THERMODYNAMIC PROPERTIES OF SOME CHLORO-FLUORO-HYDROCARBONS FROM CUBIC EQUATIONS OF STATE

Viorel FEROIU[1], Dan GEANĂ[2], Catinca SECUIANU[3]

Pentru fluidele de răcire R22 (Clorodifluorometan), R124 (2-cloro-1,1,1,2-tetrafluoroetan) şi R142b (1-cloro-1,1-difluoroetan) au fost efectuate calcule de predicţie a proprietăţilor termodinamice, inclusiv proprietăţile PVT (presiune – volum – temperatură), pe curba de saturaţie, între punctul triplu şi punctul critic. Au fost utilizate trei ecuaţii cubice de stare: Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) şi GEOS3C. A fost efectuată o comparaţie cu date experimentale. Ecuaţia de stare GEOS3C a condus la cele mai bune rezultate, forma sa generală, dar în acelaşi timp simplă, recomandând-o pentru aplicaţii.

Thermodynamic properties, including pressure – volume – temperature (PVT), were predicted along the saturation curve for refrigerants R22 (Chlorodifluoromethane), R124 (2-chloro-1,1,1,2-tetrafloroethane) and R142b (1-chloro-1,1-difluoroethane). Three cubic equations of state (EOS) were used: Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) and GEOS3C. A wide comparison with experimental data was done. The GEOS3C equation, with three estimated parameters, compares favorably to other equations in literature, resting simple enough for applications.

Keywords: equation of state, thermodynamic properties, refrigerants

1. Introduction

Refrigerants are the working fluids in refrigeration, air-conditioning and heat pumping systems. The development of models for representation and prediction of physical properties and phase equilibria, as well as the improvement of current equations of state (EOS) is of particular interest for the refrigeration industry [1, 2].

A refrigerant must satisfy many requirements: chemical stability, heat transfer ability, low toxicity, efficiency, reduced environmental consequences. No single fluid satisfies all the attributes desired for a refrigerant; as a consequence, a

[1] Prof., Dept. of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: v_feroiu@catedra.chfiz.pub.ro
[2] Prof., Dept. of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania
[3] Lect., Dept. of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: tina@catedra.chfiz.pub.ro

variety of refrigerants is used. Refrigerant selection involves compromises between conflicting desirable thermodynamic properties.

In the thermodynamic framework it is possible to develop equations to calculate the Helmholz and Gibbs free energies, enthalpies, entropies, fugacity coefficients and other thermodynamic properties of fluids. Such relationships together with equations of states can be applied to obtain estimation techniques for thermodynamic property departure functions [3]. Then the "true" thermodynamic properties for pure components and mixtures are calculated.

In previous works [4-6], thermodynamic properties of pure refrigerants and refrigerant mixtures were predicted by cubic equations of state.

In this work, PVT and thermodynamic properties were predicted, along the saturation curve for three refrigerants: R22 (Chlorodifluoromethane), R124 (2-chloro-1,1,1,2-tetrafloroethane) and R142b (1-chloro-1,1-difluoroethane). Three cubic equations of state were used: Soave-Redlich-Kwong (SRK) [7], Peng-Robinson (PR) [8] and GEOS3C [4-6]. A wide comparison with experimental data was done. The GEOS3C equation, with three estimated parameters, compares favorably to other equations in literature, resting simple enough for applications.

2. The GEOS3C Equation of State

The GEOS3C equation of state is a general form [3] for the cubic equations of state with two, three and four parameters:

$$P = \frac{RT}{V - b} - \frac{a}{(V - d)^2 + c} \tag{1}$$

The four parameters a, b, c, d for a pure component are expressed by:

$$a = a_c\, \beta^2(T_r), \quad a_c = \Omega_a \frac{R^2 T_c^2}{P_c}, \quad b = \Omega_b \frac{RT_c}{P_c} \tag{2a}$$

$$c = \Omega_c \frac{R^2 T_c^2}{P_c^2}, \quad d = \Omega_d \frac{RT_c}{P_c} \tag{2b}$$

The temperature function is given by the following equations:

$$\beta(T_r) = 1 + C_1 y + C_2\, y^2 + C_3\, y^3 \qquad \text{for } T_r \le 1 \tag{3}$$

$$\beta(T_r) = 1 + C_1 y \qquad \text{for } T_r > 1 \qquad \text{where } y = 1 - \sqrt{T_r}$$

The expressions of the parameters Ωa, Ωb, Ωc, Ωd are:

$$\Omega_a = (1 - B)^3 \qquad \Omega_b = Z_c - B$$
$$\Omega_c = (1 - B)^2 (B - 0.25) \qquad \Omega_d = Z_c - 0.5(1 - B) \tag{4}$$

$$B = \frac{1 + C_1}{\alpha_c + C_1} \qquad \alpha_C \text{ - Riedel's criterion} \tag{5}$$

Using experimental values of the critical constants and of the acentric factor for the calculation of α_C from the equation:

$$\alpha_C = 5.808 + 4.93\omega \tag{6}$$

the C_1, C_2 and C_3 parameters were obtained by fitting points on the saturation curve (vapor pressures together with the corresponding liquid molar volumes). The following features of GEOS3C parameterization are important:

- It gives exactly the experimental critical point of any substance, and also the experimental critical compresibility factor Z_c;
- The prediction of the liquid volume is improved, without translation, by means of the parameter C_1 from the temperature function of the attractive term;
- The three parameters C_1, C_2 and C_3 can provide properly the saturation pressure curve;
- The involving of the parameter C_1 in the expressions of a and b, leads to a "coupling" between the repulsive and attractive terms in the cubic equation of state.

The equations for the departure (residual) functions from ideal gas state, based on GEOS equation (or GEOS3C), are presented in another paper [9]. These expressions may be also used for other cubic equations, which can be converted to the GEOS form.

As pointed out previously [4], the cubic GEOS equation is a general form for all the cubic equations of state with two, three and four parameters. This is the meaning of the statement “general cubic equation of state” used for GEOS.

For example, to obtain the parameters of the Soave-Redlich-Kwong (SRK) equation of state we set the following restrictions: $\Omega_c = -\left(\Omega_b/2\right)^2$ and $\Omega_d = \Omega_b/2$. It follows:

$$\Omega_c = (1-B)^2(B-0.25) = -(Z_c - B)^2/4 \tag{7}$$

$$\Omega_d = Z_c - 0.5(1-B) = (Z_c - B)/2 \tag{8}$$

It results $Z_c\left(SRK\right) = 1/3$, and the relation for $B\left(SRK\right)$:

$$B = 0.25 - \frac{1}{36}\left(\frac{1-3B}{1-B}\right)^2 \tag{9}$$

Solving iteratively this equation gives $B\left(SRK\right) = 0.2467$, and correspondingly: $\Omega_a\left(SRK\right) = \left(1-B\right)^3 = 0.42748$ and

$$\Omega_b\left(SRK\right) = Z_c - B = 0.08664 .$$

For Peng-Robinson (PR) equation of state we set the restrictions: $\Omega_c = -2\left(\Omega_b\right)^2$ and $\Omega_d = -\Omega_b$. It results:

$$B = 0.25 - \frac{1}{8}\left(\frac{1-3B}{1-B}\right)^2, \qquad Z_c = \frac{1+B}{4} \tag{10}$$

giving $B\left(PR\right) = 0.2296$ and $Z_c\left(PR\right) = 0.3074$.

3. Results and discussion

The prediction of thermodynamic properties of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) is of importance in relation to their use as refrigerants. Three equations of state have been used to calculate the phase equilibrium and the thermodynamic properties along the saturation curve for R22 (Chlorodifluoromethane), R124 (2-chloro-1,1,1,2-tetrafloroethane) and R142b (1-chloro-1,1-difluoroethane): Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) and GEOS3C. The calculations have been compared with recommended data of the ASHRAE collection [10]. Ideal gas heat capacities were taken from Reid et al. [11]. The values of the critical data, acentric factor and C1, C2 and C3 parameters of the GEOS3C equation for the investigated refrigerants are presented in Table 1.

Table 1

Values of critical data, acentric factor and C_1, C_2 and C_3 parameters (GEOS3C) for R22, R124 and R142b

Comp.	T_c (K)	P_c (MPa)	$V_c \times 10^3$ (m^3/kg)	ω	C_1	C_2	C_3
R22	369.3	4.99	1.91	0.2210	0.2722	0.5876	-0.2413
R124	395.6	3.634	1.81	0.2863	0.3490	0.5789	-0.0423
R142b	409.6	4.33	2.3	0.251	0.4964	0.7563	-2.5055

Table 2

PVT and thermodynamic function deviations on the saturation curve for R22. Temperature range (K): 143.15 – 369.29. Pressure range (MPa): 6×10^{-5} – 4.99 . Number of data points: 70

EOS	AAD %				AAD			
	P^S	V^L	V^V	$\Delta^V H$	H^L(kJ/kg)	H^V(kJ/kg)	S^L(kJ/kg/K)	S^V(kJ/kg/K)
GEOS	0.4	3.1	1.3	1.9	3.65	1.88	0.01	0.007
SRK	0.8	13.5	1.9	2.5	2.89	5.02	0.01	0.017
PR	1.4	3.1	2.2	2.	2.77	2.81	0.01	0.01

The results of the calculations for R22, R124 and R142b are summarized in Tables 2-4. In each table the number of data points, the pressure and

temperature ranges are indicated. The two-phase region properties have been calculated at temperatures from the triple point to the critical point.

In these tables, the average absolute deviations for a property Y are relative (%):

$$AAD\% = \frac{\sum_{i=1}^{N} \left| (Y_i^{eos} - Y_i^{\exp}) / Y_i^{\exp} \right| \cdot 100}{N} \tag{11}$$

excepting for the enthalpy and entropy where the following equation was used:

$$AAD\ H\ or\ S = \frac{\sum_{i=1}^{N} \left| H_i^{eos} - H_i^{\exp} \right|}{N} \tag{12}$$

Table 3

PVT and thermodynamic function deviations on the saturation curve for R124. Temperature range (K): 213.15 – 395.62. Pressure range (MPa): 8×10^{-3} – 3.63. Number of data points: 67

EOS	AAD %				AAD			
	P^S	V^L	V^V	$\Delta^V H$	H^L(kJ/kg)	H^V(kJ/kg)	S^L(kJ/kg/K)	S^V(kJ/kg/K)
GEOS	0.4	2.1	1.9	2.2	3.60	2.22	0.01	0.008
SRK	0.8	13.4	2.2	2.8	2.30	4.70	0.007	0.015
PR	0.5	3.7	1.8	2.1	1.28	2.47	0.004	0.008

Table 4

PVT and thermodynamic function deviations on the saturation curve for R142b. Temperature range (K): 223.15 – 409.6. Pressure range (MPa): 1.5×10^{-2} – 4.33. Number of data points: 73

EOS	AAD %				AAD			
	P^S	V^L	V^V	$\Delta^V H$	H^L(kJ/kg)	H^V(kJ/kg)	S^L(kJ/kg/K)	S^V(kJ/kg/K)
GEOS	1.3	2.1	2.1	3.4	3.58	8.11	0.01	0.02
SRK	5.1	5.3	2.4	5.6	10.54	18.53	0.03	0.06
PR	4	7	2.1	4.7	8.64	15.16	0.028	0.05

The following observations can be made on the basis of the results of the Tables 2 - 4:

- the vapor pressures and saturated volumes are better predicted by GEOS3C, compared to the results obtained using other equations;
- the difference in performance between the EOS is less noticeable for the other properties.

The SRK and PR equations can be used with the same temperature function (eq. 3) with three parameters. This fact leads to better values for vapor pressures but the values of saturated volumes can not be improved without a

translation procedure. The advantage of the GEOS3C equation is that the prediction of the liquid volume is improved without translation by the parameter C_1 as mentioned above.

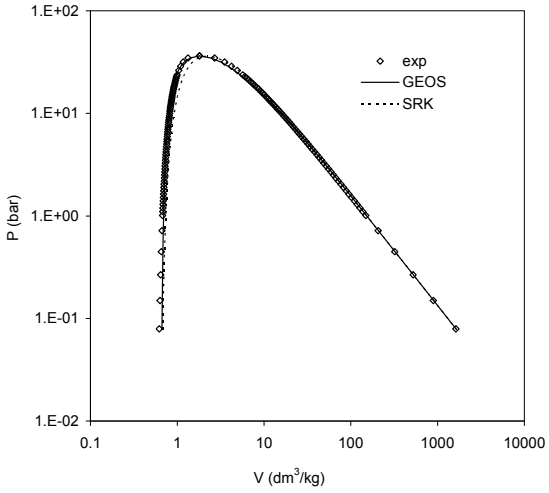

Fig. 1. Pressure - volume diagram (saturation curve) for R124; Points:Ashrae collection [10]

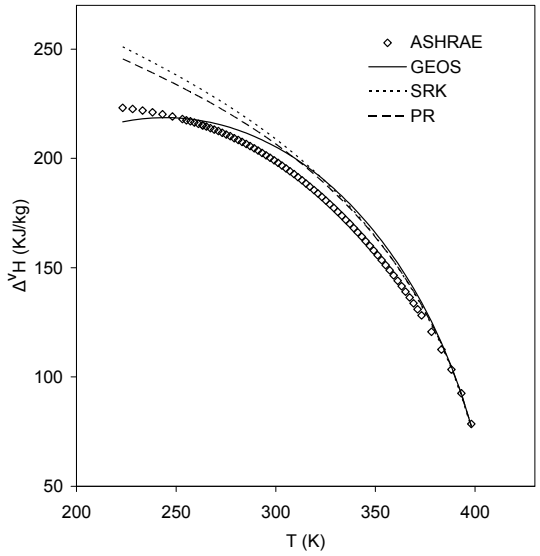

Fig. 2. Enthalpy of vaporization-temperature dependence for R142b; Points:Ashrae [10]

Examples of calculated properties are presented in Figs. 1-4. In Fig. 1, the P-V diagram calculated with the GEOS3C and SRK equations is plotted together with experimental saturation data for R124 (PR equation performs identically with the SRK equation). As can be seen, the difference between the performances of the equations is important on the liquid curve, the GEOS3C equation being in better agreement with experimental data. In Fig. 2, the enthalpy of vaporization – temperature dependence is presented for R142b. The points are experimental data and calculations are performed with all three equations of state. The GEOS equation performs better than the SRK and PR equations (see also the deviations in Table 4).

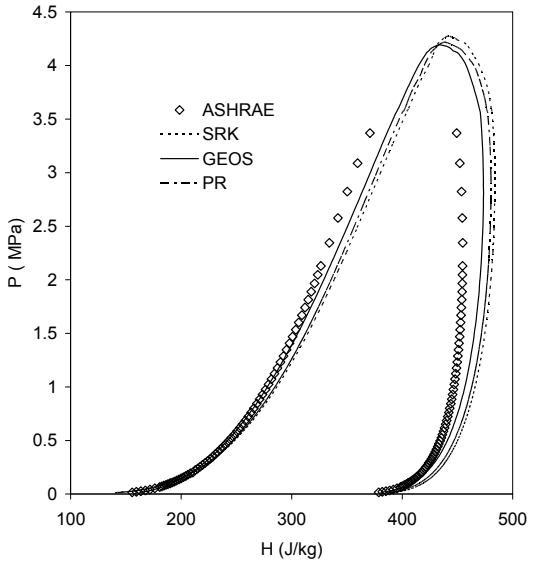

Fig.3. Pressure-enthalpy dependence along the saturation curve, for R142b;
Points:Ashrae collection [10]

Figs. 3 and 4 show the pressure – enthalpy and the temperature – entropy dependences, calculated by all three EOS, along the saturation curve, for R142b and R124. It can be seen that the GEOS3C equation reproduces better the enthalpy, while the entropy is well reproduced by all three EOS.

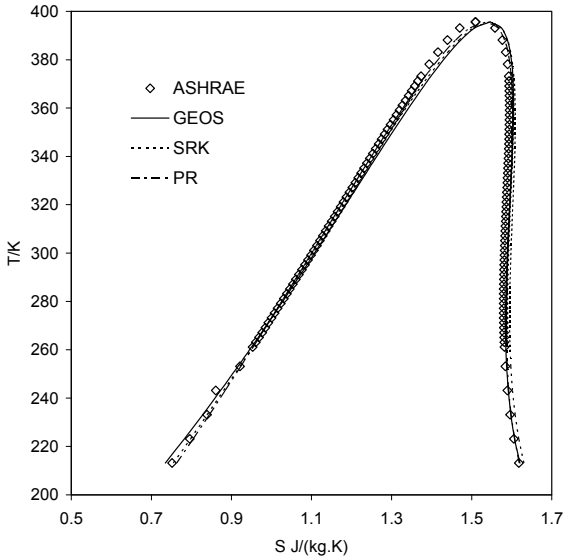

Fig. 4. Temperature-entropy dependence along the saturation curve, for R124;
Points: Ashrae collection [10]

4. Conclusions

The thermodynamic properties (including PVT properties) of refrigerants R22, R124 and R142b were predicted by three equations of state SRK, PR, and GEOS3C along the saturation curve. A comprehensive comparison with experimental data was done. The GEOS3C equation gives better predictions of vapor pressure and saturated liquid volume than the other equations of state. The saturated vapor volume is well reproduced by all three equations of state. The thermodynamic properties are well predicted by all three EOS. Although the SRK and PR equations give generally poor predictions of vapor pressure and saturated liquid volume, they lead to surprisingly good results for other properties (enthalpy and entropy). So far, GEOS3C with three estimated parameters compares favorably to other equations in literature, being simple enough for applications.

Acknowledgments

The authors are grateful to the National University Research Council (CNCSIS) of Romania for financial support (grants ID 1088, A 83).

List of symbols

a, b, c, d	- parameters in GEOS
AAD	- absolute average deviation
B	- dimensionless parameter in GEOS3C, eq. (5)
C_1, C_2 and C_3	- parameters in GEOS3C temperature function
H	- enthalpy
M	- molar mass
P, P^S	- pressure, saturation pressure
R	- universal gas constant
S	- entropy
T	- temperature
V, V^L, V^V	- molar volume, liquid volume, vapor volume
Y	- thermodynamic function (general notation)
Z	- compresibility factor

Greeks

α_c	- Riedel's criterium (parameter in GEOS)
β	- reduced temperature function in GEOS
Ω_a, Ω_b, Ω_c, Ω_d	- parameters of GEOS
ω	- acentric factor

Subscripts

c	- critical property
r	- reduced property

R E F E R E N C E S

[1]. *H. Madani, A. Valtz, C. Coquelet, A. H. Meniai, D. Richon*, "Vapor–liquid equilibrium data for the (hexafluoroethane +1,1,1,2-tetrafluoroethane) system at temperatures from 263 to 353 K and pressures up to 4.16 MPa", Fluid Phase Equilibria, **vol. 268**, iss. 1-2, 25 June 2008, pp. 68-73

[2]. *J. S. Lim, J. M. Jin, K.-P. Yoo*, "VLE measurement for binary systems of CO2 + 1,1,1,2-tetrafluoroethane (HFC-134a) at high pressures", J. Supercritical Fluids, **vol. 44**, iss. 3, April 2008, pp.279-283

[3]. *D. Geană, V. Feroiu*, Ecuații de stare. Aplicații la echilibre de faze (Equations of State. Applications to Phase Equilibria), Ed. Tehnică, București, 2000

[4]. *D. Geană, V. Feroiu*, "Thermodynamic Properties of Pure Fluids using a General Cubic Equation of State", Fluid Phase Equilibria, **vol. 174**, 2000, pp. 51-68
[5]. *D. Geană, V. Feroiu*, "Volumetric and Thermodynamic Properties for Pure Refrigerants and Refrigerant Mixtures from Cubic Equations of State", Fluid Phase Equilibria, **vol. 207**, 2003, pp. 283-300
[6]. *V. Feroiu, D. Geană, C. Secuianu*, „Properties of refrigerants from Cubic Equations of State" Rev. Chim. (Bucharest), **vol. 59** no.5, 2008, pp. 554-557
[7]. *G. Soave*, "Equilibrium Constant from a modified Redlich-Kwong Equation of State", Chem. Eng. Sci., **vol. 27**, 1972, pp. 1197-1205
[8]. *D.Y. Peng, D.B. Robinson*, "A new two-constant Equation of State", Ind. Eng. Chem. Fundam., **vol. 15**, 1976, pp. 59-64
[9]. *D. Geană, R. Tănăsescu*, "The computation of fluid thermodynamic Properties", Rev. Chim. (Bucharest), **vol. 40**, 1989, pp. 682-688
[10]. ASHRAE Handbook, Fundamentals, SI Edition, Ashrae Inc., Atlanta, 1997
[11]. *R. Reid, J.M. Prausnitz, B. Poling*, The Properties of Gases and Liquids, McGraw-Hill, New York, 1986.