

1 **Vapor-liquid equilibria for binary systems carbon dioxide + 1,1,1,2,3,3-hexafluoro-**
2 **3-(2,2,2-trifluoroethoxy)propane or 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane**
3 **at 303.15 – 323.15 K**

4

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1 **ABSTRACT**

2 The phase behavior of binary mixtures of carbon dioxide (CO_2) and hydrofluoroethers
3 (HFEs) has been studied. In particular, experimental vapor-liquid equilibrium (VLE) data
4 for $\text{CO}_2 + 1,1,1,2,3,3$ -hexafluoro-3-(2,2,2-trifluoroethoxy)propane (HFE-449mec-f) and
5 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (HFE-7200) at temperatures of 303.15,
6 313.15, and 323.15 K are reported. The VLE data were measured using a static-type
7 apparatus and then correlated using the Peng-Robinson equation of state with the van der
8 Waals one fluid and Wong-Sandler-NRTL mixing rules. Reasonable correlation results
9 were obtained from the Peng-Robinson equation of state with both the van der Waals one
10 fluid and the Wong-Sandler-NRTL mixing rules. The GC-SAFT-VR equation also gave
11 good predictions of the phase behavior. Additionally, the group contribution SAFT-
12 VR (GC-SAFT-VR) equation was used to predict the experimental VLE in good
13 agreement with the experimental data, as well as the full p, T phase diagram for
14 both systems.

15

16 *Keywords:* Vapor-liquid equilibria; carbon dioxide; hydrofluoroether; GC-SAFT-VR;
17 HFE-7200; HFE-449mec-f, correlation, group contribution

1. Introduction

2 Chlorofluorocarbons (CFCs) have been utilized extensively as refrigerants, blowing
3 agents, and cleaning solvents due to their chemical stability and physical properties.
4 However, the Montreal Protocol (1989) requested that the use of CFCs be phased-out
5 prior to 1996 because of ozone layer depletion and global warming. Thus, CFC
6 alternatives have been investigated heavily in subsequent years.
7 Hydrochlorofluorocarbons (HCFCs) have been used as interim replacements for CFCs
8 because of similar physicochemical properties and lower ozone depletion potential (ODP)
9 values; however, it should be noted that they have higher global warming potential (GWP)
10 values. Thus, they are to be phased-out by 2020 according to the updated Montreal
11 Protocol. Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) have been used as
12 alternatives to CFCs and HCFCs, because they have zero ODP and high thermal
13 stabilities; however, they still have high GWP values. Therefore, HFCs and PFCs were
14 included in the set of six major greenhouse gases whose use should be reduced in the
15 Kyoto Protocol (2005). As a result, hydrofluoroethers (HFEs) have been utilized as third
16 generation alternatives to replace CFCs, HCFCs, HFCs, and PFCs due to their zero ODP,
17 low GWP, and short atmospheric lifetimes [1-5]. Industrially HFEs are also used as
18 cleaning solvents in electronic and magnetic devices, as a protective gas in the melting of
19 alloys, for decontamination of fluids, and as heat transfer fluids in heat exchangers [6, 7].
20 However, pure HFE's are flammable and toxic. Thus, a mixture of HFE's with another
21 refrigerant could retain desirable properties, whilst negating some of the more undesirable
22 ones, and has been a successful strategy in the past (e.g., hydrofluoroolefins [8, 9]).

23 Carbon dioxide (CO₂) is a well-known natural refrigerant that can be used as an
24 alternative to the above-mentioned CFCs, HCFCs, HFCs, and PFCs, making it a possible
25 refrigerant to use in mixtures with HFE's. CO₂ is a natural, nontoxic, readily available

1 and inflammable gas with zero ODP. Because of these favorable physical properties, CO₂
2 has already been used as a working fluid for heat pumps [10]. However, one of the main
3 disadvantages is that CO₂ run heat pumps need to be operated in a trans-critical cycle, i.e.,
4 at a very high pressure (typically within 15 MPa of the maximum operating pressure),
5 due to its relatively low critical constants ($T_c = 304.12$ K, $P_c = 7.374$ MPa [11]) [12, 13].
6 Mixtures of CO₂ and HFEs may thus also provide a promising alternative by reducing the
7 need for a high operating pressure whilst retaining the more favorable properties of CO₂.

8 In order to evaluate the performance of mixtures of CO₂ and HFEs and determine
9 optimal operating conditions for refrigeration processes using mixtures of CO₂ and HFEs,
10 an understanding of the mixture vapor-liquid equilibrium (VLE) data is crucial. Several
11 studies report experimental VLE data for binary mixtures of CO₂ + CFCs [13-22].
12 However, limited VLE data is available in the literature regarding binary systems CO₂ +
13 HFEs. The object of this work is thus to measure the VLE data for binary systems CO₂ +
14 HFEs, i.e., 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane (HFE-449mec-f) and
15 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (HFE-7200). The structures of the two
16 HFEs studied are shown in Fig. 1. These two HFEs were chosen because HFE-449mec-f
17 can also be used as an alternative cleaning solvent [2, 22, 23] and HFE-7200 has lower
18 values of GWP and atmospheric lifetime compared to other HFEs (60 and 0.77 years,
19 respectively [1]). It can be used not only as a working fluid for refrigerants and heat
20 transfer, but also as a cleaning solvent and lubricant carrier, etc. [7, 24]. We determined
21 the isothermal VLE for CO₂ + HFE-449mec-f or HFE-7200 at temperatures 303.15,
22 313.15, and 323.15 K using a static-circulation apparatus. The experimental VLE data
23 were correlated by the Peng-Robinson (PR) equation of state (EOS) [25] coupled with
24 the van der Waals one fluid (vdW1) mixing rule and Wong-Sandler (WS) [26] mixing
25 rules combined with the non-random two-liquid (NRTL) model [27]. The systematic

1 series of experimental data are also described with the group contribution (GC) based
2 SAFT-VR [28] equation of state (GC-SAFT-VR) that combines the SAFT-VR [29]
3 equation with a group contribution [28] approach. The GC-SAFT-VR equation describes
4 chains composed of neutral non-polar square-well spheres of different sizes and/or
5 interaction energies (including dispersion and association), with monomer properties
6 computed from perturbation theory using a reference system of hard spheres of arbitrary
7 composition and size. Using this hetero-segmented approach, GC-SAFT-VR parameters
8 have been determined in prior work for a wide range of functional groups (i.e., CH₃, CH₂,
9 C=O, CH₂O, OH, etc.) and used to study the thermodynamics and phase behavior of
10 alkanes, alkenes, ketones, aromatics, acetates, esters, polymers, and other associating and
11 non-associating fluids (see for example [5, 28, 30-32]). We note that the cross interactions
12 between simple groups such as CH₃-CH₂ are given by the simple Lorentz-Berthelot
13 combining rules; however, for cross interactions with polar groups, such as the carbonyl
14 group, where deviations from “ideal behavior” are expected, the cross interactions are
15 fitted to pure component experimental data for molecules that contain the functional
16 groups under consideration. In this way, in contrast to the traditional equation of state and
17 SAFT-based approaches, when deviations from the Lorentz-Berthelot combining rule are
18 seen, parameters do not need to be fit to experimental mixture data. Additionally, by not
19 averaging the group parameters on chain formation, as in other group-contribution based
20 SAFT approaches [33-35], the connectivity of functional groups and location of
21 association sites can be specified in the GC-SAFT-VR approach.

22 Multiple SAFT approaches have been proven effective in the study of a wide variety
23 of refrigerants, including fluorinated systems, such as the SAFT-VR study by Galindo et
24 al. [36] and the work of Avendaño et al. [37] who studied pure refrigerants with the SAFT-
25 gamma group-contribution approach. Additionally, fluorinated refrigerant mixtures have

1 also been studied using GC-SAFT-VR and PC-SAFT in work by Haley et al. [5] and
2 Fouad and Vega [9], respectively. In this work, we expand upon previous work with the
3 GC-SAFT-VR approach in order to predict the phase behavior of the CO₂ + HFE binary
4 mixtures studied and provide a wider examination of their phase behavior than is possible
5 with correlative approaches.

6

7 2. Experimental section

8 2.1. Materials

9 The chemicals used in this work are summarized in Table 1. The CO₂ was passed through
10 a 0.5 μ m inline filter (Nepro Company, Japan) before use to avoid undesirable particles.
11 The purity of the HFE-449mec-f and HFE-7200 was verified by gas chromatography
12 (GC) (GC-14A, Shimadzu Co. Ltd., Kyoto, Japan) with a thermal conductivity detector.
13 Existence of two isomers has been reported in the literature [7, 38-41]. Thus, the
14 composition of binary isomers of HFE-7200 was determined by ¹H NMR analysis (JNM-
15 ECX400, JEOL Ltd., Tokyo, Japan). The obtained mole fraction of the isomer with CAS
16 number 163702-06-5 was 0.614, whereas that of the isomer with CAS 163702-05-4 was
17 0.386. The densities (ρ) of the esters at 298.15 K was measured using a precision digital
18 oscillating U-tube densimeter (DMA 4500, Anton Paar GmbH, Graz, Austria) with a
19 reproducibility of 10⁻² kg m⁻³. The experimental ρ at 298.15 K for the chemicals used in
20 this work are reported in Table 1 together with the literature values [7, 42].

21

22 2.2. Apparatus and procedure

23 We used a static-circulation apparatus to measure the VLE. A schematic diagram of
24 the apparatus is shown in Fig. 2. It is composed of three parts, i.e., a variable volume
25 equilibrium cell, sampling unit for vapor and liquid phases, and GC. The equilibrium cell

1 1 was immersed in a thermostated water bath with three windows (THOMAS KAGAKU
2 Co. Ltd., Japan). There are six visual sapphire windows (23 mm in diameter and 11.5 mm
3 thick) in the equilibrium cell for the visual observation of the phase behavior.

4 The temperature of the apparatus was controlled within ± 0.1 K. The equilibrium
5 cell was made from stainless steel (SUS 316) and measurements can be made at
6 temperatures up to 473 K and pressures up to 20 MPa. The inner volume was 500 cm³. A
7 calibrated Pt 100 Ω platinum resistance thermometer 4 with an accuracy of ± 0.01 K was
8 used for measurements of the sample temperature. The pressure was determined by a
9 pressure indicator (DPI 145, Druck Co., Kirchentellinsfurt, Germany) with an accuracy
10 of ± 0.04 % F.S. Two GCs were used for the analysis of the vapor and liquid phase samples,
11 respectively. Further details regarding the experimental apparatus and procedure have
12 been described in previous work [21].

13 During measurement, first, the equilibrium cell (labelled 1 in Fig. 2) was evacuated
14 by the vacuum pump, and HFE-449mec-f or HFE-7200 was charged into the equilibrium
15 cell. Next, CO₂ was added until the desired pressure is achieved. Then, the liquid phase
16 was continuously recirculated (through circulation 14 in Fig. 2). The interface of the vapor
17 and liquid phases were observed during the measurements by the visual glass windows
18 equipped in the cell. The system was regarded as reaching equilibrium when temperature
19 and pressure fluctuations of no more than ± 0.01 K and ± 0.001 MPa, respectively, were
20 observed for 30 min. The equilibrium measurement of temperature and pressure before
21 sampling was up to about 6 hours.

22 Once equilibrium was reached, the vapor and liquid samples were taken (Sample
23 injector 15 in Fig. 2). Finally, the compositions of the vapor and liquid phases were
24 determined by GC.

25

1 2.3. Analysis

2 The vapor and liquid phase samples were analyzed by a GC (GC-14A, Shimadzu Co.,
 3 Ltd., Kyoto, Japan) with a thermal conductivity detector (TCD). Porapak Q (2.0 m × 3.0
 4 mm inside diameter, Shinwa Chemical Industries Ltd., Kyoto, Japan) was used as the
 5 column packing. Helium was used as the carrier gas at a flow rate of 50.0 mL min⁻¹. The
 6 temperature in the TCD was maintained at 623 K. Compositions were determined using
 7 the absolute area method with a calibration curve. The accuracy for the mole fraction was
 8 ± 0.002.

9

10 3. Models and theory

11 3.1 Peng-Robinson Equation of State

12 The correlations of the experimental VLE data were performed with the PR EOS
 13 combined with the vdW1 or WS-NRTL models as the mixing rule. The PR EOS is given
 14 by,

$$15 P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (1)$$

16 where P is the pressure, R is the ideal gas constant, T is the temperature, v is the molar
 17 volume, a is the energy parameter and b is the size parameter. These parameters for pure
 18 components i , were calculated using

$$19 a_{ii}(T) = \frac{0.45724R^2T_{c,i}^2}{P_{c,i}} \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right] \quad (2)$$

$$20 m_i = 0.37464 + 1.5422\omega_i - 0.26992\omega_i^2 \quad (3)$$

21 and

$$22 b_i = \frac{0.07780RT_{c,i}}{P_{c,i}} \quad (4)$$

23 where $T_{c,i}$ and $P_{c,i}$ are the critical temperature and critical pressure for pure component,

1 respectively, and ω_i is the acentric factor. The pure component parameters $T_{c,i}$, $P_{c,i}$ and ω_i
 2 [11, 42, 43] used to calculate the a and b values for the pure components CO₂, HFE-
 3 449mec-f, or HFE-7200 are provided in Table 4. The acentric factor, ω_i , for HFE-449mec-
 4 f and HFE-7200 was estimated from pressure-temperature data.

5 The vdW1 and WS mixing rules were used to calculate the mixture energy
 6 parameter, a , and the size parameter, b . The vdW1 mixing rule is given by,

$$7 a = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \quad (k_{ij} = k_{ji}, \ k_{ii} = k_{jj} = 0) \quad (5)$$

8 and

$$9 b = \sum_{i=1}^{NC} x_i x_j \left(\frac{b_i + b_j}{2} \right) (1 - l_{ij}) \quad (l_{ij} = l_{ji}, \ l_{ii} = l_{jj} = 0) \quad (6)$$

10 where k_{ij} and l_{ij} are binary interaction parameters. The WS mixing rule for the PR EOS is
 11 given by,

$$12 \frac{a}{b} = \sum_{i=1}^{NC} x_i \frac{a_{ii}}{b_i} + \frac{A_{\alpha}^E}{C} \quad (7)$$

$$13 b = \frac{\sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \sum_{i=1}^{NC} x_i \frac{a_{ii}}{bRT} - \frac{A_{\alpha}^E}{CRT}} \quad (8)$$

$$14 \left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_{ii}}{RT} \right) + \left(b_j - \frac{a_{jj}}{RT} \right) \right] (1 - k_{ij}) \quad (k_{ij} = k_{ji}, \ k_{ii} = k_{jj} = 0) \quad (9)$$

15 with the constant C in Eq. (8) as

$$16 C = \frac{\ln(\sqrt{2} - 1)}{\sqrt{2}} \quad (10)$$

17 where A_{α}^E is the excess Helmholtz free energy at infinite pressure, and k_{ij} is the second
 18 virial coefficient binary interaction parameter. The NRTL model [27] was applied to
 19 calculate A_{α}^E given by,

$$A_{\alpha}^E = \sum_{i=1}^{NC} x_i \frac{\sum_{j=1}^{NC} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{NC} x_k G_{ki}} \quad (11)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (\alpha_{ij} = \alpha_{ji}, \alpha_{ii} = \alpha_{jj} = 0) \quad (12)$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \quad (\tau_{ii} = \tau_{jj} = 0) \quad (13)$$

where $g_{ij} - g_{jj}$ is the binary interaction parameter of the NRTL model. The value of 0.3 was used for α_{12} according to recommendation by Renon and Prausnitz [27]. k_{12} and l_{12} in the vdW1 mixing rule, and k_{12} , $g_{12} - g_{22}$ and $g_{21} - g_{11}$ in the WS-NRTL mixing rule were treated as fitted parameters, and were regressed by minimizing the following objective function (F_{obj}):

$$F_{\text{obj}} = \sum_{k=1}^{\text{NDP}} \left(\frac{P_{\text{exptl.}} - P_{\text{calcd.}}}{P_{\text{exptl.}}} \right)_k^2 \quad (14)$$

where NDP is the number of experimental data points, and “exptl.” and “calcd.” are the experimental and calculated values, respectively.

12

3.2. GC-SAFT-VR

In the GC-SAFT-VR approach [28], the functional groups in molecules are represented by tangentially bonded segments that each have individual size and energy parameters. The functional group i in molecule k interacts with functional group j in molecule l through dispersive interactions via the square-well potential as described by,

$$u_{ki,lj}(r) = \begin{cases} +\infty & \text{if } r < \sigma_{ki,lj} \\ -\varepsilon_{ki,lj} & \text{if } \sigma_{ki,lj} \leq r \leq \lambda_{ki,lj} \sigma_{ki,lj} \\ 0 & \text{if } r > \lambda_{ki,lj} \sigma_{ki,lj} \end{cases} \quad (15)$$

where r is the distance between the two groups, $\sigma_{ki,lj}$ is the segment diameter, and $\varepsilon_{ki,lj}$ and $\lambda_{ki,lj}$ are the dispersion energy well depth and range parameters, respectively. The cross

1 interactions for size and energy between unlike segments can be expressed by Lorentz-
 2 Berthelot combining rules,

3
$$\sigma_{ki,lj} = \frac{\sigma_{ki,ki} + \sigma_{lj,lj}}{2} \quad (16)$$

4
$$\varepsilon_{ki,lj} = \xi_{ki,lj} \sqrt{\varepsilon_{ki,ki} \varepsilon_{lj,lj}} \quad (17)$$

5
$$\lambda_{ki,lj} = \gamma_{ki,lj} \left(\frac{\sigma_{ki,ki} \lambda_{ki,ki} + \sigma_{lj,lj} \lambda_{lj,lj}}{\sigma_{ki,ki} + \sigma_{lj,lj}} \right) \quad (18)$$

6 where $\xi_{ki,lj}$ and $\gamma_{ki,lj}$ are binary interaction parameters that enable adjustments to the cross
 7 interactions from the geometric and arithmetic mean values, respectively.

8 The definition if the Helmholtz free energy for a non-associating fluid in the GC-
 9 SAFT-VR approach is given by,

10
$$\frac{A}{Nk_B T} = \frac{A^{\text{ideal}}}{Nk_B T} + \frac{A^{\text{mono}}}{Nk_B T} + \frac{A^{\text{chain}}}{Nk_B T} \quad (19)$$

11 where N is the total number of molecules in the system, k_B is the Boltzmann constant, T
 12 is the absolute temperature, A^{ideal} , A^{mono} , and A^{chain} are the contributions to the Helmholtz
 13 free energy from the ideal, monomer, and hetero-segmented chain interactions,
 14 respectively. The reader is referred to the original publications [28, 44] for details of the
 15 terms in equation (19), here we provide only the main expressions and a brief description
 16 of each term.

17 The ideal contribution to the Helmholtz free energy is given by,

18
$$\frac{A^{\text{ideal}}}{Nk_B T} = \sum_{k=1}^{n_{\text{components}}} x_k \ln(\rho_k \Lambda_k^3) - 1 \quad (20)$$

19 where $n_{\text{components}}$ represents the number of pure components in the system, x_k is the mole
 20 fraction of component k , ρ_k is the molecular number density, N_k/V , where N_k is the number
 21 of molecules of component k and V is the volume of the system, and Λ_k is the de Broglie
 22 wavelength of component k .

1 The monomer contribution to the Helmholtz free energy is given by the
 2 temperature expansion of the second order Barker Henderson perturbation theory for
 3 mixtures [45],

4
$$\frac{A^{\text{mono}}}{Nk_B T} = \sum_{k=1}^n \sum_{i=1}^{n'_k} m_{ki} x_k \left(a^{\text{HS}} + \frac{a_1}{k_B T} + \frac{a_2}{(k_B T)^2} \right) \quad (21)$$

5 where n'_k is the number of types of functional groups i in a chain of component k and
 6 m_{ki} is the number of segments of type i in chains of component k . a^{HS} , a_1 , and a_2 represent
 7 the hard-sphere reference term and the first and second order perturbation terms,
 8 respectively.

9 Finally, the contribution to the Helmholtz free energy from chain formation from
 10 the hetero-segmented monomer fluid is represented by,

11
$$\frac{A^{\text{chain}}}{Nk_B T} = - \sum_{k=1}^n x_k \sum_{ij} \ln y_{ki,kj}^{\text{SW}} (\sigma_{ki,kj}) \quad (22)$$

12 where the first sum is over all of the components, n , in the mixture, x_k is again the mole
 13 fraction of component k , the second sum considers the chain formation and the
 14 connectivity of the segments within a given component k . The background correlation
 15 function $y_{ki,kj}^{\text{SW}}$ is given by.

16
$$y_{ki,kj}^{\text{SW}} (\sigma_{ki,kj}) = \exp \left(\frac{-\varepsilon_{ki,kj}}{k_B T} \right) g_{ki,kj}^{\text{SW}} (\sigma_{ki,kj}) \quad (23)$$

17 where $\varepsilon_{ki,kj}$ is the segment-segment dispersion energy well depth and $g_{ki,kj}^{\text{SW}} (\sigma_{ki,kj})$ is the
 18 radial distribution function for the square-well monomers at the contact distance of $\sigma_{ki,kj}$
 19 and is approximated by a first-order high temperature expansion [29].

20 Once the Helmholtz free energy is obtained, other thermodynamic properties,
 21 such as chemical potential and pressure can be calculated through standard
 22 thermodynamic relationships.

23

1 **4. Results and discussion**

2 *4.1. Experimental VLE data for the binary systems CO₂ + HFE-449mec-f or HFE-7200*

3 VLE data for the binary systems CO₂ (1) + HFE-449mec-f or HFE-7200 (2) were
 4 measured at temperatures 303.15, 313.15, and 323.15 K. The experimental VLE data are
 5 listed in Tables 2 and 3, respectively. Plots of pressure (P) as functions of the liquid or
 6 vapor mole fraction of CO₂ (x_1 or y_1) for two systems are also presented in Figs. 3 and 4,
 7 respectively. The pressure was measured up to about 8.6 MPa in this work. To our best
 8 knowledge, the experimental VLE data of these systems have not been previously
 9 reported in the literature. A comparison of Figs. 3 and 4 shows that the P - x_1 diagram of
 10 the system CO₂ + HFE-7200, which has a higher carbon number, shifts to higher pressures,
 11 compared to the CO₂ + HFE-449mec-f system.

12

13 *4.2. Correlation*

14 The determined parameters in both mixing rules along with the percentage average
 15 relative deviations of the experimental and calculated P , $|\Delta P/P|_{\text{av.}}$ and the average absolute
 16 deviations of the experimental and calculated y_1 , $|\Delta y_1|_{\text{av.}}$, are provided in Table 5. These
 17 parameters were determined per system and are temperature independent. The vdW1
 18 mixing rule gave $|\Delta P/P|_{\text{av.}} \times 100$ and $|\Delta y_1|_{\text{av.}}$ of less than 2.9 % and 0.017, respectively for
 19 each dataset, whilst using the WS-NRTL mixing rule resulted in values of 3.1 % and 0.012.
 20 Thus, both models show reasonable correlation of the results at all temperatures
 21 investigated. Figs. 5 and 6 shows the relative deviations between the experimental and
 22 calculated P defined as $(P_{\text{exptl.}} - P_{\text{calcd.}})/P_{\text{exptl.}} \times 100$ (%), and the absolute deviation
 23 between the experimental and calculated y_1 defined as $y_{1,\text{exptl.}} - y_{1,\text{calcd.}}$, as a function of
 24 liquid phase CO₂ mole fraction, x_1 in the systems CO₂ + HFE-449mec-f and CO₂ + HFE-
 25 7200, respectively. The values of $(P_{\text{exptl.}} - P_{\text{calcd.}})/P_{\text{exptl.}} \times 100$ (%) and $y_{1,\text{exptl.}} - y_{1,\text{calcd.}}$

1 were generally within the uncertainties of the experimental pressure and vapor-phase
2 mole fraction for both models; however, higher values were detected in some data of both
3 systems, especially at temperature 323.15 K. The results of calculations using the vdW1
4 and WS-NRTL mixing rules are summarized graphically in Figs. 3 and 4.

5

6 *4.3. Prediction using the GC-SAFT-VR*

7 As shown in Fig. 1, where each functional group is circled, HFE-449mec-f and HFE-
8 7200 are both composed of CF₃, CF₂, CHF, CH₃, and ether CH₂O groups. The parameters
9 for these functional groups were taken from previous work [5, 28, 30] and reported for
10 completeness in Tables 6-8. Since CO₂ is a small molecule, it is not broken up into
11 individual groups and represented by the SAFT-VR parameters proposed by Ramos et al.
12 [46] as reported in Tables 6-8. Using these parameters, an average absolute deviation in
13 the pressure ($|\Delta P/P|_{av.} \%$) for pure HFE-7200 of 2.02 % and 19.35 % for pure HFE-
14 449mec-f compared to experimental data [3] are obtained. Likely, the high $|\Delta P/P|_{av.} \%$
15 value for pure HFE-449mec-f is due to the additional CF₃ functional group present in the
16 HFE-449mec-f molecule, instead of the smaller CH₃ functional group in HFE-7200. In
17 Figs. 7 (a) and (b) respectively the constant temperature predictions of the CO₂ + HFE-
18 449mec-f and CO₂ + HFE-7200 phase diagrams at 303.15, 313.15, and 323.15K are
19 shown. From the figures, it can be seen that the predictions are in good agreement with
20 the experimental data, specifically for the CO₂ + HFE-449mec-f mixture (Fig. 7(a)). In
21 order to quantitatively compare the experimental mixture data to the GC-SAFT-VR
22 predictions, the average absolute deviation in the vapor phase mole fraction of CO₂
23 ($|\Delta y_1|_{av.}$) are reported in Table 5 along with the $|\Delta P/P|_{av.} \%$ values for the mixtures at 303.15,
24 313.15, 323.15 K. The $|\Delta y_1|_{av.}$ values are averaged across the 3 examined temperatures
25 and deviations of 0.012 and 0.086 are obtained for the CO₂ + HFE-449mec-f and CO₂ +

1 HFE-7200 systems, respectively. We note that this fit is purely predictive, since all
2 parameters were obtained from a fit to pure component data, which is one of the
3 advantages of using a group-contribution based SAFT approach. However, since the
4 molecule set used to determine the interactions in fluorinated ether systems in the work
5 of Haley et al. [5] was small, the use of an adjusted cross interaction between CO_2 and
6 the CF_2 group was investigated to see if a better prediction of the $\text{CO}_2 + \text{HFE-7200}$
7 mixture could be obtained. The optimized cross interaction was fitted to the $\text{CO}_2 + \text{HFE-}$
8 7200 system at 303.15 K and is reported in reported in Tables 7 and 8. Although, the
9 adjustment of this cross interaction away from the Lorentz-Berthelot value has a minimal
10 effect on the $\text{CO}_2 + \text{HFE-449mec-f}$ mixture ($|\Delta y_1|_{\text{av.}}$ of 0.012 to 0.047), as shown in Fig.
11 8 (a), it significantly improves the agreement with experimental data for the $\text{CO}_2 + \text{HFE-}$
12 7200 system ($|\Delta y_1|_{\text{av.}}$ of 0.086 to 0.016) as can be seen in Fig. 8 (b) and reported in Table
13 5. Note that the cross interaction between CO_2 and CF_2 was fitted using the $|\Delta y_1|_{\text{av.}}$ values
14 because of the small to nonexistent changes in the $|\Delta P/P|_{\text{av.}}\%$ values.

15 Finally, the p, T projection of the fluid phase diagram was predicted for both mixtures
16 with the parameter set that includes the optimized CO_2-CF_2 cross interaction and can be
17 seen in Fig. 9. As can be seen from the figure type I phase behavior is found according to
18 the scheme of Scott and van Konynenburg [47]. We note that both sets of parameters, i.e.,
19 with and without the adjusted CO_2-CF_2 cross interaction yield very similar phase
20 diagrams. The GC-SAFT-VR approach, like all analytical equations of state, over predicts
21 the critical point [49-52] and so the predicted critical line is likely somewhat higher than
22 the experimental values; however, we anticipate the type of phase diagram to be
23 unaffected.

24

25 **5. Conclusions**

1 The experimental VLE data were obtained for two binary systems $\text{CO}_2 + \text{HFE-449mec-f}$
2 or HFE-7200 at temperatures 303.15, 313.15, and 323.15 K and at pressure up to 9.0 MPa.
3 This study furthers our understanding of these refrigerant mixtures as no experimental
4 data were previously available for these two binary systems. The experimental VLE data
5 were well correlated by the PR EOS with the vdW1and WS-NRTL mixing rules. These
6 models provide reasonable agreements with the experimental data. The GC-SAFT-VR
7 approach was also found to be able to correctly predict the phase behavior of the $\text{CO}_2 +$
8 HFE binary mixtures. Due to the molecular polarity of the HFEs studied, optimization of
9 the cross interaction between CO_2 and CF_2 was found to allow for better representation
10 of the phase behavior than using Lorentz-Berthelot combining rules alone. Utilizing the
11 fitted cross interaction the full phase diagram of the $\text{CO}_2 + \text{HFE-449mec-f}$ and $\text{CO}_2 +$
12 HFE-7200 systems was also predicted and type 1 phase behavior observed.

13

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19

20

21 *List of symbols*

22 a energy parameter in the PR EOS ($\text{Pa m}^6 \text{ mol}^{-2}$)

23 A Helmholtz free energy (J mol^{-1})

24 b size parameter in the PR EOS ($\text{m}^3 \text{ mol}^{-1}$)

25 C constant in the WS model

1	A, B, C	Antoine constants
2	F_{obj}	objective function
3	$g_{ij} - g_{jj}$	binary interaction parameter in the NRTL model (J mol^{-1})
4	k_{12}	second virial coefficient binary interaction parameter in the WS model
5		
6	k_{12}	binary interaction parameter in the PR EOS
7	l_{12}	binary interaction parameter in the PR EOS
8	m_i	parameter in the PR EOS
9	NC	number of pure components in the system
10	NDP	number of data points per system
11	P	pressure (Pa)
12	P^s	saturated vapor pressure (kPa)
13	$ \Delta P/P $	relative deviation between experimental and calculated equilibrium pressures
14		
15	R	gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
16	r	distance between the two groups
17	T	absolute temperature (K)
18	v	molar volume ($\text{m}^3 \text{ mol}^{-1}$)
19	x	liquid phase mole fraction
20	y	vapor phase mole fraction
21	$ \Delta y_1 $	absolute deviation between experimental and calculated vapor phase mole fractions of component 1
22		
23		
24	<i>Greek letters</i>	
25	α_{12}	non-randomness parameter in the NRTL model

2 ρ density (kg m^{-3})

3

4 *Superscript*

5 E excess property

6 ideal ideal

7 s saturated

8

9 Subscripts

11 ∞ infinite pressure condition

12 av. average

13 c critical

14 calcd. calculated

15 exptl. experime

16 r reduced

17

18

18 References

19 [1] W. -T. Tsai, J. Hazard. Mater. 119 (2005) 69-78,

20 <https://doi.org/10.1016/j.jhazmat.2004.12.018>.

21 [2] A. Sekiya, S. Misaki, J. Fluor. Chem. 101 (2000) 215-221,

22 [https://doi.org/10.1016/S0022-1139\(99\)00162-1](https://doi.org/10.1016/S0022-1139(99)00162-1).

23 [3] M. Yasumoto, Y. Yamada, J. Murata, S. Urata, K. Otake, *J. Chem. Eng. Data* 48

24 (2003) 1368-1379, <https://doi.org/10.1021/je0201976>.

25 [4] Y. Uchida, M. Yasumoto, Y. Yamada, K. Ochi, T. Furuya, K. Otake, *J. Chem. Eng.*

1 Data 49 (2004) 1615-1621, <https://doi.org/10.1021/je0499723>.

2 [5] J. D. Haley, C. McCabe, Fluid Phase Equilib. 440 (2017) 111-121,
3 <https://doi.org/10.1016/j.fluid.2017.01.013>.

4 [6] D. Fang, Y. Li, X. Meng, J. Wu, J. Chem. Thermodyn. 69 (2014) 36-42,
5 <https://doi.org/10.1016/j.jct.2013.09.035>.

6 [7] M. H. Rausch, L. Kretschmer, S. Will, A. Leipertz, A. P. Fröba, J. Chem. Eng. Data
7 60 (2015) 3759-3765, <https://doi.org/10.1021/acs.jced.5b00691>.

8 [8] C. G. Albà, L. F. Vega, F. Llovell, Int. J. Refrig. 113 (2020) 145 - 155,
9 <https://doi.org/10.1016/j.ijrefrig.2020.01.008>.

10 [9] W. A. Fouad, L. F. Vega, AIChE J. 64 (2018) 250-262,
11 <https://doi.org/10.1002/aic.15859>.

12 [10] P. Nekså, Int. J. Refrig. 25 (2002) 421-427, [https://doi.org/10.1016/S0140-7007\(01\)00033-0](https://doi.org/10.1016/S0140-7007(01)00033-0).

14 [11] B. E. Poling, J. M. Prausnitz, J. P. O'Connell, The Properties of Gases and Liquids
15 (5th ed.), McGraw-Hill, New York (2001).

16 [12] R. Akasaka, J. Therm. Sci. Tech-Jpn. 4 (2009) 159-168,
17 <https://doi.org/10.1299/jtst.4.159>.

18 [13] K. Djebaili, E. E. Ahmar, A. Valtz, A. H. Meniai, C. Coquelet, J. Chem. Eng. Data
19 63 (2018) 4626-4631, <https://doi.org/10.1021/acs.jced.8b00683>.

20 [14] G. Silva-Oliver, L. A. Galicia-Luna, Fluid Phase Equilib. 199 (2002) 213-222,
21 [https://doi.org/10.1016/S0378-3812\(01\)00816-0](https://doi.org/10.1016/S0378-3812(01)00816-0).

22 [15] C. Duran-Valencia, G. Pointurier, A. Valtz, P. Guilbot, D. Richon, J. Chem. Eng.
23 Data 47 (2002) 59-61, <https://doi.org/10.1021/je010075y>.

24 [16] A. M. A. Dias, H. Carrier, J. L. Daridon, J. C. Pàmies, L. F. Vega, J. A. P. Coutinho,
25 I. M. Marrucho, Ind. Eng. Chem. Res. 45 (2006) 2341-2350,

1 <https://doi.org/10.1021/ie051017z>.

2 [17] J. S. Lim, J. M. Jin, K. -P. Yoo, *J. Supercrit. Fluids* 44 (2008) 279-283,
3 <https://doi.org/10.1016/j.supflu.2007.09.025>.

4 [18] S. A. Kim, J. S. Lim, J. W. Kang, *J. Chem. Eng. Data* 55 (2010) 4999-5003,
5 <https://doi.org/10.1021/je100583z>.

6 [19] G. Raabe, *J. Chem. Eng. Data* 58 (2013) 1867-1873,
7 <https://doi.org/10.1021/je4002619>.

8 [20] S. A. Gornati, D. D. Bona, P. Chiesa, *Fluid Phase Equilib.* 498 (2019) 94-103,
9 <https://doi.org/10.1016/j.fluid.2019.06.024>.

10 [21] K. Tochigi, T. Namae, T. Suga, H. Matsuda, K. Kurihara, M. C. dos Ramos, C.
11 McCabe, *J. Supercrit. Fluids* 55 (2010) 682-689,
12 <https://doi.org/10.1016/j.supflu.2010.10.016>.

13 [22] S. Urata, A. Takada, T. Uchimaru, A. K. Chandra, *Chem. Phys. Lett.* 368 (2003)
14 215-223, [https://doi.org/10.1016/S0009-2614\(02\)01718-9](https://doi.org/10.1016/S0009-2614(02)01718-9).

15 [23] R. C. Deka, B. K. Mishra, *J. Mol. Graph. Model.* 53 (2014) 23-30,
16 <https://doi.org/10.1016/j.jmgm.2014.07.003>.

17 [24] 3M Novec 7200 Engineered Fluid Datasheet,
18 http://multimedia.3m.com/mws/media/199819O/3mtm-novectm-7200-engineered-fluid.pdf&fn=prodinfo_nvc7200.pdf (accessed December 24, 2019).

20 [25] D. Peng, D. B. Robinson, *Ind. Eng. Chem. Fundam.* 15 (1976) 59-64,
21 <https://doi.org/10.1021/i160057a011>.

22 [26] D. S. H. Wong, S. I. Sandler, *AIChE J.* 38 (1992) 671-680,
23 <https://doi.org/10.1002/aic.690380505>.

24 [27] H. Renon, J. M. Prausnitz, *AIChE J.* 14 (1968) 135-144,
25 <https://doi.org/10.1002/aic.690140124>.

1 [28] Y. Peng, K. D. Goff, M. C. dos Ramos, C. McCabe, *Fluid Phase Equilib.* 277
2 (2009) 131-144, <https://doi.org/10.1016/j.fluid.2008.11.008>.

3 [29] A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson, A. N. Burgess,
4 *J. Chem. Phys.* 106 (1997) 4168-4186, <https://doi.org/10.1063/1.473101>.

5 [30] Y. Peng, K. D. Goff, M. C. dos Ramos, C. McCabe, *Ind. Eng. Chem. Res.* 49
6 (2010) 1378-1394, <https://doi.org/10.1021/ie900795x>.

7 [31] M. C. dos Ramos, J. D. Haley, J. R. Westwood, C. McCabe, *Fluid Phase Equilib.*
8 306 (2011) 97-111, <https://doi.org/10.1016/j.fluid.2011.03.026>.

9 [32] G. M. C. Silva, P. Morgado, J. D. Haley, V. M. T. Montoya, C. McCabe, L. F. G.
10 Martins, E. J. M. Filipe, *Fluid Phase Equilib.* 425 (2016) 297-304,
11 <https://doi.org/10.1016/j.fluid.2016.06.011>.

12 [33] S. Tamouza, J. P. Passarello, P. Tobaly and J. C. de Hemptinne, *Fluid Phase Equilib.*
13 222 (2004) 67-76, <https://doi.org/10.1016/j.fluid.2004.06.038>.

14 [34] A. Lymeriadis, C. S. Adjiman, A. Galindo and G. Jackson, *J. Chem. Phys.* 127
15 (2007) 234903, <https://doi.org/10.1063/1.2813894>.

16 [35] F. S. Emami, A. Vahid, J. R. Elliott and F. Feyzi, *Ind. Eng. Chem. Res.* 47 (2008)
17 8401-8411, <https://doi.org/10.1021/ie800329r>.

18 [36] A. Galindo, A. Gil-Villegas, P.J. Whitehead, and G. Jackson, *J. Phys. Chem. B* 102
19 (1998) 7632-7639, <https://doi.org/10.1021/jp9809437>.

20 [37] C. Avendaño, T. Laffitte, C. S. Adjuman, A. Galindo, E. A. Müller, G. Jackson, *J.*
21 *Phys. Chem. B* 117 (2013) 2717-2733, <https://doi.org/10.1021/jp306442b>.

22 [38] N. Muñoz-Rujas, F. Aguilar, J. M. García-Alonso, E. A. Montero, *J. Chem.*
23 *Thermodyn.* 131 (2019) 630-647, <https://doi.org/10.1016/j.jct.2018.12.018>.

24 [39] G. S. Grubbs II, S. A. Cooke, *Chem. Phys. Lett.* 495 (2010) 182-186,
25 <https://doi.org/10.1016/j.cplett.2010.07.004>.

1 [40] I. Bravo, Y. Díaz-de-Mera, A. Aranda, K. Smith, K. P. Shine, G. Marston, Phys.
2 Chem. Chem. Phys. 12 (2010) 5115-5125, <https://doi.org/10.1039/B923092K>.

3 [41] M. B. Shiflett, A. Yokozeki, J. Chem. Eng. Data 52 (2007) 2413-2418,
4 <https://doi.org/10.1021/je700365z>.

5 [42] K. Tochigi, C. Kikuchi, K. Kurihara, K. Ochi, J. Murata, K. Otake, J. Chem. Eng.
6 Data 47 (2002) 830-834, <https://doi.org/10.1021/je0102560>.

7 [43] The Dortmund Data Bank (DDB), DDBST Software and Separation Technology;
8 GmbH Oldenburg: Germany, Version 2019.

9 [44] Y. Peng, H. Zhao, C. McCabe, Mol. Phys. 104 (2006) 571-586,
10 <https://doi.org/10.1080/00268970500475901>.

11 [45] P. J. Leonard, D. Henderson, J. A. Barker, Trans. Faraday Soc. 66 (1970) 2439-
12 2452, <https://doi.org/10.1039/TF9706602439>.

13 [46] M. C. dos Ramos, H. Docherty, F. J. Blas, A. Galindo, Fluid Phase Equilib. 276
14 (2009) 116-126, <https://doi.org/10.1016/j.fluid.2008.09.025>.

15 [47] R. L. Scott and P. H. van Konynenburg, Discuss. Faraday Soc. 49 (1970) 87-97,
16 <https://doi.org/10.1039/DF9704900087>.

17 [48] Design Institute for Physical Property Data (U.S.) and Knovel (Firm), *DIPPR*
18 *Project 801, full version evaluated standard thermophysical property values*,
19 2005, BYU DIPPR, Thermophysical Properties Laboratory: Provo, Utah.

20 [49] S. B. Kiselev and J. F. Ely, Ind. Eng. Chem. Res. 38 (1999) 4993-5004,
21 <https://doi.org/10.1021/ie990387i>.

22 [50] C. McCabe and S. B. Kiselev, Fluid Phase Equilib. 219 (2004) 3-9,
23 <https://doi.org/10.1016/j.fluid.2004.01.011>.

24 [51] C. McCabe and S. B. Kiselev, Ind. Eng. Chem. Res. 43 (2004) 2839-2851,
25 <https://doi.org/10.1021/ie034288n>.

1 [52] L. Sun, H. Zhao, S. B. Kiselev, C. McCabe, J. Phys. Chem. B 109 (2005) 9047-
2 9058, <https://doi.org/10.1021/jp044413o>.
3

1 **Figure captions**

2

3 **Fig. 1.** Structures of HFE-449mec-f and HFE-7200.

4

5 **Fig. 2.** Schematic diagram of the experimental apparatus for measuring isothermal VLE.6 1, equilibrium cell; 2, water bath; 3, stirrer; 4, thermometer; 5, pressure indicator; 6,
7 sampling valve; 7, ribbon heater; 8, CO₂ cylinder; 9, in-line filter; 10, sample installation;
8 11, vacuum pump; 12, six-way valve; 13, gas chromatograph; 14, circulation pump; and
9 15, sample injector.

10

11 **Fig. 3.** Experimental VLE data for the system CO₂ (1) + HFE-449mec-f (2) at 303.15,
12 313.15, and 323.15 K. Experimental data at liquid phase ; ● 303.15 K; ▲ 313.15 K; ■
13 323.15 K, vapor phase ; ○ 303.15 K; Δ 313.15 K; □ 323.15 K. Results obtained from —
14 PR EOS with vdW1 mixing rule.

15

16 **Fig. 4.** Experimental VLE data for the system CO₂ (1) + HFE-7200 (2) at 303.15, 313.15,
17 and 323.15 K. Experimental data at liquid phase ; ● 303.15 K; ▲ 313.15 K; ■ 323.15 K,
18 vapor phase ; ○ 303.15 K; Δ 313.15 K; □ 323.15 K. Results obtained from — PR EOS
19 with vdW1 mixing rule.

20

21 **Fig. 5.** Relative deviations between the experimental and calculated results vs. CO₂ mole
22 fraction for the system CO₂ (1) + HFE-449mec-f (2). PR EOS with vdW1 mixing rule at
23 ● 303.15 K; ▲ 313.15 K; ■ 323.15 K. PR EOS with WS-NRTL mixing rule at ○ 303.15
24 K; Δ 313.15 K; □ 323.15 K. (a) $(P_{\text{exptl.}} - P_{\text{calcd.}})/P_{\text{exptl.}} \times 100 (\%)$ and (b) $y_{1,\text{exptl.}} -$
25 $y_{1,\text{calcd.}}$.

1

2 **Fig. 6.** Relative deviations between the experimental and calculated results vs. CO₂ mole
 3 fraction for the system CO₂ (1) + HFE-7200 (2). PR EOS with vdW1 mixing rule at •
 4 303.15 K; ▲ 313.15 K; ■ 313.15 K. PR EOS with WS-NRTL mixing rule at ○ 303.15 K;
 5 Δ 313.15 K; □ 323.15 K. (a) $(P_{\text{exptl.}} - P_{\text{calcd.}})/P_{\text{exptl.}} \times 100$ (%) and (b) $y_{1,\text{exptl.}} - y_{1,\text{calcd.}}$.

6

7 **Fig. 7.** P_x slices of (a) CO₂ (1) + HFE-449mec-f (2) and (b) CO₂ (1) + HFE-7200 (2) at
 8 constant temperatures of 303.15, 313.15, and 323.15 K. Solid lines correspond to
 9 predictions from the GC-SAFT-VR approach. Points correspond to experimental data
 10 presented here at liquid phase: • 303.15 K, ▲ 313.15 K, ■ 323.15 K, and vapor phase: ○
 11 303.15 K, Δ 313.15 K, □ 323.15 K.

12

13 **Fig. 8.** P_x slices of (a) CO₂ (1) + HFE-449mec-f (2) and (b) CO₂ (1) + HFE-7200 (2) at
 14 constant temperatures of 303.15, 313.15, and 323.15 K with a binary interaction
 15 parameter between CO₂ and CF₂. Solid lines correspond to predictions from the GC-
 16 SAFT-VR approach. Points correspond to experimental data presented here at liquid
 17 phase: • 303.15 K, ▲ 313.15 K, ■ 323.15 K, and vapor phase: ○ 303.15 K, Δ 313.15 K,
 18 □ 323.15 K.

19

20 **Fig. 9.** Projected pressure-temperature diagram of HFE-449mec-f + CO₂ (----) and HFE-
 21 7200 + CO₂ (.....) where the dotted lines represent the GC-SAFT-VR predicted critical line
 22 of both the mixtures utilizing the CO₂-CF₂ binary interaction parameter, the experimental
 23 data [3, 48] for the pure components are shown as open symbols for CO₂ (○), HFE-
 24 449mec-f (◊), and HFE-7200 (□), and the solid lines are the GC-SAFT-VR predictions
 25 for the pure components presented here.

