Possibilities of heat pulse probing method for determining the phase diagram of partially-miscible liquid mixtures

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Abstract. In the course of this research, the liquid-liquid equilibrium line for binary solutions characterized by the upper critical solution temperature was developed by the traditional method of visual observation and the method of heat pulse probing. The objects of study were solutions of perfluoromethylcyclohexan/hexene-1 and perfluorodimethylcyclohexan/hexene-1. Heat pulse probing mode was found, which allows us to recognize the approaching to the temperature of liquid-liquid phase separation. The possibility of pulse technique with a characteristic time of several milliseconds to determine the phase state and estimate the actual concentration of solutions in opaque vessels was revealed.

1. Introduction
Liquid solutions with a significant deviation of properties from the ideal approximation are important and complex objects for experimental study [1]. In this regard, it was planned to study significantly non-ideal binary solutions like “unsaturated hydrocarbon–fluorinated hydrocarbon”, see subsection “Objects”. It can be expected that this class of solutions is characterized by the presence of an upper critical solution temperature (UCST). The existence of their lower critical solution temperature (LCST) currently has not been detected.

Fluoro-organic liquids (FOL) are unique in the set of their properties. They have high chemical, thermal and radiation resistance, fire-safe and harmless to the human body. Using fluorine as a structural element of organic chemistry highly increases the number of possible combinations of chemical compounds. This circumstance opens up wide possibilities for the synthesis of new substances and, at the same time, makes the task of developing methods for the experimental study of the properties of the FOL in a wide range of state parameters change relevant.

2. The main part
Two articles of the Universities of Lisbon and Braga scholars [2, 3] are known, containing data on liquid–liquid and liquid-vapor equilibrium for the system “unsaturated hydrocarbon–fluorinated hydrocarbon”, obtained in a narrow temperature range. More complete information is available on pure components. In the study of phase equilibria and properties of FOL and their solutions with hydrocarbons, a great influence was exerted by the Ural Thermophysical School under the supervision of Academician V.P. Skripov [4]. The results obtained by the members of the School for properties of FOL (75 compounds) are summarized in the handbook [5]; the results on liquid-liquid phase equilibrium of n-alkan/perfluoroalkane systems can be found in [6, 7].

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2.1. Goals and Objectives of the Study
The study is aimed at the research of the liquid–liquid phase equilibrium of two practically significant solutions of the fluorinated component with unsaturated hydrocarbon by two complementary methods throughout the whole range of concentration.

2.2. Research Subjects
Perfluorinated solution components: perfluoromethylcyclohexane (PFMCH) and perfluorodimethylcyclohexane (PFDMCH), which are transparent, light-boiling liquids. They have high chemical resistance to acids and alkalis; they are incombustible and explosion-proof, do not dissolve in most solvents, and resistant to hydrocarbon, organochlorine, and oxygen-containing (alcohols and ketones) solvents.

Unsaturated hydrocarbon hexene-1 at a temperature of 298 K and pressure of 100 kPa is a colorless liquid that does not dissolve in water but dissolves well in almost every organic solvent (including ethers and alcohols). Hexene-1 is used as a comonomer in the production of polyethylene, aldehydes, etc.

2.3. Methods for determining phase separation
The method of visual observation allows determining the temperature of the phase separation onset of homogeneous solution into two phases of different composition \( T_{ll} \). The process of occurrence and disappearance of the solution opacity during its slow cooling and, accordingly, during its heating was tracked through the transparent walls of the container. The error of \( T_{ll} \) measurement is mainly occurring due to the non-reproducibility of its value in cooling and heating processes and can be taken as 1 K. In the concentration range from 10 to 90 vol % the values of the onset temperature of the phase separation \( T_{ll} \) are obtained and the position of the UCST is estimated, see figure 1. It was found that these values for the PFMCH/hexene-1 solution are higher than the corresponding values for the PFDMCH/hexene-1 solution. The critical solution temperatures are 293 K and 282 K, respectively.

![Graph](image)

**Figure 1.** Data from the method of binodal position visual determination for the hexene-1 solutions in perfluorinated components: 1 – PFMCH; 2 – PFDMCH.

Heat pulse probing method is based on the selection of an indirect sign that is unambiguously related to the sought-for property of the system. Due to its speed and applicability under technological conditions, its varieties have found application in solving extraordinary problems of experimental thermophysics [8-11]. The operations of devices implementing this method are based on recording the response to powerful local heat release in liquid media. The determination of the boundary of single-
phase states of two-component solutions with UCST in this study was carried out in the framework of the relative measurement option. In the case of fluorinated solutions, the complexity of the problem is due to the proximity of the temperature of the onset of solution separation by the liquid–liquid mechanism and the temperature of its attainable superheat in the course of pulse heating [4], see figure 2.

![Diagram showing phase states of two-component solutions with UCST](image)

**Figure 2.** Pulse probing area and phase diagram of the PFMCH/hexene solution: 1 – liquid–liquid binodal; 2 – liquid-vapor binodal. The dashed area is the characteristic range of the probe re-heating temperature $T_L$ in the course of the second stage of its heating.

The prototype of the device was an apparatus for pulse probing of energy oils for quick detection of traces of moisture [10]. The sensitive element is the platinum wire (length of 3 mm, diameter of 20 µm), which is immersed in the investigated substance and heated according to the specified time-power conditions. The heating of the probe and consequently the boundary layer of the substance occurs in two stages. At the first stage, a short pulse of duration $t_1$ heats the probe to a given temperature $T_L$. This is followed by a configurable pause and the resulting decrease in the probe temperature. At the second stage, the probe is re-heated to the temperature $T_L$ with a pulse of lower amplitude. The characteristic heating curves of the probe are shown in figure 3. Apparently, the higher the re-heating time $t_L$ value for a given conditions of heat release, the higher the corresponding value of the heat flux density through the probe surface. An analysis of the responses revealed that $t_L$ values in the course of decreasing initial temperature of the solution $T_0$ show a local maximum. It turned out that the position of this maximum on the temperature axis $T_0$ corresponds to the vicinity of the liquid-liquid phase separation. It is natural to associate the nonmonotonicity of the $t_L(T_0)$ curve with violation of the homogeneity of the system. Indeed, nearly any violation of the homogeneity of the system, according to experimental experience (see Refs. [12–14] and bibliography therein), serves as an additional barrier to heat conduction and consequent decrease in its intensity relative to formal extrapolation along the $T_0$ axis, see points 4 and 5 in figure 3-b. The convective stage of phase separation, which occurs, sooner or later, is accompanied by an increase in heat transfer, see point $5^*$ in figure 3-b and does not require any further explanation.
Figure 3. Characteristic probe heating curves, plot (a): 1, 2 and 3 – temperature curves in a homogeneous sample at the initial temperatures of the sample $T_{01}$, $T_{02}$, $T_{03}$, correspondingly; 4 and 5 – temperature curve in a phase-separating sample at the temperatures $T_{04}$, $T_{05}$, correspondingly. The initial temperature $T_0$ is taken as a parameter. The cross-hatching areas show the character of the current in the probe circuit (right axis) at two stages of heating. Plot (b): duration of the probe re-heating to the selected value $T_{L}(t)$ against the initial temperature. The points 1–3 correspond to homogeneous solution; the points 4 and 5 correspond to phase separating mixture.

For serial measurements, the original methodology and related software were developed, see figure 4. The software is used to control the device microcontroller, record primary signals digitally, and determine probe temperature change; its purpose is also to process and store data related to the details of the experiment. The graphical interface can be used to calibrate the necessary settings, make adjustments, and changes in the heating modes of the probe to optimally select the parameters for determining the temperature of the phase separation.

Figure 4. Software GUI: 1 – the window for setting, adjusting and modifying probe heating modes, data storage management; 2 – the window for visualizing probe temperature changes and comparison to previous measurements; 3 – field for monitoring the duration of re-heating the probe from the initial temperature to the selected value $T_L(t)$. 
2.4. Results and Discussion

The fragment of the primary data array in a series of pulse experiments is presented in figures 5 and 6. In particular, the behavior of the key parameter \( t_L \), which is the duration of the probe re-heating pulse to the selected value \( T_L(t) \) is shown. The argument on the graphs was the value of the initial temperature of the sample \( T_0 \). The vertical solid line in figures 5 and 6 corresponds to the value of the liquid–liquid equilibrium temperature of the solution. The region of homogeneous states and the region of phase-separating solution can be observed to the right and the left side of this line, respectively. The data were obtained when approaching the equilibrium temperature values from the region of homogeneous states. The maximum of \( t_L(T_0) \) values (indicated by an asterisk) on experimental \( t_L(T_0) \) dependence is clearly defined. The data obtained, taking into account the data of preliminary experiments on samples with a known concentration, make it possible to track the approach to the liquid-liquid equilibrium line and determine the actual solution concentration.

Figure 5. The dependence of the probe heating time \( t_L(T_L = 388 \text{ K}) \) on the initial temperature \( T_0 \) in the PFMCH solution at hexene-1 content, vol %: 1 – 30; 2 – 50; 3 – 70. The solid lines correspond to the temperature values on the binodal. \( \Delta T \) is the length of the temperature area with characteristic signs of approaching the binodal.

Figure 6. The dependence of the probe heating time \( t_L(T_0) \) up to the selected value \( T_L(t) = 386 \text{ K} \) on the initial temperature \( T_0 \) in the hexene-1/PFDMCH solution. The other symbols are as in Figure 5.

Figure 7 shows the liquid-liquid phase equilibrium lines of hexene-1/PFMCH solutions in the concentration range from 10 to 90 vol % and hexene-1/PFDMCH in the concentration range from 20 to 80 vol %, obtained by two methods. It can be seen that the data are consistent. In the case of a solution of hexene-1/PFMCH, the pulse method allows us to “feel” the approximation of the liquid–liquid phase separation temperature from 1 K to 5 K in advance, depending on the concentration. This feature is practically important for solving problems of remote monitoring the homogeneity of a solution of variable composition in opaque vessels of chemical reactors.

Conclusions

The liquid–liquid binodal of practically important solutions of hexene-1 in perfluoromethylcyclohexane and perfluorodimethylcyclohexane was determined by visual observation method and the position of UCST was estimated.
Figure 7. Phase diagrams of hexene-1/PFDmCH (1) and hexene-1/PFMCH (2) solutions. Red lines correspond to the pulse method; black lines correspond to the visual method.

Based on a highly sensitive device, an original express technique and software for determining the liquid–liquid binodal of these solutions by an indirect sign were developed. Satisfactory agreement between the measurement results by two methods is shown. The pulse method can be used to automate the control of such type solutions phase separation in technological processes, accompanied by a change in both the temperature in the reactor and the concentration of the reactive component.

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