

EXPERIMENTAL STUDY OF THERMOPHYSICAL PROPERTIES OF LIQUIDS AND LIQUID MIXTURES

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Abstract. The apparatus for original experimental investigation of the complex thermophysical properties (isochoric heat capacity and pressure-volume – temperature PVT dependence) of liquids and their mixtures in critical and supercritical states is reported. The basis of the method is a high – temperature adiabatic calorimeter- piezometer .

INTRODUCTION

Investigation of characteristic behaviour of different thermophysical properties (heat capacity, density, PVT-dependencies) at parameters, corresponding to these states of substance is one of effective methodics to study critical and supercritical states of liquid and liquid mixtures.

Generally, thermal properties (PVT- dependencies) and caloric ones (heat capacity) are studied by different authors on different experimental devices. It is stipulated by the features those requirements that are laid to the techniques of calorimetric and piezometric measurements. Now, there is known numerous experimental methodic applying to determine the heat capacity of liquids [1, 2] and to measure the PVT- dependencies [3, 4] . To derive the equations of states authors use these various data of features, obtained by different researchers with different error estimations and in different ranges of state parameters (T, P, ρ).

The heterogeneity of obtained in that way experimental data on caloric and thermic properties leads to difficulties at their mutual concordance and use, especially, in such extremal states as critical and supercritical ones.

I-MATERIALS AND METHODS

We worked out on experimental method, which allows to measure simultaneously heat capacity and PVT- dependencies of a researched liquid and mixture.

Previously [5], it was in detail described a construction of high-temperature adiabatic calorimeter, designed by Kh.I. Amirkhanov, and measurement method using to measure isochoric heat capacity (heat capacity at constant volume).

Peculiarities of Amirkhanov's high-temperature adiabatic calorimeter allow to use it for measurement of pressure dependence upon temperature. Measurements for heat capacity $C_v = f(T)$ and pressure $P = f(T)$ are carried out along isochors $\rho = \text{const}$ in one experiment using the same measuring cell, the same experimental apparatus, and the same sample of studied substance.

Thus, on the basis of high-temperature adiabatic calorimeter- piezometer is worked out the experimental methodic permitting to obtain the interconsistent data about temperature dependence of studied substance heat capacity and pressure. This methodic allows to capacity out the measurement in wide range of temperature T and pressure P value and also in critical and supercritical states.

A schema of main elements of experimental apparatus - high-temperature calorimeter-piezometer is represented in figure 1.

The triple - layers adiabatic calorimeter-piezometer consists of inner spherical calorimetric vessel 4 and outer spherical shell vessel 2, between which is pressed a layer 3 of semiconductive material.

The inner spherical vessel 4 is made of the stainless steel and wall thickness is $0.5 \div 1.5$ mm. for different calorimeter-piezometer. The outer spherical vessel 4 has also the stainless steel and a wall thickness $5 \div 10$ mm.

As a semiconductive material is used cooper oxide. A thickness of semiconductor layer 3 is $1.5 \div 2.5$ mm.

The semiconductor layer serves as adiabatic shell. An application semiconductor layer in common with high precise automatic temperature regulators permits to thermostating the system with error within $\pm 2 \cdot 10^{-5}$ K.

A intensive mixing of studied liquid sample is made by thin perforated steel foil 10 placed inside the calorimeter – piezometer at return motion around the axis.

The measurement of heat capacity and pressure is carried out along the isochores.

The volume V_{T_0, P_0} of empty calorimeter internal vessel defined at room temperature T_0 and atmospheric pressure P_0 , by placing a deaerating bidistillate of water into the calorimeter-piezometer.

Since the measurements were carried out in wide range of states parameters, the calorimeter – piezometer volume was determined versus temperatures T and pressures P

$$V_{T,P} = V_{T_0, P_0} + \Delta V_{T-T_0} + \Delta V_{P-P_0}$$

A change of the calorimeter – piezometer volume owing to thermal and baric expansion of calorimeter – piezometer $dV = (\partial V / \partial T)_p dT + (\partial V / \partial P)_t dP$ was determined experimentally using the method described in [6] and calculation method for spherical vessel [7].

At pressure inside the calorimeter – piezometer $P = 30$ MPa at baric change of volume was $\Delta V_p = 0.15 V_0$.

The maximum value of the calorimeter – piezometer volume change at temperature 680 K was $\Delta V_t = 0.02 V_0$.

A common uncertainty of the calorimeter – piezometer volume value with account of uncertainties of baric and thermal corrections is within from 0.05 percent to 0.09 percent in temperature range from 300K to 650K and pressure to 25 MPa.

The measurement of heat capacity and pressure is carried out along the isochores.

For the research the PVT dependence the piston gauge was connected to calorimeter – piezometer with valve system through the differential membrane pressure transducer. The pressures were measured by use of compensation method with a piston gauge and by means of electrical pressure transducer complex with 0.05 % precision.

The values of specific isochoric heat capacity C_v are calculated from the relation

$C_v = (Q / \Delta T - q_c) / m$, where Q is quantity of heat transferred to system (calorimetric cell and studied sample) by inner heater, when the temperature increases by ΔT , m is mass of the test liquid. $q_c = \sum m_i C_{vi}$; m_i , C_{vi} represents the masses and heat capacities of all the elements of the inner vessel and the part of semiconducting layer that takes part in heat balance.

A detail estimation of measurement errors of isochoric heat capacity is given [5]. An error in determination of isochoric heat capacity and density not exceeds 2 % and 0.1 % correspondingly.

On the basis of high – temperature calorimeter – piezometer created an automatized experimental plant. Experimental plant gives an opportunity to carry out measurements on thermophysical properties in wide states range: in liquid phase, in vapour phase, vapour-liquid equilibria, by phase transitions, in critical and supercritical states.

By the worked out technique are studied thermophysical properties of large class of liquid systems: individual liquids – n-alkanes [5], water [2], carbon dioxide ,etc, binary mixtures [8] in range of critical and supercritical states.

The comparison of isochoric heat capacity values for n-hexane, obtained by our method and calculated by Span [9] equation of state is shown in figure 2.

The mean-square deviation of isochoric heat capacity values calculated by Gerasimov [10] crossover equation of state from our experimental results for n-alkanes is approximately 2.8 %.

CONCLUSION

The worked out methods for measure of complex C_v , PVT thermophysical properties considerably reduce an experimental time and cut down material expenses necessary for carrying out of autonomous piezometric and calorimetric researches in a region of the critical and supercritical states of liquid.

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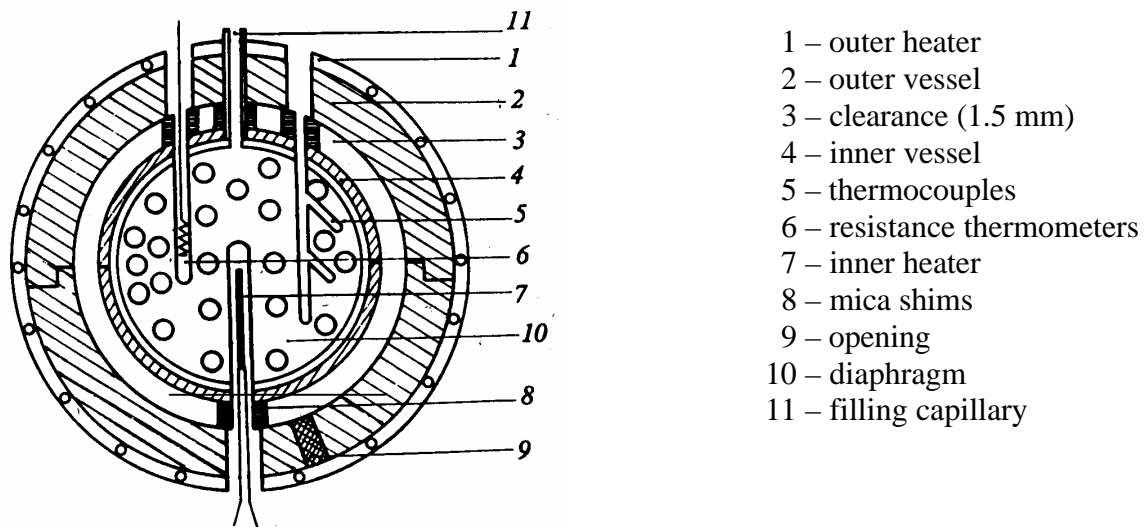


Figure 1. Schematic of calorimeter-piezometer.

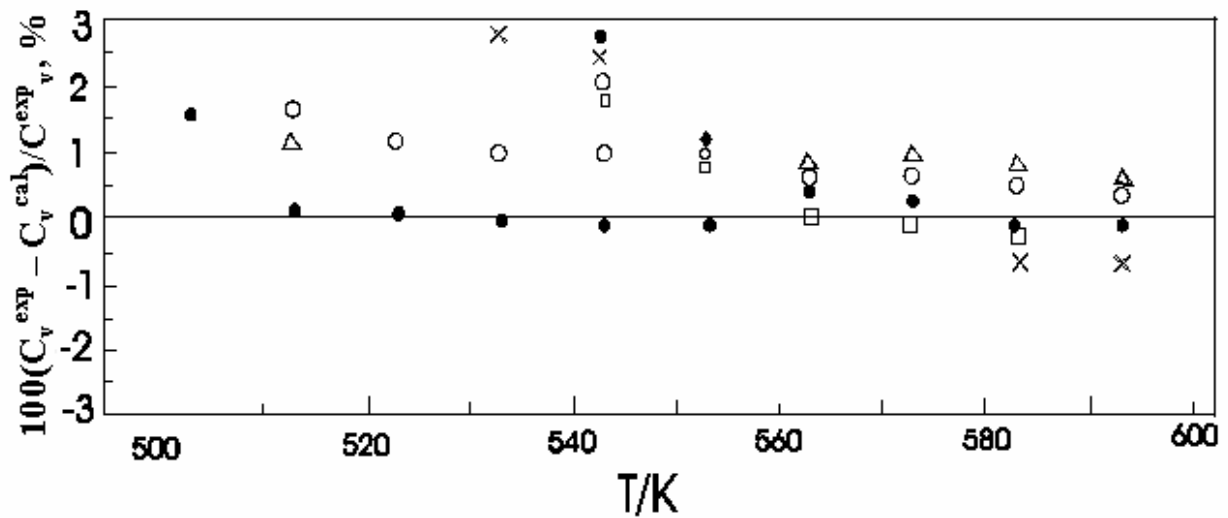


Figure 2. Relative deviations of calculated by equation [9] from experimental isochoric heat capacity γ_v for n – hexane on isochors: Δ - 62,50 kg/m³; \bullet - 83,33 kg/m³; \circ - 100,00 kg/m³; \circ - 165,84 kg/m³; \circ - 210,08 kg/m³; + - 222,22 kg/m³; \blacklozenge - 234,08 kg/m³.

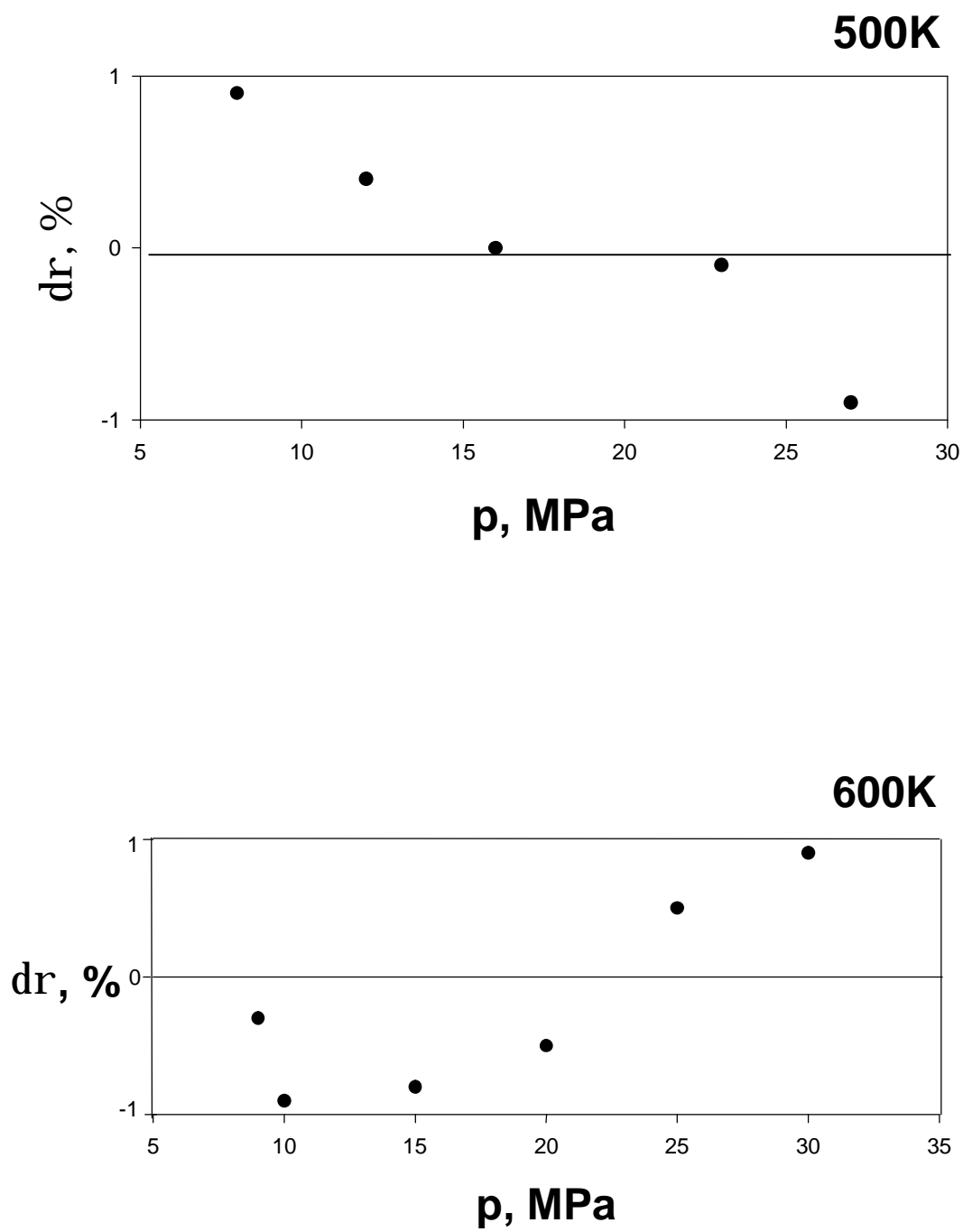


Figure 3. Comparison of our vapour pressures values with • - reported in [11] for n-pentane.