

Predicting vapor-liquid equilibria of CO₂+HFC binary mixtures by the PR EOS combined with a group contribution model

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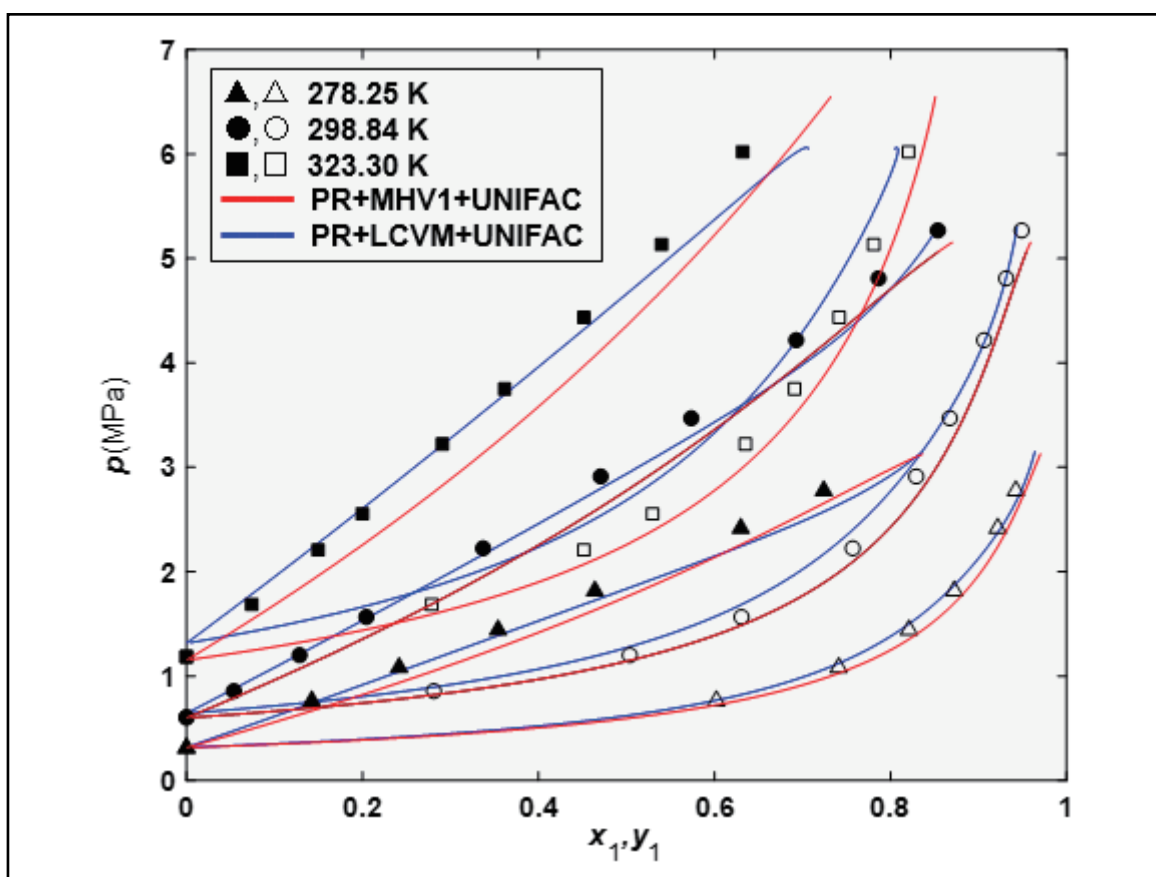
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Graphical abstract



Prediction of the vapor-liquid phase equilibrium for CO₂+R152a at three temperatures.

Public summary

- The prediction accuracy of the PR+LCVM+UNIFAC model for CO₂+HFC binary mixtures is more accurate.
- For CO₂+R32 binary mixtures, the PR+MHV+UNIFAC prediction model has higher calculation accuracy.
- It is further explained that for CO₂+HFC binary systems with very different molecular structures, the LCVM mixing rule obtains better results than the MHV1 mixing rule.

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Abstract: CO₂+HFC binary mixtures have good performance and environmental friendliness and are considered good alternative working fluids in cooling and power cycle systems. The vapor-liquid phase equilibrium properties are key to the calculation of the enthalpy and entropy of mixtures, which is critical for the analysis of cooling and power cycle systems. To accurately predict the vapor-liquid equilibrium of CO₂ and HFC (R23, R32, R41, R125, R134a, R143a, R152a, R161, and R227ea) binary mixtures, a group contribution model based on the excess free energy (G^E) mixing rules (PR+MHV1+UNIFAC and PR+LCVM+UNIFAC) is established in this paper. The interaction parameters between groups such as -CO₂, -Alkane, -CHF, and -CHF₃ are obtained by the vapor-liquid phase equilibrium experiment of CO₂ and HFC refrigerants, and these group parameters are critical for predicting their vapor-liquid phase equilibrium properties (the pressures and vapor phase molar fractions). The AARD_p value calculated by the PR+LCVM+UNIFAC model is 5.53%, the value of AAD_{y1} is 0.0132, and the AARD_p and AAD_{y1} values of the PR+MHV1+UNIFAC model are 7.40% and 0.0229, respectively. However, for the CO₂+R32 system, the PR+MHV+UNIFAC prediction model can reproduce the experimental data with lower deviations, and the values of AARD_p and AAD_{y1} are 1.53% and 0.0045, respectively. In summary, for CO₂+HFC binary mixtures, the PR+LCVM+UNIFAC group contribution model can reproduce the experimental data with lower deviations, but for individual CO₂ binary mixtures (such as CO₂+R32), the PR+MHV1+UNIFAC model also has unique advantages. According to the prediction results of the group contribution model, the PR+LCVM+UNIFAC model has significantly improved the calculation progress compared with the PR+MHV1+UNIFAC model used in the previous system.

Keywords: cooling and power cycles; CO₂+HFC binary mixtures; vapor-liquid equilibrium; the group contribution model; PR+MHV1+UNIFAC model; PR+LCVM+UNIFAC model

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Nomenclature

Symbols

a	energy parameter, J·cm ³ ·mol ⁻²
b	covolume, cm ³ ·mol ⁻¹
f_i	the fugacity of the component i
G^E	excess free energy
M	number of CO ₂ -based binary mixtures
p	pressure, MPa
PR	Peng and Robinson
HV	Huron-Vidal mixing rule
MHV1	Modified Huron-Vidal-1 mixing rule
MHV2	Modified Huron-Vidal-2 mixing rule
WS	Wong-Sandler mixing rule
LCVM	Linearity combine Huron-Vidal and Modified Huron-Vidal-1 mixing rule
UNIFAC	Original Group Contribution Model
UNIQUAC	Gibbs Excess Model
PSRK	Predictive Soave-Redlich-Kwong
VTPR	Volume-translated Peng-Robinson
NRTL	Non-Random Two-Liquid activity coefficient model
Q_k	area parameters of the group
R_k	volume parameters of the group
R	universal gas constant, 8.314472 J·mol ⁻¹ ·K ⁻¹
T	temperature, K
x	mole fraction of liquid phase
y	mole fraction of vapor phase
v	molar volume (cm ³ ·mol ⁻¹)

Abbreviations	
AARD _p	average absolute relative deviation of pressure
AAD _{y₁}	average absolute deviation of vapor phase molar fractions
EOS	equations of state
GWP	global warming potential
HFCs	hydrofluorocarbons
ODP	ozone depletion potential
<i>OF</i>	objective function
VLE	vapor-liquid equilibrium
CO ₂	carbon dioxide
R125	pentafluoroethane
R134a	1,1,1,2-tetrafluoroethane
R143a	1,1,1-trifluoroethane
R152a	1,1-difluoroethane
R161	fluoroethane
R23	trifluoromethane
R227ea	1,1,1,2,3,3,3-heptafluoropropane
R32	difluoromethane
R41	fluoromethane

Greek letters	
$\alpha(T)$	temperature-dependent alpha function
γ	activity coefficient
ω	acentric factor

Subscripts	
cal	calculated value
exp	experimental value
pre	predicted value

1 Introduction

Carbon dioxide (CO₂) is widely used as a working medium in refrigeration cycles, power cycles, supercritical Brayton cycles, and other applications due to its high thermal stability, natural working fluid, safety, environmental protection, and high energy density to achieve miniaturization of components^[1,2]. However, CO₂ is a working medium with the disadvantages of high operating pressure and low system thermal efficiency during system operation. Hydrofluorocarbon (HFC) refrigerants are highly thermally efficient in refrigeration cycles and power cycles but have high ozone depletion potential (ODP) and global warming potential (GWP)^[3]. Mixing CO₂ with other HFC refrigerants (with low GWP, zero ODP, and no toxicity) is one of the prospective ways to gain the advantages of CO₂ and minimize its disadvantages. CO₂+HFC binary mixtures can not only reduce operating pressure and improve system thermal efficiency but also reduce the ODP value and GWP value^[4]. Due to this good performance and environmental friendliness, CO₂+HFC refrigerant binary mixtures have received extensive attention and

research as alternative working media in refrigeration cycles and power cycles^[5].

The vapor-liquid phase equilibrium (VLE) data are key to the calculation of the enthalpy and entropy of CO₂+HFC refrigerant binary mixtures, which is critical for the analysis of refrigeration cycles and power cycles. Due to the simplicity of the form and the accuracy of the calculation of the cubic equation of state, it is widely used in the simulation and calculation of the thermophysical properties of various working fluids^[6]. For CO₂+HFC refrigerant binary mixtures, the cubic equation (Peng-Robinson equation^[7]) of state must be combined with the mixing rules to predict the vapor-liquid phase equilibrium properties. At present, there are many concerns and studies on the mixing rule. In general, the mixing rule is mainly divided into excess free energy mixing rules^[8] and van der Waals^[9] mixing rules.

Due to the simplicity of the form and the accuracy of the calculation, the cubic equation of state with mixing rules is widely studied in VLE properties. In the mixing rules, the cubic equations of state have a continuous and consistent description of supercritical and subcritical regional components, but the prediction accuracy of complex systems (such as highly nonideal systems and strong polarity systems) is not advanced, while the activity coefficient model has very good descriptive ability for highly nonideal systems and strong polarity systems but only for low-pressure conditions. Therefore, combining these two approaches to form an EOS/*G^E* model can play to their respective advantages and establish a broader range of mixing rules^[6].

The mixing rules of the excess gibbs free energy mainly include the HV^[10] mixing rules, WS^[11] mixing rules, MHV1^[12] mixing rules, MHV2^[13] mixing rules, and LCVM^[14] mixing rules. The activity coefficient is the key to calculating the mixing rules. Many activity coefficient models have been proposed, such as Wilson^[15], NRTL^[16], and the group contribution model (such as UNIQUAC^[15] and UNIFAC^[17]). The group contribution model mainly includes original UNIFAC and modified UNIFAC (Dortmund)^[18–21], PSRK^[22–25], and VTPR^[26–28], which have been widely used to predict the VLE properties of binary mixtures^[6].

At present, there are some studies on the group contribution theory based on CO₂-based binary mixtures. Hou et al.^[29] used the MHV1+UNIFAC group contribution model to predict the vapor-liquid phase equilibrium properties of CO₂ and five HFC refrigerants, with high prediction accuracy. Gao et al.^[30] used the MHV1+UNIFAC and MHV2+UNIFAC group contribution models to predict the VLE properties of CO₂+hydrocarbons, but the prediction accuracy was poor. Horstman et al.^[31] used the PRSK group contribution model to predict the VLE properties of CO₂+n-alkane. Schmid et al.^[28] used the VTPR group contribution model to predict the vapor-liquid phase equilibrium properties of CO₂+CH₄. The prediction accuracy was high, but only the CO₂+CH₄ working medium was not representative. In summary, the LCVM+UNIFAC group contribution model has not been used to predict the vapor-liquid phase equilibrium properties of CO₂+HFC binary mixtures. Since vapor-liquid phase equilibrium experiments require considerable time and effort, it is also of great significance to propose a prediction model suitable for CO₂

binary mixtures.

In this work, based on the background of the power cycle of CO₂ binary mixtures, the experimental vapor-liquid phase equilibrium data of 9 CO₂+HFC binary mixtures were collected, including CO₂+HFC (R23, R32, R41, R125, R134a, R143a, R152a, R161, R227ea). Based on the group contribution model (UNIFAC), the VLE data of these 9 binary mixtures were predicted by using the PR equation combined with two different forms of mixing rules (MHV1 and LCVM^[14]). By comparing the predicted values with the experimental values published in the literature, the relative deviation between the prediction results and the experimental results is obtained to analyze and discuss the applicability of different mixing rules to various types of CO₂+HFC binary mixtures.

2 Thermodynamic equations

2.1 PR equation of state

Peng and Robinson^[7] proposed the PR equation of state in 1976, which can be used to predict the VLE properties of CO₂+HFC refrigerant binary mixtures.

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}, \quad (1)$$

where R represents the universal gas constant (8.314472 J·mol⁻¹·K⁻¹); T is the temperature (K); v is the molar volume (cm³·mol⁻¹); and p is the pressure (MPa).

The two parameters a and b represent the energy parameter (J·cm³·mol⁻²) and covolume (cm³·mol⁻¹), and their expressions are shown:

$$a = 0.45724 \frac{R^2 T_c^2}{p_c} \alpha(T), \quad (2)$$

$$b = 0.0778 \frac{RT_c}{p_c} \alpha(T), \quad (3)$$

$$\alpha(T) = [1 + (0.37646 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2, \quad (4)$$

where T_c and p_c denote the critical temperature (K), and critical pressure (MPa), respectively. $\alpha(T)$ represents the temperature-dependent alpha function, ω is the acentric factor, and $T_r = T/T_c$ is the reduced temperature.

2.2 EOS/ G^E mixing rules

2.2.1 HV mixing rule

The first EOS/ G^E mixing rule was proposed by Huron and Vidal^[10],

$$\frac{a_m}{b_m RT} = \sum_i x_i \frac{a_i}{b_i RT} + \frac{1}{C^{EOS}} \frac{G^E}{RT}, \quad (5)$$

$$b_m = \sum_i x_i b_i, \quad (6)$$

where C^{EOS} is a constant related to the state equation; for the PR equation, $C^{EOS} = -0.62323$. G^E represents the excess Gibbs free energy under infinite pressure, which can be calculated by the activity coefficient model.

2.2.2 MHV1 mixing rule

The MHV1 mixing rule was proposed by Michelse^[12], which is an improved mixing rule based on the HV mixing rule.

$$\frac{a_m}{b_m RT} = \sum_i x_i \frac{a_i}{b_i RT} + \frac{1}{q_1} O, \quad (7)$$

$$b_m = \sum_i x_i b_i, \quad (8)$$

$$O = \frac{G^E}{RT} + \sum_i x_i \ln \left(\frac{b_m}{b_i} \right), \quad (9)$$

where q_1 is a constant related to the state equation; for the PR equation, $q_1 = -0.528$.

2.2.3 LCVM mixing rule

Boukouvelas^[14] found that for some binary systems, the HV mixing rule tends to give a negative bias, while the MHV1 mixing rule gives a positive deviation. Boukouvelas linearly combines two mixing rules to form a new LCVM mixing rule, combined with the UNIFAC activity coefficient model, which gives highly accurate predictions for many systems.

$$\frac{a_m}{b_m RT} = \left(\frac{\lambda}{C_{HV}} + \frac{\lambda}{C_{MHV1}} \right) \frac{G^E}{RT} + \frac{\lambda}{C_{MHV1}} \sum_i x_i \ln \left(\frac{b_m}{b_i} \right) + \sum_i x_i \frac{a_i}{b_i RT}, \quad (10)$$

$$b_m = \sum_i x_i b_i, \quad (11)$$

where the value of λ is generally 0.36. C_{HV} and C_{MHV1} are constants related to the state equation, $C_{HV} = -0.62323$ and $C_{MHV1} = -0.528$.

2.3 Activity coefficient model

In 1968, Renon and Prausnitz^[16] modified the local composition expression of the solution and proposed the NRTL activity coefficient model on the basis of two-fluid theory, which can well describe the phase equilibrium properties of binary systems, and the expressions for common binary systems are

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_1 + x_1 G_{12}} \right), \quad (12)$$

$$G_{12} = \exp(\alpha_{12} \tau_{12}), G_{21} = \exp(\alpha_{21} \tau_{21}). \quad (13)$$

The UNIFAC^[32] model is proposed on the basis of the UNIQUAC^[33] model, which is used to calculate the activity coefficients for CO₂+HFC binary mixtures. The UNIFAC model obtains the interaction parameters between groups by fitting the experimental data and then calculates the activity coefficient of the binary mixture through the interaction parameters.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R, \quad (14)$$

where γ_i is the activity coefficient of component i ; γ_i^C is the combinatorial part; and γ_i^R is the residual part.

The combinatorial part of the activity coefficient is the same as the UNIQUAC model, which depends on the molecule's size and shape.

$$\ln \gamma_i^C = \ln \left(\frac{\phi_i}{x_i} \right) + \frac{Z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j, \quad (15)$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j}, \quad (16)$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}, \quad (17)$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1), \quad (18)$$

$$r_i = \sum_k v_k^{(i)} R_k, \quad (19)$$

$$q_i = \sum_k v_k^{(i)} Q_k, \quad (20)$$

where ϕ_i is a section fraction similar to the volume fraction; x_i denotes the mole fraction; θ_i represents the area fraction; Z is the number of coordinates; $v_k^{(i)}$ is the number of group k ; r_i and q_i are structural parameters of the pure component; and R_k and Q_k are volume parameters and area parameters of the group, respectively.

The residual part of the activity coefficient is the basis for the group contribution model.

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}), \quad (21)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \psi_{mk} \right) - \sum_m \frac{\Theta_m \psi_{mk}}{\sum_n \Theta_n \psi_{nm}} \right], \quad (22)$$

$$\Theta_m = \frac{\Theta_m X_m}{\sum_n \Theta_n X_n}, \quad (23)$$

$$X_m = \frac{\sum_i x_i v_{mi}}{\sum_i x_i \sum_m v_{mi}}, \quad (24)$$

$$\psi_{mn} = \exp \left(-\frac{a_{mn}}{T} \right), \quad (25)$$

$$\psi_{nm} = \exp \left(-\frac{a_{nm}}{T} \right), \quad (26)$$

where Γ_k represents the group activity coefficient; a_{mn} and a_{nm} are the group partner energy parameters; Q_m is the area parameter; Θ_m is the area fraction; and X_m denotes the molar fraction of group m .

2.4 Thermodynamic conditions

The thermodynamic condition for the VLE is the equality of the fugacities of each component in each phase, which is expressed as

$$f_i^L = f_i^V, \quad (27)$$

where f_i^L and f_i^V represent the fugacity of component i in the

vapor phase and liquid phase, respectively.

Fig. 1 shows the group contribution prediction model that predicts the VLE properties of the binary mixture. Based on the known temperature and liquid phase components and the assumed pressure and vapor phase components, the fugacity, specific pressure and vapor phase components are calculated by the cubic equation of state (PR EOS) combined with the mixing rule (MHV1 and LCVm) and the group contribution activity coefficient model (UNIFAC).

2.5 Objective function

The objective function (OF) is expressed as follows:

$$OF = \frac{1}{N} \sum_{i=1}^N \left(\left(\frac{P_{\text{exp},i} - P_{\text{cal},i}}{P_{\text{exp},i}} \right)^2 + (y_{\text{exp},i} - y_{\text{cal},i})^2 \right)^{\frac{1}{2}}, \quad (28)$$

where the subscript “cal” indicates the calculated value; the subscript “exp” indicates the experimental value; the subscript “ i ” indicates component i ; p is the pressure; and y is the vapor phase molar fraction. The bubble-point pressure and the vapor phase molar fraction are obtained according to the temperature and liquid phase molar fraction.

$$\text{AARD}p = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_{\text{exp},i} - P_{\text{cal},i}}{P_{\text{exp},i}} \right| \times 100\%, \quad (29)$$

$$\text{AAD}y_1 = \frac{1}{N} \sum_{i=1}^N |y_{\text{exp},i} - y_{\text{cal},i}|, \quad (30)$$

where $\text{AARD}p$ is the average absolute relative deviation of pressure; $\text{AAD}y_1$ is the average absolute deviation of vapor phase molar fractions; and N is the number of experimental data.

3 Results and discussion

3.1 Prediction model comparison

Table 1 lists the thermodynamic parameters of the working fluid, mainly including critical pressure, temperature, and acentric factors. By referring to the group assignments law of the UNIFAC model, the group assignments of all working fluids are illustrated in Table 2^[29].

Table 1. Thermodynamic parameters of the working fluid^[6].

No.	Component	T_c (K)	p_c (MPa)	ω
	CO ₂	304.13	7.3773	0.22394
HFCs				
	R23	299.29	4.8320	0.2630
	R32	351.26	5.7820	0.2769
	R41	317.28	5.8970	0.2004
	R125	339.17	3.6177	0.3052
	R134a	374.21	4.0593	0.3268
	R143a	345.86	3.761	0.2615
	R152a	386.14	4.5168	0.2752
	R161	375.25	5.0460	0.2200
	R227ea	374.90	2.925	0.357

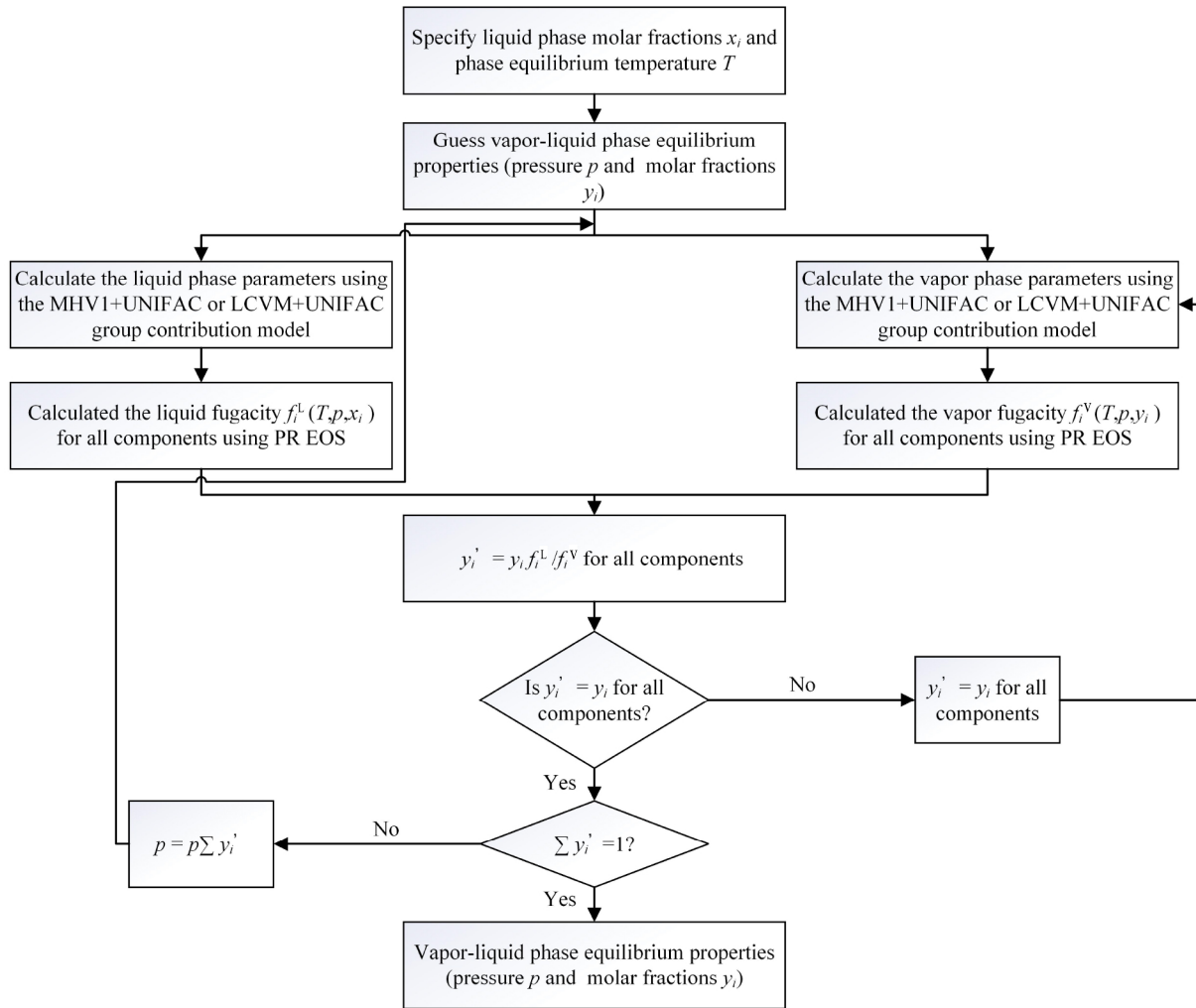


Fig. 1. Flow diagram of the VLE calculation.

Table 2. Group assignment for refrigerants^[29].

Main groups	subgroups	R_k	Q_k
-CO ₂	-CO ₂	1.300	0.982
-Alkane	-CH ₃	0.9011	0.848
	-CH ₂	0.6744	0.540
-CHF	-CH ₂ F	1.0699	1.000
	-CHF ₂	1.238	1.232
-CHF ₃	-CF ₃	1.406	1.380
	-CHF ₃	1.6335	1.608
	-CF ₃ CH ₂	2.0804	1.920

The group parameters of CO₂ and the group interaction parameters among -CO₂, -Alkane, -CHF, and -CHF₃ are determined by regressing the VLE data, as shown in Table 3.

The VLE properties of 9 CO₂+HFCs (R23, R32, R41, R125, R134a, R143a, R152a, R161, and R227ea) were predicted by the PR+MHV1+UNIFAC model and the PR+LCVM+UNIFAC model. Table 4 lists the predicted values and deviations for the group contribution model. Using the PR+MHV1+UNIFAC group contribution model, the value of AARD_p is 7.40%, and the value of AAD_{y1} is

Table 3. The group interaction parameters^[6].

	-CO ₂	-Alkane	-CHF	-CHF ₃
-CO ₂	0	-38.67	641.97	1011.83
-Alkane	719.80	0	480.72	198.36
-CHF	-255.59	50.17	0	2509.83
-CHF ₃	-267.33	108.23	896.52	0

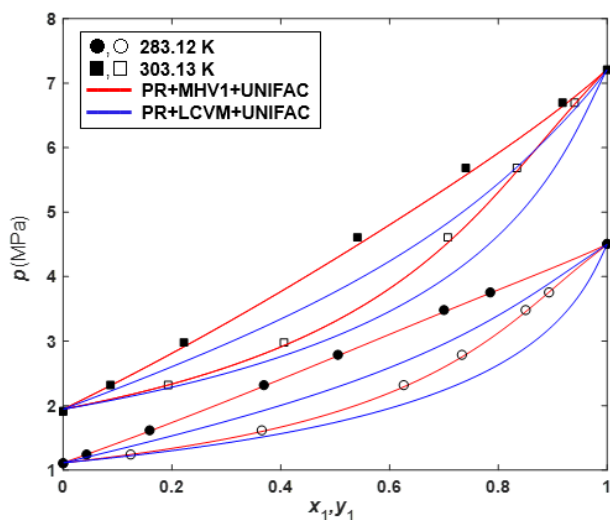
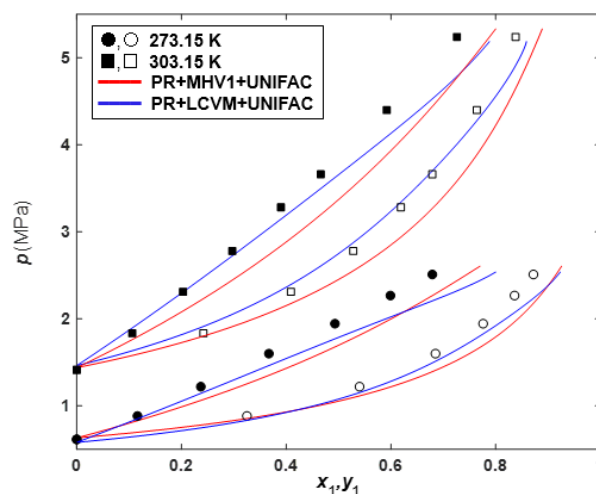
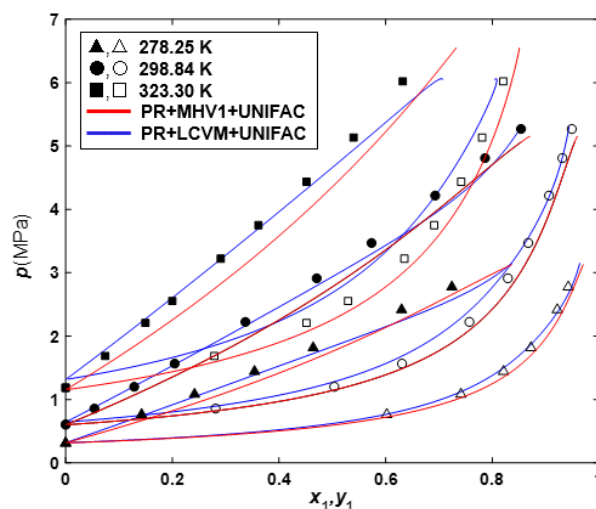
0.0229; using the PR+LCVM+UNIFAC group contribution model, the value of AARD_p is 5.53%, and the value of AAD_{y1} is 0.0132. According to the prediction results of the group contribution model, the PR+LCVM+UNIFAC group contribution model has significantly improved the calculation progress compared with the PR+MHV1+UNIFAC group contribution model used in the previous system. However, for CO₂+R32 binary mixtures, the PR+MHV1+UNIFAC prediction model has higher calculation accuracy, and the values of AARD_p and AAD_{y1} are 1.53% and 0.0045, respectively. In summary, for CO₂+HFC binary mixtures, the PR+LCVM+UNIFAC group contribution model has higher prediction accuracy overall, but for individual CO₂ binary mixtures (such as CO₂+R32), the MHV1+UNIFAC model also has unique advantages.

Table 4. The predicted values and deviations for the group contribution model.

Mixture	MHV1+UNIFAC		LCVM+UNIFAC		<i>N</i>
	AARD _{<i>p</i>}	AAD _{<i>y</i>} ₁	AARD _{<i>p</i>}	AAD _{<i>y</i>} ₁	
CO ₂ +HFCs					
CO ₂ +R23 ^[34]	8.96%	0.0145	3.04%	0.0083	33
CO ₂ +R32 ^[35]	1.53%	0.0045	5.70%	0.0079	41
CO ₂ +R41 ^[34]	4.11%	0.0520	1.50%	0.0077	5
CO ₂ +R125 ^[36]	10.92%	0.0161	8.13%	0.0022	4
CO ₂ +R134a ^[4,37]	6.71%	0.0403	6.79%	0.0320	50
CO ₂ +R143a ^[38]	9.20%	0.0152	5.43%	0.0185	51
CO ₂ +R152a ^[39]	8.50%	0.0140	4.14%	0.0129	60
CO ₂ +R161 ^[40]	5.33%	n.a.	5.37%	n.a.	31
CO ₂ +R227ea ^[41]	11.38%	0.0262	9.66%	0.0160	77
Average	7.40%	0.0229	5.53%	0.0132	

3.2 Prediction of the vapor-liquid phase equilibrium properties of CO₂+HFC binary mixtures

Based on the group contribution prediction model (PR+MHV1+UNIFAC and PR+LCVM+UNIFAC), the vapor-liquid phase equilibrium properties of CO₂+HFC binary mixtures are predicted. Figs. 2–4 show the vapor-liquid phase equilibrium of CO₂+R32^[35], CO₂+R143a^[38], and CO₂+R152a^[39] binary mixtures, respectively. It can be seen from the figure that the predictive model (PR+LCVM+UNIFAC) and the known experimental data have a good match. It can be seen from Fig. 2 that the vapor-liquid phase equilibrium properties of the CO₂+R32 binary mixture are predicted well by the PR+MHV1+UNIFAC group contribution model, which is consistent with the previous calculation results. From Fig. 3 and Fig. 4, the vapor-liquid phase equilibrium of the CO₂+R143a and CO₂+R152a binary mixtures predicted by the PR+LCVM+UNIFAC group contribution model is better than that predicted by PR+MHV1+UNIFAC.


Fig. 2. Prediction of the vapor-liquid phase equilibrium properties for CO₂+R32 at three temperatures. Experimental data^[35]: *T*=283.12 K (●,○); *T*=303.13 K (■,□). Solid red line represents the PR+MHV1+UNIFAC model; solid blue line represents the PR+LCVM+UNIFAC model.

Fig. 3. Prediction of the vapor-liquid phase equilibrium properties for CO₂+R143a at three temperatures. Experimental data^[38]: *T*=273.15 K (●,○); *T*=303.15 K (■,□). Solid red line represents the PR+MHV1+UNIFAC model; solid blue line represents the PR+LCVM+UNIFAC model.

Fig. 4. Prediction of the vapor-liquid phase equilibrium properties for CO₂+R152a at three temperatures. Experimental data^[39]: *T*=278.25 K (▲,△); *T*=298.84 K (●,○); *T*=323.30 K (■,□). Solid red line represents the PR+MHV1+UNIFAC model; solid blue line represents the PR+LCVM+UNIFAC model.

4 Conclusions

In this work, to accurately predict the VLE of CO₂ and HFC (R23, R32, R41, R125, R134a, R143a, R152a, R161, and R227ea) binary mixtures, a group contribution model based on the excess free energy (*G*^E) mixing rules (PR+MHV1+UNIFAC and PR+LCVM+UNIFAC) is established. Based on the interaction parameters between groups such as -CO₂, -Alkane, -CHF, and -CHF₃, the vapor-liquid phase equilibrium properties of CO₂ and HFC refrigerants were predicted, and the value of AARD_{*p*} calculated by the PR+LCVM+UNIFAC model was 5.53%, the value of AAD_{*y*}₁ was 0.0132, and the AARD_{*p*} value and AAD_{*y*}₁ values of the PR+MHV1+UNIFAC model were 7.40% and 0.0229, respectively. The prediction accuracy of the PR+LCVM+UNIFAC model for CO₂+HFC binary mixtures

is more accurate. However, for CO₂+R32 binary mixtures, the PR+MHV+UNIFAC prediction model has higher calculation accuracy, and the values of AAD_{Rp} and AAD_y are 1.53% and 0.0045, respectively. In summary, for CO₂+HFC binary mixtures, the PR+LCVM+UNIFAC group contribution model has higher prediction accuracy overall, but for individual CO₂ binary mixtures (such as CO₂+R32), the PR+MHV1+UNIFAC model also has unique advantages. It can be seen from the figure that the predictive model (PR+LCVM+UNIFAC) and the known experimental data have a good match. It is further explained that for CO₂+HFC binary systems with very different molecular structures, the LCVM mixing rule obtains better results than the MHV1 mixing rule.

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Conflict of interest

The authors declare that they have no conflict of interest.

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