure transmission. It is placed in a pressure chamber where excess pressure is created. The digital control signal from the computer is converted into the analog one and fed to the microcircuit contacts. As a result, the wire probe is heated under the given heat release conditions. The feedback system makes it possible to control the heat release parameters with high accuracy throughout the entire pulse. The analog signal-response from the platinum wire probe is converted to the digital one and transmitted back to the computer.

The essence of the method is to maintain the specified conditions of heat release from the probe surface in the course of heating. The diameter of the probe is 22 μm and the length is approximately 1 cm. The primary values acquired in the experiment are as follows: the voltage drop across the probe $U(t)$ and the current $I(t)$ passing through the probe circuit (Figure 3a). The software allows real-time monitoring and recording not only of the mentioned primary data, but also of the power dissipated by the probe $P(t) = U(t) \cdot I(t)$ and its resistance $R(t) = U(t)/I(t)$. The evolution of the average temperature of the probe $T(t)$ is calculated based on the thermometric calibration of platinum (Figure 3b). The heating power $P(t)$ is maintained with an accuracy of 99.95%. The total measurement errors $U(t)$ and $I(t)$ do not exceed 0.2%. The total measurement error of the calculated probe resistance $R(t)$ is 0.4%. The total calculation error $T(t)$ is 1% [13].

## 4. Experimental results

Let us consider the main results obtained in the course of heating of the water/PPG-425 mixture. The mass content of PPG-425 in mixture and the excess pressure value served as parameters of the experiments.
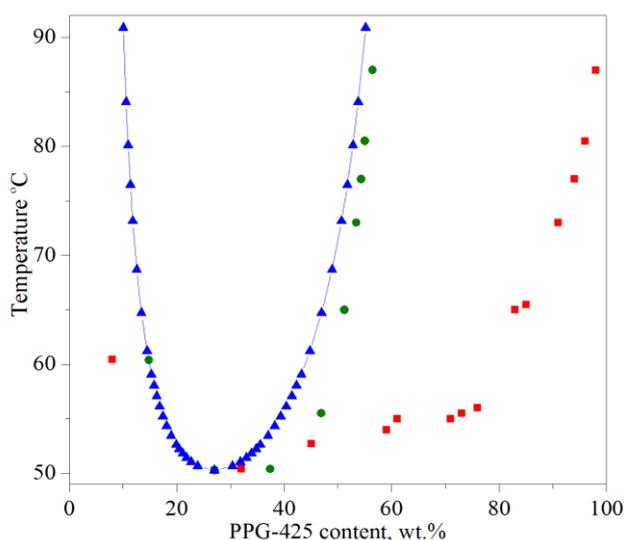


**Figure 1** Phase diagram of water/PPG-425 mixture. The red squares indicate the measured position of the binodal by the cloud point method, the green circles indicate the calculated diffusion spinodal according to the regular solution approximation [11], and the blue triangles indicate the calculation result according to the Flory-Huggins approximation at $\alpha$ = 1.61 and $\beta$ = −33.76.

The initial temperature in the measuring cell was kept constant, at the level $T_0$ = 25 °C. The first results were obtained for the mixture with a PPG content of 10 wt.% (Figure 4a). The heating of the wire probe is accompanied by a perturbation of the temperature curves.

This area is highlighted in Figure 4a. A time differentiation operation was performed for a more detailed analysis of the temperature curves (Figure 4b). In section I, the rate of temperature change slows down significantly, which is probably caused by the release of the latent heat of nucleation during the separation of the metastable mixture.



**Figure 2** Simplified scheme of the experimental setup. Explanations are given in the text.
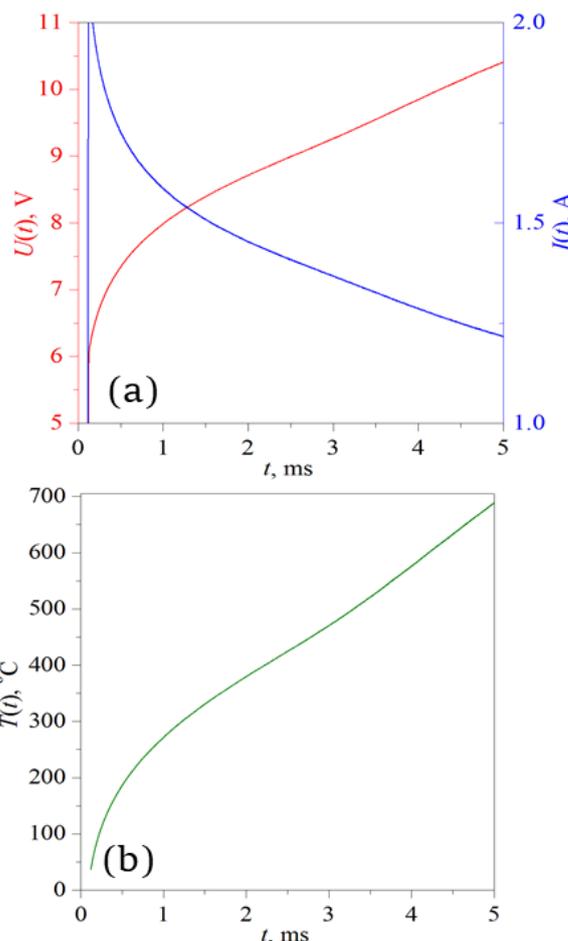


**Figure 3** Primary experimental data: voltage drop across the probe (red line) and current in the probe circuit (blue line) at a constant heating power and a pressure value of 60 MPa (a). The evolution of the probe temperature, immersed in a deionized water at a pressure value of 60 MPa, calculated from primary data (Figure 3a) (b).

Then, the mixture decomposes according to the mechanism presented in the Introduction. The rate of temperature change increases due to the heating of individual clusters adjacent to the heater with compositions close to equilibrium values. Further heating is accompanied either by boiling up of one of the mixture components in the pressure range of 16–20 MPa, or by a supercritical transition in the pressure range of 22–30 MPa. A more detailed picture of heat transfer in the course of non-stationary heating in a wide pressure range is presented in [14]. As it can be seen, the supercritical transition occurs at an excess pressure of 22 MPa and a probe temperature of 370–380 °C. The phase transition parameters (spontaneous boiling-up temperature and supercritical transition parameters) correspond to the heat transfer to water, which is due to the content of the initial substance in the mixture (about 90 wt.%).

Similar results were obtained for the mixtures with a PPG content of 40 and 50 wt.% (Figure 5). Such a heat transfer pattern corresponds to superheating of an initially stable binary mixture relative to the liquid-liquid equilibrium line (Figure 1).

From the heat transfer point of view, more interesting results were obtained for the mixtures with a PPG content of 20 and 30 wt.%. An analysis of the PD lead us to assume that in this case the mixture is transferred to the region of unstable or labile states. Let us consider the results obtained in the course of pulsed heating (Figure 6). In this case, the characteristic heating curves tend to level off. Moreover, the curves shift upwards with increasing pressure, i.e., lower values of the heat transfer intensity begin to correspond to higher pressure values. Taking into account the presence of a limited mixing region on the PD, this phenomenon may be due to the action of spinodal decomposition (SD). The SD phenomenon is the most probable relaxation mechanism in this region of PD and, at the same time, the most powerful one. SD of an unstable mixture is accompanied by the formation of phase boundaries of individual domains, which begin to move towards each other under the influence of nonequilibrium thermocapillary forces [15].

Similar results were also obtained for pressures up to 1 MPa. The study of the SD phenomenon for the water/PPG-425 mixture at relatively low pressure values is complicated by premature spontaneous boiling-up of water.
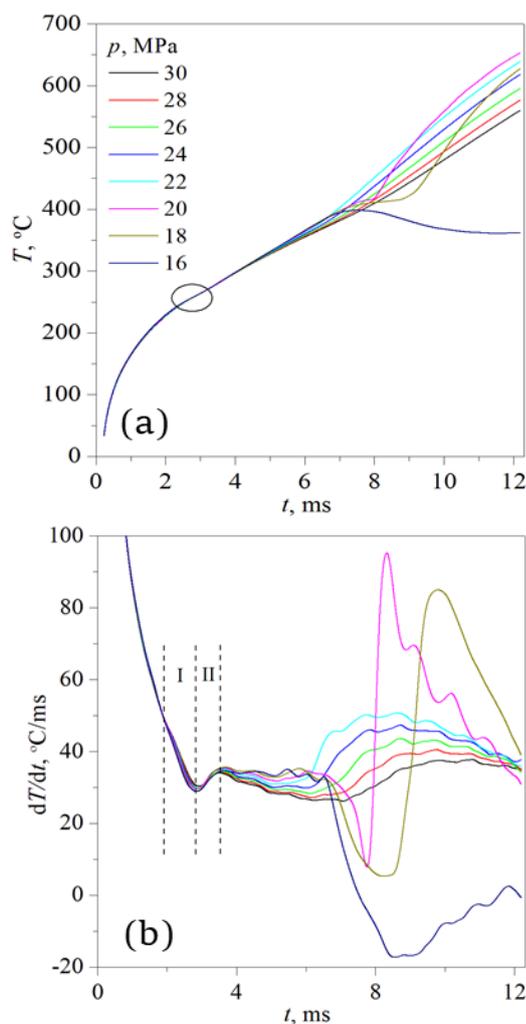


Figure 4 Heating curves for the mixture with a PPG content of 10 wt.% under constant power mode. The circle marks the area in which the course of the temperature curves changes (a). Derivatives of the probe temperature with respect to time for the mixture with a PPG content of 10% wt.% under constant power mode (b).
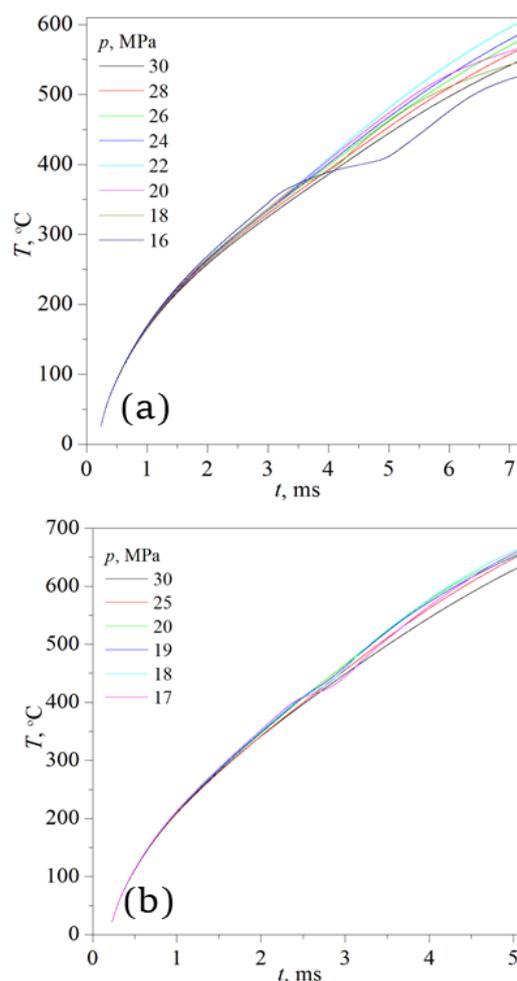


Figure 5 Heating curves for the mixture with a PPG content of 40 wt.% under constant power mode (a). Heating curves for the mixture with a PPG content of 50 wt.% under constant power mode (b).
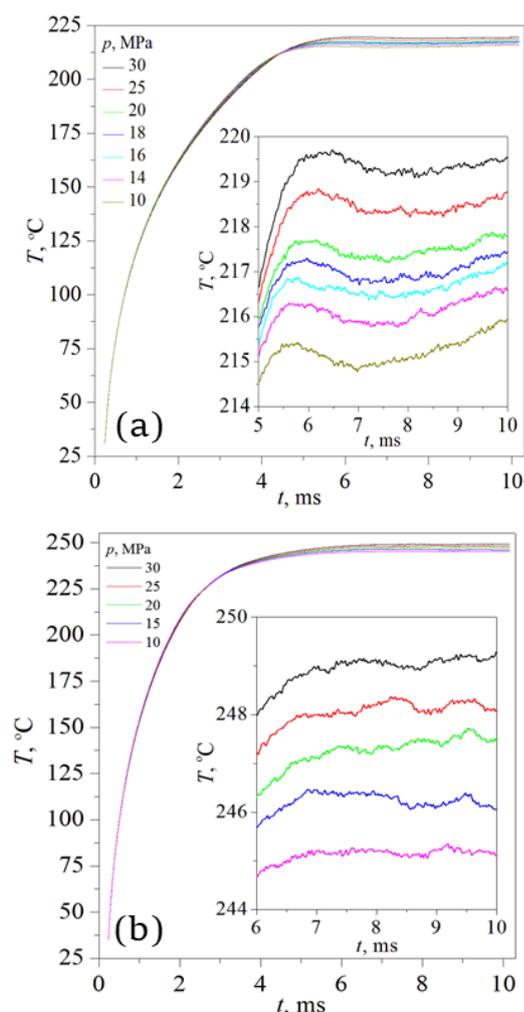
**Figure 6** Heating curves for the mixture with a PPG content of 20 wt.% under constant power mode (a). Heating curves for the mixture with a PPG content of 30 wt.% under constant power mode (b).

Thus, based on the temperature history curves analysis, it is hypothetically possible to predict the position of the diffusion spinodal of the mixture on the scale of the mixture component ratio. The essence of the phenomenon is due to the threshold change in the heat transfer pattern to the mixture under study with a change in the content of components in it. Despite the fact that the position of the diffusion spinodal was calculated at atmospheric pressure, the authors of this paper believe that such a comparison with experimental data is reasonable. Indeed, the effect of external pressure on the key elements of PD for aqueous solutions of polypropylene glycols is insignificant [16].

## 5. Conclusions

The physico-chemical properties of the water/PPG-425 mixture were analyzed. Based on these data, the position of the diffusion spinodal was calculated by means of the regular solution and Flory-Huggins approximations. The heat transfer characteristics of the mixture were studied in a wide range of component contents and pressures via the method of pulsed heating of a wire probe. An analysis of the temperature curves suggests that the proposed method can

be potentially used to estimate the position of the spinodal of two-component mixtures with LCST on the scale of the mixture component ratio. This representation is based on the threshold change in the heat transfer pattern when crossing the phase coexistence curve and the diffusion spinodal.

The elaborate choice of the heating power variation as a function of time and pulse duration creates a practical basis to select the conditions under which the phase separation of the mixture will manifest itself as a temperature-confined signal at a sufficiently small depth of entry into the region of unstable states. The mastering of such a selection technique and its development will serve as the basis to improve the technique for predicting the position of a limited mixing region of components in temperature-concentration coordinates.

## Supplementary materials

No supplementary materials are available.

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## Author contributions

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## Conflict of interest

The authors declare no conflict of interest.

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# References

1. Sengers JL. How Fluids Unmix: Discoveries by the School of Van Der Waals and Kamerlingh Onnes. Royal Netherlands Academy of Arts and Sciences: Amsterdam; 2002. 302 p.

2. Andreyeva VM, Tager AA, Tyukova IS, Golenkova LF. Study of the spinoidal mechanism of phase separation of polystyrene solutions in decalin. Polym Sci USSR. 1977;19(11):3005–3013. doi:10.1016/0032-3950(77)90322-7

3. Tager AA. Thermodynamics of concentrated polymer solutions. Polym Sci USSR. 1971;13(2):531–552. doi:10.1016/0032-3950(71)90020-7

4. Tager AA, Anikeyeva AA, Andreyeva VM, Gumarova TY, Chernoskutova LA. Phase equilibrium and light scattering in polymer solutions. Polymer Sci USSR. 1968;10(7):1926–1940. doi:10.1016/0032-3950(68)90387-0

5. Volosnikov DV, Povolotskiy II. Possibilities of heat pulse probing method for determining the phase diagram of partially-miscible liquid mixtures. J Phys Conf Ser. 2020;1677:012100. doi:10.1088/1742-6596/1677/1/012100

6. Skripov PV, Starostin AA, Volosnikov DV, Zhelezny VP. Comparison of thermophysical properties for oil/refrigerant mixtures by use of pulse heating method. Int J Phys Refrig. 2003;26(8):721–728. doi:10.1016/S0140-7007(02)00163-9

7. Rowlinson JS. The Theory of regular solutions. Proc Royal Soc A Math Phys Eng Sci. 1942;214(1117):192–206. doi:10.1098/rspa.1952.0161

8. Flory PJ. Thermodynamics of high polymer solutions. J Chem Phys. 1942;10(1):51–61. doi:10.1063/1.1723621

9. Huggins ML. Some properties of solutions of long-chain compounds. J Chem Phys. 1942;46(1):151–158. doi:10.1021/j150415a018

10. Igolnikov AA, Rutin SB, Skripov PV. Investigation of binary liquids in unstable states—an experimental approach. Liquids. 2021;1:36–46. doi:10.3390/liquids1010003

11. Volosnikov DV, Povolotskiy II, Igolnikov AA, Vasin MG, Son LD, Skripov PV. Intensification of heat transfer during spinodal decomposition of a superheated aqueous oligomer solution. J Phys Conf Ser. 2021;1787:012032. doi:10.1088/1742-6596/1787/1/012032

12. Rutin SB. An voltage-controlled precision electronic power regulator. Rev Sci Instr. 2021;92:124708. doi:10.1063/5.0071683

13. Rutin SB. An apparatus for studying nonstationary heat exchange in liquid media. Instr Exp Tech. 2021;64:781–784. doi:10.1134/S0020441221050109

14. Rutin SB, Igolnikov AA, Skripov PV. Title High-power heat release in supercritical water: insight into the heat transfer deterioration problem. J Eng Thermophys. 2020;29:67–74. doi:10.1134/s1810232820010063

15. Skripov PV, Igolnikov AA, Rutin SB, Melkikh AV. Heat transfer by unstable solution having the lower critical solution temperature. Int J Heat Mass Transf. 2022;184:122290. doi:10.1016/j.ijheatmasstransfer.2021.122290

16. Taniguchi Y, Suzuki K, Enomoto T. The effect of pressure on the cloud point of aqueous polymer solutions. J Coll Int Sci. 1974;46(3):511–517. doi:10.1016/0021-9797(74)90061-7