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A comparison between four cubic equations of state in predicting the inversion curve and spinodal curve loci of methane

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Abstract

Four equations of state, the Redlich–Kwong (RK), Peng–Robinson (PR) modified by Melhem et al., Trebble–Bishnoi (TB), and Jan–Tsai, were compared in predicting the inversion and spinodal curve loci of methane. The inversion locus of methane was also generated from a PVT framework based on the experimental data of gaseous methane. This enables us to judge the accuracy of the results obtained from the different equations of state. The calculated inversion curves were also compared to that fitted by the Gunn–Chueh–Prausnitz correlation. Results predicted by the PR equation modified by Melhem et al. showed good agreement with the experimental behavior up to a reduced pressure of 10. The RK equation shows a clear underestimate of the high pressures (above a reduced pressure of 9.5). The TB equation shows a comparable behavior to that of RK but with better predictions in high-pressure regions. The TB equation shows a good performance up to a reduced temperature of 2.3 after which it shows a deviation from the experimental data. The Jan–Tsai equation was found to be the poorest among the four equations considered in this work.

Keywords: Cubic equation of state; Inversion locus; Joule–Thomson coefficient; Spinodal locus

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Abbreviations

EOS	equation of state
GCP	Gunn–Chueh–Prausnitz correlation

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PR	Peng–Robinson
PVT	Pressure–Volume–Temperature
RK	Redlich–Kwong
TB	Trebble–Bishnoi

Symbols

a	equation of state parameter
A	equation of state parameter
b	equation of state parameter
B	equation of state parameter
c	equation of state parameter
C	equation of state parameter
d	equation of state parameter
D	equation of state parameter
m	equation of state parameter
n	equation of state parameter
P	absolute pressure/MPa
R	universal gas constant
T	absolute temperature/K
u	equation of state parameter
V	molar volume/$\mathrm{cm}^3\ \mathrm{mol}^{-1}$
w	equation of state parameter

Greek symbols

α	equation of state parameter
μ	Joule–Thomson coefficient
Ω	equation of state parameter
ζ	predicted critical compressibility
ω	acentric factor

Subscripts

c	critical state variable
H	constant enthalpy
r	reduced state variable
T	constant temperature
V	constant volume

1. Introduction

Storage tanks containing liquefied vapor are usually considered as a potential source of hazards. Sudden mechanical failure leading to a rapid pressure drop is always a possibility. It has been noticed, from several case studies [1,2], that such an abrupt pressure relief is immediately followed by an explosion that may initiate shock waves, damaging equipment and causing personnel injury. Similar characteristics are observed for accidents involving a contact of extremely hot liquids with extremely cold ones [1,2,3,4]. This phenomenon has been described in the literature by various terms, e.g., boiling-liquid expanding-vapor explosion (BLEVE), thermal explosions, fuel–coolant interaction (FCI) and rapid phase transformation (RPT). This phenomenon has been tackled by investigators from two different perspectives: the thermodynamic and the kinetic. This work is concerned with the thermodynamic approach. According to thermodynamics, for such an explosion to occur, the temperature of the stored liquid must attain or exceed the superheat limit. The superheat limit represents the intrinsic stability limit of the material at the prevailing conditions of temperature and pressure, i.e., the temperature beyond which the material becomes unstable and must change its state [5]. The locus of all superheat limits constitutes what is known as the "spinodal curve." Also, in many pressure-relief situations, the Joule–Thomson effect becomes important, and in a parallel fashion, the inversion curve that represents the locus of all zeroth Joule–Thomson coefficients becomes of practical importance. Along with the practical importance of these loci, in particular the spinodal curves which are difficult to obtain experimentally, the prediction of these loci represents a severe test for the PVT predictive capability of the equations of state. This is so because both the inversion and spinodal loci are based on derived properties [6,7].

In this work, we employ four different cubic equations of state to predict the spinodal and inversion curve loci of methane ($T_c = 190.55$ K, $P_c = 4.595$ MPa, $V_c = 98.92$ cm^3 mol^{-1}, $\omega = 0.01001$). The objective is to evaluate the predictive capability of these equations in the light of these severe tests. The studied equations of state are the Trebble–Bishnoi [8,9], Redlich–Kwong [5], Peng–Robinson as modified by Melhem et al. [10], and Jan–Tsai [11]. The equations and their derivatives are listed in the Appendix. The inversion locus was also generated from experimental data for methane [12].

2. Theroretical background

According to the criterion mentioned previously, the inversion points are obtained when

$$\mu_H = \left[\frac{\partial T}{\partial P}\right]_H = 0. \tag{1}$$

where μ_H is the insenthalpic Joule–Thomson coefficients, T is the absolute temperature, and P is the absolute pressure. A more detailed derivation is reported by Juris and Wenzel [6]. According to their work, Eq. (1) is simplified as in Eq. (2) below. The derivatives corresponding to each equation of state are listed in the Appendix

$$T\left[\frac{\partial P}{\partial T}\right]_V + V\left[\frac{\partial P}{\partial V}\right]_T = 0. \tag{2}$$

where V is the molar volume of the components.

Applying Eq. (2) to an equation of state yields a formula for the inversion loci. In order to get a complete distribution of the inversion points, temperatures are assumed with an incremental variation between successive values. Then, Eq. (2) is solved for the volume using the Newton–Raphson iterative method. Then, the equation of state is applied to calculate the pressure at this temperature and volume.

Gunn, Chueh, and Prausnitz [13] used a sufficiently large experimental PVT data base of argon, methane, ethane, carbon monoxide, nitrogen and xenon, and used the least-squares curve fitting of 89 experimental inversion points to get the correlation

$$P_r = -36.275 + 71.598\, T_r - 41.56\, T_r^2 + 11.826\, T_r^3 - 1.6721\, T_r^4 + 0.091167\, T_r^5 \tag{3}$$

The low temperature and high pressure parts of the inversion curve correlated by Eq. (3) are well-defined; the upper part is based on carbon monoxide only. However, since the acentric factors, ω, of the fluids used are close to zero, Eq. (3) is only valid for simple fluids.

The spinodal curve locus is obtained when the first derivative of the pressure with respect to the volume equals zero, i.e.

$$\left[\frac{\partial P}{\partial V}\right]_T = 0. \tag{4}$$

Eq. (4) is combined with an equation of state to give a formula for the spinodal curve loci. The derivatives corresponding to each equation of state are listed in the Appendix. To have a complete distribution of the spinodal points, volumes are assumed and varied in an incremental way. The formula corresponding to Eq. (4) is solved for the temperature using the Newton–Raphson method. The pressure is calculated by substituting the values of the temperature and the volume in the original equation of state.

3. Results and discussion

The inversion curve locus predicted using the Seivers–Schulz equation which is fitted on experimental PVT data of methane is very close to the GCP correlation. Therefore, the Seivers–Schulz equation can safely be considered as a reference for the evaluation of the inversion loci predicted by other equations of state. Fig. 1 shows a comparison between the GCP correlation and the inversion locus predicted by the Seivers–Schulz equation of state.

The inversion curve predicted by the Trebble–Bishnoi equation of state (see Fig. 1) shows good predictions at low temperatures. This equation shows deviation from the Seivers–Schulz equation above a reduced temperature of 2.3. This deviation remains at a constant magnitude after a reduced temperature of 3.5, resulting in an underestimate of the maximum inversion temperature. The maximum inversion pressure is comparable to that estimated from the Seivers–Schulz equation. Therefore, the effect of pressure on the ability of this equation to predict the derived properties is negligible.

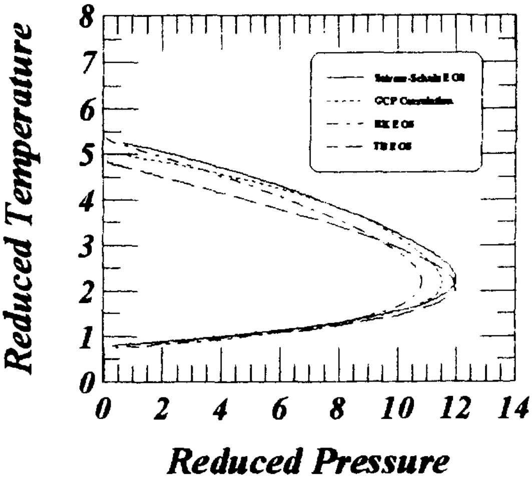

Fig. 1. Inversion curves for methane showing the RK and TB EOS with respect to the GCP correlation and the Seivers–Schulz EOS.

The inversion locus predicted by the RK equation is as good as that predicted by the TB equation of state at low temperatures; a comparison is shown in Fig. 1. The inversion locus generated from the RK equation of state shows an underestimate of the maximum inversion pressure. The deviation of RK predictions from experimental data occurs at reduced pressures above 9.5. Therefore, the RK equation is not as accurate as that of TB in high pressure regions. The RK predictions in high temperature regions are better than those of the TB equation.

The inversion locus predicted by the Peng–Robinson equation modified by Melhem et al. shows a good agreement with the Seivers–Schulz equation at reduced pressures below 10. At higher pressures, a clear overestimate of the inversion pressure is noticed. The maximum inversion pressure predicted by this equation is considerably higher than the value estimated by the Seivers–Schulz equation. The deviations from the experimental inversion data at high temperatures are small. Therefore, compared to the effect of pressure, the effect of temperature is negligible. Fig. 2 shows the inversion locus predicted by the PR equation modified by Melhem et al.

The inversion locus predicted by the Jan–Tsai equation of state does not agree with the Seivers–Schulz equation in any region. The predicted inversion temperatures are considerably above the reference values especially at high temperatures. The maximum inversion pressure is considerably less than the reference value. Therefore, the weakness of this equation cannot be set within reliable limits of operating conditions. The comparison for this equation is shown in Fig. 3.

Studying the spinodal curve loci plotted in Fig. 4, the Trebble–Bishnoi equation of state and the Peng–Robinson equation modified by Melhem et al. are highly consistent. These two equations predict an accurate value of the critical point, i.e., predicting a critical point at a reduced volume and a reduced pressure of 1.00 for each. So, the spinodal curve locus predicted by each of these equations can safely be taken to predict

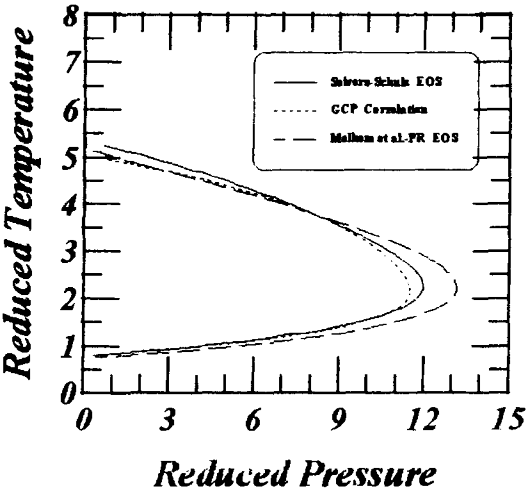

Fig. 2. Inversion curves for methane showing the PR equation modified by Melhem et al. with respect to the GCP correlation and the Sievers–Schulz EOS.

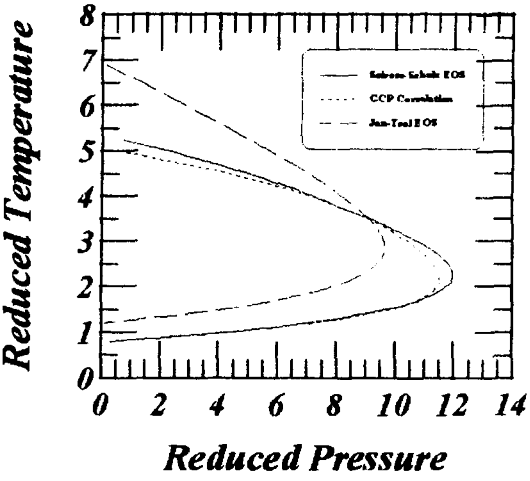

Fig. 3. Inversion curves for methane showing the Jan–Tsai EOS with respect to the GCP correlation and the Seivers–Schulz EOS.

the liquid superheat limit and the gas subcooling limit with a very good accuracy under all conditions.

RK predictions of the spinodal curve show a slight overestimate in the critical volume. The predicted critical point using RK EOS was at a reduced pressure of 1.00 and a reduced volume of 1.17.

The spinodal curve locus predicted by the Jan–Tsai equation is inaccurate, as expected from the results of the inversion curve locus. The critical reduced pressure predicted by this equation is about 0.3 and the reduced critical volume about 2. These

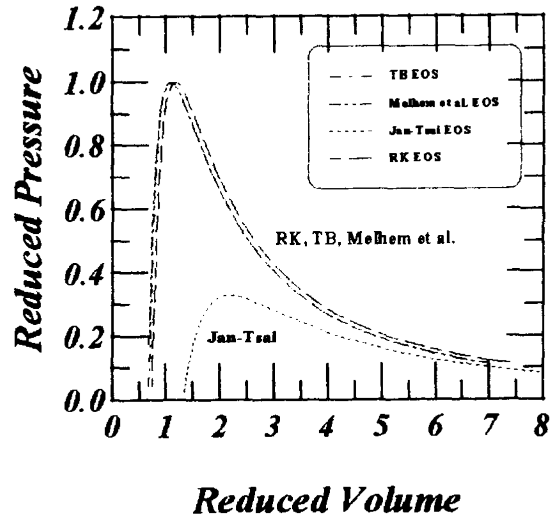

Fig. 4. Spinodal curves for methane.

trends are equivalent to the underestimate of the inversion pressures and the overestimate of the inversion temperature as noticed in Fig. 3. Therefore, the Jan–Tsai equation of state clearly fails to predict the spinodal curve locus of methane.

4. Conclusions

Four cubic, pressure-explicit equations of state, the Redlich–Kwong, Peng–Robinson modified by Melhem et al., Trebble–Bishnoi and Jan–Tsai, were compared in predicting the inversion and spinodal curve loci for methane. As a result of these comparisons, the reliability ranges of these equations to predict the various derived properties were determined. The Trebble–Bishnoi predictions were reliable at reduced temperatures below 2.3, whereas the RK equation and the PR equation modified by Melhem et al. were reliable at reduced pressures below 9.5 and 10, respectively. The Jan–Tsai equation could not produce reliable predictions.

The spinodal loci were best predicted by the Trebble–Bishnoi equation and the PR equation modified by Melhem et al. The Redlich–Kwong equation produced fair predictions with a slight overestimate in the critical volume. The Jan–Tsai equation failed in predicting the spinodal locus of methane.

Appendix: The equations of state used and their derivatives

A1. Redlich–Kwong equation of state

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)}$$

$$\left(\frac{\partial P}{\partial T}\right)=\frac{R}{V-b}+\frac{a}{2T^{1.5}V(V+b)}$$

$$\left(\frac{\partial P}{\partial V}\right)=\frac{-RT}{(V-b)^2}+\frac{a(2V+b)}{T^{0.5}(V^2+bV)^2}$$

$$a=\frac{0.42748R^2T_C^{2.5}}{P_C}$$

$$b=\frac{0.08664RT_C}{P_C}$$

A2. Jan–Tsai equation of state

$$P=\frac{RT}{V-b}-\frac{a}{V^2+ubV+wb^2}$$

$$\left(\frac{\partial P}{\partial T}\right)=\frac{R}{V-b}-\frac{a'}{V^2+ubV+wb^2}$$

$$\left(\frac{\partial P}{\partial V}\right)=\frac{-RT}{(V-b)^2}+\frac{a(2V+ub)}{(V^2+ubV+wb^2)^2}$$

$$\alpha=[1+m_1\ln(T_r)]^2$$

$$\alpha'=\frac{2m_1}{T}[1+m_1\ln(T_r)]$$

$$m_1=-0.3936-0.6353\,\omega+0.1132\,\omega^2+0.07673/Z_C$$

$$a=a_C\alpha$$

$$a'=a_C\alpha'$$

$$a_c=\frac{\Omega_a R^2T_c^2}{P_c}$$

$$b=\frac{\Omega_b RT_c}{P_c}$$

$$\Omega_b=\frac{1-3\zeta_c}{u-1}$$

$$\Omega_a=3\zeta_c^2+(u-w)\Omega_b^2+u\Omega_b$$

$$\zeta_c=0.0889+0.750\,Z_c$$

$$u=\frac{2.277}{Z_c}-5.975$$

$$w=-u(\Omega_b+1)-\zeta_c^2\frac{3-\zeta_c/\Omega_b}{\Omega_b}$$

A3. *Trebble–Bishnoi equation of state*

$$P=\frac{RT}{V-b}-\frac{a}{V^2+[b+c]V-[bc+d^2]}$$

$$\left(\frac{\partial P}{\partial T}\right)=\frac{R}{V-b}+\frac{RTb'}{(V-b)^2}-\frac{a'}{V^2+[b+c]V-[bc+d^2]}$$
$$+\frac{ab'(V-c)}{(V^2+[b+c]V-[bc+d^2])^2}$$

$$\left(\frac{\partial P}{\partial V}\right)=\frac{-RT}{(V-b)^2}+\frac{a(2V+b+c)}{(V^2+[b+c]V-[bc+d^2])^2}$$

$$a=a_c\exp\left[q_1(1-T_r)\right]$$

$$b(T_r\leq 1.0)=b_c[1.0+q_2(1-T_r+\ln T_r)]$$

$$b(T_r>1.0)=b_c$$

$$a'=-a_cq_1\exp\left[q_1(1-T_r)\right]/T_c$$

$$b'(T_r\leq 1.0)=b_cq_2(-1/T_c+1/TT_c)$$

$$b'(T_r>1.0)=0.0$$

$$q_1(\mathrm{CH_4})=0.3322$$

$$q_2(\mathrm{CH_4})=0.1363$$

$$c=RT_c(1-3\zeta_c)/P_c$$

$$d/\mathrm{cm^3\,mol^{-1}}=0.341V_c/\mathrm{cm^3\,mol^{-1}}-5.0$$

$$Z_c^3-3\zeta_cZ_c^2+3Z_c\zeta_c^2-\zeta_c^3=0$$

$$C_c-1=-3\zeta_c$$

$$A_c-2B_cC_c-B_c-C_c-B_c^2-D_c^2=3\zeta_c^2$$

$$B_c^2C_c+B_cC_c-A_cB_c+D_c^2(B_c+1)=-(\zeta_c)^3$$

$$B_c^3+(2-3\zeta_c)B_c^2+3\zeta_c^2B_c-[D_c^2+\zeta_c^3]=0$$

$$D_c=dP_c/RT_c$$

$$a_c=A_cR^2T_c^2/P_c$$

$$b_c=B_cRT_c/P_c$$

A4. *Peng–Robinson equation of state modified by Melhem et al.*

$$P=\frac{RT}{V-b}-\frac{a\alpha}{V(V+b)+b(V-b)}$$

$$\left(\frac{\partial P}{\partial T}\right)=\frac{R}{V-b}-\frac{a\alpha'}{V(V+b)+b(V-b)}$$

$$\left(\frac{\partial P}{\partial V}\right)=\frac{-RT}{(V-b)^2}+\frac{2a\alpha(V+b)}{[V(V+b)+b(V-b)]^2}$$

$$\ln\alpha=m[1-T_r]+n[1-\sqrt{T_r}]^2$$

$$\alpha'=[(n-m)/T_c-n/\sqrt{TT_c}]\alpha$$

$$m(CH_4)=0.4045$$

$$n(CH_4)=0.1799$$

$$a=\frac{0.45724R^2T_c^2}{P_c}$$

$$b=\frac{0.07780RT_c}{P_c}$$

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