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Application of a new equation of state to liquid refrigerant mixtures

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Abstract

A new general equation of state recently reported for pure liquids has been developed to predict the volumetric and thermodynamic properties of six binary and two ternary liquid refrigerant mixtures (including HCs and HFCs mixtures) at different temperatures, pressures, and compositions. The results show this equation of state can be used to reproduce and predict different thermodynamic properties of liquid refrigerant mixtures within experimental errors. The composition dependence of the parameters of this equation of state has been assumed as quadratic functions of mole fraction. Using these mixing rules, the agreement between calculated and experimental densities is better than 0.6% for binary mixtures and 2.3% for ternary mixtures. To compare the performance of this new equation of state against other well-known methods such as the COSTALD method, the density of some refrigerant mixtures, for which the parameters of COSTALD were available, has been computed and compared with those of this new equation of state.

Keywords: GMA EoS; Liquids; Internal pressure; Refrigerant mixtures; Statistical thermodynamics; Volumetric properties

1. Introduction

During the last two decades, following the realization of the effect of refrigerants in the destruction of the ozone layer, many researchers have measured thermophysical properties of these compounds, aiming to find proper substitutes [1]. An alternative refrigerant must satisfy several requirements: its coefficients of ozone depleting potential (ODP) and global warming potential (GWP) are low, its thermodynamic efficiency or coefficient of performance (COP) in a cooling cycle is to be equal to COP of CFC12, the values of the compressor power, N_{comp} and the evaporator capacity Q are to be comparable with those of CFC12 if it has to substitute in cooling equipment [2]. For example, R12 is supposed to contribute to the depletion of the stratospheric ozone layer. The mixture (R134a+R152a) may be used as a substitute in certain application because its thermodynamic properties are similar to those of R12 [3]. HCFC-22, which is one of the most widely used working fluids in air-conditioning systems, is scheduled to be phased out before 2030 by international agreement. Binary mixtures of HFC-32/134a and HFC-32/125 and ternary mixtures of HFC-32/125/134a are considered as candidates to replace HCFC-22 [4]. Hydrocarbons (HCs) have some advantages as alternative refrigerants in spite of their flammability. Their ODP is zero and their GWP is vanishing small. HCs such as propane (R-290), *n*-butane (R-600), isobutane (R-600a) and their binary and ternary mixtures are expected to be alternative refrigerants.

There is a strong demand for reliable thermodynamic properties of these alternative working fluids. The most convenient form for representation of PVT behavior for process design and optimization calculations are analytic equations of state [5].

A general equation of state for liquids recently derived by Goharshadi et al. [6] (Goharshadi–Morsali–Abbaspour “GMA EoS”) has been found to be valid for polar, nonpolar, and hydrogen-bonded fluids [6,7]. The equation of state is based on the average potential energy and is given as

$$(2Z-1)V_{\mathrm{m}}^{3}=A(T)+B(T)\rho \qquad (1)$$

where Z, V_{m}, and ρ are compressibility factor, molar volume, and density, respectively. The intercept and slope of this equation depend on temperature via the equations:

$$A(T)=A_0-\frac{2A_1}{RT}+\frac{2A_2\ln T}{R} \qquad (2)$$

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$$B(T) = B_0 - \frac{2B_1}{RT} + \frac{2B_2 \ln T}{R} \qquad (3)$$

where A_0–A_2 and B_0–B_2 are constants. To use the equation of state for a liquid, the A and B parameters must be known. To find these parameters, $(2Z-1)V_\mathrm{m}^3$ is plotted against ρ for different isotherms. The slope and intercept of the straight lines fitted to Eqs. (2) and (3) give A_0–A_2 and B_0–B_2, respectively. According to one-fluid approximation, this EoS can be extended to refrigerant mixtures but the parameters of EoS (A and B) are dependent on composition as well as temperature [8]. This paper first, examines the linearity of $(2Z-1)V_\mathrm{m}^3$ versus ρ and the temperature dependency of the parameters of EoS at any fixed composition for different refrigerant mixtures, second, calculates the volumetric properties of different binary and ternary liquid refrigerant mixtures at various temperatures, pressures, and compositions, and finally determines the composition dependence of the parameters of the equation of state.

2. Results and discussion

2.1. Experimental test of GMA EoS

Experimental PVT data of liquid refrigerant mixtures at various temperatures and compositions are used to examine the linearity of $(2Z-1)V_\mathrm{m}^3$ versus ρ (Eq. (1)). Fig. 1 shows the results at 303.15 K for the R152a–R134a refrigerant mixture [3,9] at different mole fractions and Fig. 2 for a mixture of R600a+R600 ($x_\mathrm{R600} = 0.250$) [12] at different temperatures. The linearity holds very well for all mixtures and the slope and the intercept both depend on the temperature as well as the composition of the mixture. The results are summarized in Supplementary Table S1, including the intercept and slope of the fitted straight line (Eq. (1)) at each temperature and composition, the square of the correlation coefficient (R^2), and the pressure range of the experimental data for binary mixtures. The values of R^2 show that this linearity is valid especially when similar classes of refrigerants are mixed and non-ideality effects are small. Supplementary Table S2 shows the values of the constants of Eqs. (2) and (3) for tested binary liquid refrigerant mixtures, and the square of the correlation coefficients of these equations. The ranges of pressure and temperature of this table are the same as Supplementary Table S1. The values of R^2 of this table show the temperature dependence of the parameters of equation of state, namely A and B for all mixtures is the same as that of pure components.

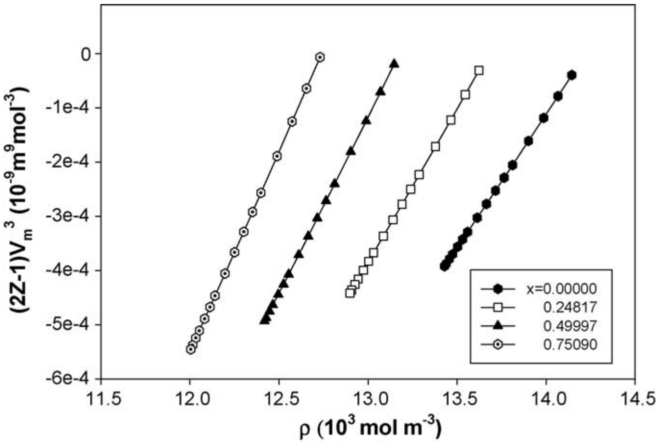

Fig. 1. $(2Z-1)V_\mathrm{m}^3$ vs. ρ for the R152a–R134a refrigerant mixture for different mole fractions at 303.15 K [3,9].

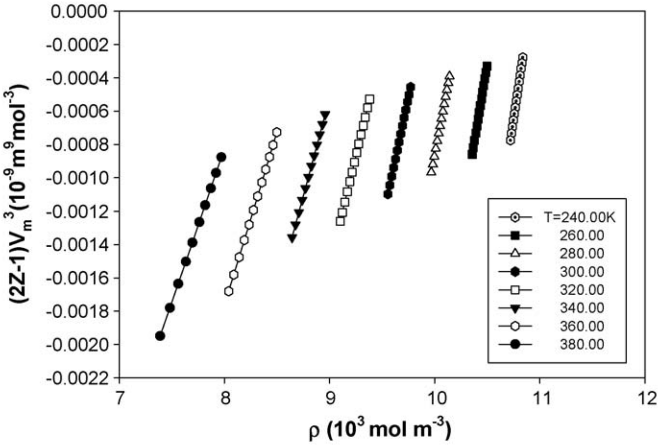

Fig. 2. Isotherms of $(2Z-1)V_\mathrm{m}^3$ vs. ρ for a refrigerant mixture of R600a+R600 ($x_\mathrm{R600} = 0.250$) [12].

The ability of this EoS to predict density at different temperatures, pressures, and compositions for all refrigerant mixtures may be evaluated by absolute average deviation (AAD). Calculated densities (NP) and the AAD values between calculated and experimental densities are reported in Supplementary Table S2. The values of AAD show that GMA EoS can predict density of liquid refrigerant mixtures at any temperature, pressure, and composition with relatively high precision. Figs. 3 and 4 show three dimensional plots of percent deviations of calculated densities for R600a+R600 refrigerant mixture at

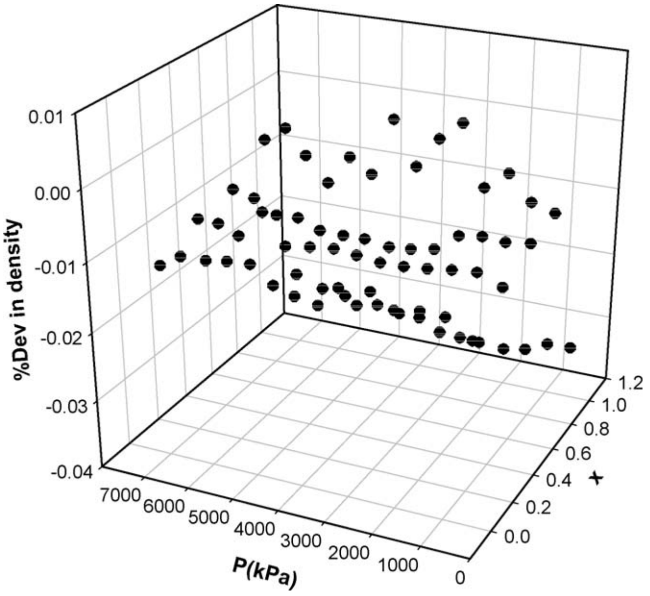

Fig. 3. Three-dimensional deviations of our calculated and experimental liquid densities of R600a+R600 refrigerant mixture at 240.0 K for different pressures and mole fractions [11,12].

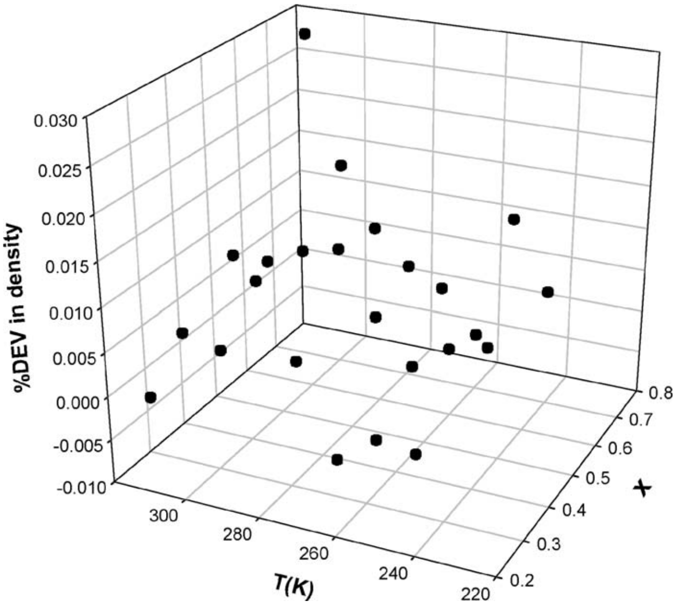

Fig. 4. Three-dimensional deviations of our calculated and experimental liquid densities of R152a–R134a refrigerant mixture at 13.87 M Pa for different temperatures and mole fractions.

240.0 K and R152a–R134a refrigerant mixture at 13.87 M Pa, respectively.

2.2. *EoS functions for liquid properties*

The density, ρ, expansion coefficient, $\alpha = (1/V)(\partial V/\partial T)_P$, isothermal compressibility, $\kappa_T = -(1/V)(\partial V/\partial P)_T$, and internal pressure, $P_i = (\partial U/\partial V)_T$, and the difference between isobaric and isochoric heat capacities of some refrigerant mixtures have been calculated at different temperatures, pressures, and compositions. The functions used for calculating these properties using GMA EoS are given as Eqs. (4)–(8), respectively.

$$B(T, x)\rho^5 + A(T, x)\,\rho^4 + \rho - \frac{2P}{RT} = 0 \tag{4}$$

$$\alpha = \frac{(2B_1 + 2B_2T)\rho^5 + (2A_1 + 2A_2T)\rho^4 + 2P}{5\rho^5(RT^2B_0 - 2B_1T + 2T^2B_2 \ln\, T) + 4\rho^4(A_0RT^2 - 2A_1T + 2A_2T^2 \ln\, T) + RT^2\rho} \tag{5}$$

$$\kappa_T = \frac{2}{\rho RT + 4\rho^4(RTA_0 - 2A_1 + 2TA_2 \ln\, T) + 5\rho^5(B_0RT - 2B_1 + 2B_2T \ln\, T)} \tag{6}$$

$$P_i = (B_1 + B_2T)\,\rho^5 + (A_1 + A_2T)\,\rho^4 \tag{7}$$

$$C_p - C_v = \frac{T\alpha^2}{\kappa_T\rho} \tag{8}$$

Supplementary Table S3 represents a typical calculation of these properties for R152a–R134a ($x = 0.49997$) refrigerant mixture at different temperatures and pressures. As far as the authors are aware, there are no corresponding experimental data to which the present calculations can be compared.

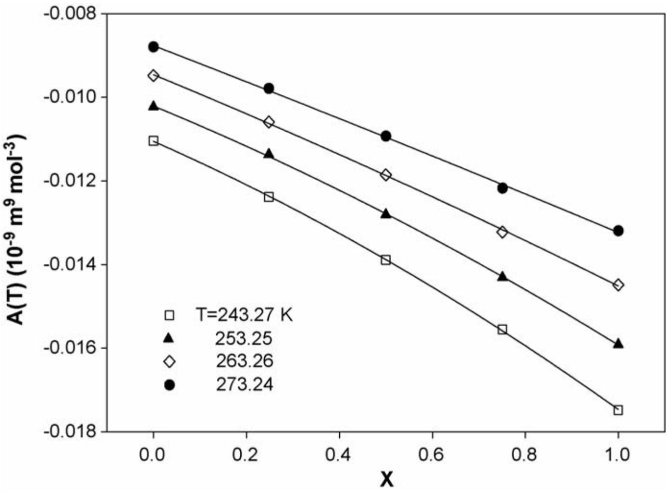

Fig. 5. Quadratic composition dependence of the parameter, A for R152a (1 − x)–R134a (x) at different temperatures.

2.3. *The composition dependence of the parameters of GMA EoS*

When applying an equation of state to mixtures it is necessary to specify mixing rules for the parameters of the EoS. Quadratic mixing rules, originally proposed by van der Waals, are used extensively in mixture calculations involving equations of state. Applying the quadratic mixing rule to the parameters of GMA EoS, namely A and B gives

$$A_{\text{mix}} = \sum_i \sum_j x_i x_j A_{ij} \tag{9}$$

$$B_{\text{mix}} = \sum_i \sum_j x_i x_j B_{ij} \tag{10}$$

The values of A_{ij} and B_{ij} when $i = j$ can be obtained from experimental P–V–T data of pure refrigerants. The parameters A_{ij} and B_{ij} refer to the pair of molecules $i - j$. The use of a quadratic mixing rule brings up the problem of evaluating these parameters. In this work, this is accomplished by using one binary refrigerant mixture. We have examined the quadratic composition dependence of the parameters A and B (Eqs. (9) and (10)) using experimental data [3,9–12] for different binary refrigerant mixtures.

To show the performance of these mixing rules, the parameters A and B versus composition have been plotted and fitted by quadratic functions of mole fraction. Figs. 5 and 6 show the values of A and B as a function of composition for the refrigerant mixture of R152a (1 − x)–R134a (x) at different temperatures, respectively. For all the systems, A and B are fitted well by

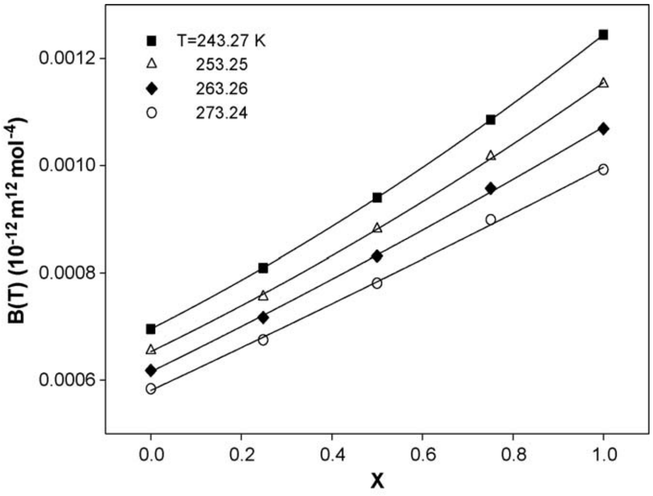

Fig. 6. Same as Fig. 5 for the parameter, *B*.

quadratic functions. A second evidence for showing the ability of these mixing rules (Eqs. (9) and (10)) is the AAD values of calculated densities using these rules. Table 1 shows the values of AAD of calculated densities using the mixing rules.

To compare the performance of GMA EoS for mixtures against other well-known methods such as the COSTALD method [13,14], we try to compare liquid molar density obtained from these two models for some refrigerant mixtures, for which the parameters of COSTALD are available. Table 2 gives the AAD values between experimental densities and those predicted using GMA EoS and COSTALD method. Although the AAD values calculated based on GMA EoS for refrigerant mixtures of R600a+R290 are greater than those of COSTALD, the maximum absolute percent deviations are lower in all cases.

2.4. Ternary mixtures

For ternary mixtures, the parameters of GMA EoS are assumed to be quadratic functions of composition (Eqs. (9) and (10)). We have used the experimental PVT data of ternary mixtures of R143a–R32–R125 [10] and R600a–R600–R290 [11,12] at various temperatures and pressures to examine Eq. (1) for ternary refrigerant mixtures. The results are given in Table 3, including the intercept and slope of the fitted straight line (Eq. (1)) at each temperature and composition, and the square of the correlation coefficient (R^2). Table 4 shows the values of the constants of Eqs. (2) and (3) for tested ternary liquid refrigerant mixtures, and the square of the correlation coefficients of Eqs. (2) and (3), and the number of calculated densities (NP) and the absolute average deviations between calculated and cor-

Table 1
The absolute average deviations between experimental and calculated densities based on mixing rules for binary and ternary refrigerant mixtures

x		AAD	NP
R600+R290 (*x*)			
0.250		0.219	39
0.750		0.538	38
R152a–R134a (*x*)			
0.24817		0.239	62
0.75090		0.456	62
R600a+R600 (*x*)			
0.250		0.011	54
0.751		0.059	53
x_1	x_2	AAD	NP
R600a (x_1)–R600 (x_2)–R290			
0.200	0.200	2.238	49
0.330	0.330	1.72	50
0.200	0.600	1.205	52

Table 2
The AAD values between experimental density data and those predicted using our work and COSTALD method [13,14]

x	AAD (GMA)	AAD (COSTALD)	NP
R600a+R600 (*x*)			
0.25	0.011 (0.034)[a]	0.163 (0.383)	54
0.751	0.059 (0.133)	0.143 (0.329)	53
R600a+R290 (*x*)			
0.25	0.500 (0.681)	0.376 (0.771)	39
0.751	0.503 (0.692)	0.335 (1.068)	34

[a] The numbers in parentheses show the maximum absolute percent deviation.

Table 3
The parameters and square of correlation coefficient (R^2) of Eq. (1) for ternary mixtures

x_1	x_2	T (*K*)	$-A(T)$ (10^{-9} m^9 mol^{-3})	$B(T)$ (10^{-12} m^{12} mol^{-4})	R^2
R600a (x_1)–R600 (x_2)–R290 [11,12]					
0.200	0.200	240.000	0.02601900	0.00211747	0.9999
		260.000	0.02244710	0.00188831	1.0000
		280.000	0.01919980	0.00167115	1.0000
		300.000	0.01633220	0.00147433	1.0000
		320.000	0.01394920	0.00131023	1.0000
		340.000	0.01180180	0.00115769	1.0000
		360.000	0.00980238	0.00101033	1.0000
0.330	0.330	240.000	0.03315330	0.00283809	0.9993
		260.000	0.02928650	0.00258625	1.0000
		280.000	0.02500900	0.0022813	1.0000
		300.000	0.02143320	0.00202344	1.0000
		320.000	0.01836400	0.00179928	1.0000
		340.000	0.01561980	0.00159357	1.0000
		360.000	0.01327720	0.00141627	1.0000
0.200	0.600	240.000	0.03885810	0.00338983	1.0000
		260.000	0.03386100	0.0030442	1.0000
		280.000	0.02888260	0.00267838	1.0000
		300.000	0.02485070	0.00238207	0.9998
		320.000	0.02141800	0.00212664	1.0000
		340.000	0.01832550	0.00188975	1.0000
		360.000	0.01561450	0.00167911	1.0000
		380.000	0.01325480	0.00149529	1.0000
R143a (x_1)–R32 (x_2)–R125 [10]					
0.333	0.335	279.99	0.00634005	0.000450343	0.9997
		289.99	0.00558030	0.000404995	1.0000
		299.99	0.00521307	0.000389338	0.9999
		309.99	0.00478602	0.000367798	1.0000

Table 4
The values of constants of GMA EoS, the correlation coefficients of Eqs. (2) and (3), the number of calculated densities, and AAD in density for ternary mixtures

x_1	x_2	A_0 ($L^3\,mol^{-3}$)	A_1 (L^4 atm mol^{-4})	A_2 (L^4 atm $mol^{-4}\,K^{-1}$)	R^2	B_0 ($L^4\,mol^{-4}$)	B_1 (L^5 atm mol^{-5})	B_2 (L^5 atm $mol^{-5}\,K^{-1}$)	R^2	NP	AAD[a]
R600a (x_1)–R600 (x_2)–R290											
0.200	0.200	0.0240453	0.480704	−9.85E-06	0.9999	0.00385	−0.02354	−3.08E-05	0.9997	86	0.034
0.330	0.330	−0.0389826	0.47618	0.00040386	0.9994	0.010875	−0.02051	−7.56E-05	0.9991	91	0.063
0.200	0.600	0.0475001	0.71969	−0.0001004	0.9998	0.004557	−0.03955	−3.87E-05	0.9997	101	0.031
R143a (x_1)–R32 (x_2)–R125											
0.333	0.335	0.794757	1.59865	−0.0048197	0.9929	−0.06052	−0.11808	0.000369	0.9843	17	0.040

[a] $\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N} 100 \left| \frac{\rho_{\exp}-\rho_{\mathrm{cal}}}{\rho_{\exp}} \right|$.

responding experimental densities on the basis of GMA EoS directly (Eq. (1)).

For applying the mixing rules for a ternary mixture, we need the *P*–*V*–*T* data of pure components plus one composition for any of their binary mixtures. Table 1 shows the average absolute percent deviations of density calculated using the mixing rules for R600a–R600–R290 in comparison with corresponding experimental densities for the ternary mixtures of R600a, R600, and R290.

3. Conclusions

In general, GMA EoS provides a simple procedure for prediction of thermodynamic properties of liquid refrigerant mixtures especially for which the similar classes of refrigerants are mixed and non-ideality effects are small. This is a significant benefit in practical applications.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.05.017.

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