Phase transitions and critical properties of 1-propanol–n-hexane system

E A Bazaev, A R Bazaev
Institute for Geothermal Research of the Daghestan Scientific Center of the Russian Academy of Sciences, Shamil 39A, Makhachkala, Daghestan Republic, 367030, Russia
E-mail: emilbazaev@gmail.com

Abstract. By using experimental data on \( p, T, x \) and \( \rho, T, x \) relations of 1-propanol–n-hexane mixtures (0.2, 0.5, 0.8 and 0.9 mol. fraction of n-hexane \( x \)) and the method of isochore fracture(p) = f(T) at two-phase (liquid-gas), one-phase (liquid, gas), near-critical and supercritical region liquid ↔ gas (\( p_c, \rho_c, T_c \)) phase transition parameters are determined. And parameters of critical points (\( p_c, \rho_c, T_c \)) are determined by the grapho-analytical method combining with scaling behavior. The dependence of pressure from temperature, density and composition along the phase coexistence curve is described by three parameter polynomial represented by expansion of the compressibility factor \( Z = p/RT\rho \) into a power series of density \( \omega = \rho/\rho_k \) and temperature \( \tau = (T - T_k)/T_k \) and

\[
p = RT\rho_m \left[ 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk}\omega^i\tau^j \right].
\]

The average relative deviation of calculated values of pressure from experimental ones is 1%. The dependence of temperature from density along the liquid ↔ gas phase coexistence curve is described by equations: far from critical points \( \rho = \rho_k (1 \pm B_0\omega^{\beta_0} + B_1\omega^{\beta_1} \pm B_2\omega^{\beta_2} + \ldots) \), and in the symmetrical part of equilibrium curve \( (\rho_f - \rho_g)/2\rho_k = B_0\omega^{\beta_0} + B_2\omega^{\beta_2} + B_4\omega^{\beta_4} + \ldots \), where \( \tau = (T - T_k)/T_k \) and \( \omega = (\rho - \rho_k)/\rho_k \). Average relative error is 1.47%.

1. Introduction
Experimental data on phase behavior and critical properties of 1-propanol–n-hexane binary mixture is a big interest of theory of solutions and practical application. The values of saturated vapor pressures of the mixture components in the diapason of temperatures till the critical one of n-hexane (\( T_k = 507.82 \) K) are similar.

Some data on \( p, \rho, T, x \) – measurements of 1-propanol–n-hexane binary mixture are given in literature sources [1–10].

In our work for the purpose of determination of phase transition (PT) parameters and determination of critical state depending on the composition experimental data on \( p, T, x \) and \( p, T, \rho, x \) – relations of 1-propanol–n-hexane binary mixture in the wide diapason of state parameters is given.

2. Experimental part
\( p, T, x \) and \( p, \rho, T \) – measurements of 1-propanol–n-hexane binary mixtures are made on the reworked accurate free-ballast volume piezometric experimental setup. Unlike other analogs our piezometer has no ballast volume and whereby whole sample is in the area of test temperature,
that is necessary for accurate determination of PT and coexistence curve (CC). Describing of experimental setup and the technique is given in [11].

The 1-propanol (CAS #71-23-8) and n-hexane (CAS #110-54-3) samples, used in this work were supplied by “Reactive” and “ReaChim” (Moscow). \( p, \rho, T, x \) – measurements were performed in the diapason of temperatures 373.15 – 573.15 K; pressures up to 50 MPa; densities 15 – 660 kg/m\(^3\); and composition \( (x) \) 0.2, 0.5, 0.8 and 0.9 molar fraction of n-hexane.

3. Experiment analysis

As one can (see figure 1) \( p, T \) phase diagram of individual substance is similar to those of binary mixture. Other values of composition have same pattern of \( p, T \)-dependency.

The parameters of PT points liquid \( \leftrightarrow \) gas \( (p_s, \rho_s, T_s) \) are determined by graph-analytical method and parameters of CC \( (p_k, \rho_k, T_k) \) are determined by including scaling behavior as a function of composition (table 1, figure 1).

Experimental critical line of the system (figure 3) is curved for the composition 0.8 – 0.9 mole fractions of n-hexane. Received data of critical pressure and temperature is consistent well with literature [12–15], that is shown on figure 4.

The dependence of pressure from temperature and composition of mixtures on saturation curve is described by three-parameter polynomial equation represented by expansion of the compressibility factor \( Z = p/RT\rho \) into a power series of density and temperature:

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

and

\[
p = RT\rho_m \left[ 1 + \sum_{i=1}^{m} \sum_{j=0}^{n} \sum_{k=0}^{s} a_{ijk} \omega^i x^k / \tau^i \right], \tag{2}
\]

![Figure 1](image-url)

Figure 1. Isochores (28.12–610.69 kg/m\(^3\) (1–30)) of pressure – temperature dependency of 1-propanol–n-hexane binary mixture (0.5 mole fraction). LP – liquid phase, SCL – supercritical liquid, GP – gas phase, SCG – supercritical gas.
Figure 2. $p$, $\rho$, $T$ – diagram of coexistence curves of 1-propanol–n-hexane binary mixture.

Figure 3. Dependence of density from temperature and composition along the coexistence curve of 1-propanol–n-hexane and their mixtures. $K^{0}_{1} - K^{0}_{2}$ – critical points of 1-propanol and n-hexane; $K_{3} - K_{6}$ – critical points of 1-propanol–n-hexane binary mixture ($x = 0.2, 0.5, 0.8 - 0.9$ mol. fractions of n-hexane); $K^{0}_{1} - K^{0}_{2}$ – projection of critical line.

where $a_{i,j}$, coefficients, $\rho_{m}$ is a molar density (mol/m$^3$), $\omega = \rho / \rho_{k}$, $\tau = T / T_{k}$, – is reduced density and reduced temperature; $\rho_{k}$, $T_{k}$ – critical density and critical temperature; $R = 8.314$ J/(mol·K) is the universal (molar) gas constant. The average relative deviation of calculated values of pressure from experimental ones is 1.1%.

Coefficients of equation (2) ($a_{i,j}$) are calculated by less square method [16, 17] and also conditions of critical state ($dp/d\rho$)$_{T}^{k} = 0$; ($d^{2}p/d\rho^{2}$)$_{T}^{k} = 0$; ($dp/dT$)$_{T=T_{k},\rho=\rho_{k}}$ = 0; ($\partial p/\partial T$)$_{T=T_{k},\rho=\rho_{k}}$ = 0.
were taken into account. The average relative deviation of calculated values of pressure from experimental ones is 1%. We used next equations [18] to describe the dependence of density of mixtures among the CC in the range of temperatures ($\tau > 0.3$):

$$\rho_{f,g} = \rho_k(1 \pm B_0 \tau^{\beta_0} + B_1 \tau^{\beta_1} \pm B_2 \tau^{\beta_2} + \ldots), \quad (3)$$

and in the symmetrical part of equilibrium curve

$$\frac{(\rho_f - \rho_g)}{2\rho_k} = B_0 \tau^{\beta_0} + B_2 \tau^{\beta_2} + B_4 \tau^{\beta_4} + \ldots, \quad (4)$$

while data handling using equations (3) and (4) the value $\beta_i$ was changed in interval $0.3 - 0.5$, and parameter $B_i$ was trimming [19]. Results of our calculations are given on table 2.
Figure 4. Dependence of critical temperature (a), critical pressure (b) and critical density (c) from composition of 1-propanol–n-hexane binary mixture. • – our work; X – [12]; ◦ – [13]; △ – [14]; ⊓ ⊔ – [15].

Table 2. The values critical indexes and amplitudes (3) and (4).

| Mixture     | $\beta_0 \pm 0.002$ | $B_0 \pm 0.002$ | $\beta_1$ | $B_1$  | $\beta_2$ | $B_2$  | $\beta_3$ | $B_3$  | $\beta_4$ | $B_4$  |
|-------------|----------------------|------------------|-----------|--------|-----------|--------|-----------|--------|-----------|--------|
| 1-propanol  | 0.338                | 2.144            | 0.838     | −0.231 | 0.676     | 0.000  | 0.909     | 0.467  | 0.974     | −0.500 |
| 0.2 mole fr.| 0.338                | 2.061            | 0.838     | −0.122 | 0.676     | 0.003  | 0.909     | 0.000  | 0.974     | −0.840 |
| 0.5 mole fr.| 0.338                | 1.925            | 0.838     | 0.244  | 0.676     | 0.007  | 0.909     | 0.018  | 0.974     | −1.040 |
| 0.8 mole fr.| 0.338                | 1.967            | 0.838     | −0.105 | 0.676     | 0.003  | 0.909     | 0.000  | 0.974     | −0.829 |
| 0.9 mole fr.| 0.338                | 1.820            | 0.838     | 0.039  | 0.676     | 0.004  | 0.909     | 0.042  | 0.974     | −0.411 |
| n-hexane    | 0.338                | 2.022            | 0.838     | −0.147 | 0.676     | 0.137  | 0.909     | 0.548  | 0.974     | −0.077 |

Equations (3) and (4) describe experimental data for researched systems with the average relative error 1.47% for values of $\beta_0 = 0.338 \pm 0.002$.

4. Conclusion
a) Thermodynamic behavior of binary mixtures of all diapason of composition is same to thermodynamic behavior of pure components (1-propanol, n-hexane).
b) Critical line of 1-propanol–n-hexane binary mixtures in the 0.8 – 0.9 mole fraction of n-hexane diapason is curved i.e. passes through the minimum.

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