Isochoric heat capacity and PVT properties of n-heptane – water binary azeotropic system

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Abstract. The isochoric heat capacity and the pressure of n-heptane – water binary layering system were measured using the high-temperature adiabatic calorimeter-piezometer method. Characteristic properties of a change in the temperature dependences of the heat capacity and the pressure along the isochores were revealed in a region of phase transitions. These features allow for fixing the azeotropy state in the system and for estimation of the influence a polar component (water) on a change in the azeptrope state temperature.

The study of n-heptane – water system is interesting from the perspective of the further development in the theory of solutions for complex systems composed of substances of various molecular natures as well as the determination of an influence of polar component impurities on a change in phase diagrams for hydrocarbon compounds. The studies are urgent in terms of practical application of results. The main components of gas-condensate systems, hydrocarbons, contact with water during oil production, transportation, and processing. The precise data on a behavior of the water-hydrocarbon phase are required when solving challenges of enhancing oil recovery, technologies for deep processing of raw hydrocarbon, at design and operation of natural gas processing facilities, raw oil processing plants and gas condensate.

The literature and reference data review has shown that there is very few information on azeotrope compositions for n-heptane – water system. The most of reported data on the azeotrope composition and azeotrope boil temperature have been obtained at the atmospheric pressure [1–3]. There are almost no experimental data for the dependence of the azeotrope composition on a pressure. Hence, this work is aimed to experimentally determine azeotrope parameters \( (X_{az}, T_{az}, P_{az}, \rho_{az}) \) and the influence of a polar component on values of these parameters.

The dependence of the heat capacity and pressure on temperature were determined on an experimental apparatus for studying the isochore heat capacity and PVT properties using the high-temperature adiabatic calorimeter-piezometer method. The experimental facility is completely automated by means of LakeShore temperature controller, Kethly digital multimeters, Kurant DI-V digital pressure sensor, and a personal computer. A detailed description of experimental technique was reported in works [4, 5]. In this research, a spherical calorimeter with a volume \( V_0 = 423.89 \text{ cm}^3 \) was used as the measurement cell. The calorimeter was made of 1Cr18Ni9Ti stainless steel. The internal volume of the calorimeter was determined by the water calibration. The temperature was measured with the use of specially made and graduated platinum resistance thermometer mounted into the tube inside the calorimeter. The
uncertainty of temperature measurements was less than 15 mK. The systems studied were prepared from bidistilled water and reference n-heptane by weighing the components on the Vibra AB (R)CE analytical balance within an accuracy of not more than 0.005–0.025 per cent. The prepared mixture was placed into the measurement cell using the high-vacuum system. An error in the detection of the density did not exceed 0.1 per cent. An analysis established [6] that the research technique and apparatus used have provided the tools for measuring the heat capacity \( C_v \) with an error of 1–3 per cents depending on a region of research, with account of reference uncertainties, corrections to non isochoric behavior, and others. The pressure was measured using the Kurant DI-V pressure unit. Kurant DI-V is the digital, high-temperature (up to 623 K), small strain gauge pressure transducer. The range of a measured pressure was 0–20 MPa with an error of 0.15 per cent.

The components of n-heptane-water system are mutually insoluble under normal conditions. The mixture is the heterogeneous three-phase system liquid-liquid-vapor with internal interfaces. Consequently, the system has a layering area, as it has appeared, in a quite wide temperature range.

According to the Van-Konynenburg classification of binary system fluid phase diagrams, the n-alkane-water phase diagrams belong to III type. This type is characterized by the absence of continuous critical point line connecting the critical points of pure components and the presence of two critical lines. One critical line starts at the critical point of a more volatile component (in this case – hydrocarbon) and ends at the upper end critical point of the mixture. The second critical line begins at the critical point of less volatile component (water) and continues to high pressures region [7]. For n-heptane-water system, the pressure on the three-phase equilibrium

![Figure 1](image-url)

**Figure 1.** Temperature dependence of the heat capacity of the \([1-x]C_7H_{16}+xH_2O\) system, \(x=0.295\) m.f., along the different isochors: (a) \( \rho = 214.2\) kg/m\(^3\), (b) \( \rho = 370.0\) kg/m\(^3\).
line is higher than the saturation pressure of both components. This indicates that the system has the heteroaazeotropy [8].

The temperature dependences of the isochoric heat capacity and the pressure of the system \((1-x)\text{C}_7\text{H}_{16} + x\text{H}_2\text{O}\) with content of polar component (water) \(x\), \(0 \leq x \leq 0.420\) mole fractions, in heptane were studied along the isochores for several constant compositions. The measurements were performed in the range of densities of 166.07 kg/m\(^3\) – 415 kg/m\(^3\) and temperatures of 400 K – 553 K.

The restricted mutual solubility of the components leads to that under normal conditions, the mixture is the binary layering system consisting of three phases: liquid 1 – L1 (n-heptane), liquid 2 – L2 (water), vapor – V. The measurements of the heat capacity and pressure along isochores were started from a region of three-phase state liquid-liquid-vapor L1L2V to the temperature increasing.

There are found some characteristics in the behavior of the heat capacity and pressure dependences on temperature for the hydrocarbon-water system. As it was previously reported [9, 10], phase transitions liquid-gas (lg) and liquid-liquid (ll) occur along the isochores with increase in the temperature in the n-heptane-water system figure 1.

The transitions are recorded by discontinuous variation of heat capacity values: a sharp jump at the liquid-gas \((T_{lg})\) phase transition and a vague jump in some temperature interval \(\Delta\) at liquid-liquid \((T_{ll})\) transition.

The phase transitions on pressure isochores are fixed by a change of slope along the function \(P = f(T)\): a sharp break at the liquid-gas phase transition and a smooth bend at the liquid-liquid transition figure 2.

The sequence of phase transitions and a value the temperature interval between \(|T_{lg} - T_{ll}|\) are different and depend on the density value of isochore studied.

For all considered compositions of the n-heptane-water system the isochore \((\rho = \rho_{az})\) is found, at approximation to which both from isochores \(\rho \leq \rho_{az}\) and from isochores \(\rho \geq \rho_{az}\) the value of the temperature interval between phase transitions \(|T_{lg} - T_{ll}|\) → 0. The isochore \((\rho = \rho_{az})\) reveals one jump of the heat capacity figure 3, and one break on the temperature dependence of pressure figure 4.

![Figure 2](image-url)  

Figure 2. The isochors of pressure \([(1-x)\text{C}_7\text{H}_{16} + x\text{H}_2\text{O}]\ x=0.147\) m.f., \(\rho=225.1\) kg/m\(^3\).
Figure 3. Temperature dependence of the heat capacity of the \([(1-x)C_7H_{16}+xH_2O]\) system, \(x=0.295\) m.f., \(\rho=361.1\) kg/m\(^3\).

Figure 4. The isochors of pressure \([(1-x)C_7H_{16}+xH_2O]\) \(x=0.147\) m.f., \(\rho=464.2\) kg/m\(^3\).

Figure 5. Coexistence curve of mixture \([(1-x)C_7H_{16}+xH_2O]\), \(x=0.295\) m.f.: 2 – liquid-vapour (Tlg), 3 – liquid-liquid (Tll1), 4 – liquid-liquid (Tll2), 1 – liquid-vapour coexistence curve of n-heptane.

Figure 6. Dependence of temperature \((T_{az})\) and pressure \((P_{az})\) of the azeotrope on the composition \((X)\) for the mixture \([(1-x)C_7H_{16}+xH_2O]\).

It means that a transition from the three-phase state liquid-liquid-gas into the homogeneous state liquid-gas takes place. A behavior of the heat capacity temperature dependence along this isochore is becoming similar to the behavior of the heat capacity temperature dependence of previously studied pure components of n-heptane-water mixture [6, 11]. We think that it corresponds to the azeotrope state. The azeotrope state is characterized by the equality in liquid and vapor phase compositions that explains the presence of one phase transition, which exhibits a behavior similar to the isochoric heat capacity temperature dependence of an individual substance.

The lines of phase equilibria \(\rho = f(T)\) liquid-liquid and liquid-gas for mixture studied are plotted in the heat capacity maxima temperatures on isochores and temperatures corresponded to breaks and bends on the \(P = f(T)\) dependence figure 5. As is evident from the figure, the lines of the phase equilibrium, for the considered mixture of constant composition \(x=\text{const},\)
Table 1. The values of the temperature, pressure, density and composition on the azeotrope line for the n-heptane-water mixture.

| x, m.f. | T, K | P, MPa | ρ, kg/m³ |
|--------|------|--------|----------|
| 0.147  | 485.65 | 3.32 | 464.2 |
| 0.295  | 515.50 | 5.81 | 361.0 |
| 0.355  | 518.85 | 6.16 | 299.8 |
| 0.382  | 519.17 | 6.16 | 269.8 |
| 0.420  | 520.35 | 6.18 | 222.4 |

intersect at one point (ρ = ρaz).

The character of the heat capacity and pressure dependence on temperature described above allow the determination the parameters of azeotrope formation: (Taz) temperature, (Paz) pressure and (ρaz) density for the constant composition mixture.

When increasing the content of the polar component X in the mixture within the measured interval of compositions the temperature Taz and the pressure Paz rise figure 6 and move to lesser values of the density table 1.

So, in this study we offer new approach for the estimation of the azeotrope state in binary systems with the stratifying area using the results of Cv, x, T, P, ρ measurements. It is shown that the experimental technique of the high-temperature adiabatic calorimeter-piezometer provides a possibility to define the presence of the azeotropy in the system, evaluate the Taz, Paz, ρaz parameters of its formation, and establish the displacement dynamics of the azeotrope state with a change in the mixture temperature.

Acknowledgments
The work is supported by grants from Russian foundation of Basic Researches (17-08-00800)

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