The effect of water traces on heat transfer in liquid hydrocarbons under pulse heating mode

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Abstract. The peculiarities of heat transfer and spontaneous boiling-up of pure hydrocarbons (n-hexane, n-decane, and n-hexadecane) and those with water traces have been studied under the pulse heating mode. The pulse lengths were from 5 to 25 ms; the pressure was elevated up to the critical one. The phenomenon of strong sensitivity of heat transfer intensity to the presence of water traces has been revealed in the vicinity of spontaneous boiling-up temperature. The hypothesis on the initiating action of water traces on macroscopic phase transitions is assumed.

1. Introduction
In view of the general trend towards an increase in the intensity of technological processes and the miniaturization of heat exchangers, the task of finding new classes of heat transfer agents that are applicable under conditions of high-power heat release is relevant [1–3]. The use of solutions separating into two liquid phases with increasing temperature, the so-called systems with a lower critical solution temperature (LCST) is considered as one of the options for increasing the heat exchange intensity [4].

Our study is carried out within the framework of the general formulation of the problem of heat transfer under high-power heating of liquids [5, 6]. This work is devoted to clarifying the features of the response of a system to the pulse heating, which accompany the introduction of small additives (at the level of the traces) that are partially compatible with the base fluid. We are talking about consistently reproducible effects confined with respect to temperature and time, which are observed when moisture is added in saturated hydrocarbons at the level of 30-40 ppm (0.003–0.004%). In particular, we found an unexpectedly large (about 10%) increase in the heat transfer coefficient from a pulse-heated wire probe to a watered sample relative to the initial “dry” sample [7]. The effect manifested itself when approaching the temperature of attainable superheat of the liquid \( T^* \) or, in other words, to the temperature of its spontaneous boiling-up at a given pressure and heating rate. The pressure in the experiments was atmospheric. The probe (being simultaneously a resistance thermometer) was heated from room temperature \( T_0 \) to the selected value of \( T_1 \leq T^* \) for a time of about 0.1 ms and was kept heated in the vicinity of the \( T_1 \) value for about 10 ms. To correctly estimate the relative heat transfer coefficient, the measurements were performed with similar heating regimes.

The purpose of this study was to find an explanation for this effect through additional experiments. As a first step, in this work, experiments were performed at elevated pressures, up to a critical value. It is known that pressure can significantly affect the kinetics of processes...
of separation into two liquid phases and spontaneous boiling-up, which are the most natural relaxation processes with increasing temperature in the initial solutions.

2. Experimental

We used the method of heating the wire probe with two pulses, see figure 1. Current pulses of high (first pulse) and low (second pulse) amplitude are successively applied to the probe. The first short pulse heats the probe to the selected temperature $T_1$. The second longer pulse holds the probe in this temperature region until the next time of reaching the $T_1$ value. In the course of second pulse, the dependence of the probe temperature on time is determined by heat transfer across the probe surface. The method allows one to estimate small changes in the heat transfer coefficient from the probe surface by the relative changes in the temperature curve recorded during the second pulse. For this purpose, we developed a technique for digital fitting of the current of the second pulse to compensate for changes in heat transfer from the surface of the probe due to the addition of moisture. As a result, we managed to conduct a comparison of samples with different moisture content in similar temperature-time heating conditions.

![Figure 1.](image)

**Figure 1.** The double pulse technique: sequence of current pulses (above) and the probe temperature evolution (below) in the course of heat exchange in single-phase liquid (left) and in the course of spontaneous boiling-up in the range of temperature $T_1^*$. The timing $t_0$, $t_1$, $t_2$, $t_{\text{max}}$ mark the onset ($t_0$) and the end of current pulses with amplitude $I_1(t_1)$ and $I_2(t_2, t_{\text{max}})$ [7].

2.1. Materials

Samples of saturated hydrocarbons were used in the experiments. Samples of hexane, decane, and hexadecane were preliminarily purified with silica gel. Then, the purified volume of each sample was divided into two parts, one of which was further saturated with moisture at room temperature from the vapor phase. As a result, samples were obtained with different moisture content from 5 to 40 ppm. Moisture content was determined by the Karl Fischer method.

2.2. Experimental procedure

Samples of liquid hydrocarbons were placed in a pressure chamber in a thin-walled PTFE container. The transfer of pressure from the working fluid to the sample through such a
container is performed with an accuracy of about 1 kPa. The wire probe was located in the sample container. Electrical connections were made through sealed insulated contacts on the pressure chamber flange. The pressure was supplied by a piston with a screw drive. At each pressure value, at least ten experiments were conducted, the results were averaged. The initial temperature of the sample was measured by a sensor located directly in the container. The probe heating and response signal registration were performed at the automated apparatus described earlier [7]. Each measurement contained up to 100 heating cycles with a sequential increase in the set value of the probe temperature $T_1$. For each cycle, the evolution of the probe temperature was recorded in the second pulse region. By adjusting the current of the second pulse, it is possible to reproduce almost exactly the temperature-time dependence of the heating for watered and “dry” samples of the chosen hydrocarbon. To determine the relative heat transfer coefficient, the voltage drop on the probe and the current in the probe circuit were recorded. Then, the time dependence of the heat release power in the probe was determined. Assuming the end losses to be negligible, this dependence was related to heat transfer from the probe to the liquid. It turned out that the relative heat transfer coefficient (of the watered sample relative to the “dry” one) in such temperature-time heating conditions remains almost unchanged during the second pulse and its average value can be used to evaluate the heat transfer in a liquid under given conditions. As a result, we obtain the dependence of the relative heat transfer coefficient from the surface of the probe to the samples under study, depending on a number of the set $T_1$ values.

Figure 2. Second pulse: experimental probe temperature histories for $n$-hexadecane. The value of $T_1$ (dashed lines) serves as a parameter. Solid lines indicate the “dry” sample, dotted lines – watered sample.

3. Results and discussion

3.1. Results at atmospheric pressure

Figure 2 shows the curves of the probe heating in hexadecane at atmospheric pressure and different temperatures 1. As can be seen in figure 2a, the heating curves for watered (40 ppm)
Figure 3. The values of heat transfer coefficient for the watered sample reduced to that of “dry” sample for three saturated hydrocarbons against $T_1$ values.

and dry (5 ppm) samples are almost the same. Increasing the temperature $T_1$ to 270°C and higher leads to significant differences between them (figures 2b, 2c, 2d).

Accordingly, the relative heat transfer coefficient for hexadecane (figure 3) has the value about unit up to $T_1 \approx 250°C$. At higher temperatures $T_1$ it increases so that the maximum increment value before boiling-up reaches 10% for samples with a moisture content of only 0.004%. Similar dependences were obtained for all three samples, mentioned above. A characteristic feature of the dependences obtained is an increase in heat transfer as the probe temperature approaches the values of the boiling-up temperature. The boiling-up, according to generally accepted provisions, is preceded by the formation of a bubble of critical diameter. The number of molecules in a critical bubble calculated within the framework of the homogeneous nucleation theory\(^1\) increases by an order of magnitude when the pressure increases from atmospheric to $p/p_c \approx 0.5$ [11], where the index “c” refers to the thermodynamic critical point. This circumstance stimulated experiments with changes in external pressure.

3.2. Results at elevated pressure

The application of the described procedure for studying samples subjected to pressure showed a decrease and subsequent disappearance of the effect under discussion with increasing in external pressure. Figure 4 shows curves for the probe temperature changes in the region of the second pulse for the “dry” and “watered” samples of hexadecane ($p_c \approx 1.4$ MPa), which are similar to those shown in figure 2. An increase in pressure up to 0.7 MPa practically eliminated the difference between samples in the heat transfer intensity values. Figure 5 shows the corresponding change in the relative heat transfer coefficient for hexadecane over a wide range in temperature $T_1$. The parameter is the pressure that rises until the difference between

\(^1\) In our experiments, boiling-up takes place apparently according to a heterogeneous mechanism [8–10], but this circumstance does not change the qualitative side of the proposed approach
Figure 4. The comparison of probe temperature histories for “dry” sample (solid line) and watered sample (dotted line) of \( \text{n}-\text{hexadecane} \) at pressure of 0.7 MPa.

Figure 5. The values of heat transfer coefficient for the watered sample reduced to that of “dry” sample for \( \text{n}-\text{hexadecane} \) against \( T_1 \) values. The pressure serves as a parameter.

samples disappears. Similar dependencies were obtained for hexane and decane. The suppression of the discussed effect occurred at reduced pressure from 0.3 to 0.5.
4. Conclusion
Experiments on pulse heating of saturated hydrocarbons, both pure and with additions of trace amounts of moisture, gave an unexpected result. It has been found that in a certain temperature range near the temperature of attainable superheat $T^*$ of the liquid, the additives significantly intensify the heat exchange between the probe and the substance. They also reduce the temperature $T^*$, and the scale of such a decrease significantly exceeds the corresponding scale observed even for gas-saturated polymer melts [12,13]. The sharp dependence of the effect scale on the reduced pressure suggests that the effect is due to the action of additives that are incompatible with the primary liquid in this temperature range. The introduction of water vapor into the hydrocarbon liquid leads to the formation of clusters consisting of several water molecules [14], which may develop in the course of approaching the boiling-up temperature and thus may facilitate a macroscopic phase transition. This hypothesis will be tested in future experiments.

Acknowledgments
The study was supported by the Russian Foundation for Basic Research, grant No. 16-08-00381.

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