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PVTx properties of the binary 1-propanol + *n*-hexane mixtures in the critical and supercritical regions

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ABSTRACT

PρTx relationship of the binary 1-propanol + *n*-hexane mixture were measured. Measurements were concentrated in the immediate vicinity of the critical and supercritical regions in order to closely observe the features of the mixture critical curve behavior (critical phenomena in the 1-propanol + *n*-hexane mixture) and other derived thermodynamic properties. The measurements have been made over the temperature range from (403 to 573) K for liquid and vapor isochores between (92 and 564) kg·m^{-3} up to 61 MPa using a high-temperature and high-pressure constant-volume piezometer. The combined expanded uncertainty of the density, ρ, pressure, P, temperature, T, and concentration, x, measurements at the 95% confidence level with a coverage factor of $k = 2$ is estimated to be 0.15%, (0.02 to 0.05) %, 10 mK, and 0.01 mole %, respectively. The critical curve data $(T_C - x)$, $(P_C - x)$, and $(\rho_C - x)$, were extracted from the measured *PρTx* data. The extracted critical curve and direct measured $P - x$ data along the critical isochore-isotherm were used to estimate the value of the Krichevskii parameter for the mixture when 1-propanol is solvent at the critical state. The measured *PρTx* data were used to calculate excess and partial molar volumes of *n*-hexane near the critical point of pure 1-propanol. The isomorphic thermodynamic behavior of the mixture have been studied on the bases of critical curve data and the critical amplitudes of the pure solvent (1-propanol).

1. Introduction

Supercritical fluid technology allowed considerable improved industrial processes. Optimization of the processes taking place at supercritical conditions is required accurate thermodynamic properties data for the binary mixtures. In various technological processes supercritical fluids contain two and more components. Therefore, besides the critical properties of pure components the critical curve data are very important for supercritical fluid technology. *PVTx* and critical properties data are very important in industry for design, simulation, and optimization processes. The thermodynamic properties of alcohol + *n*-alkane mixtures are using as additives to gasoline and entrainers or co-entrainers in modified rectification processes for binary azeotropes. Reliable EOS for supercritical fluids can be developed only based on accurate *PVTx* experimental data. Experimentally observed critical anomalies of the thermodynamic properties of fluids and fluid mixtures near and supercritical regions are very important for phase diagram modeling. It is very difficult to accurately predict properties polar and nonpolar binary mixtures (complex mixture, dissimilarity between the component structure and chemical nature) based on pure component properties due to complexity of the intermolecular interaction (H-bonding effect in alcohol solutions) between their molecules. Most cases molecular-based EOS are fail to accurate predict properties of the supercritical fluids. The experimental study *PVTx* relationship in the near- and supercritical regions is also interesting in fundamental scientific point of view to check and confirm the reliability and predictive capability of the various molecular-based fundamental EOS and accurately determine the molecular parameters of the EOS or to modify the structure of the models and their physical bases. In the present work, the measurements were focused on near- and supercritical region to precisely determine critical locus data and study of the critical phenomena in the binary 1-propanol + *n*-hexane mixture.

1.1. Brief review of the reported critical properties and PVTx data of 1-propanol + n-hexane mixture

1.1.1. Experimental critical lines data

Five data sources [1–5] for the critical properties, $P_C(x)$ and $T_C(x)$ or $P_C - T_C$ data were found in the literature for binary 1-propanol + *n*-hexane mixture. The literature search was based on the TRC/NIST archive [6]. These sources are representing 47 critical temperature data and 37 critical pressure data in the whole concentration range. All these critical properties data were used to compare with the present

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results and to estimate the value of the Krichevskii parameter. All previous reported critical properties data were obtained using visual opalescence method which less reliable than direct *PVTx* measurements. The most widely used experimental method of determining parameters of the critical parameters is visual observation of the meniscus disappearance which lacks objectivity. Moreover, approaching the critical point, where the difference between the liquid and vapor phases vanishes, and the visual determination of the moment at which the critical state occurs becomes ever less reliable. In addition, the observations are impeded by the development of critical opalescence. Therefore, the region of temperatures near the critical point (within 1 K of T_C) becomes virtually unattainable for investigation.

Xin et al. [1] reported critical properties data (T_C-x and P_C-x) for 1-propanol + *n*-hexane binary mixture. The measurements were made using critical opalescence observation method. The uncertainty of the critical temperature and the critical pressure measurements claimed by the authors are 0.4 K and 0.01 MPa, respectively. The measured critical lines data were fitted to

$$T_C(x) = xT_{C2} + (1-x)T_{C1} + T_1x(1-x) + T_2x(1-x)(2x-1) + T_3x(1-x)(2x-1)^2, \quad (1)$$

$$P_C(x) = xP_{C2} + (1-x)P_{C1} + P_1x(1-x) + P_2x(1-x)(2x-1) + P_3x(1-x)(2x-1)^2, \quad (2)$$

where T_{C1}, T_{C2}, P_{C1}, $P_{C2}$are the critical temperature and pressure of 1-propanol and *n*-hexane, respectively, T_i and P_i are the fitting parameters determined from measured critical lines data. These equations were used to estimate the value of the Krichevskii parameter (see below Section 3.3) and isomorphic characteristic densities and temperatures (see Section 3.4). Gil et al. [2] used the same method to accurate measured liquid-gas critical locus, T_C-x and P_C-x, in the whole range of mole fractions for 1-propanol + *n*-hexane mixture. The repeatabilities in the critical temperature and the critical pressure measurements for the mixture were <0.15 K and <0.013 MPa, respectively. The concentration minimum of the T_C-x critical curve was observed near the 0.6055 mol fraction of *n*-hexane. This minimum is appeared in the P_C-T_C locus as a temperature minimum at temperature of 502.886 K and at pressure of 3.544 MPa for concentration of 0.6055 mol fraction. Oh et al. [3] reported isothermal VLE (for four temperatures) and critical properties data for three 1-propanol + *n*-hexane mixtures. The values of the critical pressure and temperature were determined for three concentrations of 0.599, 0.786, and 0.319 mol fractions using visual method (critical opalescence observation). The uncertainty in the temperature and pressure measurements are 0.03 K and 0.05%, respectively. Young [4] and Hicks and Young [5] reported the critical temperature T_C-x data for eight concentrations (from 0.095 to 0.894 mol fractions). No the critical density data were found in the literature for 1-propanol + *n*-hexane mixture. As one can see from P_C-T_C projection of the critical locus, this mixture shows I type fluids phase behavior according to the classification van Konynenburg and Scott [7]. Llovell and Vega [8] developed crossover soft-SAFT EOS for 1-propanol + *n*-hexane mixture. This model shows good prediction VLE and critical line data reported by Oh et al. [3]. Most reported VLE data in the literature are include low temperature and low pressure ranges and far from the critical point. The critical properties of mixture *n*-alkane (*n*-hexane) with other alcohols (methanol, ethanol, *etc.*) were measured by other authors [2,9–12].The critical phenomena of methanol with *n*-hexane (and other *n*-alkane) was studied by de Loos et al. [9]. They studied the L-G critical P_C-T_C curve shape changes in the alcohol + *n*-alkane mixtures. Zawisza [10] found that L-G critical P_C-T_C curve for methanol + *n*-alkane mixtures runs through a temperature minimum. Liu et al. [11] also reported T_C-x and P_C-x data for methanol + *n*-hexane mixture. Sauermann et al. [12] studied critical properties of ethanol + *n*-hexane mixture.

1.1.2. Density measurements

In this review we did not included 19 reported VLE (*PTxy*) data sources for the mixture. All these studies were made at low temperatures (near the room temperature) and low pressures far from the critical point. A literature survey revealed that there are no reported density data for this mixture under pressure (NIST/TRC search). Most one phase density measurements in the literature were made in the liquid phase at low temperatures (below 313 K) or at 298.15 K. Heintz et al. [13] measured the density of liquid 1-propanol + *n*-hexane mixture at low temperatures (from 283 to 313 K) and at atmospheric pressure using VTD. The uncertainty of the liquid density measurements with such method is within 2×10^{-5} g·cm^3. The measured densities were used to calculate excess molar volume data. These data were not used in the present work due to different experimental temperature and pressure ranges. Orge et al. [14] reported the measured densities of 1-propanol + *n*-hexane mixture at 298.15 K and atmospheric pressure as a function of concentration. The measurements were made with Anton Paar DSA-48 densimeter with the uncertainty of 2×10^{-5} g·cm^3. These data also were not used in the present work due to large difference in the experimental range. Iglesias et al. [15] also reported the same type measurements for the mixture at 298.15 K and atmospheric pressure. The same type measurements (density and excess molar volumes) were made by Jimenez et al. [16] for 1-propanol + *n*-hexane mixture at 298.15 and 101 kPa. Thus, all previous reported density data were performed in the very limited temperature range (from 293 K to 353 K) and at atmospheric pressure. No high-temperature and high-pressure density measurements were performed previously for the mixture. Only VLE measurements in [3,9] were performed at high temperatures near the critical point. Thus, there are no reported *PVTx* data in the one-phase near- and supercritical regions for 1-propanol + *n*-hexane mixture. In the present work we considerable expanded the available thermodynamic database for the mixture. We reported accurate *PVTx* data for 1-propanol + *n*-hexane mixture over the temperature range from (403 to 573) K for liquid and vapor isochores between (92 and 564) kg·m^{-3} up to 61 MPa using a high-temperature and high-pressure constant-volume piezometer.

2. Experimental

The experimental details of the method (procedure of measurements and uncertainty assessment) and apparatus have been described in our earlier publications [17–27]. Only a brief review will be given here. *PVTx* relationship for 1-propanol + *n*-hexane mixture were measured with a high-temperature and high-pressure constant volume piezometer developed in our previous series publications [17–27]. This method and experimental apparatus was previously successfully employed for study of the *PVTx* properties various molecular fluids and fluid mixtures such as hydrocarbons [18,24], alcohols [25,27], and aqueous solutions [17,19–24,26] in the critical and supercritical regions. The piezometer made of a special heat-and corrosion-resistant high-strength steel alloy (ХН77ТЮРУ-ВД) on the nickel bases of 77%. The inner volume of the piezometer at various temperatures and pressures were determined during a calibration procedure that used the *PVT* of reference fluid (water, for example [28]) with well-known properties (IAPWS formulation, with an uncertainty of <0.1% for density and pressure at high temperatures). For example, at temperatures of (373.15 and 673.15) K and pressures of (38.35 and 0.3) MPa, the piezometer volumes were (32.56 and 32.059) cm^3, respectively. In the present experimental temperature and pressure ranges the inner volume of the piezometer was changed from (32.38 to 32.80) cm^3. All masses were determined with an uncertainty of 5×10^{-4} g or (0.003 to 0.040) % (in this work we use a coverage factor $k = 2$). The volume of the piezometer at reference temperature T_0 and pressure P_0 was determined with uncertainty of 0.12% ($\delta V_{P_oV_o} = \delta m + \delta\rho_{H_2O}$). This calibration was checked using other pure fluids. The resulting value of the piezometer volume was essentially the same as determined previously with water

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