



Measurement and prediction of high-pressure vapor–liquid equilibria for binary mixtures of carbon dioxide + *n*-octane, methanol, ethanol, and perfluorohexane

Katsumi Tochigi^{a,*}, Tooru Namae^a, Tooru Suga^a, Hiroyuki Matsuda^a, Kiyofumi Kurihara^a, M. Carolina dos Ramos^b, Clare McCabe^{b,c}

^a Department of Materials and Applied Chemistry, Nihon University, 1-8 Surugadai, Kanda, Chiyoda-ku, Tokyo 101-8308, Japan

^b Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, USA

^c Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA

ARTICLE INFO

Article history:

Received 29 July 2010

Received in revised form 13 October 2010

Accepted 13 October 2010

Keywords:

Experimental data

Vapor–liquid equilibria

Modified SRK equation

Adachi–Sugie mixing rule

SAFT-VR

Equation of state

Carbon dioxide

ABSTRACT

We report the measurement of high-pressure vapor–liquid equilibrium data for binary mixtures of carbon dioxide + *n*-octane, +methanol, and +ethanol systems at 313.14 K and carbon dioxide + perfluorohexane at 303.15–323.15 K. The experimental data were collected using a new simple apparatus for measuring high-pressure vapor–liquid equilibria and correlated using a modified SRK equation with the three-parameter conventional mixing rule proposed by Adachi and Sugie. The SAFT-VR equation of state has also been used to predict the phase behavior and found to be in good agreement with experimental data. For the carbon dioxide + methanol, carbon dioxide + ethanol and carbon dioxide + perfluorohexane systems simple Lorentz–Berthelot combining rules can be used to determine the cross interactions and predict the phase behavior. For the carbon dioxide + *n*-octane system cross interaction parameters fitted to experimental data are needed in order to capture the non-ideal phase behavior exhibited by this system.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Knowledge of the phase behavior of systems containing carbon dioxide are of growing importance due to the increased use of supercritical CO₂ as an environmentally benign solvent alternative to volatile organics in chemical processes [1], and more recently, in the development of new and improved methods for carbon capture and storage [2,3]. Here we report the measurement of high-pressure vapor–liquid equilibrium data for binary mixtures of carbon dioxide + *n*-octane, +methanol, +ethanol, and +perfluorohexane using a new equilibrium cell apparatus similar to that reported by Sako et al. [4]. The experimental measurements have been performed at 303.15–323.15 K and the measured data have been correlated using the modified Soave–Redlich–Kwong (MSRK) equation of Sandarusi et al. [5] with the simple mixing rule of Adachi and Sugie [6].

Cubic equations of state based on the pioneering work of van der Waals [7], such as the SRK [8] and Peng–Robinson [9] equations, are widely used in process and product design calculations, and have been applied to study the vapor–liquid equilibria

(VLE) of CO₂ containing systems; however, while these equations perform well in the correlation of experimental data, they typically fail in their ability to predict the phase behavior of non-ideal mixture systems based on pure component parameters alone. As a result, increasingly industrial and academic groups alike are turning to molecular based equation of state, like the statistical associating fluid theory (SAFT) [10,11] as such equations directly take into account the effects of molecular shape and interactions on the thermodynamics properties. Furthermore, because of the physically based nature of the model parameters, such equations are generally more successful in predicting phase behavior. The SAFT approach in particular has been applied in recent years to study the thermodynamic properties and phase behavior of a wide range of fluid systems [12–14].

In this work, we have applied the SAFT-VR [15,16] equation, which was developed in the late 90s to model fluids as hard chains that interact through a potential of variable attractive range, to examine the carbon dioxide binary mixtures studied experimentally and test the ability of the theory to predict the phase behavior. The SAFT-VR approach has been successfully applied to study the phase behavior of a wide range of fluids and in particular CO₂ + *n*-alkanes have been studied by Galindo and Blas [17,18], while Colina et al. [19] have studied both CO₂ + alkanes and CO₂ + perfluoroalkanes.

* Corresponding author. Tel.: +81 3 3259 0814; fax: +81 3 3293 7572.

E-mail address: tochigi@chem.cst.nihon-u.ac.jp (K. Tochigi).

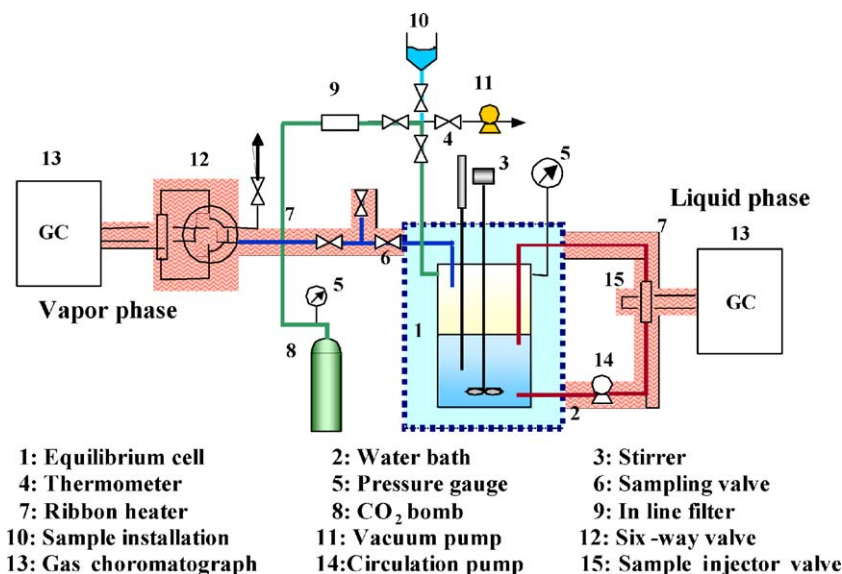


Fig. 1. Schematic diagram of the experimental apparatus.

2. Experimental

2.1. Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. The apparatus is similar to that used by Sako et al. [4] and is a static-type apparatus composed of three parts; the equilibrium cell, the vapor–liquid sampling system, and the analyzing system. The experimental equipment was designed to permit the determination of equilibrium phase compositions in a temperature range from 295 to 323 K and at pressures up to 15.0 MPa.

In the equilibrium system, the cell has an internal capacity of approximately 500 cm³ and is equipped with a Pyrex glass bull's-eye window to observe the interface between the phases. The equilibrium cell and sampling system are in a thermostated water bath. The injector valve shown in Fig. 1 (#15) is used to sample the liquid phase, while the sample valve (#6) is used for the vapor phase. The equilibrium temperature is measured with a calibrated platinum resistance thermometer (Pt 100 Ω) with an accuracy of ±0.03 K and the equilibrium pressure measured using a pressure sensor (DPI-145, Druck Co.) with an accuracy of ±0.040% F.S. (full scale). Compositional analysis of the vapor and liquid samples is performed with a Shimadzu gas chromatograph type GC-14A equipped with a thermal conductivity cell. Porapak Q was used as the column packing and helium as the carrier gas. The composition was determined using the relative area method with an accuracy of ±0.005 in mole fraction.

2.2. Procedure

Solvent (*n*-octane, methanol, ethanol, perfluorohexane) was placed in the equilibrium cell and CO₂ added until the desired pressure is achieved. After confirmation that the pressure in the equilibrium cell is constant, the temperature and pressure are measured. At that time, small samples in the vapor and liquid phases are removed using the sampling valves and introduced into the sampling system. After all the samples are introduced into the gas chromatograph, the composition of each sample can be determined. Special-grade *n*-octane, methanol, ethanol, perfluorohexane of 99.6 mol% purity were supplied by Wako Pure Chem. Co. Ltd. Carbon dioxide gas with a purity of 99.99 + mol% was supplied from Showa Tansan Co. Ltd. All reagents were used without further purification.

3. Experimental results

VLE measurements have been made for the binary systems of CO₂ + *n*-octane, CO₂ + methanol, and CO₂ + ethanol at 313.14 K. The experimental VLE data for the CO₂ + *n*-octane system are reported in Table 1 and are represented graphically in Fig. 2. Fig. 2 shows the agreement between the experimental data and the literature values at 313.15 K by Weng et al. [20] and at 313.2 K by Yu et al. [21]. The average absolute deviations in total pressure between these measurements and the experimental data reported herein are 3.4 and 4.7% at 313.15 K and 313.2 K respectively.

The experimental VLE data for the CO₂ + methanol system are given in Table 2 and are shown graphically in Fig. 3(a). Fig. 3(a) shows the agreement between the experimental data and the literature values at 313.14 by Chang et al. [22], at 313.15 by Ohgaki et al. [23], at 313.15 by Joung et al. [24], and at 313.2 K by Yoon et al. [25], respectively. The average absolute deviations in total pressure in comparison to each of these previously

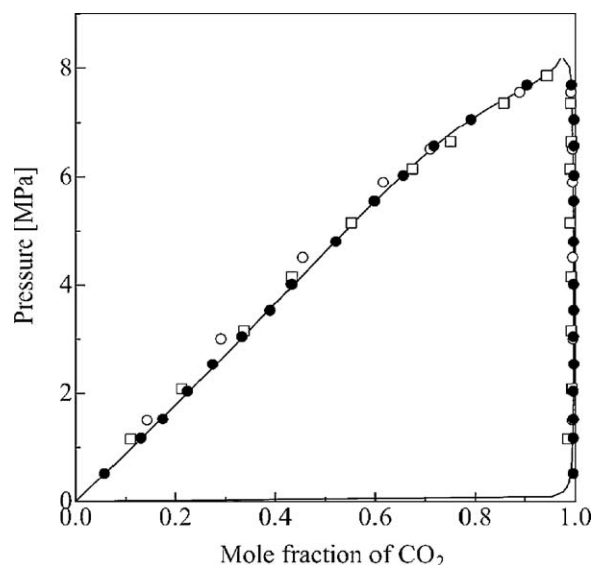
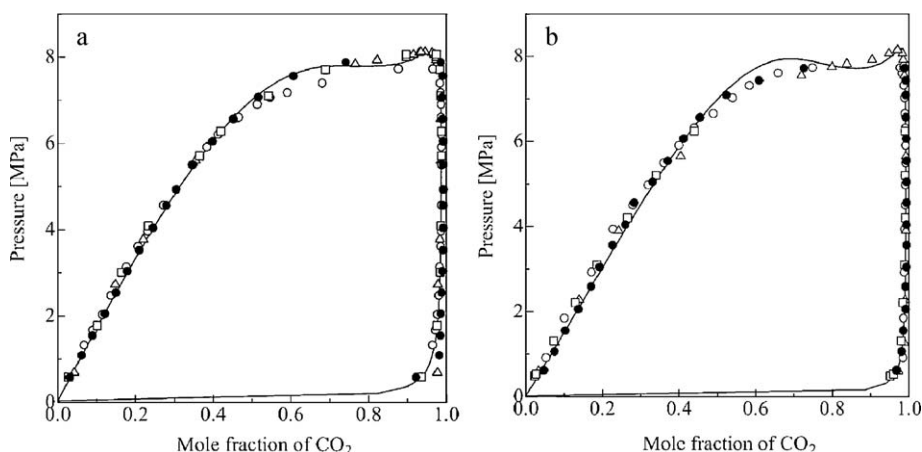


Fig. 2. Experimental VLE data for CO₂ + *n*-octane system at 313.14 K. •, this work; ○, Weng et al. [20]; □, Yu et al. [21]; ---, MSRK equation.

Table 1
Experimental VLE data for CO₂ (1) + *n*-octane (2) system at 313.14 K.

<i>P</i> [MPa]	<i>x</i> ₁	<i>y</i> ₁	<i>P</i> [MPa]	<i>x</i> ₁	<i>y</i> ₁
0.520	0.0588	0.9966	4.011	0.4333	0.9973
1.167	0.1311	0.9969	4.797	0.5219	0.9971
1.521	0.1752	0.9970	5.541	0.5990	0.9975
2.035	0.2249	0.9966	6.019	0.6565	0.9981
2.532	0.2744	0.9979	6.558	0.7187	0.9981
3.040	0.3337	0.9971	7.051	0.7920	0.9985
3.522	0.3905	0.9976	7.683	0.9049	0.9928

**Fig. 3.** Experimental VLE data for (a) CO₂ + methanol and (b) CO₂ + ethanol systems at 313.14 K. (a) ●, this work; ○, Chang et al. [22]; □, Ohgaki et al. [23]; ⊗, Joung et al. [24]; ◇, Yoon et al. [25]; ----, MSRK equation. (b) ●, this work; ○, Chang et al. [22]; □, Galicia-Luna et al. [26]; ⊗, Yoon et al. [25]; ----, MSRK equation.

reported studies are 3.9, 4.1, 3.1 and 0.7% at 313.14, 313.15, 313.15, and 313.2 K respectively. The experimental VLE data for the CO₂ + ethanol system are presented in Table 3 and shown graphically in Fig. 3(b). From Fig. 3(b), the agreement between the experimental data and the literature values at 313.14, 313.15, and 313.2 K by Chang et al. [22], Galicia-Luna et al. [26], and Yoon et al. [25] respectively can be seen. The average absolute deviations in total pressure are 8.3% at 313.14 K, 8.0% at 313.15 K and 9.8% at 313.2 K.

As can be seen from Figs. 2 and 3, the new experimental data is in all cases in good agreement with the literature values, validat-

Table 2
Experimental VLE data for CO₂ (1) + methanol (2) system at 313.14 K.

<i>P</i> [MPa]	<i>x</i> ₁	<i>y</i> ₁	<i>P</i> [MPa]	<i>x</i> ₁	<i>y</i> ₁
0.573	0.0315	0.9225	4.554	0.2798	0.9923
1.085	0.0624	0.9826	4.926	0.3055	0.9926
1.542	0.0898	0.9853	5.504	0.3490	0.9920
2.048	0.1220	0.9864	6.041	0.3989	0.9920
2.536	0.1504	0.9888	6.557	0.4522	0.9906
3.032	0.1796	0.9903	7.066	0.5165	0.9899
3.521	0.2104	0.9920	7.556	0.6069	0.9909
4.036	0.2456	0.9922	7.873	0.7418	0.9864

Table 3
Experimental VLE data for CO₂ (1) + ethanol (2) system at 313.14 K.

<i>P</i> [MPa]	<i>x</i> ₁	<i>y</i> ₁	<i>P</i> [MPa]	<i>x</i> ₁	<i>y</i> ₁
0.613	0.0480	0.9685	4.552	0.2832	0.9948
1.054	0.0751	0.9813	5.044	0.3313	0.9947
1.546	0.1031	0.9859	5.533	0.3709	0.9943
2.051	0.1375	0.9922	6.061	0.4123	0.9938
2.582	0.1710	0.9916	6.558	0.4550	0.9928
3.041	0.1933	0.9942	7.087	0.5236	0.9926
3.555	0.2267	0.9948	7.427	0.6095	0.9925
4.037	0.2606	0.9942	7.716	0.7261	0.9890

ing the use of the new apparatus for additional systems for which experimental data is not currently available. In this vein, experimental VLE data for the CO₂ + perfluorohexane binary mixture has been measured at 303.15, 313.15 and 323.15 K and are reported in Table 3 and presented graphically in Fig. 4. Fig. 4 shows the agreement between the experimental data and the data of Lazzaroni et al. [27] at 313.14 K. The average absolute deviations in total pressure between the data reported herein and that previously reported is 11.2%, which although higher than that seen for the other systems studied is primarily due to the scatter in the literature data at higher pressures (Table 4).

Table 4
Experimental VLE data for CO₂ (1) + perfluorohexane (2) system.

P [MPa]	x ₁	y ₁	P [MPa]	x ₁	y ₁
303.15 K					
0.479	0.1003	0.8741	3.528	0.6274	0.9798
1.069	0.2247	0.9436	3.986	0.6857	0.9830
1.546	0.3148	0.9570	4.493	0.7517	0.9833
2.159	0.4186	0.9728	4.995	0.8159	0.9861
2.589	0.4883	0.9768	5.445	0.8559	0.9869
2.973	0.5486	0.9806	5.982	0.9117	0.9890
313.15 K					
0.516	0.0961	0.8989	3.979	0.6209	0.9777
1.166	0.2183	0.9480	4.622	0.6970	0.9808
1.454	0.2684	0.9501	5.497	0.7864	0.9818
2.098	0.3512	0.9660	6.016	0.8364	0.9815
2.450	0.4256	0.9662	6.518	0.8719	0.9825
3.032	0.5052	0.9673	7.166	0.9201	0.9798
3.454	0.5588	0.9740			
323.15 K					
0.565	0.0911	0.8467	3.497	0.5232	0.9780
1.083	0.1808	0.9382	4.022	0.5747	0.9769
1.526	0.2551	0.9274	4.488	0.6293	0.9757
2.070	0.3280	0.9564	4.998	0.6763	0.9808
2.545	0.3906	0.9628	5.789	0.7439	0.9890
3.016	0.4720	0.9687	6.296	0.7828	0.9814

4. Discussion

4.1. Correlation of VLE using modified SRK equation

The modified Soave-Redlich-Kwong equation of state proposed by Sandarusi et al. [5] and given by Eq. (1) was used to correlate the VLE results.

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

Using the simple conventional mixing rule proposed by Adachi and Sugie [6] to calculate the cross interactions, the pure component parameters a and b are given by,

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} \quad (2)$$

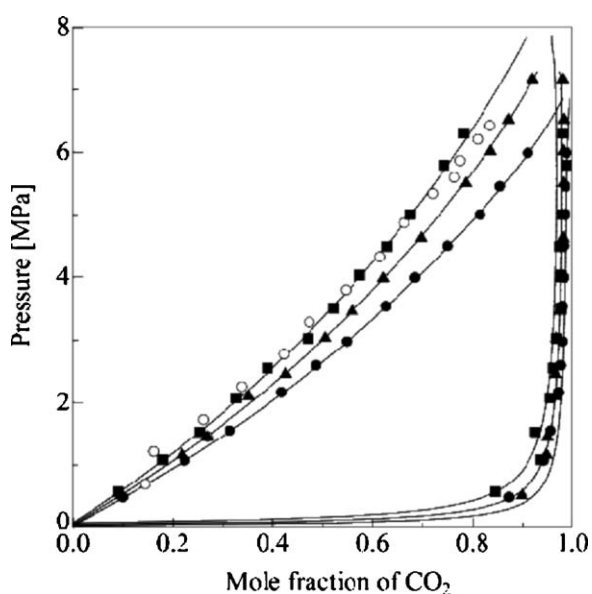


Fig. 4. Experimental VLE data for CO₂ + perfluorohexane system at 303.15, 313.15, and 323.15 K. this work: ●, 303.15 K; ▲, 313.15 K; ■, 323.15 K; ○, Lazzaroni et al. [27]; ---, SRK equation.

$$a_{ij} = \{1 - k_{ij} - l_{ij}(x_i - x_j)\} \sqrt{a_{ii}a_{jj}} \quad (3)$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij} \quad (4)$$

$$b_{ij} = (1 - m_{ij}) \frac{b_i + b_j}{2} \quad (5)$$

where

$$a_{ii} = \frac{0.42748R^2T_{c,i}^2}{P_{c,i}} \alpha_i(T) \\ = \frac{0.42748R^2T_{c,i}^2}{P_{c,i}} \left\{ 1 + (T_{r,i}) \left(m_i + \frac{n_i}{T_{r,i}} \right) \right\} \quad (6)$$

$$b_i = \frac{0.08664RT_{c,i}}{P_{c,i}} \quad (7)$$

and were calculated using Sandarusi et al.'s generalized correlation [5] and are reported in Table 5. The optimized values of k_{ij} , l_{ij} , m_{ij} and the average deviations in the total pressure and vapor composition are given in Table 6. The correlated VLE employing these values are shown in Figs. 2–4, from which we can see that although the theory is in good agreement with the experimental data, it incorrectly predicts liquid–liquid immiscibility for both for the CO₂ + methanol and CO₂ + ethanol mixtures near the critical point.

4.2. Prediction of VLE using the SAFT-VR equation

In the SAFT-VR approach, molecules are described as chains of m tangentially bonded hard spherical segments of diameter σ that interact via a square well potential of depth ε and width λ and short range association sites to mimic hydrogen bonding as appropriate. For the n -alkanes and alcohols, a simple empirical relationship is

Table 5
Pure component parameters used in the modified SRK equation of state [5].

Compound	T _c [K]	P _c [bar]	m	N
CO ₂	304.1	73.8	0.5809	0.2727
n -octane	568.8	24.9	0.8253	0.3164
Methanol	512.6	80.9	1.3013	0.2005
Ethanol	513.9	61.4	1.1545	0.4047

Table 6
Binary parameters used in the Adachi and Sugie mixing rule and deviations between experimental and calculated vapor compositions and total pressures.

System	T [K]	k_{ij}	l_{ij}	m_{ij}	$ \Delta y_1 _{av}$ [mol%]	$ \Delta P/P _{av}$ [%]
CO ₂ + n-octane	313.14	0.1200	−0.0069	0.0012	0.2	0.7
CO ₂ + methanol	313.14	0.1054	−0.0164	0.0555	0.8	0.7
CO ₂ + ethanol	313.14	0.0616	0.0319	−0.0185	0.2	2.0
CO ₂ + perfluorohexane	303.15	0.0639	−0.0121	0.0348	0.76	0.38
CO ₂ + perfluorohexane	313.15	0.0636	−0.0132	0.0391	0.36	1.03
CO ₂ + perfluorohexane	323.15	0.0523	0.0072	0.0347	1.20	1.27

used to determine the number of spherical segments m in the model chain in relation to the number of carbon atoms, viz $m = 0.33(C-1) + 1$ for n -alkanes [28,29] and $m = 0.33(C-1) + 1.2$ for alcohols [30]. The remaining model parameters are determined by fitting to pure component experimental vapor pressure and saturated liquid density data. The optimized parameters for n -octane were taken from earlier work [31] and those for carbon dioxide taken from the work of Blas and Galindo [17,18], those for perfluorohexane taken from the work of Colina et al. [19]. SAFT-VR parameters for methanol and ethanol were determined in this work by fitting to vapor pressure and saturated liquid density data for each pure component using a 3-site model to mimic the hydrogen bonding interactions between the alcohol molecules. The pure component parameters used for CO₂, n -octane, methanol and ethanol are reported in Table 7.

In the SAFT-VR approach the Helmholtz free energy for a fluid mixture of associating chain molecules is given by,

$$\frac{A}{NkT} = a^{\text{Ideal}} + a^{\text{Mono.}} + a^{\text{Chain}} + a^{\text{Assoc.}} \quad (8)$$

where a^{Ideal} is the ideal free energy, $a^{\text{Mono.}}$ is the excess free energy due to the monomer segments, a^{Chain} is the contribution due to the formation of chains from the monomer segments, and $a^{\text{Assoc.}}$ the contribution due to association interactions.

The ideal Helmholtz free energy for a mixture with n components is given by,

$$a^{\text{Ideal}} = \sum_{i=1}^n x_i \ln \rho_i \Lambda_i^3 - 1 \quad (9)$$

where n is the number of species, $\rho_i = N_i/V$ is the molecular number density, x_i the mole fraction and Λ_i the thermal de Broglie wavelength of component i .

The monomer free energy is written as a high temperature perturbation expansion about the hard-sphere (HS) reference system, viz [32–34]

$$a^{\text{Mono.}} = a^{\text{HS}} + \beta a_1 + \beta^2 a_2 \quad (10)$$

where $\beta = 1/kT$, and a_1 and a_2 are the first and second perturbation terms associated with the attractive energy $-\varepsilon_{ij}$. When dealing with mixtures based on equations for pure fluids, appropriate mixing rules are necessary to specify the composition dependence and in this work the van der Waals one-fluid mixing rule [35,36] is used in the perturbation terms for the monomer interactions, which corresponds to the MX1b mixing rule of Galindo et al. [13].

Table 7
SAFT-VR parameters for CO₂, n -octane, methanol (3 sites), ethanol (3 sites) and perfluorohexane.

Parameter	CO ₂ [17]	n -octane [31]	methanol	ethanol	Perfluorohexane [19]
M	2.0	3.333	1.2000	1.533	2.850
λ	1.515727	1.574	1.5374	1.4838	1.439
σ	2.7864	3.945	3.6568	3.7965	4.529
ε	179.27	250.3	340.4	337.6	277.33
ε_{HB}	–	–	1966	2087	–
K_{HB}	–	–	0.2900	0.2873	–

The contribution to the free energy due to the formation of chain molecules from square-well segments is given by,

$$a^{\text{Chain}} = - \sum_{i=1}^n x_i (m_i - 1) \ln [g_0^{\text{HS}} \{ \sigma_{ii}^{\text{eff}}(\lambda_{ii}) + \beta \varepsilon_{ii} g_1^{\text{ii}}(\sigma_{ii}) \}] \quad (11)$$

where the term $g_1^{\text{ii}}(\sigma_{ii})$ is obtained from a self-consistent calculation of the pressure using the Clausius virial theorem and the first derivative of the free energy with respect to the density [12].

Finally, the contribution due to association is obtained as [7]:

$$\frac{A^{\text{Assoc.}}}{NkT} = \sum_{a=1}^s \left(\ln X_a - \frac{X_a}{2} \right) + \frac{s}{2} \quad (12)$$

where the sum is over all s sites of type a on a molecule and X_a is the fraction of molecules not bonded at site a :

$$X_a = \frac{1}{1 + \sum_{b=1}^s \rho X_b \Delta_{a,b}} \quad (13)$$

The function $\Delta_{a,b}$ characterizes the association between site a and site b on different molecules and can be written as

$$\Delta_{a,b} = K_{a,b} f_{a,b} g^M(\sigma) \quad (14)$$

where, $g^M(\sigma)$ is the contact value of the monomer–monomer radial distribution function, $f_{a,b} = \exp(-\varepsilon_{a,b}^{\text{HB}}/kT)^{-1}$ is the Mayer f function of the a – b site-site bonding interaction $\varepsilon_{a,b}^{\text{HB}}$, and $K_{a,b}$ is the volume available for bonding [8]. For full details of the expressions of the SAFT-VR equation of state for the square-well potential the reader is directed to the original references [12,13].

The unlike or cross interactions needed to study mixture phase behavior were obtained from the Lorentz–Berthelot combining rules:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (15)$$

$$\varepsilon_{ij} = \xi_{ij} (\varepsilon_{ii} \varepsilon_{jj})^{1/2} \quad (16)$$

where deviations from the geometric mean can be accounted for through the binary interaction parameter ξ_{ij} . The unlike range parameter was determined from the arithmetic mean, viz

$$\lambda_{ij} = \gamma_{ij} \left(\frac{\sigma_{ii} \lambda_{ii} + \sigma_{jj} \lambda_{jj}}{\sigma_{ii} + \sigma_{jj}} \right) \quad (17)$$

When ξ_{ij} and γ_{ij} are unity the SAFT-VR approach becomes completely predictive in the sense that no parameters are fitted to experimental data for the mixtures being studied.

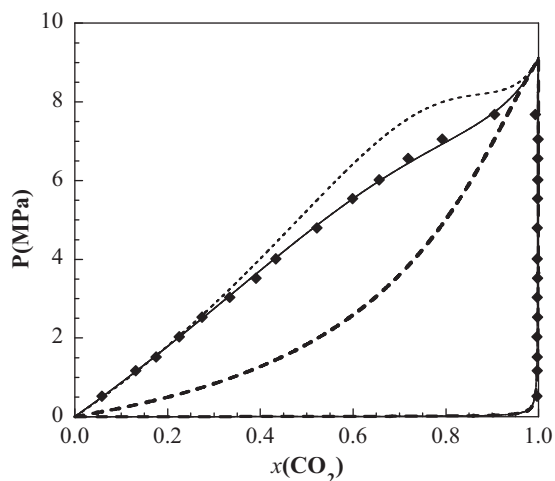


Fig. 5. P - x slice of the $\text{CO}_2 + n$ -octane phase diagram at 313.14 K. Dashed lines correspond to SAFT-VR predictions using Lorentz–Berthelot combining rules, dotted lines to predictions using $\xi_{12} = 0.88$ and $\gamma_{12} = 0.989$ obtained from the work of Galindo and Blas [17,18], and solid lines using $\xi_{12} = 0.7089$ and $\gamma_{12} = 1.079$ fitted to the experimental data.

In Fig. 5 we present the SAFT-VR predictions for the $\text{CO}_2 + n$ -octane system at 313.15 K. From the figure it can be seen that using Lorentz–Berthelot combining rules the theory significantly over-predicts the liquid phase compositions. This is to be expected given the non-ideal nature of the $\text{CO}_2 + n$ -octane binary mixture, which exhibits type II phase behavior in the classification scheme due to van Konynenburg and Scott [37,38]. Blas and Galindo [17,18] performed an extensive study of the continuous transition of phase behavior from type I to types II, III and IV for carbon dioxide + n -alkane binary mixtures with the SAFT-VR equation and proposed a set of transferable parameters for use in Eqs. (8) and (10). Using these values ($\xi_{12} = 0.88$ and $\gamma_{12} = 0.989$) better agreement with experimental data is obtained at low carbon dioxide concentrations; however, the cross interactions optimized by Blas and Galindo [17,18] were determined using parameters re-scaled to the experimental critical point and by fitting to the high pressure critical lines of the carbon dioxide + n -tridecane system and so some deviation is to be expected. Of course, if the cross interactions are fitted to the experimental data reported, very good agreement is obtained; the

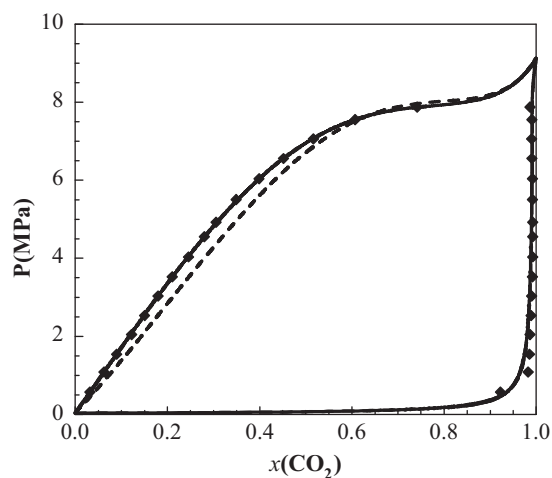


Fig. 6. P - x slice of the $\text{CO}_2 + \text{methanol}$ phase diagram at 313.14 K. Dashed lines correspond to SAFT-VR predictions using Lorentz–Berthelot combining rules and solid lines obtained using $\xi_{12} = 0.9316$ and $\gamma_{12} = 1.0230$ fitted to the experimental data.

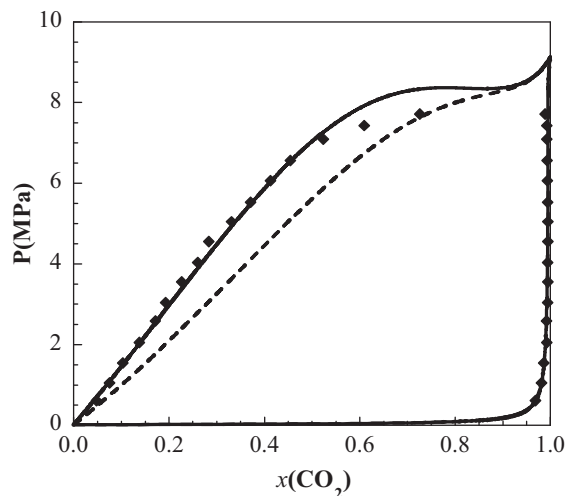


Fig. 7. P - x slice of the $\text{CO}_2 + \text{ethanol}$ phase diagram at 313.14 K. Dashed lines correspond to SAFT-VR predictions using Lorentz–Berthelot combining rules and solid lines obtained using $\xi_{12} = 0.9723$ and $\gamma_{12} = 0.9972$ fitted to experimental data.

average deviations between the experimental compositions and total pressures are 0.12 mol% and 1.4%, respectively. We note that since the CO_2 is supercritical at 313.14 K the theory over-predicts the vapor pressure of CO_2 , this could be avoided by rescaling the optimized model parameters to the experimental pure component critical points, as in the work of Blas and Galindo, or by incorporating a crossover treatment into the theory as in the SAFT-VRX approach [39,40].

For $\text{CO}_2 + \text{methanol}$ and $\text{CO}_2 + \text{ethanol}$ systems at 313.15 K, the VLE have again been predicted using Lorentz–Berthelot cross interactions. As can be seen from Figs. 6 and 7 good agreement with the experimental data is observed, since both the methanol and ethanol phase diagrams display type I phase behavior in the classification scheme due to Scott and van Konynenburg [37,38]. A deviation of only 0.6% in composition and 12% in pressure is seen for the $\text{CO}_2 + \text{methanol}$ system, while deviations of 0.34% and 25% are seen for the $\text{CO}_2 + \text{ethanol}$ system. We note that although the deviations

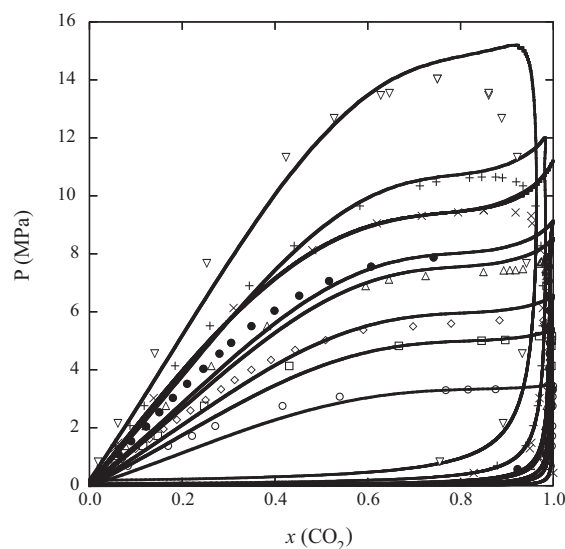


Fig. 8. P - x slices of the $\text{CO}_2 + \text{methanol}$ phase diagram at different temperatures. Solid lines correspond to SAFT-VR predictions using Lorentz–Berthelot combining rules, while symbols correspond to the experimental data: \circ , 273.15 K [41]; \square , 290.00 K [41]; \diamond , 298.15 K [23]; \triangle , 310.00 K [41]; \bullet , 313.14 K (this work); \times , 323.20 K [42]; $+$, 330.00 K [41]; ∇ , 352.60 K [42].

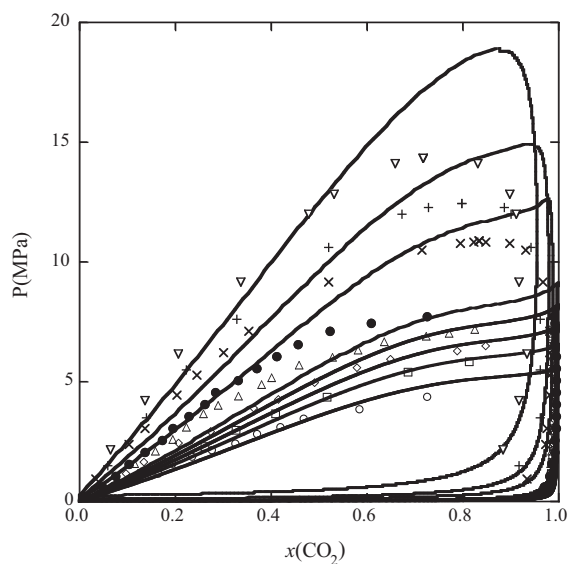


Fig. 9. P - x slices of the CO_2 + ethanol phase diagram at different temperatures. Solid lines correspond to SAFT-VR predictions using Lorentz–Berthelot combining rules, while symbols correspond to the experimental data: \circ , 291.15 K [43]; \square , 298.16 K [43]; \diamond , 303.18 K [43]; \triangle , 308.15 K [43]; \bullet , 313.14 K (this work); \times , 333.75 K [30]; $+$, 348.40 K [21]; ∇ , 373.00 K [30].

in pressure are significant, these are pure predictions and the theory predicts the correct type of phase behavior. Again a more accurate representation of the phase diagram can be obtained by fitting the cross interactions. For CO_2 + methanol we obtain $\xi_{12} = 0.9316$ and $\gamma_{12} = 1.0230$, which results in deviations of 0.51% and 0.46% in the composition and pressure respectively. Similarly, for CO_2 + ethanol if the cross interaction parameters are fitted to the experimental data we obtain $\xi_{12} = 0.9723$ and $\gamma_{12} = 0.9972$ with deviations of 0.18% and 4.03% in the composition and pressure respectively. The greater deviations observed for the CO_2 + ethanol system can be explained by the increased over-prediction in the critical region.

With the SAFT-VR approach we have also predicted the phase behavior for the CO_2 + methanol and CO_2 + ethanol binary mixtures

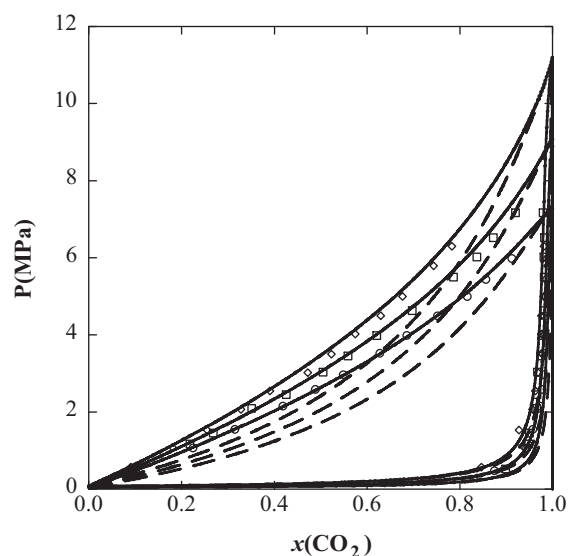


Fig. 10. P - x slices of the CO_2 + perfluorohexane phase diagram at different temperatures. Dashed lines correspond to SAFT-VR predictions using Lorentz–Berthelot combining rules, and solid lines obtained using $\xi_{12} = 0.9723$ and $\gamma_{12} = 0.9972$ fitted to the experimental data. Symbols correspond to the experimental data: \circ , 303.15 K (this work); \square , 313.15 K (this work); \diamond , 323.15 K (this work).

using the Lorentz–Berthelot cross interactions at other temperatures and pressures and compare the results with the available experimental data in Figs. 8 and 9. From the figures we can see that the phase behavior in both systems is correctly predicted to be type I, with no liquid–liquid immiscibility, as seen at 313.14 K in the experimental data reported herein and predicted by the SAFT-VR equation.

Finally in Fig. 10 we consider the CO_2 + perfluorohexane system at 303.15 K, 313.15 K and 323.15 K. From the figure, it can be seen that although the correct phase behavior is predicted using the Lorentz–Berthelot cross interactions, the theory slightly under-predicts the liquid phase compositions. Again, better agreement with the experimental data can be obtained by fitting the cross interactions to the experimental data. By fitting to the experimental data at 303.15 K, we obtain cross interactions of $\xi_{12} = 0.8107$ and $\gamma_{12} = 1.0470$, which can then be used to predict the phase behavior at the other temperatures studied. Using these modified cross interactions, the average deviation between experimental compositions and total pressures are 0.78 mol% and 2.79%, respectively.

5. Conclusions

High-pressure vapor–liquid equilibrium data for carbon dioxide + n -octane, +methanol, and +ethanol systems at 313.14 K and carbon dioxide + perfluorohexane at 303.15–323.15 K have been measured using a newly developed equilibrium still. The measured data have been correlated using a modified SRK equation by Sandarusi et al. with a simple mixing rule by Adachi and Sugie and predicted using the SAFT-VR equation. While the modified SRK equation is able to accurately correlate the experimental data, liquid–liquid immiscibility is predicted at high pressures that is not seen experimentally. The SAFT-VR equation is able to predict the correct phase behavior for the carbon dioxide + methanol, +ethanol and +perfluorohexane systems without fitting any cross interactions to experimental data; however, for the carbon dioxide + n -octane system, where the phase diagram shows significant deviations from ideality, fitted binary interaction parameters are needed to predict the correct phase behavior.

References

- [1] Y. Arai, T. Sako, Y. Takebayashi, *Supercritical Fluids*, Springer, Berlin, Germany, 2001.
- [2] R.S. Haszeldine, *Science* 325 (5948) (2009) 1647–1652.
- [3] S. Chu, Carbon capture and sequestration, *Science* 325 (5948) (2009) 1599–11599.
- [4] T. Sako, T. Sugeta, N. Nakazawa, K. Otake, M. Sato, K. Ishihara, M. Kato, High pressure vapor–liquid and vapor–liquid–liquid equilibria for systems containing supercritical carbon dioxide, water and furfural, *Fluid Phase Equilibria* 108 (1995) 293–303.
- [5] J.A. Sandarusi, A.J. Kidnay, V.F. Yesavage, Compilation of parameters for a polar fluid Soave–Redlich–Kwong equation of state, *Industrial Engineering Chemistry, Process Design & Development* 25 (1986) 957–963.
- [6] Y. Adachi, S. Sugie, A new mixing rule – modified conventional mixing rule, *Fluid Phase Equilibria* 28 (1986) 103–118.
- [7] J.D. van der Waals, Thesis, University of Leiden, 1873; English translation and introductory essay by J.S. Rowlinson, *On the Continuity of Gaseous and Liquid States*, *Studies in Statistical Mechanics*, vol. 14, North Holland, Amsterdam, 1988.
- [8] G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, *Chemical Engineering Science* 37 (1972) 1197–1203.
- [9] D.Y. Peng, D.B. Robinson, A new two-constant equation of state, *Industrial Engineering Chemistry, Fundamentals* 15 (1976) 59–64.
- [10] W.G. Chapman, G. Jackson, K.E. Gubbins, Phase-equilibria of associating fluids chain molecules with multiple bonding sites, *Molecular Physics* 65 (1988) 1057–1079.
- [11] G. Jackson, W.G. Chapman, K.E. Gubbins, Phase-equilibria of associating fluids—spherical molecules with multiple bonding sites, *Molecular Physics* 65 (1988) 1–31.
- [12] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, Statistical associating fluid theory for chain molecules with attractive potentials of variable range, *J. Chemical Physics* 106 (1997) 4168–4186.

- [13] A. Galindo, L.A. Davies, A. Gil-Villegas, G. Jackson, The thermodynamics of mixtures and the corresponding mixing rules in the SAFT-VR approach for potentials of variable range, *Molecular Physics* 93 (1998) 241–252.
- [14] E.A. Muller, K.E. Gubbins, Molecular-based equations of state for associating fluids: a review of SAFT and related approaches, *Industrial Engineering Chemistry, Research* 40 (2001) 2193–2211.
- [15] I.G. Economou, Statistical associating fluid theory: A successful model for the calculation of thermodynamic and phase equilibrium properties of complex fluid mixtures, *Industrial Engineering Chemistry, Research* 41 (2002) 953–962.
- [16] C. McCabe, A. Galindo, SAFT Associating Fluids and Fluid Mixtures, in: J.V. Sengers, A.R.H. Goodwin, C.J. Peters (Eds.), *Applied Thermodynamics of Fluids*, Royal Society of Chemistry, Cambridge, 2010.
- [17] A. Galindo, F.J. Blas, Theoretical examination of the global fluid phase behavior and critical phenomena in carbon dioxide + n-alkane binary mixtures, *J. Physical Chemistry B* 106 (2002) 4503–4515.
- [18] F.J. Blas, A. Galindo, Study of the high pressure behaviour of CO₂ + n-alkane mixtures using the SAFT-VR approach with transferable parameters, *Fluid Phase Equilibria* 194/197 (2002) 501–509.
- [19] C.M. Colina, A. Galindo, F.J. Blas, K.E. Gubbins, Phase behavior of carbon dioxide mixtures with n-alkanes and n-perfluoroalkanes, *Fluid Phase Equilibria* 222/223 (2004) 77–85.
- [20] W.L. Weng, M.J. Lee, Vapor–liquid equilibrium of the octane/carbon dioxide, octane/ethane, and octane/ethylene systems, *J. Chemical Engineering Data* 37 (1992) 213–215.
- [21] J. Yu, S. Wang, Y. Tian, Experimental determination and calculation of thermodynamic properties of CO₂ + octane to high temperatures and high pressures, *Fluid Phase Equilibria* 246 (2006) 6–14.
- [22] C.J. Chang, K.-L. Chiu, C.-Y. Day, A new apparatus for the determination of P–x–y diagrams and Henry’s constants in high pressure alcohols with critical carbon dioxide, *J. Supercritical Fluids* 12 (1998) 223–237.
- [23] K. Ohgaki, T. Katayama, Isothermal vapor–liquid equilibrium data for binary systems containing carbon dioxide at high pressures: methanol–carbon dioxide, n-hexane–carbon dioxide, and benzene–carbon dioxide systems, *J. Chemical Engineering Data* 21 (1976) 53–55.
- [24] S.N. Joung, C.W. Yoo, H.Y. Shin, S.Y. Kim, K.P. Yoo, C.S. Lee, W.S. Huh, Measurements and correlation of high-pressure VLE of binary CO₂–alcohol systems (methanol, ethanol, 2-methoxyethanol and 2-ethoxyethanol), *Fluid Phase Equilibria* 185 (2001) 219–230.
- [25] J.-H. Yoon, H.-S. Lee, H. Lee, High-pressure vapor–liquid equilibria for carbon dioxide + methanol, carbon dioxide + ethanol, and carbon dioxide + methanol + ethanol, *J. Chemical Engineering Data* 38 (1993) 53–55.
- [26] L.A. Galicia-Luna, A. Ortega-Rodríguez, New apparatus for the fast determination of high pressure vapor–liquid equilibria of mixtures and accurate critical pressures, *J. Chemical Engineering Data* 45 (2000) 265–271.
- [27] M.J. Lazzaroni, D. Bush, J.S. Brown, C.A. Eckert, High-pressure vapor–liquid equilibria of some carbon dioxide + organic binary systems, *J. Chemical Engineering Data* 50 (2005) 60–65.
- [28] G. Jackson, K.E. Gubbins, Mixtures of associating spherical and chain molecules, *Pure Applied Chemistry* 61 (1989) 1021–1026.
- [29] A. Galindo, P.J. Whitehead, G. Jackson, A.N. Burgess, Predicting the high-pressure equilibria of water + n-alkanes using simplified SAFT theory with transferable intermolecular interaction parameters, *J. Physical Chemistry* 100 (1996) 6781–6792.
- [30] M.N. Garcıa-Lisbona, A. Galindo, G. Jackson, A.N. Burgess, An examination of the cloud curves of liquid–liquid immiscibility in aqueous solutions of alkyl polyoxyethylene surfactants using the SAFT-HS approach with transferable parameter, *J. American Chemical Society* 120 (1998) 4191–4199.
- [31] C. McCabe, G. Jackson, SAFT-VR modelling of the phase equilibrium of long-chain n-alkanes, *Physical Chemistry, Chemical Physics* 1 (1999) 2057–2064.
- [32] J.A. Barker, D. Henderson, Perturbation theory and equation of state for fluids—square-well potential, *J. Chemical Physics* 47 (1967) 2856–2861.
- [33] P.J. Leonard, D. Henderson, J.A. Barker, Perturbation theory and liquid mixtures, *Transaction Faraday Society* 66 (1970) 2439–2452.
- [34] J.A. Barker, D. Henderson, What is liquid: understanding states of matter, *Reviews of Modern Physics* 48 (1976) 587–671.
- [35] L.L. Lee, *Molecular Thermodynamic of Nonideal Fluids*, Butterworth, London, 1988.
- [36] J.S. Rowlinson, F.L. Swinton, *Liquid and Liquid Mixtures*, Third ed., Butterworth Scientific, London, 1982.
- [37] R.L. Scott, P.H. van Konynenburg, 2. Static properties of solutions. Van der Waals and related models for hydrocarbon mixtures, *Discussion Faraday Society* 49 (1970) 87–97.
- [38] P.H. van Konynenburg, R.L. Scott, Critical lines and phase equilibria in binary van der Waals mixtures, *Philosophical Transactions of the Royal Society of London, Series A* 298 (1980) 495–540.
- [39] C. McCabe, S.B. Kiselev, Application of crossover theory to the SAFT-VR equation of state: SAFT-VRX for pure fluids, *Industrial Engineering Chemistry, Research* 43 (2004) 2839–2851.
- [40] L. Sun, H. Zhao, S.B. Kiselev, C. McCabe, Predicting mixture phase equilibria and critical behavior using the SAFT-VRX approach, *J. Physical Chemistry B* 109 (2005) 9047–9058.
- [41] J.H. Hong, R. Kobayashi, Vapor-Liquid Equilibrium Studies for the Carbon Dioxide–Methanol System, *Fluid Phase Equil.* 41 (1988) 269–276.
- [42] Leu, S.Y.-K. Chung, D.B. Robinson, The equilibrium phase properties of (carbon dioxide + methanol), *J. Chem. Thermody.* 23 (1991) 979–985.
- [43] C.J. Chang, S.-Y. Day, C.-M. Ko, K.-L. Chiu, Densities and P–x–y diagrams for carbon dioxide dissolution in methanol, ethanol, and acetone mixtures, *Fluid Phase Equil.* 131 (1997) 243–258.