



Modified Equation of State Applied to Refrigerants: Part II

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Abstract

The present work is the successful extension of an improved equation of state (EOS) to refrigerant fluids. The objective is the prediction of isothermal and saturated liquid densities of refrigerants. 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 densities of studied refrigerants over the temperature range from 100-400 K and pressures up to 187 MPa, with AADs equal to 2.16% and 2.66%, respectively. The surface tensions and sound velocities of saturated refrigerants were also estimated through the simple relations with AADs equal to 4.76% and 5.66%.

Keywords: Equation of state, Refrigerant, Speed of sound

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.

During the years, several researchers have presented EOS to predict thermodynamic

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properties of refrigerants [1-3]. Moreover, some empirical correlations for the liquid densities of refrigerants have been presented [4-6]. Song and Mason's (SM) EOS [7] has been developed to predict volumetric behaviours of refrigerant fluids and refrigerant fluid mixtures by Papari et al. [8]. Following the method, Eslami [9] showed that the EOS for halogenated paraffins could be expressed in terms of the minimum input information, namely, the normal boiling temperature and the liquid density at the normal boiling temperature. Also, numerous studies [8, 10-13] were carried out yet to apply the analytical equations of state for thermodynamic properties of refrigerant fluids based on the various approaches from the work of Fermeglia et al. [10] to the very recent work by Maftoon-Azad et al. [12]. 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.

An analytical equation of state has been previously modified by Papari et al. [14] 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 [14]. This study aims to extend that equation to liquid refrigerants to predict their densities at isothermal and saturated states. Our calculation results are compared with the literature data [15]. The surface tensions and velocity of sounds of saturated refrigerants are also estimated through the simple relations [16, 17].

2. Equation of State

Recently, the attractive part of some van der Waals (vdW) family EOSs [14] have been modified for correlating the volumetric data of non-polar and polar molecular fluids. One of them was that well-known Carnahan-Starling-van der Waals (CS-vdW) EOS which is as:

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

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:

$$\eta = \frac{b\rho}{4} \quad (3)$$

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 [14]:

$$\frac{P}{\rho k_B T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{a(T)\rho}{k_B T^{(\beta+1)}} \quad (4)$$

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

$$\beta = c_1 + c_2 \omega + c_3 \omega^2 \quad (5)$$

The values of coefficients c_1 - c_3 were found to be different for vapour and liquid phases as demonstrated by Papari et al. [14] and reported as follows

For vapour phase:

$$c_1 = -0.0397 \quad c_2 = 0.7619 \quad c_3 = 0.8589$$

For liquid phase:

$$c_1 = 0.2606 \quad c_2 = 3.0517 \quad c_3 = -2.191$$

When $\beta = 0$ the CS-vdW EOS is recovered. The Eq. (4) has been called "CS-vdW- β ". The

Table 1: The critical constants along with the acentric factors of studied refrigerants to be used in Eqs. (5) and (7).

Refrigerant	T _c (K)	P _c (MPa)	ω
Trichlorofluoromethane (R11)	471.11	4.408	0.188
Dichlorofluoromethane (R12)	385.12	4.136	0.176
1,1,2-Trichloro-1,2,2-trifluoroethane (R113)	487.21	3.392	0.255
1,2-Dichloro-1,1,2,2-tetrafluoroethane (R114)	420.60	3.352	0.246
Chloropentafluoroethane (R115)	353.10	3.129	0.249
Dichlorodifluoromethane (R21)	452.72	5.289	0.202
Chlorodifluoromethane (R22)	369.29	4.990	0.215
1-Chloro-1,2,2,2-tetrafluoroethane (R124)	395.42	3.625	0.300
1,1-Dichloro-1-fluoroethane (R141b)	477.50	4.212	0.217
Tetrafluoromethane (R14)	227.39	3.762	0.176
Hexafluoroethane (R116)	293.03	3.048	0.255
Trifluoromethane (R23)	299.29	4.832	0.253
1,1,1,2-Tetrafluoroethane (R134a)	374.21	4.059	0.326
1,1-Difluoroethane (R152a)	386.41	4.517	0.259
2,2-Dichloro-1,1,1-trifluoroethane (R123)	456.83	3.662	0.2819
Pentafluoroethane (R-125)	339.17	3.617	0.305
Chlorotrifluoromethane (R-13)	302.03	3.879	0.172
Difluoromethane (R32)	351.25	5.780	0.276

parameters a and b were previously obtained by solving the usual critical point equations [14], giving:

$$a = 0.496388 \frac{R^2 T_c^{(2+\beta)}}{P_c} \quad (6)$$

$$b = 0.187294 \frac{R T_c}{P_c} \quad (7)$$

The critical parameters of studied refrigerants to be used in Eqs. (6) and (7) were taken from literature [15] and reported in Table 1.

3. Results and discussion

3.1. Estimation of liquid densities

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 110-400 K and pressure range from 0.001 to 1870 bar has been checked. In this work,

we have calculated isothermal and saturated liquid densities of pure refrigerants using the proposed EOS. Our calculation results were summarized in Table 2 as the average absolute deviations (%AAD) from the literature data [15]. For 13 refrigerants, the AAD of the calculated isothermal liquid densities from the literature values have been obtained using the modified EOS. From Table 2, it was found that for 667 data points, the AAD of the calculated densities from the ones literature ones [15] was equal to 2.16%.

Our calculation results have also been compared with those obtained from the well-known Peng-Robinson (PR) EOS [18] and reported in Table 2. It was found that the present EOS is favourably 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 (i.e., 6.51%).

The densities of saturated liquid refrigerants were also estimated using Eq. (4) over the pressure range up to 1.34 MPa

Table 2: The AAD (in %)^b of the calculated compressed liquid densities of studied refrigerants using CS-vdW- β (Eq. (4)) [14] and PR [18] EOSs, both were compared with literature values [15].

Refrigerant	$\Delta T(K)$	$\Delta P(\text{bar})$	NP ^a	Eq. (4)	PR EOS
Trichlorofluoromethane (R11)	250-380	0.50-30.0	109	1.30	7.05
Dichlorofluoromethane (R12)	200-336	0.50-187	52	1.64	10.44
Chlorotrifluoromethane (R13)	160-260	0.62-32.	22	1.92	8.36
Tetrafluoromethane (R14)	110-200	4.00-49	50	2.11	9.02
Dichlorodifluoromethane (R21)	230-370	0.60-102	30	3.33	6.44
Difluoromethane (R32)	130-175	0.00-70	66	2.77	8.33
1,1,2-Trichloro-1,2,2-trifluoroethane (R113)	230-400	0.00-100	63	1.33	5.01
1,2-Dichloro-1,1,2,2-tetrafluoroethane (R114)	200-320	2.00-80	22	2.55	6.57
Chloropentafluoroethane (R115)	210-315	40.00-60	15	2.74	8.40
2,2-Dichloro-1,1,1-trifluoroethane (R123)	230-370	4.00-400	74	2.80	2.69
1-Chloro-1,2,2,2-tetrafluoroethane (R124)	200-330	6.00-400	37	2.67	2.92
Pentafluoroethane (R125a)	240-330	0.302-600	53	3.25	4.01
Hexafluoroethane (R116)	130-270	4.00-400	74	2.66	7.45
Overall			667	2.16	6.15

^a NP represents the number of examined data points.

^b $\text{AAD} = 100/\text{NP} \sum_{i=1}^N |\bar{n}_{\text{Calc.}} - \bar{n}_{\text{Lit.}}| / \bar{n}_{\text{Lit.}}$

and temperatures within 137-400 K. Our calculation results were shown in Figure 1 as the relative deviation (in %) of estimated values from the literature data [15]. The relative deviation is defined as:

$$\text{Relative deviation} = \left(\frac{\rho^{\text{Calc}}}{\rho^{\text{Lit}}} - 1 \right) \times 100 \quad (8)$$

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%. Figure 1 also shows how the CS-vdW- β passes thorough the literature data points. As it clears from Fig. 1, the relative deviations (in %) of the estimated isothermal and saturated liquid densities are within $\pm 5.41\%$.

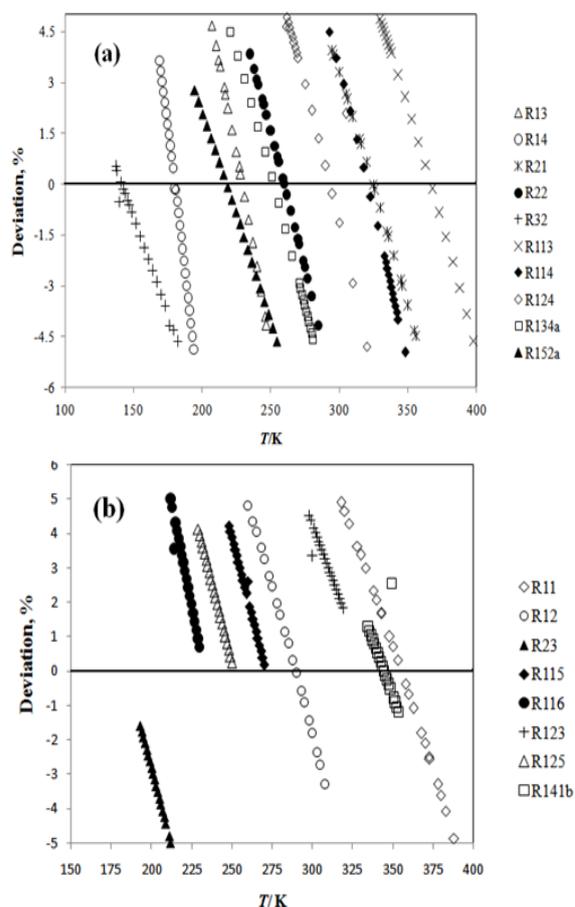


Fig. 1. Two deviation plots for the estimated saturated liquid densities of 19 refrigerants by the use of Eq. (4) from the literature data [15].

3.2. Surface tension estimation

Having liquid and vapor densities, (ρ^l and ρ^v) one can estimate the surface tensions of non-polar and polar liquids through Escobedo-Mansoori relation [17]. That relation can be reads as:

$$\gamma = \left(P_0 (\rho^l - \rho^v) (1 - T_r)^{0.37} T_r \text{Exp}(0.30066 T_r^{-1} + 0.86442 T_r^9) \right) \quad (9)$$

where, T_r is reduced temperature ($=T/T_c$) and P_0 is a temperature-independent constant characteristic of the fluid under consideration similar to the Sugden's parachor [19]. In this study, Hugill-Welsenens [20] expression for Sugden's parachor was adopted which is as:

$$P_0 = 4.01684(0.151 - 0.0464\omega) \frac{T_c^{1.083}}{P_c^{0.833}} \quad (10)$$

The surface tension of 8 saturated refrigerant liquids were estimated by Eqs (9) –(10) over the temperature range from 169- 388 K with relative deviations from the literature data [15] within $\pm 10.91\%$. To show how the proposed EOS passes through the literature data, a deviation plot is shown in Figure 2 as the relative deviation percent in the estimated

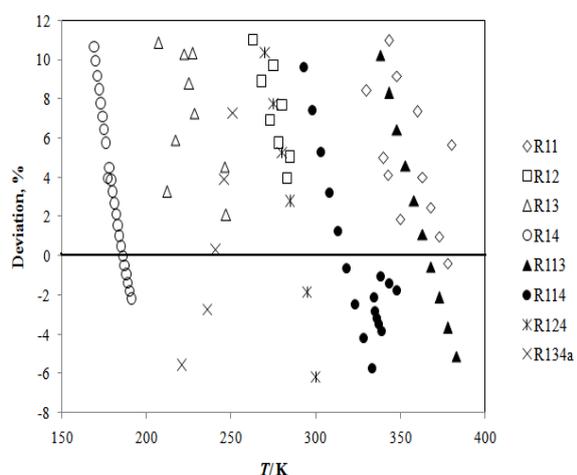


Fig. 2. Deviation plot for the estimated surface tensions of some selected liquid refrigerants using Eq. (9) from the literature data [15].

surface tensions from the literature data [15]. From 98 data points examined, the AAD of estimated surface tensions was found to be 4.76%.

3.3. Estimation of sound velocity

Having liquid densities and surface tensions, one can easily estimate the sound velocities, u (in m/s units) of non-polar liquids through Auerbach relation [16]. That relation can be reads as:

$$u = \left(\frac{\gamma}{6.3 \times 10^{-10} \cdot \rho} \right)^a \quad (11)$$

where, γ and ρ are the surface tension and the liquid density, respectively. However, Gardas-Coutinho [21] reconsidered that equation for polar liquids by re-evaluating a -power. They estimated value of a - exponent approximately equal to 0.6714. The derived liquid densities from Eq. (4) together with predicted surface tension values from Eq.(9) were employed to estimate sound velocities of 8 refrigerant liquids at saturated states. The corresponding results were shown in Figure 3 as the relative deviation percent in the estimated sound

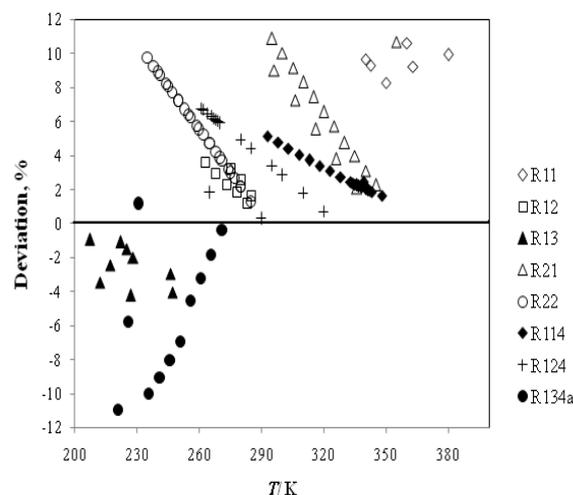


Fig. 3. Deviation plot for the estimated sound velocities of some selected liquid refrigerants using Eq. (11) from the literature data [15].

velocities from the literature data [15]. As it's demonstrated by that figure, Eq. (11) estimates the sound velocities of studied liquid refrigerants over the temperature range from 207- 380K with relative deviations up to 10.96%. From 61 data points examined, the AAD of estimated sound velocities was found to be 5.66%. It should be noted that, to predict the isothermal and saturated liquid density of refrigerants, the second set of coefficients c_1 - c_3 is taken into account, those were adjusted for "liquid phase".

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 CS-vdW- β EOS made it capable for estimating the surface tensions and sound velocities of refrigerant fluids with reasonably good accuracies.

Acknowledgments

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Nomenclature and units

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

Greek letters

γ	surface tension/ N/m
u	sound speed/ m s^{-1}
ω	acentric factor

ρ molar density, mol/m^3

Subscripts

C critical

References:

- [1] V. Feroiu, D. Geana, Rev. Roum. Chim, 56 (2011) 517-525.
- [2] J. Avsec, M. Marcic, HIGH TEMP ERATURES HIGH PRESSURES, 33 (2001) 319-328.
- [3] N. Matsuda, A. Mizuoka, K. Morita, H. Sato, in Measurements of PVT Properties and Development of Thermodynamic Equations for Difluoromethane (R32), pp. 1-4.
- [4] R.W. Hankinson, G.H. Thomson, AIChE, 25 (1979) 653-663.
- [5] C.F. Spencer, R.P. Danner, J. Chem. Eng. Data, 18 (1973) 230-234.
- [6] G.A. Iglesias-Silva, K.R. Hall, Fluid Phase Equilib., 131 (1997) 97-105.
- [7] Y. Song, E. Mason, The Journal of chemical physics, 91 (1989) 7840-7853.
- [8] S. Sheikh, M.M. Papari, A. Boushehri, Industrial & engineering chemistry research, 41 (2002) 3274-3281.
- [9] H. Eslami, International journal of refrigeration, 27 (2004) 649-655.
- [10] M. Fermeglia, A. Bertucco, D. Patrizio, Chemical engineering science, 52 (1997) 1517-1527.
- [11] M.-A. Leila, M. Javanmardi, A. Boushehri, Fluid Phase Equilib., 236 (2005) 237-240.
- [12] L. Maftoon-Azad, Z. Yazdanpanah, H. Mohamadi-Baghmolayi, J. Mol. Liq., 208 (2015) 388-393.
- [13] H. Eslami, M. Farrokhnia, International journal of refrigeration, 28 (2005) 1057-1063.
- [14] M.M. Papari, J. Moghadasi, S.M. Hosseini, F. Akbari, J. Mol. Liq., 158 (2011) 57-60.
- [15] E. Lemmon, M. McLinden, D. Friend, webbook. nist. gov (accessed October 28, 2012), (2011).
- [16] R. Auerbach, Experientia, 4 (1948) 473-474.
- [17] J. Escobedo, G.A. Mansoori, AIChE, 42 (1996) 1425-1433.
- [18] D.-Y. Peng, D.B. Robinson, Industrial & Engineering Chemistry Fundamentals, 15 (1976) 59-64.
- [19] S. Sugden, Journal of the Chemical Society, Transactions, 125 (1924) 32-41.
- [20] J. Hugill, A. Van Welsenes, Fluid Phase Equilib., 29 (1986) 383-390.
- [21] R.L. Gardas, J.A. Coutinho, Fluid Phase Equilib., 267 (2008) 188-192.