Fluid Phase Equilibria 418 (2016) 44–49

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Scaled equation of state and specific thermodynamic behavior of near-critical methane–pentane binary mixture

M. Yu. Belyakov [a], E.E. Gorodetskii [a, b, *], V.D. Kulikov [a], V.P. Voronov [a], B.A. Grigoriev [b, c]

[a] *Oil & Gas Research Institute of the Russian Academy of Sciences, 3 Gubkin Street, Moscow 119333, Russia*
[b] *Gubkin Russian State University of Oil and Gas, 65 Leniskii Prospect, Moscow 119333, Russia*
[c] *Gazprom VNIIGAZ LLC, Moscow Region, Razvilka 142717, Russia*

ARTICLE INFO

Article history:
Received 26 June 2015
Received in revised form
4 August 2015
Accepted 14 August 2015
Available online 20 August 2015

Keywords:
Liquid–vapor critical point
Scaling theory
Dew–bubble curve
Isochore
Heat capacity jump
Tricritical point

ABSTRACT

Phase behavior of methane–pentane mixture and anomalies of the isochoric heat capacity $C_{\rho,x}$ and the derivative $(\partial P/\partial T)_{\rho,x}$ have been studied experimentally in the vicinity of liquid–vapor critical point at three pentane concentrations, namely, for 0.0196, 0.0345, and 0.096 mol fraction of pentane. It has been shown that for two low pentane concentrations the behavior of the heat capacity $C_{\rho,x}$ and $(\partial P/\partial T)_{\rho,x}$ differs substantially from both theoretically predicted and experimentally observed behavior of the properties in other mixtures. We suggest that the reason of such unusual behavior is caused by the proximity of the mixture critical locus to the tricritical point at low pentane concentrations. On the other hand dew–bubble curves (DBC) of the methane–pentane mixtures for all studied concentrations do not exhibit any special features and thus can be described theoretically within the scope of the conventional scaling approach.

1. Introduction

Critical fluids are a subject of intensive investigations in the last fifty years. Relevant references can be found in [1–4]. At the present time the critical fluids are used for various industrial applications. In particular, the critical fluids due to their specific properties are being increasingly used in supercritical fluid technologies [5,6], food [7], medical [8] and other industries. Significant number of hydrocarbon- fluid deposits in near-critical thermobaric conditions exist in nature. Traditional methods used in these technologies for the description of the properties of critical fluids are usually based on certain modifications of van der Waals cubic EOS [9,10], which is known to be inaccurate near the critical point due to the lack of accounting for effect of density fluctuations.

Fluctuation theory of fluids presents an alternative approach to the classical equations of state. The fluctuation nature of anomalous behavior of thermodynamic quantities near the critical point implies the insensitivity of the thermodynamic potential to the details of intermolecular interaction and is responsible for the universal behavior of fluids in the critical region [11]. The approach based on the scaled equation of state has been successfully employed by different authors for the description of near-critical properties of both pure fluids and binary and ternary mixtures [12–15]. Recently, we proposed a new approach for the description of near-critical properties of mixtures with fixed composition, which does not depend on the number of components in mixture [16,17]. The approach is based on the fluctuation theory of phase transitions and isomorphism of critical phenomena. It has been shown that all thermodynamic properties of a multicomponent mixture can be parameterized in a universal way by means of two scaling fields of 3D-Ising model provided that the fluid mixture exhibits two-phase near-critical coexistence. The analysis of the results of experimental studies within the scope of the proposed theoretical model led to the EOS, which was in a quantitative agreement with existing experimental data on various fluid mixtures. The approach suggested in present work has been applied for the analysis of the properties of methane–pentane system. In contrast to previously studied mixtures this system does not reveal the typical near-critical anomalies in the isochoric heat capacity $C_{\rho,x}$ and the derivative $(\partial P/\partial T)_{\rho,x}$ in the range of low pentane concentrations.

2. Theoretical model

Let us briefly outline the theoretical background of the proposed approach (for the detailed discussion see Refs. [16–19]). It is well-known that fluids and fluid mixtures in the vicinity of their

---

* Corresponding author at: Oil & Gas Research Institute of the Russian Academy of Sciences, Moscow 119333, Russia. Fax: +7 499 135 54 65.
E-mail addresses: gorod@orgi.ru, gorod41@mail.ru (E.E. Gorodetskii).

http://dx.doi.org/10.1016/j.fluid.2015.08.016
0378-3812/© 2015 Published by Elsevier B.V.

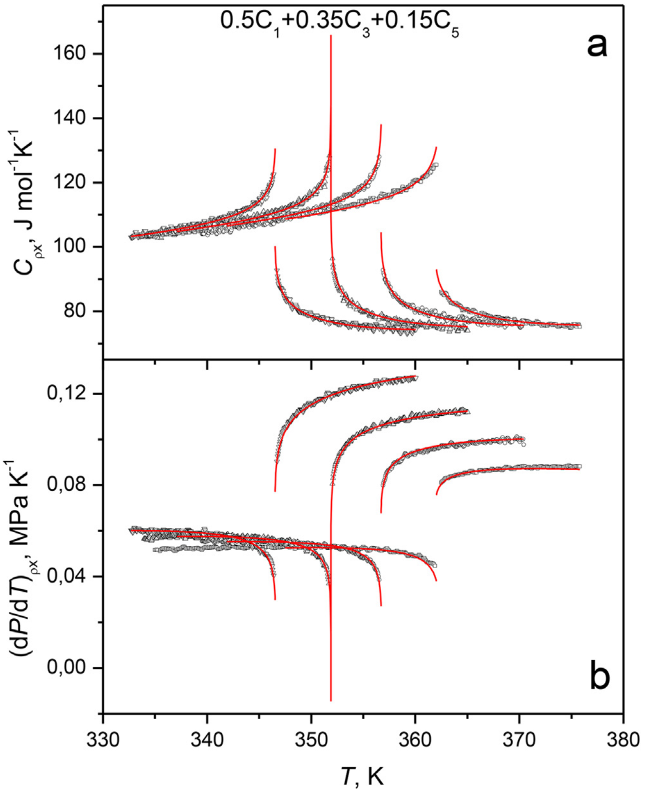

Fig. 1. The typical behavior of the isochoric heat capacity $C_{\rho,x}$ (a) and the derivative $(\partial P/\partial T)_{\rho,x}$ (b) in one- and two-phase regions measured along the near-critical isochores. Solid lines on both pictures represent the dependencies calculated within the framework of the developed approach [4].

critical points belong to the 3D-Ising model universality class [20]. In the framework of the Ising-model, three scaling fields h_1, h_2, and h_3 were introduced, so that the critical point corresponds to the condition $h_1 = h_2 = h_3 = 0$. Any two fields are considered to be independent whereas the third field plays the role of the appropriate thermodynamic potential of the system. If the scaling field h_3 was chosen for this purpose, it can be written as the known function of the fields h_1 and h_2 as follows

$$h_3 = |h_2|^{2-\alpha} f(z), z = \frac{|h_1|}{|h_2|^{\beta+\gamma}}. \qquad (1)$$

Here $\alpha = 0.11$, $\beta = 0.325$ and $\gamma = 2 - \alpha - 2\beta$ are the universal critical exponents of 3D-Ising model [21].

Scaling densities φ_1 and φ_2 conjugated to the scaling fields h_1 and h_2 can be defined from the relation

$$dh_3 = \varphi_1 dh_1 + \varphi_2 dh_2. \qquad (2)$$

Next essential point is the assumption that all scaling fields h_k are the analytical functions of the reduced temperature $\tau = T/T_c - 1$, reduced pressure $\Delta P = (P - P_c)/\rho_c RT_c$ and the reduced chemical potentials of the mixture components $\Delta\mu_i = (\mu_i - \mu_{ic})/RT_c$. Therefore, in the critical region the fields $h_k(\Delta P, \tau, \Delta\mu_i)$ can be expanded in a power series in thermodynamic fields, i.e.

$$h_k = h^{(c)}_{k\tau}\tau + h^{(c)}_{kP}\Delta P + \Sigma^n_{i=1} h^{(c)}_{ki}\Delta\mu_i + ...(k = 1, 2, 3) \qquad (3)$$

where $h^{(c)}_{mn}$ designates the derivatives taken at the mixture critical point, so that these values may be considered as some non-universal parameters. Note that such expansions correspond to the concept of the thermodynamic fields mixing in a quite general formulation of the “complete scaling” [22–24]. Using Eqs. (1)–(3), one can express all necessary thermodynamic variables in the following form [19]

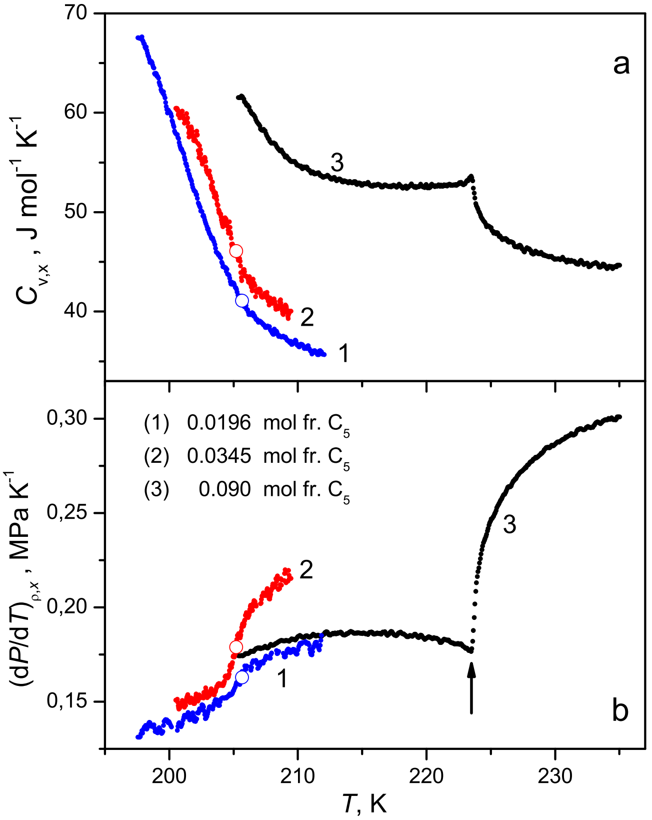

Fig. 2. The temperature dependencies of the isochoric heat capacity $C_{\rho,x}$ (a) and the derivative $(\partial P/\partial T)_{\rho,x}$ (b) in methane–pentane mixture measured along the near-critical isochores for three studied mixture compositions. The corresponding density values are equal to: (1) 0.2112; (2) 0.2488; (3) 0.3223 g/cm^3. The phase transition points for the mixtures (1) and (2) are marked by empty circles. The phase transition point for the mixture (3) is indicated by arrow.

$$\begin{aligned}
\Delta\rho &= c_{\rho 1}\varphi_1 + c_{\rho 2}\varphi_2 + c_{\rho 3}h_2 + c_{\rho 4}h_1 + c_{\rho 5}h_3 + c_{\rho 6}\varphi_1^2 + \ldots \\
\tau &= c_{\tau 1}\varphi_1 + c_{\tau 2}\varphi_2 + c_{\tau 3}h_2 + c_{\tau 4}h_1 + c_{\tau 5}h_3 + c_{\tau 6}\varphi_1^2 + \ldots \\
\Delta P &= c_{P1}\varphi_1 + c_{P2}\varphi_2 + c_{P3}h_2 + c_{P4}h_1 + c_{P5}h_3 + c_{P6}\varphi_1^2 + \ldots \\
\Delta\mu_i &= c_{i1}\varphi_1 + c_{i2}\varphi_2 + c_{i3}h_2 + c_{i4}h_1 + c_{i5}h_3 + c_{i6}\varphi_1^2 + \ldots \qquad (4)
\end{aligned}$$

where $\Delta\rho = \rho/\rho_c - 1$ is the reduced density of a mixture and the coefficients c_{mn} are considered as non-universal parameters of the model. In fact, the system (4) represents the expansions of thermodynamic variables in scaling variables. To apply these equations for the calculation of thermophysical properties of a real mixture it is necessary to define the explicit form of scaling fields and scaling densities. For this purpose the well-known parametric linear model has been used to specify the form of the scaling densities and the scaling fields in the critical region [25]

$$\begin{aligned}
h_3 &= r^{2-\alpha}(1 - a_2\theta^2 + a_4\theta^4) \\
h_1 &= a_1 r^{\beta+\gamma}\theta(1 - \theta^2), \varphi_1 = r^\beta\theta \\
h_2 &= r(1 - b^2\theta^2), \varphi_2 = a_3 r^{1-\alpha}(\theta_s^2 - \theta^2). \qquad (5)
\end{aligned}$$

Here b^2, θ_s^2, and a_i are the universal parameters of the linear model which can be expressed through the universal critical exponents only (see for example [19]).

Various physical values, including the isochoric heat capacity $C_{\rho,x}$ and the derivative $(\partial P/\partial T)_{\rho,x}$ can be calculated in analytical form in the framework of the proposed model [19]. The derived