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Vapor–Liquid Equilibria Predictions for New Refrigerant Mixtures Based on Group Contribution Theory

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Vapor–liquid equilibria (VLE) for new refrigerant mixtures containing hydrofluorocarbons, alkanes, alkenes, dimethyl ether, CO₂, and perfluoroalkanes are of great interest. Those mixtures generally exhibit azeotropes, high nonideality, association effects, and contain supercritical compounds. The modified Soave–Redlich–Kwong equation of state is used with zero reference pressure G^E–EoS mixing rules and the UNIFAC group contribution model in this study to form a group contribution model for predicting vapor–liquid equilibria. A new functional group assignment strategy is used, and the values of interaction parameters between groups are provided. These parameters are optimized from selected binary vapor–liquid equilibria data to give good representations of the experimental VLE data. A ternary system was also accurately predicted using the group contribution model. The method is totally predictive because only the structures and the critical constants of the pure components are needed to calculate the thermodynamic properties of new refrigerant mixtures.

1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which have been widely used as solvents, refrigerants, foaming agents, and propellants, can produce activated chlorine due to photolytic decomposition by ultraviolet radiation, which destroys the ozone in the stratosphere.¹ Therefore, the Montreal Protocol and the London and Copenhagen Amendments prohibit the production of CFCs and HCFCs.^{2,3} In response to the Montreal Protocol and its amendments, a new generation of alternatives such as hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons (HCs), and their mixtures have been recently developed for industrial applications. These alternatives should be evaluated for their toxicity, insulating ability, flammability, physical stability, solubility, cost, ozone-depletion potential (ODP), and global warming potential (GWP) before being put into use.⁴ Accurate knowledge of the thermophysical properties of these potential alternatives is essential for selecting refrigerants, determining optimal compositions and evaluating the performance of refrigeration systems. The importance of vapor–liquid equilibria (VLE) properties for refrigerant mixtures was stressed during the second IUPAC Workshop on refrigerants (Ecole des Mines, Paris, France) and the third IUPAC Workshop held during the ICCT conference (Rostock, Germany).⁵

Recently, extensive experimental studies have been conducted to measure vapor–liquid equilibria data for several potential alternative mixtures, mostly alkanes + HFCs binaries, alkenes + HFCs binaries, ethers + HFCs binaries, and CO₂ + HFC binaries.^{6–9} VLE experiments are very time consuming and

expensive, so it is difficult if not impossible for researchers to obtain all of the needed experimental VLE data.

Theoretical and predictive models are valuable tools for estimating the thermodynamic properties of such mixtures, thus reducing the time, resources, and overall cost of the selection and utilization of process fluids. Generally, two basic approaches are applied to predict the thermodynamic properties of mixtures. The first are methods based on the interpolation or extrapolation of a given set of experimental thermodynamic data for the targeted systems. Empirical correlations and correlations based on corresponding states can be attributed to this approach.^{10–14} Second are methods independent from experimental thermodynamic data for the given systems.^{15–22} These predictions are obtained from molecular structure information only. Considering the wide variety of possible refrigerant mixtures and the limited availability of experimental data, predictive methods are often used. Considerable work has been done on the *ab initio* approach for a priori predictions of VLE utilizing direct molecular dynamics or Monte Carlo simulation techniques, which are very time consuming, have enormous computational burdens, involve several approximations, and are yet to be tested for extension to a wide range of systems. Another method belonging to the second approach is the conductor-like screening model for real solvents (COSMO-RS),^{16–18} which is solely based on unimolecular quantum chemical calculations of the individual species in the system and does not consider the mixture itself. COSMO-RS uses eight adjustable parameters and one additional parameter for each element. Although the COSMO-RS^{17–18} theory can discern between isomers, taking the proximity effects into consideration and giving accurate representations of LLE, it sometimes fails to describe the VLE of even simple organic systems.²³ Group contribution methods like UNIFAC,¹⁹ Mod. UNIFAC,^{20,21} and ASOG²² and other prominent approaches belonging to the second class have been widely used

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in recent years. These methods are based on the concept that a solution is composed of a mixture of functional groups rather than molecules. The interaction parameters between functional groups are obtained from analyses of phase equilibria data of systems containing the same functional groups, avoiding the direct consideration of the interactions between pure compounds in the mixtures, thus making the model predictive.

These models alone can describe the VLE of systems at low pressures in the Gamma-Phi (γ - ϕ) approach with high accuracy. The development of the so-called G^E -EoS mixing rules first proposed by Huron and Vidal²⁴ made it is possible to incorporate the solution models with the commonly used equation of states; thus, making high-pressure VLE prediction possible. Huron and Vidal based their approach on infinite pressure assumptions, Michelsen²⁵ and Dahl and Michelsen²⁶ developed the MHV1 and MHV2 mixing rules based on zero-pressure assumptions, which enable the use of available group contribution parameters for the prediction of high-pressure phase equilibria. Holderbaum and Gmehling²⁷ and Ahlers and Gmehling²⁸ further developed the PSRK and VTPR group contribution models based on the same approach.

The widely used group contribution method in its most recent modifications such as UNIFAC,²⁹ Modified UNIFAC (Dortmund),³⁰ and PSRK³¹ do not include all of the group assignments and interaction parameters for the new refrigerants' related compounds. Jadot and Frère³² presented a predictive method based on UNIFAC for HFCs containing mixtures. Fransson et al.³³ developed a group contribution EoS based on the Abdoul-Rauzy-Pénéloux method originally developed for alkanes for 47 refrigerant mixtures covering CFCs, HCFCs, HFCs, and alkanes. Kleiber³⁴ developed a group contribution method based on the Gamma-Phi (γ - ϕ) approach with the original UNIFAC for a large number of binary refrigerant mixtures. Kleiber and Axmann³⁵ further extended their work to the modified UNIFAC and discussed using an evolutionary algorithm for the parameter optimization. Barolo et al.³⁶ derived a group contribution model using the SRK EoS and the Huron-Vidal mixing rules and interaction parameters from infinite dilution activity coefficient data. Elvassore et al.³⁷ further extended Barolo's work with a revised version of UNIFAC and several new HFCs + HCs binary mixtures. Tochigi et al.^{38,39} proposed an isobaric VLE prediction method for HFE-containing systems with the ASOG group contribution model, which is essentially also a Gamma-Phi (γ - ϕ) approach. However, few new refrigerant mixtures have been included in these works and sometimes too many main groups are used for the involved refrigerants.

The purpose of this work is to develop a predictive method for the description of vapor-liquid equilibria of new refrigerant mixtures containing HFCs, alkanes, alkenes, dimethyl ether, CO₂, and perfluoroalkanes. Those mixtures exhibit azeotropes, high nonideality, association effects, and contain supercritical compounds, which were rarely or not at all included in previous studies.

2. Model Development and Evaluation

The intermolecular interactions derived from the behavior of the liquid and vapor phases at high pressures are described by cubic equations of state incorporated with the G^E -EoS-type mixing rules model to develop a predictive group contribution model. The Soave-Redlich-Kwong (SRK) equation of state (EoS),⁴⁰ known for its ability to describe the VLE of nonpolar and polar compounds, has the following form:

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

where p is the pressure, R is the gas constant, T is the temperature, and a and b are the energy and covolume parameters for the equation of state expressed as

$$a(T) = (0.42748R^2T_c^2/p_c)\alpha(T) \quad (2)$$

$$b = 0.08664RT_c/p_c \quad (3)$$

with

$$\alpha(T) = [1 + (0.480 + 1.574\omega - 0.1767\omega^2)(1 - T_r^{0.5})]^2 \quad (4)$$

where T_c and p_c denote the critical temperature and pressure for the pure compounds, ω is the acentric factor, and $T_r = T/T_c$ is the reduced temperature. The critical properties and acentric factors for the compounds used in this work are given in Table 1.

Because most pure refrigerant compounds are polar substances, the $\alpha(T)$ expression proposed by Mathias and Copeman⁴¹ is used to accurately reproduce the vapor pressures for the pure compounds, thus to improve the quality of the VLE predictions for mixtures.

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3]^2 T_r \leq 1 \quad (5)$$

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5})]^2 T_r > 1 \quad (6)$$

The constants c_1 , c_2 , and c_3 are adjustable parameters obtained by fitting the EoS to the pure component vapor pressure data. The values of these constants for the compounds related to the mixtures in this study are also summarized in Table 1. The vapor pressure data for the pure compounds was taken from REFPROP 7.1,⁴² except for *n*-pentane and dimethyl ether, where the values from the DIPPR⁴³ were used.

The SRK EoS was extended to mixtures using the group contribution solution model with zero reference pressure G^E -EoS mixing rules. The molar excess free energy at zero pressure from the two-parameter cubic equation of state is given by⁴⁴

$$\left(\frac{G^E}{RT}\right)_{\text{EoS}} = \sum_i x_i \ln \frac{b_i}{b_m} + q(\alpha) - \sum_i x_i q(\alpha_i) \quad (7)$$

with

$$q(\alpha) = q(a/(bRT)) = \ln(f_0/RT) + \ln b \quad (8)$$

where f_0 denotes the fugacity at zero pressure.

Mollerup⁴⁵ suggested that eq 7 could be used to represent a given activity coefficient model by setting

$$\left(\frac{G^E}{RT}\right)_{\text{EoS}} = \left(\frac{G^E}{RT}\right)_{\text{SM}} \quad (9)$$

where 'SM' stands for the solution model. Then the expression for $q(\alpha)$ becomes

$$q(\alpha) = \sum_i x_i q(\alpha_i) - \sum_i x_i \ln \frac{b_i}{b_m} + \left(\frac{G^E}{RT}\right)_{\text{SM}} \quad (10)$$

Eq 10 implicitly defines a mixing rule for the α parameter. However, a problem arises with this and other zero-pressure

Table 1. Thermodynamic Parameters for the Pure Compounds

compound	ASHRAE Code	T_c (K)	p_c (MPa)	c_1	c_2	c_3	v_i^L (dm ³ /mol)	b_i (dm ³ /mol)	u_i
methane	R50	190.56	4.5992	0.55761	-0.49921	0.83864	0.0379	0.0268	1.414
ethane	R170	305.33	4.8718	0.71868	-0.74064	1.42642	0.0553	0.0405	1.365
propane	R290	369.83	4.2471	0.76683	-0.44389	0.84994	0.0758	0.0627	1.209
butane	R600	425.13	3.796	0.85436	-0.59024	1.14319	0.0966	0.0807	1.198
isobutane	R600a	407.82	3.64	0.76806	-3.06632	5.26603	0.0979	0.0807	1.213
propylene	R1270	364.76	4.6126	0.77559	-0.68387	1.47403	0.0691	0.0507	1.363
<i>n</i> -pentane ^a		469.7	3.37	0.92983	-0.57909	1.13750	0.1183	0.1003	1.180
tetrafluoromethane	R14	227.51	3.75	0.87397	-1.21649	2.79070	0.0549	0.0392	1.400
trifluoromethane	R23	299.29	4.832	0.96910	-0.84682	1.87418	0.0484	0.0446	1.085
difluoromethane	R32	351.26	5.782	0.98726	-0.70201	1.13307	0.0429	0.0438	0.980
hexafluoroethane	R116	293.02	3.0537	0.94040	-0.73379	1.79760	0.0858	0.0621	1.382
pentafluoroethane	R125	339.17	3.6177	1.00028	-0.53785	1.19744	0.0793	0.0675	1.174
1,1,1,2-tetrafluoroethane	R134a	374.21	4.0593	1.04041	-0.59662	1.23686	0.0741	0.0665	1.115
1,1,1-trifluoroethane	R143a	345.86	3.761	0.94985	-0.60175	1.07633	0.0721	0.0662	1.088
1,1-difluoroethane	R152a	386.41	4.5168	0.97363	-0.63208	1.12630	0.0653	0.0616	1.060
1,1,1,2,3,3,3-heptafluoropropane	R227ea	374.8	2.926	1.08977	-0.67073	1.50248	0.1100	0.0923	1.192
1,1,1,2,3,3-hexafluoropropane	R236ea	412.44	3.502	1.22931	-1.84998	4.57076	0.1026	0.0848	1.209
1,1,1,3,3,3-hexafluoropropane	R236fa	398.07	3.2	1.12132	-0.72558	1.74427	0.1052	0.0896	1.174
1,1,1,3,3-pentafluoropropane	R245fa	427.2	3.64	1.09913	-0.61233	1.59151	0.0982	0.0845	1.161
carbon dioxide	R744	304.13	7.3773	0.89199	-1.01130	3.79296	0.0336	0.0267	1.258
dimethyl ether ^a	RE170	400.10	5.37	0.92871	-1.53132	4.19254	0.0632	0.0537	1.177

^a Denotes critical properties of the compounds taken from DIPPR, whereas the critical properties for the other pure compounds were taken from REFPROP 7.1.

mixing rules at high temperatures where there is no liquid root to the equation of state for some of the pure compounds or mixtures. Michelsen²⁵ solved this problem by replacing $q(\alpha)$ with a linear approximation,

$$q(\alpha) = C_0 + C^{\text{MHV1}}\alpha \quad (11)$$

thus producing the widely used MHV1 mixing rules. Later, a quadratic extrapolation was proposed²⁶ for $q(\alpha)$ in the form,

$$q(\alpha) = C_0 + C_1^{\text{MHV2}}\alpha + C_2^{\text{MHV2}}\alpha^2 \quad (12)$$

which constitutes the basis of the MHV2 mixing rules. However, the quadratic approximation is not guaranteed to give a better representation of VLE properties, with less satisfactory results at low pressures and for polar systems.⁴⁶ MHV2 was found to be the least-accurate model among several G^E-EoS-type mixing rules for a series of binary systems.⁴⁷ In this work, the linear approximation in eq 11 was used for the α parameter with a linear combining rule for the covolume parameter b to form the following mixing rules:

$$a_m = b_m \left[\frac{G_0^E}{C} + \frac{RT}{C} \sum_i x_i \ln \left(\frac{b_m}{b_i} \right) + \sum_i x_i \frac{a_i}{b_i} \right] \quad (13)$$

$$b_m = \sum_i \sum_j x_i x_j \frac{b_i + b_j}{2} \quad (14)$$

where G_0^E is the excess molar Gibbs function expressed by a low-pressure solution model, which in this work was the group contribution model UNIFAC. C is a constant that needs to be determined to provide a better representation of the systems in this study. Fischer and Gmehling⁴⁸ demonstrated that an equation similar to eq 13 could be derived from the excess Helmholtz function approach,

$$a_m = b_m \left[\frac{A^E}{\ln \frac{u}{u+1}} + \sum_i x_i \frac{a_i}{b_i} \right] = b_m \left[\frac{G_0^E + \sum_i x_i \ln \left(\frac{b_m}{b_i} \right)}{\ln \frac{u}{u+1}} + \sum_i x_i \frac{a_i}{b_i} \right] \quad (15)$$

following the assumption proposed by Pénélox et al.⁴⁹ and Abdoul et al.⁵⁰ that

$$u = u_i = \frac{v^L}{b} = \frac{v_i^L}{b_i} \quad (16)$$

The liquid molar volume at the normal boiling point, the covolume parameter from eq 3, as well as the packing fraction u for the pure compounds are listed in Table 1. The average value of $u = 1.10$ seems reasonable for the pure compounds considered. Then, the constant C in eq 13 takes the value -0.64463, which is accidentally equal to the constant used in the PSRK model²⁷ obtained by fitting to the experimental vapor-liquid equilibria data.

G_0^E in eq 13 is expressed by the UNIFAC solution model.¹⁹ A detailed description of the UNIFAC model is given in the Appendix. a_{mm} and a_{nm} in eq A.12 are the interaction parameters between different groups that need to be evaluated in this work. Other temperature-dependent interaction parameters were also tried but with little success for the systems considered in this work.

3. Group Assignment and Interaction Parameter Optimization

Group contribution methods are powerful tools for estimating thermodynamic properties.^{27,34,37-39} The group assignments are essential for successful development of a group contribution method. Wu and Sandler⁵¹ discussed the theoretical basis for defining functional groups based on ab initio quantum mechanic calculations and suggested the general principles for group

assignments in the UNIFAC method. The main ideas can be summarized as follows:

(1) The geometry of a functional group shall be the same, independent of the molecules in which the group occurs.

(2) Each atom in a functional group should have approximately the same charge in all of the molecules in which the group occurs, and the group should have approximately zero charge.

(3) Each functional group should be the smallest entity for a molecule that can be divided into a collection of electroneutral groups.

Some of the group contribution methods developed for refrigerant mixtures^{32,33,36,37} that are reviewed in the introduction do not fulfill or even contradict these principles. As a result, the predictive ability of the group contribution models cannot be guaranteed.³⁴ Following these principles, for HFCs, the fluorine atom cannot be defined as a main group as also stated by Kleiber,³⁴ because the fluorine atom has a strong negative charge and there are many possible combinations of molecular fragments in the vicinity of the fluorine atom that are strongly affected, making the interactions between groups difficult to balance. Hence, it is not advisable to divide the fluorinated methane derivatives into smaller segments. In this work, the methane derivatives such as R14, R23, and R32 are taken entirely as separate groups, in a way consistent with the second principle listed above. Some of the methane derivatives should be incorporated into the same main group to keep the number of interaction parameters as small as possible and to improve the predictive ability of the model. All combinations of pairs of methane derivatives were systematically investigated, but no pairs were found that could be combined into the same main group. Therefore, CHF₃, CH₂F₂, and CF₄ were assigned to three different main groups.

For the ethane derivatives considered in this work, because several halogen atoms may be connected to the same carbon atom, the electronic distribution in the molecular segments beyond the carbon atom related segments can be influenced as well. In this work, the *ab initio* calculational results for the electronic charge distributions show that all of the ethane derivatives including R152a and R143a can be split into two subgroups because they are affected little by the so-called proximity effects as will be discussed in the next section. The problems become cumbersome when it comes to the propane-derivative hydrofluocarbons because the proximity effects induced by the neighboring segments become difficult to analyze, and there are no *ab initio* quantum mechanical calculational results for the propane derivatives at present. To utilize an important capability of the UNIFAC method, that is the calculation of the properties of a molecule using the properties of its constituting groups, it is advantageous to combine the subgroups from the propane derivatives into the existing common main groups. The CF₃ group is the most-electronegative group among the segments related to the propane derivatives. For example, the neighboring segment CHF in R227ea is certainly strongly influenced by such a group. Therefore, the CHF and CF₃ segments were empirically combined to form an independent subgroup CHF₃, which then must be assigned to a main group. If the CF₃ segment is replaced by fluorine, then the CHF₂ group corresponding to the CHF main group is formed. An investigation of VLE correlations and predictions for HFCs + HCs also suggests that better VLE results can be obtained by assigning the CHF₃ to the CHF main group, which is further confirmed by the VLE description for Alkene + HFC, CO₂ + HFC, and RE170 +

Table 2. Group Assignments for New Refrigerants

main groups	subgroups	R_k	Q_k
alkane	CH ₄	1.1292	1.124
	CH ₃	0.9011	0.848
	CH ₂	0.6744	0.540
	CH	0.4469	0.228
CHF	CHF	0.842	0.688
	CH ₂ F	1.0699	1.000
	CHF ₂	1.238	1.232
	CH ₂ F ₂	1.4654	1.460
	CF ₃ CHF	2.248	2.068
CHF ₃	CHF ₃	1.6335	1.608
	CF ₃	1.406	1.380
	CF ₃ CH ₂	2.0804	1.920
CF ₃	CF ₃ ^a	1.406	1.380
	CF ₄	1.780	1.820
C=C	CH ₂ =CH	1.3454	1.176
	CH=CH	1.1167	0.867
CH ₃ CO	CH ₃ CO	1.6724	1.488
CO ₂	CO ₂	1.300	0.982

^a Subgroup designed for perfluorocarbons.

HFC binary mixtures, as will be detailed in the following section. In a similar manner, for the propane derivative R245fa, the CF₃ and CH₂ segments can be combined into a subgroup CF₃CH₂. This time, if the CH₂ segment is replaced by hydrogen, the CHF₃ group corresponding to the CHF₃ main group is formed. Assigning the newly developed subgroup into the CHF₃ main group gave more-satisfactory VLE results for the systems considered. To our knowledge, such a concept cannot be generalized to other propane derivatives. Instead, for these compounds, a splitting strategy consistent with the ethane derivatives is more favorable.

The alkanes and alkenes involved in the binary systems are grouped as is commonly done in the UNIFAC¹⁹ and Mod. UNIFAC models.^{20,21} The CO₂ involved in the refrigerant mixtures is taken as a separate main group naturally. For the RE170 (dimethyl ether, DME), which is the constituent compound in the RE170 + HFCs systems, Soave et al.⁵² suggested separating it with the etheric group -O-. In this work, the DME is grouped consistently with the strategy adopted by the UNIFAC¹⁹ and Mod. UNIFAC models^{20,21} with the two subgroups CH₃CO and CH₃. The group assignments for all of the compounds are illustrated in Table 2.

The vapor-liquid equilibria were modeled, and the interaction parameters were evaluated based on a database including both pure compounds and mixtures. Table 1 lists the critical temperatures and critical pressures for the pure compounds. For the VLE data of the mixtures, only those that passed the thermodynamic consistency tests were used in the following parameter generalization. Most of the VLE systems in this work are high-pressure systems, thus as discussed by Raal and Mühlbauer,⁵³ the extension of the low-pressure thermodynamic consistency tests to high-pressure data leads to complications such as supercritical volatile components, significant vapor-phase nonidealities, and evaluations of the liquid molar volume or the excess molar volume arise. As a result, the commonly used methods, such as those used in the DECHEMA data series and DIPPR manuals, may have difficulties when applied to the high-pressure systems.⁵⁴

Having surveyed the literature for thermodynamic consistency test methods for high-pressure systems,⁵⁴⁻⁵⁸ the thermodynamic consistency test procedures similar to those proposed by Jackson and Wilsak⁵⁴ were selected. These tests make use of the SRK EoS to account for the vapor-phase nonideality and the modified

Margules equation⁵⁹ to account for the liquid-phase nonideality through liquid activity coefficients and neglect the differential of the total pressure term in the isothermal differential Gibbs–Duhem equation. The critical properties, acentric factors, and the volumetric properties were taken from REFPROP 7.1,⁴² except for *n*-pentane and dimethyl ether, for which the critical properties and acentric factors from DIPPR⁴³ were used, and the volumetric properties were calculated with the volume-translated PR EoS.⁶⁰ In practice, the extended area and points test procedures are both used. Compared to the extended area test, the extended points test procedure gives more-valuable and useful information about the quality of a set of isothermal VLE data. Nevertheless, the area test is still useful because the $\ln(\gamma_1/\gamma_2)$ data can be accurately fitted, and at the same time, the $\ln\gamma_1$ and $\ln\gamma_2$ curves can be depicted in the same figure, which can serve as an additional test, as elegantly discussed by Wisniak et al.⁶¹ The consistency of each data set was judged on the basis of the generally adopted consistency test criteria, as detailed by Jackson and Wilsak⁵⁴ and Wisniak et al.⁶¹ Table 3 lists the VLE data of 43 systems covering 140 isothermal sets (more than 1500 data points) that passed the thermodynamic consistency test, which were used in the following parameter estimation. The original VLE data collected in this study can be obtained upon request.

The group interaction parameters a_{mn} and a_{nm} were determined using the following objective function:

$$OF = \sum_{i=1}^N \left(\frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{p_i^{\text{exp}}} \right)^2 \quad (17)$$

where p_i^{exp} and p_i^{cal} are experimental and calculated pressures and N is the number of data points. Because the data sets used in parameter optimization were evaluated for thermodynamic consistency, the form of the objective function has little influence on the parameter optimization. The parameter optimization procedure was performed using both the Levenberg–Marquardt algorithm⁹¹ and the Simplex algorithm⁹² as the optimization methods, to ensure that the optimum interaction parameters were obtained. The optimized interaction parameters are listed in Table 4.

4. Results and Discussion

4.1. Alkanes + HFCs Systems. Mixtures of alkanes and hydrofluorocarbons (HFCs) are considered to be promising refrigerants, foaming agents, and propellants. Several such mixtures are in commercial use with a number of published vapor–liquid equilibria data sets for these systems. The systems in this class used for the parameter estimation are categorized in Table 3. As shown in Table 3, for all the sets of data, the average deviations of the pressure and vapor-phase composition are 3.24% and 0.0125, respectively. The largest pressure deviation is 7.39% for the R143a + R290 binary system, a value that is a bit larger than the general case. Considering that the other R143a related binaries all give rather acceptable results, the group assignment strategy was not modified to introduce a new special maingroup so as not to reduce the predictive ability of the group contribution model. At the same time, all of the other ethane derivative related systems are accurately described by this group assignments strategy. Furthermore, the VLE calculations for all of the propane-derivative HFCs related systems are quite satisfactory and encouraging with examples shown graphically in Figures 1 and 2. Therefore, the group

Table 3. VLE Database and the Calculated Results from the Group Contribution Model

systems	<i>N</i>	<i>T</i> (K)	$\Delta p(\%)^a$	Δy^b	data sources
R23+R600a	11	283.15	3.88	0.013	6
R32+R290	72	248.13–293.15	1.52	0.011	62
R32+R600	43	263.15–293.15	1.38	0.008	63
R32+R600a	20	301.80	3.84	0.019	64
R125+R290	117	253.15–323.15	1.06	0.007	65
R125+R600a	40	293.15–313.15	3.06	0.015	66
R134a+R290	29	254.997–298.011	5.36	0.017	67
R134a+R600a	28	293.66–303.68	3.77	0.016	68
R143a+R290	16	283.18	7.39	0.022	69
R143a+R600a	20	323.15–333.15	3.83	0.016	6
R152a+R600a	40	303.20–333.20	1.64	0.004	64
R152a+n–Pentane	39	303.90–384.61	5.22	0.015	70
R227ea+R290	38	303.15–343.15	2.48	0.008	71
R227ea+R600a	43	303.15–323.15	4.84	0.021	66
R236ea+R290	43	283.12–313.21	2.43	0.008	8
R236fa+R290	49	283.13–323.26	1.89	0.005	72
R236fa+R600a	15	303.68	5.00	0.019	68
R245fa+R290	32	293.18–313.22	2.98	0.010	73
R245fa+R600a	40	293.15–313.15	1.53	0.007	74
R23+R1270	17	250.994–265.013	4.31	0.016	67
R32+R1270	90	273.15–313.15	2.23	0.019	7
R134a+R1270	79	273.15–313.15	2.09	0.007	75
R152a+R1270	36	254.996–285.004	2.87	0.009	67
R23+CO ₂	41	254.00–293.15	2.26	0.009	76
R32+CO ₂	56	222.04–283.15	1.94	0.005	9
R125+CO ₂	5	284.48–304.99	4.37	0.005	77
R134a+CO ₂	30	252.95–292.95	2.51	0.005	78
R227ea+CO ₂	24	276.01–293.15	4.25	0.012	79
R32+RE170	30	258.15–293.15	4.40	0.015	80
R125+RE170	46	258.15–303.15	2.39	0.022	81
R134a+RE170	48	293.18–358.15	7.99	0.027	82
R143a+RE170	46	313.15–343.15	4.39	0.012	83
R152a+RE170	26	257.994–298.009	2.34	0.012	84
R227ea+RE170	41	278.15–308.15	3.42	0.015	85
R236ea+RE170	40	283.12–313.22	1.79	0.011	8
R236fa+RE170	37	283.12–303.68	5.66	0.017	86
R14+R50	27	169.38–178.93	4.88	0.006	87
R14+R170	37	179.68–210.03	4.13	0.010	88
R14+R290	7	173.666–173.795	3.05	0.013	84
R116+R170	34	199.64–242.93	1.57	0.011	89
R23+R116	27	209.60–227.60	0.84	0.013	90
R32+R116	14	253.55	0.64	0.006	90
R134a+R116	18	250.992–275.013	1.84	0.009	67

$$^a \Delta p\% = \frac{1}{N} \sum_{i=1}^N \left| \frac{p_i^{\text{cal}} - p_i^{\text{exp}}}{p_i^{\text{exp}}} \right| \times 100, \text{ where } N \text{ denotes the number of data points.}$$

$$^b \Delta y = \frac{1}{N} \sum_{i=1}^N |y_i^{\text{cal}} - y_i^{\text{exp}}|, \text{ where } N \text{ denotes the number of data points.}$$

Table 4. Interaction Parameters a_{mn} and a_{nm} (K) between the Maingroups Listed in Table 2

	alkane	CHF	CHF ₃	CF ₃	C=C	CH ₂ CO	CO ₂
alkane	0	378.32	172.85	151.69	86.02 ^a	251.50 ^a	n.a.
CHF	85.17	0	2789.31	59.93	−52.06	−149.45	−250.93
CHF ₃	127.02	483.65	0	21.19	−141.45	−46.50	−266.01
CF ₃	59.41	405.61	191.02	0	n.a.	n.a.	n.a.
C=C	−35.36 ^a	384.70	830.95	n.a.	0	214.50 ^a	
CH ₂ CO	83.36 ^a	253.56	−37.81	n.a.	26.51 ^a	0	26.51 ^a
CO ₂	n.a.	587.17	924.16	n.a.	n.a.	214.50 ^a	0

^a Interaction parameters taken from original UNIFAC.¹⁹ n.a. denotes parameter not available or not used in this work.

divisions for these compounds were deemed to be reasonable and acceptable.

The VLE predictive ability of the model was tested for the seven systems not used in the parameter estimation. The prediction results are listed in Table 5. These systems were picked because they are either directly from Kleiber⁸⁴ or from recently published data in the open literature. As shown in Table

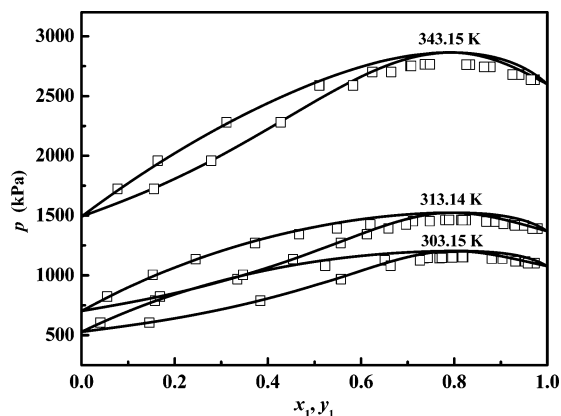


Figure 1. VLE prediction results for the R290(1) + R227ea(2) system using the group contribution model. □: Experimental data from Valtz et al.⁷¹

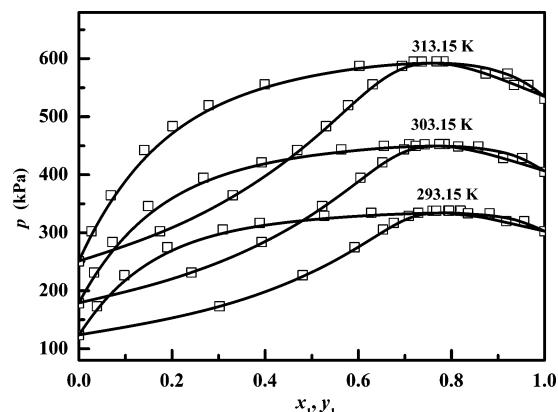


Figure 2. VLE prediction results for the R600a(1) + R245fa(2) system using the group contribution model. □: Experimental data from Bobbo et al.⁷⁴

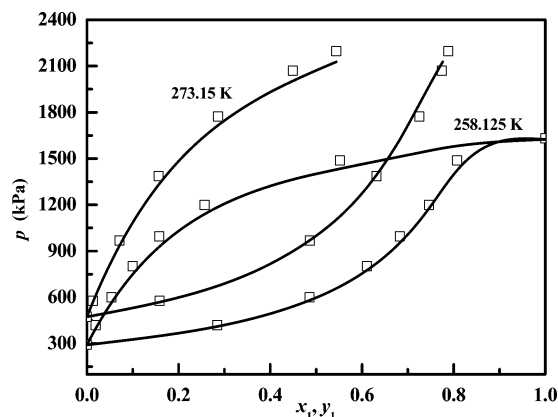


Figure 3. VLE prediction results for the R23(1) + R290(2) system using the group contribution model. □: Experimental data from Kleiber.⁸⁴

5, the systems are adequately predicted by the group contribution model with an average absolute pressure deviation of 3.51%, which illustrates the inherent predictive ability of the group contribution theory. Even systems containing R170, which is not one of the four alkanes (R290, R600, R600a, and *n*-pentane) in the alkane + HFC binaries considered in the parameter generalization, are accurately predicted, as listed in Table 5. The prediction results and the experimental VLE data for the R23 + R290 and R134a + R600 systems are also given in Figures 3 and 4. It should be noted that the isomeric effects may affect the results, because R600 and R600a are isomers. However, as illustrated above and listed in Tables 3 and 5, the correlation and prediction results are still quite accurate.

Table 5. VLE Prediction Results for Binary Systems Based on the Group Contribution

systems	<i>N</i>	<i>T</i> (K)	Δp (%) ^a	Δy ^b	data sources
R23+R170	20	228.50–243.76	3.99	0.009	93
R23+R290	15	258.125–273.150	3.48	0.011	84
R143a+R600	37	313.15–363.15	3.77	0.021	94
R152a+R290	62	273.15–313.15	2.45	0.019	84,95
R125+R600	64	278.15–323.15	1.44	0.009	96,97
R134a+R600	47	313.15–333.15	4.94	0.016	97
R152a+R600	28	293.15–303.15	4.52	0.010	98

$$^a \Delta p\% = \frac{1}{N} \sum_{i=1}^N \left| \frac{p_i^{\text{cal}} - p_i^{\text{exp}}}{p_i^{\text{exp}}} \right| \times 100, \text{ where } N \text{ denotes the number of data points.}$$

$$^b \Delta y = \frac{1}{N} \sum_{i=1}^N |y_i^{\text{cal}} - y_i^{\text{exp}}|, \text{ where } N \text{ denotes the number of data points.}$$

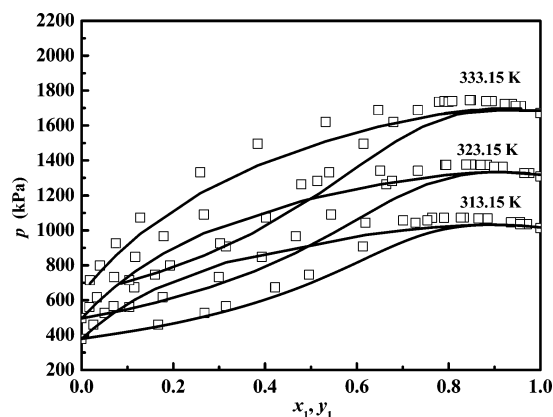


Figure 4. VLE prediction results for the R134a(1) + R600(2) system using the group contribution model. □: Experimental data from Im et al.⁹⁷

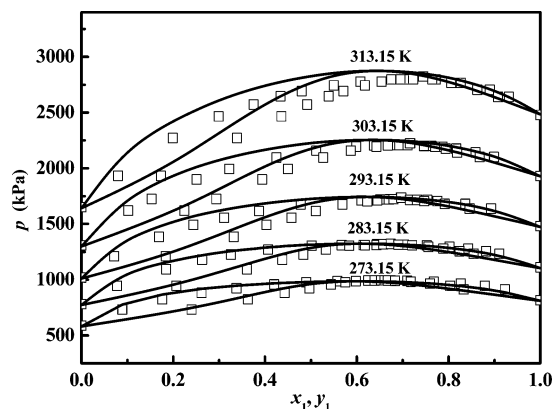


Figure 5. VLE prediction results for the R32(1) + R1270(2) system using the group contribution model. □: Experimental data from Ho et al.⁷

4.2. Alkenes + HFCs Systems. The most-common alkene, which has been developed as a promising refrigerant component, is R1270 (propylene). The VLE predictions for the alkenes + HFCs binary systems are listed in Table 3. The interaction parameters between the CH₂=CH and CH₃ main groups were taken from the original UNIFAC parameters.¹⁹ The interaction parameters between the CH₂=CH and CHF main group and the CH₂=CH and CHF₃ main group were optimized in this work, as shown in Table 4. The results show that the model yields a good reproduction of the experimental data. The R32 + R1270 and R152a + R1270 systems are illustrated in Figures 5 and 6.

4.3. CO₂ + HFCs Systems. CO₂ has long been considered as a potential refrigerant substitute. Its mixtures with HFCs have

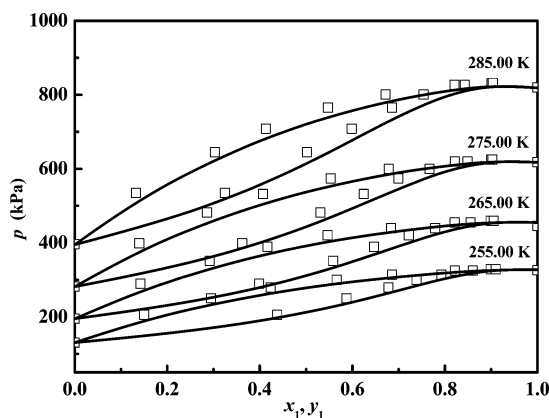


Figure 6. VLE prediction results for the R1270(1) + R152a(2) system using the group contribution model. □: Experimental data from Kleiber.⁶⁷

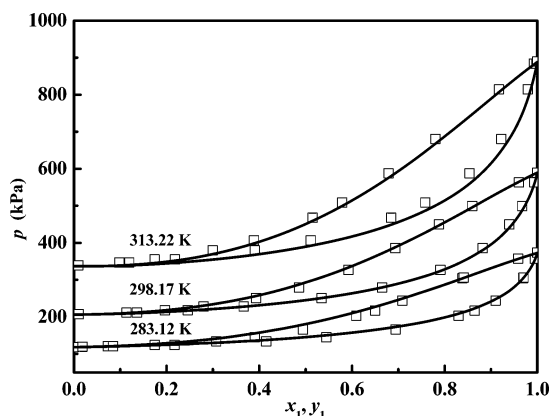


Figure 7. VLE prediction results for the RE170(1) + R236ea(2) system using the group contribution model. □: Experimental data from Bobbo et al.⁸

attracted a special interest in recent years. For the VLE calculations, CO₂ is normally a supercritical component. The VLE calculational results for the CO₂ + HFCs binary systems using the interaction parameters obtained in this work are also listed in Table 3. The group assignment strategy, especially the treatment of R227ea as in the HCs+HFCs binaries, is further validated by these results.

4.4. RE170 + HFCs Systems. Dimethyl ether (RE170) has been extensively used in industrial refrigeration systems. Systems formed by RE170 + HFCs may form hydrogen bonds, thus exhibiting association effects and strong negative deviations from Raoult's law.⁹⁹ Eight RE170 + HFCs systems were found in the literature, including three propane-derivative HFCs containing systems, for a good validation of the group assignments strategy developed here. The R236ea + RE170 and R152a + RE170 binary systems are shown in Figures 7 and 8. The R236ea + RE170 system exhibits negative deviations from Raoult's law and minimum azeotropic points. The R152a + RE170 system has a rather usual phase diagram, as illustrated in Figure 8, which is also adequately described by the present model. The interaction parameters between the CH₃CO and CH₃ main groups were taken from the original UNIFAC parameters.¹⁹ The interaction parameters between the CH₃CO and CHF main groups and the CH₂CO and CHF₃ main groups were estimated here. Table 3 shows that the calculation results for the methane, ethane, and the propane derivatives' related binaries are in the range of generally applied group contribution methods, such as UNIFAC¹⁹ and Mod. UNIFAC models.^{20,21}

4.5. Perfluoroalkanes Related Systems. Perfluoroalkanes (PFCs) are usually used as refrigerants for low-temperature

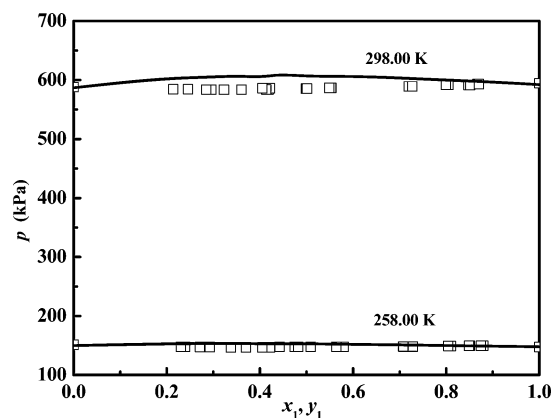


Figure 8. VLE calculation results for the R152a(1) + RE170(2) system using the group contribution model. □: Experimental data from Kleiber.⁸⁴

Table 6. Comparison of VLE Prediction Results Using Kleiber's Group Contribution Parameters and $k_{ij} = 0$ in the Classical Mixing Rules for HFC + HFC Binaries

system	Δp (%) ^a	Δp (%) ^b	system	Δp (%) ^a	Δp (%) ^b
R23+R32	2.67	2.59	R125+R134a	4.98	1.02
R23+R125	11.33	0.89	R125+R143a	0.54	1.07
R23+R134a	8.40	1.05	R125+R152a	1.76	4.05
R23+R143a	2.03	1.44	R125+R236ea	n.a.	0.97
R23+R152a	4.97	4.12	R125+R236fa	n.a.	1.17
R23+R227ea	n.a.	1.04	R134a+R152a	5.28	2.39
R32+R125	2.20	0.91	R134a+R227ea	n.a.	0.98
R32+R134a	2.80	1.59	R134a+R236fa	n.a.	1.21
R32+R143a	2.72	1.27	R134a+R245fa	n.a.	0.96
R32+R152a	2.52	3.14	R143a+R134a	1.25	1.84
R32+R227ea	n.a.	2.13	R143a+R152a	0.51	1.10
R32+R236ea	n.a.	4.65	R143a+R236fa	n.a.	3.39
R32+R236fa	n.a.	2.08	R152a+R227ea	n.a.	2.63

^a Δp (%) represents the average absolute pressure deviation calculated using the model used in this work and the group contribution interaction parameters from Kleiber.³⁴ ^b Δp (%) represents the average absolute pressure deviation calculated using the SRK EoS and the classical mixing rules with the binary interaction parameters in the classical mixing rules equal to zero.

refrigeration systems. Altogether, seven PFCs related binary systems were used in this study including PFCs + HCs and PFCs + HFCs. As shown in Table 3, the present model also gives a good representation of the experimental data for these systems with the optimized interaction parameters listed in Table 4.

4.6. Ternary Systems. Ternary and multicomponent mixtures have long been considered as potential refrigerant alternatives. Ternary mixtures account for a large part of the potential refrigerants listed by the EPA¹⁰⁰ and ASHRAE Handbook Fundamentals.¹⁰¹ However, experimental VLE data for such mixtures are rather scarce in the literature. The R32 + R290 + R227ea ternary system¹⁰² is the only one involving both HCs and HFCs that can be found in the literature. To make VLE predictions for this system possible, the interaction parameters between the HFC binaries R32 and R227ea should be available. The group contribution model developed by Kleiber³⁴ can be used to describe the HFC + HFC binaries. However, the available parameters cannot describe all of the HFCs, and the predicted results from Kleiber's model do not seem to perform better than merely assuming that the binary interaction parameter k_{ij} in the classical mixing rules is equal to zero, as shown in Table 6. The results illustrate that with $k_{ij} = 0$ in the SRK EoS with the classical mixing rules model, the VLE predictions for HFC + HFC binaries are comparable and in most cases are better than those from the commonly used group contribution

Table 7. VLE Prediction Results for the Ternary System R32 + R290 + R227ea

T (K)	$x_{1,\text{exp}}$	$x_{2,\text{exp}}$	p_{exp} (MPa)	p_{cal} (MPa)	$y_{1,\text{cal}}$	$y_{2,\text{cal}}$
308.25	0.322	0.123	1.444	1.389	0.430	0.267
319.95	0.322	0.123	1.881	1.801	0.422	0.243
328.35	0.322	0.123	2.255	2.144	0.414	0.225
269.85	0.135	0.174	0.415	0.697	0.205	0.435
273.18	0.135	0.174	0.457	0.437	0.206	0.484
286.34	0.135	0.174	0.672	0.483	0.206	0.474
301.55	0.135	0.174	1.004	1.025	0.202	0.391
310.69	0.135	0.174	1.25	1.269	0.198	0.365
329.15	0.135	0.174	1.876	1.887	0.189	0.313
298.55	0.493	0.127	1.411	1.367	0.580	0.260
313.85	0.493	0.127	2.025	1.950	0.578	0.233
307.75	0.493	0.127	1.761	1.699	0.579	0.244
303.75	0.493	0.127	1.597	1.548	0.580	0.251

methods. Though new evaluations of the interaction parameters will somewhat improve the VLE predictions given by Kleiber,³⁴ we decided not to follow this procedure. Then, one problem with ternary systems composed of both HCs and HFCs is how to describe such systems in a uniform and consistent model. To make this model fully predictive, VLE data for the R32 + R227ea binary system was generated for temperatures from 270.0 to 330.0 K, using the SRK EoS and the classical mixing rules with the binary interaction parameters $k_{ij} = 0$. These data were then used to obtain the group interaction parameters between the groups for R32 and R227ea based on the present group assignments strategy. These obtained parameters were then incorporated with the interaction parameters listed in Table 4 to predict the VLE for the ternary system. The predicted results are listed in Table 7 along with the experimental data, with an average pressure deviation of 3.47%. Because the experimental data for the ternary system was obtained using the synthetic method, the experimental vapor-phase compositions are not available. Nevertheless, the current predictions are rather similar to the predictions of Coquelet et al.,¹⁰² which were directly based on the data for the corresponding binary systems. These results are rather encouraging, indicating that this method can be used to fully predict the related ternary systems.

5. Conclusions

A group contribution model was developed to predict vapor–liquid equilibria of refrigerant mixtures containing hydrofluorocarbons, alkanes, alkenes, dimethyl ether, CO₂, and perfluoroalkanes. A new group assignment strategy was developed for these systems. Optimized interaction parameters between seven main groups were used to accurately predict the VLE for the five types of refrigerant mixtures. Extension of the group contribution method to a ternary system gives rather encouraging prediction results. The results indicate that this group contribution method is suitable for predicting vapor–liquid equilibria of new refrigerant mixtures and can be used for preselecting mixtures for experimental studies, screening alternative refrigerant mixtures, determining optimal compositions, and evaluating refrigeration cycles.

Nomenclature

A^E = excess Helmholtz free energy

a = EoS energy parameter

b = covolume parameter

a_m, b_m = EoS parameters for mixtures

C = constant in the zero pressure mixing rules

c_1, c_2, c_3 = coefficients of $\alpha(T)$ function

f = fugacity

k_{ij} = binary interaction parameter in the classical mixing rules

N = number of data points

p = pressure

$q(\alpha)$ = approximation function

R = universal gas constant

T = temperature

U = packing fraction

v = volume in molar units

x = molar fraction in the liquid phase

y = molar fraction in the vapor phase

Abbreviations

DME = dimethyl ether

EoS = equation of state

HC(s) = hydrocarbon(s)

HFC(s) = hydrofluorocarbon(s)

PFC(s) = perfluorocarbon(s)

SM = solution models

SRK = Soave–Redlich–Kwong EoS

VLE = vapor–liquid equilibria

Greek Letters

Δ = deviation

$\alpha = a/(bRT)$

$\alpha(T)$ = EOS temperature-dependent function

φ = fugacity coefficient

γ = activity coefficient

Subscripts

c = critical point

i, j = component i, j and data point i

m = mixture

r = reduced property

0 = zero pressure reference state

Superscripts

cal = calculated value

E = excess property

exp = experimental value

L = liquid phase

Appendix

The UNIFAC model¹⁹ is an extension of the UNIQUAC model to a solution-of-groups model. Its fundamental aim is to utilize existing phase equilibria data for predicting the phase equilibria of systems for which no experimental data are available. The activity coefficient is separated into a combinatorial and a residual part

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (\text{A.1})$$

with the combinatorial part providing the contribution due to differences in molecular size and shape and the residual part providing the contribution due to group interactions.

The combinatorial part is given by

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

with

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (\text{A.3})$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (\text{A.4})$$

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \quad (\text{A.5})$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (\text{A.6})$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (\text{A.7})$$

where Z is the coordination number, usually taking the value of 10. $v_k^{(i)}$ is the number of group k in molecule i . R_k and Q_k are the van der Waals volumes and surface areas, calculated based on the methods given by Bondi,¹⁰³ as listed in Table 2.

The residual part was obtained using the following relations:

$$\ln \gamma_i^R = \sum_i v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (\text{A.8})$$

with

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \psi_{mk} \right) - \sum_m \frac{\Theta_m \psi_{mk}}{\sum_n \Theta_n \psi_{nm}} \right] \quad (\text{A.9})$$

$$\Theta_m = \frac{\Theta_m X_m}{\sum_n \Theta_n X_n} \quad (\text{A.10})$$

$$X_m = \frac{\sum_i x_i v_{mi}}{\sum_i x_i \sum_m v_{mi}} \quad (\text{A.11})$$

$$\psi_{mn} = \exp \left(-\frac{a_{mn}}{T} \right) \quad (\text{A.12})$$

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