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Modelling of the Isothermal Vapor-Liquid Equilibrium of Alternative Refrigerants: Determination of Phase Diagrams (High-pressure/Low-pressure) and Optimized Binary Interaction Parameters

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Abstract

In this work, a thermodynamic model for caluclation of Vapor-Liquid Equilibrium (VLE) at moderate pressures (up to 19 bar) and different temperatures (288-323 K) is developed by using Soave-Redlich-Kwong (SRK) and Peng-Robenson (PR) equations of state (EoS) in combination with the classical van der Waals (vdW) mixing rules. Four refrigerant binary systems have been considered in this study (R134a+ R1336mzz (E)), (R600a+R1234ze (Z)), (R600a+R1243zf), (R744+R152a). Also, a new method was used to improve binary interaction parameters (k_{ij}). A comparison of experimental phase equilibrium data in the literature with the calculated results showed very good representation for some mixing rules where the relative deviation of the vapor mole fraction does not exceed 5.09 % with PR-vdW and 4.48 % with SRK-vdW. However, the relative deviation of the pressure does not exceed 2.79 % with PR-vdW and 2.42 % with SRK-vdW.

Keywords: Alternative refrigerants, Vapor-liquid equilibrium, Cubic equation of state, Classical mixing rule, Binary interaction parameter.

1. Introduction:

The current search for sustainable and ecofriendly refrigerants become the most important criteria in the development of new refrigerants in the industrial field and especially the refrigeration engineering.

Over the last several years, much research and development effort has been focused on potential refrigerants possessing low global warming potentials (GWPs). In this context, the blends like the binary or ternary mixtures containing refrigerants with low GWP like hydrofluoroolefins (HFOs) with either hydrofluorocarbons (HFCs) or natural fluids become the most promising types of alternative refrigerants [1]. The detailed knowledge of the thermodynamic properties of those mixtures, and particularly of their (isothermal/isobaric) vapor-liquid equilibrium (VLE) behavior, is necessary to design and optimize the thermodynamic systems involving these refrigerants blends such as refrigeration systems,

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heat pumps and air-conditioning systems [2]. For example, to design a heat exchangers with and without phase changing for a thermodynamic system (refrigeration cycle for instance), it is important to know the state of the refrigerant mixture and to evaluate the level of the temperature change during cooling process (temperature glide) [3-4]. In this case, it is important to know if the refrigerant mixture behaves like a pure component (azeotropic behavior) or not.

The determination of the thermodynamic properties of the vapor-liquid phase can be carried out by means of various experimental measurements. However, performing any experimental method will be long, expensive and not always achievable. Hence, it is essential to have a reliable thermodynamic model able to predict accurately the thermodynamic behavior for the mixture. Accordingly, several researchers have proposed various (VLE) models for the calculations behavior of mixtures [5-6]. Among the proposed models, the cubic equations of state (EoS) through the mixing rules with binary interaction parameters have been used for the (VLE) calculation of refrigerant mixtures.

Currently, the (EoS) are one of the most convenient tools to determine and to correlate the thermodynamic properties and the phase behavior of mixtures. Since van der Waals introduced his famous (EoS) in 1873 [7], the cubic equations of state have been subject to active research and improvements, where are widely used in thermodynamic models in many engineering applications, due to their accuracy and simplicity [8-9], where numbers of researches on cubic equations of state (EoS) in the literature review have proved that the cubic (EoS) like Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations are among the most cubic (EoS) which give good accuracy in thermodynamic properties for the substances [10-14].

In other hand, we can find that the key point when using cubic (EoS) to describe the high-pressure/low-pressure phase equilibrium of the complex systems like the refrigerant mixtures is to give appropriate values to the binary interaction parameters (k_{ij}), which involved in the classical van der Waals (vdW) mixing rule [15].

For these reasons, much effort has been paid to get the binary interaction values for mixtures, because of the decisive effect of this latter on the (VLE) prediction. Some models and methods have been proposed to correlate (k_{ij}) with the thermodynamic properties, which include the temperature [16], the critical temperature and critical pressure [17], the composition [18], the acentric factor [19], the ionization potential [20] and infinite dilution activity coefficients [21]. However, the existing models for (k_{ij}) cannot be applicable to all refrigerant blends. Although some methods such as the linear relationship between (k_{ij}) and temperature [16], the van Laar-type expressions of (k_{ij})relating with composition [18] are valid for various types of mixtures, experimental data are still needed to determine the equation coefficients. Other expressions of (k_{ij}) are only effective for certain kinds of blends. For example, Chen et al. [22] assumed that each component in a (HFC/HC) blend had a mixing factor and (k_{ij}) could be obtained by these two mixing factors. Based on the acentric factors of the substances and the critical compressibility factor ratio, empirical correlations were developed to predict (k_{ij}) of refrigerant blends [19]. In other study, Jaubert and Mutelet [23] have proposed a group contribution model PPR78 (predictive 1978, PengRobinson EoS) to determine (k_{ij}) from the molecular structures. At present, the new model proposed can predict the vapor liquid equilibrium of any substance containing alkanes, alkenes, aromatic compounds, cycloalkanes, permanent gasses, mercaptans and water.

From the literature reviews survey about the previous researches of (k_{ij}), which enters into the modeling of the phase equilibrium of the mixtures it was noted that the accurate value of binary interaction parameter (k_{ij}) for classical van der Waals (vdW) mixing rule is highly significant for the vapor-liquid equilibrium calculation of

refrigerants mixtures. However, the existing models for (k_{ij}) cannot be applied to all refrigerant mixtures.

The purpose of this study is to propose a new simple method to predict the binary interaction parameter for the classical mixing rule, which can provide better accuracy of the isothermal (VLE) calculation in both subcritical and supercritical regions for any binary refrigerant systems, based on the cubic equations of state (SRK-EoS and PR-EoS) widely used in the academic researches. Therefore, in order to use this method, two thermodynamic models (SRK-vdW and PR-vdW) were proposed and used to correlate the data (PTxy) of four binary systems of alternative refrigerants available in literature. Both models are used to check their ability to describe the isothermal (VLE) behavior in a wide range of temperatures and pressures.

The binary systems of refrigerants considered in this study are:(R134a+ R1336mzz (E)) [24],(R600a+R1234ze (Z)) [25],(R600a+R1243zf) [26],(R744+R152a) [27].

The binary systems mentioned above are environmentally friendly with zero ozone depletion potential (ODP) and low global warming potential (GWP).

The critical parameters, acentric factors and environmental properties of the compounds of the binary blends are presented in Table 1.

Table 1. CAS No, Mole fraction purities, critical parameters (T_c,P_c) and acentric factors (ù) of pure substance[24-27]

Compound	CAS No.	Mole fraction purities	T_c/K	P_c/MPa	ω
R600a	75-28-5	0.995	407.81	3.6290	0.184
R1234ze(Z)	29118-25-0	0.995	423.27	3.5330	0.327
R1243zf	677-21-4	0.998	376.93	3.5182	0.261
R134a	811-97-2	0.995	374.21	4.0593	0.327
R1336mzz(E)	66711-86-2	0.999	403.37	2.7664	0.405
R744	124-38-9	0,998	304.20	7.3770	0.225
R152a	75-37-6	0,995	386.35	4.4990	0.226

2. Thermodynamic models:

2.1. Cubic equations of state and conventional mixing rule:

The cubic equation of state (EoS) describes the relationship between pressure (P), temperature (T), and molar volume (V). The cubic (EoS) has prevailed in the academic and industrial domains in describing the thermodynamic properties and phase behavior of diverse fluids over a wide range of temperatures and pressures.

Their general form is [27]:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v^2 + ubv + wb^2} \qquad (1)$$

Where (u and w) are parameters, P is the pressure, R is the universal gas constant, v is the molar volume, T is the temperature and (a, b)are the attractive term and the molar co-volume respectively, which are functions of the critical temperature and critical pressure of the substance (see Table 1).

To describe the (isothermal/isobaric) vapor-liquid equilibrium of the refrigerant mixture by the cubic (EoS), an appropriate mixing rule must be selected. The mixing rule is actually used to establish the relationship between the mixed energy parameters a_m and a_i of its components as well as the co-volume parameters a_m and b_i.

All of the experimental data was linked with the EoS using the traditional van der Waals (vdW) approach, which is one of the oldest methods for improving (EoS) results.

The mixing rule of van der Waals (vdW) is as follows:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad (2)$$

$$b_m = \sum_i x_i b_i \qquad (3)$$

With

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \qquad (4)$$

Where $k_{ii} = 0$, $k_{ij}=k_{ji}$ is the binary interaction parameter.

The binary interaction parameter was developed to describe chemical interactions between molecules i and j. The most difficult aspect of using the classical mixing rule is determining the precise value of this parameter, which we can see is extremely important in the (VLE) prediction of refrigerant blends, where he attempted to reduce the error associated with (EoS) and shift the results to a higher level of precision.

As a result, the current paper focuses on the investigation of these binary interaction parameters in order to improve the calculated isothermal (VLE) findings for binary refrigerant combinations.

The classical mixing rule for binary refrigerant mixes is as follows:

$$a_m = x_i^2 a_i + 2x_i x_j (1 - k_{ij})(a_i a_j)^{/2} + x_j^2 a_j \qquad (5)$$

$$b_m = x_i b_i + x_j b_j \qquad (6)$$

The cubic equations of state (PR and SRK) are chosen in this study to correlate the experimental data in order to effectively anticipate and characterize the isothermal (VLE) behavior of binary refrigerant mixes. In the following section, a description of the cubic (PR- and SRK) will be described and established.

2.1.1. Peng-robinson Equation of State:

Peng and Robinson proposed the PR equation of state in 1976 [17]. The PR equation, which is simple in form and has just two parameters a and b, is used to calculate the thermo-physical properties of mixed refrigerants:

The PR-EoS is given by the following form:

$$p = \frac{RT}{v - b} - \frac{\alpha(T)}{v^2 + 2vb - b^2} \qquad (7)$$

$$a_i(T) = 0.457235\ \frac{R^2 T_{c,i}^2 \alpha_i(T)}{p_{c,i}} \qquad (8)$$

$$b_i = 0.077796\ \frac{RT_{c,i}}{p_{c,i}} \qquad (9)$$

Where their alpha-function, it is given by:

$$\alpha_i(T) = \left[1 + (0.37464 + 1.5422\omega_i - 0.26992\omega_i^2)\left(1 - \sqrt{\frac{T}{T_{c,i}}}\right)\right]^2 \qquad (10)$$

The fugacity coefficients in the liquid and vapor phases must be equal for the refrigerant blends to be in isothermal vapor-liquid equilibrium. The fugacity coefficient of species i can be expressed as follows when the (PR-EoS) is used with the standard mixing rule (vdW) to forecast the isothermal vapor liquid equilibrium:

$$\ln\phi_i^L = \frac{b_i}{b_m}(z-1) - \ln\left[z\left(1 - \frac{b_m}{v}\right)\right] + \frac{a_m}{2.828RTb_m}\left(\frac{b_i}{b_m} - \frac{2}{a_m}\sum_j x_i a_{ij}\right)\ln\left(\frac{1 + 2.414\frac{b_m}{v}}{1 - 0.414\frac{b_m}{v}}\right) \qquad (11)$$

The cubic form (in compressibility factor) of (PR-EoS). Defining :

$$Z^3 + (B-1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) \qquad (12)$$

Where A and B are the dimensionless coefficients defined by the following formulas, respectively:

$$A = \frac{Pa_m}{(RT)^2} \qquad (13)$$

$$B = \frac{Pb_m}{(RT)} \quad (14)$$

2.1.2. Soave-Redlich-Kwong equation of state

In the process industry, the Soave-Redlich-Kwong equation of state (SRK-EoS) is one of the most extensively used models to correlate and forecast fluid characteristics and phase equilibrium.

The SRK-EoS is written in the following form:

$$p = \frac{RT}{v - b} - \frac{a(T)}{v^2 + bv} \quad (15)$$

The attractive and co-volume parameters (and, respectively) of pure components are defined as:

$$a_i = 0.42748 \frac{R^2 T_{c,i}^2 \alpha_i(T)}{p_{c,i}} \quad (16)$$

$$b_i = 0.08664 \frac{RT_{c,i}}{p_{c,i}} \quad (17)$$

Their alpha-function is expressed as follows:

$$\alpha_i(T) = \left[1 + (0.479794 + 1.57588\omega_i - 0.19207\omega_i^2 + 0.02461\omega_i^3)\left(1 - \sqrt{\frac{T}{T_{c,i}}}\right)\right]^2 \quad (18)$$

The fugacity coefficient of species i can be written as follows when the (SRK-EoS) is combined with the standard mixing rule (vdW) to forecast the isothermal vapor-liquid equilibrium:

$$\ln \phi_i^L = \frac{b_i}{b_m}(z-1) - \ln\left[z\left(1 - \frac{b_m}{v}\right)\right] + \frac{a_m}{RTb_m}\left(\frac{b_i}{b_m} - \frac{2}{a_m}\sum_j x_i a_{ij}\right)\ln\left(1 + \frac{b_m}{v}\right) \quad (19)$$

In terms of compressibility factor, the cubic form of (SRK-EoS). Defining,

$$Z^3 + Z^2 + (A - B - B^2)Z - AB \quad (20)$$

The calculated results of the thermodynamic properties are compared with experimental data from the literature, where the deviations MRDU and BIASU are applied on vapor phase mole fraction and pressure for the refrigerant blends considered in this study, to prove the accuracy of the two thermodynamic models (PR-vdW and SRK-vdW) used in this study.

The MRDU and BIASU deviations are defined as follows:

$$\text{BIASU} = \left(\frac{100}{N}\right)\sum\left(\frac{U_{cal} - U_{exp}}{U_{exp}}\right) \quad (21)$$

$$\text{MRDU} = \left(\frac{100}{N}\right)\sum\left|\frac{U_{cal} - U_{exp}}{U_{exp}}\right| \quad (22)$$

Where N is the number of data points, and U=y_i or P.

3. Computational Methods:

3.1. Approached for Isothermal VLE Calculations

The fundamental equations often refer to two common approaches for (isothermal/isobaric) vapor-liquid equilibrium calculations: the homogeneous (φ-φ) or heterogeneous (φ-γ) approaches.

Because of its powerful calculating capacity and excellent accuracy, the homogeneous technique (φ - φ) has been frequently employed in the (isothermal/isobaric) VLE correlation in earlier investigations. We used the approach (φ -φ) since it allows for a variety of important simplifications when examining phase behavior.

3.2. Binary Interaction Parameters Algorithm and Computational Approach

In this study, a new approach for calculating the binary interaction parameters involved in the classical van der Waals (vdW) mixing rule is proposed in order to obtain a predictive model applicable to any blend.

The isothermal VLE and binary interaction parameter for each isotherm in a refrigerant

mixture are calculated using a computer program; the calculation technique is shown in Fig.1.

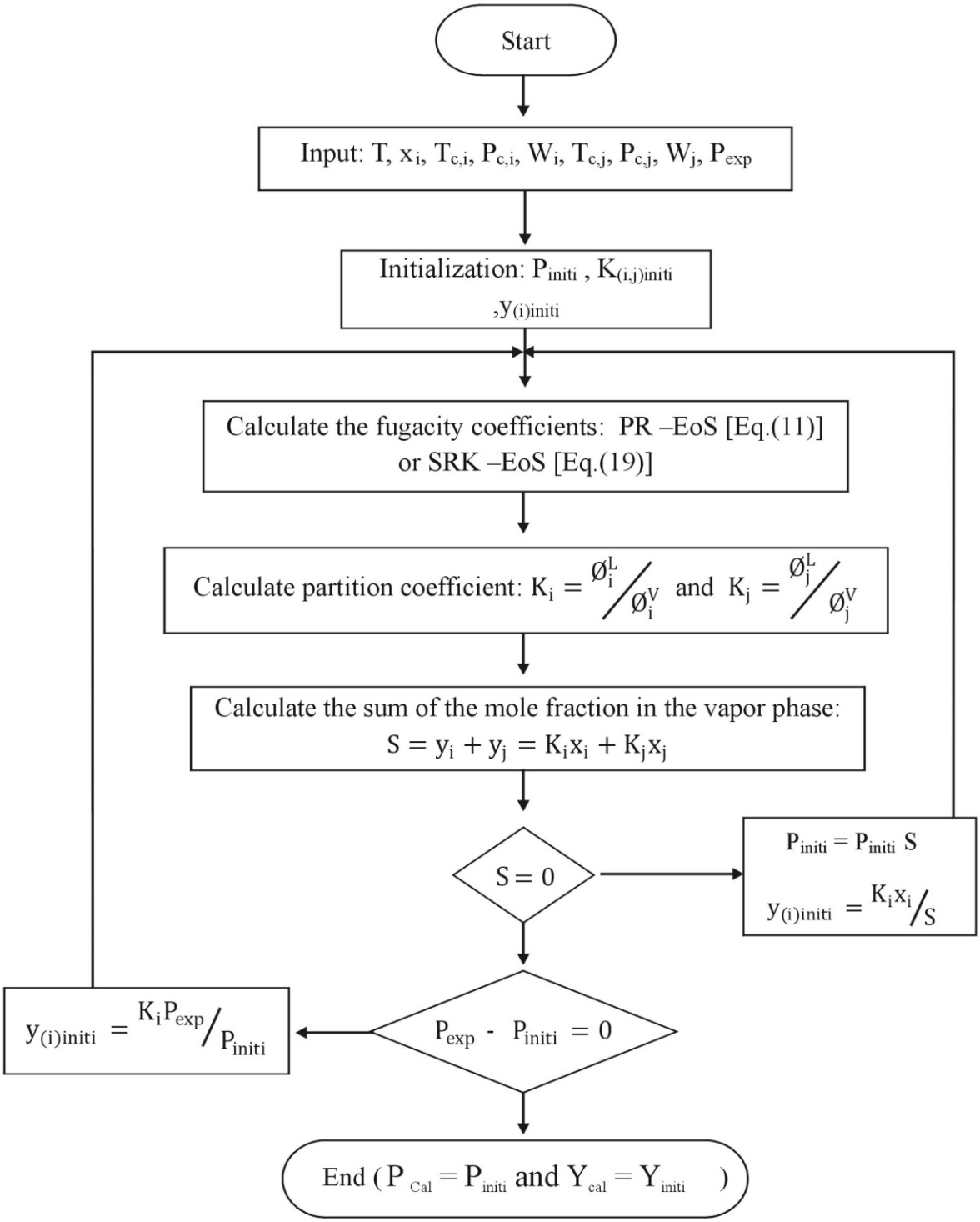

Figure 1: Calculation flowchart K_{ij} with liquid-vapor equilibrium at constant temperature.

- Enter the necessary data for the calculation, such as the temperature T, the mole fraction of the liquid phase x, and the mixture properties (Tc,Pc,vc,, ...).
- Initialization of pressure and vapor phase mole fraction y, and binary interaction parameters.
- The fugacity coefficient is calculated using the Soave-Redlich-Kwong (SRK-EoS) or Peng-Robinson (PR-EoS) equations of state, with the classical van der Waals (vdW) mixing rule.
- calculate partition coefficient :

$$k_i = \frac{\varphi_i^L}{\varphi_i^V} \qquad (23)$$

With

Yi=ki. xi so :

$$\sum_i y_i = 1 \qquad (24)$$

If the equilibrium requirement:

$$\sum_i y_i \neq 1$$

Is not met, the iterative cycle will proceed after normalizing the molar fractions using the following formula:

$$y_i = \frac{y_i}{\sum_i y_i} \qquad (25)$$

- Pressure adjustment based on the following equation:

$$P_{n+1} = P_n \cdot \sum_i y_i \qquad (26)$$

- Calculate binary interaction parameters :

$$K_{ij} = \frac{K_{ij} P_n}{P_{n+1}} \qquad (27)$$

Table 2: Temperature dependant binary interaction parameters k_{ij} of refrigerants mixtures.

Compound	Temperature/K	$k_{ij,exp}$	$k_{ij,cal}$	
			PRvdW	SRKvdW
R134a + R1336mzz [24]	313.24	0.0282	0.0298	0.0509
	333.19	0.0310	0.0323	0.0444
	353.12	0.0290	0.0300	0.0349
R600a + R1234ze(E) **[25]**	353.15	0.1462	0.1432	0.1452
	343.15	0.1461	0.1456	0.1436
	333.15	0.1451	0.1430	0.1460
	323.15	0.1467	0.1466	0.1479
	313.15	0.1430	0.1434	0.1452
	303.15	0.1429	0.1442	0.1321
R600a + R1243zf **[26]**	293.15	/	0.0771	0.0817
	283.15	/	0.0800	0.0827
	273.15	/	0.0823	0.0834
	263.15	/	0.0838	0.0834
	253.15	/	0.0848	0.0831
R744 + R152a **[27]**	258.44	/	0.0144	0.0093
	278.25	/	0.0192	0.0114
	298.84	/	0.0196	0.0166
	308.37	/	0.0173	0.0168
	323.30	/	0.0197	0.0201
	343.20	/	0.0439	0.0371

Table 3:

Experimental data			Calculated data with the PRvdW model				Calculated data with the SRKvdW model			
P_{exp}/MPa	x_{1exp}	y_{1exp}	P_{cal}/MPa	y_{1cal}	ΔP/ Mpa	Δy_1	P_{cal}/MPa	y_{1cal}	ΔP/MPa	Δy_1
R600a + R1234z(E) [25]										
					T=353.15K					
0.8592	0.0000	0.0000	0.8625	0.0000	-0.0033	0.0000	0.8744	0.0000	-0.0152	0.0000
0.9739	0.0510	0.1320	0.9890	0.1437	-0.0151	-0.0117	0.9906	0.1437	-0.0167	-0.0075
1.1664	0.1530	0.3020	1.1806	0.3169	-0.0142	-0.0149	1.1693	0.3169	-0.0029	-0.0101
1.3054	0.2550	0.4150	1.3113	0.4209	-0.0059	-0.0059	1.2943	0.4209	0.0111	-0.0078
1.4402	0.4080	0.5300	1.4341	0.5267	0.0061	0.0033	1.4150	0.5267	0.0252	-0.0028
1.5260	0.6460	0.6670	1.5162	0.6629	0.0098	0.0041	1.5006	0.6629	0.0254	0.0041
1.5267	0.6710	0.6710	1.5185	0.6896	0.0082	-0.0186	1.5032	0.6896	0.0235	-0.0067
1.5289	0.7300	0.7250	1.5166	0.7167	0.0123	0.0083	1.5039	0.7167	0.0250	0.0059
1.5139	0.7980	0.7710	1.5029	0.7670	0.0110	0.0040	1.4938	0.7670	0.0201	0.0067
1.4405	0.9210	0.8850	1.4335	0.8868	0.0070	-0.0018	1.4360	0.8868	0.0045	0.0054
1.3434	1.0000	1.0000	1.3446	1.0000	-0.0012	0.0000	1.3606	1.0000	-0.0172	0.0000
					T =343.15 K					
0.6713	0.0000	0.0000	0.6734	0.0000	-0.0021	0.0000	0.6824	0.0000	-0.0111	0.0000
0.9498	0.1580	0.3400	0.9631	0.3503	-0.0133	-0.0103	0.9553	0.3410	-0.0055	-0.0010
1.0626	0.2660	0.4500	1.0764	0.4548	-0.0138	-0.0048	1.0653	0.4480	-0.0027	0.0020
1.1651	0.4110	0.5510	1.1678	0.5460	-0.0027	0.0050	1.1565	0.5436	0.0086	0.0074
1.2311	0.6210	0.6680	1.2285	0.6531	0.0026	0.0149	1.2198	0.6563	0.0113	0.0117
1.2321	0.6400	0.6820	1.2306	0.6633	0.0015	0.0187	1.2222	0.6669	0.0099	0.0151
1.2344	0.6820	0.6950	1.2331	0.6867	0.0013	0.0083	1.2256	0.6913	0.0088	0.0037
1.2371	0.7300	0.7290	1.2319	0.7159	0.0052	0.0131	1.2256	0.7213	0.0115	0.0077
1.2270	0.7970	0.7710	1.2214	0.7625	0.0056	0.0085	1.2174	0.7688	0.0096	0.0022
1.1702	0.9200	0.8800	1.1643	0.8803	0.0059	-0.0003	1.1680	0.8856	0.0022	-0.0056
1.0874	1.0000	1.0000	1.0865	1.0000	0.0009	0.0000	1.0999	1.0000	-0.0125	0.0000
					T =333.15 K					
0.5174	0.0000	0.0000	0.5176	0.0000	-0.0002	0.0000	0.5240	0.0000	-0.0066	0.0000
0.6846	0.0970	0.2880	06876	0.2812	-0.0030	0.0068	0.6903	0.2768	-0.0057	0.0112
0.7594	0.1590	0.3760	0.7641	0.3751	-0.0047	0.0009	0.7656	0.3709	-0.0062	0.0051
0.8525	0.2690	0.4770	0.8574	0.4788	-0.0049	-0.0018	0.8584	0.4759	-0.0059	0.0011
0.9313	0.4110	0.5680	0.9277	0.5625	0.0036	0.0055	0.9292	0.5616	0.0021	0.0064
0.9798	0.6220	0.6790	0.9756	0.6608	0.0042	0.0182	0.9785	0.6625	0.0013	0.0165
0.9824	0.6520	0.6940	0.9782	0.6756	0.0042	0.0184	0.9814	0.6777	0.0010	0.0163
0.9849	0.6780	0.7010	0.9796	0.6891	0.0053	0.0119	0.9829	0.6914	0.0020	0.0096
0.9891	0.7300	0.7300	0.9794	0.7184	0.0097	0.0116	0.9832	0.7212	0.0059	0.0088
0.9805	0.7960	0.7710	0.9725	0.7619	0.0080	0.0091	0.9771	0.7651	0.0034	0.0059
0.9390	0.9180	0.8750	0.9303	0.8757	0.0087	-0.0007	0.9374	0.8784	0.0016	-0.0034
0.8690	1.0000	1.0000	0.8671	1.0000	0.0019	0.0000	0.8776	1.0000	-0.0086	0.0000

T =323.15 K

0.3918	0.0000	0.0000	0.3909	0.0000	0.0009	0.0000	0.3951	0.0000	-0.0033	0.0000
0.5373	0.0930	0.3090	0.5372	0.3049	0.0001	0.0041	0.5363	0.2983	0.0010	0.0107
0.5765	0.1420	0.3780	0.5916	0.3858	-0.0151	-0.0078	0.5894	0.3794	-0.0129	-0.0014
0.6804	0.2690	0.5100	0.6842	0.5068	-0.0038	0.0032	0.6811	0.5026	-0.0007	0.0074
0.7339	0.4130	0.5850	0.7391	0.5832	-0.0052	0.0018	0.7367	0.5810	-0.0028	0.0040
0.7750	0.6310	0.6820	0.7748	0.6699	0.0002	0.0121	0.7742	0.6725	0.0008	0.0095
0.7775	0.6790	0.7100	0.7772	0.6915	0.0003	0.0185	0.7769	0.6949	0.0006	0.0151
0.7811	0.7290	0.7340	0.7772	0.7168	0.0039	0.0172	0.7773	0.7209	0.0038	0.0131
0.7786	0.7730	0.7610	0.7744	0.7426	0.0042	0.0184	0.7751	0.7471	0.0035	0.0139
0.7750	0.7960	0.7720	0.7718	0.7577	0.0032	0.0143	0.7727	0.7624	0.0023	0.0096
0.7427	0.9170	0.8710	0.7375	0.8682	0.0052	0.0028	0.7412	0.8723	0.0015	-0.0013
0.6846	1.0000	1.0000	0.6824	1.0000	0.0022	0.0000	0.6902	1.0000	-0.0056	0.0000

T =313.15 K

0.2895	0.0000	0.0000	0.2907	0.0000	-0.0012	0.0000	0.2919	0.0000	-0.0024	0.0000
0.4630	0.1660	0.4360	0.4724	0.4417	-0.0094	-0.0057	0.4705	0.4368	-0.0075	-0.0008
0.5195	0.2610	0.5240	0.5245	0.5243	-0.0050	-0.0003	0.5224	0.5210	-0.0029	0.0030
0.5325	0.2820	0.5420	0.5329	0.5375	-0.0004	0.0045	0.5309	0.5346	0.0016	0.0074
0.5688	0.4160	0.6040	0.5702	0.6006	-0.0014	0.0034	0.5689	0.5999	-0.0001	0.0041
0.5957	0.6220	0.6890	0.5961	0.6747	-0.0004	0.0143	0.5900	0.6770	0.0057	0.0120
0.5972	0.6510	0.7020	0.5977	0.6861	-0.0005	0.0159	0.5977	0.6888	-0.0005	0.0132
0.5988	0.6810	0.7150	0.5988	0.6987	0.0000	0.0163	0.5989	0.7018	-0.0001	0.0132
0.6021	0.7300	0.7390	0.5991	0.7217	0.0030	0.0173	0.5995	0.7253	0.0026	0.0137
0.6002	0.7730	0.7600	0.5975	0.7453	0.0027	0.0147	0.5982	0.7493	0.0020	0.0107
0.5760	0.9160	0.8680	0.5713	0.8659	0.0047	0.0021	0.5740	0.8695	0.0020	-0.0015
0.5288	1.0000	1.0000	0.5309	1.0000	-0.0021	0.0000	0.5342	1.0000	-0.0054	0.0000

T =303.15 K

0.2106	0.0000	0.0000	0.2097	0.0000	0.0009	0.0000	0.2108	0.0000	-0.0002	0.0000
0.3187	0.1000	0.3670	0.3181	0.3774	0.0006	-0.0104	0.3085	0.3487	0.0102	0.0183
0.4029	0.2800	0.5550	0.4094	0.5637	-0.0065	-0.0087	0.3889	0.5473	0.0140	0.0077
0.4325	0.4140	0.6040	0.4369	0.6192	-0.0044	-0.0152	0.4183	0.6136	0.0142	-0.0096
0.4545	0.6210	0.6910	0.4553	0.6817	-0.0008	0.0093	0.4404	0.6905	0.0141	00005
0.4553	0.6540	0.7030	0.4567	0.6929	-0.0014	0.0101	0.4423	0.7037	0.0130	-0.0007
0.4555	0.6820	0.7150	0.4574	0.7033	-0.0019	00117	0.4435	0.7156	0.0120	-0.0006
0.4591	0.7570	0.7530	0.4573	0.7364	0.0018	0.0166	0.4447	0.7525	0.0144	0.0005
0.4577	0.7920	0.7700	0.4558	0.7558	0.0019	0.0142	0.4440	0.7731	0.0137	-0.0031
0.4418	0.9150	0.8640	0.4372	0.8603	0.0046	0.0037	0.4311	0.8760	0.0107	-0.0120
0.4045	1.0000	1.0000	0.4027	1.0000	0.0018	0.0000	0.4060	1.0000	-0.0015	0.0000

R744+R152a [27]

T =258.44 K

0.1440	0.0000	0.0000	0.1708	0.0000	-0.0268	0.0000	0.1704	0.0000	-0.0264	0.0000
0.3926	0.1241	0.6622	0.4121	0.6120	-0.0195	0.0502	0.4047	0.6072	-0.0121	0.0550
0.5887	0.2249	0.7794	0.6106	0.7555	-0.0219	0.0239	0.5995	0.7532	-0.0108	0.0262
0.8605	0.3586	0.8658	0.8775	0.8482	-0.0170	0.0176	0.8650	0.8481	-0.0045	0.0177
1.1022	0.4748	0.9105	1.1135	0.8947	-0.0113	0.0158	1.1028	0.8957	-0.0006	0.0148
1.3363	0.5860	0.9378	1.3436	0.9257	-0.0073	0.0121	1.3378	0.9273	-0.0015	0.0105
1.5068	0.6603	0.9516	1.5006	0.9422	0.0062	0.0094	1.4997	0.9440	0.0071	0.0076
1.7806	0.7793	0.9690	1.7599	0.9645	0.0207	0.0045	1.7690	0.9662	0.0116	0.0028
1.9646	0.8586	0.9800	1.9405	0.9777	0.0241	0.0023	1.9574	0.9790	0.0072	0.0010
2.2940	1.0000	1.0000	2.2907	1.0000	0.0033	0.0000	2.3192	1.0000	-0.0252	0.0000

T=278.25 K

0.3117	0.0000	0.0000	0.3475	0.0000	-0.0358	0.0000	0.3498	0.0000	-0.0381	0.0000
0.7628	0.1424	0.6021	0.7897	0.5809	-0.0269	0.0212	0.7742	0.5727	-0.0114	0.0294
1.0818	0.2416	0.7411	1.1052	0.7105	-0.0234	0.0306	1.0813	0.7103	0.0005	0.0308
1.4434	0.3541	0.8209	1.4714	0.8008	-0.0280	0.0201	1.4424	0.7991	0.0010	0.0218
1.8158	0.4641	0.8724	1.8395	0.8546	-0.0237	0.0178	1.8108	0.8550	0.0050	0.0174
2.4169	0.6298	0.9217	2.4193	0.9099	-0.0024	0.0118	2.4014	0.9120	0.0155	0.0097
2.7766	0.7241	0.9423	2.7690	0.9345	0.0076	0.0078	2.7626	0.9369	0.0140	0.0054
3.3002	0.8516	0.9682	3.2791	0.9644	0.0211	0.0038	3.2928	0.9665	0.0074	0.0017
3.6193	0.9245	0.9829	3.6003	0.9827	0.0190	0.0002	3.6266	0.9827	-0.0073	0.0002
3.9770	1.0000	1.0000	3.9678	1.0000	0.0092	0.0000	4.0070	1.0000	-0.0300	0.0000

T =298.84 K

0.6044	0.0000	0.0000	0.6533	0.0000	-0.0489	0.0000	0.6607	0.0000	-0.0563	0.0000
0.8566	0.0539	0.2811	0.8933	0.2711	-0.0367	0.0100	0.8961	0.2669	-0.0395	0.0142
1.2006	0.1285	0.5036	1.2322	0.4783	-0.0316	0.0253	1.2294	0.4740	-0.0288	0.0296
1.5657	0.2044	0.6306	1.5855	0.6023	-0.0198	0.0283	1.5781	0.5993	-0.0124	0.0313
2.2241	0.3370	0.7570	2.2261	0.7300	-0.0020	0.0270	2.2137	0.7293	0.0104	0.0277
2.9121	0.4707	0.8291	2.9083	0.8077	0.0038	0.0214	2.8952	0.8086	0.0169	0.0205
3.4703	0.5736	0.8673	3.4656	0.8510	0.0047	0.0163	3.4550	0.8527	0.0153	0.0146
4.2183	0.6928	0.9063	4.1607	0.8922	0.0576	0.0141	4.1560	0.8943	0.0623	0.0120
4.8098	0.7863	0.9313	4.7607	0.9215	0.0491	0.0098	4.7619	0.9236	0.0479	0.0077
5.2691	0.8537	0.9490	5.2387	0.9427	0.0304	0.0063	5.2443	0.9445	0.0248	0.0045
5.9322	0.9354	0.9741	5.9006	0.9711	0.0316	0.0030	5.9111	0.9721	0.0211	0.0020
6.5026	1.0000	1.0000	6.5403	1.0000	-0.0377	0.0000	6.5574	1.0000	-0.0548	0.0000

T =308.37 K

0.8125	0.0000	0.0000	0.8491	0.0000	-0.0366	0.0000	0.8597	0.0000	-0.0472	0.0000
1.1916	0.0722	0.3157	1.2182	0.3027	-0.0266	0.0130	1.2258	0.3002	-0.0342	0.0155
1.5738	0.1420	0.4969	1.5847	0.4677	-0.0109	0.0292	1.5897	0.4653	-0.0159	0.0316
1.9863	0.2148	0.6097	1.9781	0.5788	0.0082	0.0309	1.9808	0.5773	0.0055	0.0324
2.4474	0.2950	0.6937	2.4258	0.6630	0.0216	0.0307	2.4266	0.6625	0.0208	0.0312
3.2039	0.4194	0.7783	3.1549	0.7516	0.0490	0.0267	3.1538	0.7523	0.0501	0.0260
3.8496	0.5197	0.8239	3.7802	0.8026	0.0694	0.0213	3.7786	0.8040	0.0710	0.0199
4.5178	0.6201	0.8621	4.4498	0.8437	0.0680	0.0184	4.4482	0.8455	0.0696	0.0166
5.2406	0.7176	0.8922	5.1568	0.8782	0.0838	0.0140	5.1553	0.8803	0.0853	0.0119
5.9377	0.7994	0.9179	5.8123	0.9056	0.1254	0.0123	5.8097	0.9076	0.1280	0.0103
6.5836	0.8755	0.9387	6.5002	0.9318	0.0834	0.0069	6.4948	0.9335	0.0888	0.0052
6.9820	0.9152	0.9507	6.9042	0.9468	0.0778	0.0039	6.8964	0.9482	0.0856	0.0025
7.2005	0.9355	0.9594	7.1272	0.9550	0.0733	0.0044	7.1180	0.9563	0.0825	0.0031

T=323.30 K

1.1855	0.0000	0.0000	1.2403	0.0000	-0.0548	0.0000	1.2565	0.0000	-0.0710	0.0000
1.6868	0.0743	0.2788	1.7103	0.2659	-0.0235	0.0129	1.7221	0.2636	-0.0353	0.0152
2.2083	0.1497	0.4515	2.2020	0.4269	0.0063	0.0246	2.2095	0.4288	-0.0012	0.0227
2.5545	0.1999	0.5295	2.5382	0.5024	0.0163	0.0271	2.5429	0.5009	0.0116	0.0286
3.2220	0.2908	0.6352	3.1668	0.6022	0.0552	0.0330	3.1665	0.6019	0.0555	0.0333
3.7500	0.3615	0.6909	3.6751	0.6590	0.0749	0.0319	3.6712	0.6595	0.0788	0.0314
4.4350	0.4516	0.7417	4.3512	0.7150	0.0838	00267	4.3427	0.7165	0.0923	0.0252
5.1337	0.5398	0.7808	5.0486	0.7681	0.0851	0.0127	5.0357	0.7605	0.0980	0.0203
6.0221	0.6320	0.8206	5.8221	0.7947	0.2000	0.0259	5.8046	0.7978	0.2175	0.0228
6.9335	0.7319	0.8482	6.7158	0.8262	0.2177	0.0220	6.6949	0.8305	0.2386	0.0177
7.3614	0.7760	0.8546	7.1185	0.8362	0.2429	0.0184	7.0998	0.8413	0.2616	0.0133
7.6482	0.8088	0.8522	7.3944	0.8387	0.2538	0.0135	7.3867	0.8457	0.2615	0.0065

T =343.20 K

1.8917	0.0000	0.0000	1.9534	0.0000	-0.0617	0.0000	1.9762	0.0000	-0.0845	0.0000
2.6048	0.0826	0.2400	2.6627	0.2368	-0.0579	0.0032	2.6532	0.2313	-0.0484	0.0087
3.3138	0.1628	0.3915	3.3641	0.3767	-0.0503	0.0148	3.3264	0.3721	-0.0126	0.0194
3.9365	0.2310	0.4847	3.9698	0.4587	-0.0333	0.0260	3.9111	0.4562	0.0254	0.0285
4.6958	0.3117	0.5657	4.6956	0.5288	0.0002	0.0369	4.6166	0.5295	0.0792	0.0362
5.2202	0.3651	0.6012	5.1793	0.5638	0.0409	0.0374	5.0905	0.5669	0.1297	0.0343
6.0298	0.4491	0.6467	5.9370	0.6046	0.0928	0.0421	5.8410	0.6174	0.1888	0.0293
6.5459	0.5001	0.6640	6.3837	0.6210	0.1622	0.0430	6.2918	0.6313	0.2541	0.0327
7.1663	0.5650	0.6794	6.8961	0.6288	0.2702	0.0506	6.8332	0.6456	0.3331	0.0338
7.4117	0.5941	0.6710	7.0642	0.6226	0.3475	0.0484	7.0409	0.6455	0.3708	0.0255

:134a+R1336mzz

T =313.24 K

0.3209	0.0000	0.0000	0.3209	0.0000	0.0000	0.0000	0.3241	0.0000	0.0000	0.0000
0.4306	0.1290	0.3080	0.4279	0.3190	0.0027	-0.0110	0.4399	0.3288	-0.0093	-0.0208
0.5288	0.2520	0.5000	0.5245	0.5025	0.0043	-0.0025	0.5394	0.5077	-0.0106	-0.0077
0.6327	0.4030	0.6490	0.6360	0.6531	-0.0033	-0.0041	0.6477	0.6504	-0.0150	-0.0014
0.7222	0.5340	0.7480	0.7270	0.7488	-0.0048	-0.0008	0.7305	0.7403	-0.0083	0.0077
0.8337	0.6950	0.8480	0.8322	0.8431	0.0015	0.0049	0.8201	0.8306	0.0136	0.0174
0.8985	0.8050	0.9040	0.9010	0.9001	-0.0025	0.0039	0.8749	0.9001	0.0236	0.0039
1.0197	1.0000	1.0000	1.0197	1.0000	0.0000	0.0000	0.9607	1.0000	0.0000	0.0000

T = 333.19 K

0.5732	0.0000	0.0000	0.5732	0.0000	0.0000	0.0000	0.5807	0.0000	-0.0075	0.0000
0.7358	0.1250	0.2700	0.7310	0.2760	0.0048	-0.0060	0.7431	0.2781	-0.0073	-0.0081
0.9109	0.2710	0.4770	0.9078	0.4820	0.0031	-0.0050	0.9207	0.4819	-0.0098	-0.0049
1.1194	0.4580	0.6590	1.1230	0.6591	-0.0036	-0.0001	1.1299	0.6555	-0.0105	0.0035
1.3115	0.6330	0.7890	1.3141	0.7832	-0.0026	0.0058	1.3087	0.7766	0.0028	0.0124
1.5086	0.8240	0.9040	1.5133	0.8965	-0.0047	0.0075	1.4869	0.8912	0.0217	0.0128
1.6903	1.0000	1.0000	1.6903	1.0000	0.0000	0.0000	1.6903	1.0000	0.0000	0.0000

T = 353.12 K

0.9546	0.0000	0.0000	0.9546	0.0000	0.0000	0.0000	0.9670	0.0000	0.0000	0.0000
1.2292	0.1510	0.2780	1.2176	0.2783	0.0116	-0.0003	1.2288	0.2771	0.0004	0.0009
1.4885	0.3030	0.4710	1.4785	0.4692	0.0100	0.0018	1.4866	0.4676	0.0019	0.0034
1.8177	0.5040	0.6570	1.8188	0.6535	-0.0011	0.0035	1.8199	0.6519	-0.0022	0.0051
2.0626	0.6550	0.7720	2.0724	0.7660	-0.0098	0.0060	2.0659	0.7647	-0.0033	0.0073
2.3279	0.8170	0.8730	2.3136	0.8762	0.0143	-0.0032	2.3261	0.8753	0.0018	-0.0023
2.6483	1.0000	1.0000	2.6483	1.0000	0.0000	0.0000	2.6133	1.0000	0.0000	0.0000

R600a +R1243zf [26]

T =253.15 K

0.1262	0.0000	0.0000	0.1265	0.0000	-0.0003	0.0000	0.1263	0.0000	-0.0001	0.0000
0.1314	0.1425	0.1628	0.1321	0.1605	-0.0007	0.0023	0.1321	0.1615	-0.0007	0.0013
0.1322	0.2153	0.2201	0.1327	0.2153	-0.0005	0.0048	0.1327	0.2159	-0.0005	0.0042
0.1323	0.2549	0.2473	0.1325	0.2408	-0.0002	0.0065	0.1326	0.2410	-0.0003	0.0063
0.1323	0.2937	02719	0.1322	0.2637	0.0001	0.0082	0.1322	0.2634	0.0001	0.0085
0.1316	0.3278	0.2943	0.1317	0.2825	-0.0001	0.0118	0.1317	0.2818	-0.0001	0.0125
0.1279	0.4666	0.3699	0.1282	0.3523	-0.0003	0.0176	0.1283	0.3498	-0.0004	0.0201
0.1224	0.6093	0.4419	0.1221	0.4266	0.0003	0.0153	0.1222	0.4219	0.0002	0.0200
0.1037	0.8452	0.6256	0.1014	0.6277	0.0023	-0.0021	0.1012	0.6201	0.0025	0.0055
0.0725	1.0000	1.0000	0.0728	1.0000	-0.0003	0.0000	0.0717	1.0000	0.0008	0.0000

T= 263.15 K

0.1870	0.0000	0.0000	0.1871	0.0000	-0.0001	0.0000	0.1877	0.0000	-0.0007	0.0000
0.1942	0.1408	0.1579	0.1950	0.1576	-0.0008	0.0003	0.1953	0.1563	-0.0011	0.0016
0.1950	0.2151	0.2170	0.1958	0.2143	-0.0008	0.0027	0.1959	0.2126	-0.0009	0.0044
0.1950	0.2558	0.2467	0.1955	0.2410	-0.0005	0.0057	0.1956	0.2392	-0.0006	0.0075
0.1950	0.2942	0.2704	0.1949	0.2641	0.0001	0.0063	0.1950	0.2618	0.0000	0.0086
0.1938	0.3303	0.2940	0.1941	0.2846	-0.0003	0.0094	0.1942	0.2825	-0.0004	0.0115
0.1884	0.4809	0.3762	0.1883	0.3628	0.0001	0.0134	0.1881	0.3603	0.0003	0.0159
0.1801	0.6169	0.4492	0.1791	0.4370	0.0010	0.0122	0.1789	0.4341	0.0012	0.0151
0.1506	0.8513	0.6473	0.1482	0.6452	0.0024	0.0021	0.1477	0.6423	0.0029	0.0050
0.1085	1.0000	1.0000	0.1085	1.0000	0.0000	0.0000	0.1076	1.0000	0.0009	0.0000

T =273.15 K

0.2681	0.0000	0.0000	0.2682	0.0000	-0.0001	0.0000	0.2700	0.0000	-0.0019	0.0000
0.2778	0.1411	0.1565	0.2786	0.1558	-0.0008	0.0007	0.2794	0.1529	-0.0016	0.0036
0.2786	0.2152	0.2149	0.2796	0.2130	-0.0010	0.0019	0.2800	0.2097	-0.0014	0.0052
0.2785	0.2557	0.2464	0.2792	0.2401	-0.0007	0.0063	0.2794	0.2368	-0.0009	0.0096
0.2776	0.2939	0.2697	0.2783	0.2638	-0.0007	0.0059	0.2784	0.2606	-0.0008	0.0091
0.2761	0.3315	0.2928	0.2770	0.2858	-0.0009	0.0070	0.2770	0.2826	-0.0009	0.0102
0.2683	0.4822	0.3804	0.2683	0.3672	0.0000	0.0132	0.2679	0.3649	0.0004	0.0155
0.2560	0.6174	0.4593	0.2550	0.4441	0.0010	0.0152	0.2543	0.4428	0.0017	0.0165
0.2093	0.8757	0.6819	0.2054	0.6857	0.0039	-0.0038	0.2045	0.6864	0.0048	-0.0045
0.1570	1.0000	1.0000	0.1566	1.0000	0.0004	0.0000	0.1562	1.0000	0.0008	0.0000

T= 283.15 K

0.3735	0.0000	0.0000	0.3738	0.0000	-0.0003	0.0000	0.3775	0.0000	-0.0040	0.0000
0.3856	0.1398	0.1510	0.3870	0.1522	-0.0014	-0.0012	0.3884	0.1481	-0.0028	0.0029
0.3864	0.2156	0.2117	0.3879	0.2114	-0.0015	0.0003	0.3886	0.2070	-0.0022	0.0047
0.3857	0.2553	0.2458	0.3873	0.2386	-0.0016	0.0072	0.3876	0.2343	-0.0019	0.0115
0.3849	0.2948	0.2696	0.3859	0.2639	-0.0010	0.0057	0.3860	0.2598	-0.0011	0.0098
0.3828	0.3336	0.2933	0.3839	0.2873	-0.0011	0.0060	0.3838	0.2835	-0.0010	0.0098
0.3714	0.4822	0.3869	0.3714	0.3712	0.0000	0.0157	0.3705	0.3691	0.0009	0.0178
0.3538	0.6177	0.4636	0.3525	0.4518	0.0013	0.0118	0.3510	0.4517	0.0028	0.0119
0.2888	0.8760	0.7001	0.2827	0.7038	0.0061	-0.0037	0.2815	0.7072	0.0073	-0.0071
0.2207	1.0000	1.0000	0.2197	1.0000	0.0010	0.0000	0.2201	1.0000	0.0006	0.0000

T=293.15 K										
0.5072	0.0000	0.0000	0.5085	0.0000	-0.0013	0.0000	0.5145	0.0000	-0.0073	0.0000
0.5221	0.1400	0.1487	0.5244	0.1497	-0.0023	-0.0010	0.5267	0.1450	-0.0046	0.0037
0.5226	0.2213	0.2168	0.5251	0.2136	-0.0025	0.0032	0.5261	0.2086	-0.0035	0.0082
0.5216	0.2573	0.2425	0.5240	0.2387	-0.0024	0.0038	0.5245	0.2339	-0.0029	0.0086
0.5195	0.2956	0.2699	0.5220	0.2639	-0.0025	0.0060	0.5220	0.2594	-0.0025	0.0105
0.5179	0.3358	0.2923	0.5190	0.2891	-0.0011	0.0032	0.5186	0.2850	-0.0007	0.0073
0.5013	0.4869	0.3877	0.5007	0.3784	0.0006	0.0093	0.4991	0.3766	0.0022	0.0111
0.4776	0.6169	0.4783	0.4754	0.4594	0.0022	0.0189	0.4731	0.4602	0.0045	0.0181
0.3891	0.8796	0.7079	0.3800	0.7213	0.0091	-0.0134	0.3786	0.7265	0.0105	-0.0186
0.3022	1.0000	1.0000	0.3007	1.0000	0.0015	0.0000	0.3024	1.0000	-0.0002	0.0000

Table 4 : Pressure does not exceed 2.79 % with PR-vdW and 2.42 % with SRK-vdW

T/K	PRvdW				SRKvdW			
	MRDP	$MRDy_1$	BIASP	$BIASy_1$	MRDP	$MRDy_1$	BIASP	$BIASy_1$
R600a + R1234ze(E) [25]								
353.15 K	0.66	2.34	-0.01	-1.70	1.28	1.68	0.37	-1.03
343.15 K	0.47	1.57	-0.12	0.65	0.79	0.95	0.13	0.74
333.15 K	0.53	1.38	0.25	1.29	0.53	1.51	-0.24	1.43
323.15 K	0.56	1.56	-0.09	1.15	0.52	1.45	-0.22	1.35
313.15 K	0.50	1.39	-0.21	1.12	0.54	1.17	-0.15	1.10
303.15 K	0.59	1.76	-0.06	0.22	2.51	1.12	2.42	0.33
R600a + R1234zf [26]								
253.15 K	0.46	2.73	0.05	2.64	0.54	2.93	0,21	2.93
263.15 K	0.35	1.98	0.10	1.98	0.55	2.69	0,17	2.69
273.15 K	0.40	1.98	0.10	1.84	0.63	2.98	0,09	2.81
283.15 K	0.47	1.98	0.11	1.56	0.72	3.00	0.04	2.74
293.15 K	0.57	1.91	0.11	1.27	0.83	3.18	-0.01	2.53
R134a + R1336mzz [24]								
313,24 K	0.51	0.97	0.03	-0.63	1.99	2.00	-0.57	-0.83
333,19 K	0.37	0.97	0.03	-0.34	0.93	1.51	-0.27	-0.10
353,15 K	0.55	0.43	0.34	0.24	0.10	0.61	-0.01	0.50
R744+R152a [27]								
258,44 K	3.38	2.17	-2.79	2.17	2.65	2.21	-2.35	2.21
278,25 K	2.22	1.83	-1.88	1.83	1.64	1.94	-1.21	1.94
298,84 K	1.73	2.47	-1.10	2.47	1.90	2.65	-1.10	2.65
308,37 K	1.59	2.68	0.45	2.68	1.79	2.70	0.30	2.70
323,30 K	2.27	3.61	1.27	3.61	2.54	3.53	1.18	3.53
343,20 K	1.76	5.09	0.45	5.09	2.35	4.48	1.23	4.48

4. Results and Discussion:

In this section, we present the results of the calculated (P,T,x,y) properties and the thermodynamic behavior of the studied binary refrigerant blends.

Figs.2-5 depict the variation of bubble point pressure and dew point pressure of the binary blends: (R600a+R1234ze(Z)), (R600a+R1234zf), (R134a+R1336mzz) and (R744 + R152a) at different temperatures where the symbols denote the experimental data of the vapor-liquid equilibrium properties (P,T,x,y) collected from the literature [24-27], while the line patterns (solid line and dashed line) represent the calculated values obtained using the thermodynamic models: PR-vdW (Fig.2 (a), Fig.3 (a), Fig.4 (a), Fig.5 (a)) and SRK-vdW (Fig.2 (b), Fig.3 (b), Fig.4 (b), Fig.5 (b)) with our simple method which improves the binary interaction parameters (k_{ij}) of the classical mixing rule (vdW).

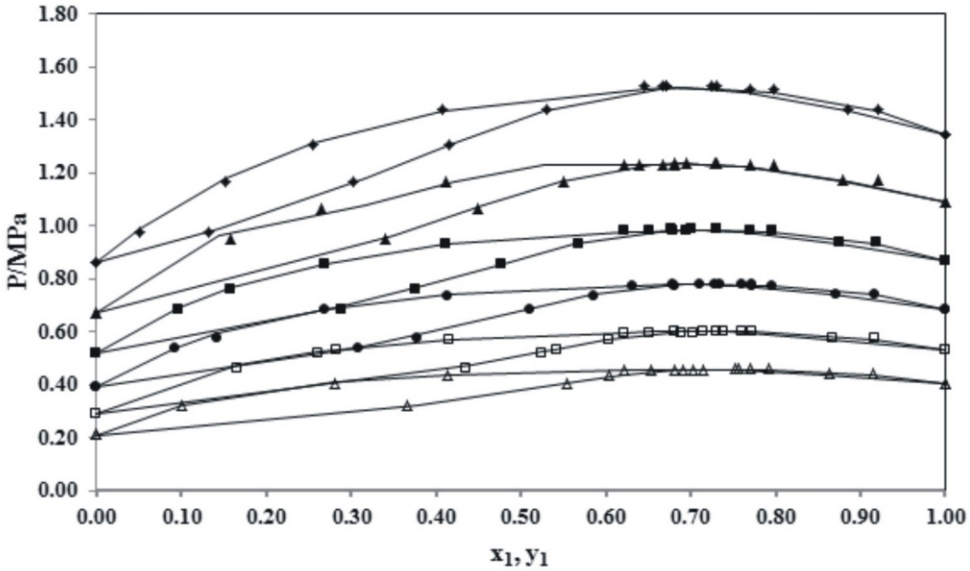

Fig.2.a.P-x-y diagram for vapor-liquid equilibrium of R600a+R1234ze (E) system Experimental data [25]: (Δ) 303.15 K; (□) 313.15 K; (•) 323.15 K; (■) 333.15 K ;(▲) 343.15 K (♦); 353.15 K; Calculated values using PR-vdW model: (—).

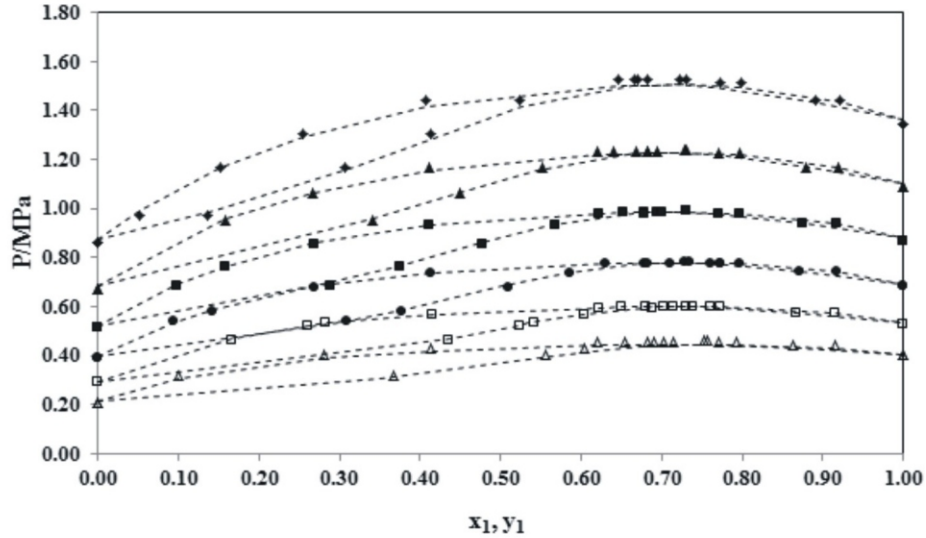

Fig.2.b.P-x-y diagram for vapor-liquid equilibrium of R600a+R1234ze (E) system Experimental data [25]: (Δ) 303.15 K; (□) 313.15 K; (•) 323.15 K; (■) 333.15 K ;(▲) 343.15 K (♦); 353.15 K; Calculated values using PR-vdW model: (—).

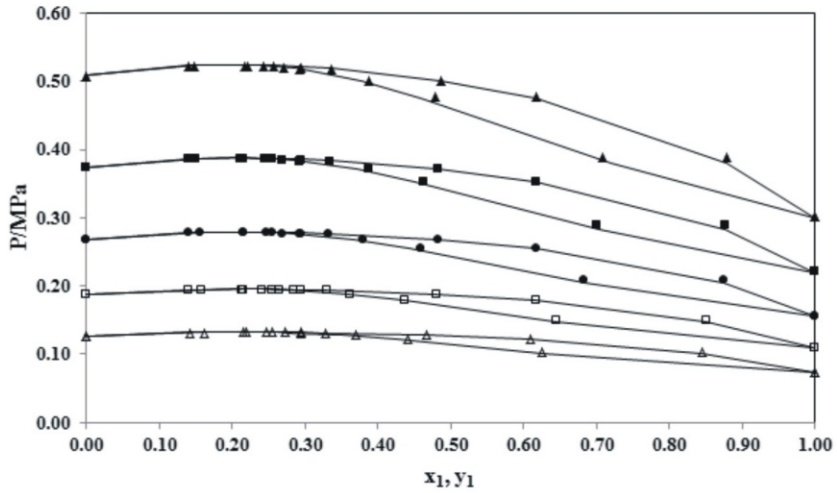

Fig.3.a.P-x-y diagram for vapor-liquid equilibrium of R600a+R1234ze (E) system Experimental data [26]: (Δ) 253.15 K; (□) 263.15 K; (•) 273.15 K; (■) 283.15 K ;(▲) 293.15 K Calculated values using PR-vdW model: (—).

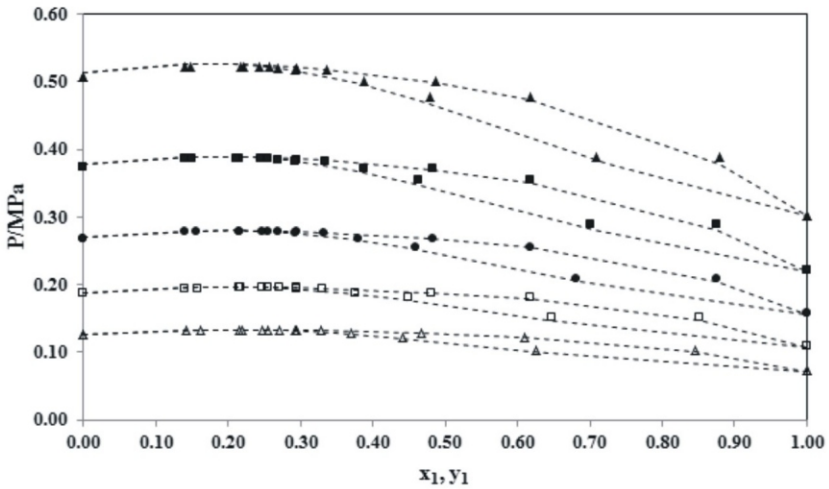

Fig.3.b.P-x-y diagram for vapor-liquid equilibrium of R600a+R1234zf system Experimental data [26]: (Δ) 253.15 K; (□)263.15 K; (•) 273.15 K; (■) 283.15 K;(▲) 293.15 K; Calculated values using SRK-vdW model: (—).

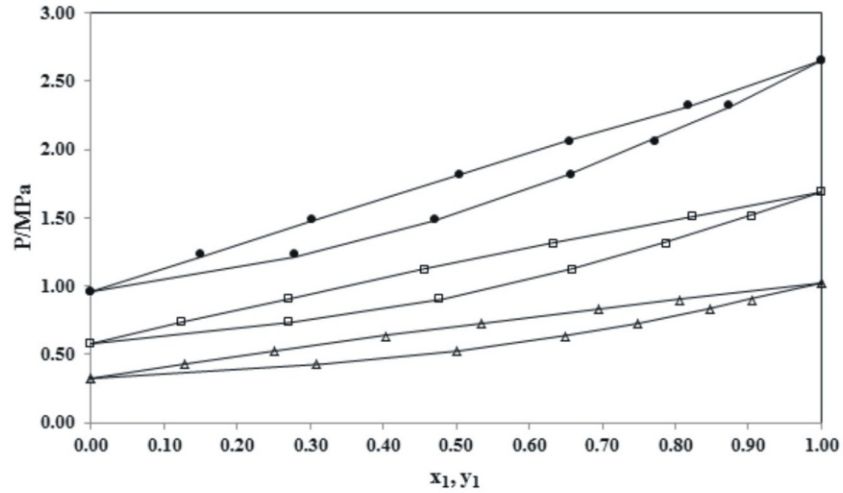

Fig.4.a.P-x-y diagram for vapor-liquid equilibrium of R134a +R1336mzz system Experimental data [24]: (Δ) 313.24 K; (□) 333.19 K; (•) 353.12 K ; Calculated values using PR-vdW model: (—).

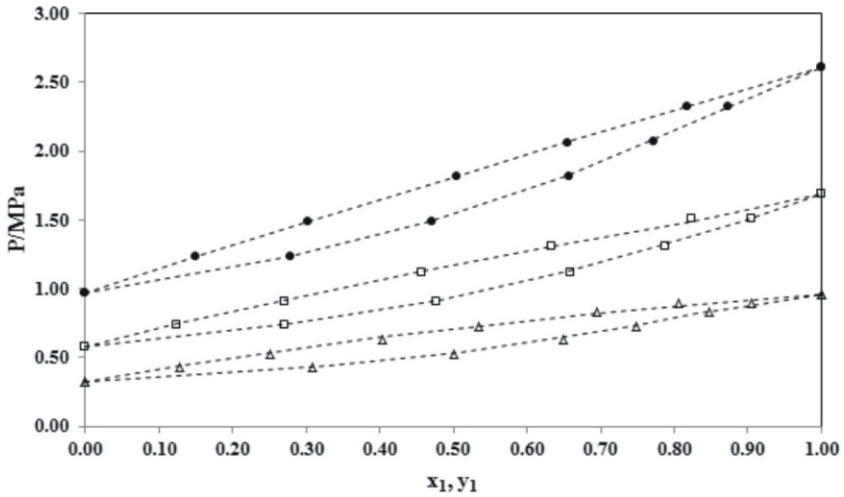

Figure 4.b: P-x-y diagram for vapor-liquid equilibrium of R134a +R1336mzz system Experimental data [24]: (Δ) 313.24 K; (□) 333.19 K; (•) 353.12 K ; Calculated values using PR-vdW model: (…).

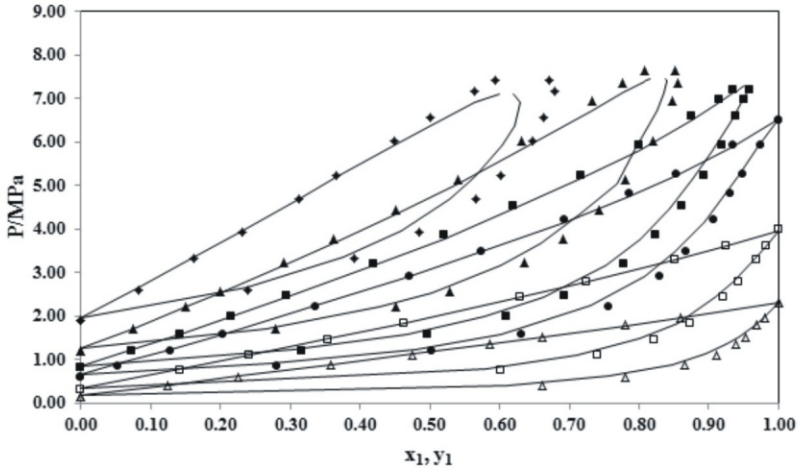

Figure 5.a: P-x-y diagram for vapor-liquid equilibrium of R744 + R152a system Experimental data [27]: (Δ) 258.44 K; (□) 278.25 K; (●) 298.84 K; (■) 308.37 K ;(▲) 323.30 K (♦); 343.20 K; Calculated values using PR-vdW model: (—).

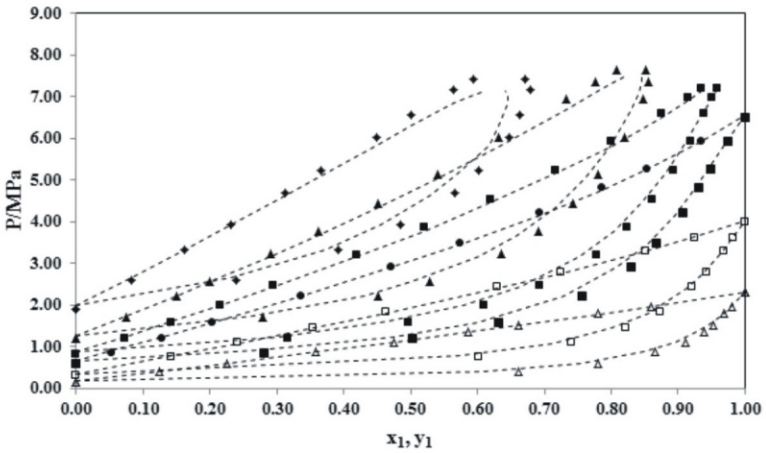

Figure 5.b: x-y diagram for vapor-liquid equilibrium of R744 + R152a system Experimental data [27]: (Δ) 258.44 K;(□) 278.25 K; (●) 298.84 K; (■) 308.37 K ;(▲) 323.30 K (♦); 343.20 K; Calculated values using SRK-vdW model: (—).

The isothermal vapor-liquid equilibrium data (P,T,x,y) of these refrigerant mixtures have been studied at different temperatures: six for R600a+R1234ze(Z) (303.15; 313.15 ;323.15; 333.15; 343.15; 353.15) K and R744+R152a (258.44; 278.25; 298.84; 308.37; 323.30 ; 343.20) K,five for R600a+R1234zf (253.15; 263.15; 273.15; 283.15; 293.15) K and three for R134a+R1336mzz (313.24; 333.19; 353.12) K.

From the curves of the phase diagrams of the studied binary blends, we can see that the binary systems((R600a+R1234ze(Z) (Fig.2 (a,b)) and (R600a+R1234zf) (Fig.3(a,b)))) exhibit an azeotropic behavior (the bubble and dew curves are tangent to each other and these two curves do not intersect) for all the temperature range, where the molar composition (x_1) of the liquid phase and the molar composition of the vapor phase (y_1) are identical (x_1=y_1) and the azeotrope corresponds to an extremum of the pressure for a constant temperature (for isothermal).The azeotropic phenomenon obtained in the both system was found between the mole fractions ((0.60 and 0.80) for R600a+R1234ze (Z)) and (0.20 and 0.40) for R600a+R1234zf) within the temperature intervals(303.15 - 353.15 K) and (253.15 - 293.15 K), respectively.

In other hand, we can observed from the (Fig.4 (a,b) and Fig.5 (a,b)) that the binary mixtures (R134a+R1336mzz) and (R744+R152a) exhibit an zeotropic behavior (the bubble and dew curves are not tangent to each other) for all the investigated isotherms. A critical behavior is observed in the binary system (R744+R152a) for the three isotherms (308.37; 323.30 and 343.20 K) above the critical temperature of carbon dioxide (R744, Tc=304.20 K) (Fig.5 (a,b)).

We can also notice from the curves shown in (Fig.2 (a,b), Fig.3 (a,b) and Fig.4 (a,b)) that the results are improved when using the two thermodynamic models (SRK-vdW and PR-vdW) with our simple method which predict the binary interaction parameter (k_{ij}) of the classical mixing rule (vdW), where the calculations accurately agree with the experimental data of the literature.A good representation of the thermodynamic behavior for binary systems (R600a+R1234ze(Z)), (R600a+R1234zf) and (R134a+R1336mzz) was obtained.

For the Fig.5 (a,b) of the (R744+R152a) system, we can see that the results of the thermodynamic behavior obtained in the subcritical isotherms are very similar with the experimental data, however, for the supercritical temperatures in the critical region, the thermodynamic behavior is not well represented, due to the intermolecular interactions occurring in the system.

In overall, the relative deviation of the vapor mole fraction does not exceed 5.09 % with PR-vdW and 4.48 % with SRK-vdW (see Table 4). However, the relative deviation of the pressure does not exceed 2.79 % with PR-vdW and 2.42 % with SRK-vdW (see Table 4).

5. Conclusions

A model for calculation the Vapor-Liquid Equilibrium was developed by using SRK and PR equations of state in combination with van der Waals mixing rules. The calculated results of the model are too close to the experimental data of the refrigerant binary systems. A new method was also developed in order to improve the estimation of the binary interaction parameters. The success of correlating Vapor-Liquid Equilibrium data using a cubic equation of state primarily depends on the mixing rule upon which the isothermal (VLE) calculations are related.The relation form between the temperature and the binary interaction parameters in all mixing rules cannot be determined correctly due to the oscillation of adjustable parameters values with changing temperature.

Superscripts

L	Liquid phase
V	Vapor phase

Abbreviations

EoS	Equation of state
GWP	Global warming potential
ODP	Ozone depletion potential
PR	Peng-Robinson
SRK	Soave-Redlich-Kwong
vdW	van der Waals
VLE	Vapor liquid equilibrium

Nomenclature

List of symbol

a	Cohesive energy parameter (J m^3mol^{-2})
b	Co-volume parameter (m^3mol^{-1})
K_{ij}	Binary interaction parameter
K_i	Partition coefficient
P	Pressure (MPa)
R	Universal gas constant (J $mol^{-1}K^{-1}$)
T	Temperature (K)
ν	Molar volume (m^3mol^{-1})
x	Liquid mole fraction
y	Vapor mole fraction
Z	Compressibility factor

Greek letters

ω	Acentric factor
α(T)	Alpha function
φ	Fugacity coefficient

Subscripts

c	Critical property
i,j	Molecular species
m	Mixture
Cal	Calculated value
Exp	Experimental value

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