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Study on the Interaction Coefficients in PR Equation with vdW Mixing Rules for HFC and HC Binary Mixtures

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Abstract The Peng-Robinson equation of state with the van der Waals mixing rules was used to correlate vapor–liquid equilibrium (VLE) data for HFC/HC, HFC/HFC, and HC/HC binary mixtures. The interaction parameter k_{ij} was obtained for every binary mixture. It was assumed that k_{ij} has contributions from the two components, and each component has its own constant contribution factor $k_i$for the mixture, and the values of k_{ij} indicate the degree in difference of properties between the two components. Therefore, the interaction parameters k_{ij} is proposed as: $k_{ij} = k_i - k_j$. The values of the mixing factor k_i for Hydrofluorocarbons (HFCs) and Hydrocarbons (HCs), including propane, isobutane, n-butane, R23, R32, R125, R143a, R134a, R152a, R227ea R236fa, R236ea, and R245fa, were obtained by least-square fitting. In total, 39 refrigerant binary mixtures were analyzed on the basis of this method, and the results showed good agreement with experimental data. The overall average absolute deviations of pressure and vapor mole fraction are 1.3 % and 0.0089, respectively.

Keywords Binary mixtures · HCs · HFCs · Interaction coefficients · PR EoS · vdW mixing rules

1 Introduction

Hydrofluorocarbon (HFC) and Hydrocarbon (HC) mixtures are promising candidates for replacement of CFC and HCFC compounds, but only limited experimental data of the vapor–liquid equilibrium (VLE) properties for HFC/HFC, HFC/HC,

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and HC/HC binary mixtures over a narrow temperature range have been reported previously in the literature [1–23]. Cubic equations of state, such as Peng-Robinson and Soave-Redlich-Kwong, with mixing rules are currently the most widely used approaches for correlating the VLE properties of mixtures. They also facilitate the simultaneous representation of volumetric properties such as density and enthalpy. But the conventional mixing rules for the cubic equation-of-state parameters, which contain empirical binary constants, are difficult to apply in a predictive mode.

In this work, the PR equation of state with van der Waals mixing rules was used to correlate VLE data for HFC/HC, HFC/HFC, and HC/HC binary mixtures. The interaction parameter k_{ij} was obtained for every binary mixture, and the mixing factors k_i of 13 different refrigerants, propane, isobutane, n-butane, R23, R32, R125, R143a, R134a, R152a, R227ea R236fa, R236ea, and R245fa, were obtained using these mixing factors. Then the interaction parameter of any binary mixture system containing these 13 types of refrigerants could be determined.

2 PR EoS with vdW Mixing Rules

In this study, the PR EoS [24] was used to correlate VLE data,

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

where

$$a(T) = a_{\mathrm{C}}\alpha(T), \tag{2}$$

$$a_{\mathrm{C}} = 0.45724\frac{R^2T_{\mathrm{C}}^2}{P_{\mathrm{C}}}, \tag{3}$$

$$b = 0.07780\frac{RT_{\mathrm{C}}}{P_{\mathrm{C}}}, \text{ and} \tag{4}$$

$$\alpha(T) = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - \left(\frac{T}{T_{\mathrm{C}}}\right)^{0.5}\right)\right]^2, \tag{5}$$

where ω is the acentric factor.

To extend the applicability of the PR equation of state to binary mixtures, one-parameter van der Waals mixing rules were used:

$$a = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j a_{ij} \tag{6}$$

$$a_{ij} = (1 - k_{ij})a_i^{1/2}a_j^{1/2}, i = 1, 2; j = 1, 2 \tag{7}$$

$$b = \sum_{i=1}^{2} x_i b_i \tag{8}$$

where k_{ij} is the binary interaction parameter. $k_{11} = k_{22} = 0, k_{21} = k_{12}$. Least-squares fitting was applied to regress the binary parameters and the following objective function was used:

$$Obj = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{p_{\text{cal}} - p_{\text{exp}}}{p_{\text{exp}}} \right| \tag{9}$$

where N is the number of experimental points.

The deviations were calculated by the following equations:

$$\delta_p = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{p_{\text{cal}} - p_{\text{exp}}}{p_{\text{exp}}} \right| \tag{10}$$

$$\delta_y = \frac{1}{N} \sum_{i=1}^{N} \left| y_{\text{cal}} - y_{\text{exp}} \right| \tag{11}$$

3 k_{ij} Correlation and Prediction for HFC and HC Binary Mixtures

The binary interaction parameter k_{ij} is usually related with temperature and composition, and is empirical and obtained by regressing experimental VLE data. Therefore, it is difficult to be given a universal relationship with T, P, or x_i for prediction. For HFC and HC binary mixtures, the values of k_{ij} usually change slightly with T, P, or x_i; here we assume it is a constant for each HFC and HC binary mixture. VLE experimental data for 39 types of binary systems (HFC/HFC, HFC/HC, HC/HC) were collected. The critical parameters, T_C and P_C, and acentric factor ω, for every component are summarized in Table 1. The interaction parameters k_{ij} in the PR equation with vdW mixing rules were obtained for each binary mixture, and are listed in Table 2. It is obvious that the values of k_{ij} are very close to 0 for HFC/HFC and HC/HC binary mixtures, while they will be much larger for HFC/HC binary mixtures.

We assume that there is a mixing factor k_i for each pure HFC and HC component, and the interaction parameter of the binary mixture k_{ij} is assumed to be the difference between the mixing factors of the pure components, which is defined as

$$k_{ij} = k_i - k_j \tag{12}$$

where k_i is the mixing factor of the component with a higher vapor pressure and k_j is the mixing factor of the component with a lower vapor pressure. For the case of a pure refrigerant, the binary interaction parameter is 0, i.e., $k_{ii} = k_i - k_j = 0$.

Table 1 Critical properties and acentric factors of pure refrigerants[a]

Refrigerant	T_C (K)	P_C (kPa)	ω
HFC23	299.07	4836	0.2634
HFC32	351.26	5782	0.2768
HFC125	339.33	3629	0.3035
HFC143a	346.04	3776	0.2611
HFC134a	374.21	4059	0.3268
HFC152a	386.41	4517	0.2752
HFC227ea	374.89	2929	0.3632
HFC236fa	398.07	3200	0.3772
HFC236ea	412.44	3502	0.3794
HFC245fa	427.2	3640	0.3724
Propane	369.85	4248	0.1524
Isobutane	407.85	3640	0.1853
n-butane	425.16	3796	0.1995

[a] From REFPROP, Version 6.0 [25]

All refrigerants are arranged by decreasing vapor pressure at constant temperature. HFC23, HFC32, HFC125, HFC143a, HFC134a, HFC152a, HFC227ea, HFC236fa, HFC236ea, HFC245fa are from Nos. 1 to 10, respectively. Propane, isobutene, and n-butane are designated as Nos. I, II, and III, respectively. About 13 different refrigerants have 13 independent variables k_i. In total, 39 equations were developed with Eq. 12 for all binary mixtures with available experimental VLE data, and these equations constitute a transcendental equation system, which can be solved by a least-squares fitting method. The values of k_i are shown in Table 3.

After the mixing factors of HFCs and HCs are obtained, all binary interaction parameters between the 13 types of refrigerants can be predicted using Eq. 12. The 78 binary interaction parameters for these HFC and HC binary mixtures are presented in Table 4. It is obvious that these interaction parameters were divided into three groups: HFC/HFC, HFC/HC, and HC/HC. Since the binary mixtures of HFC/HFC and HC/HC are homologous mixtures, their mixing factors k_i are close to each other; therefore, their absolute values of interaction parameters are really small. But for HFC/HC mixtures, the absolute values of interaction parameters are much larger.

The interaction parameters obtained by Eq. 12 were used to calculate the VLE properties again. Most deviations of pressure are less than 1.5 % with a few deviations of pressure up to 3.5 %. The overall average absolute deviations of pressure and vapor mole fraction are 1.3 % and 0.0089, respectively, a little larger than those for correlated results of Table 2. Figures 1, 2 and 3 are $P - x - y$ diagrams of typical azeotropic and zeotropic binary mixtures. The prediction results agree well with the experimental data and correlation results. The deviations between prediction results and experimental results from the literature for four types of refrigerant mixtures are shown in Figs. 4 and 5.

Table 2 Deviations of pressure and vapor mole fraction

Mixture	Number of experimental data	Correlation			Prediction		
		k_{ij}	δ_p (%)	δ_y	k_{ij}	δ_p (%)	δ_y
R32/R290	114 [1]	0.182	1.16	0.0050	0.1656	1.47	0.0080
R125/R290	117 [1]	0.154	0.62	0.0043	0.1555	0.89	0.0084
R143a/R290	18 [3]	0.135	0.53	0.0049	0.1515	1.02	0.0088
R134a/R290	29 [2]	0.166	0.56	0.0072	0.1537	0.97	0.0103
R227ea/R290	82 [4]	0.131	0.67	0.0057	0.1418	0.96	0.0099
R32/R600a	39 [8]	0.191	2.85	0.0071	0.1660	3.37	0.0135
R134a/R600a	32 [8]	0.157	1.24	0.0052	0.1541	1.29	0.0081
R152a/R600a	31 [8]	0.123	0.92	0.0133	0.1509	1.59	0.0167
R32/R600	53 [8]	0.192	2.31	0.0084	0.1753	2.53	0.0119
R125/R600	38 [8]	0.150	0.84	0.0075	0.1652	1.14	0.0106
R134a/R600	47 [8]	0.162	0.88	0.0087	0.1635	0.96	0.0110
R23/R32	16 [5]	−0.0027	0.68	0.0068	−0.0107	1.36	0.0051
R23/R125	19 [5]	0.0032	0.50	0.0044	−0.0006	0.85	0.0067
R23/R143a	16 [11]	−0.0022	0.86	0.0051	0.0034	1.18	0.0063
R23/R134a	14 [10]	0.0081	1.12	0.0064	0.0012	1.41	0.0021
R23/R152a	16 [11]	−0.019	1.25	0.0066	0.0045	1.53	0.0070
R23/R227ea	16 [10]	0.0234	2.03	0.0060	0.0131	2.79	0.0072
R32/R125	30 [12]	0.0022	0.28	0.0042	0.0101	1.24	0.0060
R32/R143a	48 [14]	0.0169	0.43	0.0057	0.0141	0.60	0.0057
R32/R134a	22 [13]	0.0042	0.39	0.0097	0.0119	1.59	0.0149
R32/R152a	14 [15]	0.0166	1.61	0.0073	0.0151	1.67	0.0087
R32/R227ea	16 [16]	0.0225	1.31	0.0059	0.0237	1.36	0.0065
R32/R236fa	18 [20]	−0.0032	0.64	0.0054	0.0130	2.04	0.0093
R32/R236ea	25 [6]	−0.0155	0.56	0.0045	0.0060	2.26	0.0134
R125/R143a	18 [7]	0.0005	0.32	0.0046	0.0040	0.56	0.0040
R125/R134a	35 [13]	0.0017	0.43	0.0044	0.0018	0.44	0.0043
R125/R152a	6 [5]	−0.0193	0.54	0.0085	0.0051	2.68	0.0193
R125/R236fa	14 [20]	0.0220	1.44	0.0095	0.0029	2.55	0.0094
R125/R236ea	23 [6]	0.0174	1.65	0.0083	−0.0041	2.40	0.0091
R143a/R134a	42 [14]	−0.0014	0.46	0.0070	−0.0022	0.48	0.0079
R143a/R152a	25 [11]	0.0102	0.68	0.0059	0.0011	1.34	0.0098
R143a/R236fa	21 [21]	−0.0009	1.15	0.0085	−0.0011	1.17	0.0084
R134a/R152a	13 [18]	−0.0044	0.82	–	0.0033	1.31	–
R134a/R227ea	39 [16,19]	0.0091	0.64	0.0068	0.0119	0.71	0.0069
R134a/R236fa	15 [6]	−0.0021	0.30	0.0037	0.0011	0.62	0.0089
R134a/R245fa	25 [17]	0.0063	0.52	0.0033	0.0063	0.52	0.0033
R152a/R227ea	16 [19]	−0.0085	0.63	0.0075	0.0086	2.23	0.0126
R290/R600a	78 [22,23]	0.0012	1.07	0.0092	0.00004	1.08	0.0092
R290/R600	16 [22]	0.0122	1.34	0.0132	0.0098	1.39	0.0119

Table 3 Mixing factors of 13 types of HFC and HC refrigerants

No.	HFC	k_i	No.	HC	k_i
1	HFC23	0.2104	I	Propane	0.0556
2	HFC32	0.2211	II	Isobutane	0.0551
3	HFC125	0.2110	III	n-butane	0.0458
4	HFC143a	0.2070			
5	HFC134a	0.2093			
6	HFC152a	0.2060			
7	HFC227ea	0.1974			
8	HFC236fa	0.2082			
9	HFC236ea	0.2151			
10	HFC245fa	0.2030			

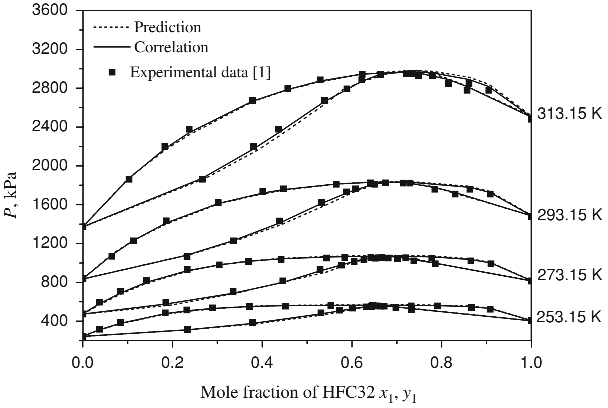

Fig. 1 $P-x-y$ diagram for HFC32/HC290

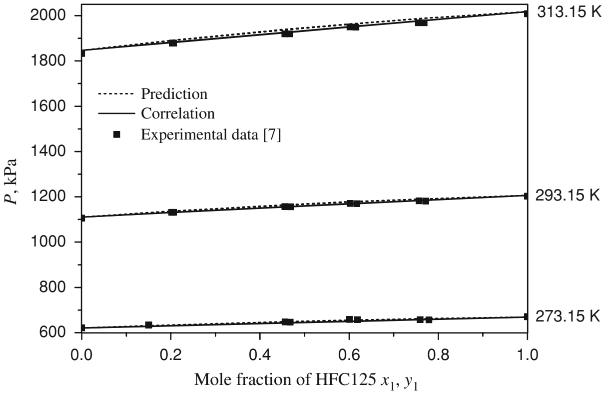

Fig. 2 $P-x-y$ diagram for HFC125/134a

Table 4 78 binary interaction parameters calculated by Eq. 12

Fluid	R23	R32	R125	R143a	R134a	R152a	R227ea	R236fa	R236ea	R245fa	R290	R600a
R32	−0.0107											
R125	−0.0006	0.0101										
R143a	0.0034	0.0141	0.0040									
R134a	0.0012	0.0119	0.0018	−0.0022								
R152a	0.0045	0.0151	0.0051	0.0011	0.0033							
R227ea	0.0131	0.0237	0.0137	0.0097	0.0119	0.0086						
R236fa	0.0023	0.0130	0.0029	−0.0011	0.0011	−0.0022	−0.0108					
R236ea	−0.0047	0.0060	−0.0041	−0.0081	−0.0059	−0.0092	−0.0178	−0.0070				
R245fa	0.0075	0.0182	0.0081	0.0041	0.0063	0.0030	−0.0056	0.0052	0.0122			
R290	0.1549	0.1656	0.1555	0.1515	0.1537	0.1504	0.1418	0.1526	0.1596	0.1474		
R600a	0.1553	0.1660	0.1559	0.1519	0.1541	0.1509	0.1423	0.1530	0.1600	0.1478	0.0004	
R600	0.1646	0.1753	0.1652	0.1612	0.1635	0.1602	0.1516	0.1624	0.1693	0.1572	0.0098	0.0093

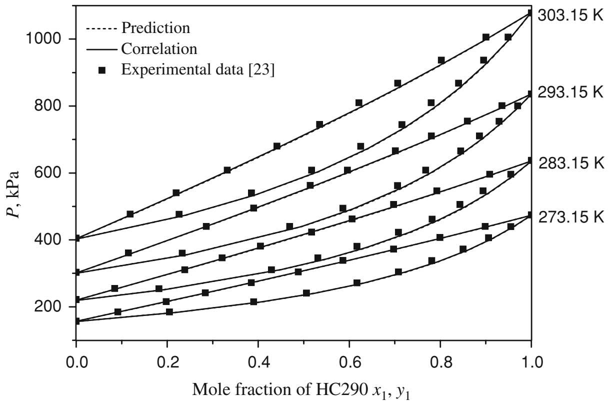

Fig. 3 $P - x - y$ diagram for HC290/600a

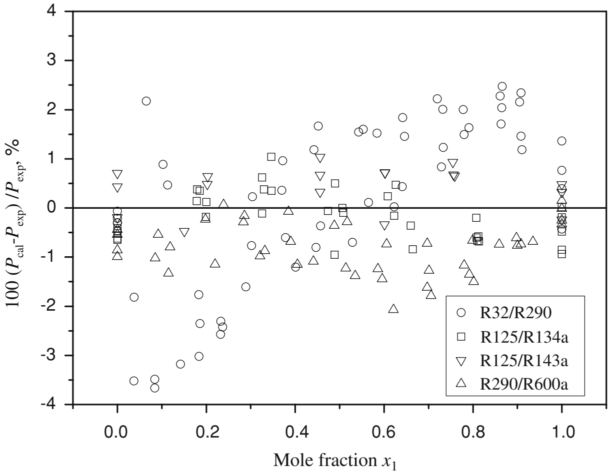

Fig. 4 Pressure deviations of four types of refrigerant binary mixtures

4 Conclusion

In this work, the PR equation of state with van der Waals mixing rules was employed to correlate VLE data for HFC/HC, HFC/HFC, and HC/HC binary mixtures. In total, 39 interaction parameters k_{ij} were obtained. A new simple model for prediction of k_{ij} was proposed: $k_{ij} = k_i - k_j$. The mixing factors k_i of 13 types of refrigerants: propane, isobutane, n-butane, R23, R32, R125, R143a, R134a, R152a, R227ea R236fa, R236ea, and R245fa were determined by least-squares fitting. Then, interaction parameters were calculated for 78 binary systems, which consist of two of these 13 types of refrigerants. There are 41 types of binary mixtures without experimental data. The predicted interaction parameters are consistent with the correlated interaction parameters. The overall average absolute deviations of pressure and vapor mole fraction

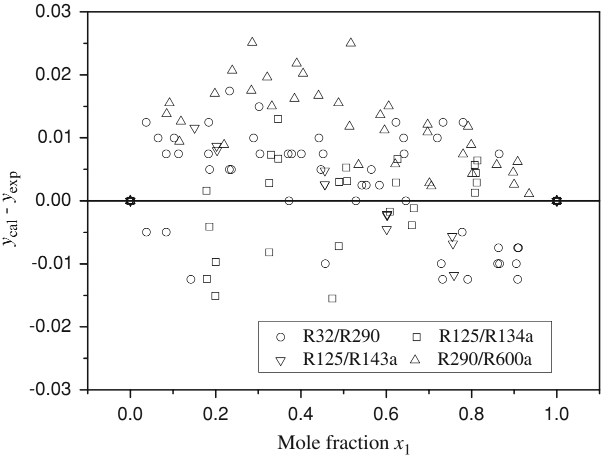

Fig. 5 Vapor mole fraction deviations of four types of refrigerant binary mixtures

using derived interaction parameters are 1.3 % and 0.0089, respectively. The accuracy can, in general, satisfy the requirements of engineering applications.

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