

A non Cubic Equation of State for Describing the ppT Properties of Pure Components and Their Mixtures

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In this work we use a non cubic equation of state proposed by *Brandani et al.*¹ to represent the volumetric properties of three pure fluids (carbon dioxide, n-pentane and toluene) at supercritical or near-critical temperatures and at pressures up to 70 MPa. The ppT properties of two binary mixtures (carbon dioxide – n-pentane and carbon dioxide – toluene) are calculated in the same range of temperatures and pressures, using the mixing rules proposed by *Brandani et al.*¹ The calculated densities are in good agreement with the literature experimental values, taking into account the wide range of temperatures and pressures at which experimental data were collected.

Key words:

Equation of state, density, carbon dioxide, n-pentane, toluene, mixtures

Introduction

A non cubic equation of state proposed by *Brandani et al.*¹ has been used for describing vapor pressures and liquid densities of pure fluids at saturation and, with suitable mixing rules, for representing successfully vapor-liquid equilibria and liquid-liquid equilibria of strongly non-ideal mixtures. More recently, this equation of state has been used for correlating the solubility of phenol in m-cresol at pressures up to 10 MPa.²

The scope of this paper is to subject this equation to a more severe test, employing the non cubic equation of state for describing the ppT properties of pure fluids at supercritical or near-critical temperatures and at pressures up to 70 MPa and the same properties for their mixtures in the same range of temperature and pressure. In fact, *Alem and Mansoori*³ have stated that a severe test of an equation of state (EOS) is its applicability for predictions of compressibility.

By comparing with the experimental data of *Pöhler and Kiran*⁴ and those of *Kiran et al.*,⁵ the predicted results are very good not only for pure fluids, but also for their mixtures.

The model

The compressibility factor, which is the sum of the ideal, repulsive, and attractive term, is given by

$$z = 1 + z^{\text{rep}} + z^{\text{attr}} \quad (1)$$

where

$$z^{\text{rep}} = \frac{4\eta - 2\eta^2}{(1 - \eta)^3} \quad (2)$$

$$z^{\text{attr}} = -\frac{4\varepsilon}{RT} \eta(1 + k_1\eta + k_2\eta^2) \quad (3)$$

with

$$\eta = \frac{b\rho}{4} \quad (4)$$

where b and ε are the size and energy parameter of the equation of state, respectively.

Moreover ρ and η are the molar and the reduced density, respectively. The constants $k_1 = -1.04387$ and $k_2 = 4.53723$ have been determined by fitting the experimental data of saturated liquid densities and vapor pressures of the following fluids: argon, xenon, methane, ethane and propane,^{6–9} in the reduced temperature range of 0.44–0.92. The mean average deviations in vapor pressures and saturated liquid densities were 0.12 % and 0.57 %, respectively.

A new evaluation of the two constants k_1 and k_2 was necessary because the values previously determined did not take into account that the attractive contribution, isolated by *Vimalchand and Donohue*¹⁰ from the overall compressibility factor in a simulation of n-butane, referred to a non-spherical molecule.

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The two parameters of the equation of state are both dependent on temperature, according to the following expressions:

$$\varepsilon = \varepsilon_c \frac{1 + \frac{\alpha}{T_R}}{1 + \alpha} \quad (5)$$

with

$$\alpha = a_0 + a_1 T_R + a_2 T_R^2 \quad (6)$$

where $T_R = T/T_c$ is the reduced temperature and

$$b = b_c \left[\frac{1 - \frac{1}{3} \exp\left(-\frac{\beta}{T_R}\right)}{1 - \frac{1}{3} \exp(-\beta)} \right]^3 \quad (7)$$

where ε_c and b_c are the two parameters at the critical point which can be determined by the conditions for the critical point

$$\left(\frac{\partial p}{\partial v} \right)_{T_c} = 0 \quad (8)$$

$$\left(\frac{\partial^2 p}{\partial v^2} \right)_{T_c} = 0 \quad (9)$$

which give

$$\frac{\varepsilon_c}{RT_c} = 2.75965 \quad (10)$$

$$\frac{b_c p_c}{RT_c} = 0.20293 \quad (11)$$

Therefore, a_0 , a_1 , a_2 and β are the parameters to be determined for any particular fluid from experimental data.

The expressions for the EOS parameters of mixtures derived from the proposed mixing rules¹ are the following:

$$\frac{\varepsilon_M}{RT} = \sum_i x_i \frac{\varepsilon_i}{RT} - \frac{\tilde{G}^E}{4\delta} \quad (12)$$

$$b_M = \frac{B_M}{1 - \sum_i x_i \frac{\varepsilon_i}{RT} + \frac{\tilde{G}^E}{4\delta}} \quad (13)$$

where

$$B_M = \sum_i \sum_j x_i x_j B_{ij} \quad (14)$$

$$B_{ij} = \frac{1}{2}(B_{ii} + B_{jj})(1 - k_{ij}) \quad (15)$$

$$B_{ii} = b_i \left(1 - \frac{\varepsilon_i}{RT} \right) \quad (16)$$

$$\delta = \eta_{\text{lattice}} \left(1 + \frac{1}{2} k_1 \eta_{\text{lattice}} + \frac{1}{3} k_2 \eta_{\text{lattice}}^2 \right) \quad (17)$$

$$\eta_{\text{lattice}} = \frac{10}{12} 0.74048 \quad (18)$$

Using for the reduced excess Gibbs energy, \tilde{G}^E , the NRTL equation¹¹ with $\alpha_{12} = 0.3$, the EOS mixture parameters are a_{12} , a_{21} and k_{12} : two binary interaction parameters and the binary parameter for the virial cross-coefficient. Since, for the two binary interaction parameters we assume a linear dependence on temperature, we use five fitting parameters to correlate all the isotherms in the entire temperature range.

The mixing rules used in this work were developed for the non-cubic equations of state,¹ but Brandani and Brandani¹² have shown that these mixing rules can be extended easily to cubic EOS.

$p/\rho/T$ properties calculation of sample systems

To test the proposed model in the description of ppT properties of pure fluids and their mixtures, we have found the experimental data of Pöhler and Kiran⁴ on the volumetric properties of carbon dioxide – toluene and those of Kiran et al.,⁵ on the volumetric properties of n-pentane – carbon dioxide, which report highly accurate data in the pressure range 0–70 MPa and various isotherms in a 100 K temperature interval.

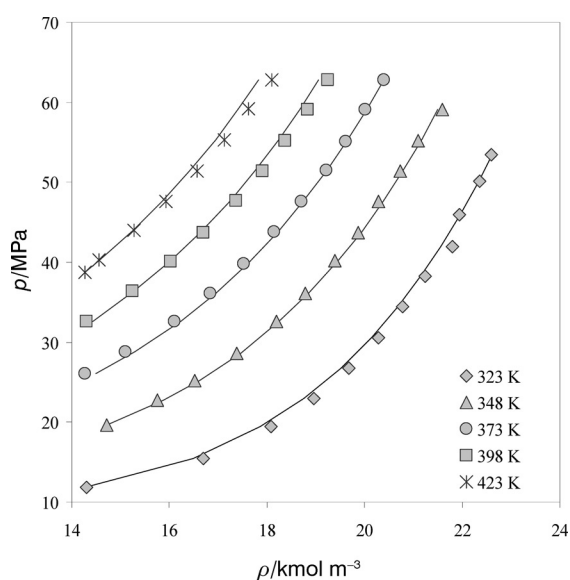
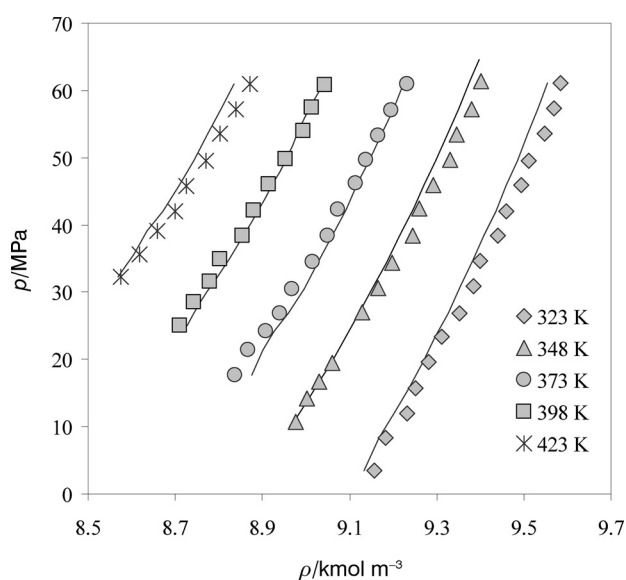
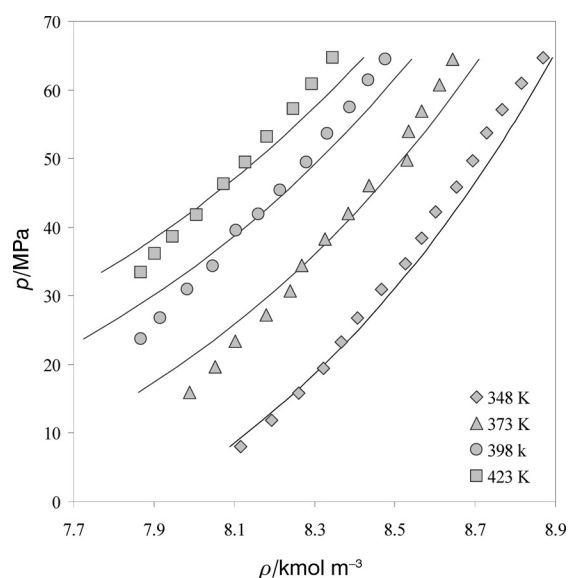
In this work, therefore, we have studied the volumetric properties of the following pure components: carbon dioxide, n-pentane, and toluene. The results of the fitting, i.e. pure fluid parameters and the average percent deviations (APD) of the experimental and calculated densities, as calculated by:

$$\text{APD} = \left(\sum_{k=1}^N \left| 1 - \rho_{k,\text{calc}} / \rho_{k,\text{exp}} \right| \right) \cdot \frac{100}{N} \quad (19)$$

are reported in Table 1, together with the temperatures of the investigated isotherms. Fig. 1–3 show the comparison between the calculated isotherms and experimental ones, for the three examined pure fluids.

Table 1 – Pure fluids EOS parameters and average percent deviation (APD) on molar density

Fluid	Carbon dioxide	n-pentane	Toluene
a_0	0.375516	0.785763	-0.070656
a_1	-0.761388	-0.607226	-0.627210
a_2	0.252439	-0.862163	1.120441
B	0.095884	0.416581	0.000791
T/K	323; 348; 373; 398; 423	348; 373; 398; 423	323; 348; 373; 398; 423
T_R range	1.06-1.39	0.68-0.91	0.54-0.91
APD on ρ /%	0.55	0.53	0.21

Fig. 1 – Diagram p/ρ for carbon dioxide at several temperaturesFig. 3 – Diagram p/ρ for toluene at several temperaturesFig. 2 – Diagram p/ρ for n-pentane at several temperatures

In Tab. 2, the percent weight fraction of carbon dioxide and the temperatures of the isotherms for the system carbon dioxide – n-pentane are reported. Tab. 3 shows the results of the fitting of the volumetric properties of the binary system carbon dioxide – n-pentane, i.e. EOS mixture parameters and APD for the densities. The mean average percent deviation ($MAPD$) on molar density is 0.72 % over the entire range of temperatures and compositions. The results are very good, taking into account that the experimental interval of temperatures is 100 K and that experimental pressures range up to 70 MPa. Fig. 4–8 show the p/ρ diagrams for the system carbon dioxide – n-pentane at various temperatures. In each isothermal diagram the lines of constant composition are reported. The composition is expressed in mass fraction of CO_2 .

Table 2 – Investigated isotherms and compositions for the system carbon dioxide – n-pentane.

Mass fraction of CO ₂ , $W_{CO_2} / \%$	Temperature, T/K
100	323; 348; 373; 398; 423
88	323; 348; 373; 398; 423
80	323; 348; 373; 398; 423
72	323; 348; 373; 398; 423
62	323; 348; 373; 398
50	323; 348; 373; 398; 423
35	323; 348; 373; 398
20	323; 348; 373; 398
10	323; 348; 373; 398
0	348; 373; 398; 423

Table 3 – Binary mixtures parameters for the system carbon dioxide – n-pentane and average percent deviation (APD) on molar density for various compositions

a_{12}/K	$(488.43 - 0.00248 T)/K$
a_{21}/K	$(27.255 - 0.00162 T)/K$
k_{12}	0.334
mass fraction of CO ₂ , $w / \%$	APD on ρ
100	0.55
88	0.68
80	0.70
72	1.21
62	0.84
50	0.63
35	0.96
20	0.56
10	0.53
0	0.53

Mean average percent deviation (MAPD) = 0.72 %

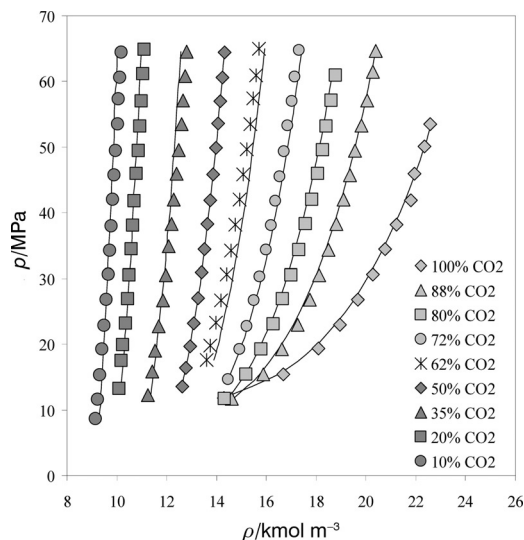


Fig. 4 – Diagram p/ρ for carbon dioxide + n-pentane mixtures at 323 K :lines of constant composition (mass fraction of CO₂)

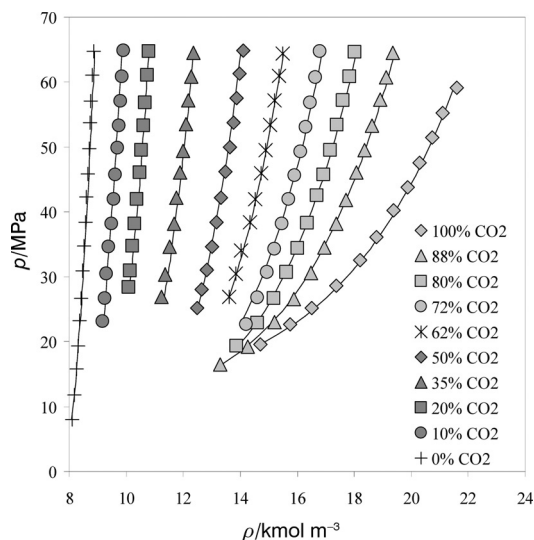


Fig. 5 – Diagram p/ρ for carbon dioxide + n-pentane mixtures at 348 K: lines of constant composition (mass fraction of CO₂)

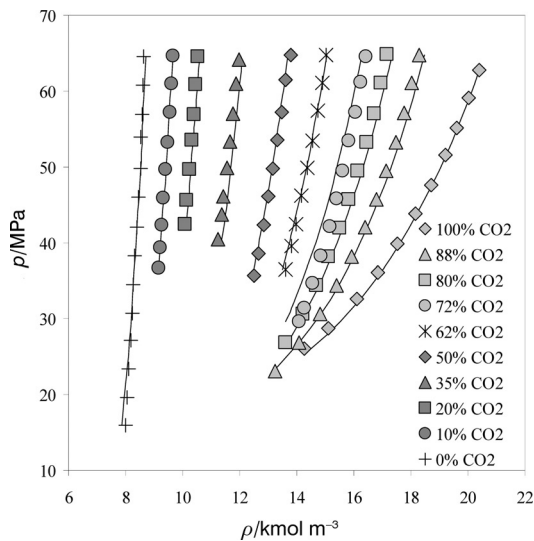


Fig. 6 – Diagram p/ρ for carbon dioxide + n-pentane mixtures at 373 K: lines of constant composition (mass fraction of CO₂)

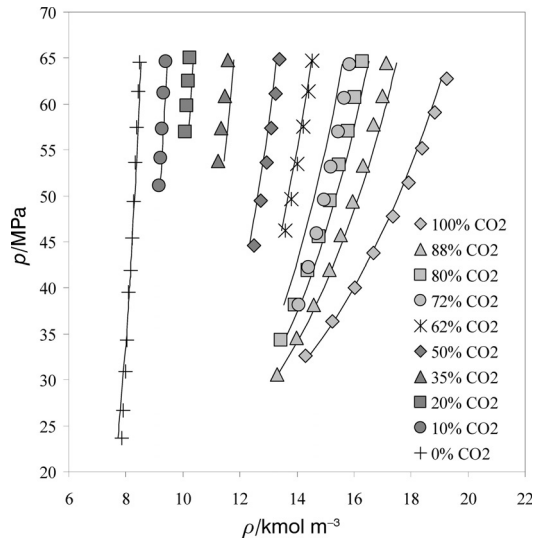


Fig. 7 – Diagram p/ρ for carbon dioxide + *n*-pentane mixtures at 398 K: lines of constant composition (mass fraction of CO_2)

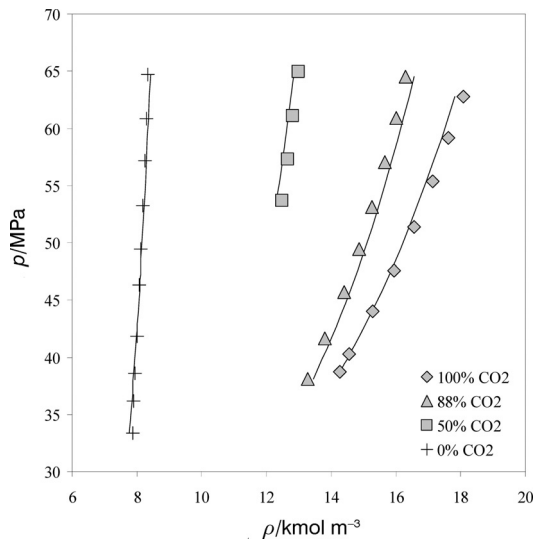


Fig. 8 – Diagram p/ρ for carbon dioxide + *n*-pentane mixtures at 423 K: lines of constant composition (mass fraction of CO_2)

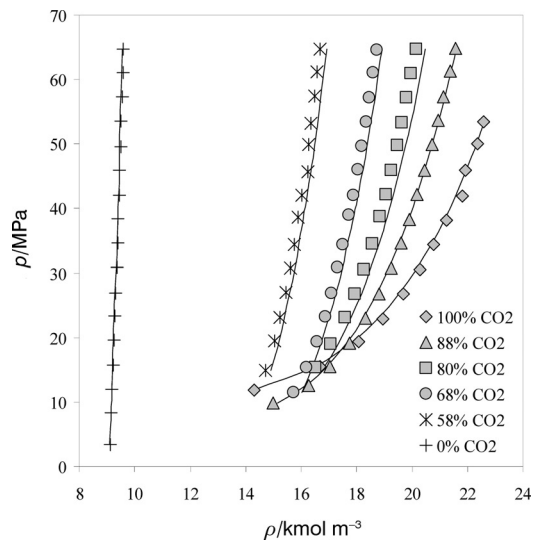


Fig. 9 – Diagram p/ρ for carbon dioxide + toluene mixtures at 323 K: lines of constant composition (mass fraction of CO_2)

Table 4 – Investigated isotherms and compositions for the system carbon dioxide – toluene

mass fraction of CO_2 , $w_{\text{CO}_2} / \%$	temperature, T/K
100	323; 348; 373; 398; 423
88	323; 348; 373; 398; 423
80	323; 348; 373; 398; 423
68	323; 348; 373; 398; 423
58	323; 348; 373; 398; 423
0	323; 348; 373; 398; 423

Table 5 – Binary mixture EOS parameters for the system carbon dioxide – toluene and the average percent deviation (APD) on molar density for various compositions

a_{12} / K	$(-112.27 + 0.00082 T)/\text{K}$
a_{21} / K	$(395.42 - 0.00559 T)/\text{K}$
K_{12}	0.384
mass fraction of CO_2 , $w / \%$	APD on ρ
100	0.55
88	0.64
80	0.68
68	0.73
58	0.86
0	0.21

Mean average percent deviation (MAPD) = 0.61 %

In Tab. 4, the mass fraction of carbon dioxide and the temperatures of the experimental isotherms for the system carbon dioxide – toluene are reported. Tab. 5 shows the fitted mixture parameters and the APD density values for the binary system carbon dioxide – toluene. The mean average deviation on molar density is 0.61 % over the entire range of temperatures and compositions, which again shows the capability of the EOS and the mixing rules to represent p/ρ in a wide temperature and pressure range. Fig. 9–13 show the p/ρ diagrams for the system carbon dioxide-toluene at various temperatures. In each isothermal diagram the lines of constant composition are reported. The composition is expressed in mass fraction of CO_2 .

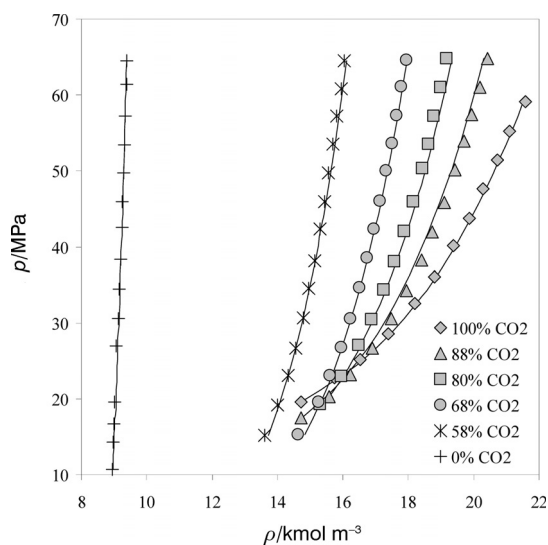


Fig. 10 – Diagram p/ρ for carbon dioxide + toluene mixtures at 348 K: lines of constant composition (mass fraction of CO_2)

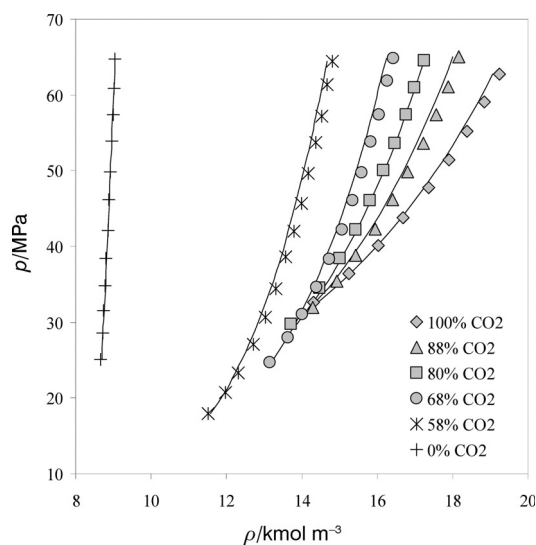


Fig. 12 – Diagram p/ρ for carbon dioxide + toluene mixtures at 398 K: lines of constant composition (mass fraction of CO_2)

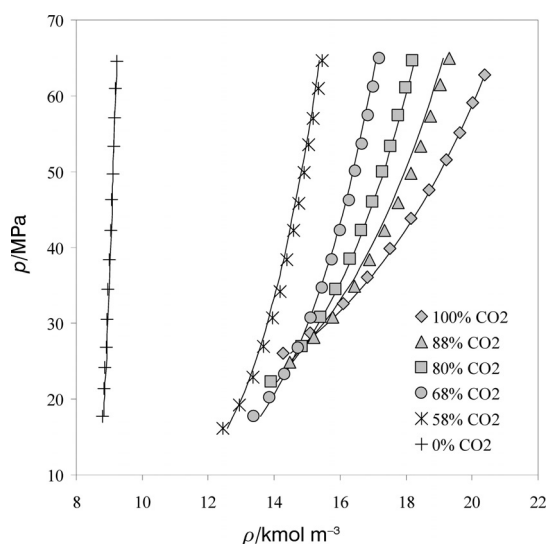


Fig. 11 – Diagram p/ρ for carbon dioxide + toluene mixtures at 373 K: lines of constant composition (mass fraction of CO_2)

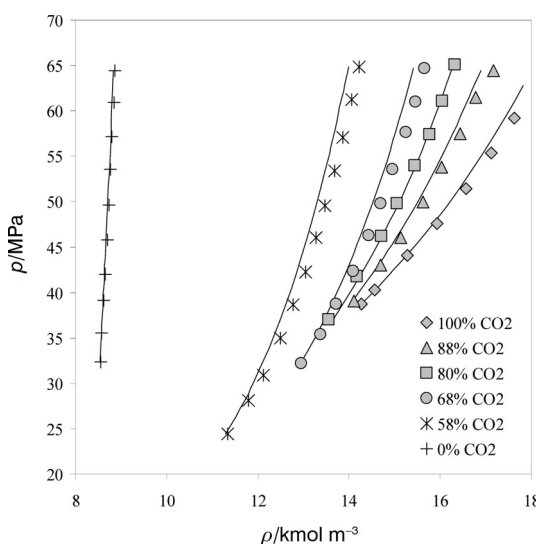


Fig. 13 – Diagram p/ρ for carbon dioxide + toluene mixtures at 423 K: lines of constant composition (mass fraction of CO_2)

Conclusions

In this work we have examined the capability of the EOS proposed by Brandani et al.¹ for correctly representing the volumetric properties of several pure fluids and their mixtures, using appropriate mixing rules. According to the results, the investigated equation of state, together with the proposed mixing rules, is capable to describe successfully the volumetric properties of pure fluids and their mixtures, in addition to its capability of correlating vapor-liquid,¹ liquid-liquid,¹ and solid-liquid² equilibria. The investigations described in this article represent a severe thermodynamic test,³ which the equation of state proposed by Brandani et al.¹ accomplishes very well.

Notation

- a_0, a_1, a_2 – individual component parameters of equation of state
- a_{12}, a_{21} – binary interaction parameters, K
- APD – average percent deviation
- B – second virial coefficient, $\text{m}^3 \text{mol}^{-1}$
- b – size parameter, $\text{m}^3 \text{mol}^{-1}$
- b_c – size parameter at the critical point, $\text{m}^3 \text{mol}^{-1}$
- \tilde{G} – reduced Gibbs energy
- k_1, k_2 – universal constants in the attractive contribution
- k_{12} – binary parameter for the virial cross-coefficient
- $MADP$ – mean average percent deviation, %
- N – number of experimental points
- p – pressure, Pa
- p_c – critical pressure, Pa

R – ideal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
 T – temperature, K
 T_c – critical temperature, K
 x – mole fraction
 z – compressibility factor
 w – mass fraction

Greek letters

α – parameter in equation (6)
 α_{12} – nonrandomness NRTL parameter
 β – individual component parameter of equation of state
 δ – defined in equation (17)
 ε – energy parameter, J mol^{-1}
 ε_c – energy parameter at the critical point, J mol^{-1}
 η – reduced density
 ρ – molar density, mol m^{-3}

Superscript

attr – attractive contribution
E – excess function
rep – repulsive contribution

Subscript

calc. – calculated quantity
exp. – experimental quantity
k – index
 i, j – components
M – mixture
R – reduced quantity

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