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Application of modified Tao-Mason equation of state to refrigerant mixtures

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Abstract−In our previous work, we modified the Tao-Mason EOS [1] to predict the volumetric properties of pure refrigerants [2]. In the present study, we have successfully extended the modified Tao-Mason EOS to refrigerant mixtures. The second virial coefficient, $B_2(T)$, and the temperature-dependent correction factor $\alpha(T)$ and van der Waals co-volume b(T) were calculated from a two-parameter corresponding-states correlation along with the enthalpy of vaporization and the molar density, both at the normal boiling point. Then the cross parameters $B_{12}(T)$, $\alpha_{12}(T)$, and $b_{12}(T)$, were determined with the help of simple combining rules. The constructed Tao-Mason EOS was employed to predict the densities and vapor pressures of several HFC, hydrocarbons and HFO mixtures. The calculated results were compared with literature data. The overall agreement between our results and literature values is remarkable.

Keywords: Refrigerant, Mixtures, Equation of State, Volumetric Properties, Corresponding States Principle

INTRODUCTION

Over the past three decades there has been an increasing interest in the use of pure and mixed refrigerants as working fluids in heat pump, refrigerating, air conditioning applications and in the geothermal power industry. They play a legitimate role in energy security, economic development and environment protection. Reliable information about the thermodynamic properties of refrigerants is essential for their application as a working fluid in the industry systems. Hydrocarbon refrigerants are natural, flammable, and nontoxic refrigerants that have advantages, including zero ozone depletion potential, very low global warming potential, excellent thermodynamic properties, leading to high energy efficiency, good compatibility with components, and low charges allowing smaller heat exchangers and piping dimensions.

HFO-1234ze (1,3,3,3-tetrafluoropropene) can widely be used for all kinds of air conditioners and refrigerators as a new generation of refrigerant. Accurate knowledge and the prediction of the thermo-physical properties of pure refrigerants and mixtures containing hydrofluorocarbons (HFCs), which are proposed as alternative refrigerants, is of great importance to evaluate the performance of refrigeration cycles and to determine the optimum composition of new working fluids. The development of models for the representation and prediction of thermophysical properties including phase equilibria as well as the improvement of current equations of state is of particular interest for the refrigeration industry [3-7].

Many researchers have pointed out the need for accurate thermophysical properties and models. Models are especially needed for refrigerant mixtures because of the limited number of experimental studies which have been reported.

In recent years, the thermodynamic properties of refrigerants and refrigerant mixtures have been investigated by several researchers [2,8-21]. Transport properties of this class of fluids have also been studied extensively [22-27]. Despite drawbacks, two of the equations of state employed for predicting the thermal properties of the pure refrigerants and their mixtures have been the ISM (Ihm-Song-Mason [28]) and original Tao-Mason EOS [2,8,9,29-31].

In this paper, we discuss the density prediction of five mixtures of refrigerants, three mixtures of hydrocarbons and one mixture of HFO presenting a modified Tao-Mason EOS for mixtures. Then this new model was employed to obtain vapor pressures of four mixtures consisting of R32+R1234yf, R32+HFO-1234ze(E), CO_2+HFO-1234yf and CO_2+HFO-1234ze(E). The modified Tao and Mason EOS, mentioned at the beginning where Tao-Mason EOS is introduced, was extended to predict the densities of both the liquid and gas phases of nine refrigerant mixtures. The results were compared with the original Tao-Mason EOS [1], ISM [28], and Peng-Robinson (PR) [32] equations of state, as well as with experimental data. The studied binary mixtures are R32+R125, R32+R134a, R125+R143a, R125+R134a, R32+R227ea, Propane+n-Butane, Propane+Isobutane, Butane+Isobutane and HFO-1234ze+CO_2 Our results show that using the modified model the molar gas and liquid densities of the studied refrigerant mixtures can be predicted to within 1.4% and 2.3%, respectively, over the temperature range of T=280-440 K and the pressure range of p=0.33-76 bar.

THEORY

1. Tao-Mason Equation of State

In 1994, Tao and Mason introduced a perturbation correction term for the effect of attractive forces and combined it with the ISM EOS [28] to present an improved equation of state (Tao-Mason

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EOS) [1]. The final form of the Tao-Mason EOS for single substances is given by:

$$\frac{p}{\rho kT}=1+(B_2-\alpha)\rho+\frac{\alpha\rho}{(1-\lambda b\rho)}+A_1(\alpha-B_2)b\rho^2\frac{\left(\exp\left(\kappa\frac{T_c}{T}\right)-A_2\right)}{(1+1.8(b\rho)^4)} \quad (1)$$

$$A_1=0.143$$

and

$$A_2=1.64+2.65[\exp(\kappa-1.093)-1], \quad (2)$$

with

$$\kappa=1.093+0.26[(\omega+0.002)^{1/2}+4.50(\omega+0.002)] \quad (3)$$

In Eq. (1), λ is an adjustable parameter, ρ is the molar density, T_c is the critical temperature, kT is the product of the Boltzmann constant, k, and the temperature, T, B_2 is the second virial coefficient, α is the scaling parameter, and b is the effective van der Waals covolume. In Eq. (3), ω is the Pitzer acentric factor. B_2, α and b parameters can be calculated from corresponding-states correlations [1, 31,33-39].

In the present investigation, we have modified the original Tao-Mason EOS to describe volumetric properties of both the liquid and gas phases of refrigerant mixtures. The remaining problem now is to find λ. We obtained λ from PVT data for pure substances at their normal boiling points. When the temperature-dependent parameters together with the values of λ are known, the entire Tao-Mason EOS can be predicted.

2. Extension of the Tao-Mason Equation of State to Mixtures

Accuracy in the prediction of properties of mixtures is one of the major concerns in scientific research and engineering applications [1,7,28]. The mixture version of Tao-Mason EOS can be read as

$$\frac{p}{\rho kT}=1+\rho\sum_i\sum_j x_i x_j(B_{ij}-\alpha_{ij})+\rho\sum_i\sum_j x_i x_j G_{ij}+\rho\sum_i\sum_j x_i x_j (I_1)_{ij} \quad (4)$$

where ρ is the molar density, x_i and x_j are mole fractions. The interaction parameters B_{ij} and α_{ij} for i≠j correspond to the values for a hypothetical single substance whose molecules interact according to a pairwise ij potential. G_{ij} is the pair distribution function at contact for real mixtures. The packing fraction of mixtures of hard-spheres is η, which is defined by the following expression:

$$\eta=\left(\frac{\rho}{4}\right)\sum_k x_k b_k. \quad (5)$$

Now the remaining problem is how to estimate the parameters G_{ij} and $(I_1)_{ij}$. The behavior of G_{ij} has been given by Ihm et al. [40] as

$$G_{ij}=\frac{1}{(1-\eta)}+\left(\frac{b_i b_j}{b_{ij}}\right)^{1/3}\frac{\rho\sum_k x_k b_k^{2/3}\left(\lambda_k-\frac{1}{4}\right)}{(1-\eta)\left(1-\rho\sum_k x_k b_k\lambda_k\right)}, \quad (6)$$

where the subscript k runs over number of fluids. $(I_1)_{ij}$ can be determined by

$$(I_1)_{ij}=\xi_{mix}(T)\,\Phi_{mix}(\rho b_{ij})\sum_{ij}(\alpha_{ij}-B_{ij}). \quad (7)$$

Tao and Mason [1] proposed that $\Phi_{mix}(\rho b_{ij})$ and $\xi_{mix}(T)$ could be approximated as

$$\Phi_{mix}(\rho b_{ij})\approx\frac{\rho\sum_k x_k b_k}{1+1.8\,\eta^4\left(\sum_k x_k b_k\right)^4}, \quad (8)$$

where

$$\xi_{mix}(T)\approx 0.143\left[\exp\left(\frac{\kappa_{mix}T_{c,\,mix}}{T}\right)-1.64\right], \quad (9)$$

$$\kappa_{mix}=\sum_k x_k\kappa_k, \quad (10)$$

$$A_{2,\,mix}=1.64+2.65[\exp(\kappa_{mix}-1.093)-1], \quad (11)$$

and

$$T_{c,\,mix}=\sum_k x_k T_{c,\,k}, \quad (12)$$

with $T_{c,\,mix}$ as the traditional pseudo-critical temperature. Now, the problem is restricted to the determination of the interaction parameters B_{ij}, α_{ij}, and b_{ij}. In principle, they can be calculated from a known ij pair potential energy [41]. This problem will be addressed in the forthcoming sections.

3. Parameter Estimation

In the present study, we have predicted the second virial coefficient using a model proposed by Sheikh et al. [31]:

$$B(T)\rho_{nb}=0.1-0.054\left(\frac{\Delta H_{vap}}{RT}\right)^2-0.00028\left(\frac{\Delta H_{vap}}{RT}\right)^4. \quad (13)$$

Here, R is the molar gas constant (8.3144621 J/mol·K [42]); hereafter, we refer to this equation as the SPB correlation. In principle, B_{ij} can be extracted from measurements of the second virial coefficient of i+j mixtures. Then α_{ij} and b_{ij} can be calculated by scaling rules. In the previous study, we also found that $\alpha_{ij}(\rho_{nb})_{ij}$ and $b_{ij}(\rho_{nb})_{ij}$ are universal functions of the reduced temperatures $\Delta H_{vap}/RT$ [2]. Therefore, these parameters in the Tao-Mason EOS have been formulated by a pair of simple equations using the heat of vaporization ΔH_{vap} and the molar density (ρ_{nb}) both at normal boiling point

Table 1. Parameters for ten refrigerants

Refrigerant	T_c (K)	$\Delta H_{vap}/R$ (K)	ρ_{nb} (mol·dm^{-3})
R32	351.255[a]	2490.14	23.315[a]
R143a	345.857[a]	2329.80	13.879[a]
R134a	374.210[a]	2737.91	13.493[a]
R125	339.173[a]	2383.93	12.611[a]
R227ea	375.950[a]	2709.04	9.072[a]
Propane	369.825[a]	2290.11	13.174[a]
Butane	425.125[a]	2695.45	10.345[a]
Isobutane	407.810[a]	2561.94	10.217[a]
CO_2	304.128[a]	3023.48	28.60[b]
HFO-1234ze	382.510[c]	2558.00	11.342[c]

[a] From Ref. [56]

[b] Determined by the extrapolation method

[c] From Ref. [57,58]

as scaling parameters. The input parameters of the Tao-Mason EOS for pure studied refrigerants are listed in Table 1. The predictive schemes outlined by Papari et al. [2] (Eqs. (5) and (6)) were employed to predict the pure parameters of α_{ij} and b_{ij}. We found that the values of the mixture parameters can also be calculated from the following equations:

$$\alpha_{ij}(\rho_{nb})_{ij} = \frac{1}{a_1 + b_1\left(\frac{T}{\frac{(\Delta H_{vap})_{ij}}{R}}\right)^{c_1-1}} \tag{14}$$

$$b_{ij}(\rho_{nb})_{ij} = \frac{1}{a_2 + b_2\left(\frac{T}{\frac{(\Delta H_{vap})_{ij}}{R}}\right)^{c_2-1}}, \tag{15}$$

where

$$(\rho_{nb})_{ij}^{\frac{-1}{3}} = \frac{1}{2}\left[(\rho_{nb})_{ii}^{\frac{-1}{3}} + (\rho_{nb})_{j}^{\frac{-1}{3}}\right] \tag{16}$$

and

$$(\Delta H_{vap})_{ij} = [(\Delta H_{vap})_i(\Delta H_{vap})_j]^{1/2}. \tag{17}$$

Here the scaling parameters are the heat of vaporization (ΔH_{vap}) and the molar density (ρ_{nb}), both at normal boiling point. The coefficients in the equations above are $a_1=-0.1053$, $a_2=2.9359$, $b_1=0.2875$, $b_2=0.4155$, $c_1=5.7862$, and $c_2=0.7966$. In addition, we set κ_{mix} equal to 1.093 in the EOS and the parameter λ was correlated by the following simple equation using high density PVT data (e.g., liquid densities):

$$\lambda = a + bT + cT^2 + dT^3 + eT^4 \tag{18}$$

The constants a, b, c, d and e for each pure refrigerant studied in this work are listed in Table 2.

RESULTS AND DISCUSSION

The goal of the present study was to modify the Tao-Mason EOS and thereafter examine the capability of the modified Tao-Mason EOS in predicting volumetric properties and vapor pressures of refrigerant mixtures in a wide range of temperature and pressure. In this respect, we adopted the macroscopic corresponding states principle for the second virial coefficient, which has been already proposed by Sheikh et al. [31] (i.e., SPB correlation), instead of the Tsonopolous correlation [43] used by Tao and Mason in their original work [1]. The benefit of this replacement is as follows. The scaling parameters in the SPB correlation are the heat of vaporization and the molar density, both at normal boiling point. These parameters are easier to measure than the critical parameters and consequently are more accessible. Additionally, the number of input parameters in the Tsonopolous correlation [43] is three (critical temperature, critical pressure, and acentric factor), whereas in the SPB correlation the number of input parameters is reduced to two (heat of vaporization and molar density). This modification is of vital importance for practical engineering applications. A technique must be devised to obtain pure component parameters for use in the equation of state before mixing and combining rules are applied. Now the parameters α_{ij} and b_{ij} can be determined by using mixing and combining rules.

The values of λ given in the Eq. (18) were found empirically from the PVT data of dense pure components. This method makes the whole procedure self-correcting, because if the input values of ΔH_{vap} and ρ_{nb} are not accurate, the effect will be largely compensated in the determination of λ. Furthermore, we found that κ in Eq. (3) is a weak function of the acentric factor so that we can approximate κ to 1.093. In light of this, A_{2mix} was modified and approximated to the value of 1.64. Note that the scaling parameter ΔH_{vap} at normal boiling point, needed in SPB correlation, is calculated using vapor pressure equations cited in the literature along with the Clasius-Clapeyron equation:

$$\frac{\partial \ln P}{\partial T} = \frac{\Delta H_{vap}}{RT^2} \tag{19}$$

To calculate ρ_{nb}, we used the saturated liquid densities reported in literature and calculated ρ_{nb} of carbon dioxide determined by the extrapolation method. After constructing the EOS, we calculated densities at single and two-phase regions and made a comprehensive comparison with experimental data over a vast range of temperatures, pressures, and compositions for several refrigerant, hydrocarbons, and HFO mixtures. It is well believed that either a binary

Table 2. Coefficients of Eq. (18)

Refrigerant	a	b	c	d	e
R32	1.844×10^{-5}	5.316×10^{-3}	-2.813×10^{-5}	6.601×10^{-8}	-5.864×10^{-11}
R143a	6.675×10^{-6}	7.111×10^{-3}	-3.729×10^{-5}	9.104×10^{-8}	-8.899×10^{-11}
R134a	1.126×10^{-5}	4.568×10^{-3}	-2.080×10^{-5}	4.146×10^{-8}	-3.057×10^{-11}
R125	2.430×10^{-6}	4.711×10^{-3}	-2.201×10^{-5}	4.223×10^{-8}	-2.796×10^{-11}
R227ea	1.536×10^{-1}	4.778×10^{-3}	-2.609×10^{-5}	6.541×10^{-8}	-7.418×10^{-11}
Propane	-4.327×10^{-1}	1.220×10^{-2}	-6.980×10^{-5}	1.750×10^{-7}	-1.700×10^{-10}
Butane	4.945×10^{-1}	-2.463×10^{-3}	1.58×10^{-5}	-4.242×10^{-8}	3.800×10^{-11}
Isobutane	5.097×10^{-1}	-2.76×10^{-3}	1.800×10^{-5}	-5.00×10^{-8}	4.640×10^{-11}
CO_2	4.050×10^{-16}	-7.122×10^{-4}	1.880×10^{-6}	2.690×10^{-8}	-1.736×10^{-11}
HFO-1234ze	2.200×10^{-16}	2.80×10^{-3}	-4.920×10^{-6}	-8.170×10^{-9}	2.070×10^{-11}

or a ternary refrigerant mixture composed of R32, R125, and/or R134a would be the optimum candidate to replace R22 [30,44], which is currently being used in air-conditioning and heat-pumping equipment but is expected to be phased out by the year 2020. Five data sets on vapor and liquid density of R32 and R125 mixtures were taken from the literature [45-49]. The results of the calculations of the gaseous and liquid densities for this mixture together with the temperatures, mixture compositions, and numbers of data points are summarized in Tables 3 and 4. It is a matter of considerable practical importance to compare the present EOS with other equations of state. In this respect, we have compared our results for this mixture with those obtained using three equations of state including the Peng-Robinson (PR) [32], original Tao-Mason [1] and ISM [28,29] equations of state. The results of the comparisons for R125+R32 mixtures in gas and liquid phase are in Tables 3 and 4, respectively. As is clear from Table 4, in most cases, the accuracy of the calculated densities using the modified Tao-Mason EOS in the liquid phase is superior with respect to those calculated from the original TM, PR, and ISM equations of state. We also extended our calculations to other binary mixtures of refrigerants. The binary mixture R32+R134a has zero ozone-depletion potential (ODP). Because of its flammable characteristics, however, R32 is not considered as a suitable working fluid for air-conditioning systems. The mixture of R32 with a nonflammable refrigerant, such as R134a, therefore, might overcome this drawback for practical applications. Tables 5 and 6 list average absolute deviations (AAD) of the calculated gaseous and liquid densities for this mixture using the modified TM, original TM, PR and ISM equations of state from the experimental ones [50]. It is evident that the average values of density

Table 3. Prediction of the saturated gas densities of R32+R125 mixtures at various temperatures and compositions

T(K)	X_{R32}	^{a}NP	AAD (%) density				Refs.
			^{b}TM (M)	TM	PR	ISM	
380	0.5001	11	0.89	0.56	0.72	2.71	[47]
370	0.5001	7	1.50	1.00	1.12	0.91	[47]
360	0.5001	7	1.80	1.28	1.07	0.29	[47]
350	0.5001	7	2.12	1.62	0.94	0.07	[47]
380	0.6977	10	1.64	1.32	0.54	0.00	[47]
360	0.6977	8	2.42	2.30	0.64	0.04	[47]
340	0.6977	8	3.56	3.10	0.30	0.00	[47]
320	0.6977	7	3.27	3.11	0.55	0.05	[47]
373.15	0.5456	6	1.54	0. 98	1.28	0.06	[45]
353.15	0.5456	6	2.13	1.47	1.25	0.22	[45]
338.15	0.5456	5	3.28	2.54	1.25	0.02	[45]
373.15	0.4320	13	0.63	0.45	0.68	2.20	[51]
353.15	0.4320	8	1.35	1.00	0.95	0.54	[51]
323.15	0.4320	8	2.26	1.78	0.37	0.07	[51]
373.15	0.5794	13	0.82	0.68	0.56	0.04	[51]
353.15	0.5794	8	1.67	1.42	0.73	0.03	[51]
323.15	0.5794	8	2.59	2.40	0.18	0.22	[51]
373.15	0.8191	12	1.16	1.07	0.25	0.01	[51]
353.15	0.8191	8	2.10	1.90	0.19	1.65	[51]
323.15	0.8191	8	2.64	2.80	0.48	0.04	[51]
330	0.36708	4	4.80	3.40	2.03	0.26	[48]
350	0.36708	4	3.25	1.89	2.58	0.27	[48]
370	0.36708	4	2.30	1.02	2.51	0.23	[48]
400	0.36708	4	1.28	0.43	2.10	0.24	[48]
420	0.36708	4	0.74	0.47	1.80	0.13	[48]
440	0.36708	4	0.27	0.73	1.50	0.87	[48]
340	0.60576	4	5.69	4.70	1.04	0.64	[48]
360	0.60576	4	4.19	3.25	1.57	0.65	[48]
380	0.60576	4	3.18	2.28	1.62	0.60	[48]
400	0.60576	4	2.37	1.50	1.51	0.43	[48]
420	0.60576	4	1.70	0.92	1.30	0.39	[48]
440	0.60576	4	1.30	0.42	1.12	0.12	[48]

[a] NP represents the number of data points examined
[b] M stands for "modified"

Table 4. Prediction of the saturated liquid densities of R32+R125 mixtures at various temperatures and compositions

T (K)	X_{R32}	^{a}NP	AAD (%) density				Refs.
			^{b}TM (M)	TM	PR	ISM	
294.68	0.7	3	1.40	1.54	8.50	9.64	[46]
313.57	0.7	3	1.67	4.55	11.47	11.26	[46]
333.55	0.7	3	4.32	5.62	17.02	9.15	[46]
294.95	0.9	3	2.22	1.82	11.37	10.29	[46]
313.84	0.9	3	0.96	0.69	13.93	12.47	[46]
333.76	0.9	3	2.48	3.79	18.81	12.51	[46]

[a] NP represents the number of data points examined
[b] M stands for "modified"

Table 5. Prediction of the gas densities of R32+R134a mixtures at various pressures and temperatures and fixed compositions

T (K)	X_{R32}	^{a}NP	AAD (%) density				Refs.
			^{b}TM (M)	TM	PR	ISM	
373.15	0.5084	6	1.51	0.86	1.26	1.68	[45]
353.15	0.5084	6	2.25	0.88	1.02	2.36	[45]
338.15	0.5084	5	1.50	1.44	0.27	1.25	[45]
360	0.39534	4	4.60	1.90	0.12	3.87	[53]
380	0.39534	4	3.00	1.29	0.85	2.05	[53]
400	0.39534	4	2.15	0.99	0.95	0.95	[53]
420	0.39534	4	1.14	0.91	0.92	0.85	[53]
440	0.39534	4	0.79	1.03	0.76	1.16	[53]
323.15	0.2502	10	0.95	0.76	1.11	1.02	[52]
373.15	0.2502	26	1.67	1.25	0.57	0.86	[52]
423.15	0.2502	20	0.29	1.68	0.46	1.01	[52]
323.15	0.4760	14	2.10	2.00	0.82	3.25	[52]
373.15	0.4760	20	2.37	1.40	0.40	1.58	[52]
423.15	0.4760	20	0.99	0.64	0.55	1.87	[52]
323.15	0.7500	15	3.56	3.44	0.43	2.84	[52]
373.15	0.7500	15	3.29	4.10	0.59	1.39	[52]
423.15	0.7500	20	2.65	1.82	0.82	2.78	[52]

[a] NP represents the number of data points examined
[b] M stands for "modified"

Table 6. Prediction of the liquid densities of R32+R134a mixtures at various pressures and temperatures and fixed compositions

T (K)	X_{R32}	[a]NP	AAD(%) density				Refs.
			[b]TM (M)	TM	PR	ISM	
280	0.3953	4	0.74	2.60	5.05	5.23	[50]
290	0.3953	5	0.64	3.20	5.60	6.55	[50]
300	0.3953	4	0.48	4.06	6.32	7.69	[50]
310	0.3953	3	0.66	4.79	7.32	8.80	[50]
320	0.3953	3	1.90	6.26	8.57	9.48	[50]

[a]NP represents the number of data points examined
[b]M stands for "modified"

Table 7. Prediction of the gas densities of R125+R134a mixtures at various pressures, temperatures, and compositions

T (K)	X_{R125}	[a]NP	AAD (%) density				Refs.
			TM[b] (M)	TM	PR	ISM	
373.15	0.495	7	0.16	0.52	3.35	3.91	[45]
353.15	0.495	4	0.30	0.59	1.27	1.84	[45]
338.15	0.495	3	0.34	0.11	0.76	0.95	[45]
323.15	0.495	2	0.31	0.23	0.33	0.87	[45]
303.15	0.495	2	0.26	0.25	0.31	1.58	[45]

[a]NP represents the number of data points examined
[b]M stands for "modified"

deviations obtained from the modified Tao-Mason EOS in the liquid phase are lower than those calculated from the original TM, PR, and ISM equations of state, but there is no superiority in the gas phase. Tables 7 and 8 report the average absolute deviations of the gaseous and liquid densities for the binary mixture R125+R134a from the measured values reported by Widiatmo et al. [50]. In the liquid state, the PR EOS outperforms the other equations of state. Fig. 1 represents the relative deviations (AAD) of the calculated

Table 8. Prediction of the liquid densities of R125+R134a mixtures at various pressures, temperatures, and compositions

T (K)	X_{R125}	[a]NP	AAD (%) density				Refs.
			TM[b] (M)	TM	PR	ISM	
279.987	0.2674	6	2.80	4.62	0.41	4.56	[50]
289.978	0.2674	6	2.60	5.51	0.97	5.60	[50]
309.987	0.2674	5	2.91	7.47	2.80	7.30	[50]
279.987	0.4603	7	2.91	4.09	0.28	5.04	[50]
289.987	0.4603	6	3.08	4.93	0.40	6.05	[50]
299.987	0.4603	5	3.28	5.78	1.27	7.08	[50]
279.987	0.6653	6	3.06	3.17	0.81	5.65	[50]
289.987	0.6653	6	3.34	3.80	0.29	6.65	[50]
299.987	0.6653	4	3.49	4.62	1.40	7.45	[50]

[a]NP represents the number of data points examined
[b]M stands for "modified"

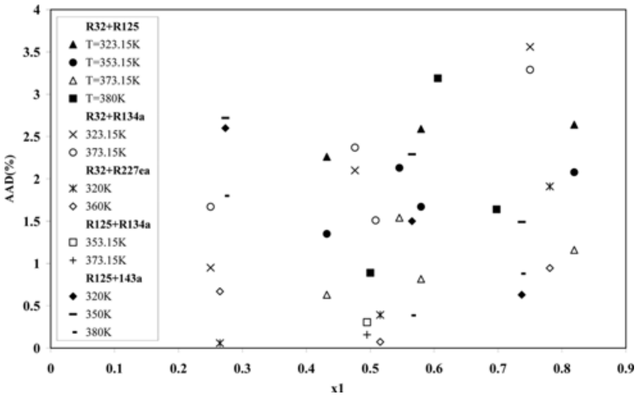

Fig. 1. The relative deviations of the calculated gas densities of R32+R125, R32+R134a, R32+R227ea, R125+R134a and R125+R143 a mixtures in terms of mole fraction and at different temperatures using the modified Tao-Mason EOS from the literature data [45,47-49,51-54]. x_1 is mole fraction of the first refrigerant mixtures.

Table 9. Results of density predictions for all considered mixtures (liquid and gaseous phases)

Mixture	Phase	ΔT (K)	ΔP (Pa)×10^5	[a]NP	AAD (%) density				Refs.
					[b]TM (M)	TM	PR	ISM	
R32+R125	Gas	320-440	0.907-52.427	217	2.20	1.68	1.08	1.36	[45,47,48,51]
R32+R134a	Gas	323.15-440	0.330-75.630	197	2.65	1.55	0.70	1.83	[45,52,53]
R32+R227ea	Gas	320 - 410	1.060-36.580	88	0.67	0.69	0.94	1.52	[54]
R125+R134a	Gas	303.15-373.15	0.550-40.310	18	0.28	0.34	1.20	1.84	[45]
R125+R143a	Gas	320 -380	1.150-47.630	102	1.43	2.40	0.57	1.58	[45,49]
R1234ez+CO_2	Gas	302.65-363.12	7.736-16.03	43	7.01	7.36	1.98	3.69	[59]
R32+R134a	Liquid	280 -320	10-30.020	19	0.62	4.18	6.57	7.33	[50]
R125+R134a	Liquid	279.98 -309.98	5.120-30.160	51	2.98	4.88	0.96	6.06	[50]
R32+R125	Liquid	294.68 -333.76	14.530-39.780	18	2.17	3.00	13.51	10.88	[46]
Propane+n butane	Liquid	240-320	4.63-70.456	111	0.17	1.89	5.61	7.31	[60]
Propane+isobutane	Liquid	240-320	3.98-70.447	108	0.52	3.94	5.69	7.80	[60]
Butane+isobutane	Liquid	240-320	4.816-70.938	121	0.32	1.09	5.59	3.92	[60]

[a]NP represents the number of data points examined
[b]M stands for"modified"

gas densities versus the mole fraction for R32+R125, R32+R134a, R32+R227ea, R125+R134a and R125+R143a using the modified Tao-Mason EOS from the literature data [45,47-49,51-54]. We can claim with confidence that the uncertainty ascribed to the calculated density is not greater than 4.6% for the refrigerant mixtures. Then we extended our calculations to other binary mixtures. Hydrocarbon refrigerants have a wide range of applications. The studied hydrocarbon refrigerants include a number of fluids including Propane+n-Butane, Propane+Isobutane, and Butane+Isobutane. HFO-1234ze is a globally compliant replacement for R134a in beverage dispensers. With respect to flammability, mixtures with CO_2 as the main component are promising. Herein, we studied the mixture of CO_2 with HFO-1234ze expected to be developed as alternatives. Table 9 summarizes our results for all binary mixtures. A close inspection of the deviations given in Table 9 reveals that, in the gaseous phase, the modified Tao-Mason EOS predicts the densities with a mean AAD of 2.4%, which, therefore, means that it does not outperform the other equations of state. In the liquid phase, the original Tao-Mason EOS is almost as accurate as the PR and ISM EOS, but the modified Tao-Mason EOS is preferable over the other three equations of state with a mean AAD within 1.1%.

In the present study, we extended the calculations to vapor pressures of refrigerant binary systems. Fig. 2 represents the deviations of the calculated vapor pressures from the literature data [55] for five mixtures consisting of R32+R1234yf, R32+R1234ze(E), CO_2+R1234yf and CO_2+R1234ze(E). We can claim with confidence that the deviation of the calculated vapor pressure compared to the simulated vapor pressures of these mixtures is not greater than 2%. For a better understanding of the performance of the model, the calculated vapor pressures of the mixtures R32+R-1234yf and CO_2+R-1234ze(E) are shown in Figs. 3 and 4. We found generally good agreement between obtained results and literature data [55].

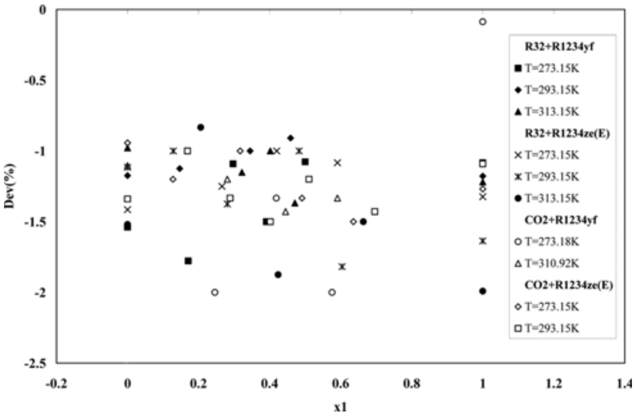

Fig. 2. The deviation of the calculated vapor pressure using the modified Tao-Mason EOS from the literature data [55] versus the mole fraction for mixtures R32 (1)+R1234yf (2), R32 (1)+ R1234ze (E) (2), CO_2 (1)+R1234yf (2) and CO_2 (1)+R1234ze (E) (2).

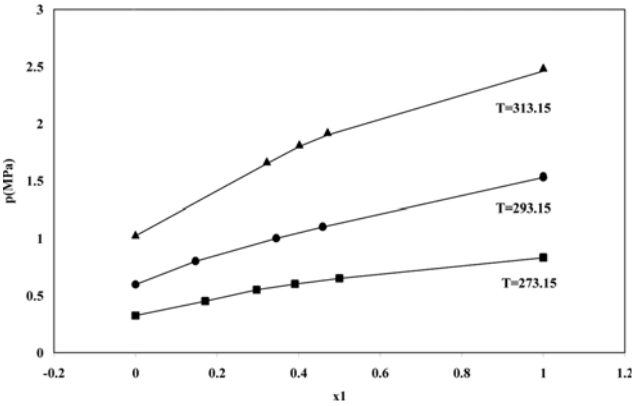

Fig. 3. Comparison between obtained results (markers) in this work and literature data [55] (solid line) for the vapor pressure in the binary system R32 (1)+R1234yf (2) at 273.15 K, 293.15 K, and 313.15 K.

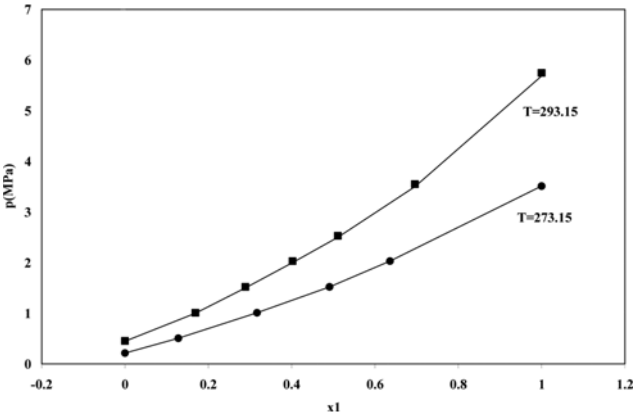

Fig. 4. Comparison between obtained results (markers) in this work and literature data [55] (solid line) for the vapor pressure in the binary system CO_2 (1)+R1234ze (2) at 273.15 K and 293.15 K.

CONCLUSIONS

We have successfully extended the modified Tao-Mason EOS to mixtures. On the basis of the results herein, the following conclusions can be drawn: (1) when tested against literature data, the calculated gas and liquid densities in the single- and two-phase regions gave mean average absolute deviations of 2.4% and 1.1%, respectively. (2) To assess the modified Tao-Mason EOS further, we compared it with the PR, ISM and original Tao-Mason EOS. In the liquid phase, the modified Tao-Mason EOS outperforms the other three equations of state. In the gas phase, there is no noticeable difference between the modified Tao-Mason EOS and the other equations of state. This study demonstrates that the mixture version of the modified Tao-Mason EOS is able to provide reliable information on the PVTx properties of both the compressed liquid phase and the gas phase of the fluid refrigerant mixtures. Additionally, the modified Tao-Mason EOS can predict vapor pressures of mixtures with satisfactory accuracy. Once the second virial coefficient from the macroscopic corresponding-states correlation, the values of λ from some high-density information, and the two constants ΔH_{vap} and ρ_{nb} for each refrigerant as well as a simple combining rule for estimating the cross values of these parameters are known, the entire EOS can be employed to predict the volumetric behaviors of fluid mixtures. The results obtained from the modified Tao-Mason EOS are remarkable in the low- and high-density regions, especially considering that they are based essentially on the second virial coefficient that characterizes the binary interaction in the low-density gas phase.

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