Phase transitions and volumetric properties of the ternary system water+1-propanol+n-hexane near the critical point

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Abstract. One-phase PVTx, phase transition \((p_s, \rho_s, T_s)\) and critical \((p_c, \rho_c, T_c)\) properties of the ternary equimolar system (0.333 mole fraction of each component) water+1-propanol+n-hexane were experimentally studied in the critical and supercritical regions. Measurements of the PVTx relationship were made using a high-temperature, high-pressure, constant-volume piezometer immersed in high precision air thermostat. The values of the phase transition parameters were determined using isochoric \(P-T\) break point technique. The standard uncertainty of the density, temperature, pressure, and concentration measurements was estimated to be 0.15%, 0.015 K, 0.05%, and 0.01 mole %, respectively. The measured PVTx data for the ternary mixture water+1-propanol+n-hexane were used to develop wide-ranged multiparametric equation of state.

1. Introduction

Accurate PVT data of fluids are crucial for understanding many industrial and natural processes. In many applications these processes are occurring at high temperatures and high pressures (near- and supercritical conditions). PVT properties of fluids are needed in many industrial applications such as a design calculation, heat and mass transfer equipment, in chemical industry, fluid flow, for developments and utilization of energy, etc. For engineering utility, the reliable methods of the thermodynamic properties calculations (an equation of state, EOS) over wide ranges of temperatures and pressures would be extremely valuable. A reliable EOS for supercritical fluids can be developed on the base of accurate PVTx experimental data. Accurate PVTx data near the critical point, the phase transition \((p_s, \rho_s, T_s)\) and the critical \((p_c, \rho_c, T_c)\) properties of ternary mixtures are important from both the fundamental (for the study of the intermolecular interactions between the different type of molecules) and the technological (supercritical fluid or enhancement of oil recovery technologies, for example) points of view. The vapor pressures of pure components (water, 1-propanol, and n-hexane) are very close to each other (see figure 1).

In previous studies [1–5] the phase equilibrium and the solubility in the ternary system water+1-propanol+n-hexane were studied at low temperatures (around room temperatures). Rasulov A. and Rasulov S. [6] used also the same technique (the difference in the design of the constant volume piezometer) to study of the volumetric properties (liquid-liquid and liquid-gas equilibrium properties) of the same system with the composition of 0.7223, 0.1535,
Figure 1. Vapor-pressure of pure water, 1-propanol and n-hexane together with measured values for ternary mixture water+1-propanol+n-hexane (this work).

and 0.124 mole fraction of water, 1-propanol, and n-hexane for six isochores. From measured data the authors estimated the values of the critical parameters. Thus, there are very limited experimental data for the ternary system under study in the critical and supercritical regions. More experimental data are required to deeply understand the physical bases (in the molecular level) of the phase transitions and critical phenomena in multicomponent systems. The present work is the continuation of our previous study of the volumetric properties of pure and multicomponent mixtures in the critical and supercritical regions at high temperatures and high pressures. In the present work, we have reported accurate PVTx data for ternary system water+1-propanol+n-hexane mixture over the wide temperature range from 373.15 to 673.15 K for liquid and vapor isochores between 25 kg/m$^3$ and 616 kg/m$^3$ at pressures up to 56 MPa using a high-temperature and the high-pressure constant-volume piezometer.

2. Experimental part

The experimental details of the method (the procedure of measurements and the uncertainty assessment) and apparatus have been described in our earlier publications. Only a brief review will be given here. PVT relationship for water+1-propanol+n-hexane mixture was measured with the high-temperature and high-pressure constant volume piezometer developed in our previous series publications. This method and experimental apparatus were previously successfully employed to study of the PVTx properties of various molecular fluids and fluid mixtures such as hydrocarbons, alcohols, and aqueous solutions in the critical and supercritical regions. The piezometer made of a special heat-and corrosion-resistant high-strength steel alloy on the nickel bases (NiCr20TiAl). The inner volume of the piezometer at various temperatures and pressures were determined during a calibration procedure that used the PVT of the reference fluid (water, for example) with well-known properties (IAPWS formulation, with an uncertainty
of < 0.1 % for densities and pressures at high temperatures). In the present experimental temperature and pressure ranges the inner volume of the piezometer was changed from 32.38 cm$^3$ to 32.80 cm$^3$. The density of the sample at a given temperature $T$ and pressure $P$ was calculated from the simple $\rho = m/V(T,P)$, where $m$ is the filling mass of the sample that immersed in the piezometer and $V(T,P)$ is the temperature- and pressure-dependent internal volume of the piezometer. In order to avoid the additional uncertainty in the density measurements which are introduced by the noxious volumes, a diaphragm-type null indicator was mounted on one of the ends of the piezometer. The standard uncertainties in the piezometer volume, mass, and temperatures were 0.05 %, 0.006 %, and 15 mK, respectively. A detailed uncertainty analysis of the method (all of the measured quantities and corrections) was given previously [7].

The measurements were made in the temperature range from 373.15 K to 673.15 K for 24 isochores between (25 kg/m$^3$ and 616 kg/m$^3$) at pressures up to 56 MPa. These temperature and density ranges are including two- and one-phases, the critical and supercritical regions.

As one can see from figures 2 and 3, the phase diagrams in $p$, $T$- and $p$, $\rho$- planes equimolar ternary system under study are similar to the phase behavior of the pure fluids, an except of a weak slope of $\rho$-dependence at a two-phase region, which is not observed for pure fluids. The values of measured PVT properties of the studied ternary system are given on table 1 and figure 4.

The temperature and composition dependences of the measured compressibility factor $Z = p/RT\rho$ for the ternary mixture along the liquid-gas coexistence curve was described by the multiparametric polynomial equation [8,9]:

\[
Z = \frac{p}{RT\rho_m} = 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk} \omega^i x^j / \tau^k, \tag{1}
\]

and

\[
p = RT\rho_m \left[ 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk} \omega^i x^j / \tau^k \right], \tag{2}
\]
Figure 3. Isotherms of pressure dependency from density.

Table 1. Measured PVT properties of the ternary mixture along the liquid-gas coexistence curve.

| T, K  | p, MPa | ρ, kg/m³ | Z = p/RTρ | T, K  | p, MPa | ρ, kg/m³ | Z = p/RTρ |
|-------|--------|----------|------------|-------|--------|----------|------------|
| 436.00| 1.36   | 25.17    | 0.8157     | 503.35| 5.45   | 304.90   | 0.2340     |
| 456.15| 2.17   | 43.87    | 0.7137     | 503.15| 5.44   | 321.92   | 0.2213     |
| 470.00| 2.80   | 62.41    | 0.6288     | 502.15| 5.41   | 350.41   | 0.2026     |
| 483.45| 3.60   | 87.08    | 0.5634     | 495.15| 4.98   | 413.77   | 0.1602     |
| 495.15| 4.43   | 125.20   | 0.4704     | 488.45| 4.50   | 445.83   | 0.1361     |
| 501.15| 5.07   | 158.36   | 0.4208     | 476.75| 3.74   | 479.39   | 0.1077     |
| 503.45| 5.33   | 190.44   | 0.3664     | 458.65| 2.73   | 517.14   | 0.0758     |
| 503.85| 5.39   | 200.29   | 0.3521     | 441.15| 1.95   | 549.67   | 0.0529     |
| 504.10| 5.44   | 224.34   | 0.3170     | 428.65| 1.48   | 573.29   | 0.0396     |
| 504.15| 5.51   | 256.15   | 0.2811     | 416.45| 1.13   | 593.03   | 0.0302     |
| 503.75| 5.48   | 275.57   | 0.2598     | 399.25| 0.76   | 616.91   | 0.0202     |
| 503.65| 5.47   | 294.66   | 0.2428     |       |        |          |            |

where $a_{i,j}$ are the fitting coefficients, $\rho_m$ is a molar density (mol/m³), $\omega = \rho/\rho_k$, $\tau = T/T_k$, $-\$ are the reduced density and reduced temperature, respectively; $p_c$, $T_c$ – are the critical density and critical temperature; $R = 8.314$ J/(mol·K) is the universal (molar) gas constant.

Coefficients of equation (2) $a_{i,j}$ were calculated by the less square method [9]. The average relative uncertainty of the calculated values of pressure from the present experimental data is less than 1.3 %. Using the grapho-analytical method of analyses, based on the scaling behavior of the coexistence curve near the critical point, the values of the critical parameters of the ternary system were estimated as ($T_c = 504.15$ K, $\rho_c = 256.15$ kg/m³, $p_c = 5.51$ MPa).

As well-known, the temperature dependence of the saturated liquid and vapor densities near
Figure 4. $p$, $\rho$, $T$-diagram of phase coexistence curve of water+1-propanol+n-hexane equimolar ternary mixture with 0.333 mole fraction in various projections. fraction of components (solid line) and its projections on coordinate planes (dotted line).

The critical point can be presented as

$$\Delta \rho = \sum_{i=0}^{n} B_i \tau^\beta_i.$$  \hspace{1cm} (3)

where $\tau = T/T_c - 1$ – is a reduced difference of temperature from the critical value; $\Delta \rho = (\rho_s - \rho_v)/\rho_c$ – is a reduced difference of saturated liquid and vapor densities from the critical value (order parameter); $\beta_0$, $\beta_1$, $\beta_2$ . . . – are the universal critical exponents; $B_0$, $B_1$, $B_2$ . . . – are the nonuniversal critical amplitudes. Since, ternary system under study behaves just like pure fluid we applied equation (3) for our ternary system, although theoretically equation (3) is not applicable for mixtures.

There are many different form of the scaling relation (3) with different values of $\beta_0$ between 0.3 and 0.5 for various molecular liquids [10–12]. In the present work we used the scaling type equation recommended in the work [12]

$$\rho_{f,g} = \rho_k (1 \pm B_0 \tau^{\beta_0} + B_1 \tau^{\beta_1} \pm B_2 \tau^{\beta_2} + \ldots),$$ \hspace{1cm} (4)

and in the symmetrical part of equilibrium curve

$$(\rho_f - \rho_g)/2 \rho_k = B_0 \tau^{\beta_0} + B_2 \tau^{\beta_2} + B_4 \tau^{\beta_4} + \ldots.$$ \hspace{1cm} (5)

The present measured values of the liquid+gas coexistence curve data were fitted to the equations (4) and (5). The optimal values of the fitting parameters are $\beta_0 = 0.33$, $\beta_1 = 0.66$, $\beta_2 = 0.97(\pm 0.01)$, $B_0 = 2.1$, $B_1 = 0.34$, $B_2 = 0.72$. The calculated values are presented in figure 5). The derived scaling type of correlation represents the present experimental saturated densities within average absolute deviation of 1.4%.
3. Conclusion
At temperature above 373.15 K the equimolar ternary mixture of water+1-propanol+n-hexane is a homogeneous and it thermodynamic behavior is very similar to pure fluids. Based on the measured PVT data near the critical point the values of the critical parameters of the ternary equimolar mixture water+1-propanol+n-hexane were determined ($T_c = 504.15$ K, $\rho_c = 256.15$ kg/m$^3$, $p_c = 5.51$ MPa).

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