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Predictions of thermodynamic properties and phase equilibria of refrigerant systems with COSMO approaches

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Abstract

The knowledge of the phase equilibrium of refrigerant mixtures is crucial for the optimization of the production processes of refrigerant molecules, and the design of energetic systems (heat pumps, Organic Rankine Cycles, …). In this work, different predictive thermodynamic models (COSMO-RS and COSMO-SAC-dsp) have been used to determine the phase behavior of mixtures of refrigerants involving alkanes, fluorinated and chlorinated compounds. The COSMO-RS model leads to rather satisfactory predictions of the vapor-liquid equilibria of mixtures and is able to capture the azeotropic behavior for most systems. However, the original COSMO-SAC model as well as the COSMO-SAC 2010 version lead to unsatisfactory predictions of VLE for these systems, as they are unable to predict the azeotropic behavior in alkane + refrigerants. By combining COSMO-SAC with a dispersion term (COSMO-SAC dsp model) and readjusting the universal parameter for the F atom, it is possible to get very satisfactory predictions of similar accuracy as COSMO-RS. In order to predict the phase behavior at high pressure, the COSMO-SAC-dsp model can be combined with the Peng-Robinson equation of state and the MHV1 mixing rule. Excellent predictions of relative volatilities can be obtained with this approach over wide temperature and pressure ranges. COSMO calculation can also be used to predict saturated liquid densities, vaporization enthalpy and boiling points of pure refrigerants.

Keywords:

HFO, HCFO, HFC, vapor-liquid equilibria, COSMO calculation, equation of state.

Nomenclature:

$\mu_{i/S}$: chemical potential of component *i* in solution *S*.

$P_{vap,i}$: vapour pressure of pure component *i*

σ_m: surface charge on segment *m*

$p_i(\sigma_m)$: sigma profile of component *i*

$p_i^{nhb}(\sigma)$: contribution to sigma profile due to non hydrogen bonding segments

$p_i^{oh}(\sigma)$: : contribution to sigma profile due to segments on O or H atoms belonging to OH groups

$p_i^{ot}(\sigma)$: : contribution to sigma profile due to segments on O atoms not belonging to OH groups, or *F* atoms

$\gamma_{i/S}$: activity coefficient of component *i* in solution *S*.

A_i: cavity surface of component *i*

$\Gamma_i(\sigma_m)$: segment activity coefficient at charge σ_m , for component *i*

$\Delta W(\sigma_m, \sigma_n)$: misfit energy between segments *m* ad *n* of charges σ_m and σ_n

$G^{ex,disp}$: dispersion contribution to the excess Gibbs free energy in the COSMO-SAC dsp model

A_{12} : Margules Constant

w: dispersion universal parameter in the COSMO-SAC dsp model

$\varepsilon_{atom,j}$: atomic dispersion energy in the COSMO-SAC dsp model

V_{cosmo} : cavity volume in Å, obtained from COSMO calculation.

1. Introduction

According to the constraints imposed by the European and International legislations, the refrigerant industry must constantly find alternative refrigerant fluids that have lower impacts on the global warming of Earth and Ozone layer. Besides the safety and environmental constraints, these alternative fluids must have proper thermodynamic properties in order to be considered as efficient refrigerants. Their energetic properties must be equivalent to the previous fluids in order to avoid important modifications of the energetic system and heavy investment costs. Working with refrigerant blends is often preferable to pure component

fluids for energy saving and flexibility. In order to select the optimal mixture composition for the design and operation of a refrigeration process, it is necessary to know the phase diagram and thermodynamic properties of mixtures. In particular, it is of crucial importance to know the location of azeotropes and the vapor-liquid equilibria (VLE) of these mixtures. Hydrofluoroolefins (HFO) and hydrochlorofluoroolefins (HCFO) have been considered for replacing the currently used hydrofluorocarbons (HFC), because they have a much lower Global Warming Potential (GWP). However, vapor-liquid equilibrium data for mixtures containing HFO and HCFOs are still scare.

Ab initio methods can be very reliable to predict the thermochemical properties of pure compounds and mixtures. Concerning refrigerant systems, Paricaud and co-workers have recently shown that ab initio calculation performed on a single molecule in vacuum can be used to accurately predict ideal gas properties of refrigerants such as ideal gas heat capacities and heats of formations [1, 2]. The aim of this work is to assess the capabilities of thermodynamic models based on ab initio COSMO calculation, for the predictions of VLE of refrigerant mixtures, containing HFCs, HFOs, HCFOS and alkanes. The VLE of such systems have been described by using molecular simulation [3], and equations of state such as the predictive E-PPR78 equation of state based on group contribution method [4], and the polar PPC-SAFT equations of state [5]. One can also mention the extensive work of Vrabec and coworkers on refrigerants systems, using both molecular simulations and equations of state [6-10]. The phase behavior of HCF mixtures were also predicted with COSMO-RS [11], with great success. However, COSMO-SAC like models have never been used for such mixtures, to our knowledge. The COSMO approach was originally developed by Klamt and coworkers [12-14] : they proposed the COSMO-RS model (COnductor -like Sreening MOdel for Real Solvent »), which is a predictive excess Gibbs free energy model. Lin and Sandler [15] proposed the COSMO-SAC (COnductoRlike Sreening MOdel – Segment Activity Coefficient) model , which includes the Staverman-Guggenheim combinatorial term and is expressed in terms of activity coefficient of segments rather than chemical potentials. Several versions of COSMO-SAC were then proposed [15-20]. Another version of the COSMO model called as COSMO-RS(ol) and based on COSMO-RS was developed by Gmehling and coworkers [21, 22]. Pye et al. [23] also proposed their own version of COSMO-RS and implemented it into the ADF software.

In this study, the 2010 version of COSMO-RS developed by Klamt's group has been used [24]. We also considered the original version of COSMO-SAC from Lin and Sandler [15], the COSMO-SAC 2010 version [19], and the COSMO-SAC dsp model developed by

Hsieh et al. [20]. The COSMO-SAC dsp has recently been used to predict flash points of fuels [25] and solvation Gibbs free energies [26]. In this study, it is used to predict the vapor-liquid equilibria (VLE) of fluorinated refrigerant mixtures. COSMO-RS has also been used for the prediction of boiling points and vaporization enthalpies of pure refrigerants, and a correlation is proposed to predict the saturated liquid densities of refrigerants.

2. Thermodynamic models

2.1. COSMO-RS

In the COSMO-RS approach [24, 27, 28], the chemical potential $\mu_{i/S}$ of component i in solution S at temperature T is given by

$$\mu_{i/S} = \int A_i p_i(\sigma)\, \mu_S(\sigma) d\sigma + \mu_{i/S}^{C} + kT \ln x_i, \tag{1}$$

A_i is the surface area of molecule i, $\mu_{i/S}^{C}$ the combinatorial contribution to the chemical potential of component i, and x_i the mole fraction of component i; $p_i(\sigma)$ is normalized the σ -profile of component i. $\mu_S(\sigma)$ is called the σ -potential of the solution. The detailed expressions of the COSMO-RS model can be found in Ref. [28]. There are several parameterizations of the model (i.e., different sets of universal parameters). In this work we use the parameterization "C21-0110" for the def-TZVP basis set. One advantage of the COSMO-RS model is the possibility of predicting vapor pressures and boiling points of pure compounds. The prediction is based on the equality of the chemical potential of the studied pure compound in both phases ($\mu_{liq} = \mu_{gas}$), where μ_{liq} is given by Eq. (1) and μ_{gas} is given by $\mu_{gas} = \mu^{id} + RT \ln P_{vap}/P_0$ where

$$\mu^{id} = E^{vaccum} - E^{COSMO} + E_{disp} + \omega_{ring} n_{ring} + n_{ig}(T). \tag{2}$$

E_{disp} is a dispersion term that is expressed as a sum of atomic contributions (types of atoms). ω_{ring} is an empirical universal parameter and n_{ring} is the number of rings of atoms in the molecule. $n_{ig}(T)$ is an empirical and universal function of T. E^{vaccum}, E^{COSMO} are the energies obtained from the quantum calculation in vacuum (isolated molecule) and inside a

cavity surrounded by a perfect conductor (COSMO calculation), respectively. As a result, two ab initio calculations have to be performed on the same molecule: one in vacuum and one inside the cavity. The value of E^{vaccum} is contained in the .energy file while E^{COSMO} is in the .cosmo file. A geometry optimization has to be performed for each file, as the geometry of the molecule is not the same in vacuum and inside the cavity. The vaporization enthalpy is obtained from the Clapeyron equation, by neglecting the molar volume in the saturated liquid phase.

The 2010 version of the def-TZVP DB database of .cosmo files developed by Klamt's group has been used with the turbomole software, which contains most of HFC and HCFC refrigerants. However, HFO and HCFO refrigerants are not included in this database. The Tmolx interface is used to generate the .cosmo and .energy files for the HFO and HFCO compounds. The options of the ab initio method are setup automatically by choosing a template for cosmo calculation. The .cosmo and .energy files were created by using the COSMO-BP-TZVP and gas-BP-TZVP templates, respectively. These templates correspond to the BP86/ TZVP DFT method. The grid size was "m3". The COSMO calculations were performed with the 6.2 Linux version of Turbomole.

2.2. COSMO-SAC

In the COSMO-SAC model of Lin and Sandler [15], the activity coefficient of component *i* is expressed in terms of the sigma profile $p_i(\sigma_m)$ as

$$\ln \gamma_{i/S} = \sum_{\sigma_m} \frac{A_i p_i(\sigma_m)}{a_{eff}} [\ln \Gamma_S(\sigma_m) - \ln \Gamma_i(\sigma_m)] + \ln \gamma_{i/S}^{SG}, \quad (3)$$

where the summation is over all possible discrete charge densities σ_m, and a_{eff}= 7.5Å^2. $\gamma_{i/S}^{SG}$ is the Staverman-Guggenheim combinatorial contribution to the activity coefficient. The surface segment activity coefficients of component *i*, $\Gamma_i(\sigma_m)$, and of solution *S*, $\Gamma_S(\sigma_m)$ are determined by solving

$$\ln \Gamma_l(\sigma_m) = -\ln\left(\sum_{\sigma_n} p_l(\sigma_n)\ \Gamma_l(\sigma_n) \exp\left(\frac{-\Delta W(\sigma_m,\sigma_n)}{kT}\right)\right), \quad (4)$$

where the index l stands for all pure compound l and for solution S.$\Delta W(\sigma_m, \sigma_n)$ describes the interaction between two surface segments of charges σ_m and $\sigma_n$and is the sum of electrostatic and hydrogen bonding contributions. The reader is directed to Lin and Sandler's paper [15] for further details. As shown in this paper, the original COSMO-SAC model cannot predict azeotropic behavior in refrigerant + alkane mixtures, so this model is not recommended for these systems.

2.3. COSMO-SAC dsp and m-COSMO-SAC dsp

The COSMO-SAC dsp version developed by Hsieh et al. [20] is based on the COSMO-SAC 2010 version [19] for which the concept of splitting the sigma profiles as a sum of different contributions was introduced. The universal parameters of COSMO-SAC dsp are the same as those of COSMO-SAC 2010. The difference between both models is the use of a dispersion contribution in COSMO-SAC dsp that corrects the deficiencies of the 2010 version. This contribution is added to the excess Gibbs free energy and is based on the simple one-parameter Margules activity coefficient model. In the COSMO-SAC dsp model the sigma profile is given by

$$p_i(\sigma) = p_i^{nhb}(\sigma) + p_i^{oh}(\sigma) + p_i^{ot}(\sigma)\,, \tag{5}$$

where $p_i^{oh}(\sigma)$ is the sigma profile that include the segments on oxygen and hydrogen atoms on hydroxyl (OH) groups; $p_i^{ot}(\sigma)$ is the sigma profile involving oxygen (not on OH group) , N, and F atoms. $p_i^{nhb}(\sigma)$ contains all the other types of atoms.

In the COSMO-SAC dsp model (as well as in COSMO-2010), the COSMO segment activity coefficient is given by

$$\ln \Gamma_{i/j}^{t}\,(\sigma_m^t) = -\ln\left(\sum_{s=nhb,oh,ot}\sum_{\sigma_n} p_j^s(\sigma_n^s)\;\; \Gamma_{i/j}(\sigma_n^s)\, exp\left(\frac{-\Delta W(\sigma_m^t,\sigma_n^s)}{kT}\right)\right), \tag{6}$$

where j denotes either the pure liquid component i or the mixture S. $\Delta W(\sigma_m^t, \sigma_n^s)$ is the energy of interaction between a segment of type t and charge σ_m, and a segment of type s and charge σ_n. Further details can be found in the original paper of the COSMO-SAC 2010 version [19]. The only difference between COSMO-SAC 2010 and COSMO-SAC dsp is the addition of the

dispersion contribution $G^{ex,disp}$ in the calculation of the excess Gibbs free energy. Hsieh et al. [20] proposed to use the one-parameter Margules model for binary mixtures,

$$G^{ex,disp} = RTA_{12}x_1x_2, \tag{7}$$

where the constant A_{12} is expressed as

$$A_{12} = w\left[\frac{1}{2}(\varepsilon_1 + \varepsilon_2) - \sqrt{\varepsilon_1\varepsilon_2}\right]. \tag{8}$$

The parameter *w* is a universal scaling factor and is equal to 0.27027. In Eq. (8) $\varepsilon_1, \varepsilon_2$ are the dispersion energy of components 1 and 2, calculated as a sum of atomic contributions as

$$\varepsilon_i = \frac{1}{N_{atom,i}}\sum_{j=1,natom_i}\varepsilon_{atom,j}N_{ji}, \tag{9}$$

where $N_{atom,i}$ is the number of atoms on molecule i, N_{ji} is the number of atoms of type j on molecule i, and $\varepsilon_{atom,j}$ the atomic contribution for atom of type j. In this work, we propose a generalization of Eq. (7) for multicomponent mixtures, given by

$$G^{ex,disp} = RT\sum_{j>i}A_{ij}x_ix_j. \tag{10}$$

where $A_{ij} = w\left[\frac{1}{2}(\varepsilon_i + \varepsilon_j) - \sqrt{\varepsilon_i\varepsilon_j}\right]$. In this study, the dispersion parameter for the *F* atom has been modified for better predictions of refrigerant + alkane VLE data. The corresponding model is then denoted as m-COSMO-SAC dsp. A fortran code of the m-COSMO-SAC-dsp, which only requires the cosmo files inputs, has been developed at ENSTA Paris and integrated into the ThermProp® [29] and Simulis thermodynamics® [30] softwares. The code can automatically recognize the molecular structure from the .cosmo file in which the positions of atoms are stored, by determining the types of bonds. For example, the code can automatically recognize carbon atoms of type sp3, sp2, sp, OH and carboxylic groups.

COSMO-SAC like models have been used with the freely available VT2005 database of .cosmo files developed by Mullins et al. [16]. For the HFO and HCFO refrigerants, the .cosmo files were created by using the Materials Studio / DMOL3 package and by following the procedure of Xiong et al. [32] and Paricaud [33]. In this procedure, the GGA-VWN-BP ab initio method is used with the DNP basis set. The whole procedure to generate .cosmo files has been explained in details by Paricaud [29]. The VLE predictions with

COSMO-SAC dsp and COSMO-RS are performed by assuming that the vapor phase is an ideal gas mixture. The VLE are then solved by considering the equality of the frugalities in both phases, namely

$$Py_i = x_i \; P_{vap,i}(T)\gamma_i(T, \boldsymbol{x}) \tag{11}$$

where $P_{vap,i}(T)$ is the vapor pressure of component i calculated with DIPPR correlations. Thus, this approach requires the knowledge of the vapor pressures of refrigerants over a wide temperature range, and it is not reliable at high pressures and close to critical points.

2.4. Combination with the PR equation of state + MHV1 mixing rule

The assumption that the vapor phase is an ideal gas mixture is valid for pressures below 1MPa. An equation of state must be used to compute the vapor-liquid equilibria of mixtures at high pressure and close to critical points. In this work, we consider a cubic equation of state based on the combination of the m-COSMO-SAC dsp, the Peng-Robinson (PR) equation of state (1978 version) [34 , 35] and the MHV1 mixing rule [36]. This model only requires the knowledge of the experimental critical temperature, pressure and acentric factors of pure refrigerants (T_c, P_c, w) as input parameters, and is available in the ThermProp software [29]. The PR Eos can be expressed in terms of the pressure P as

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{12}$$

where a and b and the covolume and cohesive energy of the mixture, T the temperature and v the molar volume. For the pure species i, the cohesive energy a_i and covolume b_i are calculated from the critical point properties (critical temperature $T_{c,i}$, critical pressure $P_{c,i}$), and the acentric factor ω_i. The PR78 α-function [35] is used to compute a. The MHV1 mixing rules [36] are given by

$$a = b\left[\sum_i x_i \frac{a_i}{b_i} - \frac{RT}{q_1}\sum_i x_i \ln\left(\frac{b_i}{b}\right) + \frac{G_\gamma^E}{q_1}\right], \quad b = \sum_i x_i b_i \tag{13}$$

where $G_\gamma^E = RT\sum_i x_i \ln\gamma_i$ is the excess Gibbs free energy of the activity coefficient model (here the m-COSMO-SAC-dsp is used), x_i the mole fraction of component i. The value of q_1 is -0.53 for the PR EoS.

3. Results and discussion

3.1. Prediction of saturated liquid densities

Following the work of Xiong et al. [32], we propose a simple correlation to predict the saturated liquid densities of pure refrigerants, which is valid over a limited temperature range around the boiling point. The correlation relates the molecular volume with the temperature, the experimental boiling point (boiling temperature at atmospheric pressure) and the COSMO cavity volume determined by COSMO ab initio calculation (DMOL3 package in the Material Studio software). The parameters of the correlation were determined on 36 refrigerants. The molar volume of the saturated liquid (in $cm^3.mol^{-1}$) is given by

$$v_{liq} = (0.43542158 \times T_r^2 - 0.3856798 \times T_r + 0.76951752) \times V_{cosmo} \qquad (10)$$

where V_{cosmo} is the COSMO cavity volume in $Å^3$ calculated with DMOL3, and $T_r = T/T_{eb}$, where T_{eb} the experimental boiling point of the pure component. The correlation is valid over the temperature range $0.6\ T_{eb} < T < 1.3\ T_{eb}$. As shown in Figure 1, a very good agreement between the DIPPR correlations [30] and Eq. (10). An average deviation of 3.04% is obtained between Eq. (10) and DIPPR reference data.

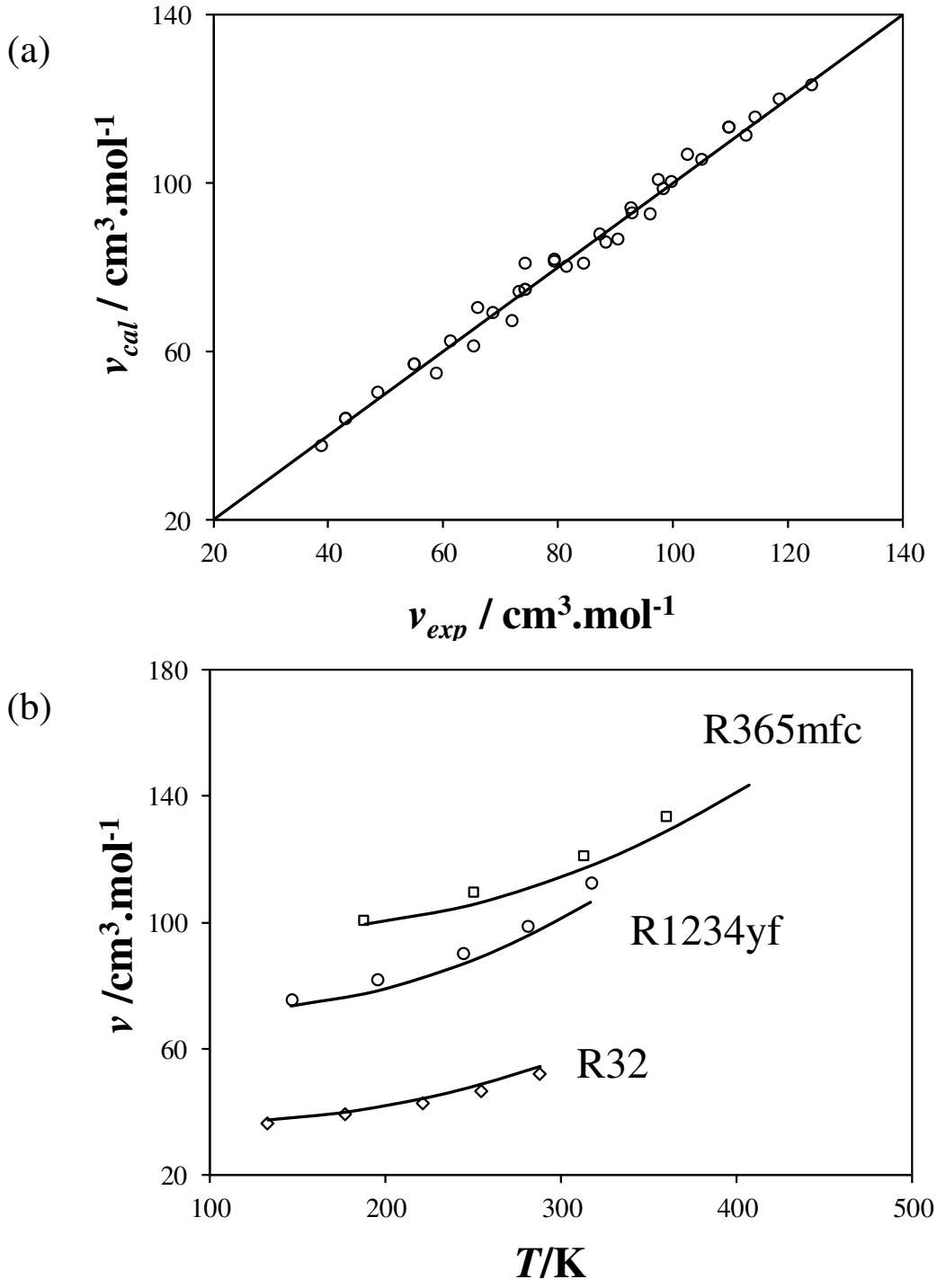

Figure 1. Predictions of the saturated liquid molar volumes of refrigerants. (a) Predictions at the boiling point at P=1atm. Comparison between Eq. (10) (v_{cal}) and DIPPR reference data [30] (v_{exp}). The line denotes the function $v_{cal}= v_{exp}$.. (b) Predictions of the saturated liquid molar volumes of different refrigerants at temperatures close to the boiling points. Comparison between Eq. (10) (lines) and DIPPR reference data [30] (symbols).

3.2. Prediction of boiling points with COSMO-RS

The COSMO-RS 2010 and the parameterization "BP_TZVP_C21_0110" + the def-TZVP database were used to predict the boiling points of some refrigerants (Eq. (2)). For the compounds like HFOs that were not included in the database, the .energy and .cosmo files (for HFO), have been determined by using Tmolx 3.4 + the def-TZVP template + the 6.2 linux version of Turbomole. The predictions of COSMO-RS have been compared with the experimental data found in the Simulis® database.

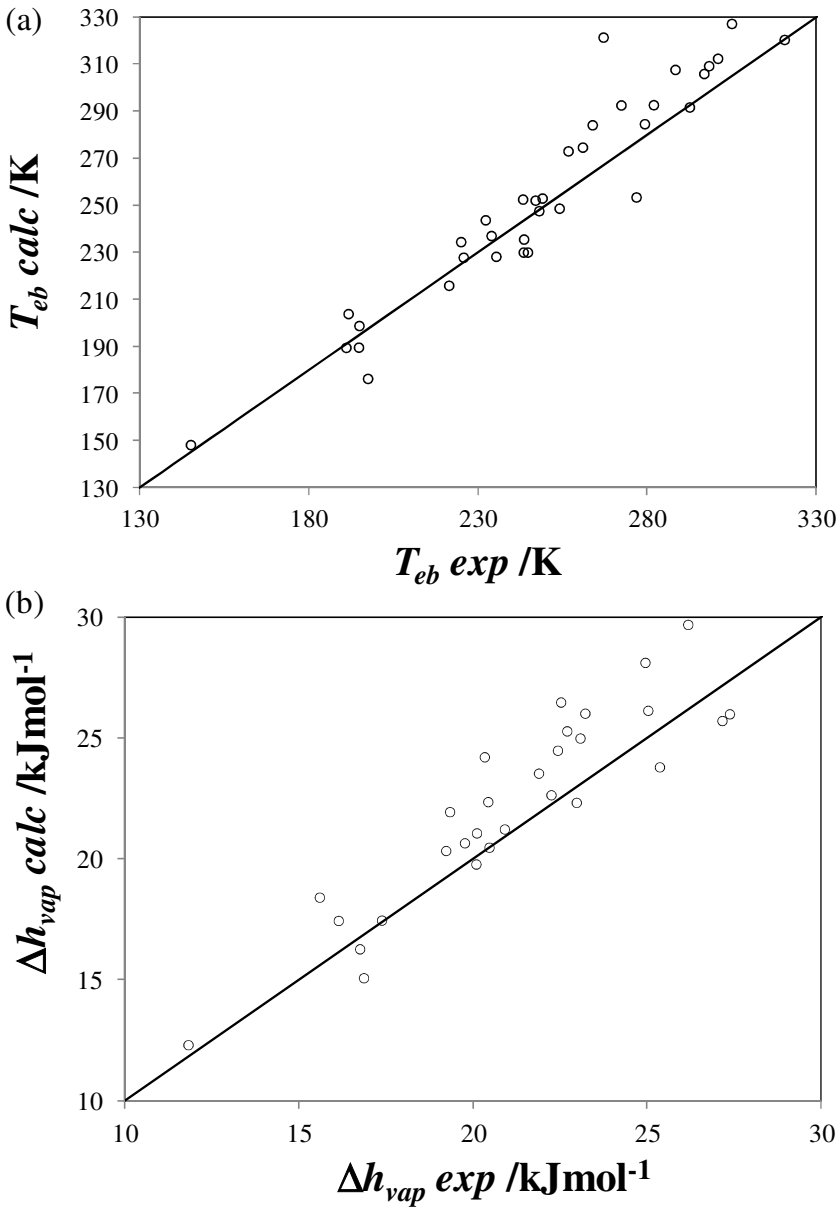

Figure 2. Prediction of the boiling points (a) and enthalpies of vaporization (b) of refrigerant fluids at atmospheric pressure, by using COMSO-RS. The lines correspond to the function y=x.

Table 1. Prediction of the boiling points and enthalpies of vaporization at atmospheric pressure by using COSMO-RS / BP_TZVP_C21_0110. Comparison between COSMO-RS predictions and Simulis® 2019 database (based on DIPPR). The bias and AAD are calculated as bias $= \frac{1}{npoint}\sum_{i=1}^{npoint}\left(X_{cal} - X_{exp}\right)$, AAD $= \frac{1}{npoint}\sum_{i=1}^{npoint}\left|X_{cal} - X_{exp}\right|$.

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Refrigerant	T_{eb} exp /K	T_{eb} calc /K	$\Delta Hvap(T_{eb})$ exp /kJ.mol^{-1}	$\Delta Hvap(Teb)$ calc /kJ.mol^{-1}
R32	221.50	215.67	20.09	19.78
R14	145.10	147.91	11.81	12.31
R11	296.97	305.74	25.00	30.46
R12	243.36	252.32	20.33	24.21
R13	191.74	203.63	15.59	18.41
R21	282.05	292.47	24.95	28.12
R22	232.32	243.51	20.43	22.36
R23	191.09	189.27	16.75	16.27
R41	194.82	189.36	17.37	17.46
R152a	249.13	252.78	21.89	23.54
R134a	247.08	251.89	22.24	22.64
R123	301.05	312.21	26.17	29.69
R124	261.05	274.42	22.70	25.29
R125	225.04	234.22	19.76	20.66
R141b	305.15	327.02	26.28	31.38
R142b	263.95	283.92	22.52	26.48
R113	320.75	320.21	27.12	31.72
R114	276.92	253.22	23.08	24.99
R115	234.04	236.83	19.33	21.95
R116	194.95	198.55	16.13	17.45
R227ea	256.79	272.83	22.43	24.48
R143a	225.81	227.60	19.22	20.34
R161	235.45	227.99	20.10	21.07
R236ea	279.40	284.39	25.36	23.80
R236fa	272.45	292.36	25.03	26.14
R245ca	298.40	309.06	27.37	25.99
R245fa	288.45	307.48	27.16	25.71
RC318	267.17	321.21	23.22	26.02
R1216	243.55	229.80	20.46	20.47
R1114	197.51	176.07	16.86	15.08
R365mfc	313.10	332.54	27.56	28.22
R1234yf	244.15	235.32	20.99	20.99
R1234ze(E)	254.18	248.45	23.00	22.45
R1243zf	248.15	247.39	22.97	22.33
R1113	244.80	229.80	20.91	21.23
Bias (K or kJ/mol)		4.98		1.47
AAD (K or kJ/mol)		11.15		1.95

Reasonable predictions of the boiling points and enthalpies of vaporization are obtained (Figure 2, Table 1), but deviations of more than 20K are observed for some compounds like RC318. This compound has a cycle, which may explain the large deviation. COSMO-RS tends to overestimate ΔH_{vap}, as the bias error is positive and close to the average absolute deviation.

3.3. Vapor pressure correlations

In order to apply the asymmetric approach (vapor phase assumed to be an ideal gas mixture), it is necessary to know the vapor pressures of pure compounds. In this work the vapor pressures were calculated by using Simulis (DIPPR) correlations. For the compounds that were not included in the Simulis database (in particular the HFO and HFCO), we fitted the parameters of the Simulis /DIPPR correlation on the experimental data available in the literature. We used the correlation labeled "101" in Simulis, which is given by

$$\ln P_{vap} = A + B/T + C \ln T + DT^E, \tag{11}$$

where T is in Kelvin and P_{vap} in Pa. The parameters are reported in Table 2.

Table 2. Parameters for vapor pressure correlations (Eq. 13), critical properties and acentric factors for HFO and HCFO refrigerants. The average (AAD%) and maximum (MaxD%) deviations are reported for the vapor pressure correlations. $\text{AAD\%} = \frac{100}{npoint}\sum_{i=1}^{npoint}\left|\frac{P_{cal}-P_{exp}}{P_{exp}}\right|$, $\text{MaxD\%} = 100\ \max_{npoint}\left|\frac{P_{cal}-P_{exp}}{P_{exp}}\right|$

Parameters	R1234yf	R1234ze(E)	R1233zd(E)	R1233xf	R1336mzz(Z)	R1336mzz(E)
T_c /K	367.85	382.51	439.6	439.98	444.5	403.37
P_c /MPa	3.3822	3.6349	3.627	3.322	2.903	2.7664
ω	0.276	0.313	0.3025	0.187	0.386	0.4053
A	66.82731	86.89877	81.9699	20.0552	94.28075	116.68995
B	-4018.959	-4902.503	-5402.550	-2963.551	-6247.890	-6477.158
C	-7.18848	-10.3159	-9.30478	0.365746	-11.50222	-14.83973
D	1.1754E-5	1.6186E-05	1.0560E-05	-2.50740E-06	1.25254E-05	1.98919E-05
E	2	2	2	2	2	2
AAD%	0.15	0.077	0.21	0.76	0.06	0.05
MaxD%	0.90	0.17	0.97	4.52	0.93	1.15
T_{min}/K	130.0	170.0	200	263.25	190.	278.18
T_{max}/K	367.85	382.51	436.9	439.98	444.5	403.37
Ref. data	[37]	[37]	[37]	[38]	[37]	[39, 40]

The Cosmotherm software that includes the COSMO-RS model also contains correlations for vapor pressures. In this work, the same vapor pressures have been used for both COSMO-RS and COSMO-SAC in most cases, for a fair comparison between both approaches.

3.4. Predictions of VLE of refrigerant mixtures

Most calculations for binary mixtures reported here were made by assuming that the vapor phase is an ideal gas mixture and by solving the equations $Py_i = x_i\ P_{vap,i}\ \gamma_i$ for components 1 and 2, as the pressure is lower than 20 bars for most systems. We have tried to predict the VLE of different refrigerant fluids by using the COSMO-RS 2010 version, and the main versions of COSMO-SAC: the original version of Lin and Sandler[15] (COSMO-SAC 2002), the modified version of Mullins et al. [16] that corresponds to a reparameterization of Lin and Sandler's version (COSMO-SAC 2006) , the COSMO-SAC 2010 version [19] that introduces the concept of non hydrogen bond (nhb) and hydrogen bond (hb) sigma profiles, and the

version of Hsieh et al. [20] called COSMO-SAC dsp, which introduces a dispersion term to correct the deficiencies of COSMO-SAC 2010. One can observed that COSMO-SAC 2002, COSMO-SAC 2006 and COSMO-SAC 2010 are unable to predict azeotopes in binary mixtures of alkanes and freon refrigerants. This is the case, for example, for the R134 + n-butane mixture (Figure 3). Besides, the predictions of COSMO-SAC 2002, COSMO-SAC 2006 and COSMO-SAC 2010 are very similar for these systems and rather poor in general. We tried to modify the

universal parameters of COSMO-SAC, such as the charge-charge and the hydrogen bonding energies. The hydrogen bonding energy do not have any significant influence on the predicted VLE curve and it was impossible to predict an azeotropic point in alkane + refrigerant mixtures.

The charge-charge energy parameter (α') can influence the phase behavior in these systems, but not in a systematic manner: if α' is increased by about 50%, the COSMO-SAC predictions of some the alkane + refrigerant mixture, like the isopentane +R365mfc mixture, are improved, but the predictions of some other mixture like R600a + R1234yf are worse. Moreover, changing this universal parameter will deteriorate the predictions of all the other systems, so we do not recommend it.

The original COSMO-SAC dsp is able to predict an azeotropic behavior in these systems, but the quantitative agreement with experimental VLE data is still not satisfactory. To better predict the VLE in refrigerant mixtures, we propose a simple modification of COSMO-SAC dsp by changing the dispersion energy $\varepsilon/$k for fluorine (F) atom, from 52.93K to 40K (Table 3). This change does not affect the predictions of mixtures with nonfluorinated compounds. The values of all the other universal parameters of COSMO-SAC dsp are kept. The corresponding model is denoted as m-COSMO-SAC dsp (modified version of COSMO-SAC dsp).

Table 3. Dispersion energy parameters of the F atom, for different versions of the COSMO-SAC dsp model

Model	ε_F/k (K)
COSMO-SAC dsp + ideal gas (vapor phase)	52.93
m-COSMO-SAC dsp+ ideal gas (vapor phase)	40
m-COSMO-SAC dsp + PR/MHV1	38

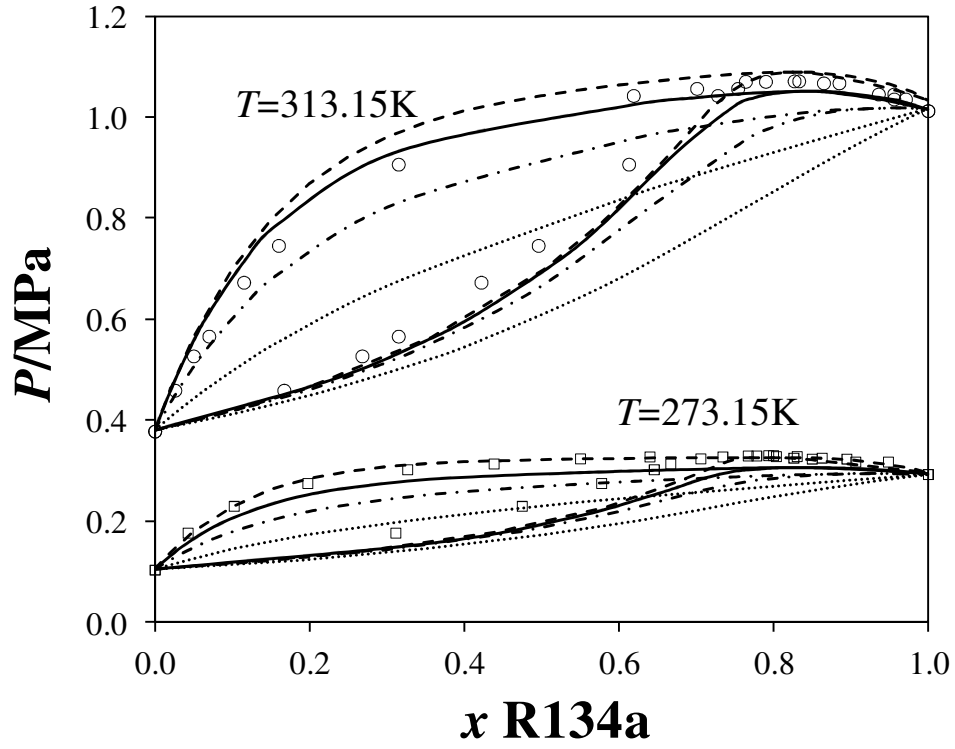

Figure 3. Vapor-liquid equilibria of the R134a + R600 (n-butane) mixture at 273.15 and 313.15K. The circles and squares denote the experimental data of Im et al. [41] and Lim et al. [42], respectively. The lines are predictions of different COSMO models, by assuming that the vapor phase is an ideal gas mixture: solid lines: m-COSMO-SAC dsp, dashed lines: COSMO-RS 2010, dash-dot lines: original COSMO-SAC dsp, dotted lines: COSMO-SAC 2010.

As shown in Figures 3, the COSMO-RS model gives good predictions of the VLE of R134a + R600 (n-butane) mixture. The COSMO-SAC 2010 predictions are rather poor as this model is unable to predict the azeotropic behavior. Similar results are obtained with COSMO-SAC 2002 and COSMO-SAC 2006. The COSMO-SAC dsp model is better than COSMO-SAC 2010, but the predictions are still not accurate enough. However, by changing the dispersion energy of the fluorine atom (m-COSMO-SAC dsp), it is possible to predict reasonably well the VLE for this binary mixture, in particular the presence of an azeotrope. This shows that the dispersion term is crucial for refrigerant systems.

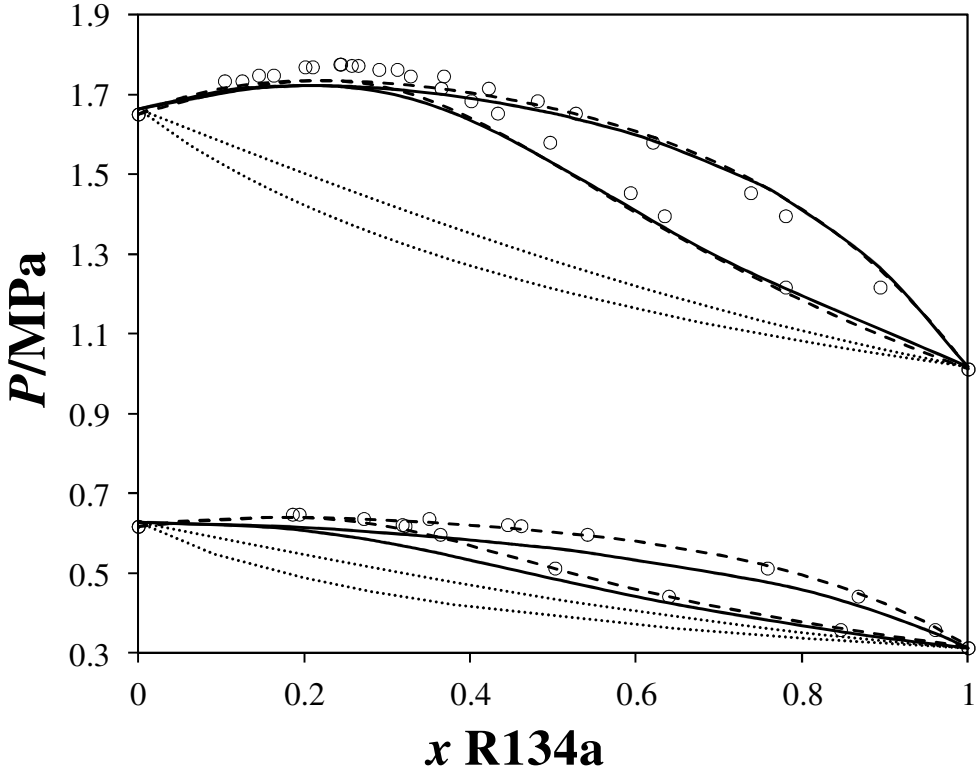

Figure 4. Vapor-liquid equilibria of the R134a + R1270 (propylene) mixture at T=275K and 313.15K. The circles denote the experimental data of Kleiber [43]. The lines are predictions of different COSMO models: solid lines: m-COSMO-SAC dsp, dashed lines: COSMO-RS 2010, dotted lines: COSMO-SAC 2010.

The m-COSMO-SAC dsp model is much better than COSMO-SAC 2010 for the R134a + propylene mixture (Figure 4). This result confirms the major role of the dispersion term in refrigerant mixtures in COSMO approaches. At higher temperatures (313K), m-COSMO-SAC dsp is close to COSMO-RS. At lower temperature (275K), the COSMO-RS model accurately predicts the phase diagrams and the location of the azeotrope, while the m-COSMO-SAC dsp model cannot predict an azeotrope. This failure can be due to the fact that the w constant in the Margules dispersion term does not depend on temperature. An improvement of the m-COSMO-SAC dsp model would be to use a temperature dependent dispersion term, or an excess Gibbs energy function more complex than the Margules model.

An interesting system to study is the R134a + DME (dimethyl ether) binary mixture as it exhibits a minimum pressure azeotrope [44] with a relative volatility close to 1. The m-COSMO-SAC dsp is in good agreement with the experimental VLE data but the results become less accurate at higher temperature (Figure 5(a)). However, the predictions are much better than COSMO-RS predictions especially for the relative volatility α_{12} (Figure 5(b)): the

m-COSMO-SAC dsp model can capture the maximum of α_{12} but not COSMO-RS. The larger deviation observed with COSMO-RS for this mixture may be explained by an overestimation of the cross association between DME and R134a.

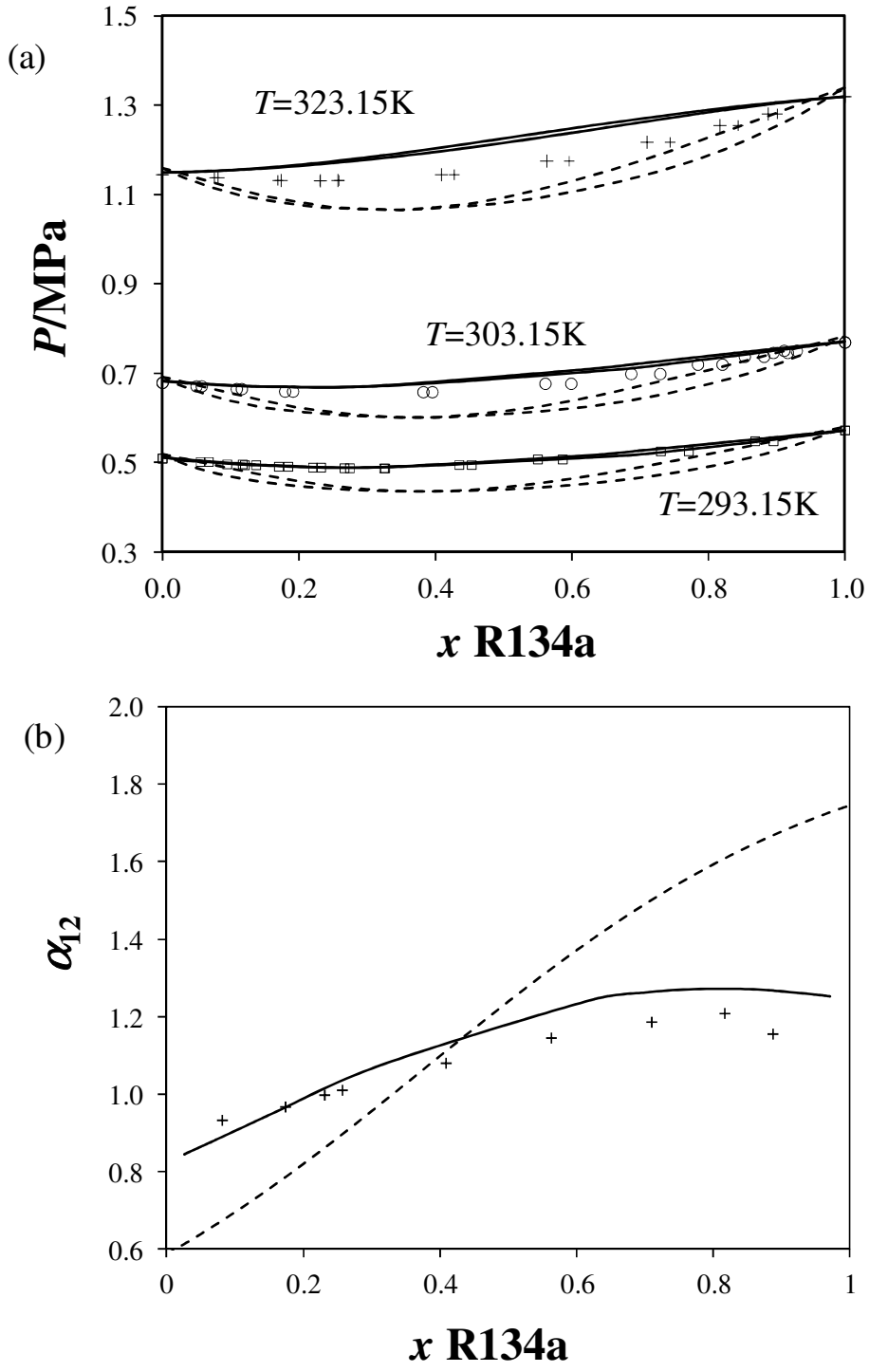

Figure 5. Vapor-liquid equilibria of the R134a + DME mixture at 293.15, 303.15 and 323.15K. (a) Pressure composition diagram. (b) Relative volatility $\alpha_{12}=y_1/x_1 \,.\, x_2/y_2$ at T = 323.15K. The

symbols denote the experimental data of Valtz et al. [44]. The solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010.

Concerning the isopentane + R245fa and isopentane + R365mfc binary systems, the COSMO-RS and m-COSMO-SAC dsp models give rather similar predictions (Figures 6 to 8), but the m-COSMO-SAC dsp model is slightly closer to the experimental data [45]. In the case of the isopentane + R365mfc mixture, we have tried two different cosmo files for R365mfc, to observe the effect of molecular conformation. The molecule R365mfc exhibits two conformations (trans and cis). The trans conformation is more stable in the gas phase (lower ab initio energy) and has a much lower dipole that that of the cis conformation. Both models predict an increase of the azeotropic pressure when the cis conformation of R365mfc is used. However, the difference between the VLE curves obtained with the trans and cis conformations is not very large (Figures 7 and 8). This result shows that conformation effects are low for this type of mixtures (alkane + refrigerant) and that the dispersion term has much more influence than polar terms in COSMO models.

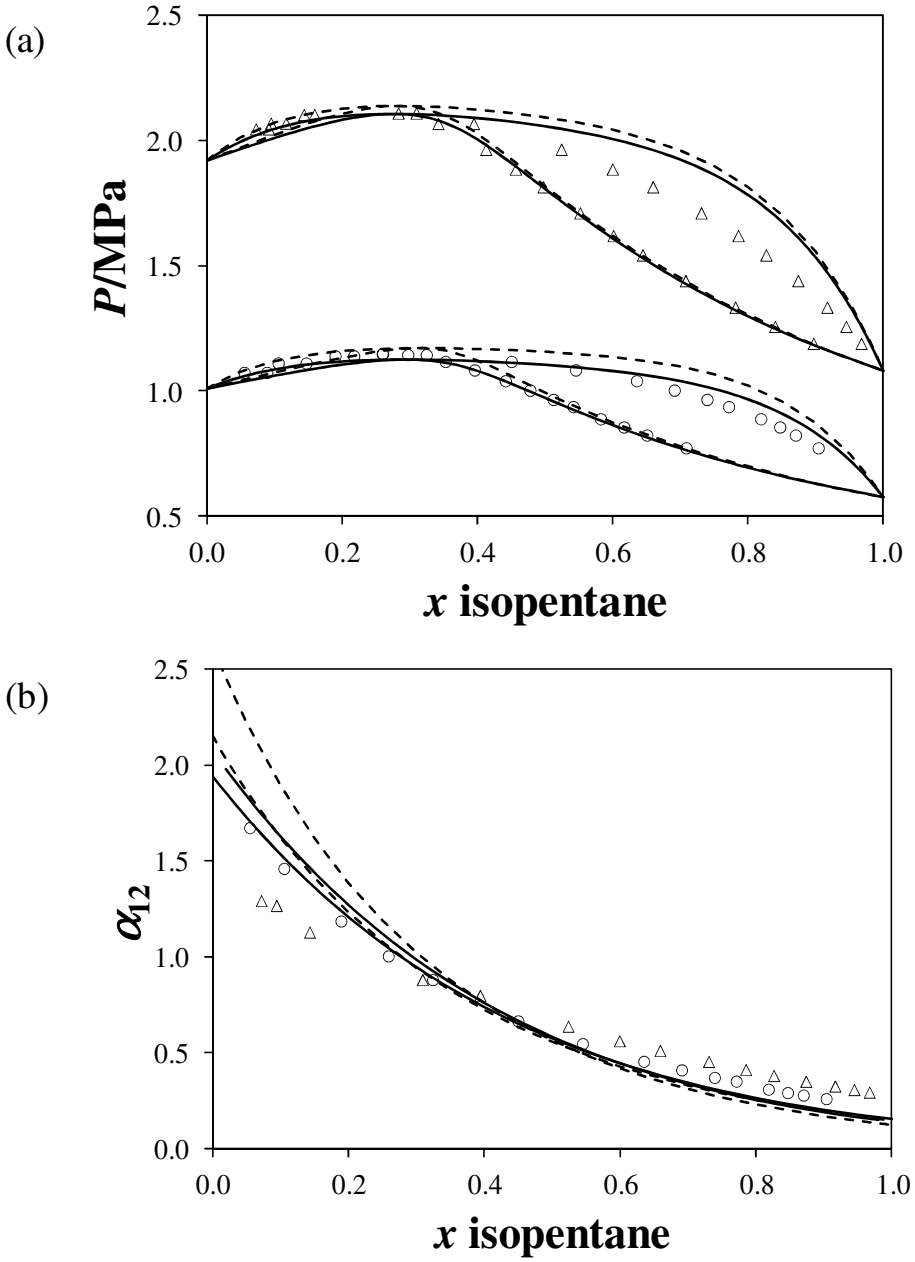

Figure 6. Vapor-liquid equilibria of the isopentane + R245fa mixture. (a) Pressure composition diagram. (b) Relative volatility $\alpha_{12}=y_1/x_1.x_2/y_2$. The symbols denote the experimental data [45]: circles: T=363.94K, triangles: T=392.87K. The solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010.

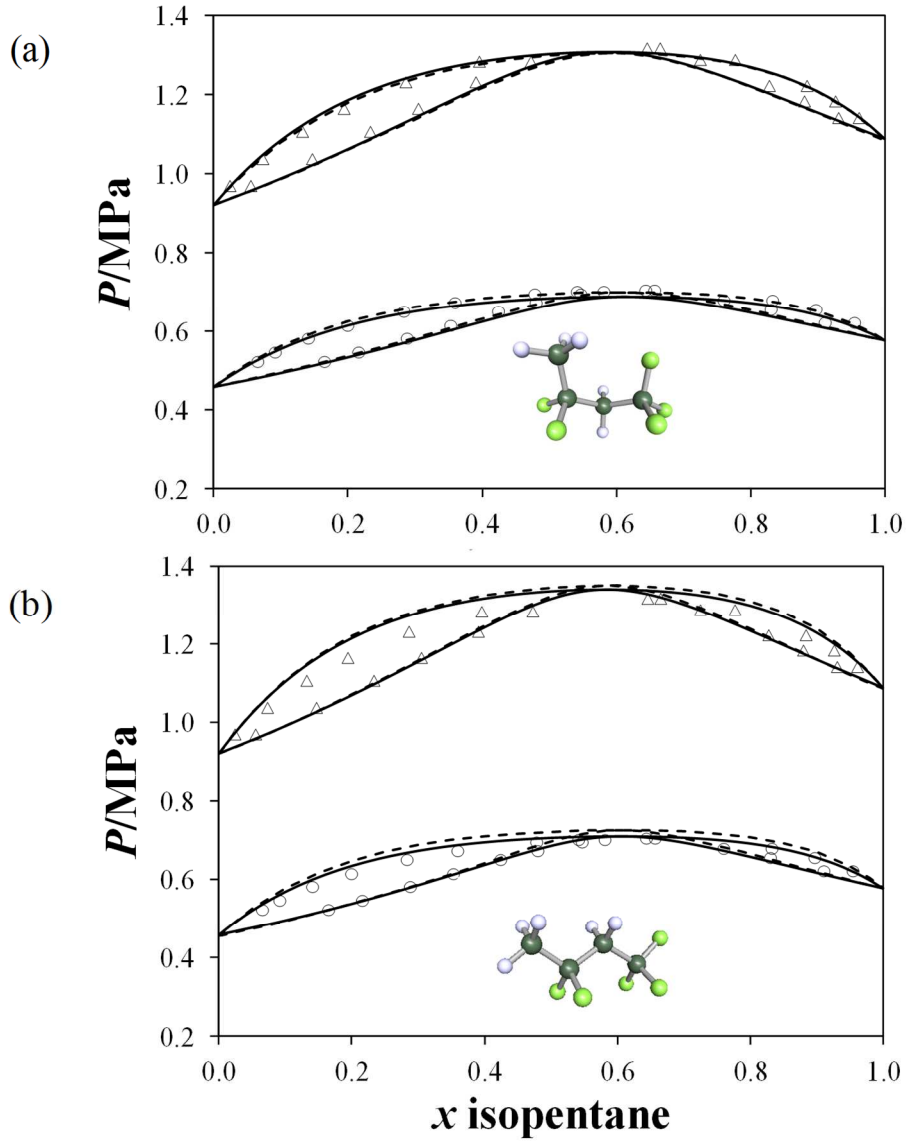

Figure 7. Vapor-liquid equilibria of the isopentane + R365mfc mixture. The symbols denote the experimental data [45]: circles: T=363.94K, triangles: T=392.87K. The solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010. Figure (a) corresponds to the predictions with the trans conformation of R365mfc, and Figure (b) corresponds to the predictions with the cis conformation of R365mfc

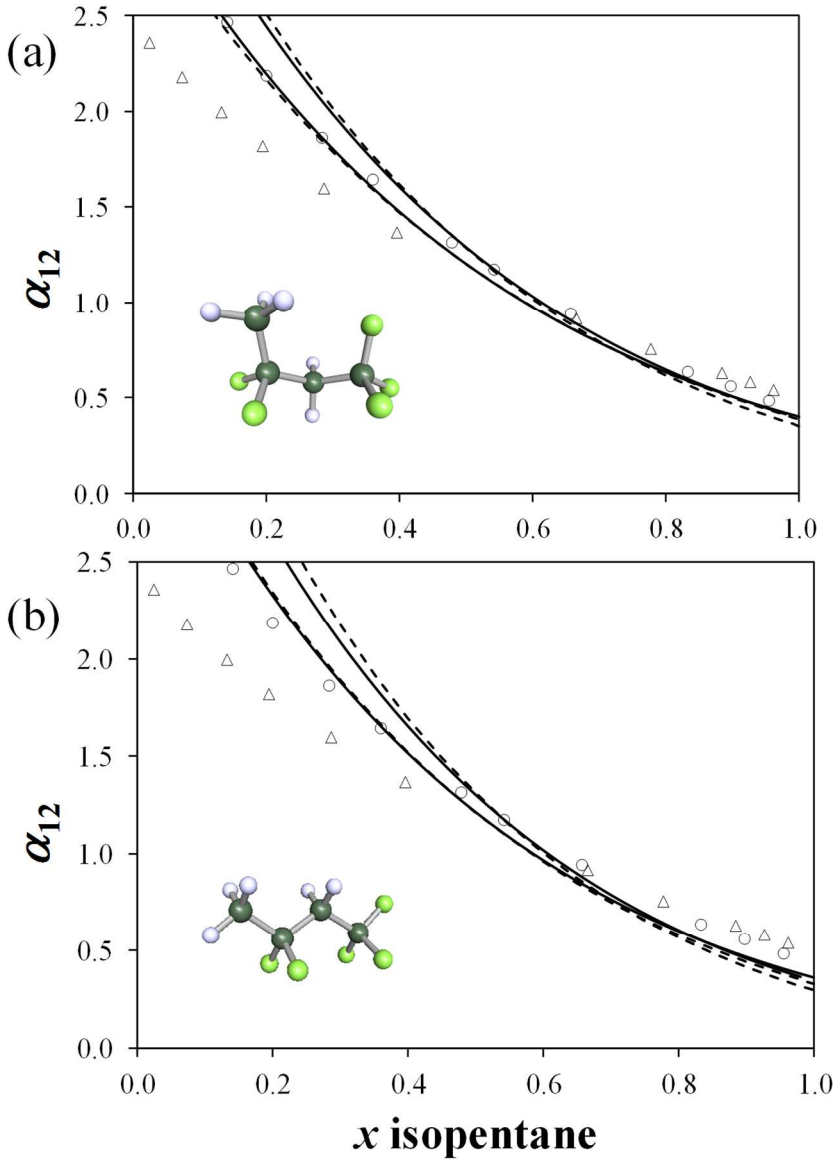

Figure 8. Relative volatility ($\alpha_{12}=y_1/x_1.x_2/y_2$) along the vapor-liquid equilibria of the isopentane (1) + R365mfc (2) mixture. The symbols denote the experimental data [45]: circles: T=363.94K, triangles: T=392.87K. The solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010. Figure (a) corresponds to the predictions with the trans conformation of R365mfc, and Figure (b) corresponds to the predictions with the cis conformation of R365mfc.

We now focus on mixtures involving the molecules of interest: HFO and HFCO refrigerants. In general, the predictions of COSMO-RS and m-COSMO-SAC dsp are quite similar. The predictions of m-COSMO-SAC dsp are usually closer to the experimental data (Figures 9 to 11), apart from the mixture R290 + R1234ze(E) (figure 12). For this mixture, m-COSMO-SAC dsp underestimates the non-ideality behavior and does not predict an azeotrope at low temperatures. One could improve the predictions by using a temperature dependent *w* constant in the Margules term, but that would involve a full re-parameterization of the m-COSMO-SAC dsp model on a large variety of systems including alkanes, alcohols, water, acids, etc.., which is beyond the scope of the current study.

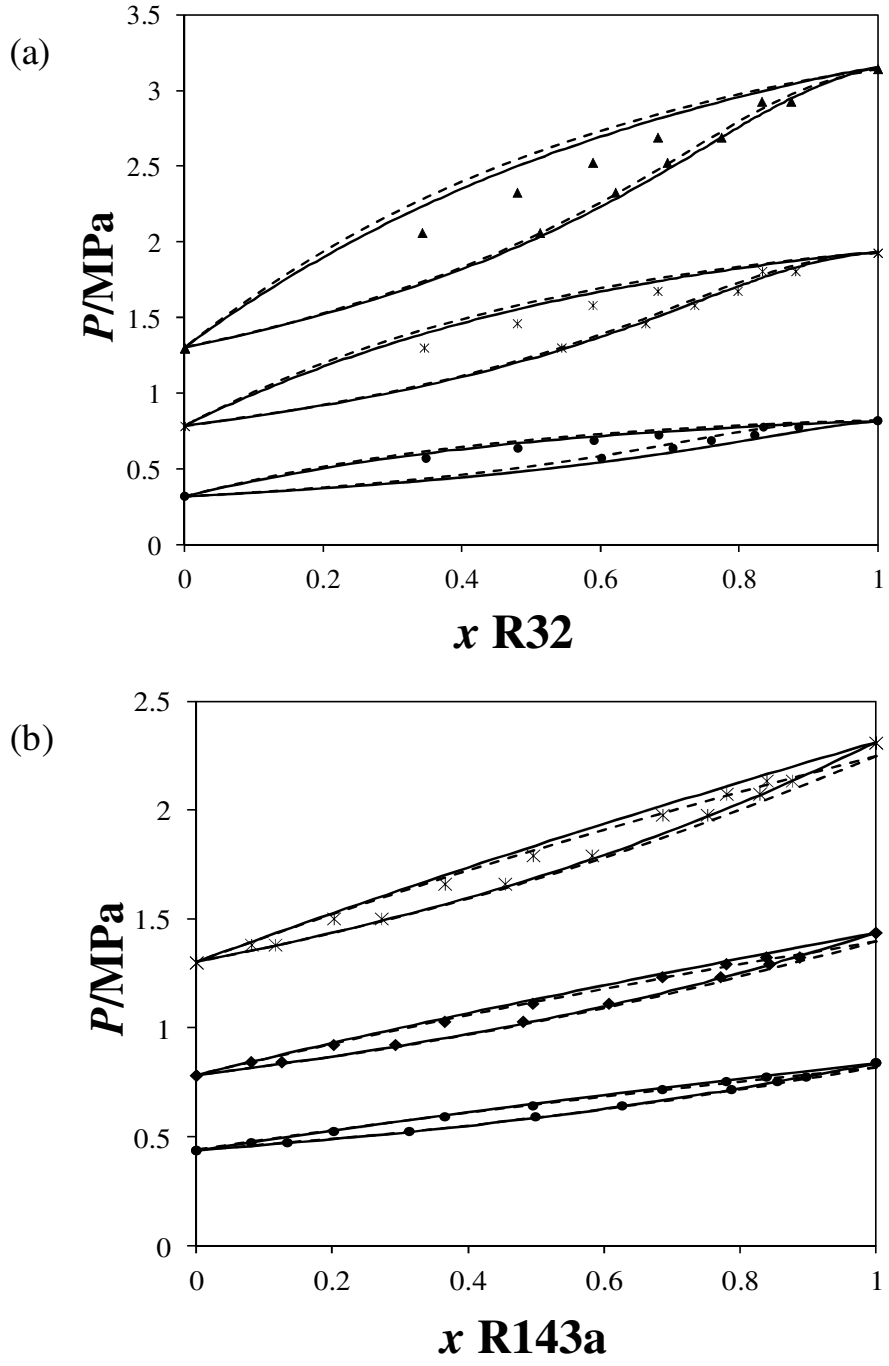

Figure 9. (a) Vapor-liquid equilibria of the R32 + R1234yf mixture. The symbols denote the experimental data [46] (circles: T=273.15K, asterisks: 303.15K, triangles: 323.15K). (b) Vapor-liquid equilibria of the R143a + R1234yf mixture. The symbols denote the experimental data [47] (circles: T=283.15K, asterisks: 303.15K, triangles: 323.15K. In both figures, the solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010.

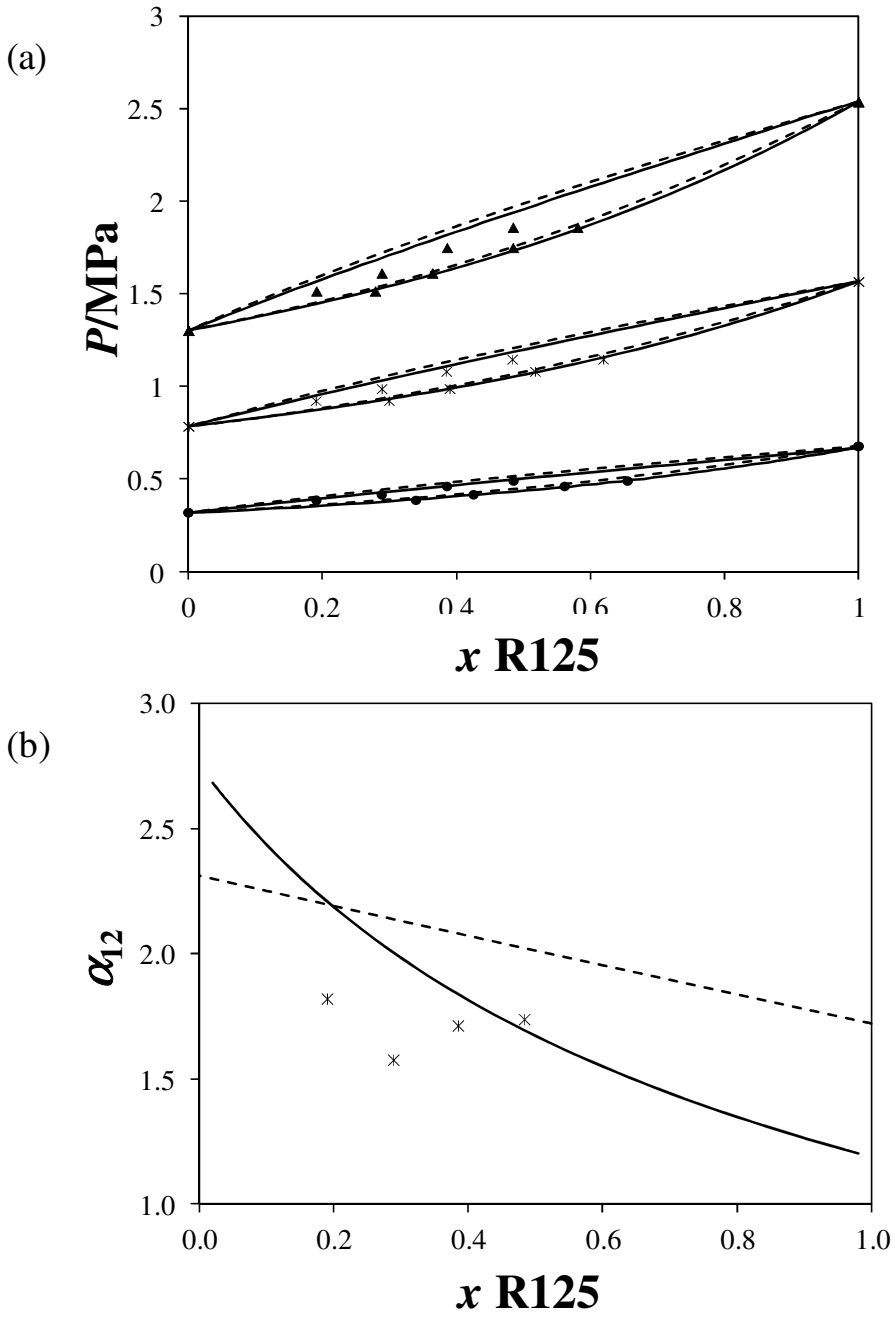

Figure 10. Vapor-liquid equilibria of the R125 + R1234yf mixture. (a) Pressure composition diagram. (b) Relative volatility ($\alpha_{12}=y_1/x_1.x_2/y_2$) at 303.15K The symbols denote the experimental data [46] (circles: T=273.15K, asterisks: 303.15K, triangles: 323.15K). The solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010.

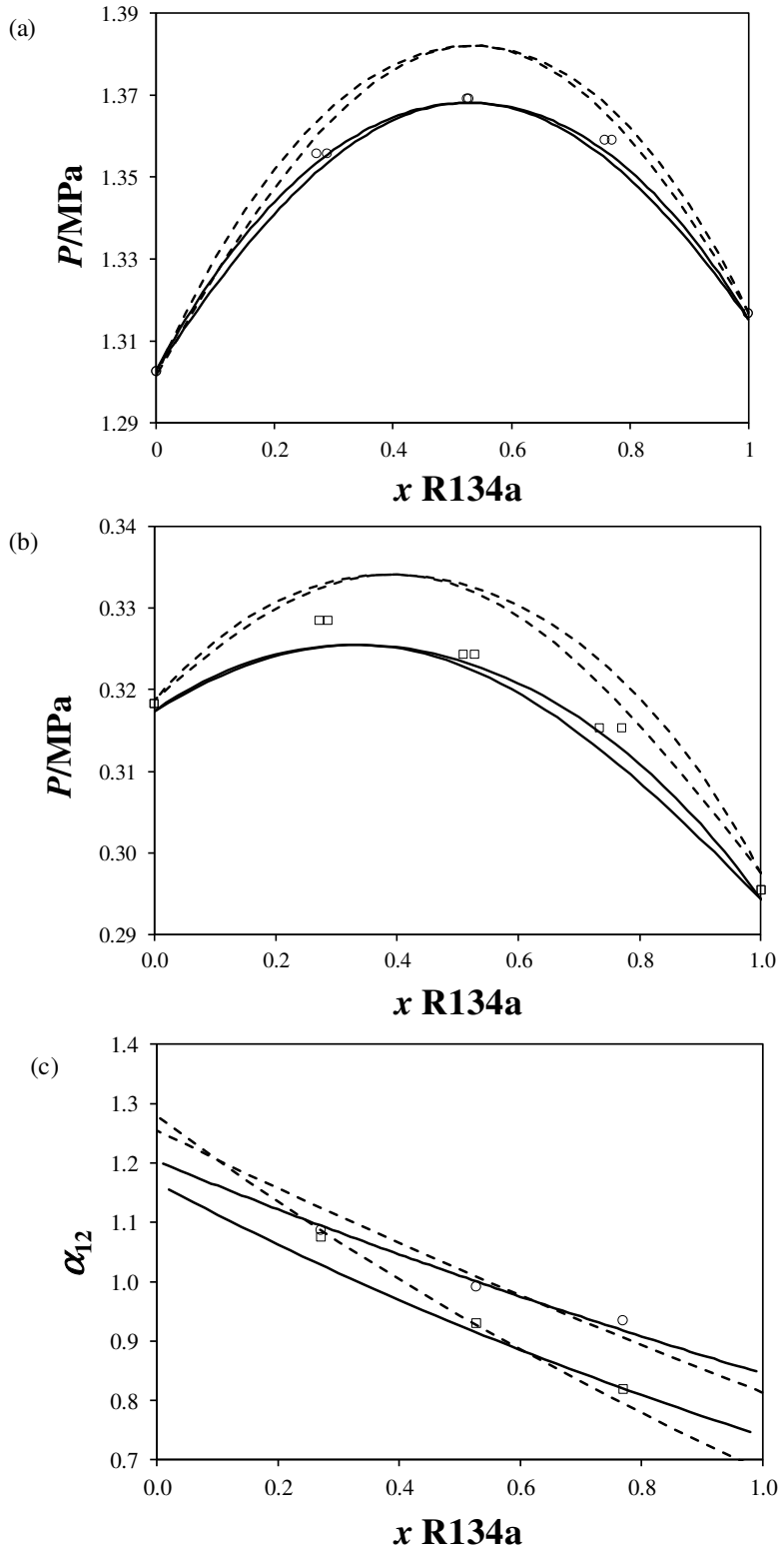

Figure 11. Vapor-liquid equilibria of the R134a + R1234yf mixture at (a) 323.15K and (b) 273.3K. (c). Relative volatility ($\alpha_{12}=y_1/x_1.x_2/y_2$) along the vapor-liquid equilibria of the R134a + R1234yf mixture. The circles and squares denote the experimental data at 323.15K and 273.3K [46], respectively. The solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010.

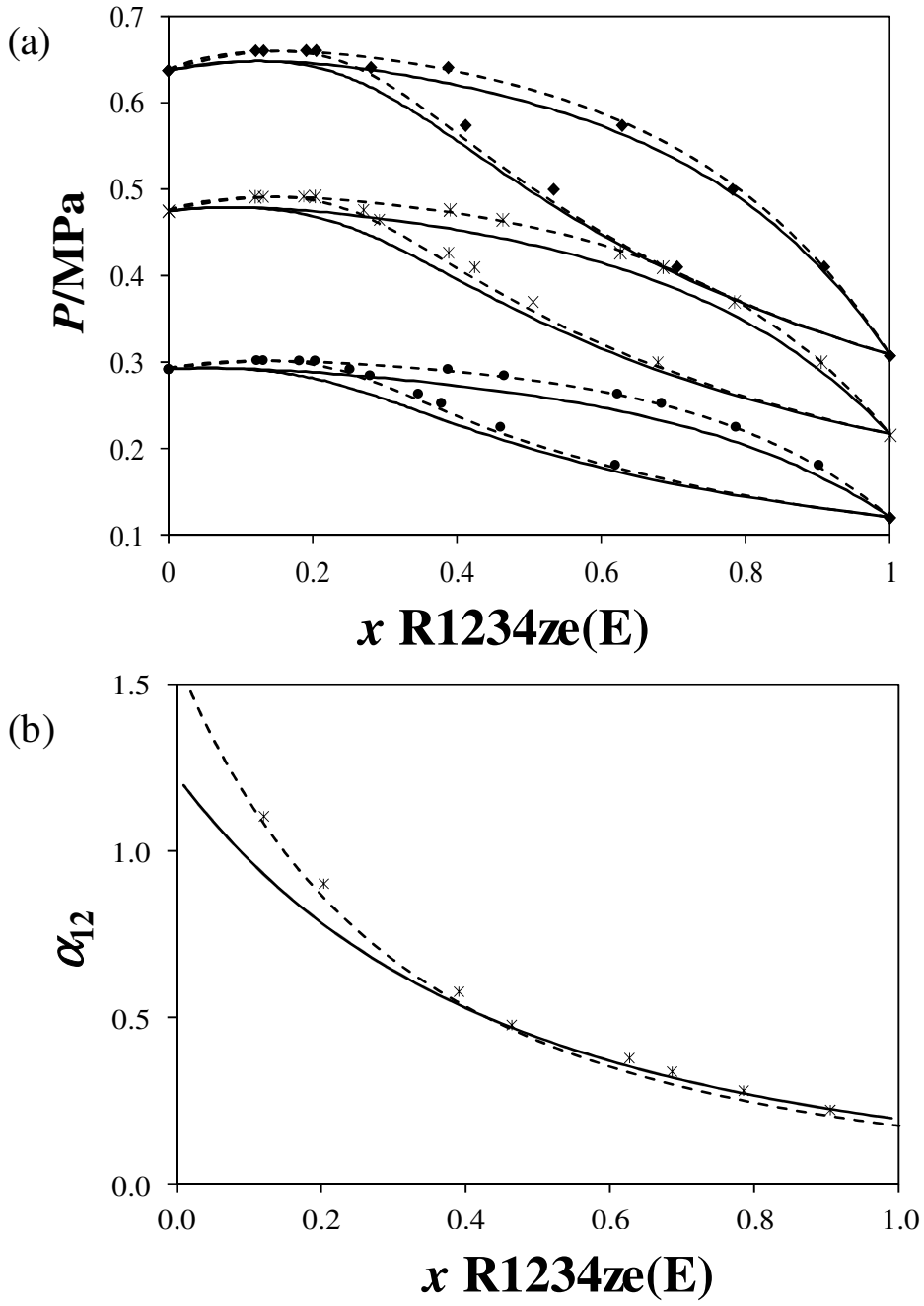

Figure 12. Vapor-liquid equilibria of the R1234ze(E) + R290 (propane) mixture. (a) Pressure composition. (b) Relative volatility ($\alpha_{12}=y_1/x_1.x_2/y_2$) at 273.15K The symbols denote the experimental data [48]. (circles: T=258.15K, asterisks T= 273.15K, diamonds: T=283.15K). The solid lines are the predictions of m-COSMO-SAC dsp and the dashed lines correspond to COSMO-RS 2010.

3.5. Predictions of VLE with the PR-MHV1 / m-COSM-SAC dsp model

The m-COSMO-SAC dsp model has been combined with the Peng-Robinson equation of state (1978 version) and the MVH1 mixing rule, in order to predict the phase behavior of refrigerant mixtures at high pressure. The critical properties and acentric factors of pure HFO and HCFO refrigerants are reported in Table 2. A slightly different value for the dispersion parameter of the F atom is found: ε_F/k = 38K (Table 3). The predictions obtained with the PR-MHV1 approach are significantly more accurate for all studied systems: the predictions of vapor phase mole fractions and relative volatilities are dramatically improved (Table 4). This is for example the case for the R600a + R1234yf and the R290 + R1336mzz(E) mixtures: excellent predictions can be obtained for both the coexistence curves and the relative relativities (Figures 13 and 14). As expected, the assymetric approach (m-COSMO-SAC dsp + vapor phase modeled as an ideal gas mixture) is unable to predict critical points (Figure 15). The PR-MHV1 / m-COSM-SAC dsp model can accurately critical points in binary systems, as shown in Figure 15 for the R23 + R1234yf mixture. The main advantage of the PR-MHV1 / m-COSM-SAC dsp model compared to other predictive equations of state based on group contribution is the possibility to provide excellent predictions of the phase behavior of refrigerant mixtures without any adjustment of binary parameters on experimental data. Note that a similar combination of COSMO-RS with the PR-MHV1 approach is theoretically possible, and similar improvements would be obtained. However, we did not perform such calculation in this paper as this combination was not possible in the 2010 version of COSMOTherm.

The PR-MHV1/m-COSMO-SAC dsp model can be used to multicomponent systems. As shown in Table 5, the VLE data of the ternary mixture (R134a +R1234yf+ R600a) are very well predicted by the model. The average deviations obtained with this model are slightly higher than those obtained with REFPROP 10 [37]. Note that REFPROP is based on a multiparameter equation of state for which the binary interaction parameters were directly fitted to experimental data. The predictions of PR-MHV1/m-COSMO-SAC dsp are better than those of the heterogenous approach (m-COSMO-SAC dsp + ideal vapor phase) and those of the E-PPR78 group contribution method [4] (Table 5).

Table 5. Predictions of VLE of the ternary mixture R134a (1) +R1234yf (2)+ R600a (3) by using three different thermodynamic models: PR-MHV1/m-COSMO-SAC dsp , m-COSMO-SAC dsp + ideal gas (vapor phase), E-PPR78 and REFPROP 10 EoS. The deviations were averaged for each temperature and each model (bold values), and the reference experimental data were taken from Hu et al. [49]. The deviations are calculated as $\mathrm{AAD\%} = \frac{100}{npoint}\sum_{i=1}^{npoint}\left|\frac{X_{cal}-X_{exp}}{X_{exp}}\right|$).

T/K	AAD/%P	AAD% y_1	AAD% y_2
PR-MHV1/m-COSMO-SAC dsp	**1.9**	**2.0**	**7.6**
283.15	3.7	1.6	7.7
293.15	2.5	2.6	6.8
303.15	1.7	2.2	7.4
313.15	0.9	2.1	7.6
323.15	0.8	1.6	8.3
m-COSMO-SAC dsp + ideal gas	**2.3**	**6.0**	**7.0**
283.15	4.2	3.8	7.3
293.15	3.0	5.6	6.3
303.15	2.2	5.9	6.9
313.15	1.4	7.0	7.1
323.15	0.7	7.8	7.6
E-PPR78	**6.6**	**6.7**	**11.8**
283.15	8.4	10.4	15.7
293.15	7.5	9.3	13.3
303.15	6.8	6.7	11.5
313.15	5.8	4.7	9.8
323.15	4.6	2.2	8.8
REFPROP 10 EoS	**1.0**	**1.6**	**6.0**
283.15	1.2	1.7	6.0
293.15	1.0	2.1	5.1
303.15	1.0	1.6	5.8
313.15	0.9	1.4	6.1
323.15	0.8	1.1	6.8

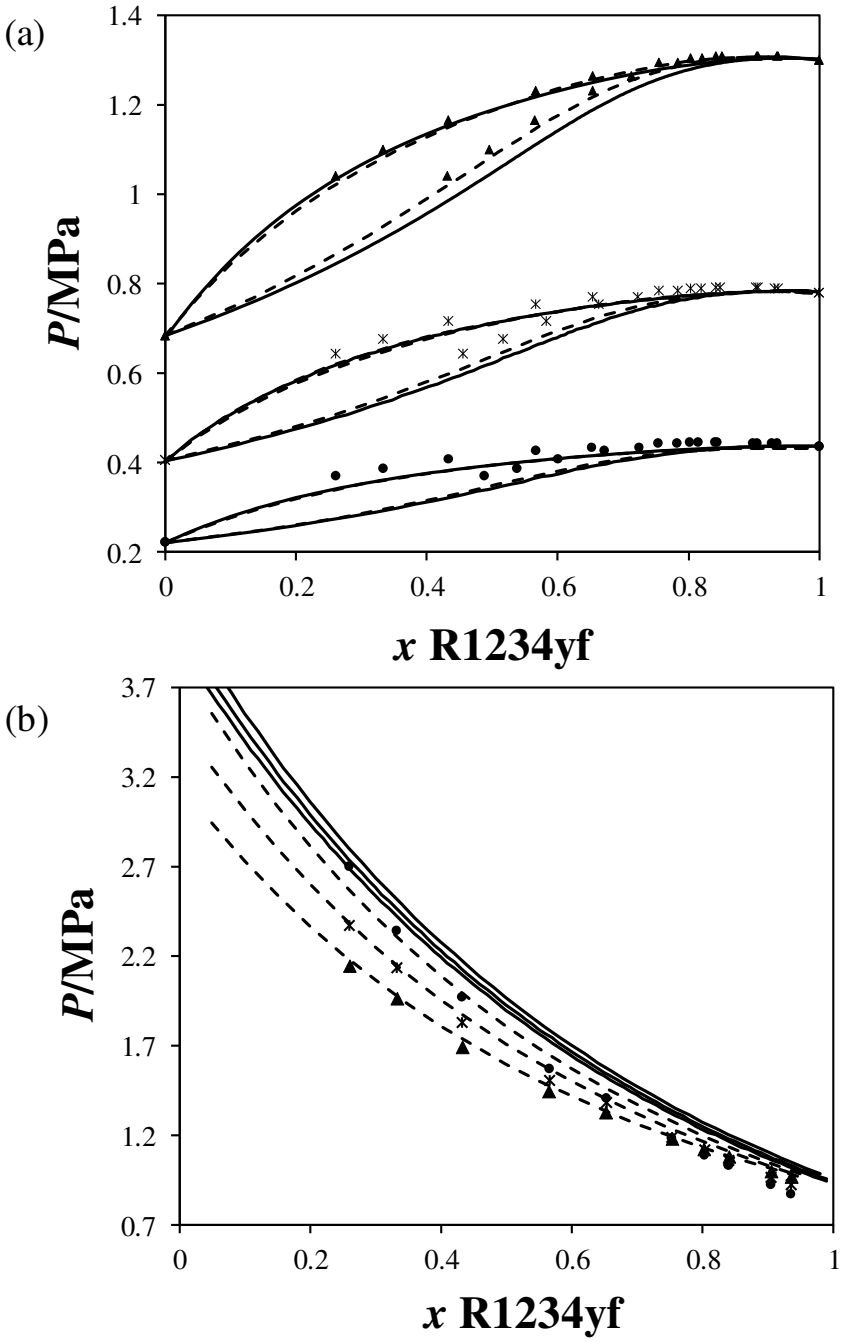

Figure. 13 Vapor-liquid equilibria of the R600a + R1234yf mixture (a) Pressure composition diagram. (b) Relative volatilities. The symbols denote the experimental data [50] (circles: T=283.15K, asterisks: T=303.15K, triangles: T=323.15K. The solid lines are the predictions of m-COSMO-SAC-dsp and the dashed lines correspond to the PR-MHV1 / m-COSMO-SAC dsp model.

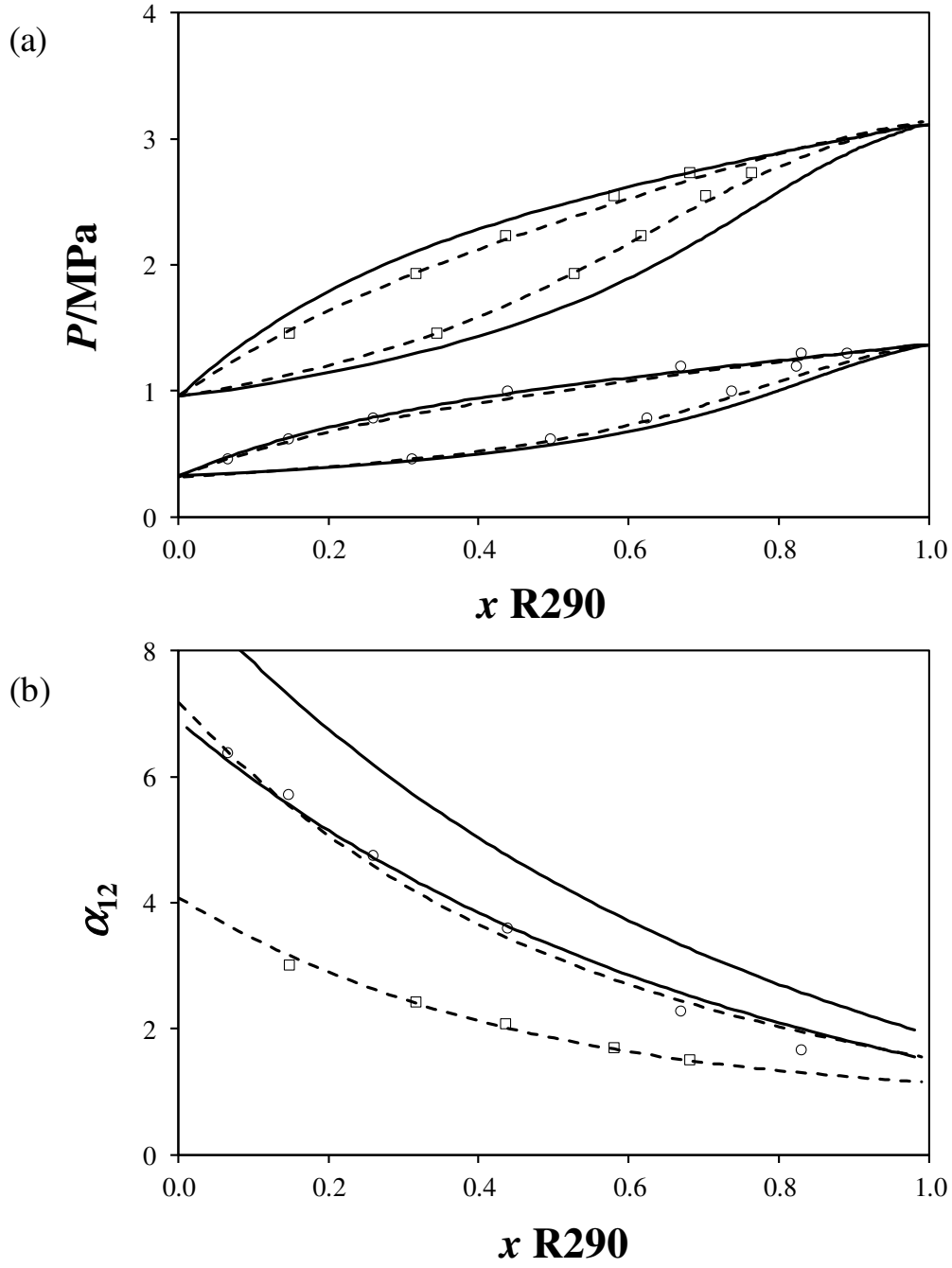

Figure. 14 Vapor-liquid equilibria of the R290 + R1336mzz(E) mixture (a) Pressure composition diagram. (b) Relative volatilities. The symbols denote the experimental data [39] (circles: T=313.19K, squares: T= 353.08K. The solid lines are the predictions of m-COSMO-SAC-dsp and the dashed lines correspond to the PR-MHV1 / m-COSMO-SAC dsp model.

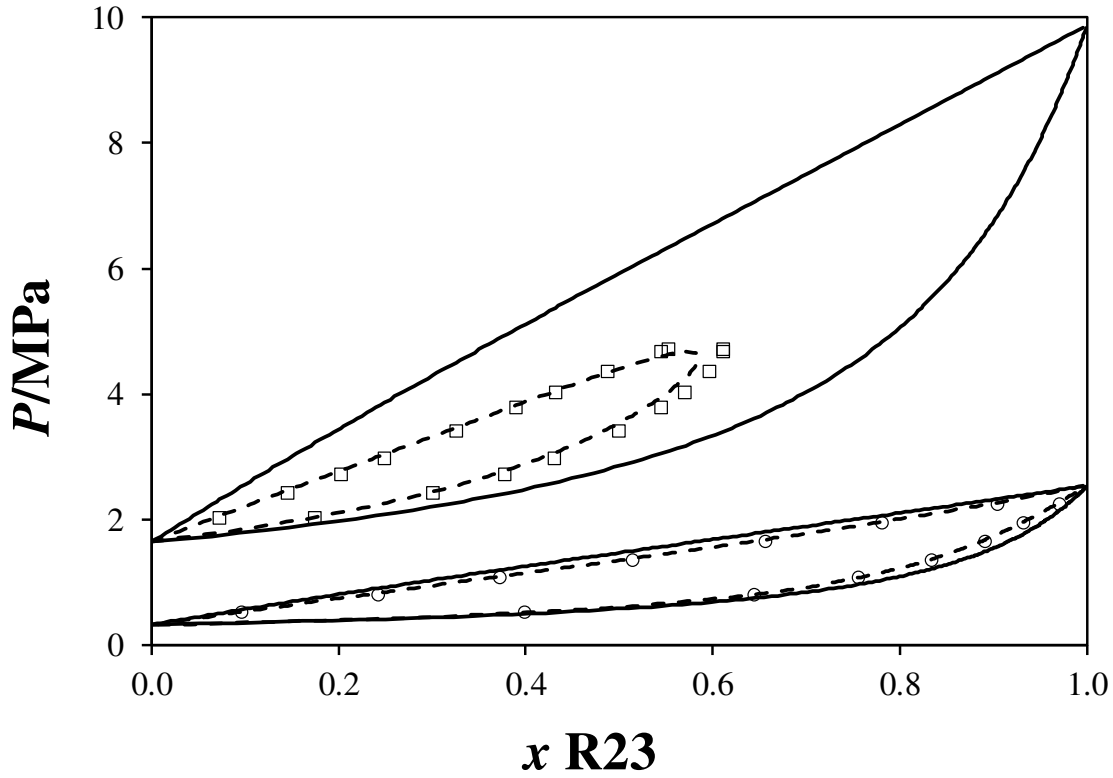

Figure. 15 Vapor-liquid equilibria of the R23 + R1234yf mixture. The symbols denote the experimental data [51] (circles: T=273.43K, squares: T=332.97K. The solid lines are the predictions of the assymetric approach (m-COSMO-SAC-dsp alone), and the dashed lines correspond to the PR-MHV1 / m-COSMO-SAC dsp equation of state.

Table 4. Predictions of vapor-liquid equilibria of refrigerant binary systems, by using the m-COSMO-SA dsp and the PR-MHV1/ m-COSMO-SAC dsp models: average absolute deviations (AAD%) between calculated and experimental data ($\text{AAD\%} = \frac{100}{npoint}\sum_{i=1}^{npoint}\left|\frac{X_{cal}-X_{exp}}{X_{exp}}\right|$).

Binary systems	Assymetric Approach m-COSMO-SAC dsp		EoS PR-MHV1 / m-COSMO-SAC dsp		Ref. Exp. Data
	AAD% P	AAD% y_1	AAD% P	AAD% y_1	
R134a + R290	2.7	6.1	2.2	2.5	[52]
R134a + R600	4.7	11.1	3.4	4.9	[41, 53]
R134a + R600a	2.7	7.4	2.0	1.8	[54]
R23 + R134a	10.5	14.4	4.9	5.0	[55, 56]
R32 + R134a	4.4	8.7	3.0	4.2	[57-60]
Isopentane + R245fa	5.3	12.7	3.4	3.3	[45]
Isopentane + R365mfc	1.3	7.9	1.3	1.1	[45]
R1234ze(E) + R290	5.3	6.6	4.4	4.3	[48]
R1270 +R134a	4.2	4.5	4.2	3.8	[43]
R32 + R1234yf	4.7	5.9	3.1	1.1	[46]
R143a + R1234yf	1.1	6.0	0.5	1.0	[47]
R125 + R1234yf	3.2	10.0	1.7	2.8	[46]
R1234yf + R134a	0.2	1.3	0.3	0.4	[46]
R1234yf + R600a	2.8	3.7	2.7	0.8	[50]
R23 + R1234yf	18.7	27.8	1.1	1.6	[51]
R1234yf + R600a	2.8	3.7	2.7	0.8	[50]
R23 + R1234yf	18.7	27.8	1.1	1.6	[51]
R1234ze(E) + R1336mzz(E)	0.5	7.4	1.2	0.2	[39]
R152a + R1336mzz(E)	2.6	7.3	4.5	2.3	[39]
R290 + R1336mzz(E)	3.9	16.2	2.9	1.1	[39]
Average over all systems	5.0	9.8	2.5	2.2	

4. Conclusions

Different COSMO approaches have been used to predict the thermodynamic properties and phase equilibria of refrigerant systems. A reasonable agreement between experimental data and the COSMO-RS 2010 version is obtained for boiling points and vaporization enthalpies of pure compounds: an average deviation of 11K is obtained for the boiling points, but deviations larger than 20K are observed for cyclic compounds like for RC318. The VLE of refrigerant mixtures have been predicted by using several versions of COSMO-SAC with COSMO-RS (2010). It is found that the COSMO-SAC 2002 [15, 16] and 2010 [19] models give poor predictions of VLE for refrigerant mixtures, and are unable to predict azeotropes in alkane + refrigerant mixtures, while the predictions of COSMO-RS are rather satisfactory for

most studied mixtures (presence of azeotrope always correctly predicted for the studied mixtures). The COSMO-SAC dsp model [20] leads to better predictions than COSMO-SAC 2010, but this model is still much less accurate than COSMO-RS. However, it is possible to make the COSMO-SAC dsp model as accurate as COSMO-RS (and even more accurate for most studied mixtures) by simply changing the value of the dispersion energy for fluorine, leading to the m-COSMO-SAC dsp model. The COSMO-RS and m-COSMO-SAC dsp models can predict well dew and bubble point curves as well as azeotropes, but they both tend to overestimate relative volatilities. The combination of m-COSMO-SAC dsp with a cubic equation of state such as PR78 by using the MHV1 mixing rule, can lead to accurate predictions of both VLE and relative volatilities at high pressures.

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