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DEFINITION OF PARAMETERS PHASE EQUILIBRIA AND IDENTIFICATION OF PHASES OF SYSTEM HYDROCARBON
Water on the basis of calorimetric measurements

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A new calorimetric method and the results of determination of binary systems phase equilibria having a region of phase stratification on the basis of calorimetric measurements are described in this paper. Isochoric heat capacity temperature dependence of binary system of hydrocarbon–water has been studied by the method of high-temperature adiabatic calorimeter. Parameters of the phase stratification region have been determined on the basis of revealed peculiarities of this dependence at phase transitions liquid–liquid and liquid–vapour and phase diagram have been made.

Keywords: *alkane, binary mixtures, calorimetric measurements, isochoric heat capacity, phase equilibria, water*

Introduction

Study of thermophysical properties and phase diagrams of water–hydrocarbon systems is important for investigation of influence of the polar component impurity on the change of the properties and phase diagrams of the hydrocarbon compounds.

These investigations are also actual for practical application of the results when solving the problems connected with refining and producting petroleum.

PVT properties and phase equilibria of aqueous mixtures *n*-alkanes were measured by De Loos, Brunner, Tian *et al.* [1–3]. Information concerning the calorimetrical study of such systems is absent. At the same time data about the heat capacity have big information on thermophysical properties, and on configuration of phase surface and phase diagrams.

The phase equilibrium of hydrocarbon–water systems has been studied on alkane (*n*-heptane)–water system on the basis of research of isochoric heat capacity at several fixed compositions.

The isochoric heat capacity of *n*-heptane–water system [xH$_2$O+(1–x)C$_7$H$_{16}$] has been experimentally researched with Amirkhanov's high-temperature adiabatic calorimeter. The construction of the calorimeter is shown in Fig. 1.

The experimental method and apparatus is described in the monograph [4] in detail. This monograph is devoted to thermophysical properties of homologous series of *n*-alkanes, and *n*-heptane is one of the researched components of the system.

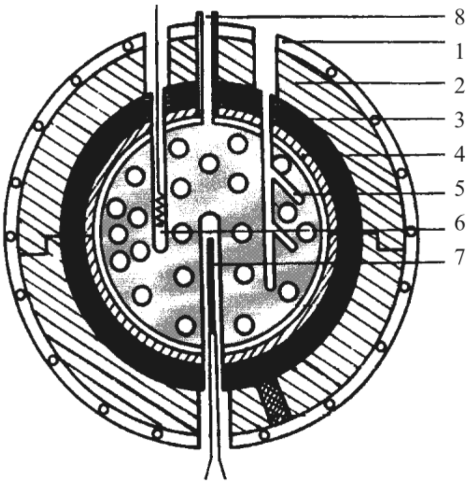

Fig. 1 Construction of calorimeter. 1 – thermal shield, 2 – outer vessel, 3 – semiconductor layer, 4 – inner vessel, 5 – platinum resistance thermometer, 6 – thermocouples, 7 – inner heater, 8 – filling capillary

This method is attested by State Standardization Service of Reference Data.

The schematic diagram of the apparatus is shown in Fig. 2.

The experimental device is automated on the basis of high-precision temperature regulators.

The isochoric heat capacity of *n*-heptane–water system has been researched by means of the calorimeter. It is made of stainless steel. The volume of

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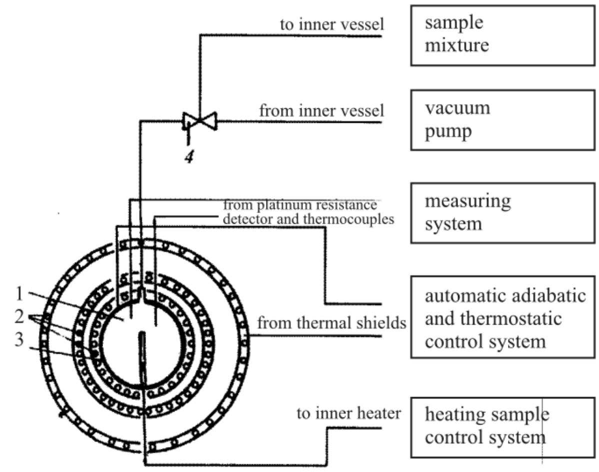

Fig. 2 Schematic diagram of the apparatus. 1 – sample mixture, 2 – thermal shields, 3 – calorimeter vessel, 4 – needle valve

calorimeter is V_0=423.57±0.05 cm^3 at temperature T_0=296.15 K and atmospheric pressure.

The calorimeter's volume V_0 is determined by filling it with air-free twice-distilled water according to the method described in [4]. Data from [5] have been used to calculate the calorimeter volume.

Amendments to the value of the initial volume V_0 were made during the experiment. These amendments are correlated with the change of volume at temperature $\Delta V_{\mathrm{T-T_0}}$ and pressure $\Delta V_{\mathrm{P-P_0}}$ extension. They have been determined by means of calculate and experimental method [4]. So the calorimeter volume is determined from correlation: $V_{\mathrm{T,P}}=V_0+\Delta V_{\mathrm{T-T_0}}+\Delta V_{\mathrm{P-P_0}}$. Error may come to 0.05–0.09%.

The sample [xH$_2$O+(1–x)C$_7$H$_{16}$] of certain composition x and mass m, corresponding to the studied isochore, was prepared in a special calibrated vessel by weighing of components: n-heptane of 'reference' without additional purification and water bidistillate. Weighing error is within $5\cdot10^{-5}$–$5\cdot10^{-3}$ g.

The calorimeter and the filling system was preliminarily vacuumized. The filling capillar was connected with a vessel containing the sample of mixture by means of special needle valve for transportation the sample mixture into the calorimeter. The density ρ is defined from correlation $\rho=m/V_{\mathrm{T,P}}$. Maximum uncertainty in ρ is 0.1%.

The temperature was measured with the use of specially made and graduated platinum resistance thermometer mounted into the tube inside the calorimeter. Uncertainty of the temperature determination is ±0.1 K.

The system [xH$_2$O+(1–x)C$_7$H$_{16}$] with x=0.147 mole fracture of water has been studied along the 10 isochores in the density range 146.0–501.5 kg m^{-3} and the temperature range from 373 to 540 K.

The immiscibility of hydrocarbons in water results in the three-phase stratification region in the mixture of these components. The mixture [xH$_2$O+(1–x)C$_7$H$_{16}$] is a three-phase system liquid–liquid–vapour at room temperature and atmospheric pressure.

The investigation of temperature dependence of the heat capacity along the isochors was started from the region of three-phase state toward the increase of the temperature.

As it is known, in the thermodynamic process at the transition across the line of coexistence, the isochoric heat capacity roughly changes. Consequently the behaviour of function $C_{\mathrm{v}}=f(T)$ when crossing the phase equilibrium curves is a good way for determination of the phase transition temperature.

The continuous method of measurement along the isochore and automatic records of thermograms and adiabatic control of the calorimetric system make possible to approach to the phase equilibrium curve up to the temperature step ($\Delta T\approx0.02$ K).

Two-phase transitions liquid–vapour and liquid–liquid as it was shown earlier are observed in the isochors of n-heptane-water system [6, 7]. The phase transitions are fixed by the corresponding jumps of heat capacity (Fig. 3). The results of the experiment show that the change in the function $C_{\mathrm{v}}=f(T)$ at phase transitions liquid–liquid, liquid–vapour are different. The phase transition liquid–vapour is accompanied by a sharp jump of heat capacity C_{v}, likewise the individual components (n-heptane and water) [4, 8]. The experiment shows, that the character of the phase transition liquid–liquid is different. It occurs at the temperature range ΔT, which achieves some degrees in some isochores. Because of this fact heat capacity jump is extended and the temperature of the beginning $\mathrm{T_{1LL}}$ and the end $\mathrm{T_{2LL}}$ of transition is fixed.

The temperature increase in the three-phase state first leads to the liquid–liquid phase transition and then to the liquid–vapour transition. It is observed in the isochors of the mixture with x=0.147 mole fracture of water in the density range $146.3\leq\rho\leq468.1$ kg m^{-3} (Fig. 3). At the increase of density, the liquid–vapour transition first takes place in isochors $469.0\leq\rho\leq501.6$ kg m^{-3} and then the liquid–liquid transition. Phase transitions temperatures are fixed by the heat capacity maxima in the isochors.

The phase diagram density–temperature and lines of phase equilibrium liquid–vapour and liquid–liquid are shown in Fig. 4.

The line ρ=*f*(*T*) of the phase equilibrium liquid–liquid of *n*-heptane–water system breaks up in two branches. One of which corresponds to the temperatures of the phase transition of the beginning and another branch relates to its end. The bifurcation of the line of the phase equilibrium liquid–liquid corresponds to the phase transition feature noted above. The experimental results show, that the region of the three-phase stratification liquid–liquid–vapour (L_1L_2V) of *n*-heptane–water system with 0.147 mol fracture of water for the density range 146.0–501.6 kg m^{-3} exists in the temperature range from 433 to 485 K.

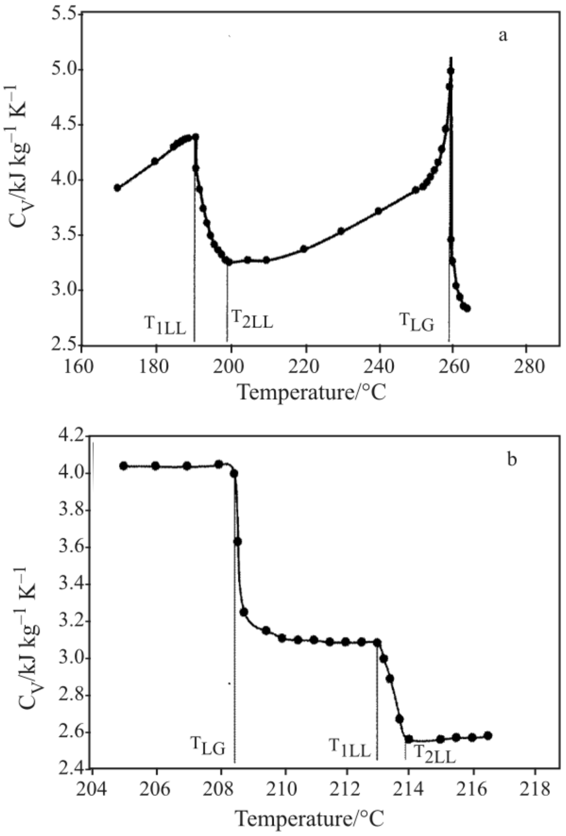

Fig. 3 The isochors of mixture [$xH_2O+(1-x)C_7H_{16}$] x=0.147 m.f. a – ρ=276.5, b – ρ=469.6 kg m^{-3}

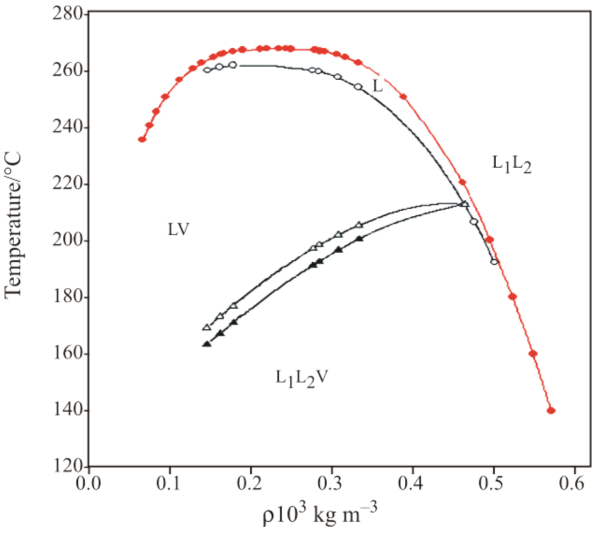

Fig. 4 Coexistence curve of mixture [$xH_2O+(1-x)C_7H_{16}$] x=0.147 m.f.: ○ – liquid–vapour, ▲ – liquid–liquid (T_{1LL}), △ – liquid–liquid (T_{2LL}), ● – liquid–vapour coexistence curve of *n*-heptane

The region of the two-phase state liquid–vapour (LV) is limited by the maximum of curve of the phase equilibria liquid–vapour. This curve is displaced to about 7 degrees below the maximum of the liquid-vapour curve of *n*-heptane. It allows to make a conclusion that water in *n*-alkane decreases temperature of the phase transition.

Acknowledgements

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