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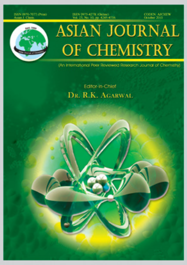

Joule-Thomson Inversion Curves Calculation by Using Equation of State

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Since the prediction of the Joule-Thomson inversion curve is known as a sever test of the equations of state (EoS). Some cubic equations of state (CEoS) can eventually have inadequate prediction for checking their ability to calculate the Joule-Thomson inversion curve. In this paper the Joule-Thomson inversion curve has been used to test the predictive capabilities of some recent equations of state. This enables us to judge the accuracy of the results obtained from different equations of state. These five equations of state are: Wang-Gmehling (WG) equations of state, modified Peng-Robinson by Twu-Coon-Cunningham (PR-TCC) equations of state, Riazi-Mansoori (RM) equations of state, Geana equations of state and modified Peng- Robinson-Stryjek-Vera proposed by Samir I. Abu-Eishah (PRSV2) equations of state. All of these equations of state are modified van der Waals (vdW) equations of state recommended in the literature for estimating volumetric properties of relevant compounds. As a corollary to the present study, we have perceived that the investigated equations of state give good prediction of the low-temperature branch of the inversion curve, except for Riazi-Mansoori and Geana equations of state. We also calculated maximum inversion temperature and maximum inversion pressure for every component used in this work.

Key Words: Equation of state, Joule-Thomson coefficient, Inversion curve.

INTRODUCTION

Any mathematical relationship between the fluid's pressure, volume and temperature is commonly called as equation of state[1]. It is therefore hardly surprising that an ability to predict accurately such equations of state and with a minimum of empiricism has been received conspicuous attentions in engineering applications[2,3]. Additionally, an ability to understand equations of state on purely molecular level[4-8], by means of some information on intermolecular potentials and the tools of equilibrium statistical mechanics, was a challenge posed of over a century ago which had been initiated by van der Waals. It also signifies that one could claim some reasonable measure of understanding of at least both the equilibrium and transport properties of gases[9-11].

The Joule-Thomson effect is of interest not only to scientists[12,13] because of its relationship to the potential function[14], but also to engineers[6,15-21] for some of its aspects such as the Linde process for liquefaction of gases and its relevance to the transport of natural gases and other hydrocarbon fluids through pipeline in arctic regions. On the other hand, the Joule-Thomson coefficients have been used for the determination of interaction potentials, though the potential parameters determined by the equilibrium properties (such as Joule-Thomson coefficients) are slightly different by those determined by non-equilibrium properties (such as viscosity). In the Joule-Thomson experiment the gas was throttled through the plug separating a thermally insulated vessel into two parts stopped up from both sides by movable plungers. If a gas in a vessel 1 at temperature T1 and pressure P1 expands slowly through a valve or porous plug into another vessel 2 where its pressure P2 < P1, one observes a temperature change, which can be positive, negative, or vanish depending on the experimental conditions. This phenomena, is known as Joule-Thomson effect. Henceforth, to pass a fluid through a porous plug is always accompanied by a decrease in pressure and a change in temperature. In an adiabatic process, the quantification of the phenomena is measured as the derivative of the temperature in relation to the pressure at constant enthalpy and is called the adiabatic Joule-Thomson effect (μ)[22-23].

$$\mu = \left(\frac{\delta T}{\delta P}\right)_H \quad (1)$$

Under appropriate conditions, adiabatic throttling of gas will cause it to lower its temperature, an endothermic effect that may be strong enough even to induce condensation[24]. For this cooling to take place, the thermodynamic state of the fluid must lie in the region bounded by the inversion curve or locus of points in which the Joule-Thomson coefficient (μ) is zero[25]. The experimental determination of inversion curves requires very precise measurement of volumetric properties at conditions up to five times its critical temperature and twelve times its critical pressure[24]. These serious experimental conditions have hindered the publication of data for even simple fluids and mixtures. Most of available data cover only the low -temperature branch of the inversion curve. This lack of experimental data is particularly troubling to theoreticians since the prediction of inversion curves is a particularly severe test of any equations of state. To date, inversion curves have been calculated for several equations of state[5,26-31]. Several studies have been performed to predict Joule-Thomson inversion curves for gas mixtures. Gunn *et al.*[32] were first to calculate inversion temperatures and pressures for cryogenic gases and their mixtures. Wisnaik[33] studied the Joule-Thomson inversion curves for gas mixtures. Moreover, Vrabec *et al.*,[34] predicted Joule-Thomson inversion curves for pure fluids and one mixture by molecular simulation. Nichita and Leibivici[35] calculated the Joule-Thomson inversion curves for two-phase mixtures. Colina *et al.*[7] used a molecular based equations of state, named as Statistical Association Fluid Theory (SAFT) equations of state, to predict complete Joule-Thomson inversion curves for carbon dioxide and the *n*-alkane series, including higher *n*-alkanes up to octatetracontane, $n-C_{48}H_{98}$. It should also be mentioned that they used the Soft-SAFT equations of state. Recently, Maghari *et al.*[36] predicted the Joule-Thomson inversion curves for polar and non-polar fluids from the cubic plus SAFT equations of state (SAFT-CP). Moreover, several studies have been recently performed to predict Joule-Thomson inversion curve[37]. There is a vast range of studies focused on the Joule-Thomson inversion curve[38]. In their first work, they have predicted the attractive branch of the effective pair interaction potential energy function by using the Joule-Thomson inversion curve[39]. Since, the prediction of Joule-Thomson inversion curve is known as a criterion to assess and rank the capabilities of the equations of state, so the performance of some equations of state is considered.

EXPERIMENTAL

By using the exact differential form of the enthalpy:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{2}$$

for an isenthalpic process (dH=0), eqn. (1) can be written in several alternative forms. We have from eqn. (1):

$$\mu = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{c_P} \tag{3}$$

Also, it is possible to write dH as

$$dH = TdS + VdP \tag{4}$$

We obtain another expression by differentiation with respect to P:

$$\left(\frac{\partial H}{\partial P}\right)_T = V + T\left(\frac{\partial S}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{5}$$

The Maxwell relationship have used in the latest equality. Now, eqn. (3) can be written as:

$$\mu = \frac{1}{c_P}[T(\frac{\partial V}{\partial T})_P - V] = \frac{V}{c_P}[T\alpha - 1] \tag{6}$$

where, α is the isobaric thermal (or cubic) expansion coefficient and has its usual definition. By combination of the following equation:

$$(\frac{\partial V}{\partial T})_P = -\frac{(\frac{\partial P}{\partial T})_V}{(\frac{\partial P}{\partial V})_T} \tag{7}$$

with eqn. (6) in conjunction to the inversion condition, $\mu = 0$, the most commonly used form of the Joule-Thomson inversion curve is obtained as:

$$T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T = 0 \tag{8}$$

By introducing the reduced volume, temperature and pressure in the aforesaid equation one can find the following equation in terms of the reduced variables:

$$T_r\left(\frac{\partial P_r}{\partial T_r}\right)_{V_r} + V_r\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = 0 \tag{9}$$

where $T_r \equiv T/T_c$, $P_r \equiv P/P_c$ and $V_r \equiv V/V_c$ are reduced temperature, reduced pressure and reduced volume, respectively. The locus of points at which the Joule-Thomson coefficient (μ) is zero is called the inversion curve. The inversion condition,$\mu = 0$ is given by the aforementioned equation[23,24]. When one equates the aforesaid equation simultaneously with any arbitrary equation of state, one can provide the locus of points for which the Joule-Thomson coefficient is zero[24]. The method of calculation is not horrendously complicated: given an equations of state on the one hand and estimating the derivatives, such as $\left(\frac{\partial P_r}{\partial T_r}\right)_{V_r}$ and $\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r}$. From this equations of state on the other hand, it is possible to show that eqn. (9) can be written as $f(T_r,V_r) = 0$. Consequently, for any chosen reduced volume, V_r the reduced inversion temperature, T_r can be found and then the reduced inversion pressure (P_r) can be calculated from the equations of state. However, the inversion curve can be obtained in terms of T_r and P_r. The maximum inversion temperature can also be found when P_r tends toward zero. In this work, we employ five different equations of state to predict the inversion curve of some fluids. The equations of state used in this work have been shown in appendix A (Can be had from authors on request).

RESULTS AND DISCUSSION

All of the calculated inversion curves are monotonous and show the pronounced humps. The figures show the prediction of the Joule-Thomson inversion curve for commonly used equations of state in the chemical and oil industry. The requested parameters of the equations of state were taken from the proposed papers. The calculated Joule-Thomson inversion curves from various equations of state are shown in Figs.1-5, for Ar, CO_2, CH_4, C_2H_6, C_3H_8, respectively. When examined for the ability to predict Joule-Thomson inversion curves, we can perform more commonly used equations of state which leads to the following conclusions:

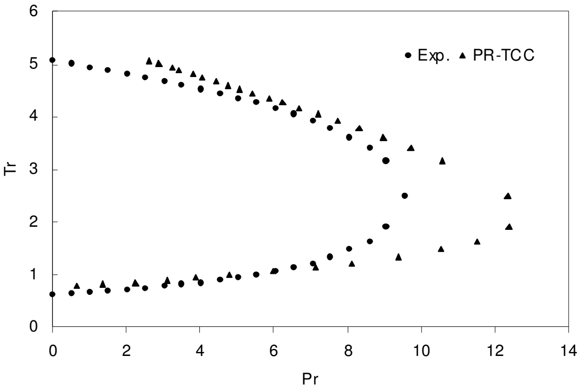

Fig. 1. Joule-Thomson inversion curves for Argon.

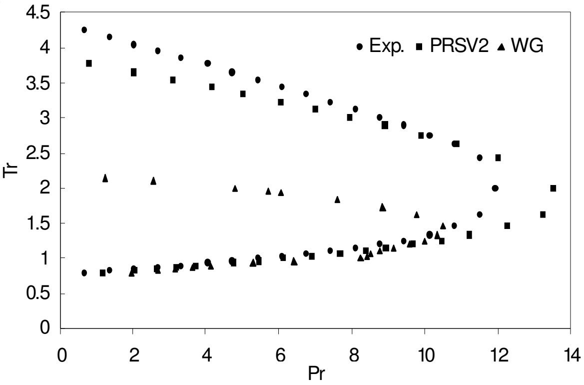

Fig. 2. Joule-Thomson inversion curves for CO_2.

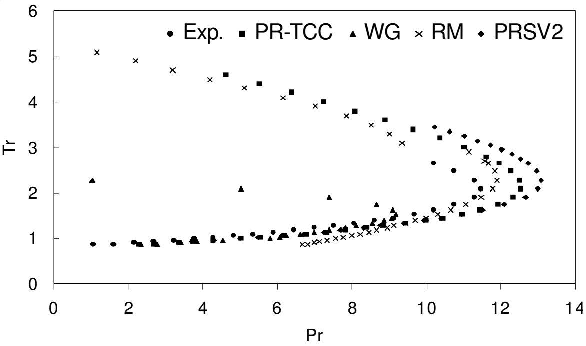

Fig. 3. Joule-Thomson inversion curves for CH_4.

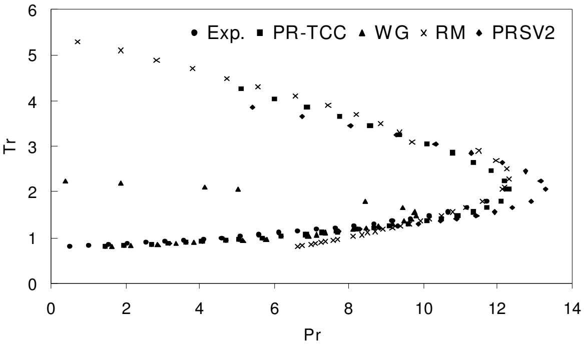

Fig. 4. Joule-Thomson inversion curves for C_2H_6

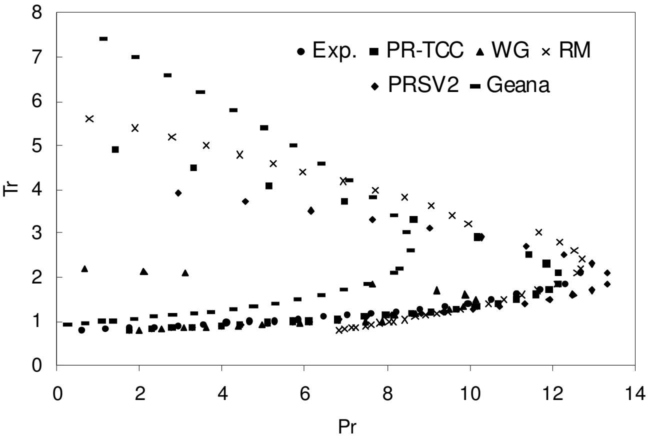

Fig. 5. Joule-Thomson inversion curves for C_3H_8

(1) All of the equations of state show the well-matched inversion curves in comparison with experimental data at low temperatures, except Riazi-Mansoori (RM) equations of state[38].

(2) The inversion curve predicted by Wang-Gmehling equations of state[39,40] does not agree with experimental data[41] in the vicinity of the maximum inversion pressure. The maximum inversion pressure is considerably less than the reference values for all fluids considered in present work. The predicted inversion temperatures are below the reference values especially at high temperatures for CO_2 and CH_4.

(3) The inversion curve predicted by modified Peng-Robinson by Twu-Coon-Cunningham equations of state[42] shows good predictions at low temperatures. The low-temperature region of the inversion curve is well matched by Peng-Robinson by Twu-Coon-Cunningham equation of state for hydrocarbons. Therefore, the Peng-Robinson by Twu-Coon-Cunningham equation can safely be considered as a reference for the evaluation of the low-temperature inversion curve predicted by the other equations of state. At high-temperature part and at the peak of the curves Peng-Robinson by Twu-Coon-Cunningham equations of state gives good predictions for hydrocarbons.

(4) The inversion locus predicted by the Riazi-Mansoori equations of state does not agree with the experimental data. The deviation of Riazi-Mansoori equations of state predictions from experimental data occurs at reduced pressure below 6 for hydrocarbons. The peak of the inversion curve is matched by Riazi-Mansoori equations of state.

(5) The inversion locus predicted by the Geana equations of state [43,44] does not agree with experimental data in any region. The predicted inversion temperatures are above the reference values especially at high temperatures for propane. The maximum inversion pressure is considerably less than the reference values. Therefore, the weakness of this equation cannot be set within reliable limits of operating conditions.

(6) The inversion curve predicted by the modified Peng-Robinson-Stryjek-Vera (RRSV2) equations of state[45] is as same as predicted by Peng-Robinson by Twu-Coon-Cunningham equations of state.

The aforesaid categorized items show that the problem of obtaining the Joule-Thomson inversion coefficients is a severe test of the capability of equations of state in cooling processes.

This, in turn, permits us to consider the ability of the equations of state more accurately than is possible by usual application of them. Albeit, there is some comments about the unnoticed pitfalls of Soave-type α-functions in equations of state[46,47]. Henceforth, this model implements discontinuity in α-function and as a result discontinuity in predicting heat capacities[47]. It should also be mentioned that Nasrifar and Bolland have introduced a new Soave-type α-function based on the square-well potential mode[48]. Nonetheless, our results show that the Joule-Thomson inversion curves serve as stringent test of the ability of utilized equations of state in cooling processes and related phenomena. The maximum inversion pressure, $P_{r,max}$ and the corresponding temperature, $T_{r,i}$ for the five equations are calculated and given in Table-1. The maximum inversion temperature, $T_{r,max}$ - the temperature below which cooling will take place as result of Joule-Thomson expansion is zero- is obtained in the ideal gas limit($P_r \rightarrow 0$) and also calculated and shown in Table-1.

TABLE-1
The calculated maximum inversion pressures P_{rmax} the corresponding temperature $T_{r,i}$ and maximum inversion temperature $T_{r,max}$

Equation of $T_{r,max}$ state	Component	$P_{r,max}$	$T_{r,i}$#	$T_{r,max}$
WG	Methane	9.1867	1.53	2.3156
	Ethane	9.8089	1.48	2.2551
	Propane	10.1559	1.49	2.2151
	Carbon Dioxide	10.5175	1.33	2.2177
PR-TCC	Argon	12.3260	2.49	5.5404
	Methane	10.9165	1.79	4.0524
	Ethane	12.3119	2.05	5.2580
	Propane	12.148	1.85	5.1104
RM	Methane	11.8991	2.29	5.2515
	Ethane	12.3175	2.3	5.3591
	Propane	12.717	2.4	5.6833
Geana	Propane	8.5725	2.6	7.6154
PRSV2	Methane	13.0905	2.29	5.2569
	Ethane	13.2637	2.05	4.5245
	Propane	13.3041	1.85	4.1985
	Carbon Dioxide	13.5442	1.998	3.8144

The number of significant figures are exactly adopted from their reference values[43]

Conclusion

Albeit, all of the equations of state are modified van der Waals (vdW) equations of state but their outcomes show small deviation between the calculated and experimental data of the Joule-Thomson inversion curves. The results resemble that most of the equations of state are more or less desirable for low temperatures. For higher temperatures they usually fail. To our best of opinion, this underlines the non- appropriateness of some of the worked out cubic equations of state for predicting Joule-Thomson inversion curves. Hence, the procedure suggested here provides a very easy mathematical method for comparison the ability of different equations of state for predicting Joule-Thomson inversion curves.

The maximum inversion temperature and the peak of the inversion curve is sensitive to the nature of the equations of state and different from one equations of state to another. Comparison of Joule-Thomson inversion curves predicted by five cubic equations of state reveals that all of them nearly give good prediction of the low-temperature region of the inversion curve. Therefore, all five equations of state can be safely considered as a reference for the evaluation of low-temperature inversion curves. For all calculations and experimental data, the results are compared with the Joule-Thomson inversion curves of non-associating fluids. This is because van der Waals type equations of state are fundamentally valid only for non-associating fluids. It is obvious that in order to apply equations of state for associating fluids they must be combined with an association theory which is out of the scope of this work.

Abbreviations:

EoS = Equation of State
WG = Wang-Gmehling
PR-TCC = Peng-Robinson- Twu-Coon- Cunningham
RM = Riazi-Mansoori
PRSV2 = Peng-Robinson- Stryjek-Vera

Symbols:

a = attraction term
b = van der Waals co-volume
c = Equation of state parameter
d = Equation of state parameter
m = Equation of state parameter
B_1, B_2 = WG EOS parameters
P = Absolute pressure
R = Universal gas constant
T = Absolute temperature
V = Volume

Greek symbols:

α = Equation of state parameter
μ = Joule-Thomson coefficient
ε = Acentric factor

Subscripts:

c = Critical state variable
H = Constant enthalpy
r = Reduced state variable

Reduced state variables:

$T_r = T/T_c$
$P_r = P/P_c$

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