

High Pressure Phase Behavior of Carbon Dioxide in Carbon Disulfide and Carbon Tetrachloride

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ABSTRACT: The knowledge about the nature of the interactions between carbon dioxide (CO₂) and different organic molecules is of relevance for designing, operating, and optimizing many industrial processes. In fact, numerous studies concerning the interactions of CO₂ with other compounds have been presented, using both experimental and theoretical approaches. As part of a continuing effort to fully understand the interactions between CO₂ and different compounds, the high pressure phase equilibria of CO₂ binary systems containing carbon disulfide (CS₂) and carbon tetrachloride (CCl₄) were here investigated, involving experimental measurements of high pressure phase equilibria and modeling with the cubic plus association (CPA) equation of state (EoS). The CCl₄ and CS₂ were chosen due to their similar structure to CH₄ and CO₂, respectively, allowing to anticipate the interactions between like and unlike molecules that can be found at binary and multicomponent systems constituted by CO₂ and/or CH₄. It was found that CO₂ + CS₂ presents strong positive deviations to ideality while the CO₂ + CCl₄ system presents an almost ideal behavior.

INTRODUCTION

Carbon dioxide, being easily available at high purity, cheap, nontoxic, and nonflammable,¹ is currently considered as an important industrial solvent for many applications. Knowledge about the nature of the interactions between CO₂ and different organic molecules is of relevance for designing, operating, and optimizing many industrial processes, such as CO₂ supercritical fluid extraction and enhanced oil recovery, through CO₂ flooding or CO₂ emissions capture and from fossil fuel-fired power plants.²

Numerous studies concerning the interactions of CO₂ with other compounds have been presented, using both experimental and theoretical approaches.^{3–13} CO₂ can be, depending on the nature of the other organic molecule, an electron acceptor or donor or a proton acceptor forming hydrogen bonds.¹⁴ In the presence of Lewis bases such as water, alcohols, ketones, amines, amides, and aromatics, CO₂ acts as a Lewis acid favoring the formation of electron donor–acceptor complexes.^{15–17} For instance, experimental spectroscopic observations put in evidence the presence of strongly attractive alcohol (OH group)–CO₂ interactions, due to highly stable complexes formed through the sp³ O-donating atoms,^{14,15,18,19} and the existence of weaker specific Lewis acid–base interactions between CO₂ and the carboxyl oxygen of esters.²⁰

Raman scattering and ab initio calculations have also shown that CO₂, a linear simple molecule with a large quadruple moment ($-15 \cdot 10^{-40} \text{ C} \cdot \text{m}^2$)²¹ forms dimers with a slipped-parallel (offset face to face) geometry.^{12,22–24}

Recently,^{3,25} it was shown that the nonideality of CO₂ solutions on low volatile compounds (heavy alcohols, alkanes, fatty acids, and fatty acid esters) and its impact on the CO₂

solubility is a result of a complex and delicate balance between the solute–solute, solute–solvent, and solvent–solvent interactions and cannot be inferred from the strength of solute–solvent interactions alone. These multiple interactions that can be found in different CO₂ systems make the description of the phase equilibria of CO₂ containing systems challenging.

The breakthrough in the modeling of polar and highly non-ideal systems in large temperature and pressure ranges came with the development of association equations of state that explicitly take into account the specific interactions between like (self-association) molecules and unlike molecules (cross-association). Molecular-based equations of state, like the statistical associating fluid theory (SAFT)^{9,26–28} and its framework derivatives, group contribution equation of state (GC-EoS)²⁹ and group contribution-associating-equation of state (GCA-EoS),²⁹ just to mention some, have been successfully used to describe the phase equilibria of a wide set of systems as well as to gain deeper insights on these systems molecular interaction. Nonetheless, one of the most successful models of that kind is the cubic-plus-association (CPA) equation of state (EoS) considering its quality, reliability, and wide range of applicability.^{27,28,30}

The CPA EoS was previously used for an adequate description of the vapor–liquid equilibrium (VLE) of an extensive series of CO₂ binary systems containing several nonself-associating, associating, and cross-associating components. A detailed investigation regarding the differing behavior of CO₂ depending on the nature of the second

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component and how the CPA EoS can best describe them was presented.^{25,31}

As part of a continuing effort to fully understand the interactions between CO₂ and different compounds, the phase equilibria of CO₂ binary systems containing CS₂ and CCl₄ were investigated in this work, involving experimental measurements of the phase equilibria at pressures up to 9 MPa and modeling with the CPA EoS. The CCl₄ and CS₂ were chosen due to their similar structure to CH₄ and CO₂, respectively, allowing to anticipate the interactions between like and unlike molecules that can be found at binary and multicomponent systems constituted by CO₂ and/or CH₄.

EXPERIMENTAL SECTION

Materials. The carbon disulfide was acquired from Panreac with mass fraction purities 99.9%, and the carbon tetrachloride was acquired from SDS with mass fraction purities 99.9%, as stated by the supplier.

The carbon dioxide (CO₂) was acquired from Air Liquide with a purity of $\geq 99.998\%$, and H₂O, O₂, C_nH_m, N₂, and H₂ impurity volume fractions were lower than $(3, 2, 2, 8, \text{ and } 0.5) \cdot 10^{-6}$, respectively, as stated by the supplier. All of the compounds were used as received from the supplier without a further purification procedure.

Experimental Equipment. The high pressure equilibrium cell used in this work is based on a cell designed by Daridon et al.^{32–36} using the synthetic method and can operate up to pressures of 100 MPa and in the (283 to 373) K temperature range. The cell consists of a horizontal hollow stainless-steel cylinder closed at one end by a movable piston and at the other end by a sapphire window. This window, along with a second sapphire window on the cell wall, through which an optical fiber lights the cell chamber, allows the operator to follow the behavior of the sample with pressure and temperature. Both the apparatus and the methodology here followed were fully described in previous works^{37–41} and shown to be adequate to accurately measure VLE in a wide range of fluids, pressures, and temperatures.^{32–40} The temperature is measured with a high precision three-wire Pt100 thermometer, with an uncertainty of 0.15 K, connected to a calibrated platinum resistance inserted inside the cell close to the sample. The pressure is measured by a piezoresistive silicon pressure transducer (Kulite) fixed directly inside the cell to reduce dead volumes, that was previously calibrated and certified by an independent laboratory with International Union of Pure and Applied Chemistry (IUPAC) accreditation, following the EN 837-1 standard, with an uncertainty of 0.05 MPa and an accuracy better than 0.2 %.

A fixed amount of solvent is introduced inside the cell; its exact mass is determined by weighing, using a high weight/high precision balance with an accuracy of 1 mg (Sartorius), by means of a flexible capillary.

The CO₂ is introduced under pressure from an ultra light-weight composite cylinder. Its mass is measured with the precision balance and introduced into the measuring cell by means of a flexible high pressure capillary.

After preparation of a mixture, of a known composition, and when the desired temperature at low pressure is reached, the pressure is then slowly increased at constant temperature until the system becomes monophasic. The pressure at which the last bubble disappears represents the equilibrium pressure for the fixed temperature.

Table 1. Experimental Solubility Data of CO₂ (1) + CCl₄ (2)

x_1	T/K	p/MPa	x_1	T/K	p/MPa	x_1	T/K	p/MPa
0.16	293.22	1.09	0.16	313.25	1.57	0.16	333.26	2.10
0.20	293.20	1.38	0.20	313.21	2.00	0.20	333.26	2.67
0.30	293.22	2.04	0.30	313.20	2.93	0.30	333.18	3.87
0.40	293.16	2.61	0.40	313.31	3.79	0.40	333.17	5.02
0.50	293.20	3.07	0.50	313.29	4.49	0.50	333.27	6.04
0.60	293.23	3.51	0.60	313.26	5.15	0.60	333.23	7.02
0.70	293.30	3.84	0.70	313.28	5.73	0.70	333.17	7.85

Table 2. Experimental Solubility Data of CO₂ (1) + CS₂ (2)

x_1	T/K	p/MPa	x_1	T/K	p/MPa	x_1	T/K	p/MPa
0.05	293.32	0.97	0.05	313.33	1.36	0.05	333.21	1.75
0.10	293.24	1.93	0.10	313.28	2.55	0.10	333.18	3.18
0.20	293.32	3.22	0.20	313.21	4.34	0.20	332.97	5.44
0.30	293.36	3.87	0.30	313.36	5.37	0.30	333.12	6.92
0.40	293.29	4.09	0.40	313.25	5.90	0.40	333.17	7.81
0.50	293.25	4.13	0.50	313.23	6.11	0.50	333.16	8.30
0.60	293.18	4.07	0.60	313.24	6.12	0.60	333.12	8.52
0.68	293.20	4.08	0.68	313.16	6.19			
0.89	293.16	4.59	0.89	313.53	7.11			
0.93	293.19	4.74	0.93	313.39	7.39			
0.96	293.33	4.91						

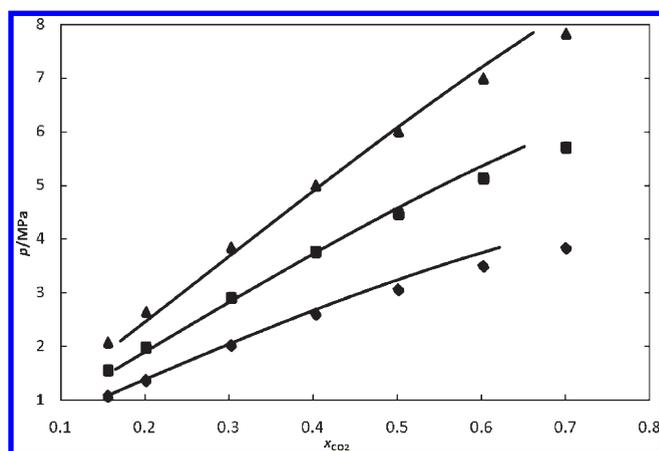


Figure 1. Pressure–composition diagram of the binary systems CO₂ + CCl₄. ♦, 293 K; ■, 313 K; ▲, 333 K. The solid lines represent the CPA EoS predictions with nonassociation.

RESULTS AND DISCUSSION

The solubility of carbon dioxide in carbon disulfide and carbon tetrachloride was measured for mole fractions ranging from (0.05 to 0.7) at 293 K, 313 K, and 333 K in the pressure range of (1 to 9) MPa, as reported in Tables 1 and 2 and depicted in Figures 1 and 2. Apart from the Reiff et al.⁴² work that reported a systematic study around the CO₂ + CS₂ system, there are no, to our knowledge, more data available in literature. As depicted in Figure 3, the data reported by Reiff et al.⁴² present the same phase behavior but with slightly lower CO₂ solubilities than those reported in this work.

The CO₂ solubility on these solvents decreases with temperature and increases with pressure as commonly observed for the

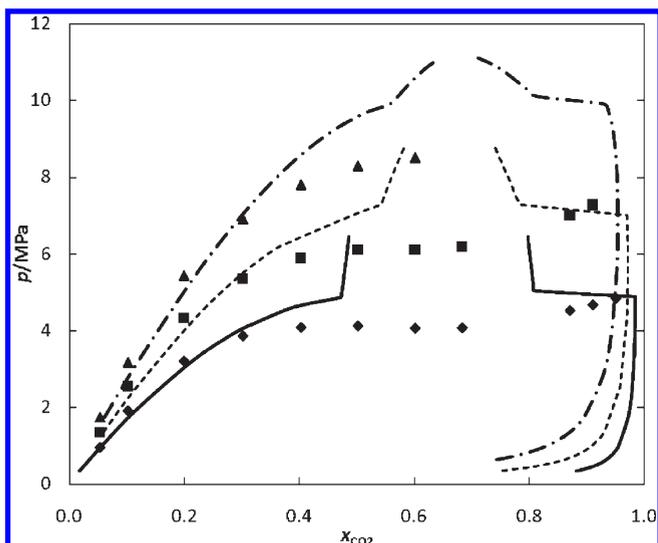


Figure 2. Pressure–composition diagram of the binary systems CO₂ + CS₂. (solid line, ◆), 293 K; (dashed line, ■), 313 K; (dash–dotted line, ▲), 333 K. The lines represent the CPA EoS predictions with nonassociation.

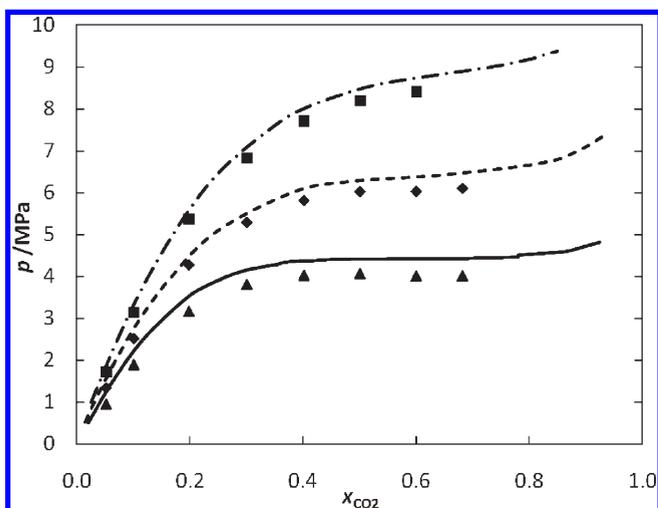


Figure 3. Pressure–composition diagram of the binary systems CO₂ + CS₂. ▲, 293 K; ◆, 313 K; ■, 333 K. The solid lines represent the data reported by Reiff et al.⁴² at solid line, 290 K; dashed line, 310 K, and dash–dotted line, 330 K.

solubility of light gases in liquids.^{37–40} In the CO₂ molar fraction region investigated, the CO₂ + CCl₄ system presents a near linear dependency of the solubility with the CO₂ concentration as shown in Figure 1. For the CO₂ + CS₂ system this linear dependency is observed only at the lowest concentrations of carbon dioxide. For CO₂ concentrations above 0.5 in molar fraction the system seems to reach a plateau in pressure, as depicted in Figure 2.

CPA EoS Modeling. The CPA EoS is composed by two terms: a physical term, that in this work is described by the Soave–Redlich–Kwong equation of state (SRK EoS), that takes into account the physical interactions between the components, and an associating term described by the Wertheim's theory, which accounts for the specific site–site interactions due to hydrogen bonding and solvation effects.²⁷

In terms of the compressibility factor, the CPA EoS is expressed by

$$Z = Z^{\text{phys}} + Z^{\text{assoc}} \quad (1)$$

$$Z^{\text{phys}} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT(1 + b\rho)} \quad (2)$$

$$Z^{\text{assoc}} = \frac{-1}{2} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (3)$$

where a is an energy parameter, b the covolume, ρ the density of the liquid, x_i the mole fraction of the component i , X_{A_i} the mole fraction of pure component i not bonded at site A , and g the simplified radial distribution function⁴³

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad (4)$$

$$\eta = \frac{1}{4} b\rho \quad (5)$$

The energy parameter for pure components is given by a Soave-type temperature dependency

$$a = a_0 [1 + c_1 (1 - \sqrt{T_r})]^2 \quad (6)$$

where T_r is the reduced temperature ($T_r = T/T_c$, T_c being the critical temperature).

X_{A_i} is the central point of the association term and is related to the association strength between two sites belonging to two different molecules

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (7)$$

where B_j represents the summation over all sites and depends on the class of the association scheme and $\Delta^{A_i B_j}$ is the association strength that can be determined by

$$\Delta^{A_i B_j} = g(\rho) \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (8)$$

CPA requires the knowledge of three pure component parameters for the physical part, a_0 , c_1 , and b , and two more for the association term, ε and β . These last two are only present in associating compounds. These parameters are estimated through a simultaneous regression of the liquid density and vapor pressure data, carried by the minimization of the objective function, OF,

$$\text{OF} = \sum_i^{NP} \left(\frac{p_i^{\text{exp}} - p_i^{\text{calc}}}{p_i^{\text{exp}}} \right)^2 + \sum_i^{NP} \left(\frac{\rho_i^{\text{exp}} - \rho_i^{\text{calc}}}{\rho_i^{\text{exp}}} \right)^2 \quad (9)$$

Using physical parameters, estimated from the pure component vapor pressure and liquid density data, represents a major improvement from the conventional cubic equations of state PR (Peng–Robinson) and SRK. In these EoS's the pure compound parameters are calculated from expressions that use component critical data originating a poor description of vapor pressures and liquid densities. On the contrary, with the CPA EoS, the pure compound parameters are estimated by a simultaneous regression of pure component data allowing an accurate description of

Table 3. CPA Pure Compound Parameters for CO₂, CCl₄, and CS₂ and Modeling Results

T range	a ₀		b · 10 ⁵		AAD %
	J · m ³ · mol ⁻²	c ₁	m ³ · mol ⁻¹	p	
CO ₂ T _{melt} – 0.9T _c	0.35	0.76	2.72	0.22	0.83
CCl ₄ 0.45T _c – 0.85T _c	1.9	0.74	8.10	1.01	0.63
CS ₂ 0.45T _c – 0.85T _c	1.14	0.60	4.95	0.76	0.74

liquid densities and especially of vapor pressures that is essential for a good representation of the VLE.

To determine the pure compound parameters of the association term, it is necessary to assign an association scheme, that is, the number and type of association sites for the associating compound. The nomenclature proposed by Huang and Radosz⁴⁴ is usually adopted.

When dealing with mixtures, the energy and covolume parameters of the physical term are calculated employing the conventional van der Waals one-fluid mixing rules.

$$a = \sum_i \sum_j x_i x_j a_{ij} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j (1 - k_{ij})} \quad (10)$$

$$b = \sum_i x_i b_i \quad (11)$$

As will be explained later, the compounds here in consideration will be taken as nonassociating; for mixtures composed of that kind of compounds the association term does not apply, and the binary interaction parameter, k_{ij} , is the only adjustable parameter. The k_{ij} parameter was estimated by minimizing the following objective function

$$\text{OF} = \sum_i^{NP} \left(\frac{x_i^{\text{calc}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right)^2 \quad (12)$$

where x_i is the mole fraction of component i in the phases selected for the optimization.

Considering the CO₂ as a self-associating molecule, applying association equations of state that explicitly take into account hydrogen bonding interactions, is a debatable issue, as discussed by Oliveira et al.²⁵ Nonetheless, from the evaluation of the CPA EoS capability to model the phase equilibria of CO₂ systems with alkanes, alcohols, esters, and acids, it is feasible to conclude that CO₂ can be considered both as an inert or as an associating compound, explicitly accounting or not for the polar interactions, depending on the nature of the other component of the binary system.

With that in mind, phase equilibria of the CO₂ + CCl₄ and CO₂ + CS₂ systems were evaluated with the CPA EoS. For both systems, the components were treated as inert compounds without explicitly accounting for their polarity. The CPA pure compound parameters of the physical term were determined from a simultaneous regression of their vapor pressure and liquid density data, taken from DIPPR.⁴⁵ A very good description for the vapor pressures and liquid densities was achieved, as seen in Table 3, with global average deviations inferior to 1 %.

Knowing the pure compound parameters, it was then possible to compute the phase equilibria of the systems. For the CO₂ + CCl₄ system, very good results were obtained using single and positive binary interaction parameters, with a global average

Table 4. Predicted Henry's Constant for the CO₂ + CCl₄ and CO₂ + CS₂ Systems

CO ₂ + CS ₂		CO ₂ + CCl ₄		
$k_{ij} = 0.1598$; x_{CO_2} AAD % = 9.6		x_{CO_2} AAD % = 3.9		
T/K	H ₁₂ /MPa	T/K	H ₁₂ /MPa	k _{ij}
293.15	18.56	293.15	7.06	0.075
313.15	24.02	313.15	9.62	0.087
333.15	30.51	333.15	12.82	0.093

deviation of 3.9 % in composition, as reported in Table 4 and depicted in Figure 1. Using a temperature-independent binary interaction parameter would lead to a significant increase on the average deviations.

Similarly, very good results were also obtained using a single, positive, and temperature-independent binary interaction parameter of 0.1598 for the CO₂ + CS₂ system, as depicted in Figure 2, with a global average deviation of 9.6 % in composition, for CO₂ molar fractions up to 0.4. Furthermore, the plateau in pressure observed for this system suggests the presence of a liquid–liquid equilibrium region for CO₂ molar fractions between 0.5 and 0.8 that decreases with increasing temperature. This hypothesis is supported by the CPA EoS prediction of a liquid–liquid phase split at this regions, by the drastic increase and change on the equilibrium pressure behavior, as depicted in Figure 2.

Henry's Constants. The Henry's law relates the amount of a given gas dissolved in a given type and volume of liquid, at a constant temperature, to the fugacity of that gas in equilibrium with that liquid and can be described as

$$H_{12}(T, P) = \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1} \quad (13)$$

where $H_{12}(T, P)$ is Henry's constant, x_1 is the mole fraction of gas dissolved in the liquid phase, and f_1^L is the fugacity of the gas in the liquid phase. As shown, eq 13 is only rigorously valid in the diluted region limit. The Henry's constants for the CO₂ in the investigated compounds were estimated by fitting the CPA EoS to the data and calculating the limiting slope as the solubility approaches zero. This approach introduces some uncertainty on the estimated Henry's constants, but the values of these constants for the two studied systems are different enough to allow a discussion of the interactions between the CO₂ and the CCl₄ and CS₂ based on these values. The estimated Henry's constant results, reported in Table 4, indicate that Henry's constant increases (i.e., CO₂ solubility decreases) with the temperature.

The results for Henry's constant of CO₂ in CCl₄ and in CS₂ were correlated as a function of temperature by an empirical equation of the type:

$$\ln(H_{12}) = A \left(\frac{1}{T} \right) + B \quad (14)$$

where the coefficients A and B are listed in Table 5, together with the Henry's constant average absolute deviations, $|\Delta H_{12}|$, obtained for each solvent.

The effect of temperature on CO₂ solubility can be related to the Gibbs energy, the partial molar entropy, and partial molar

Table 5. Coefficients A and B in eq 14 and Partial Molar Enthalpy and Partial Molar Entropy of Solvation Obtained for CO₂ + CCl₄ and CO₂ + CS₂ Systems

	A	B	$ \Delta H_{12} $ %	$\Delta_{\text{solv}}H$ kJ·mol ⁻¹	$\Delta_{\text{solv}}S$ J·mol ⁻¹ ·K ⁻¹	$-T \cdot \Delta_{\text{solv}}S _{T=298\text{K}}$ kJ·mol ⁻¹
CS ₂	-1212.900	9.359	0.29	-10.08	-77.82	23.20
CCl ₄	-1455.725	9.220	0.35	-12.10	-76.66	22.86

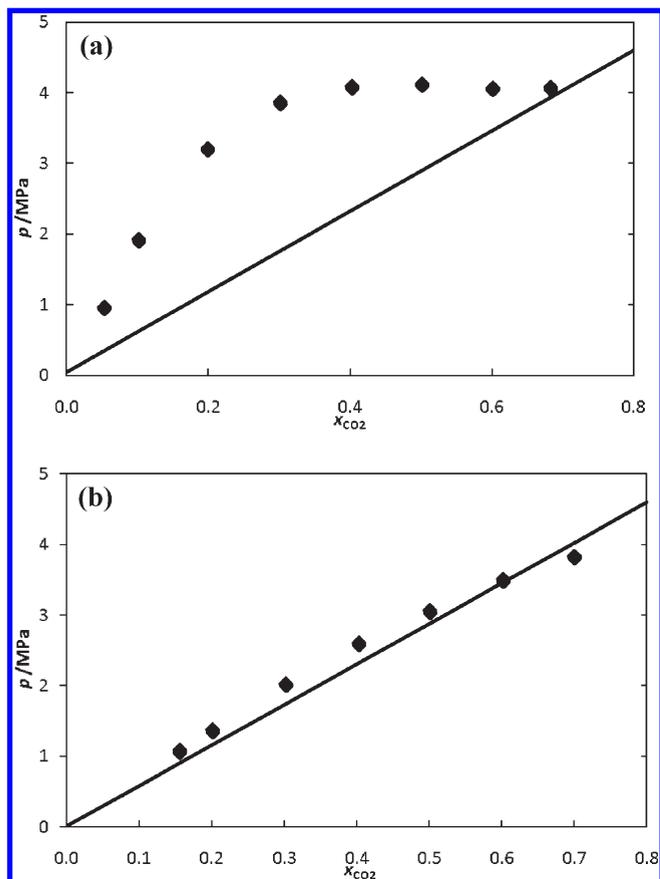


Figure 4. Pressure–composition diagram of the binary systems (a) ♦, CO₂ + CS₂ and (b) ♦, CO₂ + CCl₄, at 293 K. The solid lines represent the ideal behavior predicted by Raoult's law.

enthalpy of solvation⁴⁶ and can be calculated from an appropriate correlation of Henry's constant:

$$\Delta_{\text{solv}}G^0 = RT(\ln(H_{12}))_p \quad (15)$$

$$\Delta_{\text{solv}}H^0 = -T^2 \left(\frac{\partial \Delta_{\text{solv}}G^0}{\partial T} \right)_T = -RT^2 \left(\frac{\partial \ln H_{12}}{\partial T} \right)_p \quad (16)$$

$$\Delta_{\text{solv}}S^0 = \frac{\Delta_{\text{solv}}H^0 - \Delta_{\text{solv}}G^0}{T} = -RT \left(\frac{\partial \ln H_{12}}{\partial T} \right)_p - R \ln(H_{12})_p \quad (17)$$

The partial molar enthalpy of solvation provides an indication of the strength of interactions between the gas and the solvent, while the partial molar entropy illustrates the amount of ordering

present in the gas/solvent mixture. The results presented in Table 5 show that the partial entropies of solvation are almost identical for both systems, indicating similar structural solvation interactions. Furthermore, the higher absolute value for the partial molar enthalpy of solvation of the CO₂ + CCl₄ system indicates a more favorable interaction between the CO₂ and the CCl₄ when compared with the CS₂. The enthalpies and entropies of solvation contribution make the solubility of CO₂ in both systems nonspontaneous.

Taking into consideration the similarity between the CO₂ and the CS₂ molecules, one would expect similar interactions and a near ideal behavior. However, what is experimentally observed is that this system presents strong positive deviations to ideality, as shown by the deviations to Raoult's law, presented in Figure 4a. Nonetheless, these results can be explained if the atom electronegativities and the molecule atomic charges, dipoles, and quadrupoles are taken into account. Torii's⁴⁷ results picture a CS₂ as being an essentially nonpolar molecule due to the electronegativity of the S atom being similar to the C. On the opposite, Torii reported that the electric field around CCl₄ goes out of the chloride atom on the line extended from the C–Cl bond toward the chlorine atom on the side of the bond, due to the existence of atomic quadrupoles on the chloride atoms. The absence of charges on CS₂ leads to poor CO₂–CS₂ interactions and consequently to a strong nonideal system, while on the CO₂–CCl₄ the dipole–dipole interactions between the two molecules produce an almost ideal behavior, as shown in Figure 4b.

CONCLUSIONS

New gas–liquid equilibrium data of two binary systems, namely, carbon disulfide + CO₂ and carbon tetrachloride + CO₂, have been investigated for mole fractions ranging from (0.05 to 0.7) at 293 K, 313 K, and 333 K in the pressure range of (1 to 9) MPa, aiming at understanding the interactions between CO₂ + CS₂ and CO₂ + CCl₄ molecules.

The CPA EoS was used in the description of the measured data. The model allows a good description of the experimental data and the estimation of the Henry's constants for these systems, using only one, small, and positive binary interaction parameter.

The partial Gibbs energy, enthalpies, and entropies of solvation estimated from Henry's constants show that the solubility of CO₂ in both is nonspontaneous at standard pressure (0.1 MPa). The entropy of solvation and the partial molar enthalpy are slightly lower for the CO₂ + CCl₄ system indicating better interactions between the CO₂ and the CCl₄ than between the CO₂ and the CS₂.

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