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Modified Equation of State Applied to Refrigerants

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Abstract

An analytical equation of state has been previously modified by Papari et al. for representing the volumetric properties of molecular fluids. However the performance of that EOS has not been yet well investigated for refrigerant fluids. This study extended that equation to 19 liquid refrigerants to predict their densities at isothermal and saturated states. Two temperature-independent parameters appearing in the modified EOS are closely related to critical point properties of refrigerant fluids. Our results showed that, the proposed EOS can predict well isothermal and saturated liquid destinies of studied refrigerants over the temperature and pressure range from 137-400 K and 0.001-1870 bar, with AADs equal to 2.16% and 2.66%, respectively.

Keywords: Equation of state, Refrigerant, Liquid density

1. Introduction

Knowledge of the thermo-physical properties of refrigerant fluids is of importance in the design and fabrication of these devices. Such knowledge is also of theoretical relevance, because it provides a legitimate framework for the understanding of intermolecular forces acting in refrigerant systems. The global intention in the choice of different refrigerants for air conditioning and refrigeration applications has undergone a rapid change during the recent decades. The recycling of chloro-fluorocarbons (CFCs) has been prohibited from 2001 and this year (2015) is the deadline for removal of the maintaining existing systems. Hydro-fluorocarbons (HFCs) with zero depletion effects and very low greenhouse potentials are the best candidates for substitution of CFCs and HCFCs (hydro-fluorochlorocarbon). In this regard, equation of state (EOS) is a major tool for the correlation and prediction of thermo-physical properties of refrigerant fluids.

Numerous studies [1-5] were carried out yet to present analytical equations of state for thermodynamic proprieties of refrigerant fluids based on the various approaches from the work of Fermeglia et al. [1] to the very

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recent work by Maftoon-Azad et al. [3]. In those works two parameters appearing in the EOSs were determined based on the various approaches such as the critical point criterion, corresponding states correlations etc.

An analytical equation of state has been previously modified by Papari et al. [6] for molecular liquids from non-polar to polar ones. In that work, two parameters appearing in the EOS were determined based on the critical point criterion, where both of first and second volume derivatives of EOS at critical isotherm are equal to zero. But the performance of that EOS has not been yet satisfied for halogenated organic compounds especially the refrigerant ones. Only two refrigerant fluids were studied in that work [6]. This study aims to extend that equation to 20 liquid refrigerants to predict their densities at isothermal and saturated states. Our calculation results are compared with the literature data[7].

2. Modified CS-vdW Equation of State

Papari et al. [6] have modified the attractive part of some vdW family EOSs. One of them was that well-known as Carnahan-Starling-van der Waals (CS-vdW) EOS which is as:

$$\frac{P}{\rho k_B T} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{a\rho}{k_B T} \qquad (1)$$

Where P is the pressure, ρ is the number (molar) density, $k_B T$ is the thermal energy per molecule, a is the measure of attractive forces between molecules and η is the packing fraction defined as:

$$\eta = \frac{b\rho}{4} \qquad (2)$$

In this equation b, is the van der Waals co-volume.

The second term of the right hand of CS-vdW has been modified by Papari et al. as follows [6]:

$$\frac{P}{\rho k_B T} = \left(\frac{P}{\rho k_B T}\right)_{cs} + \left(\frac{P}{\rho k_B T}\right)_{vdW} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{a(T)\rho}{k_B T^{(\beta+1)}} \qquad (3)$$

where, β is a function of acentric factor of pure fluids as:

$$\beta = c_1 + c_2\omega + c_3\omega^2 \qquad (4)$$

c_1=0.2606 c_2= 3.0517 c_3= −2.191

When β= 0 the vdW-CS EOS is recovered. Papari et al. called Eq. (3) "CS-vdW-β".The parameters a and b were previously obtained by solving the usual critical point equations [6], giving:

$$a = 0.496388\frac{R^2 T_c^{(2+\beta)}}{P_c} \qquad (5)$$

$$b = 0.187294\frac{R\,T_c}{P_c} \qquad (6)$$

The critical parameters of studied refrigerants to be used in Eqs (5) and (6) were taken from literature [7].

3. Results and discussion

The calculation of density from the given temperature and pressure is one of the most frequently performed operations in phase equilibrium calculations. The ability of the present modified equation of state for predicting the density of studied refrigerants over the temperature range between 137-400 and pressure range from 0.001 to 1870 bar has been checked. In this work, we have calculated isothermal and saturated liquid densities of 19 pure refrigerants using the proposed EOS. Our calculation results were summarized in Table 1 as the average absolute deviations (%AAD)

Table 1 The average absolute deviation (%AAD)[b] of the calculated isothermal liquid densities from CS-vdW-β (Eq. (3)) [6] and PR EOS [8], both compared with literature values [7].

Refrigerant	ΔT(K)	ΔP (bar)	NP[a]	Eq. (3)	PR EOS
Trichlorofluoromethane (R11)	350-380	5-300	109	1.30	7.05
Dichlorofluoromethane (R12)	290-336-	5-1870	52	1.64	-
Chlorotrifluoromethane (R13)	220-260	6-320	22	1.92	8.36
Tetrafluoromethane (R14)	170-200	40-490	50	2.11	-
Dichlorodifluoromethane (R21)	330-370	6-1020	30	3.33	6.44
Difluoromethane (R32)	150-175	0.001-700	66	2.77	-
1,1,2-Trichloro-1,2,2-trifluoroethane (R113)	230-400	0.02-1000	63	1.33	-
1,2-Dichloro-1,1,2,2-tetrafluoroethane (R114)	300-320	20-80	22	2.55	6.57
Chloropentafluoroethane (R115)	290-315	40-60	15	2.74	8.40
2,2-Dichloro-1,1,1-trifluoroethane (R123)	330-370	4-400	74	2.80	-
1-Chloro-1,2,2,2-tetrafluoroethane (R124)	300-330	6-400	37	2.67	-
Pentafluoroethane (R125a)	240-330	0.3-600	53	3.25	-
Hexafluoroethane (R116)	230-270	4-400	74	2.66	7.45
Overall			667	2.16	7.39

[a] NP represents the number of examined data points.

[b] $\text{AAD}=100/\text{NP}\sum_{i=1}^{NP}|\rho_{cal}-\rho_{Lit}|/\rho_{Lit}$

from the literature data [7]. For 13 refrigerants, the AAD of the calculated isothermal liquid densities from the literature values have been obtained using the modified EOS. From Table 1, it was found that for 667 data points, the AAD of the calculated densities from the ones literature ones [7] was equal to 2.16%.

Our calculation results have also been compared with those obtained from the well-known Peng-Robinson (PR) EOS [8] and reported in Table 1. It was found that the present EOS is favorably superior to PR one. The AADs of calculated isothermal liquid densities from modified EOS (2.16%) is considerably lower than that obtained from PR EOS (7.39%).

Densities of saturated liquid refrigerants were also estimated using Eq. (3) over pressure rage from 0.001 bar up to 11 bar and temperature between 137-400K, and the calculation results were shown in Figures 1 and 2 as the relative deviation percentage of estimated values from the literature data [7]. The relative deviation is defined as:

$$\text{Relative deviation}=\left(\frac{\rho^{Calc}}{\rho^{Lit}}-1\right)\times 100 \quad (7)$$

where, superscripts “Calc” and “Lit” stand respectively, the calculated and literature values. From 382 data points examined for saturated liquid refrigerants, the AAD was equal to 2.66%. These Figures show how the CS-vdW-β passes thorough the literature data points. As Figs. 1 and 2 show, the relative deviations (in %) are within ±5.81%.

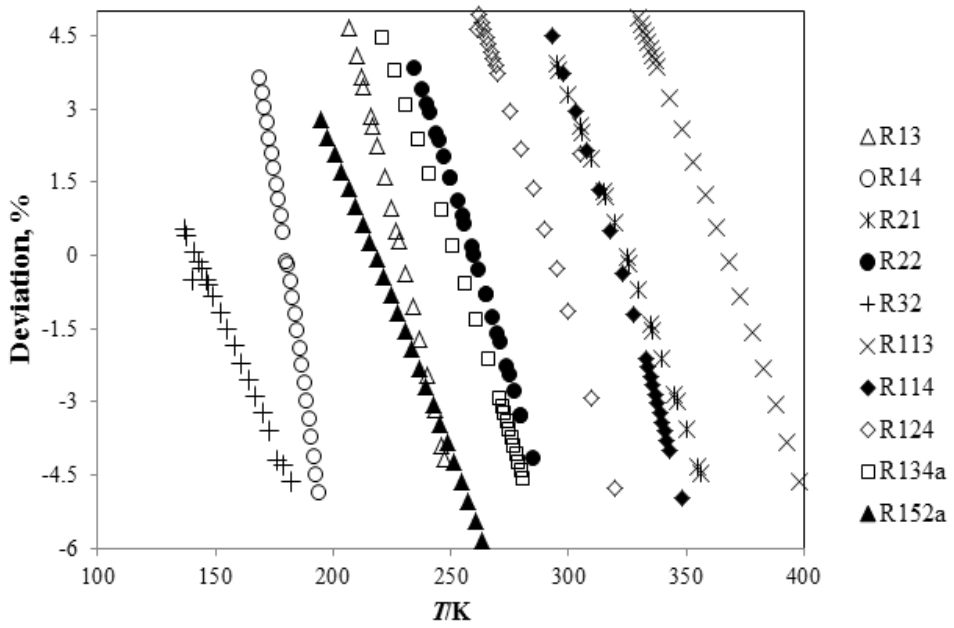

Fig. 1. Deviation plot for the estimated saturated liquid densities of 10 refrigerants from Eq. (3) from literature data [7].

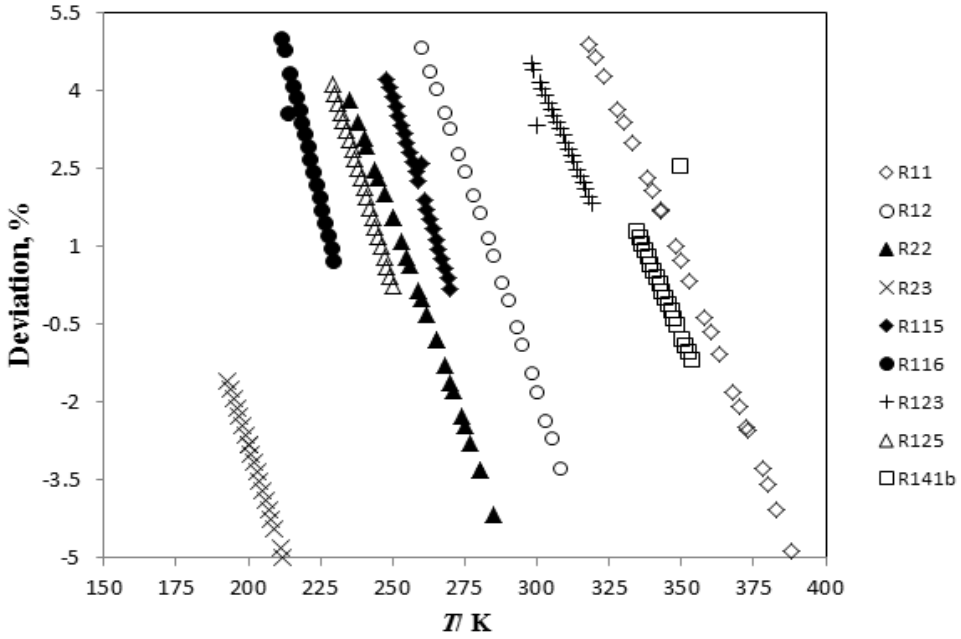

Fig.2. Deviation plot for the estimated saturated liquid densities of other 9 studied refrigerants from Eq. (3) from literature data [7].

4. Conclusion

The most striking aspect observable is the remarkable agreement achieved between the calculated results and the literature values of volumetric properties of refrigerants using the modified version of CS-vdW EOS. This clearly indicates that the modified CS-vdW EOS is superior to the PR EOS. In sum, the modified CS-vdW EOS behaves well in both isothermal and saturated states. We conclude by pointing out that the attractiveness of the modified CS-vdW EOS lies in its simplicity of calculation and its good performance in prediction of liquid densities.

Acknowledgments

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Trade name and IUPAC name of refrigerants

R134a	1,1,1,2-tetrafluoro-ethane
R11	Trichlorofluoromethane
R12	Dichlorodifluoromethane
R13	Chlorotrifluoromethane
R21	Dichlorofluoromethane
R22	chlorodifluoromethan
R32	difluoromethane
R41	Fluoromethane
R114	1,2-Dichloro-1,1,2,2-tetrafluoroethane
R113	1,1,2-Trichloro-1,2,2-trifluoroethane
R115	Chloropentafluoroethane
R116	Hexafluoroethane
R125	pentafluoroethane
R142b	1-Chloro-1,1-difluoroethane

Nomenclature and units

b	van der Waals co-volume, m^3
P	pressure, Pa
R	gas constant, J/mole K
T	absolute temperature, K
k_B	Boltzmann constant, J/K
a	attractive forces between spheres/ J m^{-3}

Greek letters

ρ	molar density, mol/m^3

Subscripts

C	critical

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